*Thermochimica Acta*, 192 (1991) 199–208
Elsevier Science Publishers B.V., Amsterdam



# Effect of electron radiation on polymer matrix systems [a]

Gregory S. Hickey

*Space Material Sciences and Engineering Section, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109 (USA)*

(Received 2 January 1991)

**Abstract**

The use of graphite–polymer composite materials in space is increasing in the number of applications and system requirements. A primary concern for any polymeric material for use in space is its environmental durability, particularly its mechanical properties. One well-documented space environmental concern is degradation by electron radiation because electrons have a high penetration ability and high natural flux rate in the space environment near the earth. Three polymer composite matrix systems were evaluated: a styrene butadiene rubber (SBR) toughened polycyanate, a carboxy terminated butyl nitrile (CTBN) toughened epoxy and a PES toughened epoxy/dicyanate. The resin systems were evaluated at electron radiation levels of zero control, 10 Mrad and 1000 Mrad total dose to evaluate changes in their glass transition, linear thermal expansion and dynamic modulus. Properties of the pure matrix were measured from $-100\,^{\circ}C$ to the glass transition temperature.

## INTRODUCTION

Polymer–matrix composites are being used in space applications because they offer high specific strength and stiffness, a designable low thermal expansion, and intrinsic damping properties. Future projects include the deployment of large precision space structures, antennas and reflectors with mission lives of 10–20 years. For example, the Precision Segmented Reflector (PSR) program is addressing the development of structural composite mirrors for space based submillimeter astronomy [1]. Such future space structures must exhibit long term dimensional stability to environmental conditions such as the radiation environment, wide thermal extremes and thermal cycling. The thermal extremes can induce microcracking in fiber reinforced composites. To minimize this, toughened polymeric systems were chosen as the baseline. One specific environmental concern is the effect of electron radiation on polymers because electrons are known to penetrate

[a] Presented at the 19th Annual NATAS Conference, Boston, MA, 23–26 September 1990.

into exposed polymer matrix systems and affect their thermal, mechanical and viscoelastic properties.

Several researchers have studied the effect of electron radiation on epoxy systems, and have found that electron radiation does not induce changes in the chemistry or mechanical properties of these systems except at doses above 100 Mrad. Below this threshold it is typically the toughening phase which undergoes degradation [2–4]. The combination of electron radiation and thermal cycling that would be expected in a low earth orbit (LEO) or geosynchronous orbit (GEO) has also been shown to induce microcracking in fiber reinforced composites. This produces mechanical and dimensional instability [5,6]. This study will look at alternatives to the traditional epoxy and toughening systems.

The level of accumulated radiation exposure for exposed materials in space will vary significantly depending on the orbit altitude and inclination [7]. Annual doses of natural trapped electron radiation can reach a maximum of 100 Mrad at an altitude of 1100 miles. The radiation decreases non-linearly to an annual radiation level of about 1 Mrad at 3500 miles altitude. Since many preferred orbits are elliptical and radiation levels vary seasonally, representative levels were chosen for this work. Electron radiation dosages of 10 and 1000 Mrad were chosen for comparative dose levels. These are expected to represent typical dose level extremes for one and ten years in a high LEO orbit.

## EXPERIMENTAL

The resin systems evaluated in this study include two developmental resins and one commercial resin. The first resin is a 175 °C cure, 230 °C postcure polycyanate resin with 5% styrene butadiene rubber (SBR) as a submicron domain-toughening phase. The second resin is a 121 °C cure 5% carboxy terminated butyl nitrile (CTBN) modified diglycidylether of bisphenol-A (DGEBA) epoxy. The third resin is a 175 °C cure 25% epoxy/75% dicyanate with 8% precipitated 10–20 $\mu$m PES as the toughening phase.

The experimental tests included in this study were differential scanning calorimetry (DSC) to measure changes in glass transition temperatures ($T_g$), thermal expansion, and dynamic tensile modulus. The DSC measurements were effected using a DuPont 910 DSC. Scans were made from −150 °C to 300 °C at a heating rate of 10 °C $min^{-1}$ under dry nitrogen. The thermal expansion measurements were carried out on a DuPont 943 thermal mechanical analyzer (TMA) using a macro probe. Scans were completed at 5 °C $min^{-1}$ from −100 °C to 100 °C under dry nitrogen. The dynamic modulus was measured using an IMASS dynastat. The dynamic modulus resin samples were tested under 1 kg tensile load with a 1 kg dynamic load. The samples were measured from −100 °C up to room temperature under dry nitrogen. The dynastat was chosen to evaluate the modulus of the resin

systems because it has been shown at low frequencies to give a true Young's modulus [8].

The resin castings were cured under 80 p.s.i.g. pressure and under vacuum. The castings were irradiated at the Jet Propulsion Laboratory under high vacuum using their Dynamatron accelerator. A description of the facility is included in the work by Anspaugh [7]. During the irradiation, the samples were maintained at 20 °C. Visually, the radiation discolored all of the resin castings, with the CTBN–epoxy and PES–epoxy–dicyanate turning black at 1000 Mrad. The 1000 Mrad exposed casting of the CTBN–epoxy was extremely brittle and was untestable for dynamic modulus.

## RESULTS

The chemical stability of the resin systems can be investigated by DSC. A summary of the changes in the glass transition temperatures as the result of electron radiation is shown in Fig. 1. Scans on all of the as-cured samples showed that the resin systems were all completely cured. The SBR–polycyanate resin showed no changes in its glass transition at 10 Mrad, but showed an increase in $T_g$ from 230 °C to about 280 °C at 1000 Mrad. The PES–epoxy–dicyanate shows the same stability of the glass transition at 10 Mrad, but a decrease in $T_g$ from 175–87 °C at 1000 Mrad. The CTBN–epoxy was the most affected by electron radiation. It showed a 10 °C decrease in its glass transition at 10 Mrad to 115 °C, and a 70 °C decrease in its glass transition temperature to 51 °C at 1000 Mrad dosage.

Figure 2 presents the average coefficients of thermal expansions for the three systems from −50 °C to 50 °C. Figures 3–5 show the TMA scans for the three systems. Note that the scans have not been normalized for differences in the sizes of specimens, therefore the slopes do not correspond directly with the coefficient of thermal expansion (CTE). The SBR toughened polycyanate was the most stable of the three resin systems at 10 and 1000

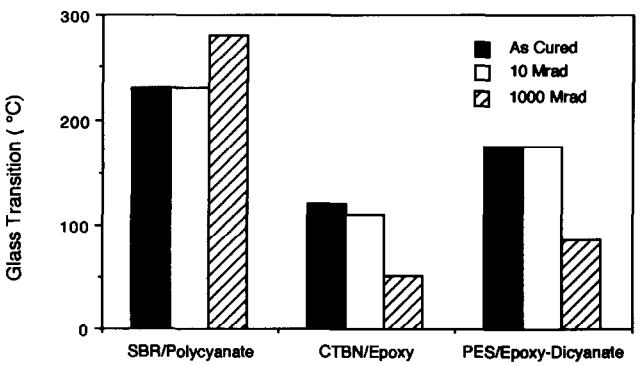


Fig. 1. Glass transition temperatures for the resin systems as a function of radiation exposure.

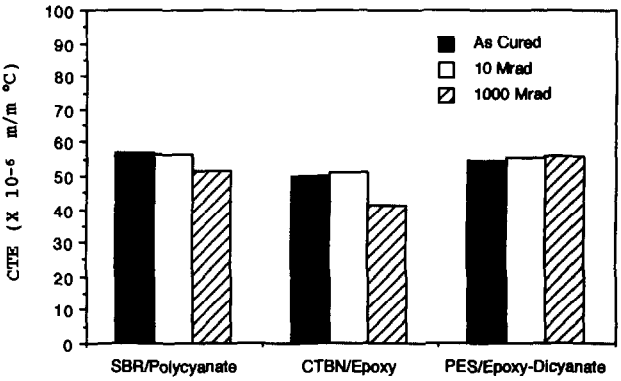


Fig. 2. Average coefficients of thermal expansion from −50 °C to 50 °C.

Mrad levels in that its thermal expansion remained linear over the 200 °C temperature range. The PES–epoxy–dicyanate was next; its thermal expansion remained linear at 10 Mrad exposure, but there was a slowly increasing non-linear expansion from room temperature up to 100 °C. This averaged out to a small net average change. The CTBN toughened epoxy was non-linear, showing an increase in expansion at 10 Mrad followed by a decrease at 1000 Mrad. This behavior for epoxides has been seen before in irradiated DGEBA epoxides, and has been related to scission within the polymer matrix followed by crosslinking [3].

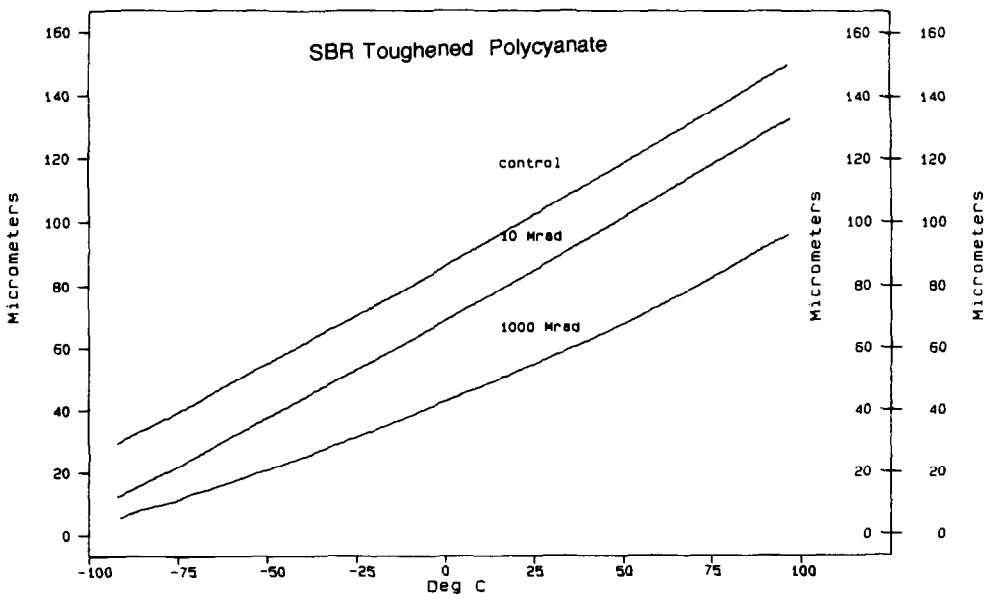


Fig. 3. Thermal expansion of SBR–polycyanate as a function of radiation exposure.

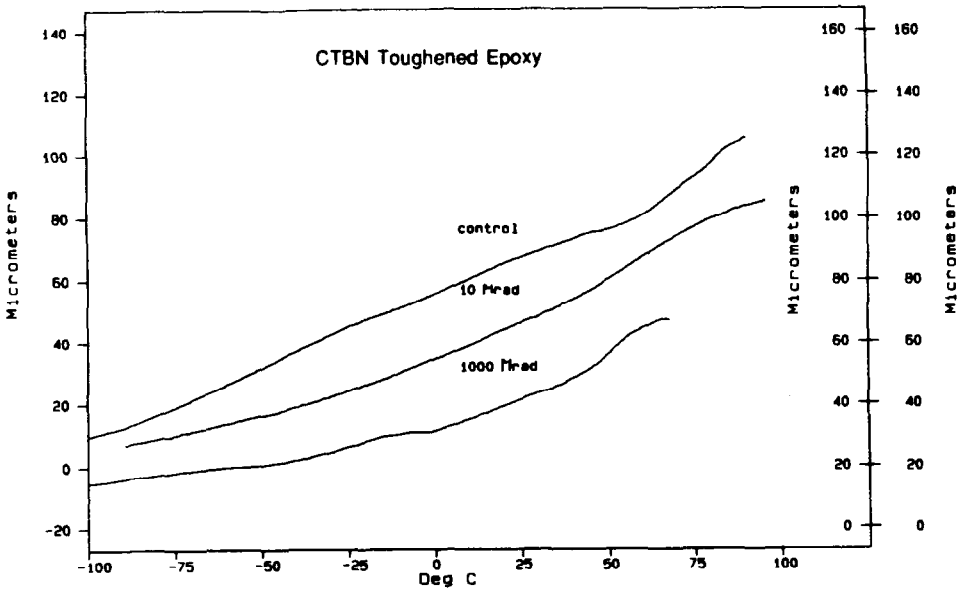


Fig. 4. Thermal expansion of CTBN–epoxy as a function of radiation exposure.

Table 1 gives a summary of the dynamic mechanical properties for the three resin systems at 1 Hz and at −50° C. This was chosen as a representative temperature for comparison because there were no transitions for any of

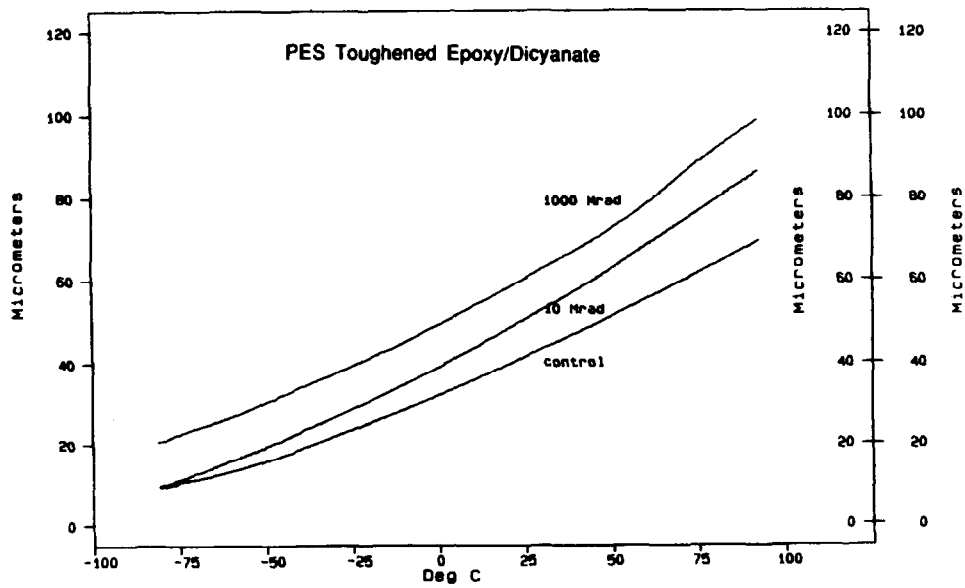


Fig. 5. Thermal expansion of PES–epoxy–dicyanate as a function of radiation exposure.

TABLE 1

Dynamic mechanical properties of matrix systems. The values in parentheses represent the percentage difference compared with the control value.

| Electron radiation level | SBR–polycyanate | CTBN–epoxy | PES–epoxy–dicyanate |
|---|---|---|---|
| | Modulus (MPa) | | |
| Control | 3044– | 4020– | 4269– |
| 10 MRad | 3008 (−1.19%) | 3792 (−5.67%) | 4134 (−3.17%) |
| 1000 MRad | 3706 (+21.8%) | – [a] | 4224 (−1.05%) |
| | Loss modulus (MPa) | | |
| Control | 56– | 100– | 750– |
| 10 MRad | 54 (−2.71%) | 83.4 (−16.5%) | 725 (−3.37%) |
| 1000 MRad | 393 (+60.2%) | – [a] | 1039 (+38.5%) |
| | Loss factor | | |
| Control | 0.0183 | 0.0250 | 0.1739 |
| 10 MRad | 0.0180 | 0.0220 | 0.1782 |
| 1000 MRad | 0.1067 | – [a] | 0.2538 |

[a] Untestable

the resin systems at this temperature, and this is an expected operational temperature for composite structural materials in a space environment. The modulus was a function of both temperature and frequency. There was a weak dependence on frequency for all resins, with the modulus increasing with frequency. Figures 6–8 present the temperature dependent complex dynamic modulus for the three systems at the three radiation levels.

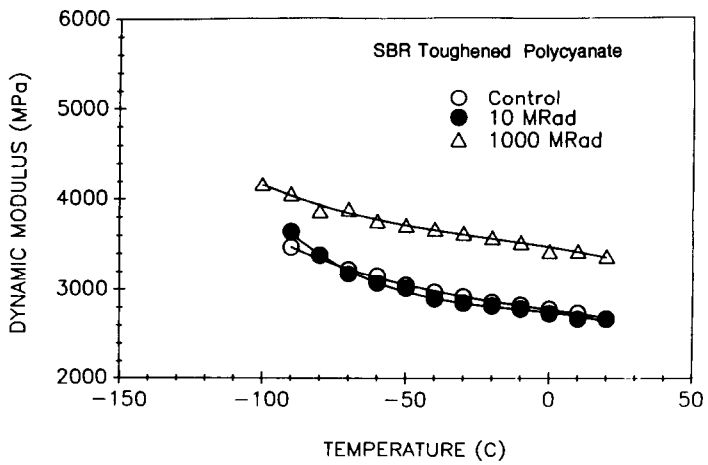


Fig. 6. Temperature dependent dynamic modulus of SBR–polycyanate as a function of radiation exposure.

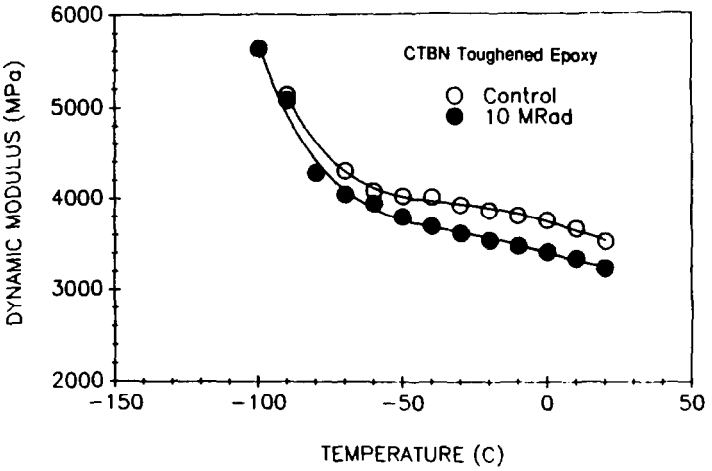


Fig. 7. Temperature dependent dynamic modulus of CTBN–epoxy as a function of radiation exposure.

The PES–epoxy–dicyanate was the most stable in terms of modulus at the cryogenic temperatures of the three systems. As seen in Fig. 8, it showed no significant degradation in dynamic modulus at any of the radiation levels. Variations of the dynamic modulus at the three radiation levels are within the accuracy and repeatability of the experimental test procedure. The SBR–polycyanate showed the same stability in dynamic modulus up to 10 Mrad. Its temperature dependent dynamic modulus is shown in Fig. 6. At the 1000 Mrad level the modulus increases at all temperatures for the PES–polycyanate. The CTBN–epoxy was the least stable of the three resins.

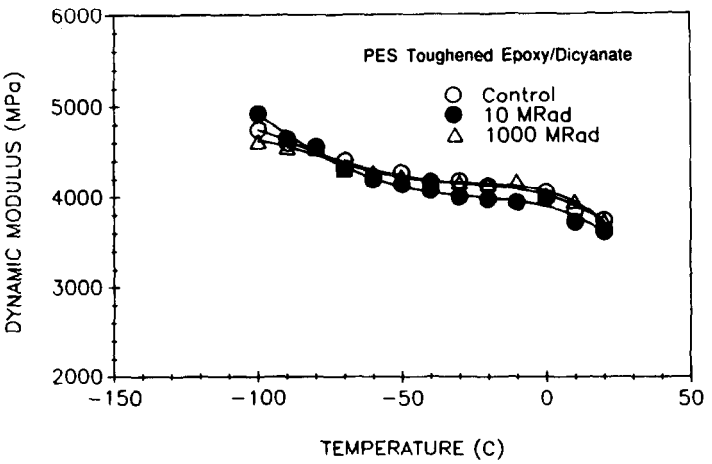


Fig. 8. Temperature dependent dynamic modulus of PES–epoxy–dicyanate as a function of radiation exposure.

As presented in Fig. 7, it showed degradation in dynamic modulus at 10 Mrad and was too brittle to be tested at 1000 Mrad exposure. The secondary transition relating to the CTBN for this system was quite apparent as a peak in the loss factor at $-65\,^{\circ}C$. Below the glass transition temperature of the toughening phase, the modulus of the resin system increased dramatically as the temperature was reduced. For the PES toughened matrix system, the glass transition for PES was below the evaluated temperature range.

## DISCUSSION

This work shows that the elastomer constituents of toughened polymer matrix systems are the most susceptible to degradation by electron radiation. The use of PES, a thermoplastic, is an improvement over the traditional elastomeric CTBN without sacrificing toughness. The CTBN elastomer is an unsaturated rubber polymer. It has been documented that CTBN has a threshold of first signs of degradation of electron radiation of $5 \times 10^5$ rad and a 25% decrease in properties at $10^9$ rad exposure level, whereas DEGBA epoxides do not start to show degradation in strength until 100 Mrad electron irradiation [9]. It is not surprising that ionizing radiation should diminish the physical and mechanical properties of the CTBN at 10 Mrad exposure. Cyanates perform as well as or better than standard epoxides in processing and general mechanical properties. They have an inherent advantage for vacuum applications over epoxides in that they have significantly less moisture absorption. This provides greater dimensional stability for composites that are used in a space environment. This improved dimensional stability comes from a minimum of hysteresis effects due to the outgassing of absorbed moisture.

Of the three resin systems, the PES–epoxy–dicyanate was the most stable as regards thermal expansion and dynamic modulus at cryogenic temperatures from degradation by electron ionizing radiation. Although the dynamic modulus did not vary by more than 3.2% from control at the highest radiation levels, dynamic testing did produce information as to how the resin was affected. For this system there was a small decrease in the loss modulus at 10 Mrad followed by a significant increase at 1000 Mrad exposure. This is shown in the loss factor as an increase in the ratio of loss modulus to the storage modulus at the two radiation exposure levels. Physically, this may be representative of the degradation of the secondary toughening phase. It should also be noted that this resin system has a significantly higher loss factor than the other two systems. The greater loss factor is directly related to improved damping ability of the resin.

The SBR toughened polycyanate was the second most stable of the three systems. It showed essentially no change at 10 Mrad but a marked increase in modulus at 1000 Mrad exposure. Along with the increase in the storage modulus, there was an order of magnitude increase in the loss factor,

resulting in an increase in the order of magnitude of the loss factor. No information was available for threshold levels for changes in the mechanical properties for the PES, but it is expected to have at least an order of magnitude higher threshold than that of the CTBN or SBR rubber because of its lack of unsaturated double bonds. Similarly, no data for electron radiation stability were available for the developmental polycyanate or epoxy–dicyanate resins without an elastomic phase.

The CTBN toughened epoxy was the least stable of the three systems. It showed a decrease in modulus at 10 Mrad exposure and was too brittle to be evaluated at 1000 Mrad. Because of the low threshold for decrease in strength for CTBN by electron radiation this was not unexpected. The decrease in dynamic modulus with radiation also produced a 3–5 °C decrease in its secondary glass transition temperature at 10 Mrad exposure.

For the SBR–polycyanate there was no change in the glass transition at 10 Mrad exposure, followed by an increase at the 1000 Mrad exposure level. This trend was observed in its measured dynamic modulus and CTE. At 10 Mrad there was no significant change in dynamic modulus or CTE. At 1000 Mrad exposure the dynamic modulus increased and the matrix thermal expansion decreased. These three trends for this system imply that it is unaffected at 10 Mrad, but that the matrix system has undergone some increased level of crosslinking at the 1000 Mrad exposure level. The PES–epoxy–dicyanate showed stability in its cryogenic modulus and thermal expansion at both 10 and 1000 Mrad radiation levels. This system exhibited a stable glass transition temperature at 10 Mrad, followed by a decrease in $T_g$ at 1000 Mrad. At temperatures approaching the $T_g$ of the 1000 Mrad exposed material, the irradiated polymer showed a non-linear increase in thermal expansion. The CTBN–epoxy system did not follow these trends, becoming grossly discolored and brittle at 10 Mrad, and difficult to handle and test at 1000 Mrad.

This level of evaluation of the polymer matrix systems serves as a first level screening in the development of new resin systems for space applications. The effect of radiation on the thermal and mechanical properties of the matrix systems will serve as an indication of how the matrices will perform in a fiber reinforced composite. At the composite level, concerns for microcracking, thermal cycling and degradation of the fiber–matrix interface need to be considered. Matrix systems which have a tendency to become brittle would be expected to perform poorly with regard to these concerns. From this work it appears that PES toughened matrix systems are an improvement over CTBN and SBR toughened systems in terms of stability in a radiation stressful environment.

## CONCLUSION

The SBR toughened polycyanate and PES–epoxy–dicyanates are both improvements over rubber toughened epoxides for space application. The

unsaturated rubber elastomers are susceptible to ionizing electron radiation at exposure levels that would be expected to be seen in a long duration mission. While the level of degradation does not reach the point of failure, it could affect structures and instrumentation that require a high level of dimensional stability.

ACKNOWLEDGMENT

Research described in this paper was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

REFERENCES

1 R. Freeland, P. McElroy, M. Paul and R. Johnston, Technical approach for the development of structural composite mirrors, SPIE Conference on Active Optical Systems, Orlando, FL, March 1989.
2 G. Sykes and D. Bowles, SAMPE Q., 17 (4) (1986) 39.
3 T. Wilson, Radiation effects on the dynamic mechanical properties of epoxy resins and graphite/epoxy composites, Ph.D. Dissertation, North Carolina State University, Raleigh, 1986.
4 S. Egusa, J. Mech. Behav. Mater., 1 (1988) 1.
5 D. Tenny and W. Slemp, Radiation durability of polymeric matrix composites, Effects of Radiation on High Technology Polymers, ACS, Washington, DC, 1989.
6 N. Takeda, M. Tahdoh and K. Kahashi, SAMPE Q. 20 (1) (1989) 27.
7 B. Anspaugh, Jet Propulsion Laboratory Solar Cell Radiation Handbook, JPL Publ. 82-069, Pasadena, CA, 1982.
8 G. Hickey, Dynamic mechanical evaluation of a rubber toughened graphite–epoxy with application for laminate analysis, North American Thermal Analysis Society Meeting, San Diego, CA, 1989; Thermochim. Acta, 166 (1990) 145.
9 M. Bruce and M. Davis, Radiation Effects on Organic Materials in Nuclear Plants, Electric Power Research Institute Rep. NP-2129, 1981.