Electron Radiation Effects on the Thermal Expansion of Graphite Resin Composites

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The effects of 1 MeV electron radiation on the thermal expansion characteristics of two graphite reinforced resin matrix composite systems were studied. Specimens of both graphite/epoxy (T300/5208) and graphite/polyimide (C6000/PMR15) were irradiated to a total dose of 6×10^9 rads at two different rates. Unidirectional, cross-ply, and quasi-isotropic laminate configurations were examined. Thermal expansion measurements were made with a laser interferometer over the temperature range of $-250°$ to $+280°$F. Dynamic mechanical analysis (DMA) tests were performed to study changes in resin chemistry. Thermal expansion results indicate that radiation did produce permanent residual strains of up to -70×10^{-6} for the graphite/epoxy when exposed to temperatures up to $+280°$F. However, no permanent changes in the coefficient of thermal expansion (CTE) were observed. No permanent residual strains or changes in the CTE attributable to radiation were observed for the graphite/polyimide specimens. No significant effects of radiation dose rate on the thermal expansion of either composite system were observed. DMA results indicate that electron radiation caused chemical changes in the epoxy matrix. These changes resulted in a lower glass transition temperature and a broader "rubbery region" which extended into the temperature range of the thermal expansion tests.

Introduction

GRAPHITE reinforced resin-matrix composites are currently being used to build space structures that require a high degree of dimensional stability, such as large communications antennas. Composites are selected because of their light weight, high stiffness, and low thermal expansion, as compared to more conventional aerospace metallic materials. The effects of the space environment on these materials is an important consideration, especially for long-life space missions of ten to thirty years. The space environment includes high vacuum, possible repeated thermal cycling between $-250°$ and 300°F, and radiation. Structures in a geosynchronous orbit (GEO) can receive doses of high energy electrons and protons, with the total dose reaching approximately 1×10^{10} rads, over a thirty-year exposure. All of these environmental factors can affect the material properties of the composite and/or cause permanent dimensional changes. These changes can have a significant effect on the performance of space structures designed to be dimensionally stable.

Research has been conducted to study the effect of thermal cycling[1-3] on the thermal and mechanical properties of resin/matrix composites. The effects of radiation on the mechanical properties of composites has also been studied.[4-6] However, only a limited amount of research has been directed at determining the effect of radiation on the thermal expansion properties of composites.[7,8] In these studies, the effect of radiation was reported on only the coefficient of thermal expansion, not on the total thermal expansion characteristics of the material.

The purpose of the current research was to study the effect of high energy (1 MeV) electron radiation on the subsequent thermal expansion characteristics of two graphite reinforced resin matrix composite systems. The two systems selected were graphite/epoxy and graphite/polyimide. Specimens were irradiated to a total dose of 6×10^9 rads at rates of 6×10^7 rads/h and 3×10^7 rads/h. Thermal expansion measurements, as well as dynamic thermal mechanical analysis (DMA), were used to detect and understand the effects of radiation on these two composite systems.

Identification of commercial products is provided in this paper in order to adequately describe the materials; it does not constitute official endorsement by NASA, expressed or implied, of such products or manufacturers.

Experimental Procedure

Materials

Panels of both T300/5208 graphite/epoxy and C6000/PMR15 graphite/polyimide were fabricated from prepreg tape and autoclave processed according to the manufacturer's recommended procedures. The 5208 (Narmco Corporation) system is a 350°F cure epoxy resin and the PMR15 system is a 600°F cure polyimide resin. Both the T300 (Union Carbide Corporation) and C6000 (Celanese Corporation) are high strength PAN (polyacrylonitrile) based graphite fibers. All of the panels were ultrasonically examined (c-scanned) after fabrication to assure a consistent high level of quality. The fiber volume contents for the T300/5208 and C6000/PMR15 panels, determined from ASTM Standard D3171-76,[9] were 70 and 69 percent, respectively, with panel thicknesses of approximately 0.04 and 0.05 in., respectively.

The four laminate configurations studied were unidirectional ($[0_8]$), cross-ply ($[0_2/90_2]_s$), and quasi-isotropic ($[0/45/90/-45]_s$, $[0/\pm45/90]_s$). The $[0_8]$, $[0_2/90_2]_s$, and $[0/45/90/-45]_s$ configurations were used for thermal expansion measurements, and the $[0/\pm45/90]_s$ configuration was used for the DMA tests. Specimens were machined from 1-ft square panels before irradiation and divided into the following three groups: baseline (no radiation); 6×10^9 rads total dose (100-h exposure); and 6×10^9 rads total dose (200-h exposure).

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Radiation Exposure

Specimens were irradiated uniformly through the thickness and over the surface with 1 MeV electrons at two dose rates, as indicated above. A dose rate of about 6×10^7 rads/h was the highest rate that could be used without exceeding a specimen temperature of 100°F during the total exposure. A dose rate of 3×10^7 rads/h was selected to investigate the effect of dose rate on the materials. This rate resulted in a 200-h exposure which was within the practical operating envelope for the radiation facility. The irradiation occurred in a clean high vacuum stainless steel chamber at pressures of 10^{-7} Torr or lower. The specimen mounting plate was cooled during the radiation exposure, and specimen temperatures did not exceed 100°F for the two dose rates used in this investigation. All specimens were vacuum dried at 120°F to a constant mass prior to radiation exposure.

Thermal Expansion Measurements

Thermal expansion measurements were made with a laser interferometer dilatometer specifically developed for measuring small thermal strains in composites.[10] The specimen geometry is shown in Fig. 1. The strain resolution with this geometry is approximately 1×10^{-6}. The repeatability of this equipment has been shown to be approximately $\pm 3 \times 10^{-6}$. The temperature cycle for all of the tests went from 75°F to a maximum of 280°F (except where noted), down to −250°F, and back up to 75°F. Thermal strain data were taken at approximately 40°F increments. There was a 30-min hold at each temperature to allow the specimen and interferometer to reach thermal equilibrium. All specimens were vacuum dried at 120°F to a constant mass prior to thermal expansion testing, and all testing was conducted with a dry N_2 purge in the oven.

Dynamic Mechanical Analysis

Dynamic thermal mechanical analysis (DMA) tests were performed on some of the specimens to help explain changes observed in the thermal expansion tests. This particular technique measures the damping capacity of a specimen as a function of temperature. Measurements were conducted over the temperature range of −185° to 600°F for the T300/5208, and up to 750°F for the C6000/PMR15, at a heating rate of 9°F/min. The specimen geometry is shown in Fig. 1. This type of measurement is useful for detecting changes in properties associated with the resin such as the glass transition temperature. DMA tests were conducted on a DuPont Model 943 Thermal Mechanical Analysis System. Again, all specimens were vacuum dried to a constant mass before testing.

Results and Discussion

Thermal Expansion

T300/5208

Thermal expansion measurements were made for one irradiated specimen from each laminate configuration and dose rate. This is because only a small number of specimens were irradiated as a result of the time required for irradiation and the limited number of specimens that can be irradiated at any one time. However, to assess the specimen-to-specimen variability for a given exposure condition, thermal expansion tests were conducted for multiple baseline specimens. A comparison of two $[0_2/90_2]_s$ T300/5208 baseline specimens is shown in Fig. 2. Data from these two samples are coincidental above −50°F. There is a maximum difference of approximately 25×10^{-6} below −50°F. These data confirm that there is very little specimen-to-specimen variability for the T300/5208.

A comparison of baseline and irradiated thermal expansion data for $[0_8]$ and $[0_2/90_2]_s$ T300/5208 is shown in Figs. 3–4. All of the baseline specimens exhibited a nonlinear thermal strain response with no significant hysteresis or permanent residual strain. Data for the irradiated specimens are

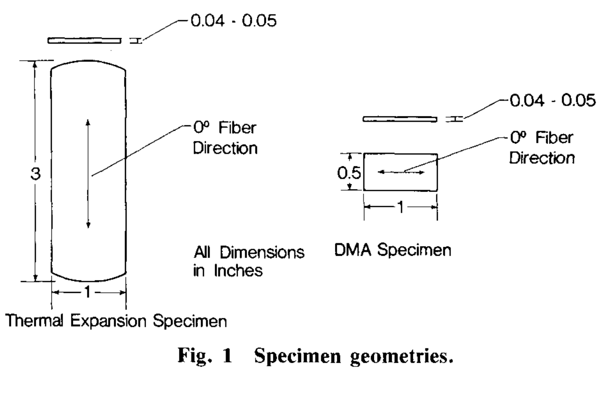

Fig. 1 Specimen geometries.

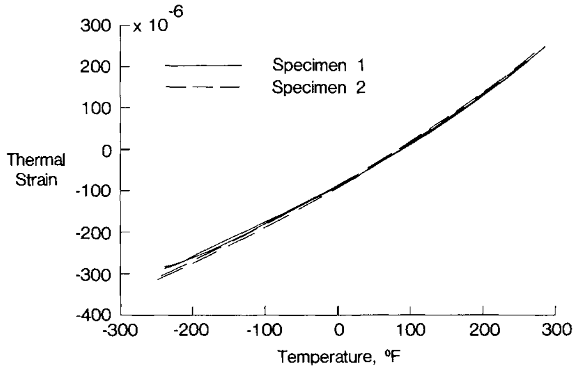

Fig. 2 Specimen-to-specimen variability in baseline thermal expansion data for $[0_2/90_2]$ T300/5208.

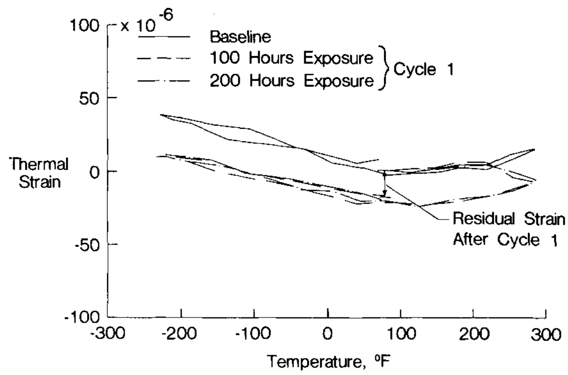

Fig. 3 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the first thermal expansion cycle of $[0_8]$ T300/5208.

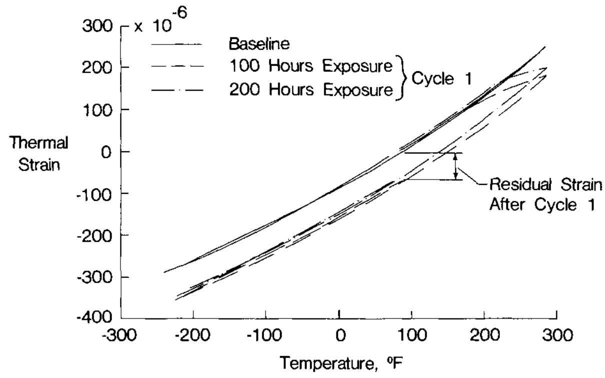

Fig. 4 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the first thermal expansion cycle of $[0_2/90_2]_s$ T300/5208.

in good agreement with their respective baseline specimens up to about 220°F. Above 220°F, however, the irradiated specimens exhibit a sudden decrease in the slope of the thermal strain curve up to the maximum test temperature of 280°F. This change in slope corresponds to a decrease in the instantaneous coefficient of thermal expansion (CTE), $d(\Delta L/L)/dT$. During the cooldown from +280° to −250°F and subsequent reheating to room temperature, the thermal strain curves for the irradiated specimens are parallel to that of their respective baseline specimens. This results in significant permanent negative residual strains in the irradiated specimens at room temperature. The $[0/45/90/-45]_s$ specimen behaved in a similar manner. The average residual strains for the $[0_8]$, $[0/45/90/-45]_s$, and $[0_2/90_2]_s$ irradiated specimens are -19×10^{-6}, -61×10^{-6}, and -67×10^{-6}, respectively. Strains of this magnitude can significantly affect the performance of dimensionally stable space structures. The cause of these residual strains is a matrix dominated phenomenon, as will be discussed. The residual strain in the irradiated $[0_8]$ specimens is smaller because the thermal expansion of this laminate is fiber dominated, and therefore is less affected by matrix changes.

Figure 5 shows the thermal strain response during the second thermal cycle of the $[0_2/90_2]_s$ T300/5208 irradiated specimen (200-h exposure). No significant additional changes in the response occur during the second cycle, and no additional permanent residual strain occurs. The curve is parallel to that of the baseline specimen. Figure 6 shows the response during a third thermal cycle when the specimen was heated above the previous maximum test temperature of 280°F to approximately 320°F. Beginning at 280°F there is another change in slope of the thermal strain curve, which results in an additional permanent residual strain of -15×10^{-6}. Data were also collected for the baseline specimen up to 320°F, and, as shown in Fig. 6, the baseline data exhibit no hysteresis or permanent residual strain.

Data from Figs. 3–6 show that only temporary changes occur in the CTE due to radiation. These changes occur when the specimen is first heated above 220°F and again at any time the previous maximum test temperature is exceeded. However, there are no significant permanent changes in the CTE due to radiation for any of the laminate configurations. No significant differences as a result of the two different dose rates were observed in the thermal response of the irradiated specimens.

Permanent negative residual strains during thermal expansion measurements have been noted by another investigator[7] for a T300/934 graphite/epoxy system irradiated to 3×10^9 rads. The 934 epoxy is a 350°F cure resin and is very similar to 5208. In this earlier work, the residual strain was assumed to be caused by a loss of moisture during the first cycle, in part because no further changes were noted after the first cycle. However, the source of this moisture was unexplained. For the present investigation, moisture loss was ruled out as a possible cause for the residual strain. Specimens were weighed before and after testing and, in all cases, weight loss was negligible. The observed negative residual strain is therefore believed to be an effect of the radiation. An explanation of the residual strain in the irradiated T300/5208 specimens will be discussed in a subsequent section. The data presented for T300/5208 point out the importance of considering the entire thermal strain response, rather than just the CTE, in order to characterize the effect of radiation on this material.

C6000/PMR15

A comparison of the thermal expansion for two $[0_2/90_2]_s$ C6000/PMR15 baseline specimens is shown in Fig. 7. The agreement between the data for these specimens is satisfactory and is typical of the laminates tested. There are small hysteresis loops of less than 12×10^{-6} in the data from each

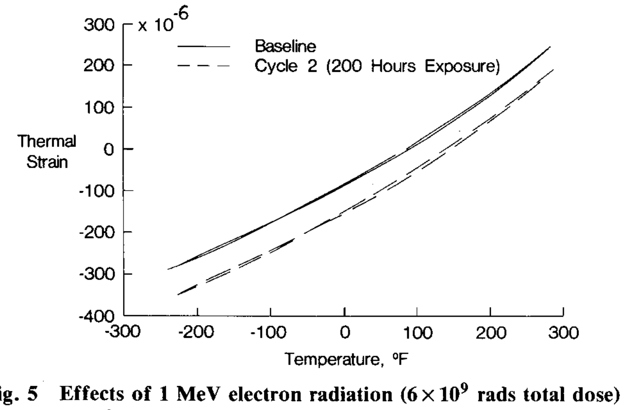

Fig. 5 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the second thermal expansion cycle of $[0_2/90_2]_s$ T300/5208.

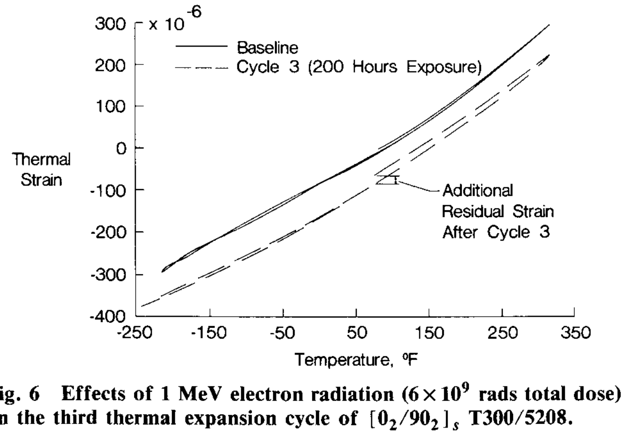

Fig. 6 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the third thermal expansion cycle of $[0_2/90_2]_s$ T300/5208.

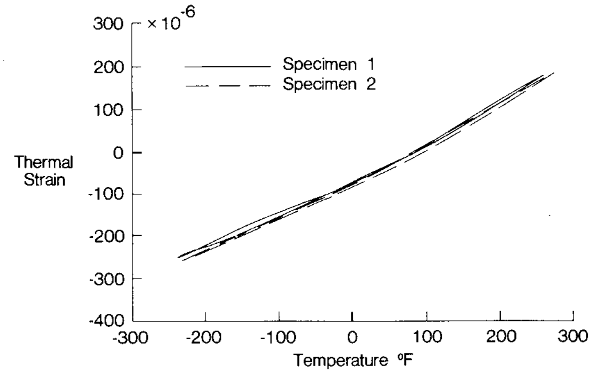

Fig. 7 Specimen-to-specimen variability in baseline thermal expansion data of $[0_2/90_2]_s$ C6000/PMR15.

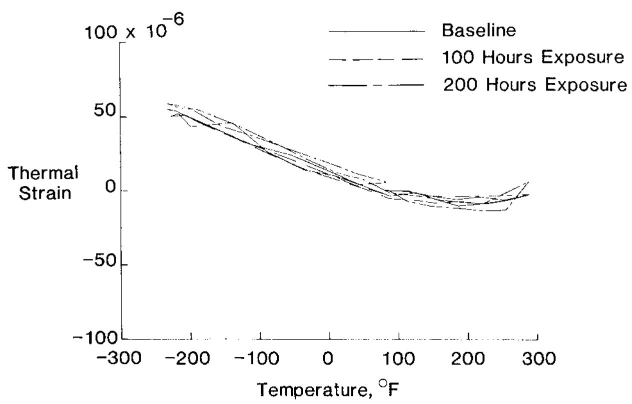

Fig. 8 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the thermal expansion of $[0_8]$ C6000/PMR15.

specimen, and the data from one specimen indicated a residual set of about 8×10^{-6}. Because all specimens were dried prior to testing, moisture loss was ruled out as a cause of the observed residual strain and hysteresis. One possible cause of this observed behavior is the microdamage that results from residual curing stresses. These residual stresses are much larger in the C6000/PMR15 specimens than the T300/5208 specimens because of the higher cure temperature of the polyimide resin.

Comparisons of baseline and irradiated thermal expansion data for the $[0]_8$ and $[0_2/90_2]_s$ C6000/PMR15 are shown in Figs. 8 and 9, respectively. There were no changes in the thermal expansion of these laminates that could be related to radiation effects. The expansion of the irradiated $[0]_8$ laminate (Fig. 8) was in good agreement with the baseline. Both irradiated specimens exhibited smaller hysteresis loops than the baseline and neither showed a residual strain. The expansion of the irradiated $[0_2/90_2]_s$ laminate (Fig. 9) was in agreement with the baseline. The spread in the data is attributed to specimen-to-specimen material variability. The expansion of the specimen irradiated for 200 h showed a residual strain of about -15×10^{-6}. However, this residual strain was not attributed to a radiation effect because a residual strain of about -8×10^{-6} was measured on a baseline specimen. The expansion of the irradiated $[0/45/90/-45]_s$ laminate (not shown) was also in agreement with the baseline. The expansion of both irradiated specimens showed a residual expansion of about -15×10^{-6}. However, a residual strain of about -8×10^{-6} was measured on a baseline specimen. The cause of the residual strain observed for both the $[0_2/90_2]_s$ and $[0/45/90/-45]_s$ laminates is not known. One possible explanation was given earlier. However, similar behavior was observed in some of the baseline specimens. Therefore, radiation was assumed not to affect the expansion of the C6000/PMR15. This is substantiated by DMA data which will be discussed in the next section. No significant differences due to the two different dose rates were observed for the irradiated C6000/PMR15 specimens.

Dynamic Mechanical Analysis

T300/5208

DMA tests were conducted on both baseline and irradiated (100-h exposure) $[0/\pm45/90]_s$ T300/5208 specimens. Although CTE data were not collected for this particular laminate configuration, trends observed in its DMA response should be representative of the laminate configurations used for the CTE tests because changes in the DMA response are primarily matrix dominated. The mechanical damping versus temperature data from these tests are shown in Fig. 10. These data confirm that the 5208 epoxy matrix chemistry was affected by electron radiation. As shown, the peak in the relative damping curve, associated with the T_g (glass transition temperature) of the epoxy, was lowered 40°F from 480°F. More importantly, the data show that the "rubbery region" (i.e., region of increasing damping and decreasing modulus) associated with this transition has been lowered and broadened for the irradiated material and extends into the temperature range studied in the thermal expansion tests.

The lower T_g and broader peak explain the hysteresis and permanent residual strain observed during the first cycle of the thermal expansion test. When the irradiated sample is heated to near 225°F and higher, the "rubbery region" is entered. The elastic modulus of the epoxy matrix would be considerably lower in this range. The thermal expansion of the composite is controlled by the CTE and modulus of both the fiber and matrix. The composite reflects the lower modulus of the epoxy by exhibiting a more fiber dominated expansion, and thus lower CTE in this temperature range. Because the heating process in the thermal expansion test occurs slowly in 40°F increments, with 30-min holds at each temperature, the irradiated specimen has sufficient time in

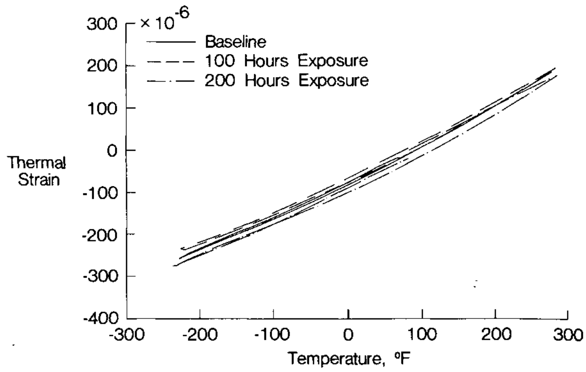

Fig. 9 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the thermal expansion of $[0_2/90_2]_s$ C6000/PMR15.

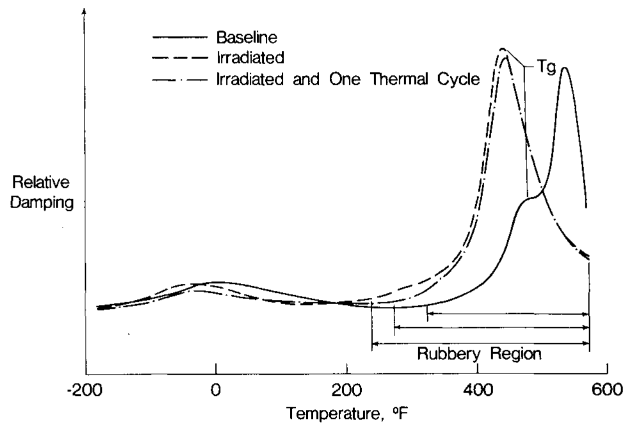

Fig. 10 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the relative damping of $[0/\pm45/90]_s$ T300/5208.

the 225°-280°F temperature range to undergo additional chemical change. The result of this chemical change moves the "rubbery region" back to higher temperatures out of the thermal expansion test range, and also raises the modulus of the epoxy back to its "glassy region" value. This increased epoxy modulus is reflected in the slope of the expansion curves during cooling and subsequent reheating of the first cycle for the irradiated specimens (Figs. 3-4), which are nearly identical to their respective baseline specimens. This observed chemical change was confirmed by conducting a DMA test on an irradiated specimen that had been exposed to one cycle of the slow heating and isothermal holds which occur in the thermal expansion tests. The mechanical damping vs temperature data for this specimen are also shown in Fig. 10. The beginning of the "rubbery region" for the cycled specimen has moved approximately 40°F higher than that of the uncycled specimen. This confirms the effect of the chemical change that occurs during the slow heating. Because the "rubbery region" has been moved above the maximum test temperature, the hysteresis effect is not observed for the second thermal cycle of the irradiated specimen (Fig. 5). Additional hysteresis and permanent residual strain are not observed until the previous maximum test temperature is exceeded and the test enters the new higher temperature "rubbery region," as in cycle 3 of the irradiated specimen (Fig. 6).

Similar DMA tests were also conducted for irradiated (6×10^9 rads, 100-h exposure) and baseline neat 5208 resin samples. The damping data from these tests are shown in Fig. 11. These experiments were performed to aid in understanding and explaining the effect of the matrix changes on the composite thermal expansion properties. The chemical change phenomenon observed in these neat resin samples was even more pronounced. The start of the "rub-

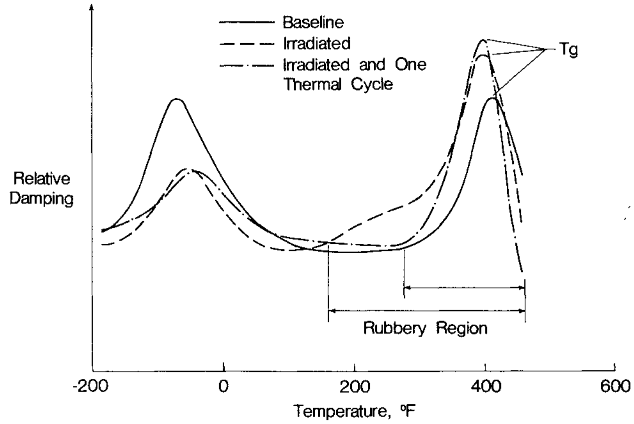

Fig. 11 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the relative damping of 5208 neat resin.

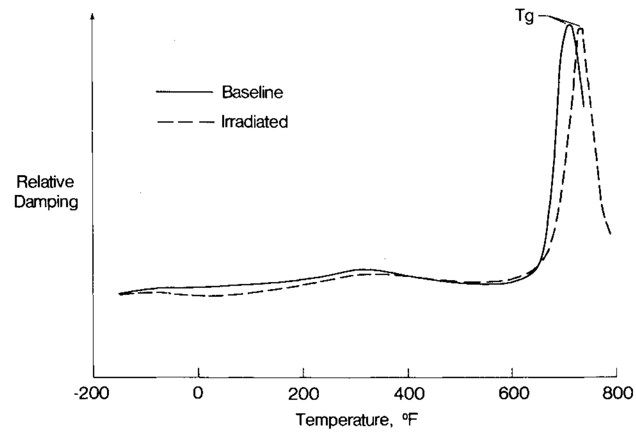

Fig. 12 Effects of 1 MeV electron radiation (6×10^9 rads total dose) on the relative damping of $[0/\pm45/90]_s$ C6000/PMR15.

bery region" for the irradiated specimen was approximately 120°F lower than that of the baseline specimen. An irradiated specimen exposed to the slow heating cycle of the thermal expansion tests again showed that the "rubbery region" moved to a significantly higher temperature, approximately back to the baseline value. These data further confirm the chemical changes observed in the composite specimens. The mechanisms associated with the chemical changes observed in both the neat resin and composite specimens have not been determined. One possible explanation is the cross-linking of free radicals that occurs during the slow heating process of the thermal expansion tests.

C6000/PMR15

DMA tests were also conducted on both baseline and irradiated (100-h exposure) $[0/\pm45/90]_s$ C6000/PMR15 specimens. These data are shown in Fig. 12. No significant differences were observed in the temperature range of the thermal expansion measurements between the damping data of the baseline and irradiated specimens. There was, however, a small increase observed in the T_g of the irradiated specimen. The corresponding T_g's of the baseline and irradiated specimens were 715°F and 735°F, respectively.

Conclusions

The effects of electron radiation on the thermal expansion characteristics of T300/5208 graphite/epoxy and C6000/PMR15 graphite/polyimide were studied. Specimens were irradiated to a total dose of 6×10^9 rads at rates of 6×10^7 rads/h and 3×10^7 rads/h. Thermal expansion measurements were made on both baseline and irradiated specimens over the temperature range $-250°$ to $+280°$F. Dynamic thermal mechanical analysis (DMA) tests were also performed. Based on the results from these tests, the following conclusions are made:

1) T300/5208 specimens, previously exposed to electron radiation, exhibited permanent residual strains of up to $-70\text{x}10^{-6}$ when thermally cycled between $-250°$ and 280°F. The magnitude of this residual strain depends upon the laminate configuration. No significant permanent residual strains attributable to radiation were observed for the C6000/PMR15 when subjected to the same thermal cycle.

2) Electron radiation did not cause any significant permanent changes in the coefficient of thermal expansion for either the T300/5208 or the C6000/PMR15.

3) No significant differences due to dose rate were observed in the thermal response of either composite system.

4) DMA data indicate that electron radiation caused chemical changes in the epoxy matrix. These changes lowered the glass transition temperature and broadened the "rubbery region" for the T300/5208, causing it to extend into the temperature range of the thermal expansion tests. After one slow thermal cycle between $-250°$ and 280°F, the "rubbery region" was raised above 280°F.

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