KINETICS OF MOISTURE DEGRADATION IN GRAPHITE-EPOXY COMPOSITES

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This study forms part of a more general program addressed to developing a better understanding of the mechanisms of interfacial bonding and environmental stability in polymer matrix composites.\(^{(1-3)}\) Several published studies have shown that exposure of graphite fiber reinforced epoxy or polyester composites to water immersion or water vapor at elevated temperature produces decreases in interlaminar shear strength accompanied by rising or falling values of fracture toughness.\(^{(2,4-6)}\)

An approach to the correction of this moisture sensitivity has been suggested by Kaelble\(^{(3,3)}\) based upon a modified Griffith-Irwin model for interfacial failure and a micro-mechanics model for fracture energy due to fiber debonding.

The first objective of this study is to evaluate the thermodynamic and kinetic aspects of shear strength degradation in uniaxial reinforced graphite-epoxy composites exposed to high moisture and elevated temperature. The second objective is to analyze the relationships between interlaminar shear strength, fracture energy and acoustic response during environmental degradation.

MATERIALS AND METHODS

The graphite fiber chosen as reinforcement was Hercules HTS\(^{®}\). BP-907\(^{®}\) a modified epoxy (Bloomingdale Division of American Cyanamid) was employed as the matrix material for Panel SCl.

Wettability measurements and surface energy analysis methods detailed in previous reports\(^{(1,2,7)}\) were applied to define the surface tension
\[ \gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p \]
properties for both fiber and cured epoxy resin components of the reinforced composites. Surface property data for the Hercules HTS® graphite fiber are \[ \gamma_{SV}^p = 25.9 \pm 1.5, \quad \gamma_{SV}^d = 25.7 \pm 3.3 \text{ and } \quad \gamma_{SV} = 51.6 \pm 2.3 \text{ dyn/cm.} \]
For the cured epoxy resin \[ \gamma_{SV}^p = 37.2 \pm 3.1, \quad \gamma_{SV}^d = 8.3 \pm 2.0 \text{ and } \quad \gamma_{SV} = 45.5 \pm 1.2 \text{ dyn/cm.} \]

Measurement of interlaminar shear strengths using the standard short beam shear test produced combinations of tensile and shear failure which indicated this test was not useful in detailed study of environmental degradation effects. The sample and test geometry shown in the upper portion of Fig. 1 was developed as a replacement of the short beam shear test. The interlaminar shear strength is described by the following relation

\[ \lambda_b = \frac{F_b}{A_0} \]  \hspace{1cm} (1)

where \( F_b \) = the compressional force at break and \( A_0 = 0.25 \text{ cm}^2 \) is the nominal cross section area of the shear plane.

Fracture energy measurements in slow crack propagation were conducted using the three point bend specimen designed by Tatersall and Tappin(9) and illustrated in the lower view of Fig. 1. The geometry of flexure loading shown in Fig. 1 generates a crack at the apex of the isosceles triangle section which propagates downward to the base of the triangle. The work of fracture per unit area \( W_b/A \) is defined as:

\[ \frac{W_b}{A} = \frac{1}{A_0} \int_{L=0}^{L_b} F \, dL \]  \hspace{1cm} (2)

where the force-displacement integral is automatically recorded by the Instron integrator accessory.

Samples were aged for varied times using 100°C and 95% R.H. vapor phase immersion over a saturated water solution of \( K_2SO_4 \) as described
FIG. 1  Test specimens for interlaminar shear strength (upper) and fracture energy (lower) measurement.
A second group of samples was subjected to full water immersion exposure at 100°C for varied times. Compression shear and fracture energy measurements were conducted at 23 ± 1°C immediately after sample withdrawal from the high moisture environment. Constant Instron crosshead speeds of 0.02 cm/min for compression shear and 0.05 cm/min for fracture energy measurement were applied. Sample weighing immediately upon removal from the high moisture environment and subsequent to extended desiccation over anhydrous calcium sulphate permits determination of moisture content at the time of fracture testing.

Subsequent to moisture exposure, fracture testing and desiccation for moisture determination all samples were subjected to ultrasonic inspection using through transmission (C-scan) at 2.25 MHz. The samples were coupled via thin films of Nonaq grease (Fisher Scientific Co.) to the signal transmission and detector transducers of a Sperry Reflectoscope UM721 (Customation Industries, Inc.). The sound transmission path was vertical in the cross section views shown in Fig. 1 with the wave front parallel (circle data points) or transverse (diamond data points) to the ply orientations. The longitudinal sound velocity $C_L$ (Km/sec) and the acoustic absorption coefficient $\alpha_L$ (nepers/cm) are determined by the following standard relations:

$$C_L = \frac{L}{\Delta t} = \frac{L}{(t_2-t_1)}$$

$$\alpha_L = L^{-1} \ln(A_1/A_2)$$

where $t_2-t_1$ is the delay time and $A_1$ and $A_2$ are signal amplitudes. These acoustic properties reflect combined effects of moisture sorption, mechanical loading, and subsequent desiccation upon the material response.

**INTERLAMINAR SHEAR STRENGTH DEGRADATION**

A. **Surface Energy Aspects**

Previous studies by us have shown that the interfacial bond between fiber and matrix under varied conditions of environmental immersion can
be expressed in terms of surface energy parameters which describe (London-d) dispersion \( \gamma^d = \alpha^2 \) and (Keesom-p) polar \( \gamma^p = \beta^2 \) contributions to liquid-vapor \( \gamma_{LV} = \gamma^d_{LV} + \gamma^p_{LV} \) or solid-vapor \( \gamma_{SV} + \gamma^p_{SV} \) surface tension. (7) Since these definitions include the surface tension properties of water where \( \gamma_{LV} = 21.8 \text{ dyn/cm}, \gamma^p_{LV} = 51.0 \text{ dyn/cm}, \) and \( \gamma_{LV} = 72.8 \text{ dyn/cm} \) at 20°C, this dispersion-polar interaction model forms the basis for predictions of the degradation of bond strength when the fiber-matrix interface is transferred from air to water immersion and comes to full equilibrium with the water immersion environment. (2)

Surface energy parameters required to define this three phase model where the matrix (or adhesive) is phase I, the environmental immersion phase (air or water) is phase 2, and the matrix (or adherend) is phase 3, are represented by the following expressions: \((1, 2)\)

\[
\begin{align*}
\gamma_1 &= \gamma_1^d + \gamma_1^p = \alpha_1^2 + \beta_1^2 \\
\gamma_2 &= \gamma_2^d + \gamma_2^p = \alpha_2^2 + \beta_2^2 \\
\gamma_3 &= \gamma_3^d + \gamma_3^p = \alpha_3^2 + \beta_3^2
\end{align*}
\]

(5) (6) (7)

The parameters \( \alpha = (\gamma^d)^{1/2} \) and \( \beta = (\gamma^p)^{1/2} \) are introduced for notational convenience. These six surface energy terms enter a detailed statement of the Griffith relation for critical stress \( \sigma_c \) for crack initiation under normal plane stress loading as defined by the following expression: \((2)\)

\[
\sigma_c \left( \frac{\pi c}{2E} \right)^{1/2} = \gamma_G^{1/2} = (R^2 - R_0^2)^{1/2}
\]

(8)

where the surface energy coefficients appear in the following supplementary relations:

\[
R_0^2 = 0.25 [(\alpha_1 - \alpha_3)^2 + (\beta_1 - \beta_3)^2]
\]

(9)
\[ R^2 = (a^2 - H)^2 + (b^2 - K)^2 \]  \hspace{1cm} (10)

\[ H = 0.50 (a_1 + a_3) \]  \hspace{1cm} (11)

\[ K = 0.50 (b_1 + b_3) \]  \hspace{1cm} (12)

and \( E \) is Young's modulus and \( C \) is the crack length. The application of Eq. 8 assumes that the change in immersion environment does not significantly influence the system modulus \( E \) or crack length \( C \) and that the significant variable is the reversible Griffith surface energy \( \gamma_G = (R^2 - R_0^2) \).

Inspection of Eq. 9 through Eq. 12 shows that the modified Griffith expression of Eq. 8 can be conveniently represented on cartesian coordinates of \( a \) versus \( b \) as shown in Fig. 2 (left portion). The left view of Fig. 2 indicates the location of the \( a \) versus \( b \) points for the matrix and fiber surfaces of Panel SCI. The vectors \( R(\text{air}) \) and \( R(H_2O) \) originate at \( H, K \) as defined by Eq. 11 and Eq. 12 and terminate at \( a = b = 0 \) for air and \( a = 4.67 \) (dyn/cm)\(^{1/2} \) and \( b = 7.14 \) (dyn/cm)\(^{1/2} \) for water which represent the surface tension properties of these two immersion phases. The \( R_0 \) vector shown in Fig. 2 also originates at \( H, K \) and describes a circle which encloses the region where \( R \approx R_0 \) and from Eq. 8 it is predicted that \( \sigma_C = 0 \).

The master function of \( \sigma_C(\pi C/2E)^{1/2} = \gamma_G^{1/2} \) versus \( R \) shown in Fig. 2 (right portion) show air and water immersion environments as two special cases. For panel SCI the prediction is that \( \sigma_C(H_2O)/\sigma_C(\text{air}) = 0.46 \) for ratio of fibermatrix debonding with constant \( (\pi C/2E) \). The diagrams of Fig. 2 graphically detail the surface energy arguments which predict that water will substantially reduce the interfacial bond strength in composite SCI.

Fracture in interlaminar shear produces shear stresses which simultaneously fracture both the fiber-matrix interface and matrix continuum between adjacent fibers. For fibers of uniform radius \( r_0 \) in regular
FIG. 2 Surface energy analysis for fiber-matrix interactions for composite SC1 with air and water immersion phases. $\sigma$ versus $\beta$ (left view). Griffith failure criteria $\sigma = \gamma_0^{1/2}$ for composite SC1 under air and water immersion (right view).
hexagonal packing the matrix distance a separating adjacent fibers is defined by the following expression: \(\text{(3)}\)

\[
a = r_0 \left[1.074 \left(\frac{\pi}{V}\right)^{1/2} - 2\right]
\]

where \(V\) = fiber volume fraction. Solving Eq. 13 with \(V = 0.40\) for Panel SCl shows that \(a = r_0\). The fractional areas for interfacial \(f_I\) and matrix \(f_M\) failure are given by the following relation:

\[
f_I = 1 - f_M = \frac{\pi r_0}{\pi r_0^2 + a} = 0.76
\]

The composite interlaminar shear strength \(\lambda_b\) interfacial failure \(\lambda_I\) and matrix failure \(\lambda_M\) is obtained from the rule of mixtures:

\[
\lambda_b = f_I \lambda_I + f_M \lambda_M
\]

Consider that an unexposed laminate under air immersion displays interlaminar shear strengths

\[
\lambda_{b0} = \lambda_{i0} = \lambda_{M0}
\]

where the zero suffix represents the respective shear strengths at zero exposure time \((t = 0)\) to water immersion. Under a condition of infinite \((t = \infty)\) exposure time under water immersion let us further assume that:

\[
\lambda_{M\infty} = \lambda_{M0}
\]

\[
\lambda_{I\infty} = \lambda_{i0} \frac{\sigma_c(H_2O)}{\sigma_c(air)}
\]

Substituting the statements of Eq. 16 through Eq. 18 into Eq. 15 we obtain the following relation:

\[
\frac{\lambda_{b\infty}}{\lambda_{b0}} = (1-f_I) + f_I \frac{\sigma_c(H_2O)}{\sigma_c(air)}
\]
For panel SCl with $\frac{\sigma_c(H_2O)}{\sigma_c(air)} = 0.463$ and $f_I = 0.76$ we obtain a prediction from Eq. 19 that:

$$\frac{\lambda_{b\infty}}{\lambda_{b0}} = 0.59 \quad (20)$$

These predictions are based upon surface energy arguments and a simplified model which translates interface degradation considerations into the composite shear failure of both interface and matrix.

### B. Kinetic Aspects

Previous studies have shown that a finite time is required to establish equilibrium between a composite material response and the environment to which it is exposed. A general procedure for expressing the cumulative damage effects of mechanical (M), thermal (T), or environmental (C = chemical or corrosive) stresses is by the relation proposed by Halpin and coworkers:(11-13)

$$\phi = \exp(-Kt^{b/a_T a_M a_C}) \quad (21)$$

where $\phi$ = the cumulative degradation function, $t = $ exposure time, $K = $ a system constant, $a_T, a_M, a_C$ = time shift factors relating to respective thermal, mechanical, or chemical effects, and $b = $ a time exponent. A specialized form of Eq. 21 applicable to analysis of degradation of interlaminar shear would take the following form:

$$\phi = \frac{\lambda_b(t) - \lambda_{b0}}{\lambda_{b0} - \lambda_{b\infty}} = \exp(-t/\tau) \quad (22)$$

where it is assumed $b = 1.0$ and the relaxation time $\tau = a_T a_M a_C/K$. Rearranging Eq. 22 we obtain the following expression for the interlaminar shear strength $\lambda_b(t)$ at exposure time $t$ by the following expression:
where the relaxation time $\tau$ is defined:

$$\tau = -\frac{t}{\ln \phi}$$ (24)

One objective of the present study was to evaluate both surface energy and kinetics aspects of interlaminar shear strength degradation as outlined by the above discussion.

C. Evaluation of Experimental Results

The experimental curves of Fig. 3 (upper portion) provide a graphical summary of the moisture content of composite panel SCl, as a function of exposure time $t$ to water vapor (95% R.H. at 100°C) and liquid water immersion at 100°C.

The effects of liquid water immersion on compressional interlaminar shear strength for composite SCl is shown in Fig. 3 (lower portion). It may be recalled from Fig. 1 that the circled points represent shear parallel and diamond points transverse to the ply orientations. The experimental data of Fig. 3 shows a monotonic decrease from initial maximum values of $\lambda_b = \lambda_0$ to final time invariant values $\lambda_b = \lambda_\infty$ which are approached at exposure times $t \geq 200$ hr. A somewhat smaller decrease in the value of $\lambda_b$ for water vapor immersion was found.

The average values of the relaxation time $\tau$ for environmental degradation appear to correlate with relatively long times required for moisture uptake as shown by the curve of Fig. 3. The liquid H$_2$O immersion condition for composite panel SCl produces an experimental value of $\lambda_{bw}/\lambda_{b0} = 0.56$ which compares well with the calculated value $\lambda_{bw}/\lambda_{b0} = 0.59$ from Eq. 19.
FIG. 3 Moisture content (in % by weight H₂O) versus exposure time (t) of composites SCL (upper view). Effects of moisture exposure time t on interlaminar shear strength λ_b of composite SCL (lower view).
DEGRADATION EFFECTS ON FRACTURE ENERGY

A. Micro-Mechanics Considerations

As shown by the data of the previous section, the effect of long term exposure to either high humidity or water immersion in graphite fiber reinforced composites follow predictive relations which point out that the state of the interfacial bond depends upon the degree of equilibrium to the adverse environment. Both the analysis and the experimental data point out that water exposure merely weakens rather than destroys the fiber-matrix shear bond strength. As noted in the Introduction, previous experimental studies have shown that water exposure with lowered interlaminar shear strength $\lambda_b(t)$ may produce both increasing or decreasing values of fracture energy $W_b/A$ for crack propagation perpendicular to the fiber axis in uniaxially reinforced composites. This rather puzzling relationship between interlaminar shear and fracture energy behavior is clarified by a consideration of the micromechanical contributions to fracture energy in fiber reinforced composites.

In a recently developed model to analyze the stress distributions and fracture energies associated with crack propagation and fiber pull-out in reinforced composites, the work of fracture $W_b/A$ per unit area of sample cross section $A$ is defined as the sum of the matrix shear work $W_{sb}$ for debonding and a frictional work $W_{fb}$ for fiber pull-out by the following relations:

$$\frac{W_b}{A} = \frac{W_{sb} + W_{fb}}{A}$$  \hspace{1cm} (25)

$$\frac{W_{sb}}{A} = f_1(V) f_2(V) \left( \frac{E}{2G} \right)^{\frac{1}{2}} \frac{\lambda_I}{\lambda_f} \left[ \frac{\sigma_b}{2} - \frac{\lambda_I (E/2G)^{\frac{1}{2}} f_1(V)}{2} \right] \geq 0$$  \hspace{1cm} (26)

$$\frac{W_{fb}}{A} = \frac{f_2(V) r_0}{2 \lambda_f} \left[ \frac{\sigma_b}{2} - \frac{\lambda_I (E/2G)^{\frac{1}{2}} f(V)}{2} \right] \geq 0$$  \hspace{1cm} (27)
where:

- fiber radius $r_0 = 4.45 \cdot 10^{-6}$ cm,
- matrix shear modulus $G = 1.19 \cdot 10^4$ Kg/cm$^2$,
- fiber tensile strength $\sigma_b = 2.46 \cdot 10^4$ Kg/cm$^2$,
- fiber volume fraction $V = 0.40$,
- fiber Young's modulus $E = 2.53 \cdot 10^6$ Kg/cm$^2$,
- volume fraction functions: $f_1(V) = 0.832$, $f_2(V) = 0.268$, $f_3(V) = 0.236$.

Since the locus of fiber tensile failure is statistically indeterminate, the range of expected fracture energy $W_b/A$ lies within upper and lower bounds specified by the following relation:

$$\frac{W_{sb} + W_{fb}}{A} > \frac{W_b}{A} > \frac{W_{sb}}{A}$$

(28)

All parameters of Eq. 26 and Eq. 28 are specified with the exception of the shear stresses $\lambda_I$ and $\lambda_F$. Information concerning the magnitude $\lambda_I$ is developed by interlaminar shear strength testing as identified in Eq. 15 and subsequent relations which lead to the kinetic expression for shear strength degradation stated by Eq. 23.

The magnitude of $\lambda_F$ and its dependences upon moisture degradation effects can only be estimated by indirect methods such as thermoelastic calculations based on resin shrinkage about the fiber as demonstrated by Broutman. (14) By introducing the constants into Eq. 26 and Eq. 27 we obtain the following specific relations:

$$\frac{W_{sb}}{A} \left(\frac{Kg}{cm}\right) = 1.025 \cdot 10^{-3} \frac{\lambda_I}{\lambda_F} (12300 - 8.58 \lambda_I)$$

(29)
\[ \frac{W_{fb}}{A} \text{(Kg/cm)} = \frac{5.96 \times 10^{-5}}{\lambda_F} (12300 - 8.58 \lambda_I)^2 \]  

(30)

where both \( \lambda_I \) and \( \lambda_F \) are expressed in Kg/cm\(^2\) units. The calculated functions of Fig. 4 present two examples of fracture energy predictions based upon Eq. 29 and Eq. 30. In upper Fig. 4 (Case I) the magnitude of \( \lambda_F = 250 \text{ Kg/cm}^2 = 3450 \text{ psi} \) is held constant while \( \lambda_I \) is variable from \( \lambda_I = 0 \) to \( \lambda_I = 1415 \text{ Kg/cm}^2 \) which characterizes fiber fracture without debonding. In the lower curves of Fig. 4 (Case II) a proportionality condition \( \lambda_F = \lambda_I/2.8 \) is applied to represent a concurrent change in \( \lambda_F \) as \( \lambda_I \) is decreased by environmental degradation. These theoretical predictions of the dependence of \( W_{fb}/A \) upon \( \lambda_I \) can be compared with measured values of \( W_{fb}/A \) versus high moisture exposure time.

The shaded regions of Fig. 4 define the upper and lower bounds for \( W_{fb}/A \) as defined by the constraints of Eq. 28.

B. Evaluation of Experimental Results

A graphical summary of the effects of water immersion on the measured fracture energy \( W_{fb}/A \) for crack propagation parallel (circles) and transverse (diamonds) to the fiber ply orientations for Panel SCl are presented in the upper view of Fig. 5. The dashed curves of Fig. 5 represent the extreme values of the experimental data. In general, the curves and data points of Fig. 5 are seen to reflect the predictions presented by the shaded regions of Fig. 4. As shown in Fig. 5, the experimental values of \( W_{fb}/A \) are low and display minimum scatter at \( t = 0 \) characteristic of high values of \( \lambda_I = \lambda_M = 1000 \text{ Kg/cm}^2 \). As exposure time increases from \( t = 0 \) to \( t = 200 \text{ hr} \) characteristic of the initial rapid degradation of \( \lambda_I \) due to water absorption, the values of \( W_{fb}/A \) increase and the scatter between maximum and minimum fracture energy increases as expected from the broadening of the shaded areas in Fig. 4. In general one finds a consistent increase in measured values of \( W_{fb}/A \) with increasing time of moisture exposure which is consistent with degradation of \( \lambda_I \) and the fracture energy model summarized by Fig. 4.
FIG. 4 Calculated fracture energy $W/A$ versus fiber-matrix shear bond strength $\lambda_I$ based on micro-mechanics analysis.
FIG. 5 Effects of moisture exposure time $t$ on fracture energy $W_b/A$ of composite SC1 (upper view). Effects of moisture exposure time $t$ on acoustic absorption coefficient $\alpha$ of composite SC1 (lower view).
This experimental study of moisture degradation effects on the work of fracture correlates closely with the results predicted by the micro-mechanics model summarized by Eq. 25 through Eq. 28. In effect, the micro-mechanics model predicts that fracture energy should increase by a factor of 2 to 5 when the interlaminar shear strength which influences $\lambda_1$ decreases by approximately one-half its original value. These predictions, as graphically displayed in Fig. 4, apply to a strongly bonded composite where the initial value of $\lambda_0 \approx 1000 \text{ Kg/cm}^2$ and the final value $\lambda_\infty \approx 400 \text{ Kg/cm}^2$.

DEGRADATION EFFECTS ON ACOUSTIC RESPONSE

An important aspect in studies of environmental degradation is the investigation of nondestructive test (NDT) methods which indicate the state of degradation of composite response. The specific objective in our experiments was to determine whether sound velocity or attenuation measurements were directly sensitive to the state of the interfacial bond as evaluated by moisture absorption, interlaminar shear strength, or fracture energy.

Sound velocity measurements on desiccated specimens subject to prior history of moisture exposure, and fracture testing for interlaminar shear or fracture energy produced averaged values of sound velocity $C_L = 3.00 \pm 0.17 \text{ Km/sec}$ at a frequency $f = 2.25 \text{ MHz}$ and temperature of $23 \pm 1^\circ C$. No significant trends were observed in the data relating to fiber ply orientation or prior moisture exposure history.

Acoustic attenuation response of composite specimens under equivalent test conditions were sensibly influenced by prior moisture exposure history. Measured attenuation data for sound wave fronts parallel (circles) and transverse (diamonds) to the fiber ply orientation are plotted versus water immersion exposure time $t$ in the lower portion of Fig. 5. Inspection of Fig. 5 shows that for transmission perpendicular to the fiber ply orientation attenuation rises to $\alpha \approx 12 \text{ nepers/cm}$. 

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The attenuation parallel to the fiber plys levels at $\alpha = 5$ to 6 nepers/cm at exposure times $t > 200$ hours.

**REVERSIBILITY OF DEGRADATION EFFECTS**

The acoustic attenuation data of the previous section appear to show that prior moisture exposure effects induce permanent changes in the composite material which are not reversed by removal of the absorbed water by desiccation. This important question of reversibility of moisture degradation effects was examined in greater detail in a series of special experiments.

In the special tests for reversibility of composite response the measurement of fracture energy was chosen as a property which increases significantly during moisture degradation and which is predicted to remain at a higher value if the damage is fully irreversible. It was found that fracture energy increases caused by interface degradation under 1000 hr water vapor exposure or water immersion are not reduced by ambient desiccation or 200°C inert atmosphere exposure.

These results tend to support a conclusion of earlier studies(2) that moisture degradation of interfaces in graphite-epoxy composites is essentially irreversible. The explanation for this finding is related to the fact that fiber-matrix bonding occurs prior to crosslinking of the epoxy matrix where local stress relaxation processes permit rheological equilibrium to be achieved at the bonded interfaces. Subsequent to curing the matrix remains in the crosslinked state and residual elastic stresses prevent rebonding of a damaged interface even when the resin is raised to above its glass transition temperature $T_g$ to provide the response characteristic of a highly crosslinked elastomer. (15)
SUMMARY AND CONCLUSIONS

The results of this study show a close correlation between analytical predictions and experimentally observed degradation of mechanical properties in graphite-epoxy composites under high moisture aging conditions. Unaged composite specimens exhibit high interlaminar shear strength \( \lambda_b \approx 850 \text{ Kg/cm}^2 \) (12,000 psi) and relatively low fracture energy \( \frac{\lambda_b}{A} = 10-20 \text{ Kg cm/cm}^2 \) (56-112 lb in/in\(^2\)). Exposure to 95% relative humidity or water immersion at 100°C for times \( t \approx 200 \text{ hr} \) produces a 30 to 50 percent reduction in interlaminar shear strength accompanied by a concurrent two to fivefold increase in fracture toughness and acoustic absorption properties. These property changes are shown to be irreversible and directly related to cumulative moisture degradation of the fiber-matrix interfacial bond. The magnitude of these property changes are consistent with surface energy analysis and micro-mechanics predictions which show that fracture energy response optimizes at intermediate values of shear bond strength.

The kinetic expression for cumulative moisture degradation of interlaminar shear strength (see Eq. 24) defines an environmental relaxation time \( \tau \) which appears to correlate with the time scales shown for water absorption into the composite test specimens. The additional parameters of this kinetic expression define relative shear strengths at exposure times \( t = \infty \) and \( t = 0 \) by a dimensionless ratio \( \frac{\lambda_b(t)}{\lambda_b(0)} \) which are calculated from equilibrium thermodynamic arguments summarized by Eq. 19.

Two technical approaches to reducing moisture sensitivity in graphite-epoxy composites are clearly identified by Eq. 24. External protective coatings which lower the diffusion rate of water into the composite material would increase \( \tau \) and thereby minimize degradation for exposure times where \( t \ll \tau \). The success of this approach would depend entirely upon the resistance of the coating to damage due to environmental exposure or mechanical damage.

The second approach to high moisture resistance is fundamentally stated by making \( \frac{\lambda_{b(\infty)}}{\lambda_{b(0)}} = 1.0 \) and the solution involves the modification of the fiber-matrix interface such that the vectors \( R(\text{air}) \) and
R(H₂O) shown by Fig. 2 display a ratio R(air)/R(H₂O) = 1.0. As discussed in previous reports implementing this second approach requires new fiber surface treatments and selection of matrix polymers which are essentially nonpolar in both surface and bulk properties.² A recent report by Gauchel and coworkers,¹⁶ wherein halogenated epoxy resins are combined with surface treated S-glass fibers to form composites with remarkable moisture resistance, appears to involve this second approach.

References:


13. J. C. Halpin, ibid, 6, 208 (1972).
DISCUSSION

DR. WILLIAM YEE (Applied Research Laboratory, Convair Aerospace):
During the aging process is the density or the velocity or both of them changing?

MR. KAELEBLE: The velocity data were constant to within about ± 5%.

DR. YEE: What about density?

MR. KAELEBLE: Our ultrasonic measurements were all made on specimens exposed to moisture and subsequently desiccated prior to measurement. Density variations should be minor.