STRUCTURAL MATERIALS FOR SPACE APPLICATIONS

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The long-term performance of structural materials in the space environment is a key research activity within NASA. The primary concerns for materials in low Earth orbit (LEO) are atomic oxygen erosion and space debris impact. Atomic oxygen studies have included both laboratory exposures in atomic oxygen facilities and flight exposures using the Shuttle. Characterization of atomic oxygen interaction with materials has included surface recession rates, residual mechanical properties, optical property measurements, and surface analyses to establish chemical changes. The Long Duration Exposure Facility (LDEF) is scheduled to be retrieved in 1989 and is expected to provide a wealth of data on atomic oxygen erosion in space.

Hypervelocity impact studies have been conducted to establish damage mechanisms and changes in mechanical properties. Samples from LDEF will be analyzed to determine the severity of space debris impact on coatings, films, and composites.

Spacecraft placed in geosynchronous Earth orbit (GEO) will be subjected to high doses of ionizing radiation which for long term exposures (20-30 years) will exceed the damage threshold (~$10^9$ Rads) of many polymeric materials. Radiation interaction with polymers can result in chain scission and/or cross-linking. For highly cross-linked 177°C cure epoxies, the primary mechanism of radiation degradation appears to be chain scission. The formation of low molecular weight products in the epoxy plasticize the matrix at elevated temperatures and embrittle the matrix at low temperatures. This affects both the matrix-dominated mechanical properties and the dimensional stability of the composite.

Plasticization of the matrix at elevated temperatures can result in permanent residual strains in composites exposed to such temperatures. Embrittlement of the matrix at low temperatures results in enhanced matrix microcracking during thermal cycling. Matrix microcracking changes the coefficient of thermal expansion (CTE) of composite laminates and produces permanent length changes. Residual stress calculations have been performed to estimate the conditions necessary for microcrack development in unirradiated and irradiated composites. These calculations show that microcracking in the transverse plies of an irradiated [$0/90_5$] Gr/epoxy laminate is predicted to occur at temperatures substantially higher than those predicted for an unirradiated laminate. Microcracking measurements were made for standard 177°C cure Gr/Epoxy, rubber toughened Gr/Epoxy, Gr/Polymide, and Gr/Thermoplastic composites. The effects of thermal cycling and irradiation followed by thermal cycling on the mechanical and physical properties of the epoxy composites were consistent with the predicted responses. The effects of UV and electron exposure on the optical properties of transparent polymer films has also been examined to establish the optimum chemical structure for good radiation resistance. Results are presented which show that these polymers have excellent resistance to both electron and UV radiation compared to more conventional polymer films, such as FEP Teflon.

Accelerated testing of space materials is a topic of great interest for the spacecraft community and is a central issue for long-life certification. Thoughts on approaches to establishing accelerated testing procedures are discussed in this paper.
Research on advanced materials development for spacecraft applications has generally been focused on three classes of materials: polymer films, coatings, and composites. High-performance polymer films such as Kapton and Mylar are widely used on current spacecraft (fig. 1). The recent concern about atomic oxygen degradation of polymer materials on spacecraft placed in low-Earth orbit (LEO) has focused attention on the development of new polymer films or coatings which are resistant to atomic oxygen erosion. Another area of research at Langley has been the development of transparent polyimide films which have very good UV and electron radiation resistance. Highlights of this research will be covered in a later section of this paper.

Coatings consist of a variety of organic-base paints, metallic materials, and ceramic materials. An extensive data base exists on the development and testing of paints that range in color from black to white. The degradation in optical properties of white paints by UV, electron and proton radiation was extensively studied in the 1960's and early 1970's. The white paint designated S13GLO is generally considered to be the best white paint available today for spacecraft applications where a low solar absorptance and high emittance are required. Atomic oxygen degradation of coatings is an area of considerable interest within NASA because space durable materials are required for Space Station (30 year design life time). Aluminum foil bonded to composite tubes has been shown to have resistance to atomic oxygen erosion. However, other metals such as silver which has been used for silver interconnects on lightweight flexible solar arrays must be protected from atomic oxygen.

Composite materials have been extensively used for spacecraft structural applications because of their combination of lightweight, high stiffness, and low thermal expansion. Composites of interest for spacecraft applications include Gr/Polymer, Gr/Al, Gr/Mg, and Gr/glass. Some of the issues and concerns with these materials will be discussed in subsequent charts.

![Types of Materials](image1)

![Spacecraft Application](image2)

Figure 1
The two major topics to be covered in this paper are space environmental effects on structural materials, and new materials development (fig. 2). Highlights of ongoing NASA research will be presented to illustrate the type of issues currently being addressed for NASA missions. Examples of new materials development will also be presented to illustrate some of the approaches being pursued to develop improved materials for space applications.

**Topics**

- Examples of space environmental effects on structural materials
  - Composites
  - Films
  - Coatings

- New materials development
  - Research focus
  - Testing issues
  - Long-life certification

Figure 2
SPACE ENVIRONMENT

The space environment is a hostile environment. It consists of atomic oxygen, ultraviolet radiation, high-energy electron, and proton radiation as well as solar flare protons, and micrometeoroids and space debris (fig. 3). For spacecraft located in low Earth orbit, atomic oxygen erosion of polymeric materials is a primary concern. This, of course, is a function of the ambient density of the atmosphere which varies with sunspot activity. Atomic oxygen degradation is a significant issue for Space Station,* which is expected to operate for 20-25 years in low Earth orbit. This topic will be covered in detail by other speakers at this symposium and therefore will not be further discussed in this paper.

Another concern for structures placed in low Earth orbit is micrometeoroids or space debris impact. Predictions based on models of the space debris environment indicate that the population density of small particles is expected to get progressively worse over the next several years. In the smaller diameter sizes the population density of space debris is expected to exceed that of micrometeoroids.

Spacecraft placed in geosynchronous earth orbit or in a high polar orbit will be subjected to high doses of electron and proton radiation. For long life missions (25-30 years) the total absorbed dose to typical composite structural elements may exceed the threshold level for damage ($10^9$ rads) for most polymeric materials. Of particular concern are changes in mechanical and physical properties of structural composites and optical properties of thermal controlled coatings or polymeric films.

![Figure 3](image)

*Space Station Freedom
The development of long-life space materials must strongly consider the dominant environmental conditions expected for the orbit where the spacecraft will be displayed. Some of the key differences for materials to be used on spacecraft placed in low Earth orbit (LEO) and Geosynchronous Orbit (GEO) are listed in figure 4. To successfully design for long-life space missions, space materials durability must be treated as a critical design requirement in the same way as requirements for mechanical, physical, or optical properties. One of the most difficult challenges in trying to engineer long life is the uncertainty associated with accelerated testing. This issue will be further discussed in a later section of this paper.

<table>
<thead>
<tr>
<th>Space Station - LEO</th>
<th>Antenna - GEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Atomic oxygen stability</td>
<td>• Radiation stability (UV, e⁻ and p⁺)</td>
</tr>
<tr>
<td>• Damage tolerance and toughness</td>
<td>• Low expansion-high precision</td>
</tr>
<tr>
<td>• Stable optical properties</td>
<td>• High stiffness and damping capacity</td>
</tr>
<tr>
<td>• Low outgassing</td>
<td>• Low outgassing</td>
</tr>
</tbody>
</table>

Figure 4
COMPOSITE TUBE AS A SYSTEM

The successful development of long-life structures in space must be based on a thorough understanding of the loads and environments that the structure will be subjected to during design lifetime. For a composite truss structure this means that the performance of composite tubes used to build the structure must be understood. The basic composite tube may be considered as a system (fig. 5) composed of: (1) the fiber-matrix composite laminate, (2) coatings for UV and atomic oxygen protection and for thermal control, (3) end fittings to attach to joints in the structure, (4) adhesives used to bond end fittings to composite laminate, and in some cases to bond coating to composites (i.e., Al foil to composite tube).

The long-term thermal and mechanical response of the tube is dependent on the performance of each of these elements. Factors which can lead to changes in the thermal response of the tube include: (1) changes in solar absorptance or emittance of coating either due to contamination or radiation degradation will alter the maximum and minimum thermal cycle that the tube will experience, loss of coating could result in UV and/or atomic oxygen erosion of composite laminate; (2) matrix microcracking resulting from thermal fatigue will change the coefficient of thermal expansion (CTE) of the composite laminate; (3) thermal fatigue failure of adhesive joints would affect both thermal and mechanical properties of the tube; (4) contaminating of coating surfaces, matrix microcracks, and coating separation from the composite laminate would change the thermal conductivity properties which could alter the temperature distribution of the composite tube as the structure goes into and out of the Earth's shadow. The long-term mechanical performance of the composite tube is obviously dependent on the properties of the composite laminate coatings, adhesives, and end fittings.

- Major Components
  - Composite Laminate
  - Coating
  - End Fittings
  - Adhesives
    - End Fittings
    - Coatings

- Response
  - Thermal
    - Coating optical properties
    - CTE of composite laminate and end fittings
    - Thermal conductivity of coatings and composite
  - Mechanical
    - Composite properties
    - Adhesive strength
    - End fittings properties

Figure 5
CTE MISMATCH IN ADHESIVE JOINTS

Coefficient of thermal expansion (CTE) mismatch in adhesive joints can result in high residual stresses and thermal fatigue failure. The truss structure of Space Station will be thermally cycled between approximately 150° and -100°F 175,000 times during 30 years in low Earth orbit. The current baseline for this structure is high-stiffness graphite/epoxy composite tubes with Al end fittings and joints. Thermal cycling tests are currently being conducted on representative composite/metal joints to evaluate their thermal fatigue resistance. CTE and elastic modulus data for three composites, high- and low-temperature adhesives, and Al and Ti are tabulated in figure 6.

![Diagram of adhesive joint](image)

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>MMC (GR/AL)</th>
<th>CerMC (GR/GL)</th>
<th>PMC (GR/EP)</th>
<th>L.T. ADHESIVE (350°F EPOXY)</th>
<th>H.T. ADHESIVE (PI)</th>
<th>AL</th>
<th>TI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE, IN/IN/°F</td>
<td>0.8* (15)**</td>
<td>-0.3 (3.6)</td>
<td>-0.6 (18)</td>
<td>30</td>
<td>20</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>ELASTIC MODULUS,</td>
<td>47</td>
<td>31</td>
<td>39</td>
<td>0.6</td>
<td>0.5</td>
<td>10</td>
<td>17</td>
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<tr>
<td>PSI X 10</td>
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</tbody>
</table>

*LONGITUDINAL **TRANSVERSE

Figure 6
LOW EXPANSION POLYMER RESINS

Residual stresses in composites are a function of the differences in coefficients of thermal expansion of the matrix resin and fibers, the elastic modulus of the matrix and fibers, and the ΔT, temperature change between the cure temperature of the composite and the use temperature of the composite. The coefficient of expansion (CTE) of some typical state-of-the-art polymers, high performance polymers, and an experimental polyimide are shown in figure 7. This chart shows that the potential exists to synthesize very low CTE (0.5 x 10^{-6}/°C) polymers. However, the aromatic thermoplastics and the dense rod-like aromatic thermoplastics must be processed at much higher temperatures than the typical 177°C cure epoxies typically used for space structures. Also the modulus of the rod-like polymers can be much higher (1-2msi) than that of the typical epoxy (0.5msi).

The combination of higher processing temperatures and higher modulus may more than offset the benefit of lowering the CTE of the polymers. Research is needed to establish the degree to which each of these properties can be varied and experimental lots of material synthesized for composite fabrication and testing. Research of this nature is currently underway at NASA Langley. The near term focus of this research is directed at understanding the structure-property relationships that determine the coefficient of thermal expansion of polymers. Promising concepts will be further explored to synthesize enough resin to fabricate composites for testing.

<table>
<thead>
<tr>
<th>State-of-the-art polymers</th>
<th>CTE (PPM/°C)</th>
<th>Structure/property relationships</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon® (TFE)</td>
<td>350°F cure epoxy</td>
<td>Aliphatic thermoplastics</td>
</tr>
<tr>
<td>Kapton® polyimide</td>
<td></td>
<td>High CTE</td>
</tr>
<tr>
<td>High performance polymers</td>
<td></td>
<td>Aliphatic thermosets</td>
</tr>
<tr>
<td>Hitachi polyimide</td>
<td>10</td>
<td>Low CTE</td>
</tr>
<tr>
<td>LaRC-TPI oriented</td>
<td>10</td>
<td>Aromatic thermoplastics</td>
</tr>
<tr>
<td>Experimental polymers</td>
<td>0.5</td>
<td>Dense, rod-like aromatic</td>
</tr>
<tr>
<td>New polyimide</td>
<td></td>
<td>thermoplastics</td>
</tr>
</tbody>
</table>

Conclusion: Potential exists for synthesizing very low CTE resins

Figure 7
During FY 88 NASA initiated a Precision Segmented Reflector Technology program at Jet Propulsion Laboratory (JPL) and Langley Research Center (LaRC) as part of NASA's new Civil Space Technology Initiative. The primary reflector shown in figure 8 is made up of hexagonal panels, each two meters in size. The panels are supported by a deployable or erectable truss backup structure and surrounded by a sunshield to keep direct solar radiation from the primary surface. Significant technical challenges exist in the areas of lightweight deployable structures, lightweight structural composite mirrors, and the control of pointing, vibration, and figure (ref. 1).

The development of lightweight, low-cost reflector panels that demonstrate high surface precision and thermal stability is considered a critical enabling technology for precision reflectors. Some of the key requirements for the reflectors panels are: aerial density ≤10 Kg/m²; surface roughness <3 µm; out-of-plane CTE ≤2 ppm/K; long-term stability in orbit <1 µm; low outgassing; good radiation stability. Much of the work to date has focused on the fabrication of lightweight honeycomb panels with Gr/Epoxy face sheets. Both E-glass and standard aluminum honeycomb core have been utilized. Coatings and polishing techniques have also been developed to improve a fabricated surface precision from 3 µm to approximately 1 µm.

Figure 8
EFFECT OF MATRIX CTE ON LAMINA PROPERTIES

A significant part of the Precision Segmented Reflector (PSR) program is the development of lightweight (<10 Kg/m²) low-cost composite panels with a surface roughness less than 0.03 μm RMS. These panels must be thermally stable during long-term (10-year) service at cryogenic temperatures in space. To accomplish these objectives research is underway to develop low expansion resins for resin matrix composites and establish fabrication procedures which minimize residual stresses in composites. Reducing through-the-thickness CTE of polymer matrix composites would help to minimize distortions in composite panel face sheets. Figure 9 shows that a reduction of CTE by an order of magnitude (CTE EP/10) would reduce the through thickness expansion of a typical graphite/epoxy laminate to approximately 1/3 the value of a Gr/Ep laminate fabricated with a typical 350°F cure epoxy. The results of figure 9 also show that the modulus of the graphite reinforcement fiber does not affect the through-the-thickness (T-T-T) CTE. Graphite/glass also has a very low T-T-T CTE which makes it a candidate material for PSR applications.

![Figure 9](image-url)
Graphite-reinforced glass is a leading candidate composite material for space applications where good dimensional stability and radiation resistance are important design considerations. The microstructure of a typical Gr/glass laminate (ref. 2) fabricated by United Technologies Research Center is shown in figure 10. Each ply of continuous fiber material is separated by a 2 mil layer of graphite scrim which was used to improve handleability of the plies prior to composite consolidation. The glass matrix is a Corning borosilicate glass (type 7740) and the reinforcing fiber was Hercules HMS, a 55 msi modulus PAN base graphite fiber. The fiber volume fraction of this laminate was approximately 0.45 ± 0.03.
The thermal expansion behavior in the x-direction of a quasi-isotropic Gr/glass laminate measured in the dimensional stability laboratory at NASA Langley (ref. 2) is shown in figure 11. The near zero CTE is evident from the slope of the stress-strain curve. Thermal cycling did not have a significant effect on the thermal expansion behavior. However, the strain hysteresis loop of $25-30 \times 10^{-6}$ was unexpected. This behavior is generally believed to be associated with either damage development in the graphite paper interply layers or changes in residual curing stresses in the laminates. Similar hysteresis phenomena was also observed for chopped fiber mat Gr/glass composites (fiber vol. fraction of 33 ±3%). The magnitude of the hysteresis was on the order of $15-25 \times 10^{-6}$. Thermal cycling of unidirectional Gr/glass samples showed that in the longitudinal direction the expansion behavior was linear and did not change with thermal cycling (100 cycles). Values of residual strain were quite low and did not change with thermal cycling. The residual strain was much more pronounced in the transversely oriented specimens. Large values were noted on the first cycles but tended to decrease in magnitude in later cycles. However, the specimen increased in length (transverse direction) during each cycle and net cumulative strains of up to $200 \times 10^{-6}$ were observed after 100 cycles. The reason for this behavior has not been established but could be associated with the development of micro damage in the composite laminate. However, microscopic and x-ray examination of the specimens after testing did not reveal any cracks.

![Figure 11](image-url)
Graphite reinforced magnesium composites are of interest for space structures because of their high specific stiffness, low thermal expansion, no outgassing, and excellent radiation resistance. The thermal expansion behavior of a typical Gr/Mg composite (ref. 2) is shown in figure 12. The composite laminate was fabricated with layers of precursor wires (Union Carbide P100 graphite fibers infiltrated with magnesium alloy AZ91C) separated by interply foils of 1.7 mil thick AZ61A Mg alloy and AZ61A Mg surface foils 2.5 mil thick. The finished panel was 80 mls thick with a fiber volume fraction of 0.47. The fiber orientation was $\pm 8^\circ$.

The thermal expansion measurements shown in figure 12 were made in a high precision Fritzeau type laser interferometric dilatometer which had a strain resolution of $1 \times 10^{-6}$. The results for the first thermal cycle were made by thermally cycling the specimen in the dilatometer by heating from room temperature to 100°F, then cooling to -200°F then reheating to room temperature. After the first cycle, the specimen was removed from the dilatometer, thermally cycled in a separate chamber and then reinserted into the dilatometer for thermal expansion measurements.

The nonlinear thermal strain behavior is attributed to plastic deformation of the matrix alloy due to thermal stress created by differential thermal expansion between the fibers and matrix alloys. The first thermal cycle produced a permanent residual strain in the specimen of $103 \times 10^{-6}$. The residual strain produced on the 5th thermal cycle was $5 \times 10^{-6}$ and on the 100th thermal cycle $8 \times 10^{-6}$. The cumulative strain after 100 cycles was $167 \times 10^{-6}$. The coefficient of thermal expansion was small ($-0.04 \times 10^{-6}$ to $0.16 \times 10^{-6}/°F$) at room temperature.

The large hysteresis loop and permanent residual strains produced in the composite clearly show that this composite could not be used for applications where it would be cooled to -200°F. Tests of this composite over a reduced temperature range of 70°F to -100°F showed that a small hysteresis loop was still present but there was no evidence of residual strain following cycling. The linear thermal expansion range of this composite can be increased by heat treating the composite to increase the yield strength of the matrix alloy or by using a higher yield strength alloy for the matrix.

![Graph showing thermal expansion measurements](image)
ELECTRON DOSE RATE IN GRAPHITE EPOXY COMPOSITE

The high energy electrons and protons present in the trapped radiation belts of the Earth can cause significant property changes in many polymer materials if the total cumulative dose exceeds approximately $1 \times 10^9$ rads. The calculated electron dose rate for a typical graphite/epoxy composite in rads/day is plotted as a function of attitude (circular orbit at zero inclination) in figure 13. The dose rate at the surface, and at 3, 6, and 15 mils below the surface are plotted. For low Earth orbit applications, such as Space Station (~550 KM), the cumulative dose over even a 30 year lifetime would not be expected to effect composite properties. However, for spacecraft placed in high Earth orbit (above 1000 KM) the absorbed dose at the surface would be approximately $7 \times 10^9$ rads in 20 years and approximately $10^{10}$ rads in 30 years. Because these levels are above the known damage threshold levels of many polymeric materials radiation damage is a significant environment factor which must be considered in material selection for long-life structures to be placed in high Earth orbits.

Selected highlights of an ongoing research program on radiation degradation of polymer matrix composites conducted at NASA Langley Research Center will be presented in subsequent figures.

Circular orbits at zero inclination

![Dose rate vs. Altitude](image)

Figure 13
EFFECT OF ELECTRON RADIATION ON AXIAL RESPONSE
OF [45°] OFF-AXIS GrEp COMPOSITES

The effect of high energy (1 MeV) electron radiation on the shear properties of a typical 177°C cure graphite epoxy composite (T300/934) is shown in figure 14. Composite specimens 0.5 inch wide by 6 inches long were cut from a 4-ply unidirectional composite laminate such that the fibers were at a 45° angle to the axis of the specimen. The specimens were dried and irradiated in vacuum (2x10⁻⁷ Torr) to 1 MeV electrons at a dose rate of 5x10⁷ rad/h and a total dose of 10¹⁰ rads. Unirradiated and irradiated specimens were tested at room temperature, +121°C and -157°C.

The results (ref. 3) in figure 14 show that radiation changes the stress strain behavior of the composite laminate at all three temperatures examined. At low temperature (-157°C) the strength and strain-to-failure of the composite are significantly reduced. At room temperature the strength and modulus are increased by irradiation and the strain-to-failure was only slightly reduced. At elevated temperature (+121°C) radiation damage of the epoxy matrix caused large reductions in strength and stiffness and a significant increase in strain-to-failure.

These changes in mechanical properties are consistent with changes expected if the primary radiation damage mechanism were chain scission. Chemical characterization tests revealed the presence of low molecular weight species in irradiated composites not found in unirradiated composites. These low molecular weight species, resulting from chain scissions, plasticize the matrix at elevated temperatures and embrittle the matrix at low temperatures. They can also have a significant effect on thermal expansion behavior which will be illustrated in subsequent figures.

![Figure 14](image_url)
The effect of irradiation on the compressive response of [0]_8 and [90]_8 laminates of T300/934 was measured (ref. 3) at -157°C, RT, and 121°C. Irradiation had very little effect on the compressive properties at -157°C and caused only a small reduction in the strength properties at room temperature, -3% axial and -13% transverse. However, irradiation caused a severe reduction in the strength of both the [0]_8 and [90]_8 laminates (-62% and -54%, respectively) at elevated temperatures. The elevated temperature stress-strain curve for the [90]_8 laminate in figure 15 clearly shows that the matrix has been degraded by irradiation. For the [0]_8 laminate the matrix stiffness is sufficient at room and cold temperature to prevent microbuckling of the fibers such that the strength of the [0]_8 composite reflects the strength of the fibers. However, at elevated temperatures the matrix stiffness is reduced to the point where lateral support for the fibers is not sufficient to achieve full fiber properties. These results are consistent with results for neat resin specimens tested at elevated temperatures with and without irradiation exposure. The DMA results for baseline and irradiated T300/934 showed that the average molecular weight and cross-link density of this material were reduced by irradiation. Both of these effects would be expected to reduce the elevated temperature stiffness of the resin and thus degrade the compressive properties of the composite.

Figure 15
THE EFFECT OF ELECTRON RADIATION AND THERMAL CYCLING ON MICROCRACK FORMATION IN T300/934 Gr/Ep

The effects of sequential radiation and thermal cycling on induced microdamage in the T300/934 Gr/Ep (ref. 4) are presented in figure 16. This figure shows typical X-ray radiographs of 4-ply [0/90/90/0] laminates after (1) 500 thermal cycles, after (2) 500 cycles followed by irradiation (10^4 Mrads), and after (3) irradiation followed by 500 thermal cycles. In each case the thermal cycles consisted of cycling the specimen between -156°C and 121°C using a 20-minute cycle period. The specimens that were thermally cycled only and thermally cycled and then irradiated had approximately 7 cracks/cm in the 0° and 90° directions. However, the specimen that was irradiated and then thermally cycled developed approximately 30 cracks/cm.

The effect of radiation on matrix microcracking was found to be even a worse problem in an elastomer-toughened 121°C epoxy system (CE 339). Exposure to 1 MeV electrons caused severe degradation of the matrix at moderate doses of radiation (ref. 5). At a total dose of 10^{10} rads the residual ultimate tensile strengths of irradiated fiber-dominated specimens were about 50 percent of those of unexposed specimens. Microcracking in irradiated and thermal cycled specimens was extensive. The elastomer used to toughen the matrix in this composite system was found to be extremely sensitive to radiation and underwent crosslinking at low (10^7 - 10^8 rads) total doses.

Figure 16
EFFECT OF THERMAL CYCLING ON CTE IN THE $0^\circ$ DIRECTION

During thermal cycling of graphite epoxy composites microcracking can result as illustrated in figure 16 from the combination of residual fabrication stresses and the thermal stresses induced by the mismatch in thermal expansion between the fibers and matrix and between adjacent plies of different orientations. Radiation damage to the resin matrix can further contribute to microcracking by creating low molecular weight polymer products which embrittle the matrix at low temperatures. The combined effect of thermal cycling and radiation damage on the CTE of a $[0, 90, 90, 0]$ T300/934 composite laminate is shown in figure 17. The composite was cycled up to 500 times between -156°C and 121°C in a baseline (or unirradiated) condition and after exposure to 1 MeV electrons for a cumulative exposure of $10^{10}$ rads. The CTE of the baseline material was essentially unchanged after 500 thermal cycles indicating that no significant damage was developed in the composite as a result of thermal cycling. However, the CTE of the irradiated composite laminate was substantially reduced by thermal cycling indicating development of damage in the composite.

X-ray microgradiography of the composites showed that the crack density in the $90^\circ$ plies was approximately 30 cracks/cm after 500 cycles. Microcracks in the $90^\circ$ plies reduce the CTE of the laminate in the $0^\circ$ direction because the $0^\circ$ plies have a more dominant role than when there are no cracks in the $90^\circ$ plies.

![Figure 17](image-url)
Radiation degradation of matrix resins combined with a cyclic thermal environment can affect the dimensional stability of polymer matrix composites in two ways. Radiation-induced chain scission can produce degradation products that plasticize the matrix at elevated temperatures which can change the way in which residual curing stresses are relieved in the composite, and degradation products can embrittle the matrix at low temperatures, resulting in matrix micro-cracking. Irradiation can also result in additional cross-linking which can embrittle the matrix resin.

Figure 18 shows the effects of radiation degradation products on the thermal expansion behavior (ref. 6) of a typical 177°C cure Gr/Ep composite ([0₂/90₂]₅ T300/5208). The irradiated specimen shows a pronounced nonlinearity at elevated temperature and a permanent negative residual strain of approximately -67×10⁻⁶ at room temperature after one thermal cycle to -157°C. Repeated cycles over the same temperature range give a strain response parallel to the unirradiated curve, but displaced by the permanent residual strain present after the first cycle. However, if the specimen was cycled to a higher maximum temperature, an additional change in slope of the thermal strain curve occurs which results in an additional permanent residual strain.

Figure 18
The elevated temperature nonlinear strain response and subsequent permanent residual strain at room temperature shown in figure 18 are related to radiation degradation products plasticizing the matrix and can be explained by the DMA results (ref. 7) presented in figure 19. The damping data for the irradiated composite show that the Tg is lowered by approximately 22°C and a broad "rubbery region" is produced compared to the unirradiated composite sample. During the thermal cycling tests the specimen was heated into the region where the matrix could flow, thus relieving residual tensile curing stresses resulting in a more fiber-dominated response at high temperature (nonlinear region) and permanent negative residual strains at room temperature. On subsequent thermal cycles no additional changes were measured. The reason for this behavior may be related to the procedure used to run the thermal expansion tests. The heating process in these tests occurred slowly in 22°C increments, with 30-minute holds at each temperature. In the 107°C-138°C temperature range, chemical changes apparently took place resulting in a movement of the "rubbery region" back to higher temperatures out of the thermal expansion test range. Thus on subsequent thermal cycles to the same temperature no additional changes were measured.

![Graph showing Young's Modulus and Loss Modulus](image)

Figure 19
Polymeric second-surface mirror coatings are so named because the reflecting coating is on the second surface (non-sun-facing side) of the polymeric film as illustrated in figure 20. To obtain a high reflectance (low solar absorptance) the polymeric film must be highly transparent to the solar spectrum from 250 to 3000 nanometers since sunlight passes through the film and is reflected back through the film into space. The reflecting coating is typically an opaque thickness of silver or aluminum with a thin over-coating of stainless steel to provide corrosion protection. An adhesive is applied to the stainless steel side of the SSM for bonding the SSM to a spacecraft.

Although the polymeric film is transparent in the solar wavelength region, it possesses infrared absorption bands characteristic to all polymers. These IR absorption bands give rise to the thermal emittance characteristics needed for this SSM to perform as a thermal control coating. As the thickness of the polymeric film increases, the emittance also increases to some limiting value near 0.9. Solar absorptances as low as 0.08 with emittance values of 0.92 have been obtained with polymeric second-surface mirror coatings.
Space durable polymeric films which have high optical transparency in the 300-600 nm range of the electromagnetic spectrum are needed for applications such as second-surface thermal control coatings, solar cell covers, and multilayer insulation blankets. Although several classes of polymers which are transparent/colorless are available, such as polyesters, aliphatic polyimides and FEP Teflon, these materials have limited long-term stability in the space environment, especially in orbits where high energy ionizing radiation is present. Aromatic polyimides have good toughness and flexibility, good thermal stability, high mechanical strength, and good radiation resistance but these polymers generally have poor transparency in the visible range. Commercial aromatic polyimide film is approximately 70% transparent (depending on thickness) in the 500 nm wavelength range which is the wavelength of interest for space applications. The transparency will also decrease with exposure time in space.

A new series of highly optically transparent linear aromatic polyimide films has been synthesized (refs. 8-9) with variations in the polymer molecular structure aimed at reducing electronic interactions between polymer chains to increase optical transparency. Polymerizations were performed with highly purified monomers with the result that several polymers were produced with good optical transparency compared to commercially available polyimide films such as Kapton as illustrated in figure 21. The more transparent films were evaluated for use in the space environment and typical results are shown in figure 22.
Several series of linear aromatic polyimide films have been synthesized and characterized.

**NEW MATERIALS DEVELOPMENT**

One of the most fundamental needs in new materials development is a clear definition of the material requirements (fig. 24) and the relative importance of each requirement. These requirements need to be as specific as possible. For example, simply to specify high strength and stiffness for structural composites is not very useful to the materials engineer. He really needs to have target mechanical, physical, optical, and electrical properties so that he can select the appropriate fibers, resins, layups, and coatings to achieve high stiffness, low CTE, good compressive strength, high resistance to thermal fatigue, low outgassing, and other critical properties as required. It is also important to define the service environment to insure that service life simulations are conducted in realistic exposure conditions. A fresh new look is needed to develop test standards for space qualification of materials for long-term (20-25 yrs.) service in space.

**Testing Issues**

- Mechanical, physical, optical property requirements
- Material property data base - What is required and when is it developed?
- Test standards - Are existing space qualification guidelines adequate?
Space durable polymeric films which have high optical transparency in the 300-600 nm range of the electromagnetic spectrum are needed for applications such as second-surface thermal control coatings, solar cell covers, and multilayer insulation blankets. Although several classes of polymers which are transparent/colorless are available, such as polyesters, aliphatic polyimides and FEP Teflon, these materials have limited long-term stability in the space environment, especially in orbits where high energy ionizing radiation is present. Aromatic polyimides have good toughness and flexibility, good thermal stability, high mechanical strength, and good radiation resistance but these polymers generally have poor transparency in the visible range. Commercial aromatic polyimide film is approximately 70% transparent (depending on thickness) in the 500 nm wavelength range which is the wavelength of interest for space applications. The transparency will also decrease with exposure time in space.

A new series of highly optically transparent linear aromatic polyimide films has been synthesized (refs. 8-9) with variations in the polymer molecular structure aimed at reducing electronic interactions between polymer chains to increase optical transparency. Polymerizations were performed with highly purified monomers with the result that several polymers were produced with good optical transparency compared to commercially available polyimide films such as Kapton as illustrated in figure 21. The more transparent films were evaluated for use in the space environment and typical results are shown in figure 22.
EFFECT OF ELECTRON RADIATION ON TRANSMISSION OF TRANSPARENT POLYIMIDE FILMS

Several series of linear aromatic polyimide films have been synthesized and characterized before and after simulated space exposure (ref. 10). To maximize optical transparency, highly purified monomers were used and several changes were made in the molecular structure to reduce the color intensity. The properties of the films were fully characterized including determination of glass transition temperatures (T_g), polymer decomposition temperature, transmission UV-visible spectra, infrared spectra, and solubility in selected organic solvents. Typical UV-visible spectra of the 6F-containing films before and after the films were exposed to 1 MeV electrons for a total dose of 5x10^9 rads representative of 20-25 years in an orbit in the trapped radiation belts such as Geosynchronous Earth Orbit (GEO) are shown in figure 22. Transmission spectra of 6F dianhydride-containing films are compared to commercially available Kapton H film. The 0.5-mil-thick films were approximately 95% transparent at 500 nm before electron exposure and were 85 to 91% transparent after exposure to 5x10^9 rads. The 6F+3,3'-ODA polyimide was especially radiation stable and showed only a 2% reduction in transparency at 500 nm after electron exposure. All of the films remained flexible after radiation exposure and no changes in molecular structure were detectable by Fourier transform infrared spectroscopy. The combination of good radiation (UV and electron) stability, good thermal stability, high optical transparency, and solubility make these polymers very attractive for space applications either as polymer films or spray coatings.

Figure 22
SPACE MATERIALS DEVELOPMENT

Space materials research and development is a continuing research thrust (fig. 23) within NASA. The objectives of this work are to develop new and improved materials for future NASA space science instruments and spacecraft for the civil space industry. The desire to increase design lifetimes combined with stringent requirements on precision, structural weight and performance have established guidelines for development of new long-life materials. However, materials development is a long-lead activity and requires long-range research programs to not only develop the materials but also conduct simulated space exposure testing to establish the long-term durability of these materials in the space environment. Short-term (2-3 yrs) "Advanced Development Programs" similar to that conducted for Space Station are not adequate to develop, test, and certify long-term space durability on new materials.

- NASA's charter is to develop technology to advance the civil space program
- NASA's customers are the civil space industry and space science community
- Materials focus should be on development of new and improved materials and long-life certification of selected existing materials
- Materials development needs to be a long-term continuing R&D effort - 2 to 3 years "Advanced Development Programs" are generally not adequate

Figure 23
NEW MATERIALS DEVELOPMENT

One of the most fundamental needs in new materials development is a clear definition of the material requirements (fig. 24) and the relative importance of each requirement. These requirements need to be as specific as possible. For example, simply to specify high strength and stiffness for structural composites is not very useful to the materials engineer. He really needs to have target mechanical, physical, optical, and electrical properties so that he can select the appropriate fibers, resins, layups, and coatings to achieve high stiffness, low CTE, good compressive strength, high resistance to thermal fatigue, low outgassing, and other critical properties as required. It is also important to define the service environment to insure that service life simulations are conducted in realistic exposure conditions. A fresh new look is needed to develop test standards for space qualification of materials for long-term (20-25 yrs.) service in space.

Testing Issues

- Mechanical, physical, optical property requirements

- Material property data base - What is required and when is it developed?

- Test standards - Are existing space qualification guidelines adequate?

Figure 24
LONG-LIFE CERTIFICATION

Established test procedures for long-life certification of space structures do not exist. Spacecraft have been designed and built for relatively short lifetimes, 3-8 years, based on limited test data. Nearly all of the environmental effects data in the literature are for exposure to a single environmental parameter such as ultraviolet radiation, electron radiation, micrometeoroid impact, etc. Very little combined exposure data exist. Also the chemical formulation of many of the polymers and composites of interest for space hardware have changed over the past decade.

For long-life (20-25 yrs.) certification acceleration methodologies (fig. 25) are required for realistic combined exposure conditions. These methodologies must be based on a fundamental understanding of damage mechanisms in the materials. Benchmark flight experiments are required to verify ground-based simulations to insure that damage mechanisms observed under accelerated exposure conditions are the same as produced in space. Space environmental effects testing is very time consuming and expensive and new approaches are required to insure that data generated on existing materials will be useful for certification of tomorrow's materials.

- Acceleration methodology - must be based on knowledge of damage mechanisms
- Benchmark flight experiments are required to verify ground-based simulations
- Long-life certification process must be cost effective - How do we accomplish this?

Figure 25
REFERENCES


