The long-term performance of polymer-based composites in the space environment is discussed. Both thermoset and thermoplastic matrix composites are included in this discussion. Previous efforts on the space environmental effects on composites are briefly reviewed. Focus of this review is placed on the effects of hygrothermal stresses, atomic oxygen, ultraviolet (UV), and space debris/micrometeoroid impacts along with the potential synergism. Potential approaches to estimating the residual strength of polymer composites after exposures to atomic oxygen erosion or space debris/micrometeoroid impact are evaluated. New ground-based data are then utilized to illustrate the effects of atomic oxygen and thermal cycling on the failure behavior of polymer composites. Finally, research needs, challenges, and opportunities in the field of space environmental effects on composite materials are highlighted.
Surface degradation of space materials has been initially attributed to neutral atomic oxygen, which has a translational kinetic energy of approximately 5 eV by virtue of the spacecraft velocity of 8 km/s (refs. 1,2,4,6,7). However, various observed orbital effects on materials have been duplicated by Whitaker and co-workers (e.g., ref. 10) in plasma reactors where translational energy is low. This observation suggests that the high kinetic energy may not be the primary cause for atomic oxygen erosion. An alternative explanation offered by spacecraft glow investigators is that the recombination energy of oxygen atoms on surfaces is responsible for the observed degradation (ref. 11). The studies conducted by Whitaker and Jang (ref. 10) also includes the development of an equation relating exposure area, atomic oxygen flux, frequency factor, and activation energy to rate of polymer mass loss. Previous studies (refs. 1-10) have placed emphasis on the causes of atomic oxygen erosion and the changes of material surfaces. The effects of such erosion on the subsequent structural performance of materials have not been studied to any significant extent.

Several experiments conducted during the first LDEF mission contained polymer-based composites, which included different reinforcing fibers (graphite, boron, Kevlar, S-glass) and a variety of resin matrices (epoxies, polyimide, polysulfone) (ref. 9). This LDEF project also contained several other monolithic polymeric materials (without reinforcement). Additional information concerning the mass loss suffered by these materials due to atomic oxygen erosion, the material darkening effect caused by UV, and the space debris/micrometeoroid impact-induced damage has just become available (refs. 12,13). These two conference proceedings contain the preliminary data obtained from the various LDEF composite experiments (refs. 14–26). Some preliminary conclusions have been drawn from these experiment (refs. 27,28). The following are considered to be more important observations from these studies:

**Atomic oxygen (AO) effect:** Matrix resins were found to erode at a higher rate than the reinforcement fibers in composites (ref. 14). The AO erosion depth was inversely proportional to the fiber content for graphite/polymer composites; fiber content was more important than fiber type in dictating the erosion rate (ref. 14). The erosion features may be a function of fiber modulus and structure (ref. 24), but no controlled experiments were designed to assess the roles that the various material factors play. The erosion depths of the uncoated polymer composites were much less than for matrix resins alone (ref. 14).

Based on a very small sampling space, a 20- to 30-percent reduction in the flexural strength and modulus for uncoated graphite/epoxy composites was observed on the leading edge of LDEF (ref. 24). An uncoated graphite/bismaleimide composite suffered a 60-percent reduction in flexural strength. The short beam shear strength of these same materials was reduced by 10 percent (ref. 24). These effects were presumably due to AO erosion; but why AO erosion on a composite surface would result in modulus or shear strength reduction remains unclear. These property degradation results were reported by the General Dynamics Space System Division (GDSSD). In contrast, the LDEF polymer composites investigated by the Lockheed Missiles and Space Company (LMSC) did not exhibit any reduction in flexural strength, modulus, or short beam shear strength (ref. 24). The preliminary data further confirmed the notion that polymer composites for long-duration-mission spacecraft in LEO would require protection from AO attack (ref. 28). All the LDEF composite experiments on the effect of AO can only be considered qualitative in nature. No study was directed toward elucidating the AO erosion kinetics or mechanisms of polymer composites, with or without surface protection. Without such a study, design against AO erosion can only be accomplished by a trial-and-error basis.

**Thermal cycling and moisture loss effect:** Boeing Defense and Space Group (ref. 19,25) estimated that the leading edge exposed (unshielded) composites had experienced thermal cycling between
-53 °F (−47 °C) and 183 °F (84 °C) while the trailing edge exposed composites between -27 °F (−33 °C) and 170 °F (76 °C) for approximately 3,400 cycles during the 69 months in space. Extensive microcracking was observed with the leading edge exposed materials, including graphite/PMR-15 polyimide and graphite/polysulfone, and with the trailing edge exposed materials, although to a slightly smaller extent. Microcracking was only observed in the multidirectional (nonunidirectional) laminates. Microcracking was believed to be caused by thermal cycling (refs. 17,19,25), but moisture content variations could have been a significant factor. Moisture induced residual stresses (or strains) may be no less important than those caused by the mismatch in coefficient of thermal expansion (CTE). This factor appears to have been neglected in the interpretation of the microcracking phenomenon.

**Space debris/micrometeoroid impact effect:** The space debris/micrometeoroid impact damaged polymer composite samples did not show the typical hemispherical craters found on metallic structures (refs. 16,26). The damage patterns are characterized by the formation of penetration holes with adjacent surface damage, some internal delaminations, and local fiber fracture. For composites containing brittle graphite fibers, the exit and impact holes exhibited cleaner fiber fractures. In contrast, aramid fiber composites failed in a “brush or broom” mode surrounding the impact damage region (ref. 26). These damage morphologies of polymer composites are very similar to what was observed in the composites subjected to low-velocity impact (refs. 29,30). Determination of post-damage residual properties of advanced polymer composites has been an active area of composites research. However, so far no data of this nature have been reported from the LDEF community.

**The effect of UV radiation:** Optical property changes on the composite surfaces were considered to be an indication of polymer degradation due to UV radiation exposure. These changes were not present where graphite fibers could have prevented penetration of UV radiation into the material. Although synergistic effects between UV and AO were speculated, no direct evidence was available for or against this speculation.

The small number of specimens recovered from the first LDEF mission has severely limited the scientists’ ability to investigate the residual properties of polymer composites exposed to the real space environment. Future space-structure design would require additional knowledge on the degree of microcracking and the changes in such critical properties as the CTE, strength, stiffness, fracture toughness, and vibrational characteristics. A better understanding of these property changes can only be achieved by conducting more ground-based simulation tests to supplement the long-duration exposure data.

**SOME GROUND-BASED SIMULATION RESULTS**

**Thermal Cycling of Polymer Composites**

Thermal cycle induced microcracking phenomena were observed on carbon fiber reinforced polymer matrix composites (epoxy-, poly(phenylene sulfide)-, and PEEK-based). One or two minute intraply cracks were observed on thermoplastic matrix composites after a single thermal cycle between −45 °C and +85 °C. Microcracks were initiated at the fiber-matrix interface, preferentially in fiber-rich (or resin-deficient) zones (Fig. 1). Microcracking appeared more severe in PPS than in PEEK composites. Microcracking was not observed in epoxy composites for the first 200 cycles. Judging from the fact that thermoplastic composites tend to have weak fiber-matrix interfacial bonding, these observations suggest that interfacial bond plays a critical role in initiating microcracks in carbon fiber reinforced thermoplastic composites. Intraply cracks are known to be the precursors to delamination cracks, the most serious life-limiting failure mode in laminated composites.
Thermal cycle cracks are caused by the hygrothermal stresses (temperature and moisture variations) present in a laminate. The residual thermal stresses in a fibrous composite may be analyzed at different levels of complexity. First, the differential thermal stresses established between a single fiber and the matrix may be estimated either analytically or numerically. Second, the residual stress fields developed within a group of regularly arrayed fibers may also be determined either theoretically or experimentally. Third, the thermal stresses that occur between laminae with different effective thermal expansion coefficients (CTE) (e.g., due to different fiber orientations) and that caused by moisture content variations may also be calculated using, for example, the classical lamination theory. In each level of study, certain assumptions have to be made to render the problem more tractable.

As a first approach (levels 1 and 2), a "thick cylinder model" (fig. 2) (ref. 31) was developed to simulate the thermomechanical behavior near a fiber in a group of fibers with a given fiber volume fraction. In this model, the stress and strain fields in a thick cylinder under uniform pressure were derived based on the classical elasticity theory. Using such a thick cylinder model, the residual stresses established in a model single fiber-matrix system representing various polymer composites were calculated.

In practically all advanced polymer composites, the matrix has a greater CTE than the fiber, which subjects the fiber to a compressive stress. For most practical volume fractions of fibers, the matrix will generally be subjected to a radial compression at the fiber-matrix interface and a tangential tensile stress. Even in the absence of a good chemical bond, this radial compression against the interface provides friction forces to assist in the load transfer process between the fiber and the matrix. These mechanical bonds are particularly important for thermoplastic composites in which chemical bonds are difficult to form. The magnitudes of such residual thermal stresses at the microscopic level have been calculated for the composite systems being considered for space applications. Equation (1) was utilized in these calculations, which were meant to estimate the orders of magnitudes of these microscopic-level stresses:

\[
P = \frac{(\alpha_m - \alpha_f) \Delta T}{E_m \left( \frac{r_f^2 + r_m^2}{r_m^2 - r_f^2 + \nu_m} \right) + \frac{1 - \nu_f}{E_f}}.
\]

In this equation, \(\alpha\), \(E\), \(r\), and \(\nu\) are, respectively, the CTE, elastic modulus, effective radius, and volume fraction of the fiber \((f)\) or the matrix \((m)\). Derivation of this equation was based on a single-fiber system, but did include the effect of fiber volume fraction (ref. 31). In the case of \(V_f = 0.6\), \(r_f^2/r_m^2 = 0.6\) and equation (1) may be further simplified to estimate the magnitudes of \(P/\Delta T\) for a variety of composites. The results of such calculations are given in Table 1.

The TCM analysis indicates that, at the microscopic level, the matrix generally is subjected to a radial compression and a tangential tensile stress at the fiber-matrix interface when the end-use temperature \((T_e)\) is lower than the curing temperature or crystallization temperature \((T_c)\). The lower the end-use temperature, the greater the magnitudes of these residual stresses. When good chemical bonding is absent, this radial compression against the interface provides a mechanical bond between the fiber and the matrix. The magnitudes of such residual thermal stresses at the microscopic level for high modulus carbon fiber-PPS composites are of approximately \(83 \times 10^3\) Pa/K (Table 1). With \(T_c = 175\) °C and \(T_e = 25\) °C, we have \(p = 12.5\) MPa. The magnitude of this interfacial compressive stress will drop to 7.47 MPa when the C/PPS specimen is heated to 85 °C. The fact that microcracks in C/PPS were observed after the second-half (heating) cycle, but not after the first-half (cooling) cycle, may be ascribed to the reduced interfacial adhesion (compressive stress) when the composite was raised to a higher temperature. Although the residual stress magnitudes caused by differential CTE's between layers would also be reduced with a higher \(T_e\), these magnitudes were obviously sufficient to overcome the weak interfacial
adhesion between carbon fibers and the PPS matrix, leading to interfacial debonding and, thus, the observed microcracking.

At the more macroscopic scale (between laminas), a change in temperature ($\Delta T$) or moisture content of a laminated composite structure causes a variation in its dimensions proportional to the change in temperature ($\Delta T$) or moisture content ($\Delta C$) and its initial dimensions. This leads to the development of a thermal strain ($\varepsilon^T$) or hygroscopic strain ($\varepsilon^H$). However, thermal deformation of a lamina is constrained by its neighboring laminae, leading to the development of residual stresses. The magnitudes of these macroscopic residual stresses in each layer of a composite for several composite systems may be estimated using the classical lamination theory. These stresses will produce additional stresses at the fiber-matrix interface and must be added to or subtracted from the microscopic interface thermal stresses mentioned earlier.

The magnitudes of the macroscopic residual thermal stresses in each layer of a composite for several composite systems (not including C/PPS system) have been estimated. The residual stresses in individual plies of a C/PPS laminate are being computed. Their values are expected to be of the same order of magnitude as obtained with the C/epoxy system. The results (Table 2) indicate that the transverse stress ($\sigma_{xx}$ in the 90° layers) is approximately 12.9 MPa at room temperature and reduced to 8.1 MPa at ~80 °C. This stress will yield a local tensile stress at the fiber-matrix interface. The interfacial compressive stress magnitudes (caused by the difference in CTE between the fiber and the matrix) for a typical C/epoxy will drop from 5.7 MPa at room temperature to 3.6 MPa at ~80 °C. This microlevel stress is not sufficient to compensate for the corresponding macrolevel contribution. Fortunately, relatively strong chemical bonds are present between carbon fibers and the epoxy resin. Thus, much higher stresses are required to induce interfacial debonding in epoxy systems. This is why the C/epoxy composite did not exhibit microcracking even after several hundred thermal cycles between -45 °C and 85 °C. The moisture effect has yet to be analyzed.

Atomic Oxygen Erosion of Polymer Composites (Residual Properties)

The response of four types of fiber-epoxy composites to atomic oxygen was investigated by Bianchi (ref. 32): carbon fiber-, aramid (Kevlar) fiber-, glass fiber-, and glass/carbon/glass hybrid composites. In terms of mass loss, the carbon fiber-epoxy composite suffered the greatest rate of degradation among this group of materials (Fig. 3). This was followed by the Kevlar, hybrid (not shown) and glass fiber systems. That the glass fiber-epoxy and the hybrid composite (with the top and bottom layers being glass fiber-epoxy laminas) suggested the glass fiber to be relatively more resistant to the AO attack. In light of flexural modulus and strength retention, the Kevlar fiber composite stood out to be the best against AO degradation for long-term exposures. Again, the carbon fiber system exhibited the highest rate of strength reduction (Fig. 4).

Surface morphology studies by optical microscopy and SEM indicated that the AO degradation process in a composite followed a two-step process. In general, the matrix resin appeared to be less resistant to AO. This observation is consistent with the LDEF findings (refs. 17,24,25). Where accessible by AO, the resin located within the interstices between fibers tended to get eroded away first (Fig. 5). This resin erosion step typically proceeded to one or two fiber diameters deep prior to any significant fiber degradation was observed. The fiber erosion step was characterized by the formation of surface pores, some larger and deeper holes, nonuniform diameter reduction (necking) and, when a long exposure time was imposed, some fiber breakages (Fig. 6). Thinner (Fig. 7) and weaker fibers appeared to be the preferential initiation sites of damaging cracks that were responsible for the reduction in mechanical properties.
RESEARCH NEEDS AND OPPORTUNITIES

Previous research efforts concerning environmental effects on polymer composites were largely limited to the observations of the chemical and physical changes taking place on the surface of materials. No systematic efforts have been made in elucidating the AO erosion mechanisms and kinetics of polymer composites. Little endeavor has been directed to assessing the subsequent (residual) performance of polymer and composite materials after various degrees of space environment exposure. With a better understanding of erosion chemistry and performance-space environment relationship, we would be better prepared to study the maintainability and repairability of space materials and structures. Also lacking is a predictive model for material durability that incorporates both material and space environmental parameters. These efforts are essential to the establishment of improved guidelines for choosing composites for space applications.

Space Environment Effects on the Material Performance

Future ground-based simulation studies should include determination of the mechanical properties of various aerospace-grade composites in relation to the space environmental factors. These properties include the resistance to foreign object impacts, CTE, strength, stiffness, fracture toughness, and damping response.

As an example, composites may be exposed to a varying but controlled degree of AO attack in a simulated space environment. Various thermomechanical properties may then be measured and correlated with the chemical and physical changes of the material surface. This effort should be aimed at identifying the most critical morphological or microstructural features of material surfaces that would govern the degradation effect. Micromechanics models may then be developed to allow for prediction of the key mechanical properties of composites.

Extensive and indepth studies on the response of various polymer composites subjected to low-velocity impacts by foreign objects have been conducted by many researchers (e.g., refs. 29,30). Many key material parameters have been identified that dictate the impact resistance of polymer composites. Studies should be extended to include high-velocity impacts, simulating the interaction between micrometeoroids and structural components. Since the data on the velocity and dimensions of space debris/micrometeoroids are becoming increasingly available, we are now in a better position to predict the impact damage state and the residual properties of polymer composites. Information acquired through these future studies will help establish scientific guidelines, based on which one judge if, when, and how to service or repair the space structures.

Model Development

The LDEF community perhaps should collaborate to develop a model having some predictive value for material durability. The development of the model may begin by considering the mass loss and surface structural changes caused by the simulated attacks of AO, radiation, and micrometeoroids/debris under the conditions of hygrothermal variations. The effect of mass loss can be related to the parameters of microstructural or morphological changes (which may generate stress concentrations, e.g.) must also be considered perhaps from the statistical fracture mechanics perspectives. This suggestion originates from the observation that characteristic AO eroded and debris impact damaged surfaces of materials contain many defects of differing severity (varying defect size and crack tip radius of curvature). All these effects should be incorporated in the model and compared with the material’s intended service
function (e.g., structural integrity) to predict the residual properties (e.g., strength) and durability of the material.

Maintenance of Space Structures

Future space missions may require development of a reliable maintenance methodology. This may be accomplished by first evaluating the surface chemical and physical states (surface functional groups and roughness profile) of potential space-bound polymers/composites exposed to AO, UV radiation, and hypervelocity impacts. These surface-eroded or damaged materials may then be coated with fresh layers of identical material or other chemically compatible materials. Different degrees of surface treatment (e.g., grit blasting or chemical cleaning) may be applied to the eroded structures prior to coating/repairing. The mechanical integrity (strength, stiffness, and impact resistance) of the repaired structures must then be measured as a function of the surface conditions. This task will produce desirable knowledge on the candidate protection/repair materials and the surface treatments required.

Future space missions may also demand development of effective techniques to cure or polymerize the protection or repair materials in a space environment. Conventional aerospace techniques such as press molding of polymers and autoclave curing of composites require a high temperature to activate the reaction and a high pressure to consolidate the microstructure. Application of a high temperature and high pressure to the structures in space is not a straightforward task. A better alternative is to take advantage of the resources in the space environment to activate and accelerate the polymerization reaction. The potential resources that can be utilized to initiate polymerization include gamma radiation, electrons, protons, other charged particles, AO, and visible/UV light. The feasibility of utilizing atomic oxygen to initiate or accelerate polymerization reactions of silicon-, epoxide-, and imide-based resins should be established.

CONCLUDING REMARKS

The spacecraft or the components placed in orbit will be subjected to constant attacks by the various space environmental agents. The degradation mechanisms and kinetics of polymer composites in the space environment must be addressed. Further evaluations of structural changes and property degradation will allow us to gain a better understanding of the material-space environment interactions. The space components may require protection, maintenance, and repair to ensure long-term reliability and survivability. One goal of future research will be the establishment of an effective methodology to maintain or service the space structures. Efforts should also be made in the future to develop a durability predictive model that incorporates both material and space environmental parameters, and hopefully to suggest improved guidelines for choosing polymer composites for space applications.

ACKNOWLEDGMENTS

This project is partially supported by the 1992 ASEE/NASA Summer Faculty Fellowship Program. B.Z. Jang would like to thank his NASA host, Mr. Roger Linton, for technical assistance and encouragement. J. Bianchi is supported by the Engineering Physics Division of Marshall Space Flight Center through a NASA Graduate Researcher Fellowship, with Dr. A.F. Whitaker being the technical monitor.
REFERENCES


Table 1. The values of $P/\Delta T$ for several fiber-resin combinations.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Matrix</th>
<th>$E_f$ (GPa)</th>
<th>$\alpha_f$ (E-6/K)</th>
<th>$E_m$ (GPa)</th>
<th>$\alpha_m$ (E-6/K)</th>
<th>$P/\Delta T$ (KPa/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-modulus carbon</td>
<td>Toughened epoxy</td>
<td>340</td>
<td>7</td>
<td>3.0</td>
<td>60</td>
<td>36</td>
</tr>
<tr>
<td>Intermediate modulus</td>
<td>Epoxy</td>
<td>270</td>
<td>8</td>
<td>3.5</td>
<td>55</td>
<td>37</td>
</tr>
<tr>
<td>High-modulus carbon</td>
<td>PPS</td>
<td>340</td>
<td>7</td>
<td>4.0</td>
<td>99</td>
<td>83</td>
</tr>
<tr>
<td>High-modulus carbon</td>
<td>PEEK</td>
<td>340</td>
<td>7</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-glass</td>
<td>Epoxy</td>
<td></td>
<td></td>
<td>3.5</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Kevlar-49</td>
<td>Epoxy</td>
<td></td>
<td></td>
<td>3.5</td>
<td>55</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Residual thermal stresses in a carbon/epoxy composite, $[0/45/90/-45]_2s$.

<table>
<thead>
<tr>
<th>Layer Number</th>
<th>$\Delta T = -97 °C$</th>
<th>$\Delta T = -154 °C$</th>
<th>$\Delta T = -222 °C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{xx}$</td>
<td>$\sigma_{yy}$</td>
<td>$\sigma_{xy}$</td>
</tr>
<tr>
<td>1($0^\circ$)</td>
<td>-195</td>
<td>8.12</td>
<td>0</td>
</tr>
<tr>
<td>2($45^\circ$)</td>
<td>93.5</td>
<td>93.5</td>
<td>102</td>
</tr>
<tr>
<td>3($90^\circ$)</td>
<td>8.12</td>
<td>-195</td>
<td>0</td>
</tr>
<tr>
<td>4($-45^\circ$)</td>
<td>93.5</td>
<td>93.5</td>
<td>102</td>
</tr>
</tbody>
</table>
Figure 1. Microcracks in carbon fiber/PPS composites due to thermal cycling, (a) optical micrograph and (b) SEM micrograph.
Figure 2. Schematic of thick-cylinder model (TCM).
Figure 3. Mass loss per surface area exposed to AO for carbon-, Kevlar, and glass-fiber reinforced epoxy composites.

Figure 4. Flexural strength reduction of composites due to AO exposure.
Figure 5. An atomic oxygen eroded surface of the glass-epoxy composite.

Figure 6. Kevlar fiber/epoxy composite surface after a long exposure to AO.
Figure 7. Postflexural test examination of an AO-eroded carbon/epoxy composite indicates necked fibers being the preferential sizes of crack initiation.