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Thermal Expansion of Selected Graphite-Reinforced Polyimide-, Epoxy-, and Glass-Matrix Composites

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

KEY WORDS: composites; dimensional stability; thermal expansion.

1. INTRODUCTION

Precision space structures often require structural materials that possess high specific stiffnesses and low coefficients of expansion to meet strict dimensional stability requirements. Graphite-fiber reinforced composites meet both of these criteria and are prime candidates for space structures. Composites can be fabricated to meet specific design requirements by proper selection of the reinforcement fibers, matrices, numbers of plies, and ply orientations. 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,

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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 −156°C to as high as 149°C depending upon the thermal control coating used. Anomalous 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 the 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 to 149°C. The effect of the type of epoxy resin used in the composite material on the dilation 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

The three graphite-epoxy (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 contains an elastomer-toughened, 121°C-cured epoxy obtained from the Ferro Corporation. The P75S/930 and the P75S/934 composites, obtained from the Fiberite Corporation, contain 135°C- and 177°C-cured epoxy resins, respectively. The graphite-polyimide (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. Unidirectional $[0]_8$ and cross-ply $[0_2/90_2]_s$ laminate panels were fabricated from each polymer-matrix composite system using procedures specified by the prepreg suppliers. Both unidirectional and $[0/60/-60]_s$ quasi-isotropic graphite-glass (Gr/glass) composite laminates, made with Hercules HMS PAN-based graphite fibers and Corning 7740 Borosilicate glass, were consolidated at about 1430°C by United Technologies Research Center [7, 8].

Specimens, nominally 2.5 × 7.6 cm, were cut from flat panels of each composite. 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 for the specimen geometry used is approximately 1×10^{-6}. The strain repeatability of this equipment has been shown to be approximately $\pm 3 \times 10^{-6}$ [9]. The test cycle for all specimens began by heating from room temperature to the maximum temperature, cooling to the minimum temperature (all below −17°C), and heating to room temperature. Thermal strain data were taken at approximately 22°C increments. There was a 30-min 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 [10] was used to compute the response of the $[0_2/90_2]_s$ laminates of the three epoxy and the polyimide composites. All unidirectional laminate properties used in the 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. Literature properties were used for P75S/CE339 [6] and C6000/PMR-15 [11]. A number of literature sources were examined for properties of the other composite materials, but a consistant 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 as plots of thermal strain as a function of temperature in Figs. 1–6 and as

Table I. Elastic Properties of Unidirectional Composite Lamina Used in Analysis[a]

Fiber/matrix	E_1 (GPa)	E_2 (GPa)	ν_{12}	G_{12} (GPa)	$\alpha_1(10^{-6}\ ^\circ C^{-1})$ at 24°C	$\alpha_2(10^{-6}\ ^\circ C^{-1})$ at 24°C	Stress-free temperature (°C)
P75S/CE339	283	7.45	0.37	3.65	-1.021	47.42	121
P75S/930	352	5.86	0.30	5.52	-1.076	31.71	135
P75S/934	269	4.83	0.40	5.52	-1.051	34.52	177
C6000/PMR-15	128	8.55	0.37	4.67	-0.212	22.42	316

[a] E_1, longitudinal Young's modulus; E_2, transverse Young's modulus; G_{12}, shear modulus; α_1, longitudinal coefficient of thermal expansion; α_2, transverse coefficient of thermal expansion; ν_{12}, Poisson's ratio.

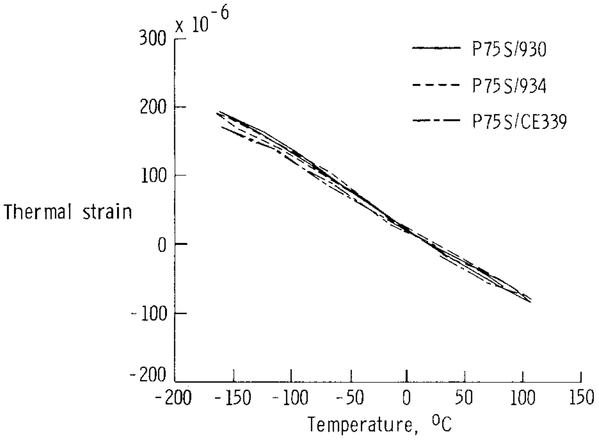

Fig. 1. Longitudinal thermal expansion of Gr/Ep unidirectional laminates.

the coefficient of thermal expansion (CTE) in Fig. 7 and Table II. These are typical data measured for each laminate of each composite system. The thermal strain for each specimen was represented by a third-order polynomial curve fit to the data. The CTE was obtained by taking the first derivative, with respect to temperature, of the 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.

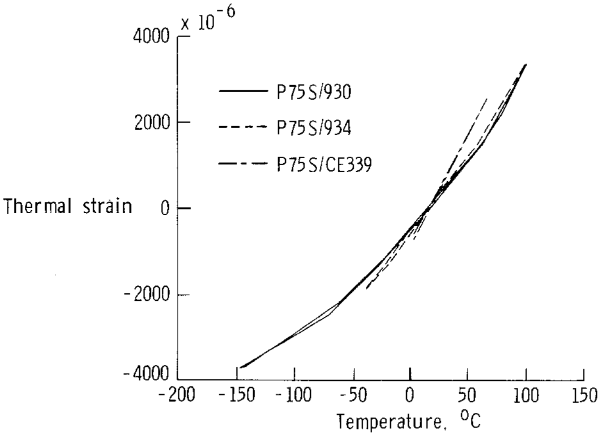

Fig. 2. Transverse thermal expansion of Gr/Ep unidirectional laminates.

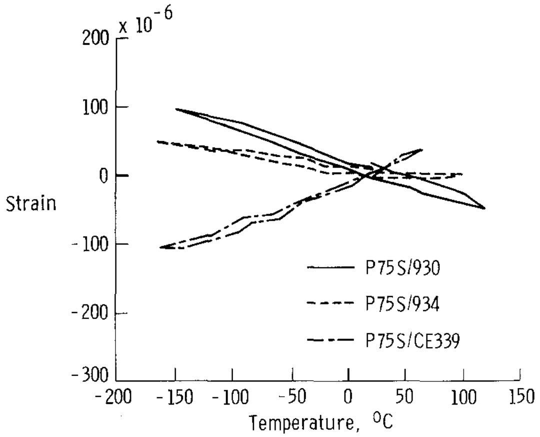

Fig. 3. Thermal expansion of Gr/Ep $[0_2/90_2]_s$ laminates in the 0-fiber direction.

5.1. Epoxy Composites

The longitudinal expansions of the Gr/Ep composites (Fig. 1) are dominated by the fiber. The CTE in the fiber direction is negative and approximately the same for the three epoxy systems, -1.03 to -1.08×10^{-6} °C^{-1}, at 24°C. The thermal expansion in the transverse direction (perpendicular to the fibers) (Fig. 2) indicates that the expansion is resin dominated. The large and positive CTEs are typical of neat epoxy

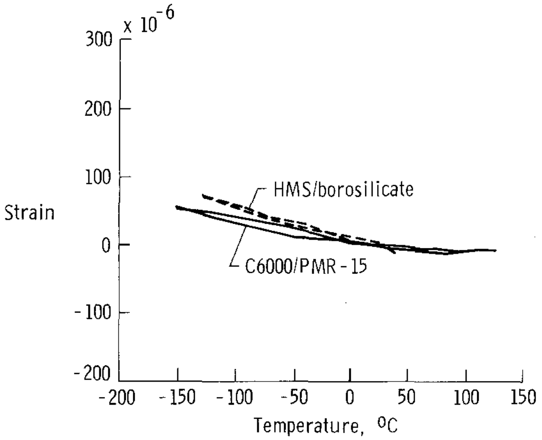

Fig. 4. Longitudinal thermal expansion of Gr/glass and Gr/Pi unidirectional laminates.

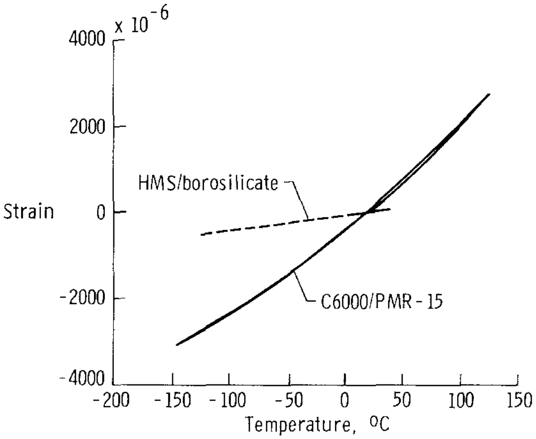

Fig. 5. Transverse thermal expansion of Gr/glass and Gr/Pi unidirectional laminates.

resins. The transverse expansions of the P75S/930 and P75S/934 composites are similar, CTEs of 32.4×10^{-6} and 34.2×10^{-6} °C^{-1} at 24°C, respectively, since the two composites have similar resin matrices (although cure temperatures differ). The transverse CTE of the P75S/CE339 system is also large and positive, $47 \times 10^{-6}\,\mathrm{C}^{-1}$ at 24°C; because of the elastomer additives for toughness it is larger than those of the other epoxy systems.

The expansion of the cross-ply $[0_2/90_2]_s$ epoxy laminates is shown in Fig. 3. The responses of the P75S/930 and P75S/934 composites are again

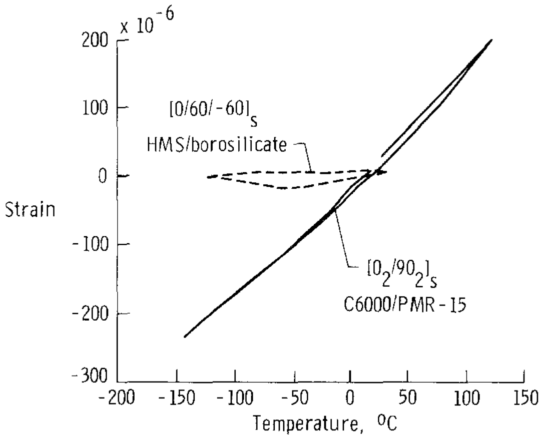

Fig. 6. Thermal expansion of $[0/60/-60]_s$ Gr/glass and $[0_2/90_2]_s$ Gr/Pi laminates in the 0-fiber direction.

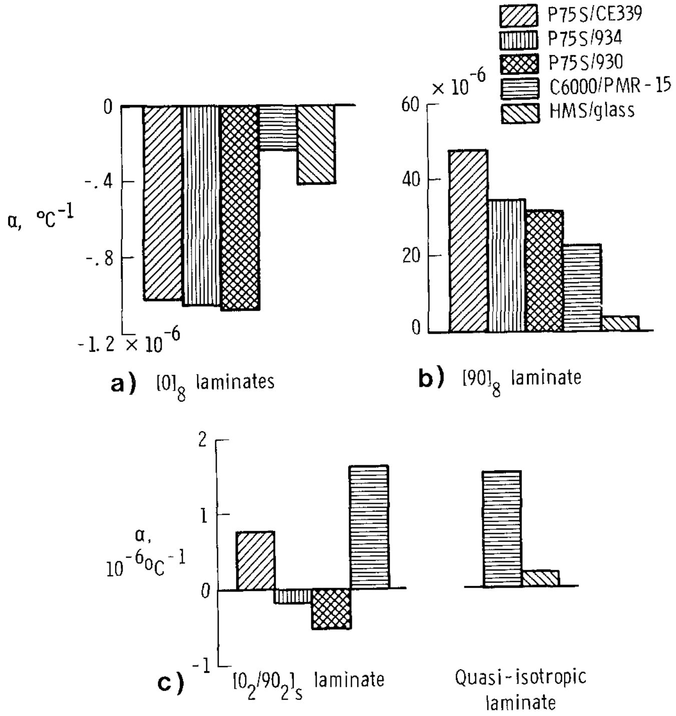

Fig. 7. Coefficients of thermal expansion, at 24°C, of epoxy-, polyimide-, and glass-matrix laminates. (a) $[0]_8$ laminates; (b) $[90]_8$ laminates; (c) cross-ply and quasi-isotropic laminates.

similar; the expansion is strongly influenced by the negative CTE of the fibers. The thermal strain hysteresis evident for the P75S/930 composite may be due to the maximum test temperature approaching the glass transition temperature of the 930 matrix. The P75S/CE339 has a positive CTE; laminate theory indicates that the positive CTE could result from a very high transverse CTE and a relatively large transverse tensile modulus compared to those of the P75S/930 and P75S/934 composites (Table I). These data clearly demonstrate the strong influence resin matrix properties can have on the thermal expansion of a $[0_2/90_2]_s$ laminate.

5.2. Polyimide and Glass Composites

The longitudinal and transverse thermal expansions of the Gr/Pi and Gr/Glass composites are shown in Figs. 4 and 5, respectively. In both systems, the longitudinal expansion is dominated by the fibers, which

Table II. Polynomial for Coefficient of Thermal Expansion[a]

Material system	Layup	Fiber content (% volume)	$\alpha = a_0 + a_1 T + a_2 T^2$ (10^{-6} °C^{-1})			α (10^{-6} °C^{-1}) at 24°C
			a_0	a_1	a_2	
P75S/CE339	$[0]_8$	54	-1.06139	1.07846×10^{-3}	2.24660×10^{-5}	-1.022
	$[90]_8$	54	43.87086	1.48554×10^{-1}	0	47.436
	$[0_2/90_2]_s$	53	0.72851	1.42919×10^{-3}	-5.26443×10^{-6}	0.760
P75S/934	$[0]_8$	48	-1.08952	1.13846×10^{-3}	2.01227×10^{-5}	-1.051
	$[90]_8$	48	32.99234	5.01059×10^{-2}	5.83457×10^{-4}	34.531
	$[0_2/90_2]_s$	50	-0.23764	1.95718×10^{-3}	1.71117×10^{-5}	-0.181
P75S/930	$[0]_8$	65	-1.11847	1.31669×10^{-3}	1.92998×10^{-5}	-1.076
	$[90]_8$	65	28.63332	1.23597×10^{-1}	2.23925×10^{-4}	31.730
	$[0_2/90_2]_s$	65	-0.54396	3.59615×10^{-4}	3.81570×10^{-6}	-0.533
C6000/PMR-15	$[0]_8$	60–65	-0.26280	1.86422×10^{-3}	8.949×10^{-6}	-0.213
	$[90]_8$		21.07760	5.37334×10^{-2}	1.11175×10^{-4}	22.432
	$[0_2/90_2]_s$		1.57261	2.51919×10^{-3}	2.96137×10^{-6}	1.635
	$[0/45/90/-45]_s$		1.46009	2.75219×10^{-3}	5.5277×10^{-6}	1.529
HMS/ borosilicate	$[0]_8$	47	-0.42372	3.81993×10^{-4}	-6.31687×10^{-6}	-0.418
	$[90]_8$	44	3.75852	-3.42241×10^{-4}	-4.49064×10^{-5}	3.724
	$[0/\pm 60]_s$	44	0.16381	1.78600×10^{-3}	-1.02264×10^{-5}	0.201

[a] a_i, coefficients in polynomial; T, temperature; α, coefficient of thermal expansion.

results in negative CTEs for the composites. (The CTEs are not as negative as those of 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 CTE is much higher for the Gr/Pi than the Gr/glass because the CTEs of the two matrix materials are so different: about 3.6×10^{-6} and $50 \times 10^{-6}\ ^{\circ}\mathrm{C}^{-1}$ at 24°C for the borosilicate glass and PMR-15 polyimide, respectively (Fig. 7). The combination of low CTEs in both the longitudinal and the transverse directions makes the Gr/glass composite a very promising candidate for dimensionally stable structures.

The expansions 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 (Fig. 7) of the Gr/glass very close to zero, about $0.18 \times 10^{-6}\ ^{\circ}\mathrm{C}^{-1}$, and the CTE of the Gr/Pi about $1.62 \times 10^{-6}\ ^{\circ}\mathrm{C}^{-1}$ (both at 24°C). Although different fibers are used in these two composites, it is the different matrix materials which more significantly influence the net response of the composites. The low CTE of the borosilicate glass combined with the low expansion fiber results in a composite with a very low CTE. The source of the thermal strain hysteresis evident in Fig. 6 for the Gr/glass composite is not known; 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 Gr/Ep and Gr/Pi. Insufficient mechanical property data were available for the glass-matrix composite to use with the laminate theory. Very good agreement was obtained between analysis and experimental data for the P75S/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, are attributed to the use of temperature-independent properties in the analysis.

Calculated and measured CTE values at 24°C are compared in Fig. 10; the agreement is good. The differences between calculated and measured CTEs are attributed to the difference between the properties assumed for the analysis and those of the specific materials tested. These differences arise from the lack of a high-quality mechanical property data base for the materials tested and the sensitivity of the analysis results to these properties. For example, a 10% decrease in E_2 for P75/934 changes

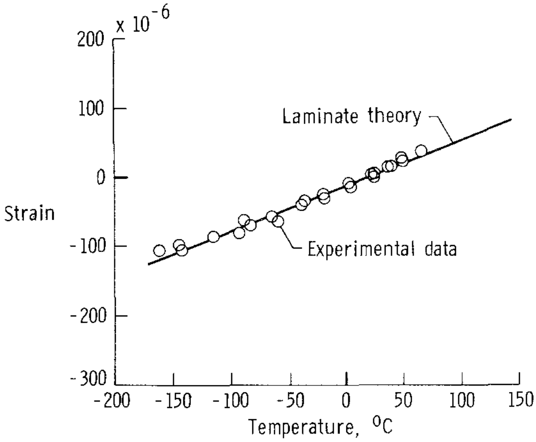

Fig. 8. Predicted and measured thermal expansion of a P75S/CE339 Gr/Ep $[0_2/90_2]_s$ laminate.

the CTE for the $[0_2/90_2]_s$ laminate from -0.185×10^{-6} to -0.27×10^{-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. 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.

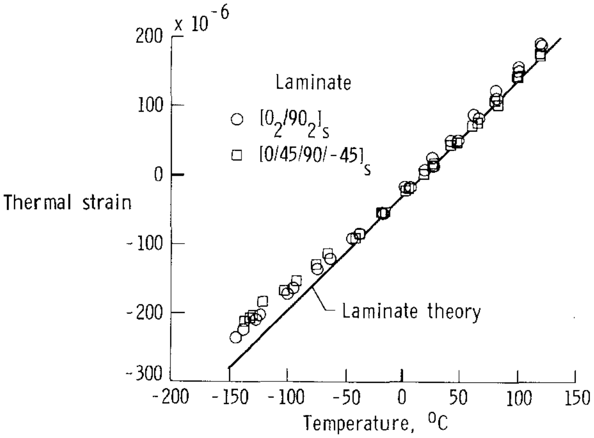

Fig. 9. Predicted and measured thermal expansion of C6000/PMR-15 Gr/Pi $[0_2/90_2]_s$ and $[0/45/90/-45]_s$ laminates.

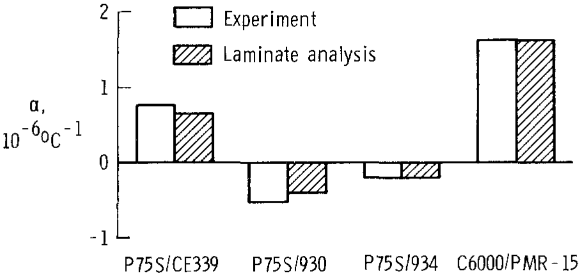

Fig. 10. Comparison of measured and predicted coefficients of thermal expansion at 24°C for Gr/Ep and Gr/Pi $[0_2/90_2]_s$ laminates.

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 [3, 6, 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 data of the Gr/glass during the 1st and 100th thermal cycles (Fig. 11) show that the expansion of this $[0/60/-60]_s$ laminate specimen was unaffected by 100 cycles between −129 and 38°C. However,

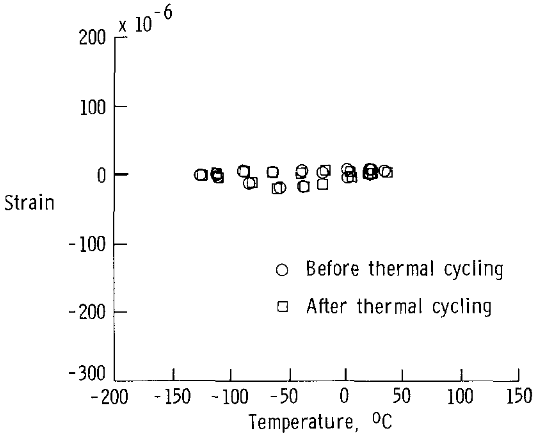

Fig. 11. Thermal expansion of a Gr/glass $[0/60/-60]_s$ laminate before and after 100 thermal cycles between −129 and 38°C.

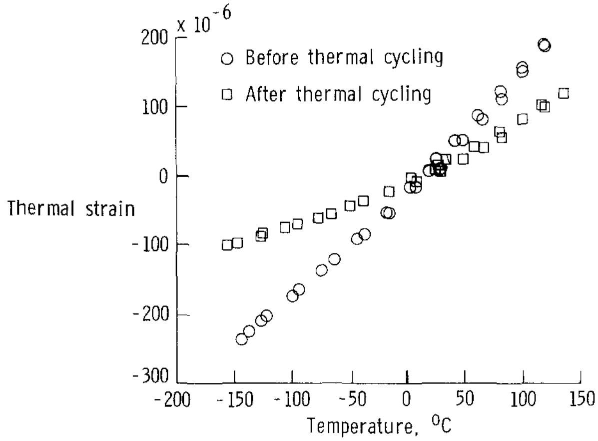

Fig. 12. Thermal expansion of a Gr/Pi $[0_2/90_2]_s$ laminate before and after 250 thermal cycles between −156 and 121°C.

the length of the specimen increased by about 76×10^{-6} cm after 100 cycles. 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 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 signigicantly reduced the CTE, from about 1.64×10^{-6} to about 0.79×10^{-6} °C^{-1} at 24°C after 250 cycles. 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 was very different from the expansion of composite laminates with single-phase epoxy-matrices and the same P75S carbon fibers, although all had the same stacking sequence $[0_2/90_2]_s$. Thus, cross-ply composite thermal expansion is sensitive to matrix material properties.

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 a 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, induced by 250 cycles between -156 and 121°C in the graphite/polyimide laminate, 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 the transverse directions. The expansion of the $[0/60/-60]_s$ Gr/glass laminate was not changed by 100 thermal cycles from -129 to 38°C; however, a residual strain of about 10×10^{-6} was measured.

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