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Moisture and viscoelastic effects on the dimensional stability of composites

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ABSTRACT

Dimensional stability is the time dependent strain response to mechanical, thermal, chemical or physical loads, whether internal or externally applied. This paper presents recent work on moisture induced strains and viscoelastic behavior of polymer matrix composite materials. Topics covered include determination of lamina coefficients of moisture expansion (CME) or β_{11} and β_{22}, and the microyield strength (MYS). It is shown that the creep recovery part of a MYS test can be a sensitive indicator of moisture level and/or matrix damage.

1. INTRODUCTION

Carbon fiber reinforced polymer matrix composite materials (CFRP) are primary candidates for many light weight, stiff and dimensionally stable components and structures. The high stiffness and low thermal expansion coefficients of carbon fibers, for example, permit design of their laminates to achieve near-zero in-plane coefficients of both thermal (CTE) and moisture (CME) expansion. In practice, it is difficult to achieve near-zero CME values because of relatively slow and anisotropic mass transfer, adsorption effects, and in the measurement of moisture distribution. Moisture and time dependent mechanical behavior such as creep and recovery or relaxation effects are interrelated for CFRP, due to the viscoelastic nature of the matrices involved. Moisture plasticizes most resins or polymers, and thus a description of viscoelastic behavior requires specification of the moisture content, gradients and/or changes.

A design parameter for precision metallic components has long been the microyield strength (MYS), or the stress value corresponding to a residual or permanent strain of 10^{-6} in/in after repeated short term loadings to successively higher stress levels. Due to the viscoelastic nature of polymers, however, it is difficult to define a "permanent" deformation. The MYS has meaning for CFRP if the loading and recovery times are specified. This reduces the study of MYS of composites to precise characterization of short term creep/recovery tests. Thus strain is described in terms of viscoelastic (linear or non-linear) parameters along with ply orientations. The same analytical framework is then modified to account for changes in moisture content and even permanent damage or degradation mechanisms, such as matrix microcracking (a possible result of extensive thermal cycling). Thus we see that the study of the dimensional stability of composites is an interdisciplinary subject, with predictive models needed to account for several simultaneous effects.

2. MOISTURE EFFECTS

2.1 Background

A major requirement in design for dimensional stability is determination of β_{11} and β_{22}, the ply input parameters for standard classical laminate plate (CLP) theory computer codes. Handbook values[1] often give β_{11}, the fiber direction CME, a value of zero. For precision applications, however, this will lead to errors, as the true value is typically closer to 50×10^{-6}/% moisture.[2] For example, a unidirectionally reinforced high stiffness graphite epoxy composite will shrink about 35 microinches per inch in the fiber direction during dryout after equilibration at about 50% relative humidity. In the transverse direction, the corresponding number is closer to $3\text{-}4 \times 10^{-3}$/% M. It should be noted that this strain figure is higher than any that might be expected from most thermal excursions for CFRP. The relative lack of specific data relate primarily to measurement and data analysis difficulties. A successful approach is described as follows.

2.2 Measurement of CME - theoretical approach

Techniques for CME measurements have received limited attention.[3,4,5] The relative merits of strain gages, transducers and interferometers were discussed.[4] We recall that the CME is the strain corresponding to a unit moisture content change at constant temperature. This applies theoretically only at infinite time, since the mode of moisture content change is diffusion limited. A good approximation to the exact equation for fractional (Fickian) change in moisture content (M) of a flat plate exposed on two sides to a new moisture environment may be given by:[6]

$$G = [M - M_0]/[M_\infty - M_0] = 1 - \exp\{-7.3\,(Dt/h^2)^{0.75}\} \qquad (1)$$

If $D = 1.8 \times 10^{-7}$ mm^2/s at an elevated temperature, such as 150°F and the plate thickness is 1.524 mm, then $G = 0.71$ in about 1.2×10^6 s. This means that 71% of the total expected weight (and approximately the strain) change will occur in two weeks. If the sample is at a uniform, evenly distributed, moisture content at the beginning of this period (e.g., completely dry) then one can extrapolate weight (and corresponding dimensional) changes to infinite time ($G = 1$) during exposure to a constant M_∞. The ratio of $\Delta L/L_0$ to ΔM at infinite time is the true CME. We have found that if diffusion is purely Fickian, and not influenced by pores, surfaces, etc., then a plot of either strain or moisture content against the lumped parameter G is generally a straight line.

Data can be readily obtained for $0.2 < G < 0.7$. The lower limit of 0.2 varies according to the time needed to equilibrate the sample temperature and/or the measurement system. If the absorption or desorption measurement commences with a non-uniform or unknown moisture distribution the true CME can still be obtained by carrying out several measurements under constant conditions (M_∞) but for various time periods, and extrapolating the results to infinite time. The appropriate value of the diffusivity D can be found from the initial slope of M versus $t^{0.5}$ curve.[6]

2.3 Measurement of CME

A convenient and relatively inexpensive strain transducer is the linear variable differential transducer (LVDT) with at least a 30 V/inch response. With a voltage sensitivity of 0.1 mv, and a 3 inch sample, we obtain a strain sensitivity of 10^{-6} in/in. This is sufficient for β_{11} measurements on unidirectional GFRP samples and, with care, also for near-zero CME laminates.

In practice, several LVDTs are mounted on low expansion ceramic blocks (such as Schott "Zerodur", Corning "ULE" glass) as shown in Figure 1. A fused quartz rod may be attached to the LVDT core rods using a suitable adhesive, which also serves to mount the LVDT to minimize the effects of periodic temperature fluctuations. Sample edges must be sealed, e.g., with Airtech "Flashbreaker" silicone coated polyester tape, because the diffusivity in fiber directions is an order of magnitude greater than the plate through-thickness value. A Zerodur reference block is measured along with the CRFP test panels to record possible discontinuities from vibrations, shocks, etc. The entire assembly is mounted inside a temperature and humidity controlled oven and left untouched for two or more weeks. Temperatures well below the (moisture reduced) glass transition temperatures[1] should be used; typically 150°F is suitable for most epoxy resins cured at 250°F or above. Humidity can be controlled by various salt solutions (ASTM Standard E104-51-71). Figure 2 gives data for 4-inch Zerodur samples, showing the stability of such a system. The corresponding weight changes are obtained from identical samples placed in an identical temperature/humidity oven. This oven is opened once or twice a day, the samples removed, cooled in a few minutes and weighed on a microbalance and replaced. The first oven (with the LVDTs) also contains witness samples which are weighed at the beginning and end of the test to corroborate the weight versus time curve at two points. Temperature (thermocouples), humidity (electronic hygrometers) and LVDT voltages are recorded continuously with a computer controlled data acquisition station.

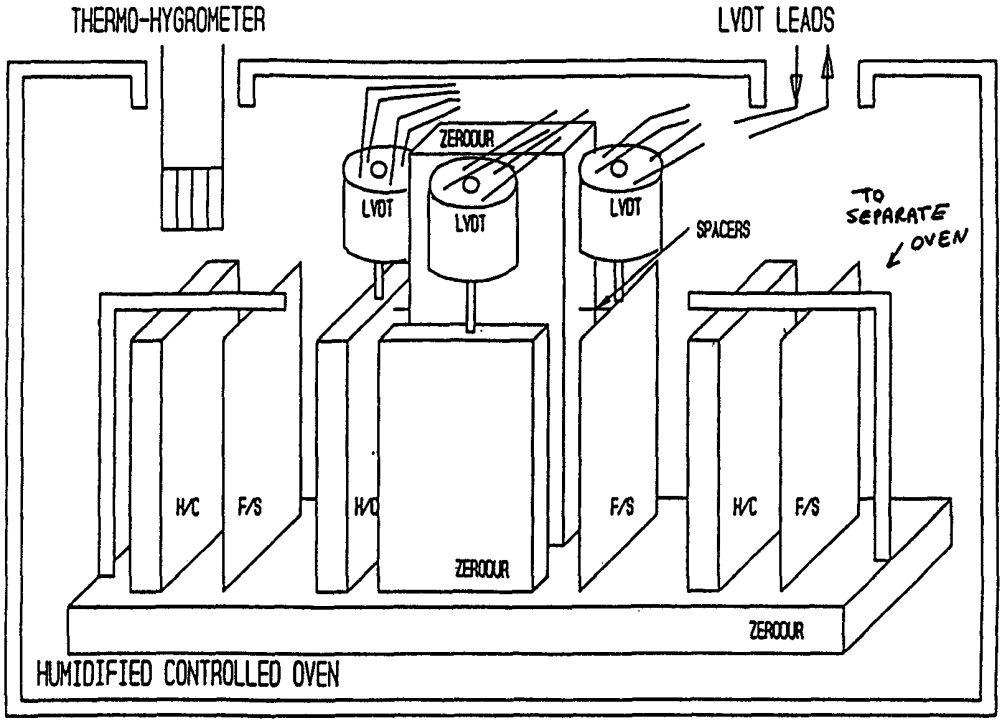

Figure 1. CME test rig showing LVDTs mounted on Schott Zerodur supports.

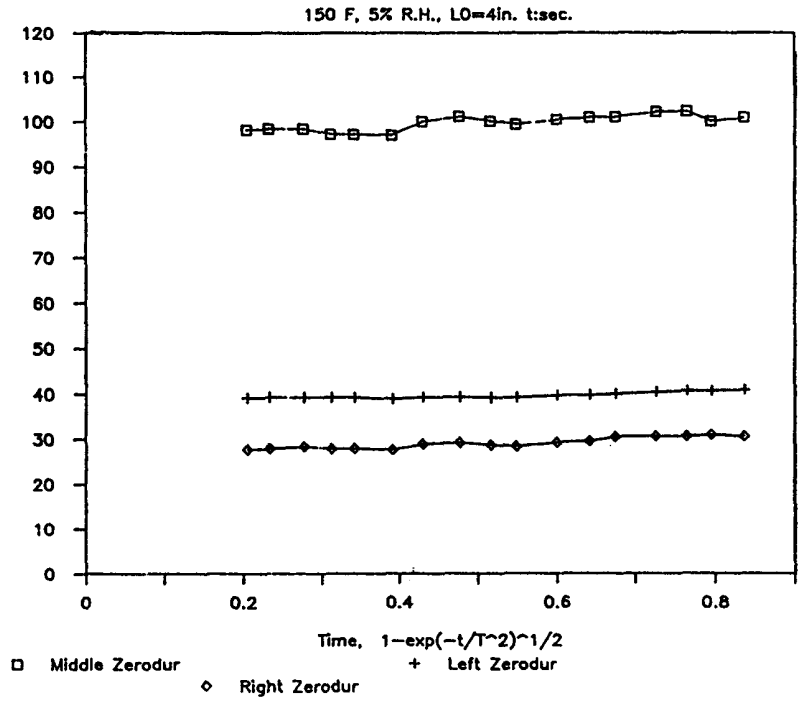

Figure 2. Microstrain ($\Delta L/L_o$) versus a time parameter. Typical 24 hour test results with the apparatus of Figure 1 on Zerodur test samples showing system and different LVDT stabilities.

2.4 Typical CME results

Results for 0.028 inch thick Hercules UHM/3501-6 plates with a $(0,\pm 45,90)_{3s}$ layup are shown in Figures 3 and 4. Two volume fractions of fibers are considered, with the third case including an aluminum honeycomb core. It is seen that there is an approximate straight line relationship for both weight and strain versus G at least up to G = 0.9. As expected, the lowest volume fraction fibers gives the highest weight and strain changes. The honeycomb core (plus adhesive layer) tends to reduce the strain but not the weight change, resulting in a lower CME value.

2.5 Ply orientation effects of absorption rates

The apparent change in slope of a strain or weight change (Figures 3 and 4) at longer times has been analyzed.[7]. Predictions suggest that changes in the slopes of these curves should be expected for thin wall laminates, due to the effects of ply orientation. Since there will always be a moisture gradient through the laminate during ab- or desorption, the orientation of the outer plies will dominate the strains (but will not affect the weight changes). This is shown in Figure 5, where a 0/90/90/0 layup is compared with a 90/0/0/90 layup of T300/5208 material during absorption. We see that extrapolations to $t = \infty$ (G = 1) would lead to different CME predictions for the two cases. However, this effect diminishes for stiffer fibers and with thicker laminates.[7]. Nevertheless, the change in slope at long times is still seen, suggesting modification of the model at nearly saturated conditions.

Figure 6, plotted with a CLP code and typical β_{11} and β_{22} values, reminds us that zero CME can be achieved, at least in one direction. It also points out that there is always a relatively high through-thickness CME which often affects the dimensional stability of end attachments to CFRP structures.

2.6 Additional moisture induced deformations

Strain measurements during desorption tend to give different results when carried out in a) dry air, b) flowing dry air or inert gas and c) vacuum. These data have been usually obtained by different techniques; e.g., a laser interferometer measures desorption in vacuum. A systematic study which accounts for boundary layer effects using the same technique is lacking. Furthermore, absorption and desorption curves should not be symmetrical because of the altered internal stress states involved. There is evidence that the diffusivity is stress dependent.[4] Absorption on AS/3501-5 composites was found to be initially slower than desorption.[8] The explanation was that the boundary layer is in compression during absorption but in tension during desorption. We have also found that samples stored in vacuum adsorb moisture during mirror attachment and setup in preparation for CTE testing in vacuum with a laser interferometer. This adsorbed moisture absorbs prior to heating, and then desorbs at temperature, altering the shape of the thermal strain versus temperature curve, at least on the first heating cycle.

Postcuring has been found to increase M_∞ and to some extent also the diffusivity. Resins which have not been post cured do not completely desorb during dryout. At high temperatures and high moisture contents, Fickian diffusion models are no longer applicable, even without the presence of surfaces, voids, etc. Transition regions still need to be defined.

3. VISCOELASTIC EFFECTS

3.1 Introduction

The viscoelastic nature of matrices in CFRP affects their dimensional stability in many ways, but particularly their creep and recovery behavior. The time dependent stress response is a combination of elastic behavior, where stress is proportional to strain (at a given strain rate) and viscous flow (as in an incompressible (Newtonian) fluid where the strain rate is proportional to the stress. The creep strain is defined as the time-dependent permanent strain under a constant load (but not necessarily a constant stress). In principle, a viscoelastic solid reaches an equilibrium deformation during

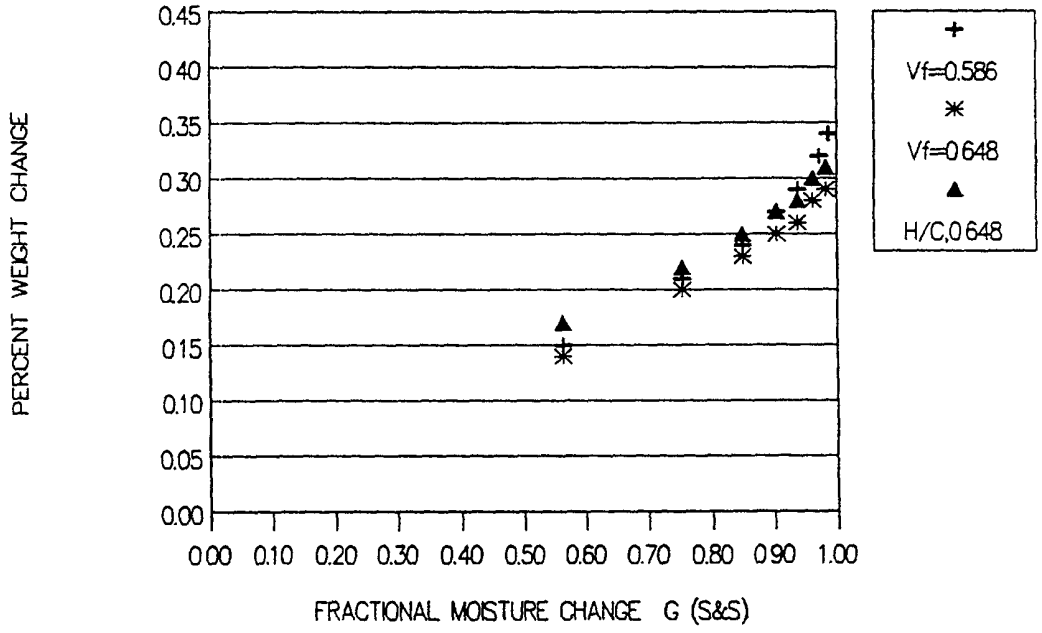

Figure 3. Percent weight change versus a time parameter G (Eq.(1)) for three samples of Hercules UHM/3501-6 $(0,\pm 45,90)_{3s}$ facesheets with different fiber volume fractions and with an Al honeycomb core.

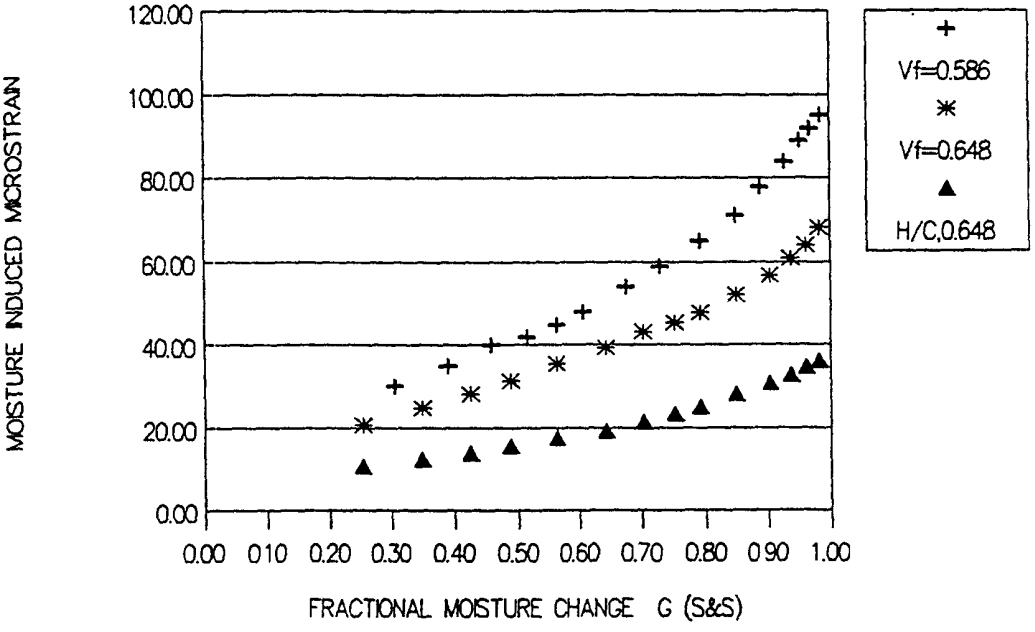

Figure 4. Microstrain versus a time parameter G (Eq. (1)) for samples in Figure 3.

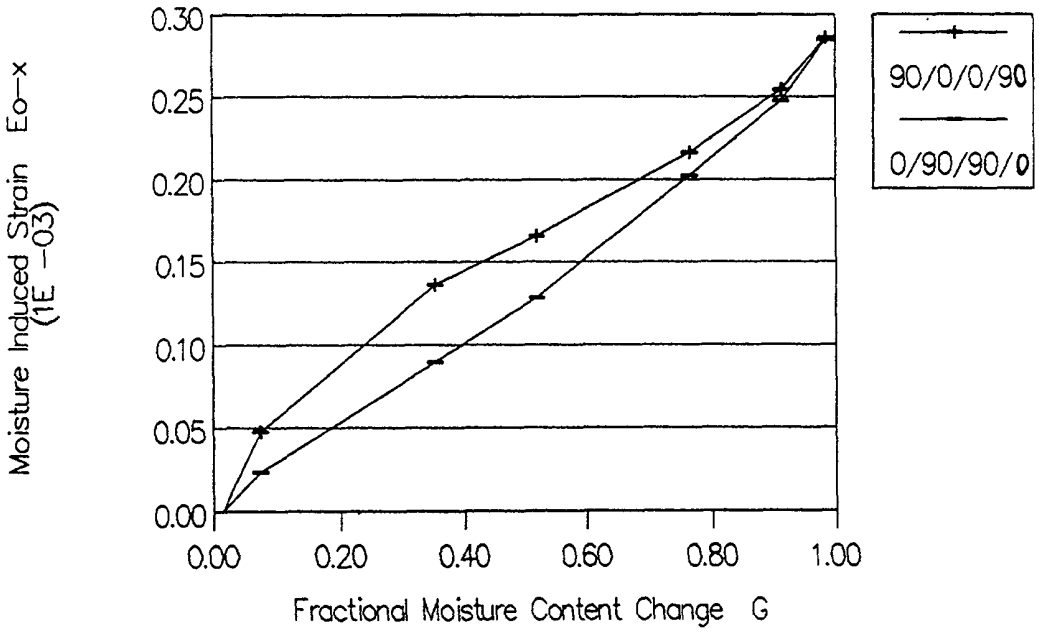

Figure 5. Predicted moisture induced in-plane strain ($\times 10^{-3}$) versus a time parameter G (Eq. (1)) for four-ply layups of T300/5208 laminates.

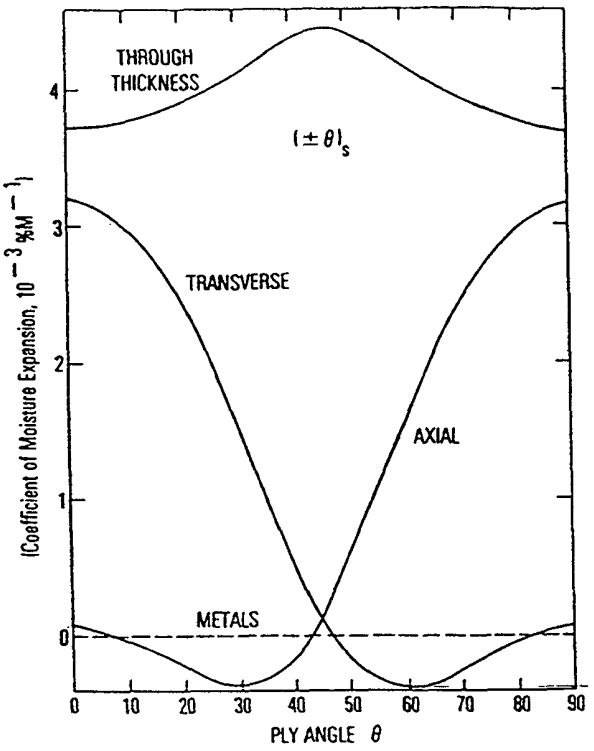

Figure 6. Predicted variation of CME with ply angle for angle-ply layups of GY70/934 laminates.

creep (ultimately no viscous flow or a zero creep rate). Viscoelastic behavior is either linear or non-linear. The former implies that the ratio of stress to strain is only a function of time, and not of stress or strain magnitude. Non-linear behavior may be expected at high temperatures and high moisture levels and in directions perpendicular to fibers. Analytically, additional terms for stress (or strain) dependence must be added to account for non-linear behavior.[9]

A design parameter commonly used for precision components is the microyield strength (MYS). In CFRP, it can be used to identify changes in dimensional response to loads caused by environmental factors such as moisture absorption and internal damage, such as thermal cycling induced microcracking.

3.2 The microyield strength of composites

The microyield strength is defined as the stress level needed to induce a permanent strain of 10^{-6} after repeated short-term loadings to successively higher stress levels. For metals which undergo plastic deformation, the MYS is both determined and used in a straight-forward manner. With viscoelastic behavior, however, the deformations after unloading are time dependent and exhibit an effective memory of the time and load level before. Early work on the MYS of composites showed that there is incomplete recovery after creep with laminates, but that honeycomb structures tend towards more complete strain recovery.[10] The sensitivity of the MYS to microcracking,[11,12] irradiation[13] and moisture[14] have been noted. The original definition of the MYS may be retained provided we specify both loading and unloading times, and regard each loading cycle as a short term creep curve as illustrated in Figure 7.[12]

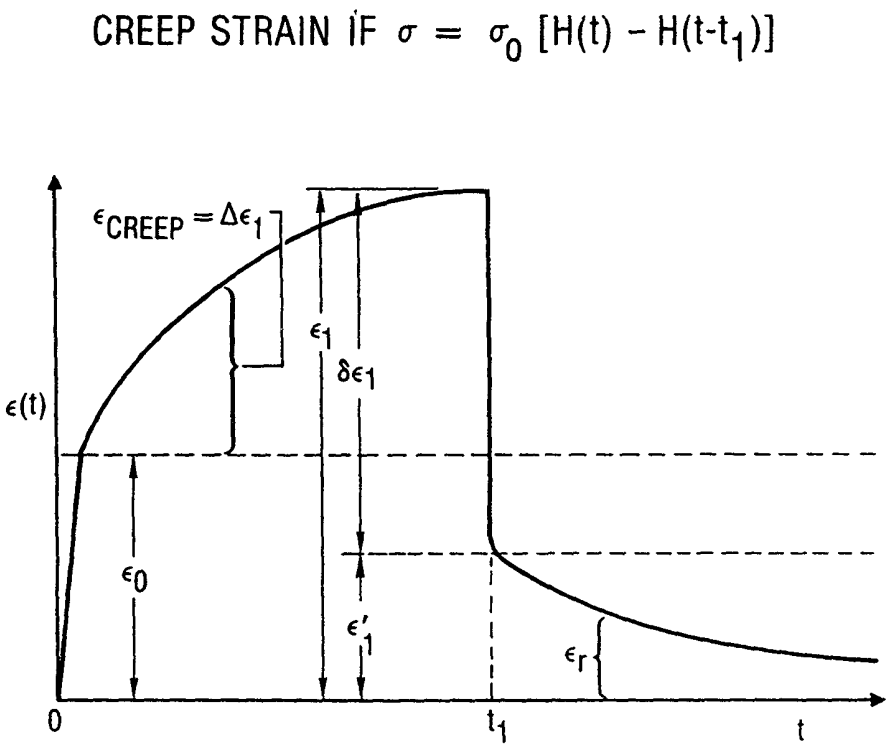

Figure 7. Typical creep response curve to a step function loading cycle.

3.3 Creep recovery

The generalized equation for non-linear creep is given as:

$$e(t) = g_o S_o \sigma + g_1 \int_o^t \Delta S(\psi - \psi') (dg_2\sigma/d\tau)\, d\tau \quad (2)$$

where S_o and $\Delta S(\psi - \psi')$ are the initial and transient components of the creep compliance and ψ, ψ' are reduced times, or time divided by a shift parameter.[15] The viscoelastic non-linearizing parameters such as g_o, g_1, g_2 and the time shift factor "a" are functions of stress, temperature and also ply orientation, but it is not clear that their use can predict the onset or effects of matrix cracking. For the response to stress (σ) alone (with different composite systems) g_2 can either decrease or increase or both. g_2 has also been expressed empirically as a hyperbolic sine function of stress.[16] The expression derived from Eq. (2) for creep recovery is;

$$e_r = g_2 C \sigma \left[\psi^n - (\psi - \psi_1)^n\right] \quad (3)$$

where C and n come from the general power law expression for the transient component of the linear viscoelastic creep compliance, namely $\Delta S(\psi) = C \psi^n$. Studies on moisture and damage effects have shown that it is difficult to attribute any particular mechanism to the effect of these non-linearizing parameters on recovery times.[13]

A method for the prediction of recovery strains ($e_r(t)$) as a function of creep loads (N = load/unit width), load time (t_1), unloading times ($t-t_1$), ply orientations and general laminae properties was recently developed.[12] It is based initially on linear viscoelasticity of the matrix and applies at low loads, low moisture contents and minor degrees of internal damage. It expresses creep and recovery in terms of time dependent laminate stiffnesses (A(t)). Studies of the effects of moisture and matrix microcracking induced by thermal cycling[13] lead to a generalized creep recovery strain relation;

$$e_r(t) = Q N m \left[(1/A(t) - (1/A(t - t_1)\right] \exp\left\{\left(b_c' + b_o'\right) N\right\} \quad (4)$$

where Q is related to the moisture content and the term in the brackets accounts for the decreasing recovery strain with time after t_1. m is a lumped stiffness parameter, essentially independent of time.[12] The exponential term accounts for the stress dependent effect of microcracking. b_c' represents the effect of internal damage and b_o' represents the non-linearizing effect of high stresses. This expression is similar to that of Eq. (3) in terms of g_2 being equivalent to Q, but adds a specific damage parameter. Consequently, Eq. (4) accounts for the general change in e_r with stress after altered moisture and/or damage as shown in Figure 8. These data were obtained from compression tests of P75/934 tubes, in this case $(\pm 45)_s$ with t_1 = 45 s and t = 90 s. The control samples were as-fabricated and stabilized at 50% R.H., while the high moisture sample was stabilized at 150°F and 80% R.H. This is equivalent to an increase of 0.7 to 0.9 wt% moisture. Matrix microcracking should occur by cooling below about -13°F.[17]. Ten cycles of 300 s immersion in liquid nitrogen were used to induce microcracking. It is seen that additional moisture raises the entire level of recovery strain at all stresses (the Q term). The effect of microcracking is apparent only at the higher stress levels.

3.4 Viscoelasticity and dimensional stability

The viscoelastic nature of CFRP further determines the nature of residual stresses. For example, changes in the original (high temperature) cure cycle can take advantage of viscoelastic recovery effects to minimize the residual stresses.[18] However, this makes it difficult to know the stress free temperature, which, for purposes of predicting thermally induced microcracking, may need to be determined independently. Once known, however, it is possible to use laminate theory to determine the temperature at which the transverse stresses in individual plies reach their ultimate strengths, thus initiating microcracking.[17].

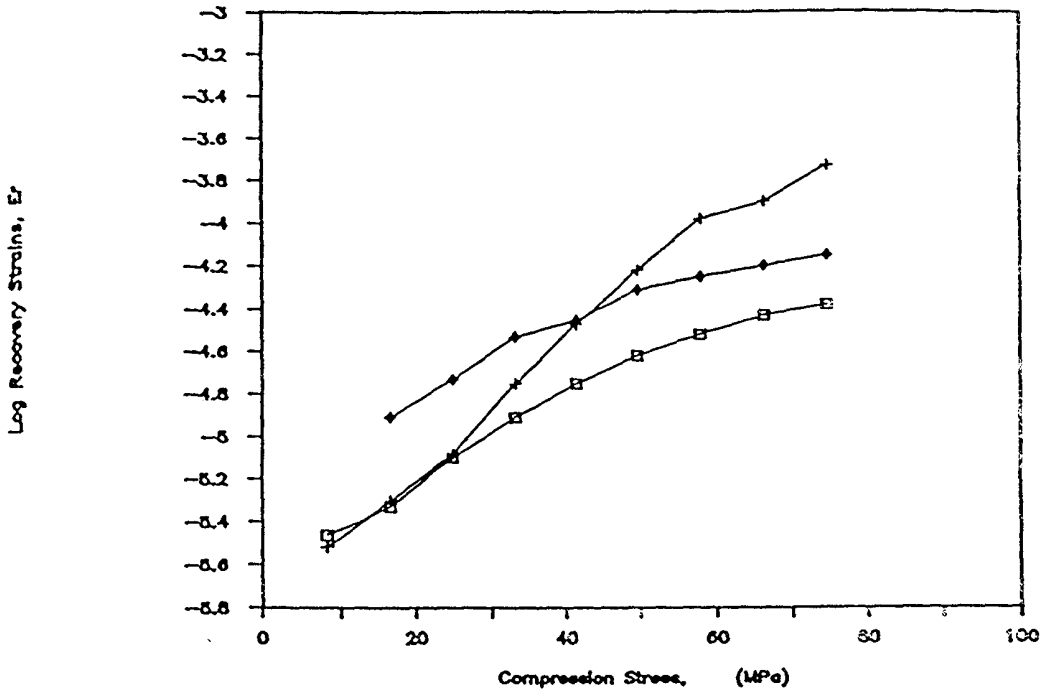

Figure 8. Log recovery strain at 45 s after unloading versus applied (compressive) stress after successive 45 s loadings in the 0° direction for P75/934 four-ply laminate tubes. Laminate orientation is $(\pm 45)_s$. o = as-fabricated, + = thermally cycled and * = added moisture.

4. CONCLUSIONS

It has been shown that the interactions of applied stress, moisture, matrix damage and the viscoelastic nature of the CFRP requires quantitative assessment of both the magnitude of definitive parameters and their time dependence. Thus the dimensional stability of CFRP has both first and second order dependence on moisture. Initially the normal time dependent stress response of a viscoelastic material depends on the moisture content, and secondly the moisture content is itself time dependent, due to the finite diffusion rates. The effects of internal damage can be estimated from stiffness changes and from altered creep recovery behavior.

5. REFERENCES

1. G.S. Springer, "Environmental Effects," pp. 17-36 in *Reference Book for Composites Technology - 2*, S.M. Lee (Editor), Technomic Publishing Co., Inc., 1989.
2. S.A. Eselun, H.D. Neubert and E.G. Wolff, "Microcracking Effects on Dimensional Stability," *24th National SAMPE Symposium*, pp. 1299-1309, May 1979.
3. E.G. Wolff and S.A. Eselun, "The Coefficient of Moisture Expansion - Its Measurement and Use," Conf. on *Advanced Composites - Special Topics* Technology Conferences, El Segundo, CA, December 1979.
4. E.G. Wolff, "Polymer Matrix Composites: Moisture Effects and Dimensional Stability," *Composites Encyclopedia, Vol. 4*, S.M. Lee (Editor), VCH Publishers, 1990/91.
5. D.S. Cairns and D.F. Adams, "Moisture and Thermal Expansion of Composite Materials," *U. Wyoming Report UWME-101-104-1*, November 1981.

6. C.H. Shen and G.S. Springer, "Moisture Absorption and Desorption of Composite Materials," *J. Comp. Mat.*, Vol. 10, p. 2, 1976.
7. E.G. Wolff, "Effect of Ply Orientation on Moisture Expansion," submitted to *Composites Science & Technology*, 1990.
8. H.T. Hahn and R.Y. Kim, "Residual Stresses in Composites," *ASTM-STP-658*, p. 98, 1977.
9. E.G. Wolff, "Creep," in *Reference Book for Composites Technology - 2*, S.M. Lee (Editor), Technomic Publishing Co., pp. 111-142, 1989.
10. N.P. Freund, "Measurement of Thermal and Mechanical Properties of Graphite-Epoxy Composites for Precision Applications," in *Composite Reliability, ASTM-STP-580*, pp. 133-145, 1975.
11. J.L. Camahort, E.H. Rennhack and W.C. Coons, "Effects of Thermal Cycling Environment on Graphite-Epoxy Composites," *ASTM-STP-602*, pp. 37-49, 1975.
12. E.G. Wolff and S.T. Crane, "Prediction of the Microyield Strength of Polymer Matrix Composites," *J. Comp. Tech. & Res.*, Vol. 10, No. 4, pp. 165-172, 1988.
13. V.F. Mazzio, "Composite Data for Spacecraft," *AFML-TR-82-4079*, June 1982.
14. E.G. Wolff and P. Gao, "Thermal Cycling and Moisture Effects on Creep Recovery in CFRP," *Int. Conf. on Comp. Mat.*, Beijing, China, August 1989.
15. Y.C. Lou and R.A. Schapery, "Viscoelastic Characterization of a Nonlinear Fiber-Reinforced Plastic," *J. Comp. Mat.*, Vol. 5, pp. 208-234, 1971.
16. C.M. Howard and L. Hollaway, "The Characterization of the Non-Linear Viscoelastic Properties of a Randomly Oriented Fibre/Matrix Composite," *Composites*, Vol. 18, pp. 317-323, 1987.
17. E.G. Wolff, "Dimensional Stability of Carbon Fiber Reinforced Plastic Tubes," *SAMPE Quarterly*, pp. 26-33, October 1984.
18. Y. Weitzmann and B.D. Harper, "Optimal Cooling of Cross-Ply Composite Laminates and Adhesive Joints," *J. Appl. Mech.*, Vol. 49, pp. 735-739, 1982.