THERMAL EXPANSION OF SELECTED GRAPHITE
REINFORCED POLYIMIDE-, EPOXY-, AND
GLASS-MATRIX COMPOSITE

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JULY 1985
Thermal expansion of selected graphite reinforced polyimide-, epoxy-, and glass-matrix composite

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AVAIL: NTIS, SAP: HC A02/MF A01

MAUS: //BOROSILICATE GLASS//CARBON FIBERS//GRAPHITE-POLYIMIDE COMPOSITES//

KINS: //DIMENSIONAL STABILITY//LAMINATES//RESIDUAL STRESS

ABB: Author
SUMMARY

The thermal expansion of three epoxy-matrix composites, a polymide-matrix composite and a borosilicate glass-matrix composite, each reinforced with continuous carbon fibers, has been measured and compared. The expansion of a composite with a rubber toughened epoxy-matrix and P75S carbon fibers was very different from the expansion of two different single phase epoxy-matrix composites with P75S fibers although all three had the same stacking sequence. Reasonable agreement was obtained between measured thermal expansion data and results from classical laminate theory. The thermal expansion of a material may change markedly as a result of thermal cycling. Microdamage, induced by 250 cycles between -156°C and 121°C in the graphite/polyimide laminate, caused a 53% decrease in the coefficient of thermal expansion. The thermal expansion of the graphite/glass laminate was not changed by 100 thermal cycles from -129°C to 38°C; however, a residual strain of about $10 \times 10^{-6}$ was measured for the laminate tested.
1. INTRODUCTION

Precision space structures often have strict tolerances on dimensional control and thus require structural materials that possess high specific stiffnesses and low coefficients of expansion. Graphite-fiber reinforced composites meet both of these requirements and are prime candidates for space structures such as large, high precision antennas and structural elements for the Space Station. Composites can be designed to meet specific design requirements by proper selection of the type of reinforcement fiber, type of matrix, number of plies and ply orientation. Currently, metal-, resin-, and ceramic-matrix composite materials are all candidates for use in space applications. The environment to which these materials will be exposed includes high vacuum, radiation, atomic oxygen and thermal cycling. The effects of high vacuum, radiation and atomic oxygen on the dimensional stability and properties of composites have been the subject of a number of studies [1-6].

Space structure temperatures may cycle from as low as of -156°C to as high as 149°C depending upon the thermal control coating used. Unexpected expansion of even a low expansion material over this temperature range could significantly alter the performance of a dimensionally critical, precision space structure. Therefore, the expansion characteristics of candidate materials in the space service environment must be defined and understood to ensure that the proper material is selected and the performance of the structure will meet design criteria. This paper presents thermal expansion data on several continuous graphite-fiber reinforced composite materials that are candidates for space applications. Data are presented for three epoxy composites reinforced with a high modulus pitch fiber, a polyimide composite reinforced with a high strength PAN-based carbon fiber and a glass composite reinforced
with a high modulus PAN-based carbon fiber. The thermal expansion of unidirectional, quasi-isotropic and cross-ply laminate configurations of these materials was measured over the temperature range of -156°C to 149°C. The effect of the type of epoxy resin used in the composite material on the dilatation is demonstrated. Comparisons of measured data with results from classical laminate theory are shown and discussed. The effects of thermal cycling on the dilatation of the polyimide and glass composites are also shown.

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2. MATERIALS AND SPECIMENS

All materials used in this study (three graphite-epoxy composites (Gr/Ep), a graphite-polyimide (Gr/Pi), and a graphite-glass (Gr/Glass)), are candidate space composite material systems. The three different Gr/Ep composite systems, each with a different epoxy resin on Union Carbide P75S pitch carbon fibers, were obtained as unidirectional prepreg tape. The P75S/CE339 composite system contains an elastomer-toughened, 121°C cured epoxy obtained from the Ferro Corporation. The P75S/930 and the P75S/934 composite systems, obtained from the Fiberite Corporation, contain 135°C and 177°C cured epoxy resins, respectively. The Gr/Pi composite, C6000/PMR-15, contains the Celion 6000 carbon fiber from the Celanese Corporation and the 316°C cured PMR-15 polyimide resin. Panels with laminate configurations of [0]₈ and [0₂/9₀₂]₈ were fabricated from each composite material system using the recommended procedures for each material system. Both unidirectional and a [0/60/-60]₈ quasi-isotropic Gr/Glass composite laminates, made with Hercules HMS PAN-based graphite fibers and Corning 7740 Borosilicate glass, were included in this study. This Gr/Glass composite material was consolidated by
United Technologies Research Center at about 1430°C, Ref. 7. Properties and fabrication techniques for the Gr/Glass material are presented in Refs. 7 and 8.

Samples, nominally 2.5 cm × 7.6 cm, were cut from flat panels of each composite material. Both ends of each specimen were then slightly rounded to minimize end effects and to provide single point contact in the test fixture.

3. TEST EQUIPMENT AND PROCEDURE

Thermal expansion measurements were made with a laser interferometric dilatometer specifically developed for measuring small thermal strains in composites [9]. The strain resolution with the specimen geometry used in this study is approximately $1 \times 10^{-6}$. The strain repeatability of this equipment has been shown to be approximately $\pm 3 \times 10^{-6}$. The temperature range over which expansion measurements were made was not the same for all of the materials studied because of the different glass transition temperature for each material or because of design criteria. However, the test cycle for all specimens began by heating from room temperature up to the maximum temperature, cooling to the minimum temperature (all well below -17°C) and heating to room temperature. Thermal strain data were taken at approximately 22°C increments. There was an approximate 30-minute hold at each temperature to allow the specimen and interferometer to reach thermal equilibrium. All specimens, except the glass matrix composite specimens, were vacuum dried at about 50°C to a constant weight prior to measurements of the thermal expansion and all tests on the dried specimens were conducted with a dry N$_2$ purge in the test chamber. Two or three thermal expansion tests were made for each laminate configuration of each composite material system.
4. LAMINATE ANALYSIS

Classical linear elastic laminate theory was use to compute the response of the \([0_2/90_2]\) lamina of the three epoxy and the polyimide composites based upon the properties of the unidirectional laminates of each of these systems. Classical laminate theory is presented in detail in many references, (such as Ref. 10), and will not be presented here. All properties used in the present analysis were assumed to be temperature independent and are given in Table I. The coefficients of thermal expansion, at 24°C, are those measured in this study. The stress free temperature was assumed equal to the cure temperature for each resin system. The other properties for P75S/CE339 and C6000/PMR-15 came from Refs. 6 and 11, respectively. A number of literature sources were examined for properties of the other composite materials, but a consistent set was not found. Therefore, these sources were used collectively to derive the set of properties shown in Table I for P75S/930 and P75S/934.

5. RESULTS AND DISCUSSION

The expansion characteristics of the composite materials are presented in plots of thermal strain as a function of temperature, Figs. 1-6, and as the coefficient of thermal expansion (CTE), Fig. 7 and Table II. These data are typical of the data measured for each laminate of each composite material system. The thermal strain for each specimen was represented by a 3rd order polynomial curve fit to the data. The CTE was obtained by taking the first derivative, with respect to temperature, of the 3rd order polynomial. The polynomials for the CTE as a function of temperature are presented in Table II and the values of the coefficients, at 24°C, are presented in Table II and Fig. 7.
5.1 Epoxy Composites

The longitudinal expansions of the Gr/Ep composites are shown in Fig. 1. The expansion of each composite is dominated by the fiber which results in a negative CTE. The CTE in the fiber direction is approximately the same for the three epoxy systems, -1.03 to -1.08 \times 10^{-6}\,°C^{-1} at 24°C. The thermal expansion in the transverse direction (perpendicular to the fibers), shown in Fig. 2, indicates that the expansion is resin dominated. The large and positive CTEs are typical of neat epoxy resins. The transverse expansion of the P75S/930 and P75S/934 composites are similar, CTEs of 32.4 \times 10^{-6} and 34.2 \times 10^{-6}\,°C^{-1} at 24°C, respectively, which is not surprising since the two composites have similar resin systems but cured at different temperatures. The CTE of the P75S/CE339 system is also large and positive, 47 \times 10^{-6}\,°C^{-1} at 24°C, and is larger than the other epoxy system because of the elastomer additives for toughness.

The expansion of the \([0_2/90_2]_s\) epoxy laminates is shown in Fig. 3. The response of the P75S/930 and P75S/934 composites are again similar; the expansion is strongly influenced by the negative CTE of the fibers. The thermal strain hysteresis evident for the P75S/930 composite was unexpected and may be due to the maximum test temperature approaching the glass transition temperature for this panel. The P75S/CE339, however, has a positive CTE, which is very different from the other epoxy systems. Laminate theory indicates that the positive CTE of the P75S/CE339 results from the very high transverse CTE and the larger transverse tensile modulus of this composite, Table I, compared to the P75S/930 and P75S/934 composite. These data clearly demonstrate the strong influence the resin properties can have on the thermal expansion of a \([0_2/90_2]_s\) laminate.
5.2 Polyimide and Glass Composites

The longitudinal thermal expansion of the Gr/Pi and Gr/Glass composite materials is shown in Fig. 4. In both systems the expansion is dominated by the fibers, which results in negative CTEs for the composites. Note the CTEs are not as negative as for the Gr/Ep composites because the fibers used in the epoxy composites have a much more negative CTE than the fibers used for the Gr/Pi and Gr/Glass composites. The transverse expansions for the latter composite systems are shown in Fig. 5. The CTE is much higher for the Gr/Pi than the Gr/Glass because the CTE of the two matrix materials are so different: about $3.6 \times 10^{-6}$ and $50 \times 10^{-6} \degree C^{-1}$ at $24^\circ C$ for the borosilicate glass and PMR-15 polyimide, respectively, Fig. 7. The very low CTE of the Gr/Glass in both the longitudinal and transverse directions make this composite a very promising candidate for dimensionally stable structures.

The expansion of a quasi-isotropic Gr/Glass laminate $[0/60/-60]_s$ and a $[0_2/90_2]_s$, Gr/Pi laminate are shown in Fig. 6. The two materials expand very differently with the CTE of the Gr/Glass very close to zero, about $0.18 \times 10^{-6} \degree C^{-1}$ and the CTE of the Gr/Pi about $1.62 \times 10^{-6} \degree C^{-1}$ (both at $24^\circ C$). (A comparison of the CTE of quasi-isotropic laminates of Gr/Glass and Gr/Pi is shown in Fig. 7.) Although different fibers were used in these two composites, the different matrix materials greatly influence the net response of the composites. The low CTE of the borosilicate glass combined with the low expansion fiber result in a composite with a very low CTE. The source of the thermal strain hysteresis evident in Fig. 7 for the Gr/Glass composite is not known, however, the discontinuous graphite fiber felt cloth, used in the prepreg for handling purposes, may contribute to this unexpected response.
5.3 Comparisons With Analysis

Classical laminate theory was used, with the properties listed in Table II, to calculate the thermal expansions and CTE of the \([0_2/90_2]_s\) laminate of the epoxy materials and the polyimide materials. There was insufficient mechanical property data available for the glass matrix composite to use with the laminate theory. Very good agreement was obtained between analysis and experimental data for the P758/CE339 \([0_2/90_2]_s\) laminate, Fig. 8, and the C6000/PMR-15 \([0_2/90_2]_s\) and \([0/45/90/-45]_s\) laminates, Fig. 9. The differences between analysis and experiment, particularly for the C6000/PMR-15 at low temperatures, is attributed to the use of temperature independent properties in the analysis.

Calculated and measured CTE values at 24°C are compared in Fig. 10 for all materials except the Gr/Glass. The agreement ranges between good to excellent. The differences are attributed to the difference between the properties used (assumed) in the analysis and those of the materials tested. These differences arise from the lack of a good quality property data base for the materials tested. For example, a 10% decrease in \(E_2\) for P75/934 changes the CTE for the \([0_2/90_2]_s\) laminate from \(-0.27 \times 10^{-6} °C^{-1}\). In addition to differences in material properties due to measurements techniques, batch-to-batch variations, etc., properties may also change due to temperature. Reference 14 reports an increase in \(E_2\) of a 934 resin composite at \(-156°C\) of about 33% above the room temperature value. This kind of change in \(E_2\) in P75/934 would change CTE for a \([0_2/90_2]_s\) laminate from \(-0.185\) to \(0.089 \times 10^{-6} °C^{-1}\), a 148% change including a change in sign. Therefore, a good data base with a consistent set of property data is required to obtain consistent agreement between predicted and measured thermal expansion over a large temperature range.
5.4 Effects of Thermal Cycling on Thermal Expansion

The thermal expansion data presented heretofore have not included the effects of any service environmental parameters other than a single thermal cycle. The service environment can significantly alter the thermal response of composites (Refs. 3, 6, and 12). Figures 11 and 12 show the effects of a limited number of thermal cycles on the Gr/Glass and Gr/Pi composites. The thermal expansion of the Gr/Glass during the 1st and 100th thermal cycles is shown in Fig. 11. These data show that the expansion of a Gr/Glass [0/60/-60]s laminate specimen was unaffected by 100 cycles between -129°C and 38°C. However, the specimen, after 100 cycles, was about $76 \times 10^{-6}$ cm longer than before the first cycle. This residual strain could be an important factor in the performance of a precision structure.

The thermal expansion of the C6000/PMR-15 composite before and after 250 cycles (two different specimens) between -156°C and 121°C is shown in Fig. 12. During thermal cycling, microdamage develops within the laminate as a result of stresses caused by the mismatch in properties between laminae of different orientation [13]. These stresses are superimposed on stresses due to fiber-matrix property mismatch. The resulting microdamage (microcracks) induced in the composite by thermal cycling significantly reduced the CTE after 250 cycles from about $1.64 \times 10^{-6}$ to about $0.79 \times 10^{-6}$ °C$^{-1}$ at 24°C. This reduction could significantly alter the performance of a dimensionally critical structure.

6. CONCLUDING REMARKS

The thermal expansion of three epoxy-matrix composites, a polyimide-matrix composite and a borosilicate glass-matrix composite, each reinforced with continuous carbon fibers, has been measured and compared. The expansion
of a 121°C cured composite laminate with a rubber toughened epoxy-matrix, containing P75S carbon fibers, was very different from the expansion of 135°C and 177°C cured composite laminates with a single phase epoxy-matrices, although all 3 have the same stacking sequence $[0_{2}/90_{2}]_{s}$. This indicates the sensitivity of the composite thermal expansion to the matrix material. Reasonable agreement was obtained between measured thermal expansion data and results from classical laminate theory for cross-ply laminates of the epoxy and polyimide composites. Good agreement between predicted and measured expansion can be obtained consistently only if there is reliable mechanical property data base available to support the laminate analysis. Although thermal expansion of a material is known and understood (i.e., predictable), expansion after thermal cycling exposure may be very different. Microdamage was induced by 250 cycles between -156°C and 121°C in the graphite/polyimide laminate which caused about a 53% decrease in the coefficient of thermal expansion. The thermal expansion of the graphite/glass composite was low in both the longitudinal and transverse directions. The expansion of the $[0/60/-60]_{s}$ Gr/Glass laminate was not changed by 100 thermal cycles from -129°C to 38°C; however, a residual strain of about $10 \times 10^{-6}$ was measured.
NOMENCLATURE

$a_i$ coefficients in polynomial

$E_1$ longitudinal Young's modulus

$E_2$ transverse Young's modulus

$G_{12}$ shear modulus

$V_f$ fiber volume content

Greek Symbols

$\alpha$ coefficient of thermal expansion

$\alpha_1$ longitudinal coefficient of thermal expansion

$\alpha_2$ transverse coefficient of thermal expansion

$\nu_{12}$ Poisson's ratio
REFERENCES


<table>
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<th>Fiber/matrix</th>
<th>$V_f$</th>
<th>$E_1$, GPa</th>
<th>$E_2$, GPa</th>
<th>$v_{12}$</th>
<th>$G_{12}$, GPa</th>
<th>$\alpha_1$, $10^{-6}\degree\text{C}^{-1}$ at 24$\degree\text{C}$</th>
<th>$\alpha_2$, $10^{-6}\degree\text{C}^{-1}$ at 24$\degree\text{C}$</th>
<th>Stress free temperature, $\degree\text{C}$</th>
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<td>P75S/CE339</td>
<td>55</td>
<td>283</td>
<td>7.45</td>
<td>0.37</td>
<td>3.65</td>
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<td>47.42</td>
<td>121</td>
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<td>5.52</td>
<td>-1.076</td>
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<td>5.52</td>
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<td>0.37</td>
<td>4.67</td>
<td>-0.212</td>
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Table II.- Polynominial For Coefficient of Thermal Expansion

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<th>Material system</th>
<th>Layup</th>
<th>Fiber content % volume</th>
<th>$a = a_0 + a_1 T + a_2 T^2, 10^{-6} \degree C^{-1}$</th>
<th>$a, 10^{-6} \degree C^{-1}$ at 24°C</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$a_0$</td>
<td>$a_1$</td>
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<tr>
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<td>[0]_8</td>
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<td></td>
<td>[90]_8</td>
<td>54</td>
<td>43.87086</td>
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<td>Borosilicate</td>
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<td>0.16381</td>
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Fig. 1. Longitudinal thermal expansion of Gr/Ep unidirectional laminates.

Fig. 2. Transverse thermal expansion of Gr/Ep unidirectional laminates.

Fig. 3. Thermal expansion of Gr/Ep [0₂/9₀₂]₅ laminates in the 0-fiber.

Fig. 4. Longitudinal thermal expansion of Gr/Glass and Gr/Pi unidirectional laminates.
Fig. 5. Transverse thermal expansion of Gr/Glass and Gr/Pi unidirectional laminates.

Fig. 6. Thermal expansion of [0/60/-60]s Gr/Glass and [02/90s]s Gr/Pi laminates in the 0-fiber direction.

Fig. 7. Coefficients of thermal expansion, at 24°C, of epoxy-, polyimide- and glass-matrix laminates.
Fig. 8. Predicted and measured thermal expansion of a P75S/CE339 Gr/Ep [0/90]laminate.

Fig. 9. Predicted and measured thermal expansion of C6000/PMR-15 Gr/Pi [0/90] and [0/45/90/-45] laminates.

Fig. 10. Comparison of measured and predicted coefficients of thermal expansion at 24°C for Gr/Ep and Gr/Pi [0/90] laminates.

Fig. 11. Thermal expansion of a Gr/Glass [0/60/-60] laminate before and after 100 thermal cycles between -129°C and 38°C.

Fig. 12. Thermal expansion of a Gr/Pi [0/90] laminate before and after 250 thermal cycles between -156°C and 121°C.
The thermal expansion of three epoxy-matrix composites, a polyimide-matrix composite and a borosilicate glass-matrix composite, each reinforced with continuous carbon fibers, has been measured and compared. The expansion of a composite with a rubber toughened epoxy-matrix and P75S carbon fibers was very different from the expansion of two different single phase epoxy-matrix composites with P75S fibers although all three had the same stacking sequence. Reasonable agreement was obtained between measured thermal-expansion data and results from classical laminate theory. The thermal expansion of a material may change markedly as a result of thermal cycling. Micro-damage, induced by 250 cycles between -156°C and 121°C in the graphite/polyimide laminate, caused a 53 percent decrease in the coefficient of thermal expansion. The thermal expansion of the graphite/glass laminate was not changed by 100 thermal cycles from -129°C to 38°C; however, a residual strain of about 10 x 10^-6 was measured for the laminate tested.