ENVIRONMENTAL EFFECTS ON POLYMERIC

MATRIX COMPOSITES

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SUMMARY

Current epoxy resins utilized in high performance structural composites absorb moisture from high humidity environments. Such moisture absorption causes plasticization of the resin to occur with concurrent swelling and lowering of the glass transition temperature. Similar effects are observed in composites. Data are presented showing the effects of absorbed moisture on Hercules AS/3501-5 graphite/epoxy composites. Prediction of moisture content and distribution in composites, along with reduction in mechanical properties, are discussed.

INTRODUCTION

The glass transition temperature, T_g, of a polymer is defined as the temperature above which the polymer is soft and below which it is hard. For epoxy resins the T_g is the temperature at which the polymer goes from a glassy solid to a rubbery solid. From a practical standpoint it is more appropriate to discuss a glass transition temperature region rather than a single glass transition temperature, as the change from a hard polymeric material to a soft material takes place over a temperature range. The concept of a T_g is for convenience and refers to the temperature at which there is a very rapid change in physical properties. As a result, there is no precise T_g.

It is well recognized (ref. 1) that the T_g of a polymer can be lowered by mixing with it a miscible liquid (diluent) that has a lower glass transition temperature than the polymer. This process is referred to as plasticization. Thus, moisture acts as a diluent in current resins being utilized in high performance structural composites, resulting in a lowering of the T_g. There are indications (ref. 2) that similar effects occur in epoxy matrix composites. Data (ref. 2) also indicates that the lowering of the T_g in both neat resins and

derived composites can be estimated from the Kelley-Bueche plasticization theory (ref. 3). Thus, absorbed moisture reduces the temperature range over which matrix dominated composite properties remain stable. From a practical standpoint, change of failure mode due to plasticization is of primary concern.

In the present paper, the prediction of moisture content in conjunction with laboratory characterization is discussed in detail. In addition, data is presented which shows the effect of absorbed moisture on the flexure strength of unidirectional Hercules AS/3501-5 graphite/epoxy composites. The flexure test is an excellent example of absorbed moisture inducing a change in failure mode.

PREDICTION OF MOISTURE DIFFUSION

Fick's Law

It has been shown (ref. 4) that moisture diffusion in laminated composites can be predicted by Fick's second law. For diffusion through the thickness of an infinite plate, the diffusion equation is given by

$$\frac{\partial m}{\partial t} = D_z \frac{\partial^2 m}{\partial z^2} \tag{1}$$

where m is the percent moisture gain per unit thickness, D_z is the diffusivity through the thickness, t denotes time, and z is the thickness coordinate. Consider the following boundary and initial conditions for a plate of thickness h

$$m(z, 0) = m_i = \text{constant} \tag{2}$$

$$m(0, t) = m(h, t) = m_1 = \text{constant} \tag{3}$$

where m_i is the initial moisture distribution in the material, and m_1 is the surface moisture concentration, which is a function of the relative humidity. A solution to equation (1) which satisfies the conditions of equations (2) and (3) can be obtained by classical separation of variables with the result

$$m(z, t) = m_1 - \frac{4}{\pi}(m_1 - m_i) \sum_{n=1}^{\infty} \frac{1}{(2n-1)}$$

$$x \left[\sin \frac{(2n-1)\pi z}{h} \exp \left[-(2n-1)^2 \pi^2 t* \right] \right] \tag{4}$$

where

$$t* = \frac{D_z t}{h^2} \tag{5}$$

The total weight gain of moisture in the plate is given by

$$M = \int_0^h m \, dz \tag{6}$$

Integration of equation (4) yields

$$M(t) = M_1 - \frac{8}{\pi^2}(M_1 - M_i) \sum_{n=1}^{\infty} \frac{\exp\left[-(2n-1)^2 \pi^2 t*\right]}{(2n-1)^2} \tag{7}$$

Application to Characterization

Consider an experiment where an initially dry specimen is exposed to a constant environment (temperature and humidity) for a given period of time t_1. It is then put in a dry environment and the temperature ramped at a constant rate to a given level at time t_2. A test is then performed on the specimen over some period of time. Such a procedure is used during laboratory characterization of moisture effects on the mechanical behavior of laminates. It is often desirable to control both the moisture content and distribution during such a characterization. Equations (4) and (7) can be modified for such a purpose.

For the interval $0 \leq t \leq t_1$, equations (4) and (7) can be used directly with $m_i = M_i = 0$ and $D_z = D_z(T_1)$, where T_1 denotes the temperature during this time interval. It should be noted that the diffusivity is a function of temperature. In the interval $t_1 \leq t \leq t_2$ the temperature will be varying with time and as a result, D_z will vary with time. This can be accounted for by defining $t*$ in the following manner (ref. 5)

$$t^* = \frac{1}{h^2} \int_{t_1}^{t} D_z(s) \, ds \tag{8}$$

Note that in the derivation of equation (8) it is assumed that the temperature gradient has negligible effect on diffusivity, as the heat diffusivity is several orders of magnitude greater than moisture diffusivity. For this interval the initial distribution can be obtained from equation (4), with the result

$$m_i(z) = m_1 \left[1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \sin \frac{(2n-1)\pi z}{h} \right.$$
$$\left. \times \exp \left[-(2n-1)^2 \pi^2 t_1^* \right] \right] \tag{9}$$

where

$$t_1^* = \frac{D_z(T_1)t_1}{h^2} \tag{10}$$

In addition,

$$m(0, t) = m(h, t) = 0 \tag{11}$$

$$D_z = D_z(T) = D_z(t) \tag{12}$$

If equation (9) is expressed as a Fourier series, then the moisture profile for this time interval becomes

$$m(z, t) = \frac{4}{\pi} m_1 \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \left\{ 1 \right.$$
$$\left. - \exp \left[-(2n-1)^2 \pi^2 t_1^* \right] \right\} \sin \frac{(2n-1)\pi z}{h} \tag{13}$$
$$\times \exp \left[\frac{-(2n-1)^2 \pi^2}{h^2} \int_{t_1}^{t} D_z(s) \, ds \right]$$

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$$M(t) = \frac{8M_1}{\pi^2} \sum_{n=1}^{\infty} \frac{1 - \exp\left[-(2n-1)^2 \pi^2 t_1^*\right]}{(2n-1)^2}$$

$$\times \exp\left[\frac{-(2n-1)^2 \pi^2}{h^2} \int_{t_1}^{t} D_z(s)\,ds\right]$$

(14)

For the interval $t_2 \leqq t$

$$m_i(z) = \frac{4m_1}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \left\{1 - \exp\left[-(2n-1)^2 \pi^2 t_1^*\right]\right\}$$

(15)

$$\times \exp\left[-(2n-1)^2 \pi^2 t_2^*\right] \sin\frac{(2n-1)\pi z}{h}$$

where

$$t_2^* = \frac{1}{h^2} \int_{t_1}^{t_2} D_z(s)\,ds$$

(16)

The boundary conditions are those of equation (11). Since equation (14) is in the form of a Fourier series, the moisture profile for this time interval becomes

$$m(z,t) = \frac{4m_1}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n-1)} \left\{1\right.$$

$$- \exp\left[-(2n-1)^2 \pi^2 t_1^*\right]\right\} \sin\frac{(2n-1)\pi z}{h}$$

(17)

$$\times \exp\left[-(2n-1)^2 \pi^2 (t_2^* + \bar{t})\right]$$

and the total moisture gain is given

$$M(t) = \frac{8M_1}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \left\{1\right.$$

$$- \exp\left[-(2n-1)^2 {}^2 t_1^*\right] \Big\} \ \exp\left[-(2n-1)^2 {}^2 (t_2^* + \bar{t})\right] \tag{18}$$

where

$$\bar{t} = \frac{D_z(T_2)}{h^2} (t - t_2) \tag{19}$$

CHANGE IN FAILURE MODES

Filament Dominated Laminates

In most engineering usage of fiber reinforced composites, laminate stacking geometry is chosen such that stiffness and strength are controlled by fiber modulus and strength, respectively. Thus, some matrix softening can be accommodated in such applications without serious consequences. If considerable matrix softening occurs, however, the ability of the resin to support the fiber is severely reduced, along with the ability to transfer load through the matrix to the fibers. The result is a change in failure mode from filament dominated to matrix dominated. The classical example is that of unidirectional compression, where a significant loss in matrix stiffness leads to local instabilities and a reduction in compression strength. Thus, any loss in resin T_g due to moisture absorption can lead to a reduction in the useful temperature range of the composite laminate.

Flexure Strength

Unidirectional flexure tests are commonly used for quality control, and 0 degree flex strength is considered to be a filament dominated property. For state-of-the-art high-performance epoxy resins, 0 degree dry flex strength is relatively insensitive to temperatures below 300°F. With increasing moisture content, however, measurable strength degradation can occur at temperatures considerably below 300°F. This is illustrated in Table I, where 0 degree flex strengths are shown for Hercules AS/3501-5 graphite/epoxy composites. These results were obtained on eight-ply composites subjected to a standard four-point bend test with a 32:1 span-to-depth ratio. A cursory examination of these results reveals that a severe loss in 0 degree flex strength occurs at a temperature as low as 200°F after exposure to equilibrium moisture content in a 95% relative humidity environment. The T_g of this material under these conditions has been shown to be approximately 210°F (ref. 2).

Under dry conditions the shear strength of the matrix, for temperatures less than 300°F, is high enough to prevent interlaminar shear failure and assure that the flex strength is governed by fiber breakage. As moisture induces matrix softening below 300°F, the high temperature flex strength becomes dominated by interlaminar shear yielding. This conclusion can be supported by examining failed specimens and noting that the 300°F wet composites did not display fiber breakage as the mode of failure, but were permanently deformed near the load noses where the shear stress was largest. Furthermore, the load deflection curves for these cases produced a classic example of an elastic-plastic material. For conditions under which brittle failure was induced, fiber breakage occured between the loading pins where the interlaminar shear stress vanishes. Thus, the 0 degree flex strength is another classic example of a change in failure mode induced by matrix softening.

Interlaminar shear stress-strain behavior relative to the 0 degree flex test is illustrated in figure 1. These 0 degree shear results were obtained from a ± 45 degree tensile test as described by Rosen (ref. 6). The entire stress-strain curve is not shown, but is terminated at the stress level where the maximum interlaminar shear stress occurs in the 0 degree flex test. This value can be calculated from classical beam theory with the following result for quarter-point loading.

$$\tau_{max} = \frac{\sigma_f}{S} \tag{20}$$

where τ_{max} is the maximum value of the interlaminar stress obtained during the flex test, σ_f is the flex strength, and S is the span-to-depth ratio of the test specimen. For the high temperature tests considerable non-linear shear stress-strain behavior is observed. For the wet tests, the non-linear behavior occurs at very low stress levels.

To further illustrate the change in failure mode, 0 degree flex strength is plotted on a log scale in figure 2 as a function of temperature for wet and dry conditions. This plot resembles typical log modulus versus temperature curves found in classical viscoelastic polymeric materials. Thus, the flex test may be useful in assessing T_g for composites or for assessing the useful temperature range of the material for various moisture contents.

CONCLUDING REMARKS

It has been shown that a solution to Fick's law can be obtained which is relavent to laboratory characterization of composite materials containing moisture. This solution provides a detailed moisture profile in addition to determining total weight gain due to moisture absorption. Data presented also indicates that the widely utilized unidirectional flexure test can be a valuable tool in assessing the useful temperature range of composite laminate: for various moisture contents.

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TABLE I.- UNIDIRECTIONAL FLEX STRENGTH, AS/3501-5 GRAPHITE/EPOXY

TEMPERATURE	σ_f(DRY)	σ_f(WET-1.1%)*	σ_f(WET-1.7%)**
RT	259 KSI	265 KSI	252 KSI
200° F	259 KSI	210 KSI	180 KSI
250° F	242 KSI	166 KSI	135 KSI
300° F	233 KSI	125 KSI	90 KSI

* EXPOSED TO EQUILIBRIUM AT 75% RELATIVE HUMIDITY AND 160°F, % WT. GAIN = 1.1%.

** EXPOSED TO EQUILIBRIUM AT 95% RELATIVE HUMIDITY AND 160°F, % WT. GAIN = 1.7%.
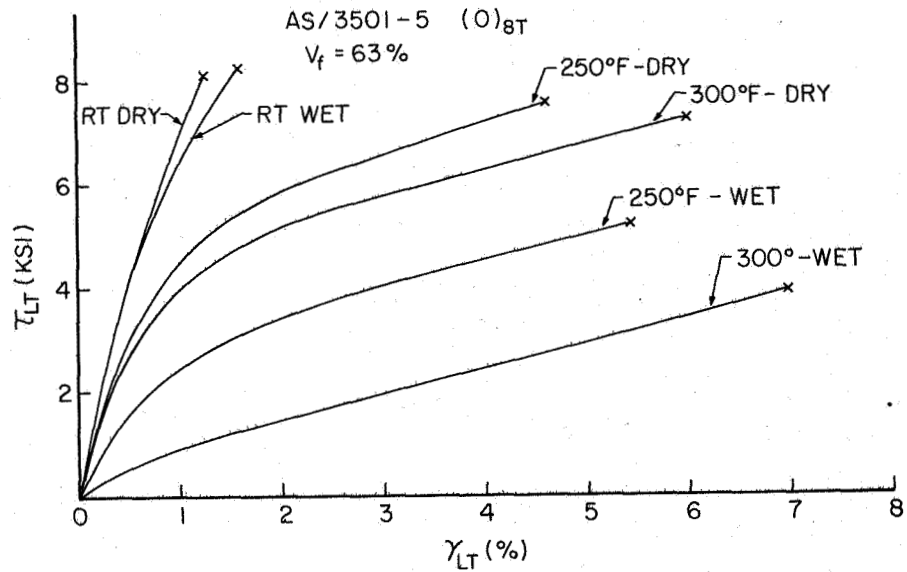
Figure 1.- Shear stress-strain curves for unidirectional
composites. Wet = 1.1% equilibrium weight gain at
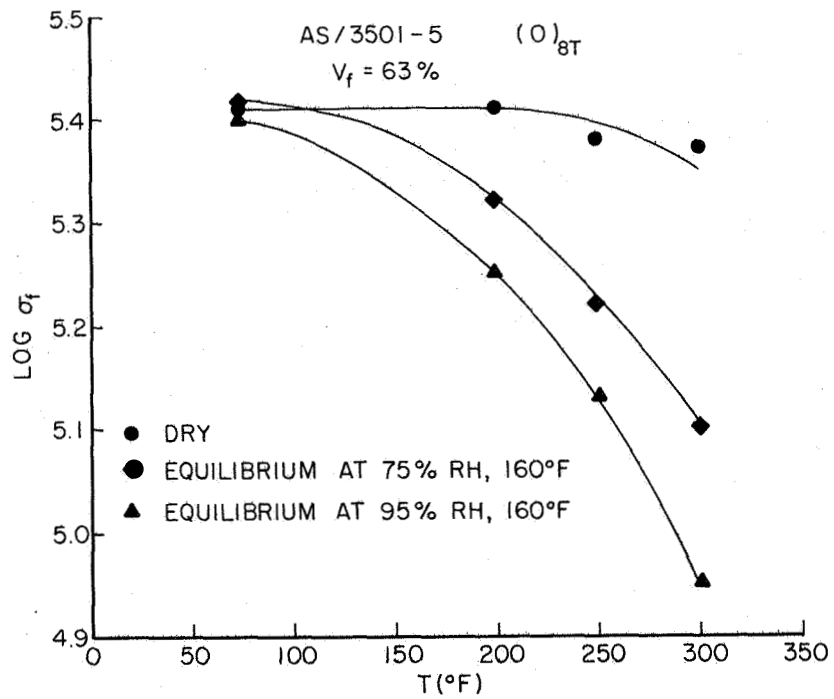75% relative humidity and 160°F.

Figure 2.- Unidirectional flex strength as a
function of temperature.