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National Aeronautics and  
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# MONITORING FIBER STRESS DURING CURING OF SINGLE FIBER GLASS- AND GRAPHITE-EPOXY COMPOSITES

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## Summary

The difference in thermal expansion characteristics of epoxy matrices and graphite fibers can produce significant residual stresses in the fibers during curing of composite materials. Tests on single fiber glass-epoxy and graphite-epoxy composite specimens were conducted in which the glass and graphite fibers were preloaded in tension, and the epoxy matrix was cast around the fibers. The fiber tension was monitored while the matrix was placed around the fiber and subjected to the temperature-time curing cycle. Two mechanisms responsible for producing stress in embedded fibers were identified as matrix thermal expansion and contraction and matrix cure shrinkage. A simple analysis based on the change in fiber tension during the curing cycle was conducted to estimate the produced stresses. Experimental results on single fiber glass- and graphite-epoxy composites show that the fiber was subjected to significant tensile stresses when the temperature was raised from the first to the second dwell period. When initial fiber pre-tension is about 60 percent of the fiber failure load, these curing-induced stresses can cause tensile fracture of the embedded fiber.

## Introduction

Several studies have been conducted to understand the cure kinetics of thermoset resins (refs. 1 and 2); in particular, the manner by which the chemical and thermal changes encountered during curing leads to residual stresses in composites (refs. 3 and 4). The effect of residual stresses is reflected in the mechanical properties of cured composites (ref. 5). In calculating the thermal residual stress in composites, a stress-free state at the highest temperature in the curing cycle is commonly assumed. Thus, attention is focused on the optimization of the cooling path to minimize these residual stresses in composites.

During the curing cycle, thermoset matrices undergo significant matrix volume changes—expansion as well as shrinkage (ref. 1). Expansion occurs with the increase in the volume of epoxy when temperature is increased. Contraction occurs with the alignment of molecular chains during the cross-linking. These matrix volume changes may produce significant stresses in a fiber at various stages of the curing cycle.

The objective of this research was to monitor the fiber stresses and identify the responsible mechanisms during a typical two-stage, thermoset epoxy matrix curing cycle in various single fiber-epoxy composites. This report presents a specific experimental technique for evaluating these residual stresses. Results on glass and graphite fibers and amine-cured epoxy systems suggest that primarily two mechanisms produce stresses in the fiber: volume expansion and contraction caused by temperature change, and cure shrinkage. Results show the significance of each mechanism at different stages of the curing cycle.

## Material

The residual stress measurements were made for glass and AS-4 graphite fibers embedded in epoxy matrix. The matrix is a diglycidyl ether of bisphenol-A (EPON 828, Shell Chemical Company) cured with 14.5 parts per hundred by weight of meta-phenylene diamine (mPDA, Aldrich Chemical Company). The matrix was mixed, debulked under vacuum for 10 min, and subjected to a two-step cure cycle in air. In the first cycle, the material's temperature was increased from room temperature to 75 °C (167 °F) and held constant for 2 hr. The temperature was then increased to a second dwell temperature at 125 °C (257 °F) and again held constant for 2 hr. After the second dwell, the heating cycle was stopped and the specimen was allowed to cool to room temperature. The first dwell allows gases and other volatiles to escape from the matrix material and allows the matrix to flow. The second dwell time allows cross-linking of the

polymer. The matrix cured in this manner has a modulus of 3.6 GPa and tensile strength of 89.6 MPa.

## Experimental Procedure

The procedure was to apply a known tension to a fiber, subject the matrix around the fiber to a given temperature-time curing cycle, and then monitor the change in the fiber tension. Figure 1 shows the schematic of the experimental setup. One end of the fiber was fixed to a rigid support; the other end, passed through a cavity in a silicone mold and glued to a load cell. The thickness of the base of the silicone mold was kept as small as possible (about 0.5 mm) to minimize the effect of silicone volume change on experimental results. The load cell was mounted on a linear stage connected to a motorized actuator, whose motion was precisely controlled with a joy-stick (not shown in the figure). The linear motion of the load cell was controlled by the motorized actuator, which was used to apply tensile load to the fiber.

A predetermined tension was applied to the fiber. The resin was heated to about 75 °C and mixed with the hardener. The resin-hardener mixture was degassed for about 10 min in a vacuum oven and then poured around the fiber in the cavity of the silicone mold. The specimen was then subjected to the two-step cure cycle described in the preceding section. Heat was applied to the resin using a strip-heater; temperature was controlled with a power distributor and a temperature controller. A ceramic plate placed between the heated zone and the load cell prevented heating of the load cell. A thermocouple placed directly above the specimen monitored the temperature. The output from the load cell and the thermocouple was recorded during the curing process. The cured single fiber-epoxy specimens were removed from the mold and examined under an optical microscope to detect fiber breaks.

## Results and Discussion

For results discussed herein, the fiber is in tension and fixed between two rigid supports. One support is a load cell (see fig. 1); therefore, any change in fiber strain during the curing cycle can be detected by this device.

An example of fiber tension change during the curing of a single fiber graphite-epoxy composite is shown in figure 2. The fiber tension was unchanged for the first 1.5 hr at 75 °C. Some increase in fiber tension occurred during the last half hour at 75 °C. The fiber tension dropped rapidly when the temperature was increased from the first dwell period (75 °C) to the second dwell period (125 °C). After the tension dropped to a minimum value, the fiber tension increased slowly again during the first half hour at 125 °C. No tension change was observed during the last 1.5 hr at 125 °C. Along the cooling path, the fiber tension again increased and stabilized at completion of the cooling.

Figure 3 illustrates the mechanisms that caused changes in fiber tension during the curing cycle. This figure shows only the effect of matrix volume change on the fiber tension curves and not the mechanical preload. There are two sources of matrix volume change: heat and matrix cross-linking. In region AB, matrix volume increased as a result of thermal expansion. However, sufficient fiber-matrix interface shear strength had not yet developed because of insufficient matrix cross-linking in this region. Therefore, when the matrix volume increased, the matrix simply flowed over the fiber without causing any change in fiber tension. Matrix polymerization is expected to begin during the second dwell period (ref. 4). However, the fiber load change in region BC indicates that the matrix polymerization had already begun late in the first dwell period. Volume shrinkage associated with matrix polymerization (ref. 6) is caused by the reaction and rearrangement of the molecules into

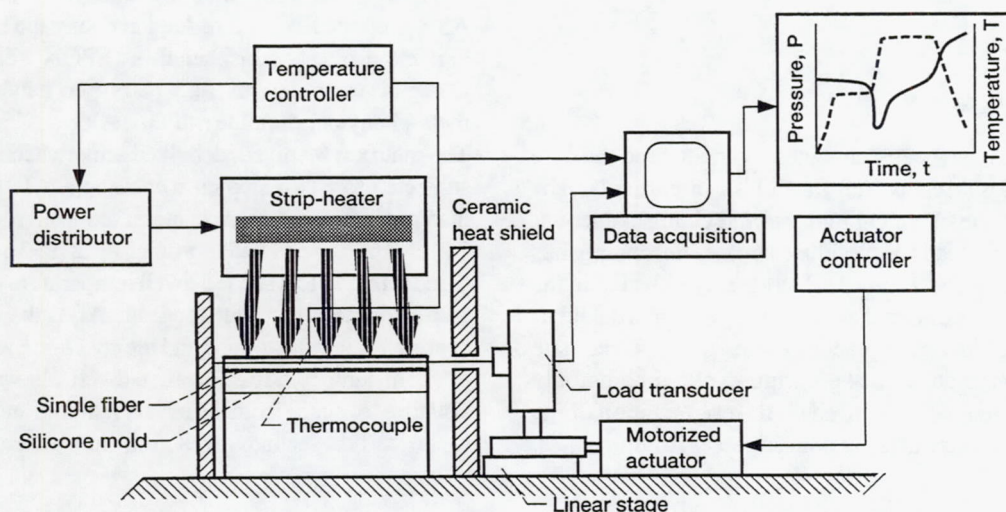


Figure 1.—Fiber load monitoring device for single fiber composite specimens.

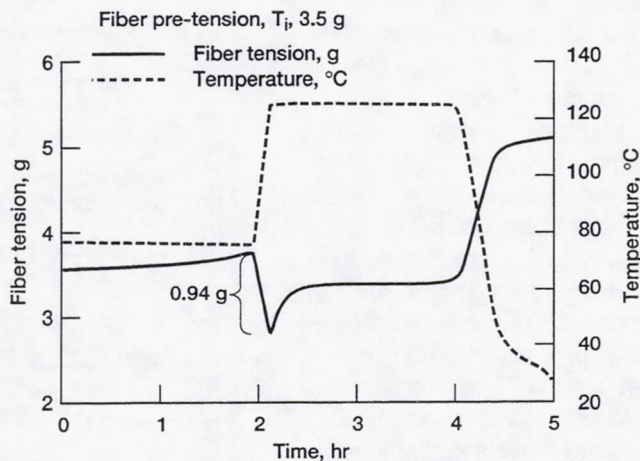
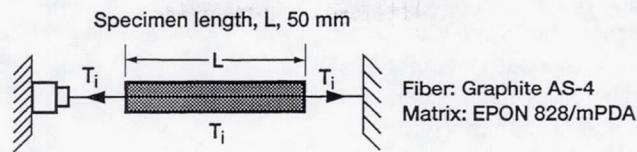


Figure 2.—Change in fiber tension detected at load cell during the curing cycle of a single fiber graphite-epoxy composite.

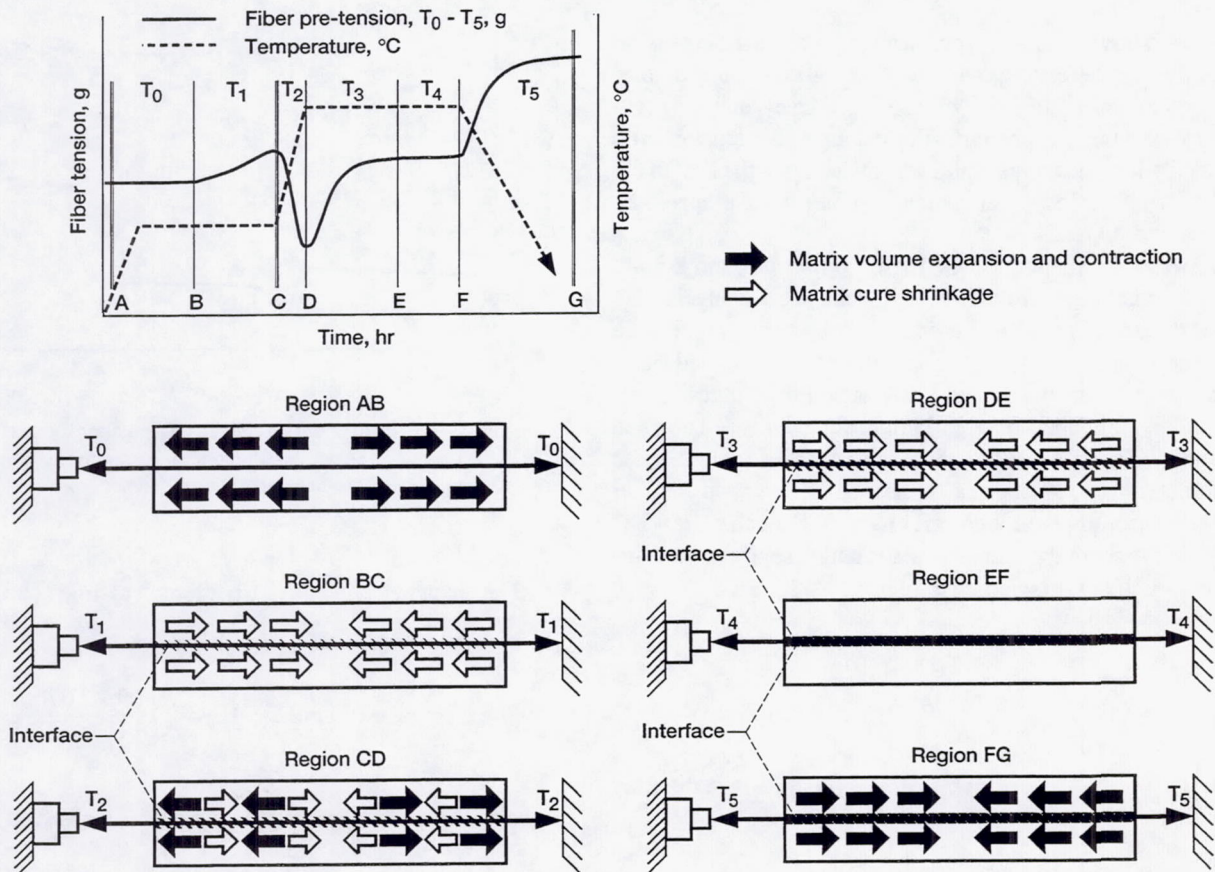


Figure 3.—Mechanisms responsible for producing fiber stress when a thermoset matrix surrounding the fiber is subjected to curing.

a more compact configuration. Since the matrix had partially polymerized, the fiber-matrix interface could respond to matrix volume changes. Matrix volume shrinkage loads the embedded fiber in compression, and thus, increases the fiber tension measured at the load cell. In region CD, when temperature was increased to 125 °C, the two mechanisms operated simultaneously. Because the matrix thermal expansion dominates the cure shrinkage, fiber tension measured at the load cell decreased. The embedded fiber experienced significant tensile stresses in this region. The matrix cross-linking process continued in region DE; the matrix shrinkage applying compressive load to the embedded fiber. Neither mechanism operated in region EF. Finally in region FG, when cooling began, the matrix volume reduction was associated only with decreasing temperature. In this region, the embedded fiber was loaded in compression.

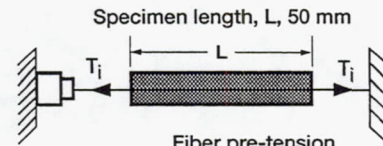
To verify these mechanisms, experiments were conducted on single fiber glass- and graphite-epoxy composites in which the specimen length and fiber pre-tension  $T_i$  were changed systematically. Figure 4 shows the effect of  $T_i$  on the fiber tension curves obtained during the curing process for glass- and graphite-epoxy composites. Within each type of composite material, the fiber tension curves are similar in that the initial pre-tension  $T_i$  does not affect the change in fiber tension during curing. Considering the mechanisms shown in figure 3, the fiber tension curves are expected to be independent of the initial fiber pre-tension.

Figure 5 shows effect of specimen length on the fiber tension curves during the curing cycle for fiber glass- and graphite-epoxy composites. In both cases, the longer matrix length caused larger tension changes. For example, the tension drop produced when the temperature was raised from the first to the second dwell period level almost doubled as the specimen length was doubled.

The average fiber stress in these composites throughout curing is calculated from simple mechanistic analysis. We assume that the fiber stresses produced in the curing process are distributed uniformly along the length of the embedded fiber. During the process, the embedded fiber length changes. Let us say that the embedded fiber end points are positioned at a and b at time  $t = 0$  (fig. 6). When the curing cycle is applied, these end points move to positions a' and b' at a time  $t = t$  and the fiber tension measured at the load cell changes to a value  $T(t)$ . The change in the normal strain in the fiber length segments not surrounded by the matrix can be expressed as

$$\Delta\epsilon(t) = \frac{T(t) - T(0)}{A_f E_f} \quad (1)$$

where  $T(0)$  is the fiber pre-tension and  $A_f$  and  $E_f$  are the fiber cross-sectional area and stiffness, respectively.



Fiber pre-tension, $T_i$ , g	
—————	3.5
- - - - -	5.0
- · - · -	7.0
- - - - -	10.0
·····	Temperature, °C

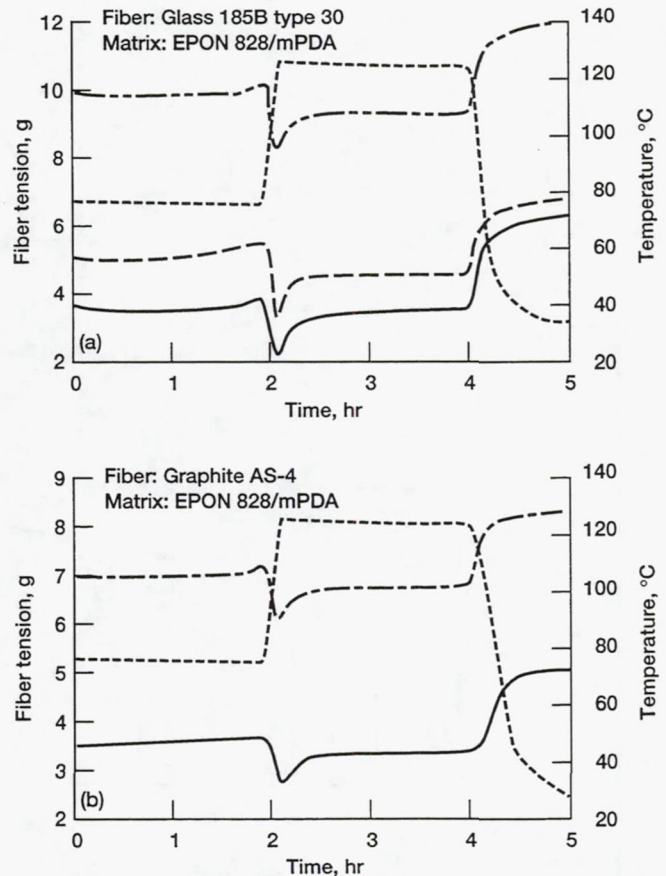


Figure 4.—Effect of fiber pre-tension,  $T_i$ , on fiber tension change during curing process. (a) Single fiber glass-epoxy composite. (b) Single fiber graphite-epoxy composite.

The change in embedded fiber length at time  $t$  can be written as

$$\delta = aa' + bb' = 2\Delta\epsilon(t)L_1 = 2 \frac{T(t) - T(0)}{A_f E_f} L_1 \quad (2)$$

where  $2L_1$  is the fiber length outside the mold (fig. 6).

Since a uniform stress distribution in the embedded fiber has been assumed, the fiber stress at a time  $t = t$  during curing can be expressed as

$$\sigma_f(t) = -\frac{\delta}{L_2} E_f - \varepsilon_{\Delta T}(t) E_f = -2 \frac{T(t) - T(0)}{A_f} \left( \frac{L_1}{L_2} \right) - \alpha_f (\Delta T) E_f \quad (3)$$

where  $\alpha_f$  is the coefficient of thermal expansion of the fiber and  $\Delta T$  is the change in temperature seen by fiber length  $L_2$  surrounded by the matrix. For many thermoset matrices, the  $\Delta T$  will also include the temperature increase resulting from the exothermic reactions during the cross-linking (ref. 7). However, since the coefficient of thermal expansion of fiber,  $\alpha_f$ , is quite small ( $\alpha_f$  for glass fiber is  $5.4(10^{-6})/^\circ\text{C}$ ;  $\alpha_f$  for graphite fiber is  $-1.6$  to  $-0.9(10^{-6})/^\circ\text{C}$ ), the second term's contribution to the fiber stress is insignificant compared with that of the first term in equation (3). Therefore, the average fiber stress is approximated as

$$\sigma_f(t) = -2 \frac{T(t) - T(0)}{A_f} \left( \frac{L_1}{L_2} \right) \quad (4)$$

Note that equation (4) does not include the stresses resulting from the fiber pre-tension  $T(0)$ .

The fiber stress calculated from equation (4) is plotted in figures 7 and 8 for fiber glass- and graphite-epoxy composites. These fiber stresses are due only to the matrix volume change; that is, fiber stresses resulting from the fiber pre-tension are not included in these curves. The embedded fiber experiences both tensile and compressive stresses during various stages of the curing cycle. Significant tensile stresses are generated when the temperature is raised from the first to the second dwell temperature. Some tensile stress is released when matrix cross-linking continues. Finally, during cooling, the matrix shrinkage applies significant compressive stresses to the embedded fiber.

According to the fiber stress plots for graphite fibers (fig. 8), the matrix volume changes produce a maximum tensile stress of about 1.5 GPa on the embedded fiber. Independent tensile tests on graphite fiber samples revealed an average fiber strength of about 3 GPa. Therefore, if these fibers are pre-tensioned to an initial stress of about 1.5 GPa, the combined tensile stress (curing-induced stress plus the initial stress) in the embedded fiber should be close to its failure stress. In those samples, a fiber fracture can occur during the curing cycle. To verify this, tests were conducted on fiber graphite-epoxy specimens in which the fiber pre-tension was about 50 percent of the expected

fiber failure load. Results on two of those specimens having pre-tensions of 6.5 g (1.3 GPa) and 7.0 g (1.4 GPa) are shown in figure 9. After the completion of the curing cycle, the specimens were examined under an optical microscope for fiber cracks. No fiber crack was detected in the 6.5-g, pre-tensioned fiber specimen. However, in the 7.0-g, pre-tensioned fiber specimen, one fiber crack was detected (see fig. 9). The fiber cracks were observed in several other specimens in which the fiber tension was larger than 7.0 g (1.4 GPa). These observations suggest that, although the analysis used to calculate the fiber stress during the curing is based on some gross assumptions, such as

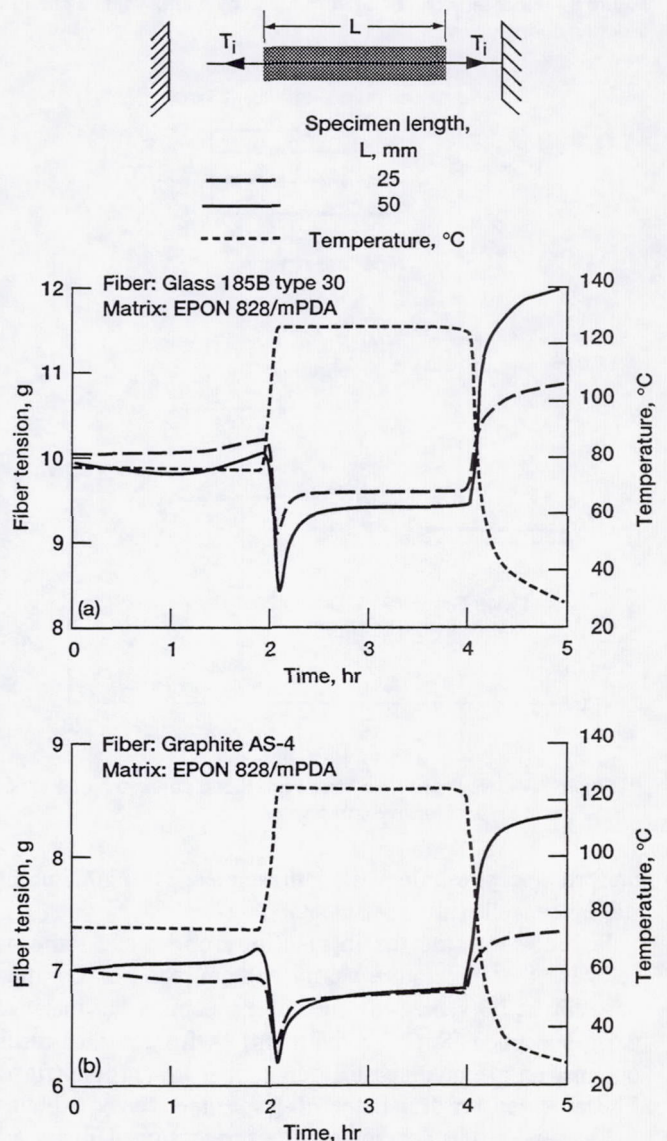


Figure 5.—Effect of fiber specimen length,  $L$ , on fiber tension change during curing process. (a) Single fiber glass-epoxy composite. (b) Single fiber graphite-epoxy composite.



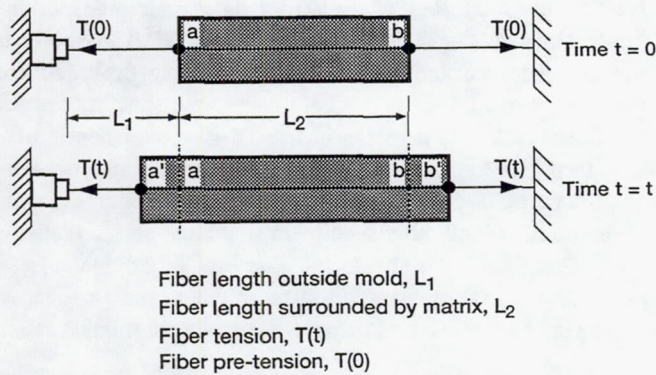


Figure 6.—Fiber tension change produced by matrix volume change during curing cycle.

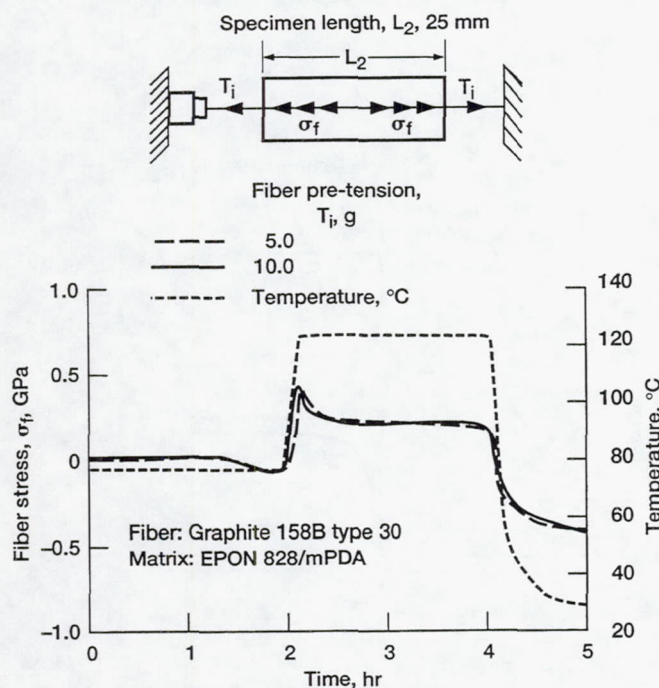


Figure 7.—Calculated fiber stress produced during the curing of single fiber glass-epoxy composites.

uniform fiber stress along the entire embedded length, findings still agree well with experimental observations.

Figure 9 shows that the fiber tension drop detected at the load cell when the temperature was raised from 75 to 125 °C is much larger in the 7.0-g, pre-tensioned fiber specimen than that in the 6.5-g specimen. Such behavior differs from earlier results obtained on specimens with different fiber pre-tensions (fig. 4). The larger tension drop in the 7.0-g specimen can be explained as follows. The tensile fracture of the pre-tensioned fiber occurs with the temperature increase from 75 to 125 °C. Because of initial tension, the fiber tries to “spring-back” after its fracture. The fiber break partially relieves the fiber stress. The viscous matrix, not completely cured, allows the fiber to partially spring back and thus to produce a relatively large fiber crack and a larger fiber tension drop at the fiber end attached to the load cell.

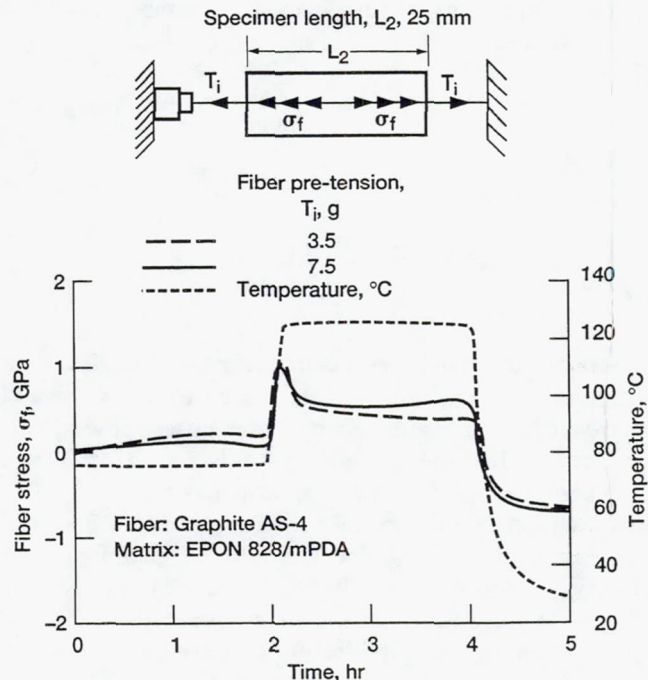


Figure 8.—Calculated fiber stress produced during the curing of single fiber graphite-epoxy composites.

Two additional experiments were conducted to verify fiber fracture occurrence within a short time interval at a temperature increase of 75 to 125 °C. In both specimens, the fibers were pre-tensioned to about 70 percent of their expected failure load. For one specimen, the test was terminated at point A in the temperature-time curve (fig. 10). The specimen was removed and immediately examined under an optical microscope. No fiber crack was detected. The other specimen, removed at point B in the temperature-time cycle and immediately examined under the microscope, did show fiber cracks (fig. 10). These experiments further verify that a large tensile stress occurs during the transition period when the temperature is raised from the first to the second dwell period.

Such experiments may be used to optimize the curing cycle to obtain the desired fiber residual stresses in the cured composite. For example, when the stresses resulting from the fiber pre-tension are superimposed on the curing-induced fiber stresses shown in figures 7 and 8, the fiber stress curve will move up. Thus, fiber compressive stress at the end of the cooling cycle can be reduced by applying a tensile load to fibers in a composite before subjecting them to the curing cycle. However, tensile stresses that occur during the transition from the first to the second dwell period will also increase, and can cause tensile fracture of the fiber with curing. According to the mechanisms shown in figure 3, two sources contribute to fiber stress during the transition period (region CD in fig. 3). These two mechanisms oppose each other. Because of the high heating rate in region CD, matrix thermal expansion dominates over matrix cure shrinkage. By reducing the heating rate, it should be possible to find the optimum rate in region CD so that these two mechanisms completely cancel each

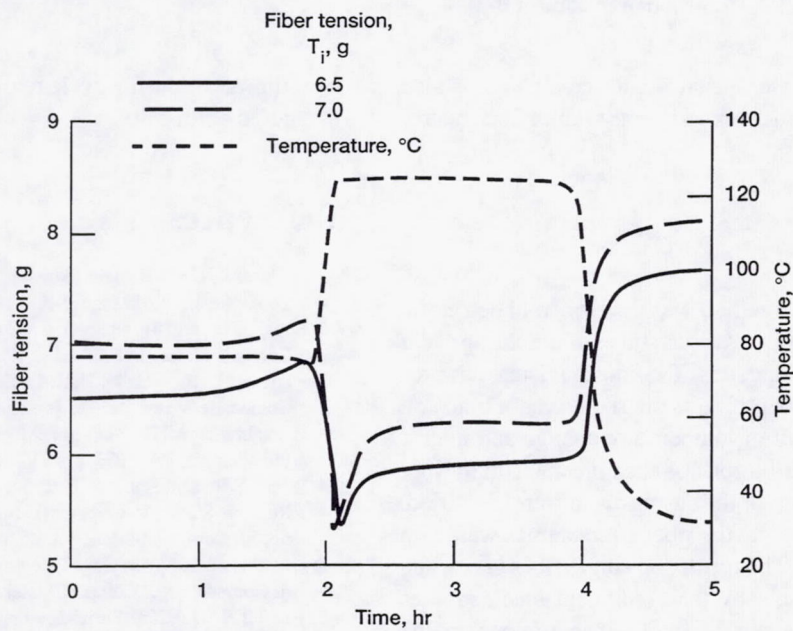
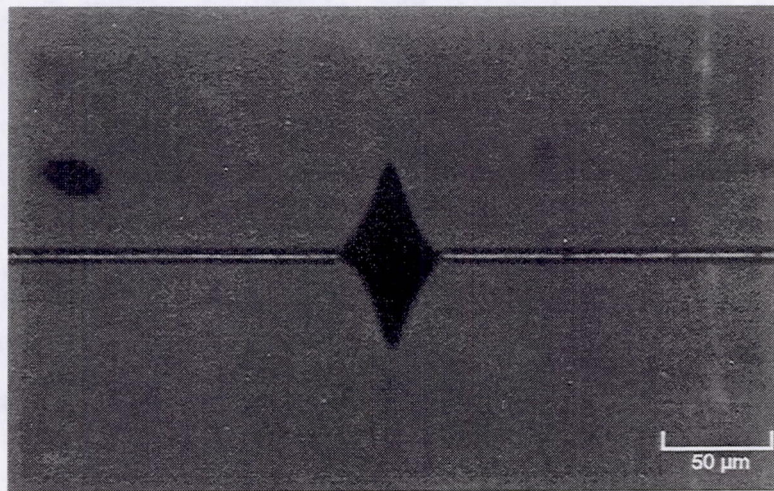
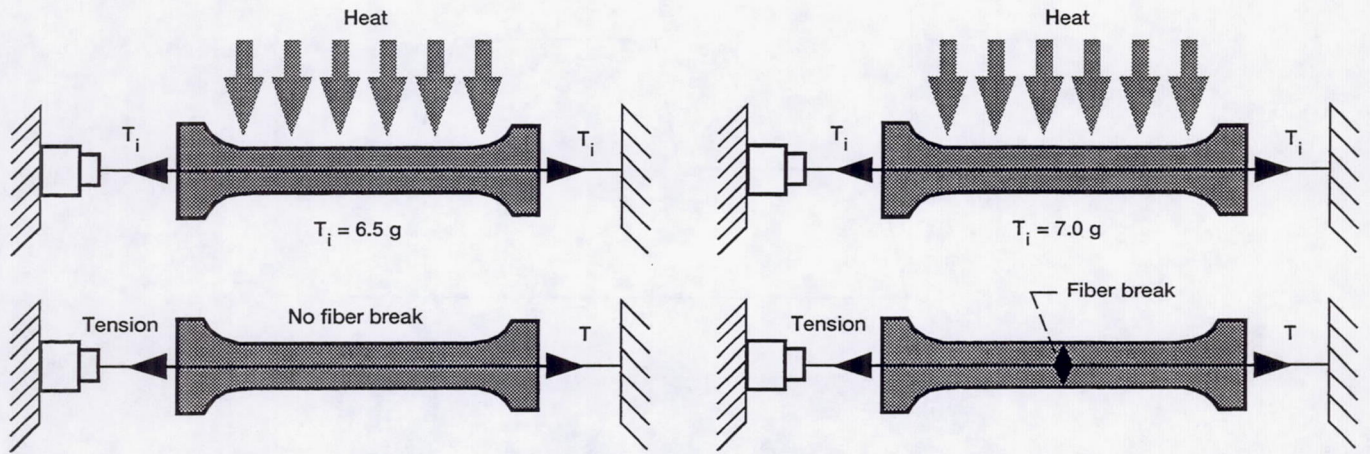


Figure 9.—Fiber tension drop curves obtained from specimens with 6.5 g (1.36 GPa) and 7.0 g (1.4 GPa) fiber pre-tensions. Photograph shows fiber crack detected in 7.0 g specimen.

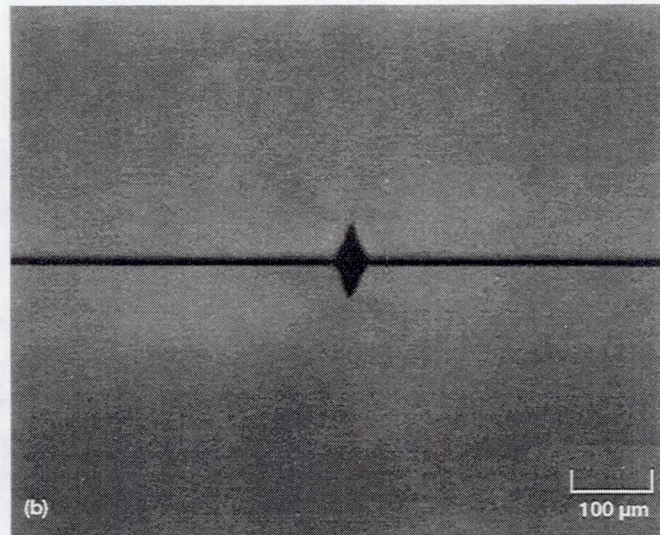
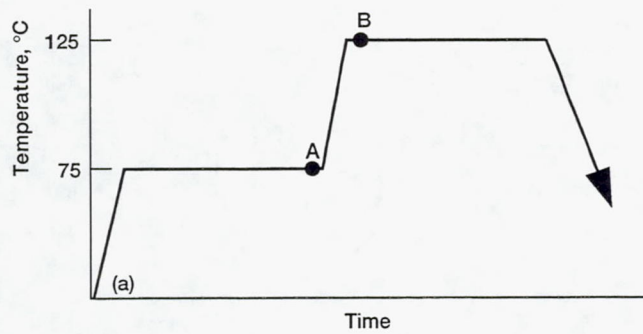


Figure 10.—Curing cycle showing points A and B at which single fiber graphite-epoxy specimens were removed to detect fiber fracture. (a) No fiber crack detected in specimen removed at point A. (b) Photograph showing fiber crack that occurred in specimen removed at point B.

other and reduce the fiber tensile stress. Research work is also currently underway to use these experiments to tailor fiber-matrix interface stresses.

## Conclusions

A simple experimental method was developed to detect the fiber stresses produced during various stages of the curing cycle of single fiber-matrix composites. Two mechanisms that produce these stresses were identified as matrix thermal expansion and contraction as a result of temperature change and matrix cure shrinkage. The contributions of each mechanism to fiber stresses in different regions of the curing cycle were identified. The analysis used to calculate the fiber stress agrees well with the experimental results. The results on single fiber glass- and graphite-epoxy composites show that significant tensile stresses are produced during the curing cycle. The regions in the temperature-time curing cycle where fiber stress occurs were identified. The experiments developed in this study can be used

to optimize the curing cycle to obtain the desired fiber stresses in a cured composite.

## References

1. Hodges, J.; et al.: Residual Stresses and the Optimum Cure Cycle for an Epoxy Resin. *J. of Mater. Sci.*, vol. 24, June 1989, pp. 1984–1990.
2. Loos, A. C.; and Springer, G. S.: Curing of Epoxy Matrix Composites. *J. Compos. Mater.*, vol. 17, Mar. 1983, pp. 135–169.
3. Pagano, N.J.; and Hahn, H.T.: Evaluation of Composite Curing Stresses. *Composite Materials: Testing and Design, Proceedings of the Fourth Conference, ASTM STP-617, American Society for Testing and Materials, Philadelphia, PA, 1977, pp. 317–329.*
4. White, S.R.; and Hahn, H.T.: Process Modeling of Composite Materials: Residual Stress Development During Cure. Part II. Experimental Validation. *J. Compos. Mater.*, vol. 26, no. 16, 1992, pp. 2423–2453.
5. Lee, S.; and Springer, G.S.: Effects of Cure on the Mechanical Properties of Composites. *J. Compos. Mater.*, vol. 22, Jan. 1988, pp. 15–29.
6. Russell, J. D.: Cure Shrinkage of Thermoset Composites. *SAMPE Q.*, vol. 24, no. 2, Jan. 1993, pp. 28–33.
7. Lee, H.; and Neville, K.: *Handbook of Epoxy Resins*. McGraw-Hill, Inc., New York, 1967.

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