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Creep Rupture of Polymer-Matrix Composites

by

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ABSTRACT

An accelerated characterization method for resin matrix composites is reviewed. Methods for determining modulus and strength master curves are given. Creep rupture analytical models are discussed as applied to polymers and polymer-matrix composites. Comparisons between creep rupture experiments and analytical models are presented.
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Introduction

Resin matrix composites are being widely examined for use as structural materials in the automotive and aerospace industries, to mention only two instances where lightweight but strong materials are desirable. Examples of the types of materials being examined are the chopped fiber sheet molding compounds (SMC) and the continuous fiber laminated composites. In the former a chopped fiber glass is common while in the latter both glass and graphite fibers are common. Both polyester and epoxy resins are customary in each situation. The principle of operation, of course, is that the fiber substantially increases both moduli and strength properties of an otherwise relatively compliant and weak matrix material. The matrix serves to bind the fibers together and to transfer loads from fiber to fiber or ply to ply.

While the fiber dominated properties of composites have, by far, received the most attention to date, it is now clear that resin dominated properties are of equal importance in many instances. The latter is especially true for long time design situations in the presence of a hostile environment. Polymer resins are adversely affected by temperature, moisture and other parameters. Also, polymers demonstrate creep or viscoelastic properties which are aggravated by temperature and moisture environments. As a result, the degradation of matrix dominated moduli and strength properties with time for resin matrix composites is both natural and obvious. Creep properties are the most affected due to the load transfer mechanisms which occur in the material.

The purpose of the present effort was to examine the time dependent creep rupture process in graphite/epoxy laminates as a function of
temperature and stress level. Moisture, though important, was not considered. Thus, materials were dried and desiccated prior to use.

Accelerated Characterization

The design process for most engineering materials is such that accelerated characterization is relatively easy. For metals as well as other materials, structural components are often sized so that linear elastic analyses can be used. Therefore, a test for modulus properties is usually simple and quick. Provided stresses and strains never depart from the linear elastic range, no change in properties are likely over the lifetime of the structure.

For repeated loading situations, fatigue failures may be a problem. Again, however, accelerated determination of fatigue life can be made in a short time by increasing the frequency of oscillations in the testing program. Assuming that properties are frequency independent allows one to determine in a few days information which can be used for long term design.

Obviously, the above comments are not appropriate for viscoelastic materials where both moduli and strength properties change with time. Thus, there is a real need for a method by which laboratory data collected in a short time can be extrapolated to the design lifetime.

That viscoelastic properties are important for graphite/epoxy laminates has been previously demonstrated and reported [1]. This result is reproduced and shown in Figure 1 which indicates that a delayed viscoelastic fracture process was observed for a graphite/epoxy $[\pm 45^\circ]_{4S}$ tensile specimen containing a circular hole. That is, a creep to failure response
occurred for individual plies and the laminate eventually fractured (separated) even though the applied laminate tensile load was relaxing in a fixed grip situation. Obviously, should the same phenomena occur in prototype structure, premature failures would occur. Figure 2 shows photographic evidence of the longer delayed fracture shown in Figure 1.

A procedure for the accelerated characterization of graphite/epoxy laminates was proposed by Brinson, Morris and Yeow [1]. The procedure which is shown in Figure 3 is based upon the well known time temperature superposition principle (TTSP) for polymer materials and the widely used lamination theory for composite materials. Using these ideas, the objective was to predict lamina and laminate moduli and strengths as a function of time using a minimum of testing.

The process outlined in Figure 3 assumes that the properties of a lamina to be used in a particular laminate could be routinely determined through normal quality control procedures. Ramp loaded properties for a particular T300/934 graphite/epoxy material reported previously [2] are shown in Figure 4. The necessary information of item A (see Fig. 3) can be obtained therefrom. An $E_2$ master curve* (item C) for the same material is shown in Figure 5. The TTSP methods used to obtain such master curves was reported previously [1,3]. Further, it was shown in earlier publications that the shift function (item C) was essentially independent of fiber angle and that master curves for arbitrary fiber angles predicted using the orthotropic transformation equation (item B)

*In our creep tests we, of course, measured compliance. However, we elected to plot our results as reciprocal of compliance so that master curves would have the units of modulus. No reciprocity between compliance is implied or intended.
agreed well with experimentally determined curves and medium term ($10^3$ minutes) test results [1,3-5]. Therefore, the information given in Figures 4 and 5, determined using only a minimum of testing, can be used to predict individual lamina modulus (compliance) master curves for arbitrary fiber angles. The resulting information can be used in the incremental lamination theory of item H.

The complicating feature of Figure 3 is the need for strength properties and strength master curves, items D and G. Figure 4 indicates that ramp loaded lamina strengths vs fiber angle can be determined reasonably accurately [2]. Further, it has been shown that a time independent failure theory can be used to accurately predict strengths as a function of fiber angle [5,6]. However, these procedures are not very useful in predicting the strength master curves in item G. Strength master curves as a function of fiber angle and temperature can only be determined by a large scale testing program or by successfully using or developing a viable creep rupture law. The present effort speaks to this process for graphite/epoxy laminates.

**Deformational Approaches to Delayed Failures (Creep Rupture)**

Deformational approaches utilize knowledge of the state of stress, strain and time. The classic approach to this phenomenon is given by Landel and Fedors [7]. In this work the authors develop a property surface in stress-strain-time space to establish the constitutive behavior for several polymers. Furthermore, they suggest that failure merely constitutes a boundary to the surface. Thus, the property surface uniquely establishes the stress-strain-time relationship for any load.
path, and the surface will also give the stress and strain at the time of failure. This visualization can be incorporated for uniaxial stress or pure shear. For the case of a polymer matrix composite this means that such a surface could be established for the macromechanical behavior of a given unidirectional off-axis orientation.

An alternate and much simpler approach was suggested in our earlier work [1]. This approach is based upon the key assumption that the strength master curve of item G would have the same form as the modulus master curves of item E with the same shift function. Thus, knowing the ramp loaded strength as given in Figure 4 and the modulus master curve of Figure 5 allows the determination of strength master curves for arbitrary fiber angle and temperature by simple changes of scale. Different temperatures can be accommodated by merely translating the master curve in accordance with the same shift factors used for modulus.

It was not recognized until recently that such an assumption is indeed a deformational theory of failure. Let us assume that an off-axis linear viscoelastic reciprocal of compliance master curve $1/S_{xx}(t)$, is known at a reference temperature $T_0$. Now presume that one failure point is known, say $\sigma_1$ and $t_1$. We now must adjust the vertical scale by some multiplicative constant, $A$, so that

$$A/S_{xx}(t_1) = \sigma_1 \quad (1)$$

It can easily be seen by rearrangement of (1) that

$$A = \sigma_1 S_{xx}(t_1) \quad (2)$$

Furthermore, it is assumed that all other rupture times and stresses are given by,
\[ A = \sigma_i S_{xx}(t_i) \]  \hspace{1cm} (3)

The right hand side of (3) represents the creep strain at failure. The left hand side is of course constant for all \( \sigma_i \) and \( t_i \). Therefore, this assumption is tantamount to saying that the total strain is constant at failure. Not surprisingly, this assumption is borne out experimentally several places in the Russian literature (for example, Stepanov [8]). In reality the compliance, \( S_{xx}(t) \), will be nonlinear in areas of interest so it is actually not strictly correct to speak of this assumption as one of constant failure strain.

Figures 6 and 7 show the results of a creep rupture testing program on T300/934 at a temperature of 160°C compared to creep rupture predictions determined using the above assumption and scaling procedures [6]. As may be recognized, reasonable agreement between experiment and prediction was obtained, considering the scatter inherent in composite testing as well as creep rupture testing in general.

**Phenomenological Approaches to Delayed Failure (Creep Rupture)**

Of primary interest here is the method that seems to be most often associated with Zhurkov and sometimes known as kinetic rate theory. This exclusive association, however, may not be entirely merited. According to several sources (Stepanov [8] and Kargin and Slonimsky [9] and others) the original form of the equation was published by Alexandrov in 1945. The Alexandrov equation provided a basis for determining the relaxation time at an arbitrary temperature and stress level of a nonlinearly viscoelastic material. According to Zhurkov [10], Zhurkov first used the relationship to predict rupture times in 1953. The most common form of
the equation is given as

$$t_r = t_0 e^{u_0 - \gamma \sigma \over KT}$$

(4)

where

- $t_r$ = rupture time
- $t_0$ = a constant normally about $10^{-12}$
- $u_0$ = a constant activation energy
- $\gamma$ = a constant
- $\sigma$ = applied uniaxial stress
- $K$ = Boltzmann's constant
- $T$ = absolute temperature

In the form originally used by Alexandrov, $t_r$, represented the relaxation time at stress and temperature levels $\sigma$ and $T$.

Zhurkov and his coworkers have successfully applied the relationship to over 50 different materials including metals and polymers in a series of papers. One can surmise from reviewing the Russian literature that the validity of the relationship is unquestioned. In fact, Regel' et al. [11] have even suggested the existence of something called the "kinetic rule of mixtures." Outside the USSR the method has received some attention. Chiao et al. [12] have found the Zhurkov relationship to be valid for composites. However, the composite they studied was only several strands of aramid fiber impregnated with epoxy primarily for protection. There is no record in the literature of anyone applying the technique to the failure of off-axis or general laminates of the type studied here.

There have been attempts at providing the legitimacy of equation (4) on a physical basis. For example, $t_0$ is generally stated to be the
period of natural oscillation, and hence is nearly constant for all materials. An energy barrier significance is associated with $u_0$. In practice all the constants must be evaluated using experimental data as described by Zhurkov [10], Chiao [12], or Bartenev and Zuyev [13]. One notices that for a certain stress level, the exponential term in equation (4) tends toward one when the quantity $\gamma \sigma$ is equivalent to the activation energy $u_0$, i.e.,

$$\lim_{\gamma \sigma \rightarrow u_0} t_0 e^{\frac{-u_0}{KT}} = t_0$$

This implies the existence of a so-called pole (common intersection) when $\log t_r$ is plotted vs. stress as shown in Figure 8. After reviewing a number of sets of data in the literature it would appear that a good bit of discretion is often required to force the data to intersect at a pole. The remaining constants, $u_0$ and $\gamma$, may be determined by plotting $KT \ln(t_r/t_0)$ vs. stress. It can be shown that the zero stress intercept of this plot yields $u_0$ and the slope yields $\gamma$ [10].

The universal nature of equation (4) is not automatically assumed in the Western scientific community. For example, after several paragraphs of discussion Knauss [14] states, "Zhurkov's impressive findings appear thus to be the somewhat fortuitous result of a particular test method." The Zhurkov method may be founded on no greater scientific basis than other classical parametric methods described subsequently. Close scrutiny of equation (4) reveals that failure will even occur at vanishing stress, admittedly at long time, which is obviously erroneous. Zhurkov's method has been modified by other investigators to suit particular needs.
For example, Slonimskii et al. [15] found that

\[ t_r = t_0 e^{\frac{u_0}{RT} - \gamma \sigma} \]  

which we shall refer to later as the modified rate equation.

Other phenomenological methods are surveyed by Conway [16] and Goldhoff [17]. The most popular of these are the Larson-Miller, Dorn, and Manson-Haferd methods. The details of these methods will not be given here. However, after careful observation it was apparent that nearly all the phenomenological approaches were similar in the way that temperature affects rupture times. For example the Zhurkov, Larson-Miller, and Dorn method all give a relation of the form

\[ \log t_r = A + \frac{B}{T} \]  

where A and B are constants for a given stress. The Manson-Haferd approach gives

\[ \log t_r = A - BT \]  

for constant stress. For typical values of \( \log t_r \) and absolute temperature, equations (7) and (8) give similar results. The differences in the phenomenological methods are primarily due to the influence of stress. It is believed that none of the above methods, including that of Zhurkov, have sufficient scientific justification at present to be considered anything more than empirical.

There are several fundamental problems with the use of a phenomenological approach on a composite material. First, it is implicitly assumed that the dominant mode of failure or the failure mechanism itself is substantially the same for all temperatures and stress levels. In creep
tests of \([\pm 45^\circ]_{4s}\) laminates described elsewhere [18] it is noted that failure at high stress levels involves little delamination while failure at low stress levels involves considerable delamination. Thus, the failure mechanisms at various stress levels are likely different. A more fundamental problem involves the state of stress in a composite. It is well known that the state of stress in the matrix material is complex (a general biaxial state at least). Furthermore, it is acknowledged that the parameters used in the Zhurkov method are functions of the type of stress (i.e., shear vs. extension, see Yartsev and Ratner [19] for one example). Therefore, for composites there may be little reason to believe that the parameters for one orientation are the same as those for another.

There is one phenomenological approach specifically tailored to the time dependent fracture of composites. Wu and Ruhmann [20] have extended the original work of Wu [21] on tensor polynomial failure surfaces to the time dependent case. This approach postulates that the failure of a unidirectional composite is governed by a failure surface in stress space where the bases of the space are the in-plane normal and shear stresses, \(\sigma_1, \sigma_2, \tau_{12}\), relative to the principal material axes. Wu postulated that the failure surface shrunk radially inward with increasing time according to a Zhurkov type dependence. The applied load is represented by a vector emanating from the origin, and when the load vector contacts the failure surface specimen failure is said to occur. This approach is more general than the other phenomenological approaches since the surface and its time dependence is invariant with respect to the geometry of loading. Of course, the Wu failure surface takes commensurately more tests to quantify, however, Wu [21] has demonstrated that
a minimum number of tests is required. To date, very little experimental evidence to support this theory is available.

**Creep Rupture Testing Program**

A creep rupture testing program on the same T300/934 composite as studied previously was undertaken. A new batch of material had to be ordered. Unfortunately it was ascertained that matrix dominated properties of the original batch and the new batch were not the same. Hence no relevant comparisons could be made. These differences are given in Table 1 and amply demonstrate some of the fundamental difficulties associated with composite test programs.

Creep rupture data for $[90^\circ]_{8S}$, $[60^\circ]_{8S}$, and $[45^\circ]_{8S}$ T300/934 materials are shown in Figures 9-11. Also shown in Figure 9 are the Larson-Miller parameter method and the modified rate equation (5) fitted to the data. As may be observed, very poor agreement with the Larson-Miller parameter method was obtained. The modified rate equation worked best but still represented the data rather poorly.

It may be interesting to note parenthetically that the constant strain to failure assumption used earlier gives predictions of the same form as the data shown in Figures 9-11.

**Summary and Conclusions**

A method of accelerated characterization of composite laminate viscoelastic modulus and strength properties is reviewed. It was shown that lamina modulus master curves can be obtained using a minimum of normally performed quality control type testing. Further, lamina strength master curves obtained by assuming a constant strain failure criterion were
presented together with experimental data. Reasonably good agreement exists between the two.

Various phenomenological delayed failure models were reviewed and two (the modified rate equation and the Larson-Miller parameter method) were compared to creep rupture data with poor results. One word of caution is in order here as we have discovered that our new batch of material was significantly affected by a postcuring phenomenon. Thus it is entirely possible that the data of Figures 9-11 are the result of a chemical time dependent strengthening process (postcuring) while at the same time suffering time dependent degradation of mechanical properties. Currently a testing program is under way to attempt to evaluate this phenomenon.

The accelerated characterization procedure as originally proposed and discussed herein was based upon concepts of linear viscoelasticity and the TTSP. It is recognized that the creep rupture process is likely nonlinear and nonlinear viscoelastic principles should be used. Recently a time temperature stress superposition principle (TTSSP) has been identified which does incorporate nonlinear effects. These efforts are reported separately [22]. For a more detailed discussion of these ideas and the postcuring effects see reference [18].

As a final note, work is currently on going to develop the incremental lamination theory shown in Figure 3 as item H. Also, an additional general laminate testing program is under way to evaluate the results of the incremental lamination theory and to give insight to creep-rupture of general laminates.
Acknowledgements

The authors gratefully acknowledge the support of NASA-Ames under grant number NSG-2038 and the many helpful discussions with our project monitor, Dr. Howard G. Nelson, and his associates.
Table 1. A Comparison of the "Old" and "New" Batches of Material

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<tbody>
<tr>
<td>[0°]_{8s} #1</td>
<td>19.88x10^6 psi</td>
<td>20.74x10^6 psi</td>
<td>207.9 ksi</td>
<td>195.6 ksi</td>
<td>0.95%</td>
<td>0.87%</td>
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<tr>
<td>[0°]_{8s} #2**</td>
<td>19.88x10^6 psi</td>
<td>20.79x10^6 psi</td>
<td>-</td>
<td>-</td>
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<tr>
<td>[90°]_{8s} #1</td>
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<tr>
<td>[90°]_{8s} #3***</td>
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<td>-</td>
<td>5.80 ksi</td>
<td>13.28 ksi</td>
<td>-</td>
<td>-</td>
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**Slipped in grip.

***For strength measurement only.
REFERENCES


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Fig. 6: Comparison of [30°]_8s Creep-Rupture Predictions and Experiment Results

PORTION OF 160°C MASTER CURVE, [30°]_8s LAMINATE

O CREEP RUPTURE DATA, 160°C

(d(0.1) vs (0.01) x 10^8 S/1

LOG TIME (Min)

(d(0.1) vs (0.01) x 10^8 S/1

22
Fig. 8. Typical Data Obeying Zhurkov's Equation
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Fig. 10. Summary of Creep Rupture Data Obtained on [60°]$_8$s Specimens, Lines Are Best Fit
Fig. 11 Summary of Creep Rupture Data Obtained on \([45^\circ]_8\) Specimens, Lines Are Best Fit