DETECTION OF HYDROTHERMAL AGING IN COMPOSITE MATERIALS*

David H. Kaelble
Rockwell International, Science Center
Thousand Oaks, California

In the title of this paper the term "hydrothermal", meaning separate or combined conditions of high moisture and temperature, is introduced to describe the complex property degradation processes in two graphite-epoxy composites. It became evident in the course of this study that important hydroelastic stresses degrade composite strength in much the same fashion that thermoelastic stresses do. In fact, the study shows that there are complex internal stress effects within the composite, probably concentrated at the fiber-matrix interface, which depend upon the detailed prior history of moisture-temperature exposure.

This program divided itself rather naturally into three parts which are listed below:

1) Prepare and degrade reinforced composite specimens with varied moisture susceptibility.

2) Characterize composites by NDE and correlate with mechanical strength.

3) Develop a mathematical model to relate physical property measurements with molecular mechanisms of moisture degradation.

The experimental methods utilized in these three phases of study are listed in Table I. The conclusions developed from the study are summarized as follows:

Part 1: Interface

* Surface energy analysis of both fiber and matrix correctly predict moisture degradation.

* Translaminar ultrasonic (2.25 MHz) sound velocity and absorption measures prior moisture exposure and strength degradation.

Part 2: Bulk Matrix

* Changes in chemical network structure produced by aging modify the matrix dynamic mechanical spectrum to lower sound velocity and increase absorption.

* Research sponsored by ARPA/AFML Center for Advanced NDE
Table I. Experimental Methods for Study of Moisture Degradation

<table>
<thead>
<tr>
<th>Part 1: Interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Surface energy analysis</td>
</tr>
<tr>
<td>- Interlaminar shear strength</td>
</tr>
<tr>
<td>- Moisture take up</td>
</tr>
<tr>
<td>- Ultrasonics-transverse (2.25 MHz)</td>
</tr>
<tr>
<td>- SEM failure surface</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Part 2: Bulk Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Differential scanning calorimetry</td>
</tr>
<tr>
<td>- Specific heat</td>
</tr>
<tr>
<td>- Infrared spectroscopy</td>
</tr>
<tr>
<td>- Dynamic mechanical spectroscopy (1.1-110 Hz)</td>
</tr>
<tr>
<td>- Thermomechanical analysis</td>
</tr>
<tr>
<td>- SEM failure surface</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Part 3: Composite System Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Thermal expansivity</td>
</tr>
<tr>
<td>- Dynamic mechanical spectroscopy (1.1 - 110 Hz)</td>
</tr>
<tr>
<td>- Ultrasonics - longitudinal (30 KHz)</td>
</tr>
<tr>
<td>- Ultrasonics - transverse (1-10 MHz)</td>
</tr>
<tr>
<td>- SEM failure surface</td>
</tr>
</tbody>
</table>
• Hydrothermal (100°C in H₂O) aging induces a temporary rubbery response state through water swelling which permits micro-defect growth in the matrix phase.

Part 3: Composite System Response

• Unaged composites display a high degree of lock-in strain along fiber axis due to fiber-matrix constraints.

• Fiber-matrix strain relaxation during aging produces major temperature shifts in the glass transition.

This paper will attempt to highlight the experimental results which support these conclusions.

The properties of the two composite materials utilized for moisture degradation NDE studies are detailed in Table II. Composite SC-2-2 was moisture sensitized by treating the graphite fiber surface with a water soluble polymer. Composite SC-2-3 was moisture stabilized by hydrogen reduction of the polar organic surface of the carbon fiber. The special interlaminar shear test geometry and the surface energy analysis applied to predict shear degradation are described in detail in workshop proceedings for last year.

The upper curves of Fig. 1 show the effects of hydrothermal (100°C in H₂O) aging time t upon the interlaminar shear strength \( \lambda_b \) of composites SC-2-2 and SC-2-3. The degradation of \( \lambda_b \) can be expressed by a simple exponential decay relation as follows:

\[
\lambda_b(t) = \lambda_{b0} \left[ r + (1-r) \exp{-t/\tau} \right]
\]

where, \( r = \lambda_{b\infty}/\lambda_{b0} \) = ratio of aged \( t = \infty \) to unaged \( t = 0 \) shear strengths and \( \tau \) = the relaxation time for the degradation process. Composite SC-2-3 with \( r = 0.67 \) and \( \tau = 52.5 \) hr. is shown to be more moisture resistant than SC-2-2 with \( r = 0.37 \) and \( \tau = 3.15 \) hr. A higher value of \( r \) guarantees a greater shear strength retention under conditions of moisture equilibration in the composite while a high value of \( \tau \) indicates a low rate of degradation. The lower curves of Fig. 1 show that SC-2-3 absorbs less moisture and at a lower rate than water sensitized SC-2-2. The equilibrium uptake of 6 to 7% H₂O correlates directly with the 12% H₂O found in the pure epoxy matrix. This result shows that the less than 3% H₂O shown for composite SC-2-3 is related to hydroelastic stresses in this moisture resistant composite that restrict equilibrium matrix swelling.

The data points of Fig. 1 are average values of two or more test specimens, and the scatter in \( \lambda_b \) values reflects the local microheterogeneous character at the locus of failure as shown by scanning electron microscopy (SEM). The failed shear test specimens were dried to remove the water and then tested for translamellar sound velocity \( C_L \) and acoustic attenuation \( \alpha_L \).
Table II. Constituents and Volume Fractions of Components in Uniaxially Reinforced Graphite-Epoxy Panels

<table>
<thead>
<tr>
<th>Reinforced Composite Panel</th>
<th>SC-2-2 Moisture Sensitive</th>
<th>SC-2-3 Moisture Resistant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber plys/cm</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>Fiber</td>
<td>HTS with Gantrez 169 Size (1)</td>
<td>HTS with Hydrogen Surface treatment (2)</td>
</tr>
<tr>
<td>Resin</td>
<td>BP907</td>
<td>BP907</td>
</tr>
<tr>
<td>Volume Fractions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiber (%)</td>
<td>59.7</td>
<td>57.0</td>
</tr>
<tr>
<td>Resin (%)</td>
<td>38.1</td>
<td>43.0</td>
</tr>
<tr>
<td>Voids (%)</td>
<td>2.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Densities:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fiber $P_F$ (gm/cc)</td>
<td>1.74</td>
<td>1.74</td>
</tr>
<tr>
<td>Matrix $P_M$ (gm/cc)</td>
<td>1.21</td>
<td>1.21</td>
</tr>
<tr>
<td>Composite $P_C$ (gm/cc)</td>
<td>1.50</td>
<td>1.51</td>
</tr>
</tbody>
</table>

(1) Gantrez 169 is a high molecular weight copolymer of maleic anhydride and methyl vinyl ether applied to the fiber tow from a 1% (by weight) solution in methyl ethyl ketone solvent and dried on the fiber surface.

(2) Graphite HTS fibers heat treated for 120 min at 1038°C in a 90/10:: hydrogen/nitrogen atmosphere.
Fig. 1. Dependence of interlaminar shear strength $\lambda_b$ (upper view) and moisture content as Wt- \% H$_2$O (lower view) on hydrothermal aging time $t$ at 100°C in H$_2$O.
The results are shown in Fig. 2. The upper view of Fig. 2 shows that $C_L$ is reduced by 30% in the course of hydrothermal degradation of $\lambda_b$. The lower view of Fig. 2 shows $\alpha_2$ increases over 100% during shear strength degradation. The primary source of scatter in the data of Fig. 2 is the above mentioned scatter in $\lambda_b$ values.

It is of importance to note that the path length averaged values of $C_L$ and $\alpha_2$ developed from ultrasonic experiments (2.25 MHz at 230°C) provide a sensitive NDE measurement of prior moisture exposure and strength degradation even after the moisture has been removed.

Under Part 2 of this program a detailed study was conducted of the pure epoxy matrix during both curing and subsequent aging. A combination of IR spectroscopy, DSC, and mechanical spectroscopy measurements show that curing produces the molecular changes indicated by the upper arrow of Fig. 3, while hydrothermal aging produces the structure change shown by the disappearance of the nitrile $\text{C}=$N$ to form a guanyl urea ring structure in one of the four arms of the crosslink between the epoxy end groups and the DICY curative. The highly polar crosslink structure shown in Fig. 3 is receptive to water via strong Van der Waals bonding. A further explanation for the high water uptake in the pure resin is accounted for by the $T_g$ lowering from $T_g(\text{dry}) = 125^\circ$C to $T_g(\text{wet}) = 80^\circ$C. In other words, the water of hydration changes the cured resin from the glass to rubber state at the standard hydrothermal aging condition of 100°C in H2O.

The modification of the crosslink structure as shown by the lower arrow of Fig. 4 is expected to modify the low temperature $\beta$ transition which is displayed at $T_\beta = -45\pm 15^\circ$C at low dynamic frequencies of $f = 1$ to 1000 Hz. The curves of Fig. 4 plot dynamical mechanical loss tangent $\tan \delta$ versus temperature as developed by 110 Hz Rheovibron measurement of unaged and aged-dried epoxy matrix. These curves show that $\tan \delta$ is higher in the aged and dried specimen at temperatures above $-50^\circ$C, indicating lower modulus or sound velocity due to the higher level of viscoelastic response. The effects of aging on composite ultrasonic response (see Fig. 2) correlate with both the results of IR spectral analysis for chemical structure (see Fig. 3) and Rheovibron measurements (see Fig. 4) of the pure resin phase.

Instron thermomechanical (TMA) measurements of stress-strain response at relaxation times $t = 15$ sec and strain $= 0.5\%$ provide thermal response data that encompass both the low temperature $\beta$ transition and high temperature $\alpha$ or glass transition. The upper curve of Fig. 5 shows the tensile relaxation modulus $E(t)$ for the cured but unaged pure matrix with a slight modulus change at $T_\beta = 60$ and a major modulus change at $T_\alpha = 122^\circ$C with a plateau response above $T_g$ characteristic of a highly cross linked rubbery state. The lower curve shows the combined effect of aging and hydration on lowering both $T_\beta = 90^\circ$C and $T_\alpha = 75^\circ$C. Redrying the sample to remove all
Fig. 2. Variation of interlaminar shear strength $\lambda_b$ (aged-hydrated) with sound velocity $C_L$ (upper view) and attenuation $\alpha_L$ (lower view) of subsequently dried composites SC-2-2 and SC-2-3.
Epoxy + Dicyandiamide (DICY)

\[
\begin{align*}
&\left[\begin{array}{c}
0 - CH_2 - H - CH_2 \\
\end{array}\right]_4 + H_2N - C - N - C = N \\
\end{align*}
\]

Fig. 3. Suggested curing mechanisms for Epoxy BP907 Resin.
Fig. 4. Temperature dependence of tanδ for cured BP907 Epoxy Matrix at 110 Hz.
Fig. 5. Tensile relaxation modulus $E(t)$ versus temperature $T$ for cured BP907 Epoxy at $t = 15$ sec.
water restores $T_B = -60$ and $T_a > 100^\circ C$ but lowers $E(t)$ at all temperatures above $T_B$. The TMA measurements for $E(t)$ above $T_a$ were prevented by premature tensile failure at low strain $\varepsilon < 0.5\%$. Examination of the failure surfaces by SEM revealed that small cavities of diameter $< 1.0 \mu m$ had evidently grown by internal crack growth to produce a network of penny-shaped cracks with length $\gg 10 \mu m$. Above $T_a$ these cracks extend to produce matrix cohesive failure at low stress. Spontaneous development of matrix microdefects during hydrothermal aging represents a new phenomena not anticipated by earlier studies.

Several examples which dramatically illustrate the importance of the internal stress states induced by hydrothermal aging are illustrated through hysteresis in thermal expansivity and dynamic mechanical response which disappears on thermal annealing above $T_a=T_g$ for the matrix. The three views of Fig. 6 show the collapse in transalaminar thickness of composite SC-2-3 subsequent to hydrothermal aging at $100^\circ C$ in $H_2O$ (above $T_a=85^\circ C$), subsequent cooling to $23^\circ C$, followed by drying (below $T_a=122^\circ C$). This sequence of hydration in the rubber state followed by desiccation in the glass state produces a length-temperature hysteresis where the sample length is $L_0 = 1.000 \, \text{in.}$ and is reduced by 0.6% following the first thermal cycle to $170^\circ C$ as shown in Fig. 6. The second thermal cycle shows reduced hysteresis and the third thermal cycle in Fig. 6 shows only a slight thermal lag effect and the normal increase in slope in $dL/dT$ characteristic of $T_g=120^\circ C$.

Thermal scans of tan\(\delta\) versus temperature where the Rheovibron places a longitudinal reinforced sample of composite SC-2-3 in dynamic flexure at $110 \, \text{Hz}$ are shown in the curves of Fig. 7. Scans 1, 2, and 3 for the unaged composite show steady shift in $T_a$ to higher temperature. The first thermal scan of the aged-dried specimen shows increase in tan\(\delta\) at temperatures below $100^\circ C$ and then a bending over of the tan\(\delta\) versus $T$ curve so that a second thermal scan shows a $T_a$ response which coincides with the thermally annealed unaged specimen.

The response shown in these last two figures (Figs. 6 and 7) is interpreted as showing the relaxation of internal stress within the composite. The unrelaxed internal stress dilates the matrix and suppresses the magnitude of $T_0$. The excess intermolecular free volume introduced on dessication of the hydrated composite below $T_a$ is one source of the stress effect and may be termed a "hydroelastic" stress. The increasing $T_a$ with thermal scans for unaged composite SC-2-3 evident in Fig. 6 shows the relaxation of thermoelastic stresses evidently introduced during the cure cycle by volume change due to crosslinking and differential fiber-matrix contraction.

The results developed in this brief examination of experimental data show that the measurement program of Table I provides a rather clear view of the effects of hydrothermal aging in graphite-epoxy composites. The conclusions of Table II are partially amplified by the experimental results shown in Figs. 1-7 and will be more fully detailed in the papers eminating from this work.
Fig. 6. Linear thermal expansivity of composite SC-2-3 transducer to fiber orientation subsequent to hydrothermal aging and drying (initial sample length 1.000 in. at 23°C).
Fig. 7. Temperature dependence of $\tan \delta$ for composite SC-2-3 parallel to fiber orientation for unaged and aged-dried specimens.
A summary of candidate standard and developmental NDE tests which appear promising in terms of development as practical field test for strength degradation in composites are listed in Table III. This listing is not exclusive of other methods, and reflects those techniques which appear most promising based upon the experience gained in this program. Ultrasonics and acoustic emission with associated frequency spectral analysis appear as sensitive and highly diagnostic methods for detection of strength degradation. Thermography and penetrants appear as excellent tools for detecting failure of protective surface treatments or degradation of surface structures exposed to environmental extremes.

Gages such as strain-density sensors or dielectrometer electrodes can, of course, be fabricated into a composite material and operated as valuable new methods for monitoring internal stress and physical response. Specific spectrographic tests that can conduct an analysis of the chemical structure state of the composite surface using optical (IR) or microwave response of the polymer matrix phase are also recommended by the very specific information deduced from IR spectroscopy in this study. In conjunction with the methods of Table III, an appropriate selection of laboratory tests for materials and subsystem response from Table II is, of course, required to isolate the physiochemical mechanism of strength degradation.

References:


Table III. Candidate Diagnostic NDE Tests for Strength Degradation in Composites

**CANDIDATE STANDARD NDE TESTS**
- Ultrasonics (Frequency Spectra)
- Acoustic Emission
- Thermography
- Penetrants

**CANDIDATE DEVELOPMENTAL TESTS**
- Strain-density Sensors
- Dielectrometry
- Radiofrequency and Microwave Tests
- Infrared Spectroscopy
DISCUSSION

DR. LACKMAN (Rockwell International, B-1 Division): I think we have time for about two or three questions.

MR. GEORGE EPSTEIN (Aerospace Corporation): Dave, have you considered nuclear quadrupole resonance which has shown promise in measuring internal stresses or changes in the stress phase?

MR. KAELBLE: This is a whole new area to me, and, in fact, I think the whole proposition of the dynamic variations in internal stress and strain needs to be looked at very sensitively. I think that spin resonance, NMR, and various other techniques which give a signature with regard to both intra and intermolecular motion are really very important, useful techniques to apply. I think that they can be applied indirectly through standard NDT measurements, and it's a matter of establishing a logic bridge between the real mechanism and the thing you're measuring.

MR. EPSTEIN: The other part of my question is: What is the possibility of developing a coating that would prevent moisture penetration in the first place?

MR. KAELBLE: Well, that is an approach. Of course, you can stabilize a system internally, and, in fact, the interface design studies seem to indicate that's a very viable approach. The protective coating approach is also viable. A criticism of this approach is stated as follows: "If we have a single defect, we've opened the whole system to ultimate degradation." But I have to reflect that steel in salt water has been protected by paint, and it's a universal solution to that particular problem. If one talks about protective coatings which are refurbished, certainly I would have to consider that an approach. It's an independent approach from internal protection.

DR. LACKMAN: All right. One more question.

MR. JIM BROWN (Rockwell International): Your work indicates the degradation is at least partially irreversible, which is quite different than most other studies. Do you explain this by the microcracking or do you have other explanation?

MR. KAELBLE: Now, it's quite clear that, depending on the system, you can involve both matrix and interface degradation; but clearly the interface is the dominant factor in these studies. The separation in the early figures of the degree and extent of degradation of the composites clearly reflects an important influence in the interface.