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ABSTRACT: Tension tests on $(0°)_8$ T300/5208 graphite/epoxy composites
were performed to determine the influence of various quality control
variables on failure strength as a function of moisture and moderate
temperatures.   The extremely high- and low-moisture contents investigated
were found to have less effect upon properties than did temperature or
the quality control variables of specimen flaws and prepreg batch-to-
batch variations.   In particular, specimen flaws were found to drasti-
cally reduce the predicted strength of the composite, whereas specimens
from different batches of prepreg displayed differences in strength as
a function of temperature and extreme moisture exposure.   The findings
illustrate the need for careful specimen preparation, studies of flaw
sensitivity, and careful quality control in any study of composite
materials.

KEY WORDS: Composite materials, graphite/epoxy composites, tensile
strength, environmental tests, moisture, quality control

The use of composite materials in commercial aircraft primary structures
is hindered by the absence of convincingly reliable techniques for predicting
composite durability under actual service conditions.   Development of such
techniques is complicated by the fact that significant changes in composite
durability can occur not only at extreme temperatures, but also at moderate
temperatures due to extreme moisture contents.   This problem is being
addressed at NASA-Ames Research Center in a program investigating the

mechanisms of deformation, strength degradation, and failure of graphite/ epoxy composites. The portion of that work to be reported here involves an assessment of the influence of various quality-control variables -- specifically prepreg batch, cure conditions, and specimen quality -- on the effect of moisture and moderate temperature on the tensile properties of $(0°)_8$ Thornel 300/NARMCO 5208 graphite/epoxy composites.

Experimental Procedure

Materials

The "T300/5208" graphite/epoxy composite was fabricated from prepreg tape manufactured by NARMCO Materials, Inc., from Union Carbide Corporation's Thornal 300 graphite fiber, and NARMCO's 5208 epoxy resin. Table 1 gives the physical and mechanical properties of the WYP-30-1/0 (zero twist) grade of Thornel 300 fiber used in the prepreg. The NARMCO 5208 epoxy resin is one of several commercial epoxies based on the TGDDM-DDS system, that is, the main constituents are tetraglycidyl 4,4'-diaminodiphenyl methane epoxy (such as Ciba Geigy MY-720) cured with 4,4'-diaminodiphenyl sulfone (such as Ciba Geigy Eporal). The 5208 system contains about 90 parts-per-hundred (pph) by weight of TGDDM, about 24 pph DDS, and about 10 pph of glycidyl ether of a bisphenol-A novolac epoxy (Celanese SU-8) [1].

Specimen Fabrication

The specimens used in this study were fabricated for NASA-Ames by an outside vendor. Large (approximately 1 m²) panels of the suitable lamination sequence were prepared from one of two different batches of 0.3-m-wide prepreg tape. These panels were cured in an autoclave held for 1/2 h at 135°C and then 2 h at 180°C, under 700 kPa pressure. The average volume percent fiber from these panels was determined to be 64.6%, with a range of 64.3 to 64.8%.

Next, vendor-fabricated tabs made from 0°/90° fiberglass fabric and epoxy resin were bonded to the panels. The tab adhesive used for the panels made from prepreg batch A was FM-143 adhesive by 3M cured for 1 h at 125°C and 50 psig. For the panels made from prepreg batch B, an unknown but reportedly comparable adhesive was used. Specimens were then cut from the panels using a dry carborundum cut-off wheel. The nominal configuration of these specimens was 12.7 mm wide, 1.2 mm thick, with a gage length of 127 mm, and 60-mm-long fiberglass tabs.

The as-received specimens were found to suffer from numerous fabrication defects. Two problems were particularly troubling: (1) extensive torn fibers stuck out from the cut sides, and numerous edge delaminations extended into the cut sides of specimens; and (2) the composite itself, or the composite plus the tabs, tended to be bowed. Because of our concern over these defects and because of reproducibility problems in our preliminary results, most of the specimens used in this study were subjected to extensive screening and rework. This procedure involved screening the specimens and rejecting any specimens that exhibited obvious bow or other irreparable defects. The specimens were then reworked by wet-polishing sufficient material off both cut sides to remove all detectable (at 30×) torn or delaminated material. This screening and rework procedure was done to bring all specimens up to the quality outlined in the ASTM Test Method for Tensile Properties of Oriented Fiber Composites (D 3039-76). The resulting width of these polished-edge specimens ranged from 10 to 12 mm. The properties of unpolished-edge specimens were also investigated. These specimens were screened for bow and for edge defects. Only specimens without visually obvious edge delaminations were retained.

In order to answer questions about the possible influence of degree of cure upon 0° properties, some of the specimens were given a postcure of 2 h at 200°C, followed by a slow oven cool.

Environmental Conditioning

As-received specimens contained 0.15 to 0.45% moisture. Specimens destined for mechanical testing were first dried in a vacuum desiccator at 100°C for 7 days, then held for at least 2 days under vacuum at room temperature. Weight gain/loss studies (on "dummy" specimens, without tabs, yet taken from the same panels) confirmed that this was sufficient time to ensure complete moisture removal from the specimens. Specimens to be tested in the "dry" condition were left in a room temperature vacuum desiccator until being tested at the appropriate temperature and <5% relative humidity (r.h.). All specimens to be tested in the "wet" condition were placed, after drying, in an environmental chamber at 60°C and approximately 100% r.h. for at least 60 days. This process produced essentially complete moisture saturation [2]. Work by Adamson, however, has shown that the so-called "reverse thermal effect" can produce an even higher moisture content than "normal" saturation in similar graphite/epoxy composites [3]. This reverse thermal effect occurs when specimens are first saturated, or nearly saturated, with water at a given temperature and then are placed in water (or high humidity) at a *lower* temperature. Thus, in order to increase moisture content to a true extreme, wet specimens were finally held at room temperature and at essentially 100% humidity for at least 45 days before testing. Weight gain from the dummy specimens confirmed such an additional increase in moisture content: specimens conditioned for at least 60 days at 60°C and 100% r.h. contained 1.57 ±0.23% of water (by weight), whereas specimens further conditioned for 45 days at room temperature and 100% r.h. contained 2.02 ±0.13%

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water.[3] All wet specimens tested in the study were subjected to this additional moisture exposure. In addition, all specimens were held at room temperature and ~100% r.h. until being tested at the appropriate temperature and ~100% r.h.

Mechanical Testing

Tension tests to failure were performed inside an environmental chamber using a 10,000-kg-capacity servo-hydraulic mechanical testing machine. The tensile grips were mounted to an alignment device consisting of a three-post ball-bearing die set. This alignment device was, in turn, mounted to the hydraulic actuator and, through a universal joint, to the load cell and load frame. Longitudinal strain was measured using an axial strain-gage extensometer; for many of the tests, transverse strain was also measured using a diametral extensometer.

All tests were done at a constant elongation rate which resulted in an actual strain rate of 3×10^{-5} s^{-1}. Time to failure (at about 1% strain) was approximately 5-1/2 min.

Experimental Matrix

The experimental conditions studied were as follows:

I.   Temperature: 25° and 96°C

II. Moisture content: Dry ≐ 0% (tested at <5% r.h. at 25°C,
                                        <2% r.h. at 96°C)

     Wet ≐ 2% (tested at ·100% r.h.)

III. Prepreg batch: Batches A and B

IV. Cure condition: Not postcured, cured as received

                        Postcured 2 h at 200°C

V. Specimen quality: Polished edges = specimens screened for
                       bow and with cut sides wet polished to
                       remove damage

                       Unpolished edges = specimens screened for
                       bow and for visually obvious damage to
                       cut sides

Nearly every permutation of conditions was studied. However, in the case of unpolished-edge specimens, only specimens from batch A, mostly not-postcured, were considered.

Results and Discussion

Our concern with the effect of prepreg batch upon properties resulted from some early findings in this study. Anomalous results from some early tests were traced to specimens prepared from prepreg batch B. A microscopic investigation of tested and untested batch B specimens and of the prepreg itself was performed. From optical microscopy, scanning electron microscopy (SEM), and consultation with NARMCO and Union Carbide, we concluded that there were indeed some differences between batch B and other prepreg such as batch A. Some of these differences are illustrated in Fig. 1. A photomicrograph of a laminate made from "normal" prepreg (such as batch A) is shown in Fig. 1a. The cut and polished filament ends reflect light very effectively and thus appear light-colored. A photomicrograph of a laminate made from prepreg batch B is shown in Fig. 1b. In this laminate, there are light and dark areas, with the transition between such areas occurring both between layers and within a single layer. In the dark areas, as can be seen from the magnified view of Fig. 1c, the individual filaments have been damaged. Figure 1c also illustrates that the dark areas are frequently connected with

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individual fiber bundles (3000 filaments to a bundle). The obvious conclu-
sion that the filaments are somehow degraded in these areas was refuted by
careful polishing and SEM work, which showed that the epoxy matrix in these
areas is somehow altered and weakened. Unless extreme care is exercised the
apparent filament degradation actually occurs during metallographic prepara-
tion. The altered epoxy matrix allows the filaments to move around and thus
be damaged during polishing. Since the altered epoxy occurs within and
around individual fiber bundles, the epoxy probably has reacted to some sur-
face effect or contaminant on *some* of the fibers used to make up the prepreg.
We suspect that this effect is related to another problem encountered on a
few occasions by other T300/5208 users and labeled "zebra tow" by them.[4] In
this case, some of the surface tows (fiber bundles) of the composite panels
tended to pull loose from the panel when the peel ply was removed. We have
noted some such surface features on specimens made from our batch B prepreg.

Figure 2 is a plot of axial elastic modulus, E_{11}, as a function of tem-
perature and moisture content at two strain levels. As can be seen from this
figure, E_{11} (as determined from the slope of the stress-strain curve) is
statistically significantly higher at an axial strain, ϵ_{11}, of 0.5% than at
$\epsilon_{11} = 0.1\%$. Other researchers have also observed this increase in modulus
with strain [2,4]. Figure 2 also illustrates that the increase holds true
for all combinations of moisture and temperature. One possible explanation
for the phenomenon is that curved filaments in the composite straighten with
increased strain so that more filaments carry the applied load [2]. Another
possible explanation is that there may be a strain-induced improvement in
orientation of the covalently bonded carbon platelets within the individual
filaments.[5]

Other findings on the behavior of E_{11} were as follows:

• There is no statistically significant effect of the cure condition or specimen quality on E_{11}.

• There may be an influence of prepreg batch upon E_{11}. The mean for batch B is systematically lower than that for batch A. For example:

		E_{11} (0.1% ϵ_{11})	E_{11} (0.5% ϵ_{11})	
25°C, wet	Batch A	129.5 ±1.9 GPa	139.5 ±2.5	(N = 12)[6]
	Batch B	127.3 ±1.6	137.1 ±1.9	(N = 9)

In this case, the mean of the batch A specimens is greater than that of batch B at the 95% confidence level.

• There is a statistically significant temperature-induced increase in E_{11} for dry specimens only. (See Fig. 2.) Since the axial thermal-expansion coefficient of the fiber is negative, that is, the fiber *contracts* axially with increased temperature, the increase in E_{11} is not surprising. However, it is not clear why no such effect is seen for wet specimens.

• There may be an effect of moisture upon E_{11}, but such an effect is not systematic. At 25°C and 0.1% strain, the mean E_{11} for the wet specimens is *higher* than that for the dry specimens to better than 95% confidence. However, at 96°C and a strain of 0.5%, the mean E_{11} for the wet specimens is *lower* than that for the dry specimens to better than 99% confidence.

Determination of the major Poisson's ratio, ν_{12}, was difficult since the diametral extensometer slipped under many conditions. It was not possible to get any "good" data on wet specimens, but the data obtained indicate no influence of any of the other variables upon ν_{12}. In particular, there appears to be no influence of strain upon ν_{12}. The mean value of ν_{12} was 0.33 ±0.01 (N = 14).

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A very important finding of this study was the magnitude of the influence of specimen quality upon 0° strength. Figure 3 compares 0° strength as a function of temperature for polished-edge and unpolished-edge batch A specimens. As can be seen, the strength is significantly increased by the improved specimen quality resulting from polished edges. It is also interesting to compare these results with strengths of specimens previously rejected as having irreparable defects:

		0° Strength	
Batch A, 25°C, dry	Polished edge	1542 ±89 MPa	(N = 9)
	Unpolished edge	1333 ±79	(N = 8)
	Rejects	1313 ±71	(N = 12)

The 0° strength of the "good" unpolished edge is no better than that of the "reject" specimens. This finding confirms that the specimen preparation procedure outlined in ASTM Method D 3039-76 is not overly conservative.

From Fig. 3, it is also seen that edge polishing produced a change in strength behavior as a function of temperature. The 0° tensile strength of dry polished-edge specimens increased significantly with an increase in temperature, whereas the small increase in mean strength for dry unpolished-edge specimens is not statistically significant. Moisture content, on the other hand, had no statistically significant effect upon strength for batch A specimens whether they were edge polished or not. Unfortunately, we were unable to get reliable strength data at 96°C wet because of end-tab failures. This was because the additional moisture content we produced using the " everse thermal effect," when combined with elevated temperature, caused tab failure to occur before composite failure. (For batch A specimens, the tabs themselves failed prior to composite failure, but for batch B specimens,

the tab adhesive failed at very low loads.) Thus, our observations on the effect of moisture content on strength are valid only at 25°C.

These findings are somewhat in disagreement with those of Lifshitz [2]. Lifshitz studied unpolished-edge specimens and reported an effect of moisture content on strength at both 25° and 96°C. Lifshitz's specimens, however, were conditioned at 60°C and ~100% r.h. only. We suspect that the additional moisture content we induced using the reverse thermal effect produced a degradation that cancelled any strength increase resulting from nominally wet conditions alone. Lifshitz also reported a statistically signficant increase in strength with temperature for his unpolished-edge specimens. However, his data only compared "room" and "wet" (without reverse thermal effect) moisture conditions, whereas ours compares dry specimens only.

Figure 4 illustrates the effect of prepreg batch upon 0° strength. The mean strength at 25°C for wet batch B specimens is less than that for dry batch B specimens at the 90% confidence level (but not at the 95% confidence level). Far more clearly significant is the difference in strength between batch A and batch B specimens at 96°C. As can be seen from Fig. 4, the batch B specimens are much weaker at this temperature. As we have explained, we were unfortunately unable to fail the composite itself at 96°C wet. Nevertheless, we suspect that the combination of temperature and moisture — each of which seems to affect the batch B specimens adversely — may have produced significant degradation in the strength of batch B specimens.

Scanning Electron Microscopy

In an attempt to understand the mechanisms that have produced the property changes described above, we have initiated scanning electron microscopy studies on the failure surfaces of the composite specimens. Figure 5 shows typical failure surfaces for dry, polished-edge, not-postcured specimens.

One specimen from each batch A and batch B was tested at 25° and 96°C. As can be seen from this figure, the appearance of the individual broken fila- ment is the same regardless of the temperature or batch. In fact, this holds true for typical failures at all conditions. Furthermore, there are few single filaments "pulled out" of any of the failure surfaces, and the amount of epoxy remaining on the surface of the filaments indicates that the inter- facial bond in all cases is reasonably strong.

It is difficult, however, to pick out differences in the specimens which might explain the observed differences in properties. Obtaining such an explanation from the failure surfaces is complicated by a number of factors. First, the elastic recoil at failure induces significant secondary damage, which complicates failure-surface analysis. Second, there is a great deal of specimen-to-specimen variability at any one condition. Third, even for a given specimen, the differences in appearance between different areas are great. Thus, no single set of micrographs such as is shown in Fig. 5 can represent the specimens.

One difference, however, appears again and again regardless of area or specimen. The matrix in the specimens tested at 96°C shows less of the smooth, cupped, and glass-like signs of conchoidal failure than does the matrix of specimens tested at 25°C. Unfortunately, this is equally true for batches A and B specimens, so it does not explain the observed strength dif- ferences between specimens of the two batches. We hope that further micro- scopy will clarify these observations.

Conclusions

Our results demonstrate that the tensile properties of T300/5208 graphite/ epoxy composites are affected by various quality-control variables. Perhaps

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the most important finding is the large effect of specimen quality (preexisting torn fibers and edge delaminations even if they are not easily detectable) on strength. Another important finding is that strength and its variation with temperature and moisture content can be influenced by prepreg batch-to-batch variations. These findings lead us to make three points about studies of mechanical properties of graphite/epoxy. First of all, the importance of careful specimen preparation technique cannot be overemphasized. The procedure outlined in ASTM Method D 3039-76 is often compromised in practice, but it is clear from our work that such a rigorous procedure is not overly stringent. Second, the influence of preexisting flaws upon properties should be an integral part of any study of composite properties. And third, the influence of such quality-control variables must either be understood or the variable itself carefully controlled in any composite destined for actual service exposure.

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Footnotes

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[3] All limits given in this paper are 95% confidence limits, based on the "t" test.

[4] Dale Black, NARMCO Materials, Inc., Costa Mesa, CA, private communication, December 1979.

[5] Myles K. Towne, Union Carbide Corp., Cleveland, Ohio, private communication, October 1979.

[6] N = number of specimens entering into statistics.

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TABLE 1 -- Physical and mechanical properties specified for WYP-30-1/0

(zero twist) grade of Thornel 300 graphite fiber[a]

Physical properties

Filaments/fiber bundle	3000
Twist	None
Filament density[b]	1.73 Mg/m^3
Filament equivalent diameter[b]	6.9 μm

Mechanical properties

Minimum tensile strength	2660 MPa (385 ksi)
Average tensile modulus	200-240 GPa (32-35 msi)
Minimum average strain to failure	1.1%

[a]Dale Black, NARMCO Materials, Inc., Costa Mesa, Calif., June 1979.

[b]Not part of specification. Taken from Union Carbide Corporation product literature.

Figure Captions

FIG. 1 — *Photomicrographs of T300/5208 laminates from "normal" (batch A) and "anomalous" (batch B) prepreg. (a) batch A, (b) batch B, and (c) batch B: anomalous fiber bundle among normal bundles.*

FIG. 2 — *Axial elastic modulus, E_{11} as a function of temperature at two different axial strains, ε_{11}, levels and moisture contents for batch A specimens. (Error bar shows 95% confidence limits. Numbers in parentheses are numbers of specimens.)*

FIG. 3 — *$0°$ tensile strength as a function of temperature for polished-edge and unpolished-edge batch A specimens at two moisture contents.*

FIG. 4 — *$0°$ tensile strength as a function of temperature for polished-edge batch A and batch B specimens at two moisture contents.*

FIG. 5 — *Scanning electron micrographs of failure surfaces of dry, not-postcured, polished-edge specimens. (a) batch A, tested at $350°C$, (b) batch B, tested at $25°C$, (c) batch A, tested at $96°C$, and (d) batch B, tested at $96°C$.*

a   b

100 μm ──▶| |◀──

c

10 μm ──▶| |◀──

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

10 μm