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MOLECULAR PROPERTIES OF POLYMERIC MATERIALS FOR SPACE APPLICATIONS

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INTRODUCTION

This report, covering the period 1 November 1989 to 15 April 1991, is divided into two sections: Section 1. Achievements (papers and talks) and 2. Summary of research activities.

1. ACHIEVEMENTS

The following publications were prepared under this cooperative agreement during the above period:

Kristen T. Kern, Edward R. Long, Jr., Sheila Ann T. Long, and Wynford L. Harries. "Effects of Electron Radiation and Thermal Cycling on Sized and Unsized Carbon Fiber - Polyetherimide Composites." Polymer Preprints, Vol. 31, No. 1, p. 611 (1990).

Phillip C. Stancil, Sheila Ann T. Long, Edward R. Long, Jr., and Wynford L. Harries. "Spectroscopic Techniques to Study Polymer-Atomic Oxygen Reactions for Low-Earth Orbit Simulations." Polymer Preprints, Vol. 31, No. 1, p. 570 (1990).

Kristen T. Kern, William G. Witte, Jr., Sheila Ann T. Long, and Wynford L. Harries. "Radiation and Vacuum Effects on Adhesive Materials in Bonded Joints." Engineered Materials Handbook Volume 3: Adhesives and Sealants. ASM International. p. 644 (1990).

Stephanie L. Gray, Kristen T. Kern, Sheila Ann T. Long, and Wynford L. Harries. "Improved Technique for Measuring Coefficients of Thermal Extension for Polymer Films." Proceedings of National Educators Workshop Update 90. NIST Special Publication 822 (1991).

Phillip C. Stancil, Edward R. Long, Jr., Sheila Ann T. Long, and Wynford L. Harries. "Effects of Atomic Oxygen on Two Polyimides and their Carbon-Fiber-Reinforced Composites." Polymer Preprints, Vol. 32, No. 1, p. 644 (1991).

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Kristen T. Kern, Edward R. Long, Jr., Sheila Ann T. Long, and Wynford L. Harries. "Effects of Radiation on the Glass Transition Temperature of Polyetherimide Resin in Composite Materials." Bulletin of the APS, Vol. 36, No. 3, p. 792 (1991).

Kristen T. Kern, Sheila Ann T. Long, Craig A. Hoogstraten, and Wynford L. Harries. "Mechanical and Molecular Properties of Epoxy-Based Materials for Space Applications." Accepted for publication in proceedings of "Space Radiation Effects on Materials, Devices, VLSI and Biosystems." March 18 to March 20, 1991 Hampton, Virginia.

Kristen T. Kern, Phillip C. Stancil, Edward R. Long, Jr., Sheila Ann T. Long, and Wynford L. Harries. "Simulated Space Environmental Effects on a Polyetherimide and its Carbon Fiber-Reinforced Composite." In preparation for submission to SAMPE Quarterly.

Kristen T. Kern, Craig A. Hoogstraten, William G. Witte, Jr., Sheila Ann T. Long, and Wynford L. Harries. "Effects of a Simulated Space Environment on Six Aerospace Adhesives." In preparation for publication as NASA Technical Paper.

The following presentations were given under this cooperative agreement during the above period:

Kristen T. Kern, Edward R. Long, Jr., Sheila Ann T. Long, and Wynford L. Harries. "Effects of Electron Radiation and Thermal Cycling on Sized and Unsized Carbon Fiber - Polyetherimide Composites." Annual Spring Meeting of the American Chemical Society, Boston Mass. April 23 to April 27 1990.

Phillip C. Stancil, Sheila Ann T. Long, Edward R. Long, Jr., and Wynford L. Harries. "Spectroscopic Techniques to Study Polymer-Atomic Oxygen Reactions for Low-Earth Orbit Simulations." Annual Spring Meeting of the American Chemical Society, Boston Mass. April 23 to April 27 1990.

Stephanie L. Gray, Kristen T. Kern, Sheila Ann T. Long, and Wynford L. Harries. "Improved Technique for Measuring Coefficients of Thermal Extension for Polymer Films." National Educators Workshop Update 90, Gaithersburg, MD November 13 to November 15, 1990.

Kristen T. Kern, Sheila Ann T. Long, Craig A. Hoogstraten, and Wynford L. Harries. "Mechanical and Molecular Properties of Epoxy-Based Materials for Space Applications." Conference: Space Radiation Effects on Materials, Devices, VLSI and Biosystems. March 18 to March 20, 1991 Chamberlain Hotel, Hampton, Virginia.

2. SUMMARY OF RESEARCH ACTIVITIES

This cooperative agreement was intended to investigate the effects of a space environment on the properties of polymeric materials. In addition, efforts have been made to understand and investigate environment simulation techniques and test methodology.

2.1 The Space Environment

Amongst the effects of the space environment which must be taken into consideration for polymers in Earth orbit are the effects of atomic oxygen (AO), the effects of energetic electrons, and the effects of thermal extremes. Atomic oxygen (AO) interacts with polymeric materials to cause effects which are characterized by a loss in polymer mass. Atomic oxygen is of particular concern for materials in low-Earth orbit (LEO). Energetic electrons may penetrate polymeric materials and cause chemical modification to their structure. Materials in Earth orbit may receive doses as high as 100 MGy during a 30-year mission. Temperature extremes, experienced by structures during their orbit, may cause microscopic mechanical damage to materials. Temperatures of materials in Earth orbit are expected to reach as high as 150 °F and as low as -150 °F.

2.2 Evaluation of Test Methodology

2.2.1 Analysis of Oxygen Plasma in a Radio-Frequency Discharge

An oxygen plasma created by a radio-frequency (RF) discharge was used to simulate the AO environment in LEO. Through the use of emission spectroscopy and transmission infrared spectroscopy of thin polymer resins, it was shown that AO in the neutral triple ground state $O(^3P)$ is the primary reactive species in the RF discharge as is observed in LEO. High resolution emission spectra also revealed the presence of O_2, H, N_2, OH and O_2+ and suggest that $O(^1D)$, $O(^1S)$, O+, N, and N+ do not exist in the discharge plasma. Identification of these species was instrumental in developing models of chemical reactions as discussed below.

2.2.2 Quantitative Dynamic Mechanical Analysis

The methods of data reduction used with Dynamic Mechanical Analysis (DMA) were investigated to further understand the temperature-dependant response of materials to low amplitude, periodic loading. Equations were derived which approximate the modulus for thin composite materials by using a no-shear bend approximation. These equations were used to develop software routines for analysis of DMA data using a microcomputer. These results have allowed the application of time-temperature superposition to analyze the DMA data for uni-directional composite materials.

2.2.3 Cure Monitoring via FDEMS

A frequency dependant electromagnetic sensor (FDEMS) was used to monitor the cure state of epoxy resins. The FDEMS uses a comb capacitor imbedded in the resin to determine the dielectric storage and loss constants of the resin. The cure state may be characterized by these values. Initial investigation indicated that the dielectric loss constant for a commercial epoxy resin, Fiberite 977-2, did not reach a constant value during the cure cycle. This indicates that complete cure was not achieved for a standard cure cycle. This type of result shows that use of FDEMS may allow the establishment of cure cycles which result in complete cure.

2.3 Evaluation of Polymer Performance in a Space Environment

2.3.1 Effects of Atomic Oxygen on Polymers

Emission spectroscopy has been used to identify reaction products from the exposure of polymers to AO. Three polymers were studied: polyetherimide (PEI), a 1-1 blend of LaRC thermoplastic polyimide and polyimidesulfone (LaRC-TPI:PISO2), and flouroethylenepropylene-polytetraflouroethylene (FEP-Teflon). The emission spectrum for PEI is shown in figure 1. The emission spectra for these polymers have indicated that the reaction products are mainly CO, CO2+, C2, OH, and H. Large molecules or chain fragments were not observed. The identification of these reaction products gives clues to the reaction mechanisms occurring. Reactivity of the polymer to AO can be measured by the emission intensity.

Two graphite fiber reinforced polymers were exposed to AO in the oxygen discharge. The systems studied were C6000/PEI and AS-4/LaRC-TPI:PISO2. Mass loss measurements and mechanical properties were studied. The results of these evaluations suggest that AS-4/LaRC-TPI:PISO2 is more resistant to AO than C6000/PEI. Changes in strength and strain properties may be explained primarily due to the loss of surface material. Infrared spectra indicate a loss of C=O bonds in PEI as a result of the AO exposure. Infrared spectra of LaRC-TPI:PISO2 suggested an increase in imide ring structures and therefore chain length due to an AO induced imidization reaction at the surface.

2.3.2 Effects of Electron Radiation and Thermal Cycling on Polymers

Six commercial structural adhesives were evaluated for use in a space environment. Glass transition temperatures (T_g) and single-lap-shear (SLS) strengths were found for each material in the following conditions: non-exposed, irradiated, thermal cycled, and irradiated and subsequently thermal cycled. In addition, spectroscopic techniques, infrared and ultra-violet, were used to characterize the changes in the materials. The SLS strengths at three temperatures for the adhesives are shown in figure 2. When tested at -150 °F, five of the six adhesives retained less than 52 percent of their room temperature SLS strength. Three of the adhesives also showed significant loss of SLS strength at 150 °F. The effects of simulated space environmental exposures on the SLS strengths of the adhesives is shown in figure 3. The SLS strength for irradiated EA 934NA was greater than the SLS strength for non-exposed EA 934NA. Radiation had the opposite effect on FM300M, while the remaining four adhesives were not affected by the irradiation. Thermal cycling had little effect on the adhesives. Exposing the adhesives to radiation and then to thermal cycling resulted in large losses of SLS strength for five of the six adhesives. Only EA 934NA was not affected by the sequential exposure. Investigation of T_g's for the adhesives indicated that three of the adhesive systems were found to form additional crosslinks as a result of the irradiation.

C6000/PEI was studied for effects due to electron radiation and thermal cycling. These studies also provided the opportunity to investigate the fiber-polymer interface properties of the material. The three-point flexural test, DMA, and interlaminar shear test were used to characterize the materials. As shown in figure 4, the use of fiber sizing resulted in lower flexural modulus values, regardless of the direction of the fibers with respect to the test loading. The results of the study on the exposed material suggest that thermal cycling may improve the interfacial properties of these fiber-polymer systems, as is evident from the data in figure 5. The glass transition temperature of the materials indicated no significant effects for doses of 75 MGy and less. See Figure 6. However, the transition temperature for materials exposed to a 100 MGy dose was distinctly higher than the transition temperature for the non-irradiated material. A higher transition temperature indicates an greater density of chemical crosslinking in the polymer portions of the material.

3. CONCLUSIONS AND RECOMMENDATIONS

The results of this cooperative agreement identified the changes in the properties of six aerospace structural adhesives, three neat high polymers, and two fiber-reinforced polymers, as caused by exposure to four simulated space environmental conditions. Significant property changes occurred for several of the systems as a result of one or more of the exposures. The following are the most significant results of this research:

1. Emission spectra of an RF discharge plasma can be used to identify the reactive species in the plasma.

2. Dielectric cure monitoring using FDEMS has indicated that a standard cure cycle for an epoxy resin did not fully cure the epoxy.

3. Emission spectroscopy was used to identify the reaction products for three polymers in an atomic oxygen environment.

4. Changes in the strength and strain properties of C6000/PEI composite materials resulting from AO exposure are primarily

due to loss of surface material.

5. Five of six epoxy-based adhesive materials investigated showed significant loss of strength when tested at -150 °F. Similar loss of strength occurred for three adhesives when tested at 150 °F.

6. Radiation exposure followed by thermal cycling resulted in significant loss of strength in five of six adhesives investigated.

7. C6000/PEI composite materials made with epoxy fiber sizing had mechanical properties which were inferior to those for C6000/PEI composites made with no fiber sizing.

8. Changes in the T_g of PEI in C6000/PEI composites do not occur linearly with absorbed radiation dose, but rather appear to have a threshold dose in the 75- to 100-MGy range above which the T_g of irradiated materials is higher than the T_g of non-exposed material.

Based on these results the following recommendations are made:

1. The dependance on temperature of the strength of the adhesive materials should be further investigated to determine temperature ranges for nominal adhesive performance.

2 The effects of radiation followed by thermal cycling on adhesively bonded aluminum-to-composite joints should be studied to determine the mechanisms for the large loss in SLS strength observed for the materials in this study.

3. Further investigations of the mechanisms for radiation-induced crosslinking in PEI which may lead to new models for radiolysis kinetics should be conducted.

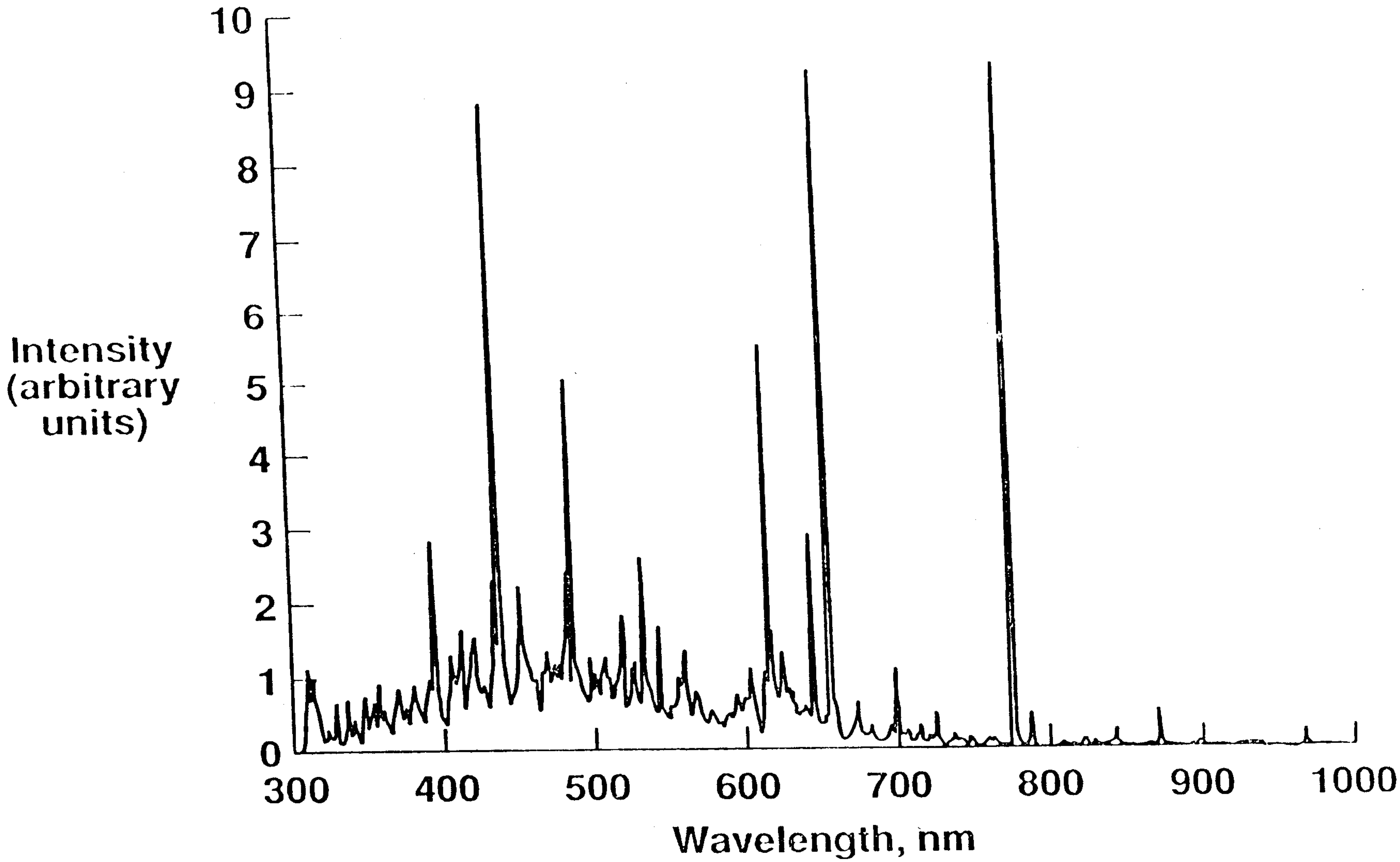

Figure 1. Emission spectrum of PEI film in RFGD.

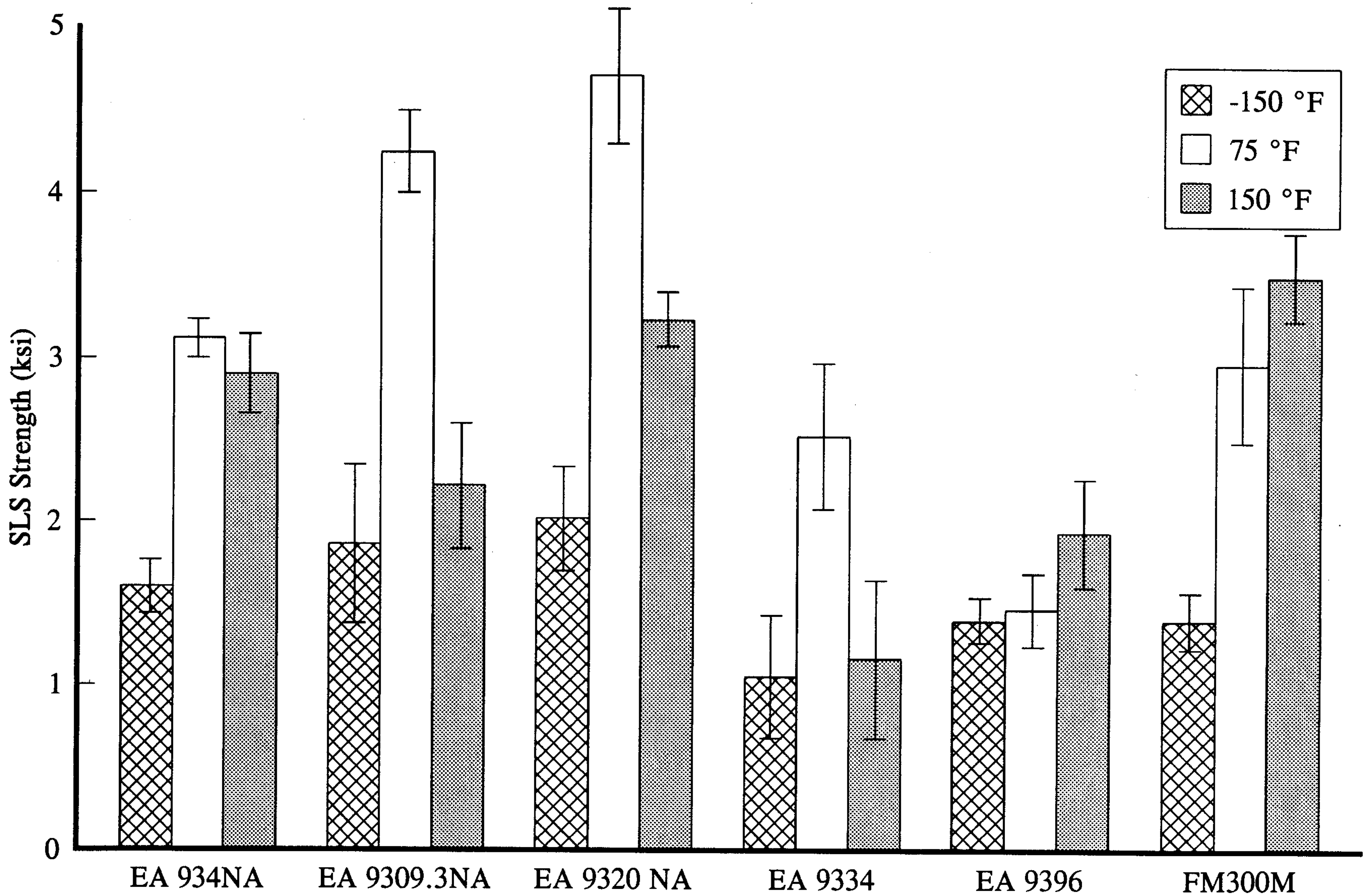

Figure 2. SLS strength at three temperatures for aluminum-to-composite SLS specimens.

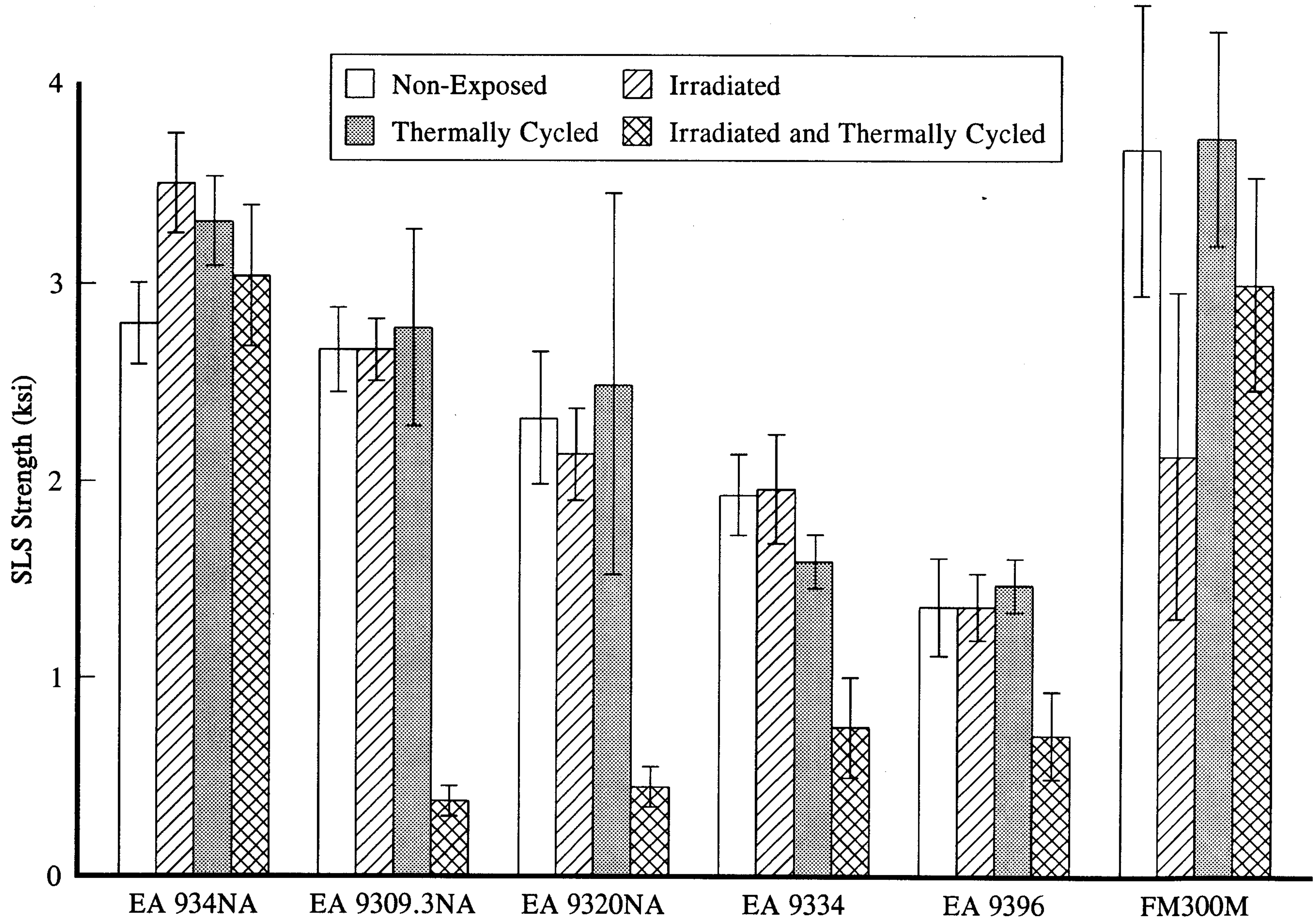

Figure 3. SLS strengths for MSLS specimens exposed to simulted space environmental conditions.

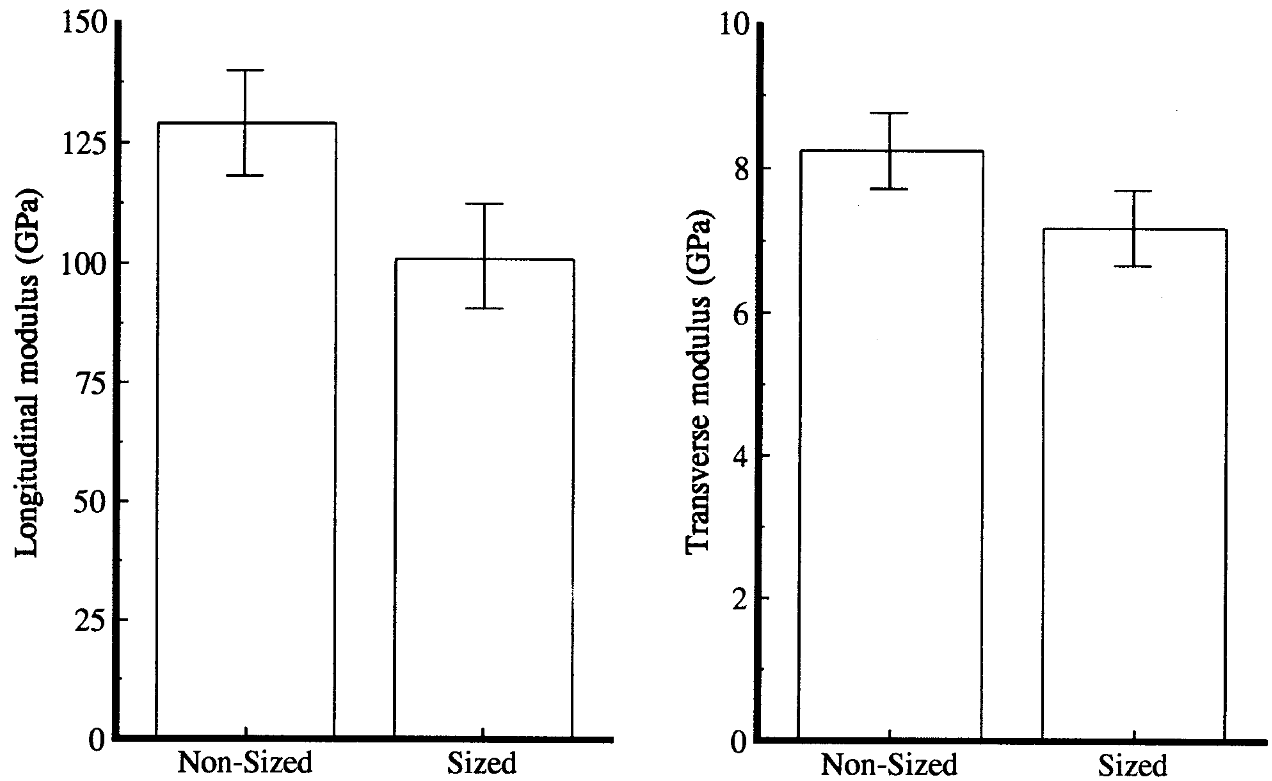

Figure 4. Flexural modulus for carbon fiber-reinforced Ultem. Modulus values in chart A are for longitudinally oriented fibers, while those in chart B are for transversely oriented fibers. The left-hand bar in each chart is for material made with non-treated fibers, while the right-hand bar is for material made with fibers pretreated with an epoxy sizing.

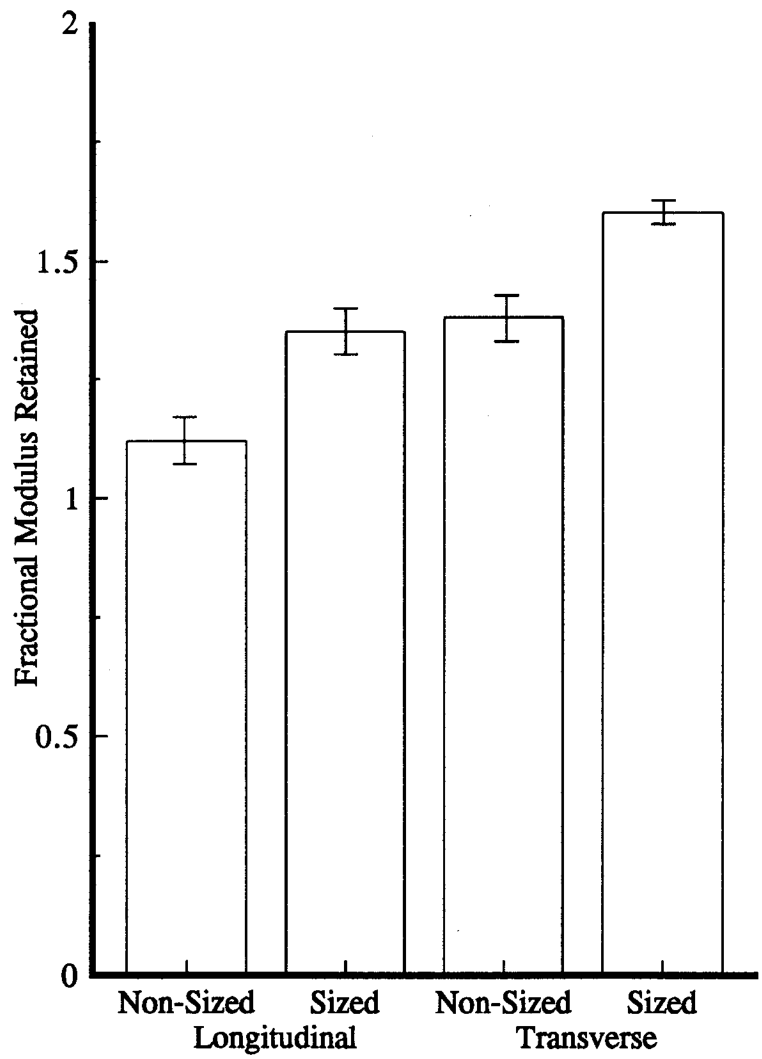

Figure 5. Longitudinal and transverse flexural modulus values for thermally cycled carbon fiber-reinforced Ultem with non-sized fibers and with sized fibers. Modulus values have been normalized to their respective non-exposed values.

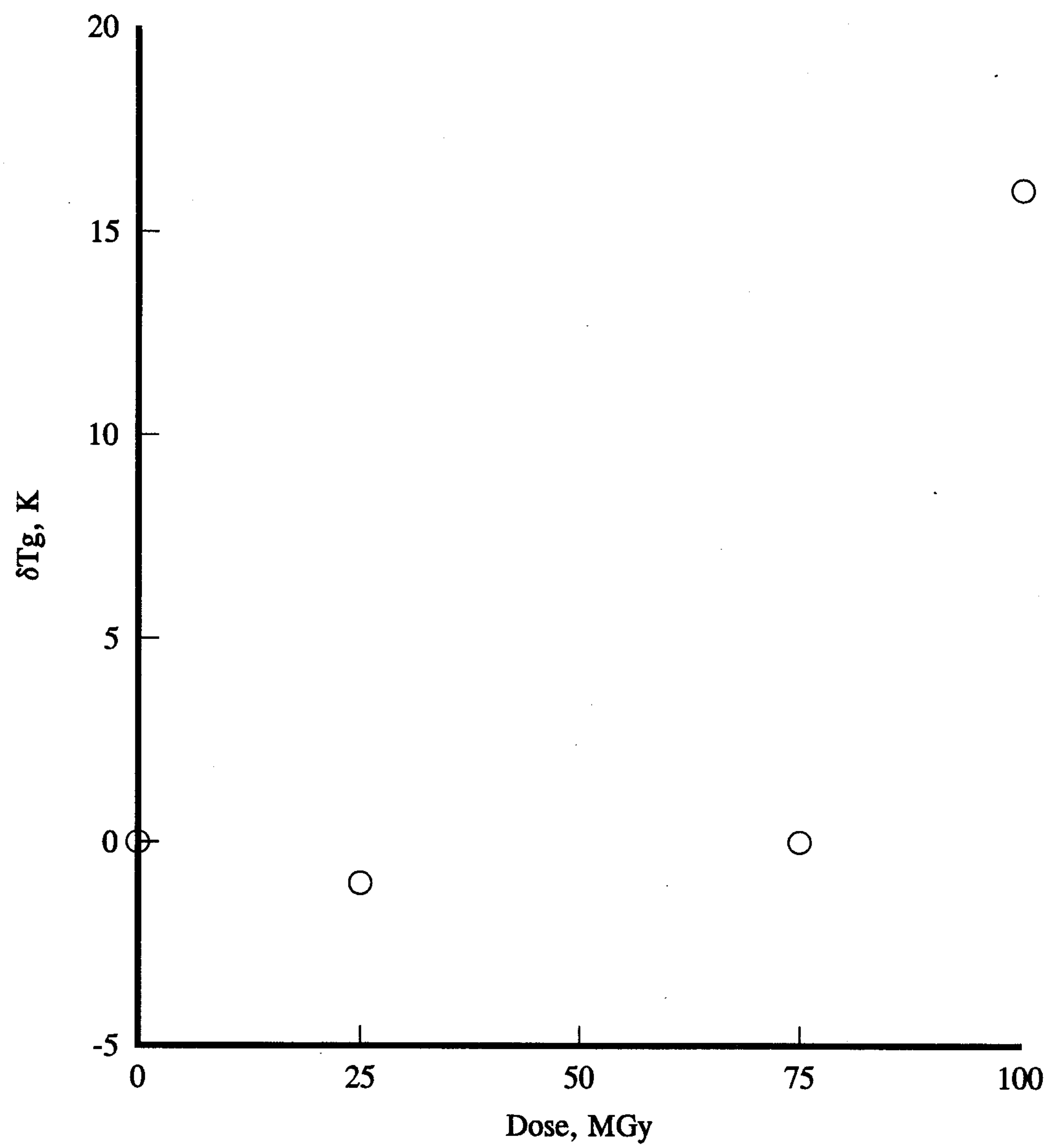

Figure 6. Change in Tg as a function of dose for C6000/PEI with non-sized fibers.