The structural performance, reliability and durability of polymer composites can now be correlated with three generic classes of internal defects. The first generic class of chemical structure defects (size 10-100Å) that control critical design properties such as glass transition $T_g$, moisture absorption, and dimensional changes can be controlled by chemical analysis of raw materials prior to manufacture. A second generic class of manufacturing defects (size greater than 10µm) include inclusions, voids and debonds which are related to manufacturing process control and recognized by ultrasonics, optical scanning and other techniques sensitive to interfacial imperfections. The interaction of these two classes of defects such as interconnected microcracks and macroscopic crack growth which can be detected by visual inspection and ultrasonic emission.

The recognition of intrinsic structural defects, and their contributions to polymer composite reliability, represents an important extension in the analytic modeling and reliability predictions for structural polymers, adhesively bonded metals and high strength fiber reinforced composites in which the physical chemistry parameters appear as primary control variables. This discussion introduces and discusses combined deterministic/statistical models for polymer composite reliability. The molecular process which determines the relation between environmental condition and macroscopic structural effect is detailed within such models and provides important criteria for chemical and manufacturing optimization of polymer composite reliability. Experimental data of aging effects on the statistical strength distributions of structure polymers, metal-to-metal joints and reinforced composites are examined and compared with model predictions.

### INTRODUCTION

Concepts of structural design for reliability are old and well used. A classical expression of these concepts is well illustrated in the following excerpt of a poem by Oliver Wendell Holmes as described in Table 1.

**THE DEACON'S MASTERPIECE:**
Or the Wonderful "One-Hoss-Shay."*

A Logical Story

Have you heard of the wonderful one-hoss-shay,
That was built in such a logical way
It ran a hundred years to a day
And the, of a sudden - ah, but stay,
I'll tell you what happened without delay,

At age one hundred years to the day
There are traces of age in a one-hoss-shay
A general flavor of mild decay,
But nothing local, as one may say,
There couldn't be, - for the Deacon's art
Had made it so like in every part
That there wasn't a chance for one to start.
And yet, as a whole, it is past a doubt
In another hour it will be worn out!

This morning the parson takes a drive.
All at once the horse stood still,
Close by the meet'n'-house on the hill.
-First a shiver, and then a thrill,
Then something decidedly like a spill,-
And the parson was sitting upon a rock,

-What do you think the parson found,
When he got up and stared around?
The poor old chaise in a heap or mound,
You see, of course, if you're not a dunce,

How it went to pieces at once,-
All at once, and nothing first,-
Just as bubbles do when they burst.

The design of high performance, reliability, and durability into mobile structures such as spacecraft, airplanes, cars, or the one-horse-shay described above is a special branch of structural engineering in which weight minimization is an important design constraint. The rapidly evolving polymer composite technology represents new inputs which make exotic advanced structures such as the man-powered airplane "Gondor", and the Space Shuttle functional within their design constraints.

One specific objective of this discussion is to review current reliability concepts and identify new approaches, particularly relevant to polymer composite materials. A second objective is to indicate the important role that predictive models and computer aided design and manufacture (CAD/CAM) can play in achieving polymer composite reliability. A final objective is to illustrate the utility of determining the molecular processes which control macroscopic reliability and define environmental aging and nondestructive evaluation (NDE) directly in terms of the molecular process.

**Current Concepts**

Current concepts of engineering design to achieve structural reliability are detailed in an excellent review edited by Swedlow, Cruse, and Halpin(2). Several of the important current

---

definitions of reliability provide valuable insight into design concepts. A widely used and generally accepted definition of reliability is described by the so-called "bathtub curve" of Fig. 1, and the following definition of reliability $R$ by the following equation:

$$ R = \exp \left( - \int_0^t \lambda (t) \, dt \right) \quad (1) $$

where $\lambda (t)$ is defined as the failure rate at time $t$, or the "bathtub curve" and Eq.(1) defines a break in period in which manufacturing defects are covered by warranty and repaired without charge. Following this break in period, the failure rate is minimized and dominated by circumstantial failure until a period where the wearout process characteristic of environmental aging begins to dominate. As pointed out by Heller(3), human existence is modeled by higher infant mortality (burn-in) followed by primarily accidental mortality during early maturity and terminating in wear out by aging as shown in Fig. 1.

With ceramic materials where time effects are nondominant and failure is primarily determined by stress initiated failure modes, the concept of structural reliability can be defined by applied and allowable stress distributions as shown by the curves of Fig. 2, and the following definition of reliability $R$ as given in the following relation:

$$ R = \int_0^\infty \phi (X) \int \phi (X) \, dx \, dx \quad (2) $$

This design strategy for structure reliability assumes that pre-existing defects are either inherent in the material or produced during fabrication. Flaw detection by nondestructive inspection (NDI) becomes of primary importance in eliminating detectable flaws. Sacrificial proof testing may be applied to eliminate all flaws above a given size. The result of both NDI with rejection at flaw size $B$ or proof testing with sacrificial failure at flaw size $A$ is to establish the determined safe crack growth curves in the right view of Fig. 3.

An intrinsic problem in designing large structures involves the extrapolation of strength and reliability data obtained from small coupon specimens to values appropriate to the large structure. In practice this problem is further complicated by the fact that manufacturing defects in the large structure may differ from those small coupon specimens manufactured separately. Materials which are not particularly sensitive to flaws, such as metals exhibit far less scatter in strength than brittle materials which are flaw sensitive. At the micro-mechanical response level the scatter in strength is due to the distribution of flaws. As discussed by Jerina and Halpin(6), the extreme value (or Weibull) statistical distribution function has now been widely applied in materials science and engineering.

The Weibull distribution function defines reliability $R$ by the following relation(6-8):
Weibull shape
the lower right
which assumes that the Weibull slope $m$ remains
strength
fundamental importance of the Weibull slope $m$ in
curves of Fig. 4, if the the Weibull slope factor
$\ln(-\ln R) = \text{constant}$ with varied $V$, $K$, and $N$. Both Eq.(5) and
structural
concentration, and numeric complexity by $N$ holes.
left views of Fig. 4 trace the progressive effects
lowering of mean strength from
$\beta_1$, $\beta_2$ and $\beta_3$ is defined by the following relation: (6)
where the ordinate becomes $\ln(-\ln R)$, the slope is
mean strength at $\ln(-\ln R) = 0$ is a reference condition
$V_i K_i V_i V_0 K_0 V_0 = 1.0$.

The several implications inherent in the
Weibull criteria for structural reliability are
graphically summarized in Fig. 4 and discussed in
greater detail by Jérima and Halpin.(6) The
lower right view of Fig. 4 point out the
fundamental importance of the Weibull slope $m$ in
structural design. As shown in the lower right curves of Fig. 4, the the Weibull slope factor $m$
displays a high value $m = 30$, the increase in
size or number complexity, such as $V_j / V_0 = 100$
or $N_j / N_0 = 100$, only slightly lowers the mean
strength with $\beta_1 / \beta_0 = 0.86$. However, where the
Weibull shape factor $m$ is lowered to represent
typical structural materials such as $m = 4$ for
aluminum, the prediction is that with $V_j / V_0 = 100$
or $N_j / N_0 = 100$, a major lowering of mean
strength with $\beta_1 / \beta_0 = 0.32$ results. Thus,
where $m$ represents a material property relating to
the distribution of microcracks, the translation of
this material property to large scale structural
reliability $R$ is well delineated in Weibull
definitions.

This section has provided a brief review of
statistical definitions of structural reliability
which form the basis of current design practice in
composite structures. The Weibull distribution
provides an entry point for translating
microscopic material responses, as defined by $m$
and $\beta_1$, into predictions of large scale
structural reliability.

\[
R = 1 - F = \exp \left[ -\frac{V_i K_i N_i}{(V_0 K_0 V_0)^{1/m}} \beta \right] 
\]

(3)

where $F$ is failure probability, $V_i$, $K_i$, $N_i$ are
respectively related to size, shape, and numeric complexity effects upon the mean strength $\beta$ at reliability level $R = 1/e \approx 0.368$. The
Weibull distribution shape factor $m$ is determined
from analysis of experimental data where the
measured strengths $\sigma$ are arranged serially, $j = 1, 2, 3, \ldots, N$ in increasing order of $\sigma$ and the reliability is defined as follows: (7)

\[
R = 1 - F = \left( \frac{V_j}{V_0} \right)^{1/m} 
\]

(4)

By taking logarithms of Eq.(3) we obtain the
following linear relation:

\[
\ln(-\ln R) = m(\ln \sigma - \ln \beta) + \ln V_i K_i N_i 
\]

where the ordinate becomes $\ln(-\ln R)$, the slope is $m$ and the intercept at $\ln(-\ln R) = 0$ is a reference condition $V_0 K_0 V_0 = 1.0$.

Dual Path Concept
The structural performance, reliability, and
durability of polymer composites can now be
 correlated with three generic classes of defects.
The first class of generic defects (size 1-200Å)
that control critical design properties such as
glass transition $T_g$, moisture absorption, and
dimensional changes can be controlled by chemical
analysis and selection of raw materials prior to
manufacture. (9-12) A second generic class of
manufacturing defects (size greater than 1μm)
include inclusions, voids, and debonds which
results from non-optimum process control in
fabrication and manufacture. This second class of
defects are detected by ultrasonics, optical
scanning and other methods sensitive to
interfacial imperfections as is well detailed by
other papers at this conference.

The interaction of these two classes of
intrinsic defects with environmental and
mechanical stresses produces a third class of
macroscopic fatigue defects such as networks of
interconnected microcracks as well as singular
macroscopic crack growth. These fatigue defects
can be detected by ultrasonic emission, moisture
diffusion analysis, and optical inspection.

Recognition that intrinsic chemical and
manufacturing defects may, in large part,
determine polymer composite reliability represents
an important extension of analytical modeling in
which physical chemistry parameters appear as
primary control variables. A preferred dual path
approach for correlating environmental (plus
mechanical) aging with macroscopic strength is
shown in Fig. 5. In addition to the statistical
correlations for structure reliability discussed
in the preceding section, the dual path approach
adds detailed spectroscopic analysis to define the
molecular process of aging and strength change.
As shown in Fig. 5, the proposition of process
scale-up characterization to define and control
manufacturing defects is inherent in the dual path
approach. Utilization of the dual path approach
usefully combines both deterministic and
statistical models for polymer composite
reliability. A highly evolved flow chart for
polymer composite reliability analysis is shown by
the block diagram of Fig. 6.(12)
Fig. 5 Preferred dual path for correlating environmental aging with macroscopic strength.

Fig. 6 Technical approach to polymer composite reliability.

The left column of Fig. 6 deals with studies of composite system response and develops the important statistical correlation between environmental aging and composite reliability. The central column of Fig. 6 defines special studies of interfacial bonding, which range from surface chemistry to macroscopic characterization of surface roughness. These studies are dominantly related to isolation and control of manufacturing defects introduced by improper surface treatment and process conditions for bonding and curing.

The right column of Fig. 6 defines essential studies in polymer properties which include chemical analysis, polymer synthesis, molecular weight characterization and mechanical spectrum analysis. In polymer studies, these four areas of study are presently closely interconnected. Failure of polymer cohesive response in composite applications is readily identified in molecular terms and corrective action involving polymer chemistry and chemical analysis becomes available to composite reliability studies.

The present problem with regard to full implementation of the technical approach shown in Fig. 6 is the failure of material scientists to convert their detailed physical data into parameters directly useful to the design engineer for large scale structures. This problem has been recognized and a semiformal approach for resolution has been proposed by Kelley and Williams (15) in the form of a morphological scheme termed the “Interaction Matrix”. The interaction matrix, as shown in Table 2, lists mechanical property requirements as defined by the design engineer as column headings. A list of molecular properties as defined by the material scientist are listed in descending order as row headings. Within the box, defined by a design requirement and a molecular property, the degree of correlation is assigned on a numeric scale such as shown in Table 2. By summing these numbers across both the rows and columns as shown by the \( \Sigma \) values in Table 2, the position of both rows and columns can be rearranged to maximize the strong correlations within a matrix as shown in the upper left section of Fig. 2. This summing and rearrangement of the interaction matrix tends to focus communications and research toward the most fruitful sector of defined engineering need and molecular response.

Table 2. Interaction matrix between molecular property and mechanical requirement; 3=Strong interaction, 2=Medium, 1=Negligible, 0=Unknown, \( \Sigma \)=Sum of Interactions

<table>
<thead>
<tr>
<th>MECHANICAL REQUIREMENT</th>
<th>Tg</th>
<th>Ee</th>
<th>T0</th>
<th>E0</th>
<th>n</th>
<th>E</th>
<th>( \Sigma )</th>
</tr>
</thead>
</table>
| Volume Fraction Plasticizer | 3  | 3  | 1  | 1  | 11
| Volume Fraction Filler | 2  | 3  | 2  | 3  | 11
| Degree of Crystallinity | 1  | 3  | 3  | 3  | 11
| Molecular Weight | 3  | 3  | 1  | 1  | 9
| Crosslink Density | 1  | 3  | 1  | 2  | 1
| Chain Stiffness | 3  | 1  | 0  | 2  | 7
| Macromolecular Friction Coefficient | 3  | 1  | 0  | 0  | 7
| Heterogeneity Index | 2  | 1  | 2  | 1  | 7
| Entanglement Molecular Weight | 1  | 3  | 1  | 1  | 7
| Solubility Parameter | 3  | 1  | 0  | 0  | 2
| E | 22  | 22  | 16  | 10

* \( T_0 \): glass temp; Modules (E) vs time (t) \( = E(t) = E_0 (1+\frac{t}{T_0})^n \), \( E_e \): glass modulus, \( E_0 \): glass to rubber transition, \( n \): exponent.

The development of quantitative and preferably deterministic relations between engineering design parameters and molecular response variables is, of course, the desired end point in the dual path approach. An illustrative reliability and durability model for the polymer subphase in composite response is detailed in the following set of six relations:

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GLASS Transition RESPONSE

\[
T_{\text{go}} = \frac{2}{R_0} \left( \frac{\Delta u_c}{\Delta h} \right) + C(t) \quad (6)
\]

\[
T_g = T_{\text{go}} + \left( \frac{\partial T}{\partial \sigma} \right)_0 + \left( \frac{\partial T}{\partial C_{\text{H}2O}} \right)_0 + \left( \frac{\partial T}{\partial m^{-1}} \right)_0 \quad (7)
\]

RHEOLOGICAL RESPONSE

\[
\log \left( \frac{1}{a_T} \right) = \frac{17.4(T-T_g)}{51.6} + t^{-T_g} \quad (8)
\]

\[
M_i = \left[ \frac{M_0 - M_{\infty}}{1 + \frac{t}{a_T} t^{-1}} \right] + M_{\infty} \exp \left( -\frac{t}{m^T} \right) \quad (9)
\]

RELIABILITY-FAILURE RESPONSE

\[
R_M = \exp \left( -\frac{m(a)}{b} \right) \exp \left( -\frac{m(e)}{b} \right) \exp \left( -\frac{t}{b_0\tau} \right) \quad (10)
\]

\[
R_t = R_M + (1-R_M) R_w \quad (11)
\]

The details of symbols and parameter definitions for this model are summarized in Table 3.

Table 3. Nomenclature for polymer reliability relations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{go}}$</td>
<td>Reference glass transition defined by monomer composition.</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Summation of molecular degrees of freedom.</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Monomer Tg, as affected by mechanical (tensile) stress, moisture concentration $C_{\text{H}2O}$, and U.V. radiation effects.</td>
</tr>
<tr>
<td>$a_T$</td>
<td>Time scale correction factor (C(t) $\approx$ 25°C).</td>
</tr>
<tr>
<td>$C(t)$</td>
<td>Time shift factor for rheological response.</td>
</tr>
<tr>
<td>$T$</td>
<td>Test temperature.</td>
</tr>
<tr>
<td>$M_0$</td>
<td>Time dependent modulus.</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Glass (solid) state modulus.</td>
</tr>
<tr>
<td>$M_{\infty}$</td>
<td>Rubber (tensile) state modulus.</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Test time and exponent.</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>Duration time for glass to rubber transition.</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>Terminal time for rubber to liquid transition.</td>
</tr>
<tr>
<td>$K_t$</td>
<td>Limiting (tensile) modulus.</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Rubber (tensile) modulus.</td>
</tr>
<tr>
<td>$K_{\infty}$</td>
<td>Limiting (tensile) modulus at infinite time.</td>
</tr>
<tr>
<td>$\sigma_T$</td>
<td>Relaxation time for Weibull failure process.</td>
</tr>
<tr>
<td>$\sigma_{\text{stress}}$</td>
<td>Stress (tensile) for Weibull failure process.</td>
</tr>
<tr>
<td>$\sigma_{\text{strain}}$</td>
<td>Strain (tensile) for Weibull failure process.</td>
</tr>
<tr>
<td>$m(a), m(e)$</td>
<td>Weibull distribution shape factors for time (t), stress (a), and strain (e) dominated failure.</td>
</tr>
</tbody>
</table>

This model starts by introducing chemical structure and measurement time contributions to define a reference $T_{\text{go}}$ in Eq.(6). This relation was empirically developed by Hayes(17) and correlated with glass transition theory by Kaelble(18). Monomer sequence distribution as discussed by Johnston(19) and semicrystallinity as discussed by Boyer(20) complicate use of Eq.(6) for some polymers. The important concept embodied in the relation is that functional group properties of the monomeric unit determine an important thermal transition relating to environmental durability.

In Eq.(7) the effects of mechanical stress, bulk moisture concentration $C_{\text{H}2O}$ and U.V. radiation effects on reciprocal polymer molecular weight $M^{-1}$ are identified. Common values for the partial derivatives:

\[
\frac{\partial T}{\partial \sigma} = -0.1 \frac{\Delta \sigma}{\text{cm}^2}{\text{ Kg}} \quad \text{(polystyrene, ref.18)}
\]

\[
\frac{\partial T}{\partial C_{\text{H}2O}} = -6.0 \frac{\text{C}}{\text{wt%H}2O} \quad \text{(epoxy, ref.21)}
\]

\[
\frac{\partial T}{\partial m^{-1}} = -0.06 \frac{\text{C}}{\text{M}^{-1}} \quad \text{(general, ref.18,22)}
\]

The fundamental issue which is directly expressed by Eq.(7) is the direct description of local or macroscopic changes in nominal values of glass temperature $T_g$ due to separate or combined effects of mechanical stress, moisture and U.V. exposure effects on $M^{-1}$. In general, one must assume effective local concentration effects in $\sigma$, $C_{\text{H}2O}$, and $M^{-1}$. As examples, stress concentrations at crack tips, or high surface moisture concentrations will locally reduce $T_g$.

The familiar WLF equation(23) is presented as Eq.(8) is a nearly universal relation for calculating the time shift factor $\eta_T$ at test temperature $T$ which characterizes all rheology dominated response of the polymer interfacial subphase. Since $T_g$ in this relation is previously defined by Eq.(7), all the comments presented above for spatially localized $T_g$ states are, of course, transformed by Eq.(8) into spatially localized time response states in terms of $\eta_T$ within both the bulk polymer and at the interface. It is particularly evident that a polymer composite at temperatures near its reference $T_g$ will display a potentially wide distribution of $\theta_T$ values with local variations in $T_g$.

The values of $\eta_T$ generated from Eq.(8) appear as time $t$ shift factors in both Eq.(9), which defines subphase modulus $M_i$ and Eq.(10), which defines the Weibull modulus $M_i$ and Eq.(10), which defines the Weibull modulus $M_i$. A modified power law relation suggested by Kelley and Williams(15) for approximate fitting of viscoelastic data in polymeric materials over extremes of time response if presented in Eq.(8). An example calculation of $M_i$ for over 30 decades of reduced time ($t/\eta_T$) for a typical amorphous polymer such as polystyrene is shown in the solid curve of Fig. 7.

In Eq.(10), which defines a reduced time function for reliability (equivalent to survival probability), the $\theta_T$ parameter appears as a time reduction factor. The complexity in time scales of failure for uniform failure conditions is presented in physical terms by the Halpin and Polley(24) model for fracture. The Halpin-Polley model describes a statistical distribution of flaws as present in all polymeric materials and mathematically connects these defects to the well known Weibull frequency distribution(25) which assumes that failure is initiated at the weakest link. Gordon(26) has
shown that time fluctuations in steady state peel fracture appear to fit a Gaussian frequency distribution which is essentially identical to the distribution defined by Eq. (3) when the Weibull shape factor exponent takes the value m = 3.67. The dashed curve of Fig. 7 presents a plot of Eq. (10) with m(t) = 1.0 which is relatively low for typical polymer failure. A simple calculation is introduced to demonstrate the fundamental propositions in terms of stress-strain behavior and failure response of a polymeric subphase. First, assume the Mf and Rf properties of this subphase are described by the curves in Fig. 7. Also assume the subphase is tested in tension somewhat below the subphase glass temperature with:

\[ T - T_g = -30^\circ C \]

\[ (\alpha T_g) = -0.10^\circ C \text{ cm}^2 \text{ kg}^{-1} \]

and with

\[ C_{H_2O} = 0 \]

By use of Eq. (7) and Eq. (8) the curves shown in Fig. 8 can be calculated to correlate stress magnitude \( \sigma \) with log \( t/\alpha T \). The curves in Fig. 8 illustrate the MFL prediction of stress effects on the time shift factor and show that tensile stresses readily supported by the cohesive or interfacial strength of a glassy polymer can change rheological response time of the material over many decades and, in fact, produce rubbery state response when \( \sigma > 300 \text{ kg/cm}^2 \) for the example shown. For a known stress-strain response for the material, such as defined by simple time dependent Hookian response:

\[ \sigma(t) = \epsilon \cdot M_f(t) \]

It follows that stress-strain curves in tensile creep can be calculated. This calculation applies for the case of instant loading to constant stress \( \sigma \), and maintaining this stress constant to a designated constant time \( t \), which we set at \( t = 1.0 \text{ sec} \) and \( t = 8.61 \times 10^8 \text{ sec} = 20 \text{ yr} \). Isochronal creep stress vs strain curves can be constructed from the curves of Fig. 7 and Fig. 8.

The 20 year life of the polymer composite reflected by tensile creep curves for \( t = 20 \text{ yr} = 6.31 \times 10^8 \text{ sec} \) shown in lower Fig. 9 can be readily generated in the same fashion as the \( t = 1 \text{ sec} \) response curves shown in upper Fig. 9. In summary, the intent of this section and the above illustrative examples is to show that the right vertical arrows which connect chemical synthesis to mechanical spectroscopy in Fig. 6 are detailed by structure-property relations. In Eq. (8) the time shift factor \( \alpha T \) can be reset by changes in temperature \( T \), stress \( \sigma \), moisture concentration \( C_{H_2O} \), and reciprocal polymer molecular weight \( M_f^{-1} \) to accelerate natural degradation processes which determine long term durability and reliability.

The data summary of Table 4 reports experimentally determined Weibull strength distributions of structural adhesives, fibrous reinforced composites, and adhesive bonded metal joints under different conditions of environmental aging. These strength distributions were obtained in conjunction with physical chemical characterizations which clarify the shift in the Weibull values of mean strength \( \sigma_0 \) and distribution shape factor \( m(\sigma) \) reported in Table 4 will, perhaps, provide practical insights into the proposed dual path concept sketched in Fig. 5.

Multiphase Structural Adhesives

Epoxy structural adhesives, toughened by a rubbery subphase, are now extensively used in aircraft structures \cite{28}. Current adhesively bonded primary structures such as Air Force PABST (primary adhesive bonded structures technology) include carboxy terminated butadiene acrylonitrile (CTBN) rubber as a chemically combined constituent of the epoxy structural adhesive \cite{29}. In CTBN modified epoxy adhesives, the rubbery subphase precipitates during curing of the adhesively bonded joint. This produces the multiphase morphology and microstructure that leads to a
to cavitation and crazing (stress-whitening) due to dilational strains in the triaxial stress field of the crack tip (34,35). Since extensive microstructure degradation precedes final failure in CTBN toughened epoxy, an important question is whether the statistical distribution of cohesive strengths is adversely modified.

A special study was undertaken to clarify the multiphase morphology effects upon the statistical distribution of cohesive strengths in the materials summarized in Table 5. Microtensile test specimens (ASTM Method 1708-66) were die cut from the cured epoxy films while they were heated to rubbery state response at 120°C. Tensile tests were conducted at a strain rate $\dot{\varepsilon}$ of 0.09 min$^{-1}$. Single specimen tests, at temperatures from -200°C to 200°C as shown in Fig. 10a, were conducted to determine the temperature dependence of nominal tensile strength $\sigma_T$. At -150°C and 100°C, which represent lower and upper service temperatures in structural applications, larger groups of specimens were tested to determine the statistical distribution of $\sigma_T$. Six groups of specimens, as summarized in upper Table 3, describe the bounds of strength variation indicated in Fig. 10a by the extreme high and low tensile strengths indicated by the bracketed error bars at -150°C and 100°C for each strength curve.

| Table 5. Co-reactants for three-dimensional epoxy-nitrite rubber block copolymers |
|---------------------------------|-----------------|-----------------|
| 1. Epoxy: DGEBA (Epon 828, Shell Chemical Company), 100 pbw (parts by weight), $M_n = 280$ g/mole |
| 2. Catalyst: Piperidine - 5 phm |
| 3. Cure program: terminated nitrite rubber (Wormal Chemical Company) - 0, 17, 29, 39, 59% by weight based on 100 pbw Epoxy + 5 pbw piperidine |
| HAC $\rightarrow$ CH = CH$_2$ $\rightarrow$ CH$_3$ + (OH$_n$ - CH$_2$ - CH$_2$)$_m$ (OH$_m$ - CH$_2$ - O) $\rightarrow$ CH$_3$ |
| $M_n = 3100$ - 3500 g/mole |
| 4. Mix items (1), (2), and (3) above, degas, and cure for 16 hours at 105°C under dry N$_2$ |

In Fig. 10b, the strength data points are arranged serially $J = 1, 2, \ldots N$ in increasing order of $\sigma_T$, and the survival probability (= reliability) is defined by Eq. (4) where $N$ is the number of observations and $F$ is the failure probability. Six groups of data show the cumulative distribution of survival probability. The ratio of extreme strength values (Table 4) for pure epoxy is not dramatically modified by either extremes of test temperature or composition. The study thus supports the view that the statistical distribution of cohesive strengths is not strongly or adversely modified by addition of CTBN. Inspection of Fig. 10 provides the following conclusions in relation to fracture integrity:

1. The effect of temperature change, from -150°C to 100°C, dominantly influences the cohesive strengths of CTBN toughened epoxy.
2. Chemical composition changes, from 0-50% by weight CTBN epoxy modifier, is the second most dominant strength determinant.

---

**Strongly enhanced fracture toughness** (30-34), where ($\delta_{IC} = 2.0$ to 4.0 kJ/m²) with 15% CTBN modifier, compared to 0.1 to 0.2 kJ/m² for unmodified epoxy resins (35).

Several detailed studies of the fracture properties of CTBN modified epoxy adhesives now show that their high fracture toughness is related

Table 4. Weibull strength distributions

<table>
<thead>
<tr>
<th>Composite Polymer</th>
<th>Test</th>
<th>$\sigma$ = exp [-(20%)&lt;@&gt;(t)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy/EPN</td>
<td>T(OC)</td>
<td>Tensile Failure</td>
</tr>
<tr>
<td>0</td>
<td>-150</td>
<td>R=15</td>
</tr>
<tr>
<td>17</td>
<td>-150</td>
<td>R=15</td>
</tr>
<tr>
<td>10</td>
<td>-150</td>
<td>R=15</td>
</tr>
<tr>
<td>0</td>
<td>-150</td>
<td>R=15</td>
</tr>
<tr>
<td>17</td>
<td>-150</td>
<td>R=15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composite Polymer</th>
<th>Test</th>
<th>$\sigma$ = exp [-(20%)&lt;@&gt;(t)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy/EPN</td>
<td>T(OC)</td>
<td>Tensile Failure</td>
</tr>
<tr>
<td>0</td>
<td>-150</td>
<td>R=15</td>
</tr>
<tr>
<td>17</td>
<td>-150</td>
<td>R=15</td>
</tr>
<tr>
<td>10</td>
<td>-150</td>
<td>R=15</td>
</tr>
<tr>
<td>0</td>
<td>-150</td>
<td>R=15</td>
</tr>
<tr>
<td>17</td>
<td>-150</td>
<td>R=15</td>
</tr>
</tbody>
</table>

---

Fig. 9 Calculated tensile creep stress $\sigma(t)$ vs. strain $e(t)$ (solid curves) and reliability $R(T)$. Reduced stress $R(T)$ vs. strain $e(t)$ (dashed curves) at $t = 1$ sec (upper view) and $t = 20$ yr (lower view).
enhancement of fracture toughness by inclusion of displays its principal adverse effect in shifting tensile strengths to lower values, without change the entire distribution of high temperature strength is physically related to the lower degree of cure as indicated by liquid chromatography and higher heat of cure indicated by differential scanning calorimetry (DSC). The numeric information of Table 6 also shows the importance of differentiating between total DDS curative as measured by IR spectroscopy and free amine as measured by quantitative molecular separation using liquid chromatography. The chemical analysis data of Table 5 forms part of the materials and processes approach to chemical defects definition as outlined in Fig. 6.

A comprehensive environmental durability characterization has been carried out on the three composites described in Table 6. Some results of this study serve to highlight the direct importance of chemical analysis in composite reliability and durability predictions.

Table 6. Chemical characterization of graphite-epoxy prepreg materials.

<table>
<thead>
<tr>
<th>This Study</th>
<th>Reference System</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Epoxy Matrix</td>
<td>Hercules 3501-5</td>
</tr>
<tr>
<td>2. Graphite Fiber</td>
<td>Hercules 3501-5</td>
</tr>
<tr>
<td>3. S Total DDS Curative</td>
<td>29.2</td>
</tr>
<tr>
<td>4. % Free DDS Curative</td>
<td>18.1</td>
</tr>
<tr>
<td>5. Epoxy Equivalent</td>
<td>299</td>
</tr>
<tr>
<td>6. MLs DDS Type Darsi</td>
<td>0.047</td>
</tr>
<tr>
<td>7. Relative Degree of Cure by Liquid Chromatography</td>
<td>22</td>
</tr>
<tr>
<td>8. Heat of Polymerization by DSC (cal/g polymer)</td>
<td>187</td>
</tr>
</tbody>
</table>

In the DSC thermograms of Fig. 11, the rate of chemical curing correlates with the amplitude of $\frac{\Delta H}{\Delta t}$, the heat release rate. The low temperature initiation of curing in 334 and 3501-5 epoxy correlates with the detected presence of the BF$_3$ catalyst as compared to uncatalyzed 5208 which requires much higher temperatures to complete the curing process.

![Fig. 10(a)](image)

The temperature and compositional dependence of the tensile strength for a rubber modified epoxy.

Fig. 10(b) The stress dependence of the survival probability for rubber modified epoxy at -150 and 100°C.

(3) Statistical strength variation, for a survival probability range from 0.05 to 0.95, is a minor strength determinant.

It thus appears that the 15-40 fold enhancement of fracture toughness by inclusion of approximately 15% CTBN in structural epoxy resins displays its principal adverse effect in shifting the entire distribution of high temperature tensile strengths to lower values, without change in shape. This adverse effect on high temperature strength is physically related to the lower crosslinking density for the three-dimensional network formed between CTBN and epoxy coreactants.

Fibrous Composite Reliability

Hydrothermal exposure (combined high moisture and temperature) of graphite reinfored epoxy matrix composites can produce irreversible reduction in shear strength and modifies the Weibull distribution of survival probabilities as shown in studies by Kanble and Dynes [36]. Comparative chemical analysis of two catalytically cured graphite-epoxy matrix composites and an aromatic amine cured epoxy matrix composite shows that curing mechanisms and epoxy network structure influence both thermal response and environmental durability. The results of chemical analysis of the three epoxy prepregs are summarized in Table 6. The chemical analysis follows standard procedures outlined in previous reports [10,12]. The data of Table 6 shows that a BF$_3$ type boron is present as a catalytic curing agent in 3501-5 epoxy (Hercules) and 934 epoxy (Fiberite) and present only as a trace constituent in 5208 epoxy (NARMCO). This BF$_3$ catalyst decomposes to initiate homopolymerization of epoxy groups at lower temperatures than co-reaction between epoxy and DDS (diaminodiphenyl-sulfone) curative which is common to all three systems. The higher level of free DDS curative in 5208 epoxy correlates with the lower degree of cure as indicated by liquid chromatography and higher heat of cure indicated by differential scanning calorimetry (DSC). The numeric information of Table 6 also shows the importance of differentiating between total DDS curative as measured by IR spectroscopy and free amine as measured by quantitative molecular separation using liquid chromatography. The chemical analysis data of Table 5 forms part of the materials and processes approach to chemical defects definition as outlined in Fig. 6.

![Fig. 11](image)

Fig. 11 DSC thermograms for curing reactions of commercial epoxy matrix materials extracted from prepreg. (DSC scan rate $\phi = 20^\circ C/min$)

200
The use of catalytically assisted curing clearly correlates with easier processability as shown in the lower temperature cure cycles shown in Fig. 11. The thermal scans of dynamic damping response in the fully cured uniaxial composites of these materials, as shown in Fig. 12, reveal that catalytic curing at lower temperatures produces a crosslinked network with substantially lower T_g. As shown in Fig. 12, the 934 epoxy displays onset of T_g response by an initial increase in tanδ at T = 200°C while cured 3501-5 epoxy shows initial rise in tanδ at 225°C and 5208 epoxy at T = 250°C for dry fully cured composite.

The effects of prior moisture exposure to full saturation is shown in the damping curves of Fig. 13 to lower the T_g related initial increase in tanδ response to about T = 140°C for 934 epoxy and T = 160°C for 3501-5, while the 5208 resin maintains low tanδ response to above 200°C.

The prediction offered by the dynamic damping response as measured by Rheovibron is that cured 3501-5 resin will display glass state response at 232°C in the dry state, and low strength rubbery response due to water plastization in the moisture saturated state at 232°C. The curves of Fig. 14 show the clearly separated interlaminar shear strength distributions for uniaxial 3501-5 epoxy matrix composite where dry and moisture exposed specimens were subjected to an equivalent 232°C thermal spike prior to strength measurement at 29°C. As predicted, the interaction of high moisture and high temperature produced internal damage which lowered both mean shear strength λ_o and also substantially lowered the Weibull distribution shape factor m.

**Fig. 12** Rheovibron thermal scans for flexural damping in cured uniaxial reinforced graphite-epoxy composite in the dry unaged condition.

**Fig. 13** Rheovibron thermal scans for flexural damping in cured uniaxial reinforced graphite-epoxy composite in the wet-aged condition.

**Fig. 14** Cumulative distribution function of survival probability.

**Metal Joint Reliability**

All metals, except gold, are chemically reactive with oxygen and moisture at room temperature and tend to form oxide or hydrated oxide surface layers [37]. In addition to oxidative chemical reaction, these high energy surface films are subject to further physical adsorption by water vapor and volatile organic contaminants. In structural metal to metal joints, the reliability of the bond may be directly related to the chemical stability of the
interfacial bond. Weibull statistical analysis has recently been applied to investigate the effects of both surface exposure time (SET) and bond exposure time (BET) on the distributions of single layer shear bonds of aluminum alloys. Smith and Kaelble have recently conducted a detailed study of combined SET and BET aging in normal (50% R.H., 230°C), and high moisture (95% R.H., 54°C). The experimental methods of the study by Smith and Kaelble are outlined in Table 7 with full details contained in the published report.

TABLE 7
Metal Joint Reliability Studies

| 1. Metal Adherends: Un clad 2024-T3 aluminum alloy surface treated by standard FPL sulfuric chromate etch and T6-600-4V titanium alloy treated by standard phosphate fluoride cleaning process. Coupon size 0.063" thick, 1" wide, and 4" long. |
| 2. Adhesive: HT 424 epoxy-phenolic film adhesive (from American Cyanamid) with glass fiber carrier and standard weight 0.0135 ± 0.005 lb/sq. ft. Unfilled HT 424 primer with parts A and B used with adhesive. |
| 3. Bonding Process: Treated metal coupons spray primed with 0.001" thickness HT 424 primer solution using clean dry argon carrier gas. Primer layers dried 30 min ambient 230°C and 60 min at 60°C. An adhesive film is placed in the 1.000"x0.500" overlap between two metal adherends. Six such joints are aligned in a bonding jig with the glass carrier acting to provide constant glue line thickness 0.008". Cure cycle with 60 min temperature rise to 1710°C and 60 min cure cycle at 1710°C followed by cooling to room temperature. |
| 4. Tensile Lap Shear Testing: 1.5" x 1.0" x 0.063" aluminum alignment shims bonded to eliminate offset. Tests at 230°C using 0.01"/min Instron crosshead rate and 4.5" jaw separation. |

In this study the surface chemistry and related wettability of both adherends and adhesive were analyzed prior to bonding. The results of this surface energy analysis can be plotted on a surface energy map where the ordinant coordinates as shown in Fig. 15 respectively refer to dispersion (monopolar) and polar components of surface energy and interfacial bonding mechanisms. The theory of interfacial adhesion experimentally verified in this analysis defines the thermodynamic work of adhesion \( W_a \) by the following relation:

\[
W_a = W_{13} = 2(\alpha_1 \alpha_3 + \beta_1 \beta_3) \tag{12}
\]

where \( \alpha_1, \beta_1 \) define the dispersion and polar surface properties of adhesive and \( \alpha_3, \beta_3 \), those of the metal adherend.

As shown in Fig. 15, and further documented in detailed kinetic studies by Kaelble and Dynes, the \( \alpha_3 \) and \( \beta_3 \) properties of aluminum alloy change dramatically with surface aging time after FPL etch. The \( \alpha_1, \beta_1 \) surface properties of HT 424 adhesive are shown to lie below the curve for Al 2024-T3 at all stages of surface aging which predicts proper bonding between adhesive and adherend in air.

The interfacial work of adhesion \( W_a \) as defined by Eq.(12) will decrease with surface aging time (SET) as shown by the upper curve of Fig. 15. As shown in the lower curves of Fig. 16, the lap shear bond strength varies with SET in a fashion that correlates closely with the predictions from work of adhesion calculations. A simple but now widely demonstrated correlation between surface energetics and fracture mechanics is available in the following relations for critical stress \( \sigma_c \) for Griffith type crack initiation under normal stress loading(41,42):

\[
\sigma_c = \left( \frac{E_\ell}{C} \right)^{\frac{1}{2}} \left( R - R_0 \right)^2 > 0 \tag{13}
\]

where \( E, C \) are a characteristic modulus and crack length which are assumed constant and the surface energy parameters \( R \) and \( R_0 \) are defined by the following relations(41,42):

\[
R_0 = 0.25 (\alpha_1 - \alpha_3)^2 + (\beta_1 - \beta_3)^2 \tag{14}
\]

\[
R^2 = (\alpha_2 - H)^2 + (\beta_2 - K)^2 \tag{15}
\]

\[
H = 0.5 (\alpha_1 + \alpha_3) \tag{16}
\]

\[
K = 0.5 (\beta_1 + \beta_3) \tag{17}
\]

In Eq.(15) two new surface energy parameters \( \alpha_2 \) and \( \beta_2 \) define the environment (phase 2) at the crack tip. The model for critical stress defined by Eq.(13) can be presented on surface energy coordinates as shown in Fig. 17.
predicted decrease in critical stress $\sigma_c$ of the HT 424 to Al 2024-T3 interface is:

$$\frac{\sigma_c(H_2O)}{\sigma_c(\text{air})} = 0.644 \quad (18)$$

$$\frac{\sigma_b(\text{aged, wet})}{\sigma_b(\text{unaged, dry})} = \frac{2275 \text{ psi}}{3300 \text{ psi}} = 0.69 \quad (19)$$

which is in close agreement with the prediction of Eq.(18).

An essentially parallel detailed study of surface aging showed a shift in $\sigma_2$ and $\sigma_3$ for phosphate-fluoride cleaned titanium alloy similar to that detailed in Fig. 15. Application of the modified Griffith analysis as shown in Fig. 19 provides the following predicted moisture degradation of bond strength at the HT 424 to Ti-6Al-4V interface:

$$\frac{\sigma_c(H_2O)}{\sigma_c(\text{dry air})} = 0.84 \quad (20)$$

Fig. 16 Dependence of interfacial work of adhesion $W_{13}$ (upper curve) and lap shear bond strength $\sigma_b$ (lower curve) at varied SET.

Fig. 17 Modified Griffith analysis of the effect of H$_2$O immersion in reducing critical failure stress $\sigma_c$ for interfacial failure between HT424 and etched Al 2024-T3 ($\phi_1 = 1 - \phi_c = 1.0$).

Fig. 18 SET and BET response surface for lap shear bond strength for Al 2024-T3-HT424.

Fig. 19 Modified Griffith analysis of the effect of H$_2$O immersion in reducing critical failure stress $\sigma_1$ for interfacial failure between HT424 and phosphate-fluoride treated Ti-6Al-4V, ($\phi_1 = 1 - \phi_c = 1.0$).
An equivalent calculation for moisture degradation of the HT 424 cohesive bond produces the following prediction:

\[
\frac{\sigma_c (H_2O)}{\sigma_c (\text{dry air})} = 0.63 \tag{21}
\]

Joint strength testing of the HT 424 to titanium alloy was carried out under conditions of separate and combined SET and BET in high moisture (95\% R.H., 540\°C). The SET vs BET response surface of shear bond strength \(\sigma_s\) is shown in Fig. 20 where each point is an average of six strength tests. As shown in Fig. 20, the shear bond strength reaches an equilibrium value under extended moisture aging. Comparing joint strengths for fully aged (22 hr SET, 1000 hr BET) and unaged (0 hr SET, 0 hr BET) for Ti-6Al-4V to HT 424 bonds (see Table 4) provides the following experimental ratio:

\[
\frac{\sigma_s \text{ (aged, wet)}}{\sigma_s \text{ (unaged, dry)}} = \frac{2873 \text{ psi}}{3640 \text{ psi}} = 0.75 \tag{22}
\]

which lies intermediate between the cohesive failure prediction of Eq.(21) and the interface prediction of Eq.(20). Microscopic visual inspection of the fracture surfaces for the HT 424 to titanium lap shear points shows predominant (above 50\%) cohesive failure for lap shear bonds described in Fig. 20.

The Weibull plots of Fig. 21 show shear bond strength distributions for unaged and fully aged aluminum (upper view) and titanium (lower view) adherends. The titanium bonds show lower Weibull m values in both unaged and aged states. Conversely, if mean strength with \(R = 0.37\) and \(\ln(-\ln R) = 0\) is applied as a design criteria, the curves show titanium alloy joints to display higher unaged and aged strengths.

Detail Test Plans

Previous sections of this discussion have presented and discussed the importance of recognizing the molecular processes which influence polymer composite reliability. A need for further development of the molecular theory of polymer reliability is also made evident in these several examples from structural polymers, fibrous composites, and bonded metal joints. The simple design concept of structural strength becomes replaced by a more sophisticated and holistic (or encompassing) design concept for reliability and durability by use of a combined molecular and mathematical modeling. If molecular theory of structure reliability were complete, the chemical analysis test plan outlined in Fig. 22 would provide sufficient design data to provide structural reliability predictions. Lacking a complete molecular theory requires that detailed experimental test programs for physical and mechanical analysis as outlined in Fig. 23 be employed in conjunction with chemical analysis, the detailed test programs outlined in Fig. 22 and Fig. 23 require advanced instrumentation and computer aided data processing.

Executing a complete chemical analysis of a polymer composite as outlined in Fig. 22 generally provides sufficient detailed information to replicate a commercial polymer adhesive or
coating. In order to improve the reliability and durability of adhesives or coatings, essentially all aspects of the detailed physical and mechanical test program of Fig. 23 need to be employed. The upper rank experiments in Fig. 23 involving DSC, surface energetics, and thermal mechanical analysis (TMA) simulate manufacturing steps for surface treating, bonding, and curing polymer composites. The central tier of experiments in Fig. 23 incorporate NDE tests, adhesive joint tests in conjunction with study of polymer material response. The lower portions of Fig. 23 outline phases of study involving aging and failure mechanisms. The lower extremity of Fig. 23 describes a data analysis with correlation of molecular process and composite response. The detailed test plans outlined by Fig. 22 and Fig. 23 are presently utilized to determine and improve polymer reliability. The challenge to both theoretical and experimental analysis is, of course, to lower the cost and increase the reliability of currently functioning test programs as detailed in Fig. 22 and Fig. 23.

Summary and Conclusion
In summary, we may return to the mythical "one-hoss-shay" of Holmes poem (see Table 1) which presents the nearly perfect example of design for structural reliability and durability. An important point presented and hopefully well illustrated in this discussion is the importance of adding the analysis of molecular processes to present statistical theory of structure reliability. Implementation of the interaction matrix (see Table 2) establishes a direct avenue for communication between the specialist in engineering design and the materials scientist. The dual path approach (see Figs. 5 and 6) with combined deterministic/statistical testing and analysis is validated by extensive studies of which several are briefly reviewed in this discussion. A more general development and application of molecular theory of polymer reliability can lower the cost and increase the efficiency in present detailed test programs (see Figs. 22 and 23) for analyzing chemical, physical, and mechanical aspects of polymer composite durability.

A recent workshop on space environment effects on polymeric matrix composites in large scale space structures provides recommendations which also serve as conclusions to this discussion(43):

1. Prior chemical analysis is necessary for materials identification.
2. Predictive modeling is mandatory.
3. All test designs should be based on the predictive model.

Implementation of the above recommendations promotes organization of present knowledge into an initial mechanistic model with molecular and macroscopic properties correlated. The model can be verified and refined as work progresses. The model elevates the engineering program to the level of conducting science and not simply data gathering.

ACKNOWLEDGEMENT
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DISCUSSION

George Martin (Consultant): Dave, have you considered the state of ionization of the air and related chemical degradation of surfaces?

David Kaelble (Science Center): Yes, of course. It appears in these models through the reciprocal molecular weight.

If you have radiation damage you are going to experience it in terms of a change in either by cross linking or scission within the polymeric phase. I don't expect that damage would be specific to the interface specifically unless you had a very high absorption cross-section for the interface itself. With orbiting space structures the radiation is from Van Allen type radiation environments. It is very difficult to model that particular situation in terms of the potential damage mechanisms in relation to the various types of energetic sources which range, of course, from photons to the high energy electron sources. The approach taken is simplify that whole argument by assuming that you are going to have surface protective mechanisms, that you will have thin foils which will essentially shield the surface from UV and, perhaps, the photon degradation and be left then with primarily the electron radiation damage effect.

George Martin: I was considering much lower levels of ionization; for instance, our Los Angeles smog here.

David Kaelble: Well, I'll tell you that, of course, is a subject of great concern and much study, even today.

Here again, protective mechanisms are obtained by molecular processes. In automobile tires, the tires are modified with a paraffin filler which actually comes out of solution and migrates to the surface to form a coherent film that replenishes itself throughout the life of the tire. Of course that is an old trick and it stabilizes the system, that is, crack growth due to ozone or combined ozone and photolytic effects.


Arthur Jonath (Lockheed Research): Dave, have you gone into studying the nature of the defect in the polymer in which the water condensation occurs, the origin of the defect, the actual molecular nature of the defect?

David Kaelble: Well, in epoxies, the only thing we have, of course, is the inference from molecular structure. One can do a sort of a cohesive energy density mapping of the molecular structure and you find that the regions or molecular sites which most closely correlate with the energy density properties of water will be the most highly interactive through physical solution. We haven't done spectroscopic studies. That is the simple answer, I guess, to that question.

Arthur Jonath: To add to that question, I guess what I am asking on a molecular level, are there sites that one could look at as being more polar in nature that would be more associated with defects, that would be more absorbent to the water?

David Kaelble: Yes, very definitely. I would say those beta hydroxyl sites on the amide crosslink and certainly ether oxygen sites on the homopolymer crosslinks would be the sites that one would look at spectroscopically and expect to find the effect of water. That is, if you could use I.R. shifts or if you could use proton N.M.R., you might expect to see modification of degrees of freedom in that region.

Robb Thomson: Other questions? We will break for lunch then.