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MOISTURE DIFFUSION ANALYSIS OF COMPOSITE STRENGTH DEGRADATION

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ABSTRACT

Moisture diffusion analysis (MDA) has been developed as a new non-destructive evaluation methodology to monitor the strength degradation of graphite-epoxy composite materials. Studies of composite strength degradation due to high moisture identify reversible strength loss due to current moisture content and irreversible strength loss related to prior moisture exposure with microstructure damage. MDA measures current moisture content, directional diffusion coefficients, and moisture concentration profiles. MDA measurement utilizes an electrolytic cell to concurrently record cumulative moisture content and moisture effusion rate. Extension of the diffusion analysis of moisture diffusion coefficients and indicates a high sensitivity of MDA to moisture degradation of the fiber-matrix interface. Extension of the methodology to analyze non-Fickian diffusion shows that MDA can be applied to locate regions of composite strength degradation related to hydrothermal cycling effects. Studies which correlate MDA with ultrasonic response, and interlaminar shear strength of composite laminates subjected to localized moisture damage, show that MDA can be applied to map and locate low strength regions of a composite structure.

Introduction

Recent studies by McKague, Hallais, and Reynolds\(^1\) showed that the moisture diffusion properties of graphite-epoxy composites are substantially altered by hydrothermal (separate or combined exposure to high moisture and temperature) cycling which simulates the service conditions of supersonic aircraft. Augl and Berger\(^2\) also report that thermal cycling of unidirectional graphite-epoxy composites previously exposed to moisture increased the moisture diffusion coefficient yet did not reduce the flexural or shear strength. In both studies the increase in diffusion coefficient is attributed to microcrack formation. In studies designed to investigate moisture degradation in graphite-epoxy composites, Kaelble and Dynes\(^4\) recognize that ultrasonic acoustic response and moisture diffusion analysis (MDA) combine as a new methodology for nondestructive evaluation of moisture exposure effects.

One of the important objectives in nondestructive evaluation (NDE) of composite materials is to clearly document and correlate the departure of a primary performance property such as strength with other physical responses which can be evaluated nondestructively. This report details the complete results of a study of hydrothermal cycling effects upon the ultrasonic velocity and attenuation, transverse dilation, moisture diffusion kinetics, and interlaminar shear strength of a uniaxial graphite-epoxy (Hercules AS Graphite-3501-5 Epoxy) composite. A portion of this study is detailed in a published report\(^3\) and will be briefly discussed here to bring the complete result into sharper focus.

Experimental

As described in an earlier report,\(^3\) a uniaxial reinforced panel of 48 plies of Hercules AS graphite fiber in 3501-5 epoxy matrix was fabricated and cured according to production optimized procedures. The resulting composite displayed a fiber volume fraction \(V_f = 0.60\) and void volume fraction \(V_v < 0.01\). This earlier report also details the chemical composition, moisture degradation mechanisms, strength loss, and NDE results for this composite designated SC4. That study showed that very precise measurement of ultrasonic wave velocity \(C_L\) and spatial attenuation \(a_L\) are required to directly detect moisture content. The longitudinal sound velocity \(C_L\) (Km/s) and spatial attenuation \(a_L\) (neper/cm) are determined by the following standard relations:

\[
C_L = \frac{T_{nt}}{T_{t2-t1}} \quad (1)
\]

\[
a_L = \frac{1}{T} \ln \left(\frac{A_1}{A_2}\right) \quad (2)
\]

where \(T\) is composite thickness, \(nt\) is delay time, and \((A_1/A_2)\) is the signal amplitude ratio. The parameters \(t_2\) and \(t_1\) are the respective arrival times (\(\mu\)sec) and amplitudes (V) without sample (subscript 1) and with sample (subscript 2). In this study water is used as the acoustic coupling material between the ultrasonic transducer and sample using ultrasonic C-scan measurement at 2.25 MHz and 23°C following the methods described by Tauchert.\(^5\)

In order to precisely evaluate varied hydrothermal cycling effects, a special experiment was designed for which a precisely machined bar of composite SC4 of dimension L by W by T = 12 by 1.0 by 0.20 in. with fibers parallel to the L axis was prepared. This bar was exposed to four simultaneous conditions of moisture exposure as shown in the schematic of Fig. 1. These varied zones of hydrothermal exposure develop a gradient of moisture content along the L axis of the bar. Subsequent to aging for 1128 hrs. in the conditions described by Fig. 1, the bar was characterized by ultrasonic C-scan at 2.25 MHz and 23°C. Additionally, precision measurements of specimen thickness \(T\) which enter calculations of Eq. (1) and Eq. (2) were conducted in conjunction with ultrasonic response at 0.5 in. (1.25 cm) intervals along the sample length.
Subsequent to this initial length characterization, a series of thermal shocks were then imposed on the bar in which the time-temperature history was uniform along the length of the bar. Measurements of $T$, $C_l$, and $\alpha_l$ were repeated as described above along the length of the bar subsequent to each thermal shock. For each thermal shock cycle the bar was wrapped in aluminum foil to enhance heat transfer and the perheated platens of a hydraulic press were closed against the 1 in. by W = 12 x 1 in. faces of the bar with a compressive stress of 100 psi. After 5 or 10 minutes the press was opened and the bar was immersed in 23°C water with repeat measurements of $T$, $C_l$, and $\alpha_l$.

The first two thermal cycles were restricted to the recommended service temperature limit of 177°C (350°F). The third and fourth thermal shock cycles involved progressively higher temperatures of 204°C (400°F) and 232°C (450°F) which approach the glass transition temperature $T_g \approx 250°C$ of fully cured dry composite SC4.

Subsequent to the four thermal shock cycles, the bar received a final length evaluation of $T$, $C_l$, $\alpha_l$ and was then dried at 110°C in vacuum and sectioned to provide 48 test specimens of dimensions L by W by T = 0.5 cm by 1.5 cm by 2.5 cm with a group of four from each 1 in. section of the bar length. A group of three specimens at bar length positions $L_1 = 0.5$, 1.5, 2.5, 11.5 in. were tested for interlaminar shear strength at 23°C and zero moisture using the compressive shear test of the earlier study. The fourth specimen was subjected to moisture diffusion analysis.

A related study of composite SC4 by moisture diffusion analysis (MDA) describes the use of the DuPont moisture evolution analyzer (Model 902H). Prior to MDA the twelve test specimens were first desicated to provide a common initial condition of zero moisture. The samples were then exposed to 1800 min. water immersion at 75°C with periodic weighing to evaluate the kinetics of water absorption by weight change measurements. After 1800 min. water immersion at 75°C the samples were individually inserted into the 75°C dry atmosphere (50 R.H.) sample chamber of the DuPont Moisture Evolution Analyzer. Measurement of water release rate $d(W/H_2O)/dt$ versus time t and determination of moisture content is automatically carried out by the instrument.

**Results**

A graphic summary of the effects of variable moisture exposure (see Fig. 1) and subsequent thermal cycles on the 23°C values of ultrasonic properties $\alpha_l$, $l$, and thickness $L$ is shown in Figs. 2, 3, and 4, respectively. For ease of inspection, the curves are separated by application of a vertical shift factor $K$ to the measured data values as indicated in the graphs. The lower curve of Fig. 2 shows that $\alpha_l$ remains relatively constant with position $L$ though moisture exposure varies with the length abscissa of Fig. 2. The 177°C (350°F) thermal shock cycles of Fig. 2 also show nearly level $\alpha_l$ values with position. With subsequent thermal shock cycles 3 and 4 where the thermal exposure exceeds the recommended service limit of 177°C (350°F) the upper curves of Fig. 2 show notable increases in $\alpha_l$ in the sections previously exposed to high moisture where $L = 6$ to 12 in. The high attenuation due to internal microstructure degradation in cycle 4 reduced $\alpha_l$ to low values characteristic of $\alpha_l > 12$ neper/cm with visible evidence of internal microcrack formation and delamination in the high moisture region $L = 6$ to 12 in. Conversely in the low moisture region $L = 0$ to 6 in. the thermal shock cycles 1 through 4 are seen to leave $\alpha_l$ substantially unchanged.
Figure 2. Effects of varied moisture exposure and subsequent thermal cycles on the acoustic attenuation $\alpha_l$ of composite SC4.

Inspection of Fig. 3 shows that ultrasonic velocity at $23^\circ C$ and 2.25 MHz is very sensitive to moisture content as indicated by the variation in $C_l$ with $L$ shown in the lower curve. Thermal shock cycles to $177^\circ C$ ($350^\circ F$) show the middle section region of $C_l$ versus $L$ is broadened. Thermal shock cycles 3 and 4 show more abrupt changes in $C_l$ in the length region $L = 5.5$ to 6.75 in. (14.0 to 17.1 cm) where a transition occurs from low to high moisture. Signal loss prevents $C_l$ measurement for $L > 6.5$ in. (16.5 cm) subsequent to cycle 4 due to internal crack formation.

The curves of Fig. 4 show that the precise thickness $T$ measurements which accompany this ultrasonic characterization are quite informative in identifying the locus of large defect development. The progressive sample thickness maximum where $L = 6$ to 9 in. (15.2 to 22.9 cm) is evident following the first thermal cycle. Subsequent thermal cycling to higher temperatures increases this local thickness maximum due to progressive internal crack growth and delamination.

The cured dry material for composite SC4 shows an ultrasonic wave velocity $C_l = 2.92$ km/s as compared to $C_l = 1.49$ km/s for bulk water at $23^\circ C$ and 2.25 MHz. The sound velocities shown in Fig. 3 are evidently dominated by the matrix and moisture constituents of the composite. Thus, regions of the composite with high moisture will display a lower sound velocity as shown in Fig. 3. The data of Fig. 3 show that sound attenuation $\alpha_l$ is primarily sensitive to internal defects rather than moisture content. Thus sound velocity is sensitive to current moisture content and attenuation to degree of microstructure degradation. The degree of interlaminar dilation as measured by $T$ in Fig. 4 is also an evident monitor of internal damage.

Figure 3. Effects of varied moisture exposure and subsequent thermal cycles on the ultrasonic velocity $C_l$ of composite SC4.

Figure 4. Effects of varied moisture exposure and subsequent thermal cycles on the thickness $T$ of composite SC4.
Following the nondestructive inspection summarized in Figs. 2-4, the composite bar was desiccated to a dry state and sectioned as described above to provide both interlaminar shear and moisture diffusion analysis (MDA) specimens. The MDA specimens were subjected to moisture absorption studies with measurement of weight fraction of water M versus liquid water immersion time t at 75°C. These typical types of moisture absorption curves are shown in Fig. 5. All MDA samples where L = 0.5 to 5.5 characteristic of low moisture exposure (23°C, 50% R.H.) prior to four thermal shocks show classical Fickian moisture absorption. A linear M versus t^2 curve which extrapolates to (M_0)_A = 0 at t = 0 and provides a constant initial slope characteristic of an apparent absorption diffusion coefficient D = 3.78·10^-8 cm^2/s is shown by the lower curve of Fig. 5.

The two upper curves of Fig. 5 show non-Fickian absorption with (M_0)_A > 0 indicative of physical penetration of bulk water into surface exposed microcracks at t = 0. A nonlinear M versus t^2 response shown in the upper curves of Fig. 5 indicates a more complicated diffusion and moisture saturation along shorter diffusion path lengths which form the microcrack structure.

Moisture effusion rate measurements as shown in Fig. 6 show that the effusion rate dM/dt versus effusion time t is highly reproducible for low moisture exposure elements of the test bar with L = 0.5 to 5.5 in. In the region of high moisture exposure L = 6.5 to 11.5 in., the effusion rate at constant time t is dramatically higher indicative of desorption enhanced by the presence of microcrack structure within the test specimen.

Table 1 summarizes the length L dependent values of interlaminar shear strength \( \tau_h \) (average and std. dev.) the intercept \( (M_0)_A \) and initial slope \( dM/dt \) for absorption. For desorption the initial moisture content \( (M_0)_D \) at cycle initiation (subsequent to 1800 min. water immersion at 75°C and the desorption time t_d at 75°C and 0% R.H.) required to reduce effusion rate to a constant level \( dM/dt = 1.0 \mu g/m/s \) (see Fig. 6) are also tabulated in Table 1.
The length profiles of absorption parameters \((M_0)\) and \(dM/dt\) are shown in Fig. 7 and show dramatic and easily recognized increases when \(L > 5.5\) in characteristic to high moisture exposure prior to thermal cycling. The length profiles of desorption parameters \((\dot{M})_0\) and \(\dot{M} \) shown in Fig. 8 display equivalent large increases when \(L > 5.5\) in characteristic of prior hydrothermal damage to composite microstructure. The curves of Fig. 7 for moisture absorption and Fig. 8 for moisture release show that low moisture exposure, \(L = 0.5\) to 5.5 in, followed by four thermal cycles, produce no evidence of change in composite microstructure and this result is consistent with the ultrasonic properties shown in Figs. 2 and 3.

Ultrasonic measurements in the high moisture region, \(L = 6.5\) to 12 in, of exposure fail due to high signal attenuation in thermal cycle 4. The data of Table 1 and curves of Figs. 7 and 8 show that MDA remains a quantitative measuring method over the whole bar length and continues to function after thermal cycle 4. The range of MDA measurement of microstructure degradation is, therefore, potentially broader than possible with ultrasonic measurements.

The detailed tabulation of \(\lambda_b\) values at varied values of \(L\) along the test bar in Table 2 permits a more detailed statistical analysis. Inspection of the two data sets, \(\lambda_b\) for \(L = 0.5\) to 5.5 for low moisture and \(L = 6.5\) to 11.5 in, for high moisture conducted by the Weibull (extreme values) statistics, produces the interesting curves shown in Fig. 10. A special statement of the Weibull argument for this shear test data states that the probability of survival \(S\) is related to applied interlaminar shear stress \(\lambda\) by the following relation:

\[
S = \exp \left( -\frac{\lambda}{\lambda_0} \right)^m V \quad (3)
\]
where $V$ is the volume for uniform shear loading and $\lambda_0$ and $m$ are Weibull parameters. For these test data the volume is constant with $V = 1.0$. By taking logarithms we obtain the following:

$$\ln(-\ln S) = m[\ln \lambda - \ln \lambda_0]$$

(4)

which predicts a plot $\ln(-\ln S)$ versus $\ln \lambda$ with slope $m$ and intercept $\lambda = \lambda_0$ when the survival probability $S = e^{-1} = 0.37$. The test data of Table 2 for $L = 0.5$ to $5.5$ and $L = 6.5$ to $11.5$ are separately arranged serially $j = 1, 2, \ldots, N$ in increasing order of $\lambda_0$ and the survival probability is defined as:

$$S = 1 - F = 1 - \frac{1 - 0.50}{N}$$

(5)

where $N$ is the number of observations and $F$ is the failure probability. The upper curves of Fig. 10 show the cumulative distributions plotted as $S$ versus $\lambda_0$ or $\ln \lambda_0$ for the two aging conditions. The lower curves of Fig. 10 show these same data linearize well on Weibull plots and conform to Weibull analysis.

Table 2: Experimental Values of $\lambda_0$ for Composite SR4 Tested Dry at 23°C After Described Hydrothermal Aging and Thermal Cycle 4

<table>
<thead>
<tr>
<th>$L$ (in)</th>
<th>$\lambda_0$ (g/cm$^2$)</th>
<th>Moisture Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>944, 1031, 1228</td>
<td>23°C, 50% RH, 1128 hr</td>
</tr>
<tr>
<td>1.5</td>
<td>1270, 660, 948</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>2.5</td>
<td>736, 986, 928</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>3.5</td>
<td>1079, 992, 868</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>4.5</td>
<td>1092, 1000, 900</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>5.5</td>
<td>933, 964, 992</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>6.5</td>
<td>632, 412, 409</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>7.5</td>
<td>635, 710, 507</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>8.5</td>
<td>492, 936, 480</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>9.5</td>
<td>996, 476, 292</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>10.5</td>
<td>874, 946, 188</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
<tr>
<td>11.5</td>
<td>197, 272</td>
<td>100°C, 100% RH or Liquid H2O, 1128 hr</td>
</tr>
</tbody>
</table>

The data and curves of Fig. 10 show that high moisture exposure, where $L = 6.5$ to $11.5$, combined with thermal cycling to 232°C (450°F) reduces shear strength $\lambda_0$ by 43 percent at survival probability $S = 0.37$. The corresponding decrease in $m$ which broadens the distribution shows that at a higher survival probability $S = 0.95$ of greater interest to a design engineer, the high moisture exposed length $L = 6.5$ to $11.5$ shows $\lambda_0$ is reduced by 79% as compared to low moisture length $L = 0.5$ to $5.5$.

Summary and Conclusions

This study clearly shows that MDA (moisture diffusion analysis) can be effectively applied to scan the area or length of a composite panel and locate regions of microstructure degradation and resultant loss in internal strength. In this study a one dimensional variation of moisture exposure and subsequent hydrothermal damage was imposed. The results obtained in the present study should also be demonstrated with more complex localizations of moisture exposure to either limited area (two-dimensional) or area plus depth (three-dimensional). When composite SC4 is thermally cycled beyond the recommended service ceiling temperature of 177°C (350°F) the region of high moisture exposure (100°C, water vapor or liquid, 1128 hr.) clearly exhibits microstructure and strength degradation.
Ultrasonic acoustic properties, thickness profiles, and MDA profiles in both adsorption and desorption modes are highly sensitive to the structure degradation. In regions of extensive internal damage, ultrasonic inspection becomes limited as a quantitative tool by high acoustic attenuation and resultant loss of signal. MDA in this instance becomes highly sensitive as a profiling method. Regions of internal microcrack formation display easily detectable non-Fickian moisture diffusion properties wherein bulk water penetrates the open capillary structure and subsequently diffuses by shortened path lengths between adjacent microcracks.

Further analysis of these newly recognized non-Fickian diffusional regimes appears to be a promising new method for analyzing the details of microstructure degradation. This type of extended MDA analysis combined with statistical analysis of strength degradation as graphed in Fig. 10 appears as the direct approach to coupling MDA and ultrasonic surveillance to quantitative predictive criteria for residual strength and service life of the composite material in critical primary structure applications.

Acknowledgement

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References


Nomenclature

\[ \begin{align*}
A_1, A_2 & : \text{ acoustic signal amplitudes (v)} \\
C_L & : \text{ longitudinal sound velocity (km/s)} \\
D & : \text{ apparent absorption diffusion coefficient (cm}^2/\text{s}) \\
F & : \text{ failure probability defined by Eq. (3) (dimensionless)} \\
j & : \text{ Weibull observation index defined by Eq. (5) (dimensionless)} \\
L & : \text{ length of specimen (in.)} \\
m & : \text{ Weibull parameter defined by Eq. (3) (dimensionless)} \\
M_A & : \text{ weight fraction of water in absorption (\%)} \\
(M_0)_A & : \text{ weight fraction of water in absorption at time } = 0 (\%) \\
M_D & : \text{ weight fraction of water in desorption (\%)} \\
(M_0)_D & : \text{ weight fraction of water in desorption at time } = 0 (\%) \\
R.H. & : \text{ relative humidity (\%)} \\
s & : \text{ survival probability defined by Eq. (3) (dimensionless)} \\
t & : \text{ time (sec)} \\
t_D & : \text{ time required to reduce moisture desorption to } 1 \text{ gm/sec (sec)} \\
t_{0.1} & : \text{ acoustic signal arrival times (usec)} \\
T & : \text{ thickness of specimen (in.)} \\
v & : \text{ volume for uniform shear loading } = 1 \text{ (dimensionless)} \\
\lambda_0 & : \text{ Weibull parameter defined by Eq. (3) (Kg/cm}^2) \\
\lambda & : \text{ interlaminar shear stress (Kg/cm}^2) 
\end{align*} \]