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# Physical Aging in Graphite Epoxy Composites

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# Physical Aging in Graphite Epoxy Composites

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# ABSTRACT

Matrix-dominated mechanical behavior of a graphite/epoxy composite has been found to be affected by sub-$T_g$ annealing. Postcured $(\pm 45°)_{4S}$ specimens of Thornel 300 graphite/Narmco 5208 epoxy were quenched from above $T_g$ and given a sub-$T_g$ annealing at 140°C for times up to $10^5$ min. The ultimate tensile strength, strain-to-break, and toughness of the composite material were found to decrease as functions of sub-$T_g$ annealing time. No weight loss was observed during the sub-$T_g$ annealing. The time-dependent change in mechanical behavior is explained on the basis of free-volume changes that are related to the physical aging of the non-equilibrium glassy network-epoxy. The results imply possible changes in composite properties with service time.

# INTRODUCTION

The long-term properties of amorphous, glassy materials, including the cross-linked thermoset of network epoxies, have been demonstrated to change as functions of annealing time at temperatures below the material glass transition temperatures, $T_g$ (1,2). This sub-$T_g$ annealing process is typically accompanied by a volume recovery phenomenon known as physical aging (3,4).

A polymer cooled from a temperature above its $T_g$ is in a non-equilibrium state and possesses excess free volume as well as excess values of state functions such as enthalpy and volume. The molecular basis for this nonequilibrium behavior arises from the "quenching" of free volume into the polymer system due to the inability of the polymer chains to achieve their equilibrium conformation as the temperature of the system is lowered through the $T_g$. That is, due to the rapidly increasing viscosity as $T_g$ is approached, the molecules essentially undergo a "log-jam effect" and excess free volume is quenched into the system.

While a polymer is at a temperature below $T_g$, there is some degree of molecular motion. With time, its molecular system will approach the true equilibrium state. Physical aging represents the thermodynamic drive toward equilibrium in the glassy state, and the recovery process involves a decrease in free volume as the material ages.

Although the nonequilibrium behavior of inorganic glasses has been recognized for many decades, it has only been in the last 20 years or so that the nonequilibrium behavior of organic polymer-glasses has been

given some attention. This latter recognition has primarily focused on linear polymeric glasses, such as polystyrene (5), poly(ethylene terephthalate) (5,6), poly(vinyl acetate) (4,7), and polycarbonate (8). Only recently has there been some attention given to network or cross-linked glasses, such as epoxies (1,2,9).

The essence of physical aging in glasses comes forth through striking time-dependent changes in a variety of properties, including mechanical, diffusional, and dielectric properties. Specifically, with increased sub-$T_g$ storage time the material becomes stiffer and less ductile (1,2,8), sorption decreases and molecular mobility is decreased, as noted through the frequency dependence of the dielectric parameters (10,11).

This paper reports the significant effects of this nonequilibrium behavior in epoxy glasses on the time-dependent mechanical behavior of a graphite/epoxy composite. These observations are particularly important in view of the growing application of graphite/epoxy composites as structural components in the aerospace and automotive industries.

EXPERIMENTAL

Materials

The material used in this study was Thornel 300/Narmco 5208 graphite/epoxy composite. This composite was fabricated from prepreg tape manufactured by Narmco Corporation from Union Carbide's Thornel 300 graphite fiber and Narmco Corporation's 5208 epoxy resin. The Narmco 5208 epoxy resin is one of several commercial epoxies based on the TGDDM-DDS system. The main constituents are tetraglycidyl 4,4' diaminodiphenyl

methane cross-linked with 4,4' diaminodiphenyl sulfone. The Narmco 5208 system also contains about 90 pph by weight of TGDDM (72.6 percent), about 24 pph DDS (19.4 percent), and in addition about 10 pph (8.0 percent) of glycidyl ether of a bisphenol-A novolac epoxy (12). The chemical structures of these components are shown in Fig. 1. Like all epoxy resins, the system can exhibit batch-to-batch variations in properties as a result of compositional variations in both major and minor constituents.

Balanced, symmetric, 16-ply ($\pm45°$)$_{4S}$ laminates by Lockheed Missiles and Space Company, Inc., Sunnyvale, California, from 12-in.-wide Narmco prepreg tape. Following lay-up, the laminate panels were cured in an autoclave held for 0.5 h at 135°C and for 2.0 h at 180°C under a pressure of 6.895 $\times$ $10^5$ Pa (100 psi). The percentage of fiber by volume of similar panels has been determined to average 64.6 percent, with a range of variation from 64.3 to 64.8 percent.

Fiberglass-fabric/epoxy end-tab material was bonded to the laminate panels, using a sheet adhesive cured for 1.0 h at 125°C under a pressure of 3.45 $\times$ $10^5$ Pa (50 psi). The end-tab material was required to prevent grip-induced damage to the specimens during the mechanical tests. Specimens (Fig. 2) were cut from the cured laminate panel, using a dry carborundum cutoff wheel.

Procedure

The glass transition temperature, $T_g$, of Narmco 5208 was determined, using differential scanning calorimetry and dynamic mechanical analysis.

The value of $T_g$ so determined was used as the basis for annealing and sub-$T_g$ annealing treatments.

With the exception of five specimens (which were to be tested in the as-received condition) all specimens were postcured for 4 h at 200°C followed by an air cool to room temperature at a rate of about 0.5°C min$^{-1}$. This postcuring schedule was performed in an effort to totally cross-link the resin and to eliminate the potential for continued chemical aging. Five of the postcured specimens were set aside; the others were heated to 260°C for 20 min and then immediately quenched in an ice-water bath. Within 1 min after quenching, all of the specimens were wiped dry. Five of these quenched specimens were immediately tensile tested; the others were sub-$T_g$ annealed at 140°C for various times up to $10^5$ min. Time zero for the sub-$T_g$ annealing or physical aging experiment was defined as the time when a thermocouple adjacent to the specimens had reached the temperature of 140°C. Five specimens were removed from the oven and air cooled at time intervals of about 10, $10^2$, $10^3$, $10^4$, and $10^5$ min. All specimens were stored at room temperature prior to tensile testing.

Tensile tests were performed, using a servo-controlled, electro-hydraulic mechanical test machine at a constant grip displacement rate of $5 \times 10^{-5}$ sec$^{-1}$. Axial strain over a 1-in. gauge section was monitored and recorded together with the applied load. All tests were performed at 23°C in accordance with ASTM D 3518-76 (13-15).

From the resultant stress-strain record, the following tensile properties were determined: ultimate tensile stress, $\sigma_u$, which is the maximum stress a specimen can withstand prior to failure; strain-to-break, $\varepsilon_B$, which is the axial strain imparted to the specimen at total

failure; yield stress, $\sigma_y$, which is the stress at a 0.1 percent strain offset; and Young's modulus, E, which is the ratio of stress to strain for the initial, linear, elastic region of the stress-strain curve. A toughness index is also used; it is the toughness values normalized to the average value of toughness observed for specimens aged for $10^5$ min.

## RESULTS AND DISCUSSION

Thermal analysis performed by differential scanning calorimetry of the graphite/epoxy laminate indicated that the epoxy matrix material was not fully cured — an exotherm was detected during the first scan from room temperature to 300°C. Because it has been demonstrated that continued chemical aging can change the mechanical behavior of an epoxy (16), it was important to this study that all possibility of continued chemical aging be eliminated to permit a full evaluation of the effect of the physical aging phenomenon on mechanical behavior. The composite specimens were given a standard postcuring treatment of 4 h at 200°C. After postcuring, differential scanning calorimetry confirmed that the epoxy matrix was in a fully cured state with a regular step-function increase in heat capacity at a $T_g$ range of 180°C to 270°C. This result was also confirmed, using dynamic mechanical analysis.

Tensile tests were performed on the $(\pm 45°)_{4S}$ laminate with the laminate in the following conditions: as-received, as-postcured, as-quenched, and aged at decade increments from 10 to $10^5$ min at 140°C. A summary of the observed matrix-dominated stress-strain behavior is shown in Fig. 3. As can be seen, the graphite/epoxy laminate was

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found to be extremely sensitive to thermal history. The as-received specimens exhibited the highest value of $\sigma_u$ and by far the greatest values of $\epsilon_R$ and toughness. As suggested previously (16), the post-curing treatment resulted in a significant reduction in these mechanical properties. This effect is undoubtably due to the completion of the cross-linking reactions in the matrix epoxy.

Oddly enough, the postcured specimens given an ice-water quench from above $T_g$ exhibited a severe loss in strength, ductility, and toughness — far greater than that of the as-postcured specimens (Fig. 3). This observation was unexpected, based on the free-volume concept. A rapid quench will result in a significant deviation from equilibrium in the epoxy; thus, a relatively large amount of free volume will be frozen into the epoxy. Because more free volume can be inter-preted to mean higher chain mobility and shorter molecular relaxation time, an increase in free volume was anticipated to result in an increase in matrix-dominated tensile properties instead of a severe decrease.

Quenched specimens given a brief thermal annealing at 140°C for 10 min were found to exhibit tensile behavior similar to that observed for as-postcured specimens (Fig. 3). This rapid recovery of mechanical properties over that observed in the as-quenched behavior is an artifact of the quenching process and not an indication of the tensile behavior of the epoxy matrix material itself. One explanation for these observa-tions is the presence of residual stresses, which can develop in the laminate as the result of rapid thermal changes. Graphite and epoxy

have significantly different thermal expansion coefficients, and rapid cooling of the laminate will not permit the time-dependent relaxation of these stresses. The fact that a brief thermal annealing results in recovery of matrix-dominated tensile properties suggests that the residual stresses have been removed and have not caused irreversible damage in the laminate. Additionally, the fact that thermally annealed as-quenched specimens and as-postcured specimens exhibit essentially identical mechanical behavior suggests that the relatively slow cool associated with the postcure treatment and the rapid cool associated with the quench treatment result in a comparable nonequilibrium state in the epoxy matrix material.

Thermal annealing at 140°C for times investigated up to $10^5$ was found to have a severe effect on the matrix-dominated tensile behavior of the graphite/epoxy laminate, as seen in Fig. 3. The continual reduction in the stress-strain curve with decrement interval increases in exposure time at 140°C is shown in Fig. 4. These observed decreases in strength, ductility, and toughness are interpreted to be the results of the physical aging process occurring in the epoxy matrix material of the laminate. As an additional check to assure ourselves that compositional changes were not occurring in the laminate with thermal exposure, specimen weights were followed. No resolvable weight change was observed in any of the aged specimens.

The detailed influences of physical aging on $\sigma_u$, $\epsilon_B$, toughness, E, and $\sigma_y$ in this T300/5208, $(\pm 45°)_{4S}$, graphite/epoxy laminate are shown in Figs. 5-9, respectively. The ultimate strength was found to

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decrease 32 percent relative to the as-postcured specimens, with the greatest incremental decrease occurring during exposure times of $10^4$ to $10^5$ min (<u>Fig</u>. <u>5</u>). Strain-to-break was found to decrease 43 percent, with the decrease occurring generally in a linear manner with time (<u>Fig</u>. <u>6</u>).

Likewise, toughness decreased linearly with time to a decrease of 68 percent at $10^5$ min (<u>Fig</u>. <u>7</u>). The scatter in the results for modulus and yield strength was significant; however, in general, E was found to remain essentially constant (<u>Fig</u>. <u>8</u>) and $\sigma_y$ was found to decrease with time (<u>Fig</u>. <u>9</u>).

## SUMMARY

Physical aging, known to influence the long-term mechanical behavior of organic polymer-glasses including network or cross-linked glasses, such as epoxies, has been demonstrated to influence the mechanical behavior of graphite/epoxy composite as well. The matrix-dominated tensile behavior of a T300/5208, $(\pm 45°)_{4S}$, graphite/epoxy laminate was followed as a function of exposure times up to $10^5$ min at a temperature (140°C) below the $T_g$ of the matrix epoxy. Significant decreases in the strength, ductility, and toughness of the laminate were observed as functions of thermal exposure. These observations suggest that the influences of physical aging of the matrix epoxy should be considered in the prediction of the long-term durability of a graphite/epoxy composite structure.

# ACKNOWLEDGMENTS

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## FIGURE CAPTIONS

Fig. 1.  Chemical structures of the constituents of Narmco 5208 epoxy resin.

Fig. 2.  Front view and side view of $(\pm 45°)_{4S}$ graphite/epoxy specimens showing end-tab reinforcement.

Fig. 3.  Comparison of stress-strain curves for $(\pm 45°)_{4S}$ graphite/epoxy composites of different thermal histories.  (Error rectangles were drawn to indicate 95 percent confidence level for both stress and strain.)

Fig. 4.  Effect of sub-$T_g$ annealing time at 140°C on the matrix-dominated tensile properties of graphite/epoxy.

Fig. 5.  Ultimate tensile strength of the $(\pm 45°)_{4S}$ laminate as a function of the sub-$T_g$ annealing time at 140°C.

Fig. 6.  Strain-to-break as a function of sub-$T_g$ annealing time at 140°C.

Fig. 7.  Normalized toughness index or relative toughness as a function of sub-$T_g$ annealing time at 140°C.

Fig. 8.  Young's modulus as a function of sub-$T_g$ annealing time at 140°C.

Fig. 9.  Yield stress as a function of sub-$T_g$ annealing time at 140°C.
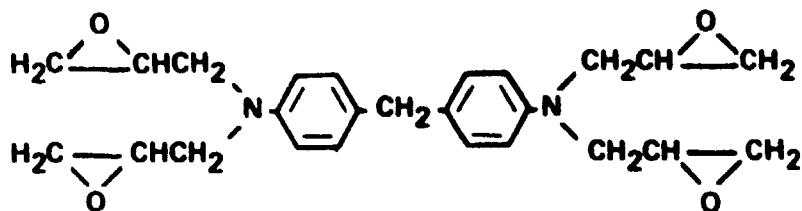
**TETRAGLYCIDYL 4, 4' DIAMINODIPHENYL METHANE EPOXY (72.6%)**
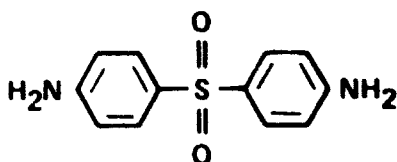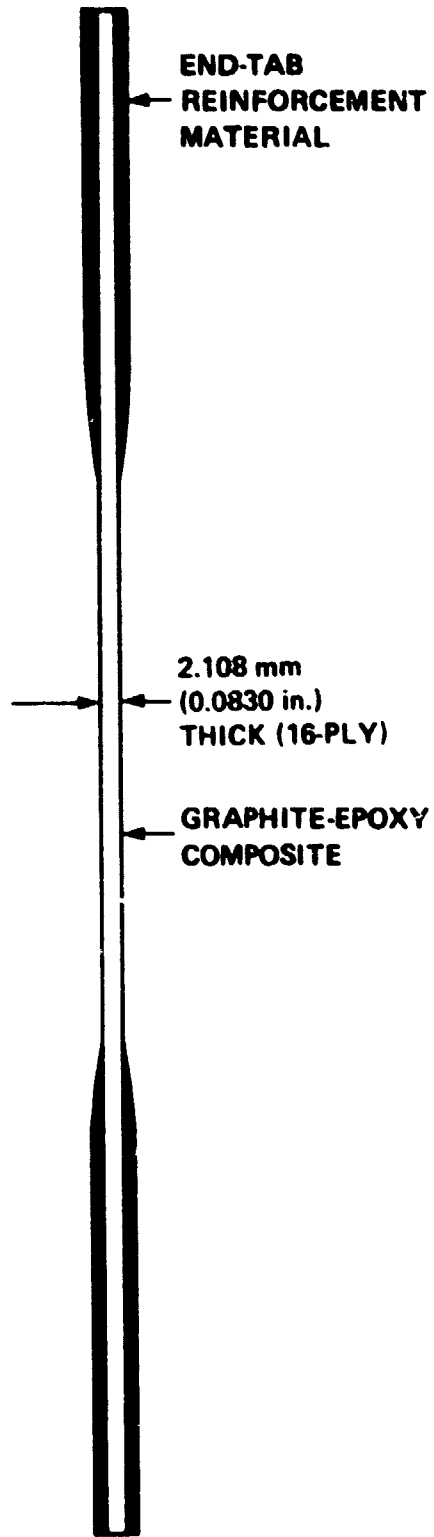


**4, 4' DIAMINODIPHENYL SULFONE (19.4%)**
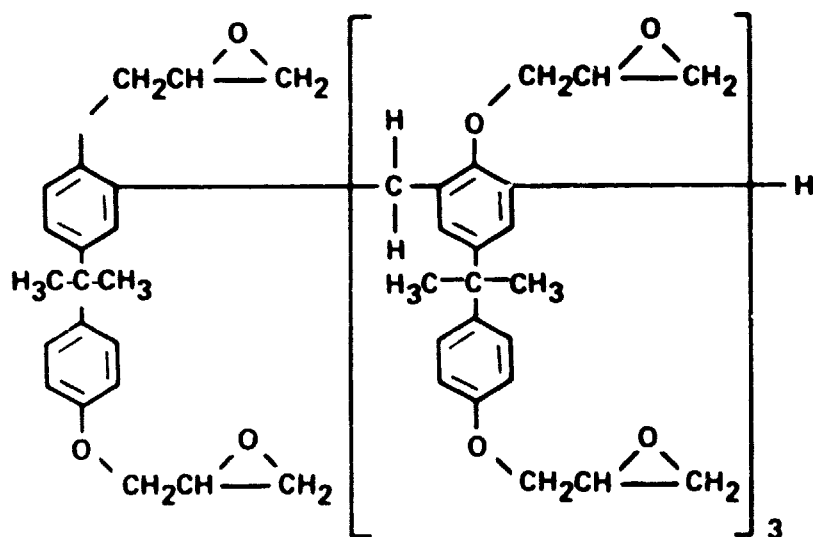


**GLYCIDYL ETHER OF A BISPHENOL-A NOVOLAC EPOXY (8.0%)**

Fig. 1

12.7 mm
(0.5 in.)

63.5 mm
(2.5 in.)

76.2 mm
(3.0 in.)

63.5 mm
(2.5 in)

FRONT VIEW

END-TAB
REINFORCEMENT
MATERIAL

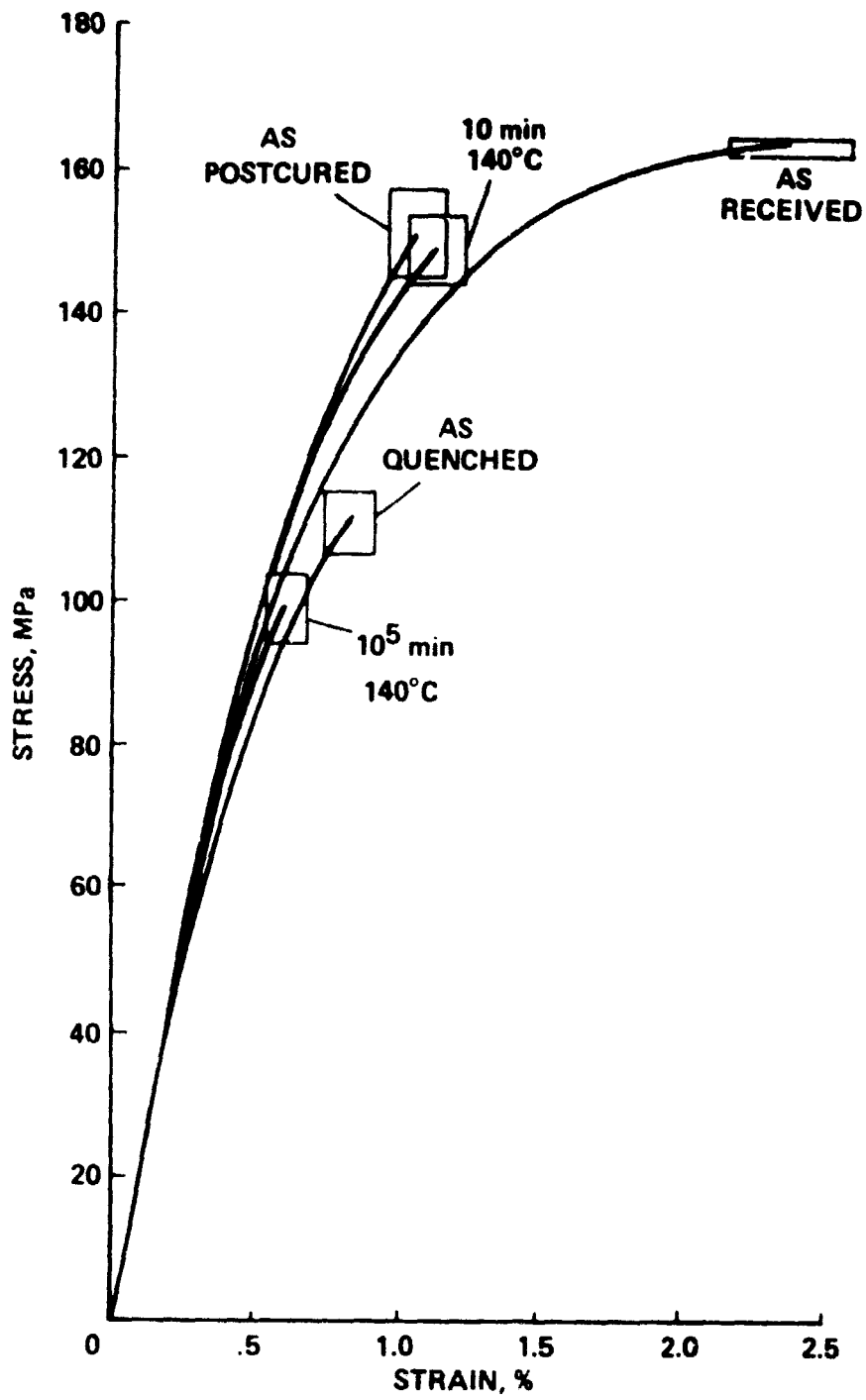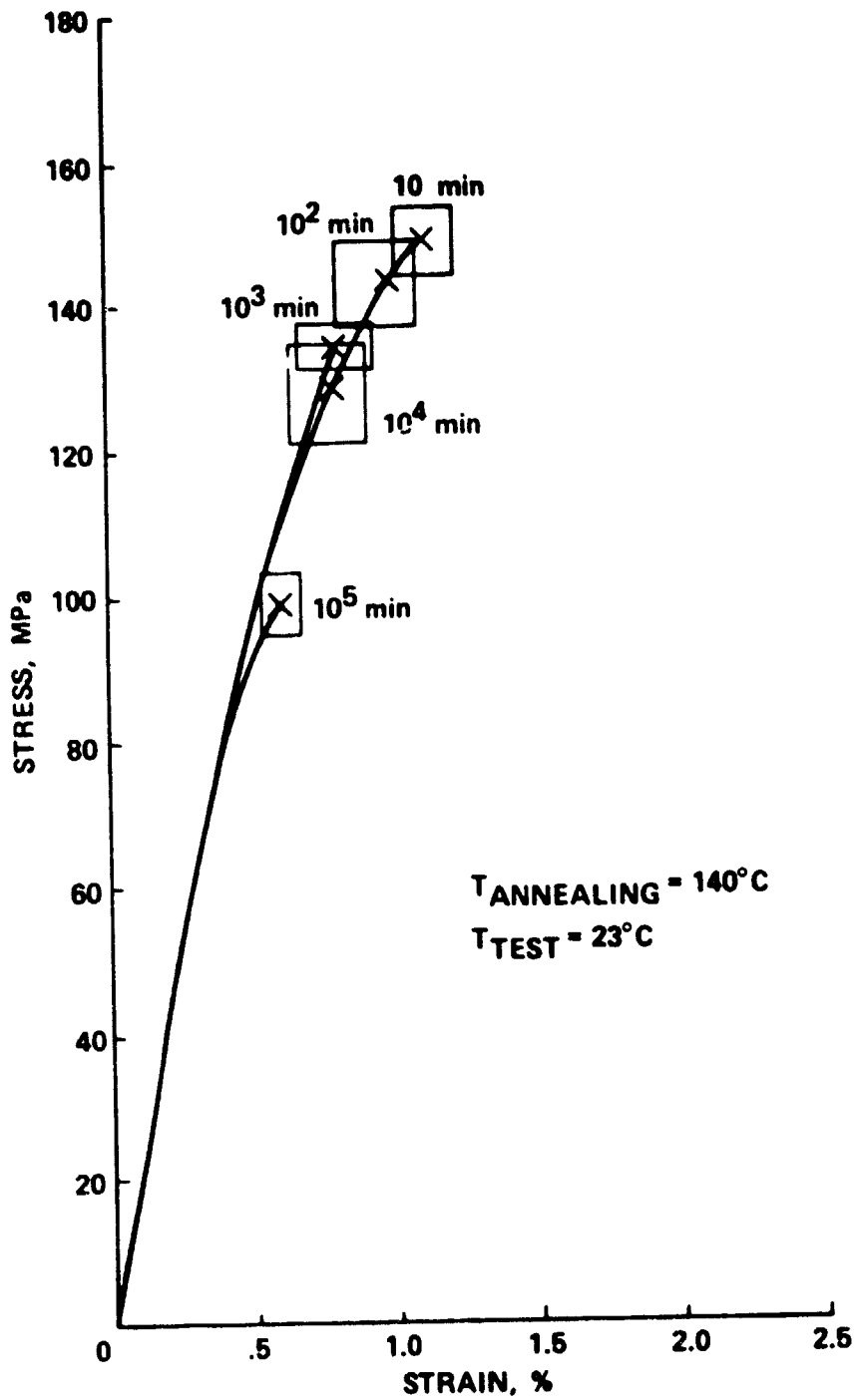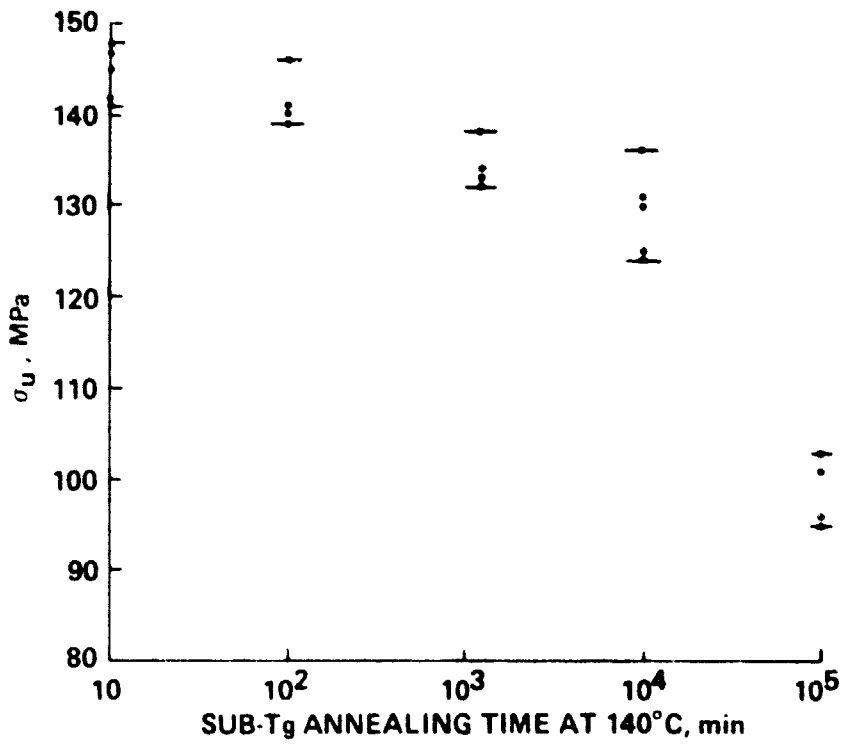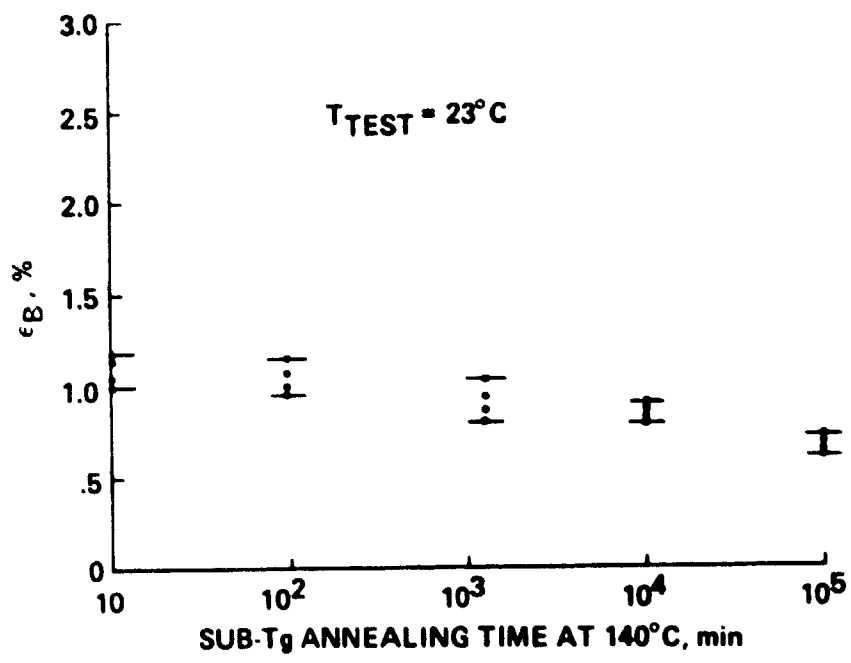2.108 mm
(0.0830 in.)
THICK (16-PLY)

GRAPHITE-EPOXY
COMPOSITE
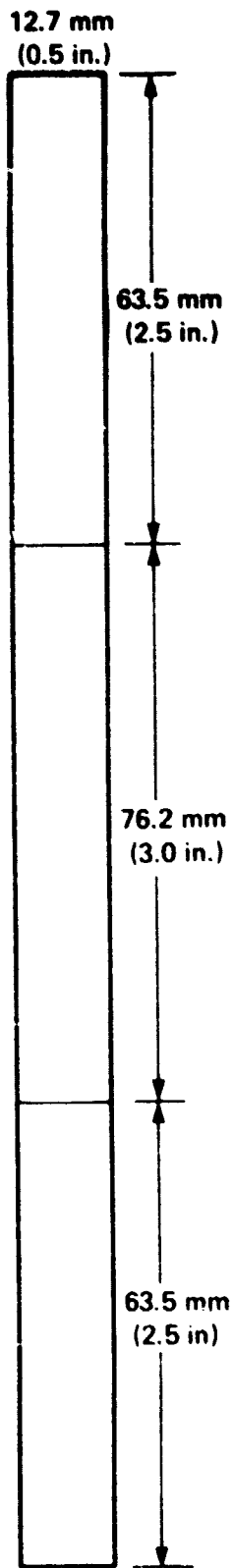
SIDE VIEW

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9