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The Accelerated Characterization of
Viscoelastic Composite Materials

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ABSTRACT

A brief review of necessary fundamentals relative to composite materials and viscoelasticity is provided. Subsequently the accelerated characterization techniques of Time Temperature Superposition and Time Temperature Stress Superposition are treated in detail. An experimental procedure for applying the latter to composites is given along with results obtained on a particular T300/934 graphite/epoxy. The accelerated characterization predictions are found in good agreement with actual long term tests. A postcuring phenomenon is discussed that necessitates thermal conditioning of the specimen prior to testing. A closely related phenomenon of physical aging is described. The effect of each on the glass transition temperature and strength is discussed.

Creep rupture results are provided for a variety of geometries and temperatures for T300/934 graphite/epoxy. The results are found to compare reasonably with a modified kinetic rate theory.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

The time dependent behavior of composite materials subject to various conditions of temperature and stress is the central theme of this investigation. Topics relevant to the theme such as viscoelasticity, time temperature superposition, creep rupture, etc., are treated in substantial detail. Other topics on composites such as lamination theory, micromechanics, etc., are discussed only briefly or peripherally. As some familiarity with composites is assumed, those interested in details not provided herein are referred to the excellent text of Jones (1975)*.

General Information

The merits of composite materials are well established and have received wide-spread attention by many investigators; but their use has been more limited. Thus far, applications seem to be in two general areas. The most wide-spread use of composites has been in the consumer products arena where they have been used increasingly for cosmetic and less important structural members. Examples include moldings for automobiles, boats, appliances, etc. Many of these applications have been with sheet molding compounds (SMC), a chopped glass fiber-polyester composite, or with woven glass fabrics in a polyester or epoxy matrix. SMC offers improvements in strength and modulus over traditional polymers and is presently the most adaptable

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*Names followed by parentheses indicate references found in alphabetical order at the end of the paper.

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to mass production of all fiber reinforced polymer based composite materials. Work is currently proceeding in the auto industry and elsewhere to extend the applications of SMC to load bearing structural members.

"Advanced" or "high performance" continuous fiber composites are of primary concern in the present investigation. These materials are much more expensive, less adaptable to mass production techniques and presently reserved, for the most part, to very high performance applications such as military aircraft. Advanced composites may contain graphite, boron, glass, or aramid fiber reinforcement in a metallic or polymeric matrix. Graphite/epoxy laminates are the most popular composites of this type and are the concern of the experimental portion of this paper. Many of the concepts, subsequently, are applicable to any polymer matrix composite.

Viscoelastic Behavior

Epoxy resins exhibit viscoelastic or time dependent effects which are accelerated by a number of environmental conditions. The best understood accelerating factor is temperature. For years, the time-temperature superposition principle (TTSP) has been used for the accelerated characterization of linear and more recently nonlinear viscoelastic materials. The literature abounds with references to this type of behavior, and the application of TTSP to form modulus or compliance master curves is commonplace. Polymers in general and epoxies in particular are susceptible to moisture-induced effects on properties. Moisture accelerates viscoelastic processes in polymers

and also gives rise to residual stresses. Recently stress has been recognized as an additional accelerating factor for nonlinearly viscoelastic polymers, and an isothermal stress time superposition principle analogous to the TTSP has also been used to produce master curves. In the foreign literature, vibratory components superimposed on static loads have been considered an accelerating factor. In general, a viscoelastic body may be subjected to all of the above accelerating factors. The manner in which these factors may be combined is not widely agreed upon. However, the literature provides some examples of combined application of some of the above factors.

Obviously polymer based composites, such as graphite/epoxy, will have properties which are time dependent and are similarly affected by the accelerating parameters of temperature, moisture, and stress. Matrix dominated mechanical properties will be the most viscoelastic. Fiber dominated properties are not entirely independent of temperature and moisture effects, but time dependent properties of unidirectional graphite/epoxy laminates loaded in the fiber direction are negligible. However, off-axis unidirectional composites with even slight angles between the load and fiber directions will exhibit significant time-dependent behavior. Hence, any graphite/epoxy composite without reinforcement in all load bearing directions will have properties which are matrix dominated in the time dependent sense.

For the most part, composite structures may be designed using linear elastic analysis. However, due to the effects of environment, there are instances where time dependent phenomena such as creep, relaxation, delayed failures, etc., may be important long-term design

considerations. Recently the Federal Government instituted a policy that aircraft structures must be certified for long-term air worthiness. This requirement is easily met for materials with time independent properties under static loading such as metals. For materials with time dependent properties under static loading, long-term integrity prediction is not easily accomplished without knowledge of properties over the design life-time of the structure. The ability to insure long-term integrity without the necessity of long-term experimentation (accelerated characterization) is of obvious merit and is the thrust of the present effort.

Goals and Objectives

Analytical and experimental procedures for the accelerated characterization of moduli and strength properties of composite materials have recently been under consideration by several research groups. Relevant literature will be discussed subsequently and, in fact, the identification and discussion of such literature was a primary objective of this investigation.

The present study is an outgrowth of the earlier efforts of Brinson, Morris and Yeow (1978). Their work identified both an analytical and an experimental procedure by which short-term laboratory tests could be used to predict long-term moduli and strength properties of composite laminates. Their program was directed toward quasi-static time and temperature properties, while those of their NASA-Ames sponsors and counterparts (see Roten and Nelson, 1978, for example) were directed toward environmentally related fatigue properties.

In previous VPI&SU efforts toward accelerated characterization, the TTSP principle was used and experimental programs were conducted such that concepts of linear viscoelasticity could be used, i.e., small stresses and strains. Obviously, when rupture occurs stresses and strains are quite likely beyond linear limits.

Initially the aims of the project were to devise a procedure to determine the nonlinear in-plane moduli properties of an individual lamina and to link these results, if possible, to a creep rupture phonomenon in either a lamina or a laminate. As time progressed the difficulty of obtaining time dependent failures in general laminates became apparent. When new materials were obtained they were found to be considerably different than those presumably prepared identically previously. Later, it became apparent that inadequate information was available on the nature of the time-temperature equivalence generally used in accelerated predictions for polymers and composites.

The above described evolutionary refinement of goals culminated in the following objectives:

1) To study the nature of the TTSP and other superposition principles.

2) To suitably define or provide a methodology for predicting the combined effects of temperature and stress level on the principal compliances in an accelerated manner.

3) To perform creep rupture testing of newly acquired uni-directional material.

4) To investigate methods of predicting time dependent failure using existing procedures, and to determine if item 2 might be useful in such endeavors.

5) To investigate the assumption of Brinson, et al (1978) that creep strength master curves are of the same form as the reciprocal of compliance master curves for unidirectional laminates.

6) To generally provide details of master curve formation necessary for the continued development of a time dependent failure predictive method for composites described in earlier publications, Brinson, et al (1978), Cartner, et al (1978), Morris, et al (1979), Yeow, et al (1978a,1979).

7) To carefully document experimental considerations and provide guidance for future work.

II. INTRODUCTION TO THE MECHANICS OF COMPOSITE MATERIALS

Nomenclature used to describe composite behavior has not been completely standardized. Generally, the symbols used here follow those of Jones (1975) wherever possible. The present discussion describes the macroscopic elastic behavior of a single lamina, or a unidirectional laminate (a laminate with all plies having the same fiber orientation). Further, this section briefly discusses the predicting of general laminate behavior from the behavior of a single ply, which is often referred to as lamination theory. The branch of study which relates the constituent response of the fiber and matrix materials separately to that of the composite is called micromechanics and will be discussed briefly later in this paper.

Constitutive Relations

Composites, by design, have properties which vary with orientation. Hence, they are by definition, anisotropic. The most general form of constitutive equation for a linearly elastic homogeneous anisotropic body is given by equation (2-1).

$$\sigma_{ij} = C_{ijk\ell}\, \varepsilon_{k\ell} \qquad i,j,k,\ell = 1 \text{ to } 3 \qquad (2\text{-}1)$$

where σ_{ij} and $\varepsilon_{k\ell}$ are components of the Cartesian stress and strain tensor respectively and $C_{ijk\ell}$ is the stiffness tensor with 81 separate values. Due to the symmetry of the stress and strain tensors there are a maximum of 36 independent constants among the 81. The remaining 36 may be reduced to 21 from strain energy arguments (Onsager's

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principle). Thus, a completely anisotropic homogeneous linear elastic body may be described with 21 independent constants.

In reality a laminated composite panel is heterogeneous but an assumption of homogeneity is usual to simplify analytical and experimental analyses. Further, individual lamina or plies are customarily assumed to be orthotropic. By definition an orthotropic body contains three planes of symmetry. The above assumptions allow one to utilize the transformation law for Cartesian tensors to show that the 21 constants may be reduced to only 9 independent ones. In such a body the shear strains are uncoupled from the extensional strains and one another (when boundary tractions are applied in the same sense as the planes of symmetry).

Advanced composites are often used as plates or panels and hence are subjected to both in-plane membrane and out-of-plane bending loads. Only in-plane loads are of interest here, so out-of-plane response will not be discussed and the out-of-plane shears and normal stress will be assumed to be zero. Under these conditions the laminate is in a state of plane stress and its constitutive relations may be reduced to the so-called collapsed or reduced form containing only four constants. As most people working with composites are engineers by training, the collapsed form is convenient as it incorporates the use of the in-plane shear strain γ_{12} instead of its tensorial counterpart $\epsilon_{12} (\epsilon_{12} = \frac{1}{2} \gamma_{12})$.

In the work described here a great deal of attention will be placed upon creep and creep rupture testing of off-axis (the load being at an angle to the fiber) unidirectional composite laminates. In a

creep test the stress is held constant while the strains are measured and hence it is most desirable to work with the compliance matrix S_{ij} (the inverse of the stiffness matrix). Furthermore, it is customary to reserve the 1 axis for the fiber direction and the 2 axis for the direction transverse to the fibers but still in the plane of the laminate. The reduced form for strain in terms of stress thus becomes,

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \gamma_{12} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & 0 \\ S_{21} & S_{22} & 0 \\ 0 & 0 & S_{66} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \end{bmatrix} \qquad (2\text{-}2)$$

where $\varepsilon_1, \varepsilon_2$ = in-plane normal strains in the one and two directions

γ_{12} = in-plane engineering shear strain

σ_1, σ_2 = in-plane normal stresses in one and two directions

τ_{12} = in-plane shear stress

S_{ij} = reduced material compliances

The compliances, S_{ij}, are often described in terms of the more conventional engineering constants given below.

$$S_{11} = \frac{1}{E_{11}}$$

$$S_{12} = -\frac{\nu_{12}}{E_{11}} = -\frac{\nu_{21}}{E_{22}} = S_{21}$$

$$S_{22} = \frac{1}{E_{22}}$$

$$S_{66} = \frac{1}{G_{12}}$$

where $\nu_{12} = -\frac{\varepsilon_2}{\varepsilon_1}$ when $\sigma_1 = \sigma$, $\sigma_2 = 0$ and E_{11}, E_{22}, and G_{12} are

customary moduli. Equation (2-2) may be thought of as the plane stress form of Hooke's law for an orthotropic body. Of course the compliance relationship may be inverted to give stress in terms of strain; however this form will not be required and is not given.

Transformations

In a continuous medium, tensorial quantities may be related to new coordinate systems by use of the transformation equation. In a heterogeneous medium the use of coordinate transformation is valid in a less rigorous sense. For example, in a unidirectional laminate the stress in the fibers and the stress in the matrix are different, but the average stress may still be transformed via coordinate transformation with good results.

In a laminate, the compliance matrix of an individual lamina (ply), S_{ij}, in material coordinates may be transformed into a compliance matrix $\bar{S}_{ij}$ in body or global coordinates through the use of the transformation matrix $[T]$. The transformation law may be developed simply by expressing stresses and strains in a lamina in body co-ordinates in terms of stresses and strains in material coordinates. When this is done the following equation is developed (see Jones (1975) for example),

$$
\begin{Bmatrix} \varepsilon_x \\ \varepsilon_y \\ \gamma_{xy} \end{Bmatrix} = [T]^T [S][T] \begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix} = [\bar{S}] \begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix} \tag{2-3}
$$

where matrix multiplication is implied, superscript T implies the matrix transpose, θ is defined as shown in Figure 2-1, and the
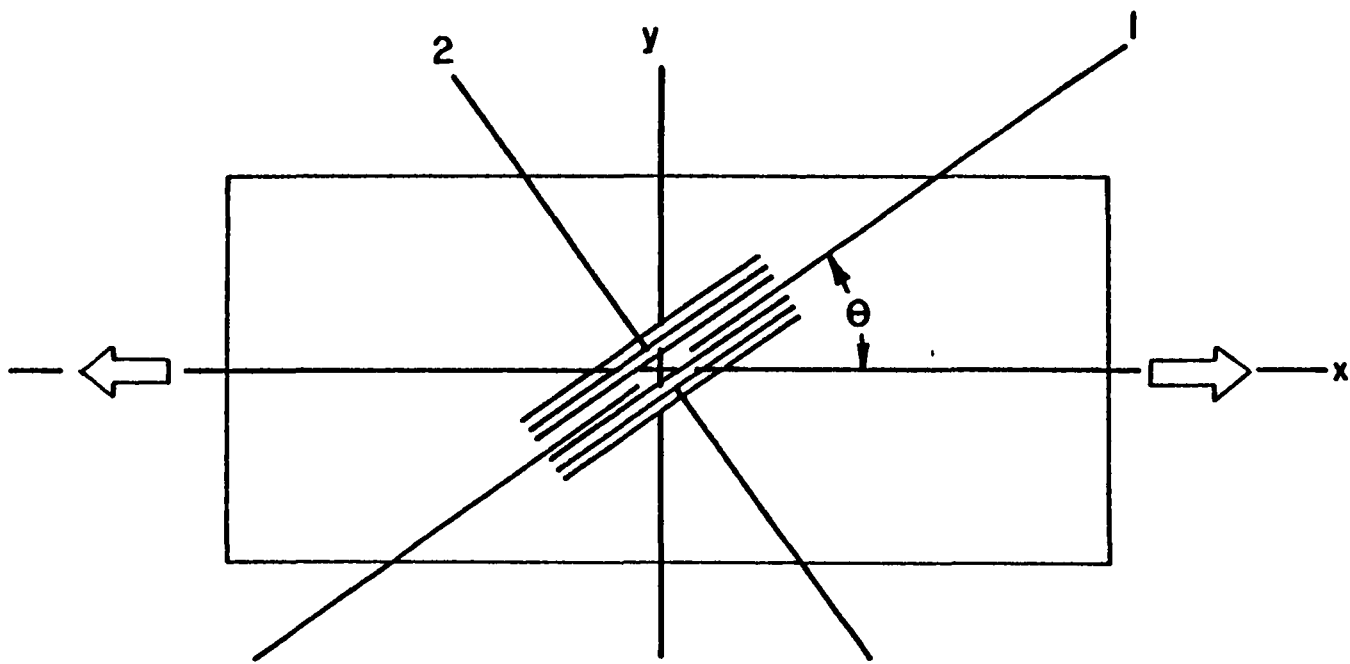
Figure 2-1. Coordinate system and fiber angle, θ, as used in transformation equations.

transformation law between $[\bar{S}]$ and $[S]$, can be written as,

$$\bar{S}_{11} = S_{11} \cos^4\theta + (2S_{12} + S_{66}) \sin^2\theta \cos^2\theta + S_{22} \sin^4\theta$$

$$\bar{S}_{12} = S_{12}(\sin^4\theta + \cos^4\theta) + (S_{11} + S_{22} - S_{66}) \sin^2\theta \cos^2\theta$$

$$\bar{S}_{22} = S_{11} \sin^4\theta + (2S_{12} + S_{66}) \sin^2\theta \cos^2\theta + S_{22} \cos^4\theta$$

$$\bar{S}_{16} = (2S_{11} - 2S_{12} - S_{66}) \sin\theta \cos^3\theta - (2S_{22} - 2S_{12}$$
$$- S_{66}) \sin^3\theta \cos\theta$$

$$\bar{S}_{26} = (2S_{11} - 2S_{12} - S_{66}) \sin^3\theta \cos\theta - (2S_{22} - 2S_{12}$$
$$- S_{66}) \sin\theta \cos^3\theta$$

$$\bar{S}_{66} = 2(2S_{11} + 2S_{22} - 4S_{12} - S_{66}) \sin^2\theta \cos^2\theta + S_{66}(\sin^4\theta + \cos^4\theta)$$

The reader should bear in mind that a slightly different transformation is used for the reduced stiffness matrix, C_{ij}, which is a result of the use of engineering shear strain.

Several points should be noted with respect to the above described property transformations. First, it should be noted that the $[\bar{S}]$ matrix will in general have no zeros. In other words, a unidirectional material when observed from an orientation other than that aligned with its symmetry axes will appear to be anisotropic. Second, when the compliance associated with an arbitrary axis x is known, as shown in Figure 2-1, an equation is provided which will yield an unknown principal compliance (associated with the 1-2 axes) factor provided the others are known. For example,

$$\bar{S}_{11} = S_{xx} = \cos^4\theta \, S_{11} + \sin^4\theta \, S_{22} + \cos^2\theta \sin^2\theta \, (2S_{12} + S_{66}) \quad (2-4)$$

may be used to solve for S_{66} if S_{11}, S_{22}, S_{12}, and θ are all known.

This in fact will be done to solve for S_{66} at a later time.

Lamination Theory

Subsequently in this paper laminated plate theory will be mentioned. Laminated plate theory provides a procedure for the approximate analysis of laminated composite plates. The principal assumption of this theory is that a line passing through a laminate normal to the mid-surface under stress-free conditions will remain a straight line normal to the midsurface after deformation. This assumption is similar to the plane sections remain plane assumption of Euler-Bernoulli beam theory. In other words, there is no relative deformation between adjacent plies of a laminate. Furthermore, when a laminate is symmetric about its mid-plane, inplane loads produce only an inplane response. For general asymmetric laminates inplane and out-of-plane responses are coupled. All of the laminates to be discussed herein will be symmetric. As discussed later, some of the creep rupture test observations seem to violate the fundamental assumption of laminated plate theory of no relative deformation between adjacent plies.

III. INTRODUCTION TO LINEAR VISCOELASTICITY

Viscoelasticity is the study of materials whose properties are time dependent. In the case of viscoelastic solid materials one is primarily interested in the time dependent strain response under constant stress (creep) and the time dependent stress response under constant strain (relaxation). Undoubtedly recent interest in the subject of viscoelasticity has been prompted by the increased use of polymers which are by nature very viscoelastic. Composite materials which use either polymeric matrices, polymeric fibers or both are similarly viscoelastic. In this paper graphite/epoxy is of primary interest and it is assumed that the viscoelastic response of the composite is entirely due to the matrix and that the fiber is elastic (Brinson, et al (1978), Yeow, et al (1979), Morris, et al (1979)).

The thrust of this paper is toward stress dependent effects which are inherently nonlinear; however, it is first necessary to describe the linear behavior. Linear viscoelastic response is often associated with small stress levels and infinitesimal strains. The most basic requirement for the linear theory to be applicable, however, is superposition. Thus, the individual responses for two arbitrary inputs may be summed to form the response for the sum of the inputs.

Constitutive Relations

The isothermal linear anisotropic theory of viscoelasticity is completely defined by the relaxation modulus, $C_{ijk\ell}(t)$, and the creep compliance, $S_{ijk\ell}(t)$. We will define these properties such that

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$$\sigma_{ij}(t) = C_{ijk\ell}(t)\, \varepsilon_{k\ell}^0 \tag{3-1}$$

and

$$\varepsilon_{ij}(t) = S_{ijk\ell}(t)\, \sigma_{k\ell}^0, \tag{3-2}$$

where we assume that the material is initially dead until time, $t = 0$, at which time an instantaneous strain, $\varepsilon_{k\ell}^0$, or stress, $\sigma_{k\ell}^0$, is applied and held constant with time. Thus the applied strain or stress history is defined by

$$\varepsilon_{k\ell}(t) = \varepsilon_{k\ell}^0\, H(t) \tag{3-3}$$

$$\sigma_{k\ell}(t) = \sigma_{k\ell}^0\, H(t) \tag{3-4}$$

where $H(t) = 0$ for $t < 0$ and $H(t) = 1$ for $t \geq 0$.

The assumption of linearity allows one to assemble solutions using superposition for varying applied strain and stress histories. For example the response of a multistep load

$$\sigma_{k\ell}(t) = \sigma_{k\ell}^0\, H(t) + \sigma_{k\ell}^1\, H(t - t_1) \tag{3-5}$$

may be found by adding the responses of both stress inputs,

$$\varepsilon_{ij}(t) = S_{ijk\ell}(t)\sigma_{k\ell}^0 + S_{ijk\ell}(t - t_1)\sigma_{k\ell}^1 \tag{3-6}$$

where by definition the values for all viscoelastic functions prior to $t = 0$ are zero. In a like manner the response to any arbitrary strain or stress input may be found by superposition using the convolution integral yielding

$$\sigma_{ij}(t) = \int_0^t C_{ijk\ell}(t - \tau)\, \frac{d\varepsilon_{k\ell}}{d\tau}\, d\tau \tag{3-7}$$

and

$$\varepsilon_{ij}(t) = \int_0^t S_{ijk\ell}(t - \tau) \frac{d\sigma_{k\ell}}{d\tau} d\tau \qquad (3\text{-}8)$$

Equations (3-7) and (3-8) completely define the isothermal constitutive laws for an anisotropic homogeneous linearly viscoelastic body. It is recognized that when the constant strain or stress inputs given in equations (3-3) or (3-4) are introduced in equations (3-7) or (3-8) that the definitions of relaxation modulus and creep compliance are retrieved as in equations (3-1) or (3-2) respectively. All of the components of relaxation modulus and creep compliance may be determined by varying the indices of applied stress and strain in equations (3-1) and (3-2). Due to the symmetry of the stress and strain tensors

$$S_{ijk\ell}(t) = S_{jik\ell}(t) \qquad (3\text{-}9)$$

and

$$S_{ijk\ell}(t) = S_{ij\ell k}(t) \qquad (3\text{-}10)$$

where similar relations are valid for $C_{ijk\ell}(t)$. Schapery (1967) has shown that the equivalent of Onsager's Principle is valid for composite materials when the individual phases satisfy similar relationships. Assuming this to be the case

$$S_{ijk\ell}(t) = S_{k\ell ij}(t) , \qquad (3\text{-}11)$$

and a similar relation is again valid for the relaxation modulus. Therefore, either viscoelastic function contains at most 21 independent functions of time. In a like manner to that used in Section II, it

can be shown that the plane stress viscoelastic response of a homogeneous orthotropic laminate may be expressed by only four functions of time. As before, we are primarily interested in the creep compliance of a unidirectional laminate.

Property Measurement

In a unidirectional laminate necessary values of compliance may be determined in three tests. Using the notation of Section II we have the following relationships.

1. For a uniaxial test of a 0° specimen

$$S_{11}(t) = \frac{\epsilon_1(t)}{\sigma_1^0} \quad \text{and} \quad S_{21}(t) = \frac{\epsilon_2(t)}{\sigma_1^0} \tag{3-12}$$

2. For a uniaxial test of a 90° specimen

$$S_{22}(t) = \frac{\epsilon_2(t)}{\sigma_2^0} \quad \text{and} \quad S_{12}(t) = \frac{\epsilon_1(t)}{\sigma_2^0} \tag{3-13}$$

3. For a uniaxial test of any orientation not 0° or 90° one may use the transformation equation and the results of tests 1 and 2 to calculate S_{66} using the measured off-axis compliance, S_{xx}.

$$S_{xx}(t) = \cos^4\theta \, S_{11}(t) + \sin^4(\theta) \, S_{22}(t)$$

$$+ \cos^2\theta \, \sin^2\theta \, (2S_{12}(t) + S_{66}(t)) \tag{3-14}$$

Alternatively, when the complete state of strain is known via a strain gage rosette S_{66} may be calculated using

$$S_{66}(t) = \frac{\gamma_{12}(t)}{\tau_{12}^0}$$

The superscript for stress has been added to indicate the value of stress which is applied at time equal zero and held constant thereafter.

Creep vs. Relaxation

Particular attention has been given the creep compliance in this section since it is experimentally easier to measure than the relaxation modulus. In a creep test the strain may be measured at the center of the specimen, the stress calculated from the applied load, and the compliance calculated directly. When the creep specimen is of adequate length, end effects negligibly perturb the stress at the center and an accurate calculation of compliance can be made. In a relaxation test several problems present themselves. First, any specimen movement in the grips or less than adequate testing machine stiffness will artificially change the relaxation function. Secondly, in a relaxation test the strain is usually measured at the center using a strain gage or extensometer. When the relaxation modulus is calculated, it is implicitly assumed that the measured strain is valid for the length of the specimen and that the specimen is free of constraints so a uniaxial stress field is present. This condition of course cannot be satisfied at the ends due to the constraint of the grips, or lack of grip rotation. Thus, creep testing is preferred since end effects can never be eliminated with reasonable length specimens in relaxation testing of anisotropic solids.

Constant Strain Rate Testing

Constant strain rate testing may also be used to determine the relaxation modulus as suggested by Smith (1962) for both linear and nonlinear characterizations of elastomers. In this type of test

$$\varepsilon_{k\ell} = R_{k\ell}\, t \, , \tag{3-15}$$

where $R_{k\ell}$ = rate of strain of $\varepsilon_{k\ell}$.

Substitution of (3-15) into (3-7) and taking derivatives yields

$$\frac{\partial \sigma_{ij}(t)}{\partial t} = R_{k\ell}\, C_{ijk\ell}(t) \tag{3-16}$$

and by use of the chain rule

$$\frac{\partial \sigma_{ij}(t)}{\partial \varepsilon_{k\ell}(t)} = C_{ijk\ell}(t) \, . \tag{3-17}$$

Thus, the instantaneous slope of the stress strain curve yields the relaxation modulus independent of the strain rate used to define the curve; however, rather slow rates must be used if moduli are to be measured for any length of time.

In the present study both creep tests and constant strain rate tests were performed on graphite/epoxy. The constant strain rate tests were shown to be less desirable than creep tests for a hard viscoelastic solid, such as our graphite/epoxy material.

Interconvertibility and Aging

One important aspect of the linear theory is the interconvertibility of the viscoelastic functions. Once the creep compliance is known, it is theoretically possible to calculate the relaxation

modulus. Ferry (1970) gives a complete discussion of these relation-
ships. More often, however, the quasi-elastic assumption of Schapery
(1967) is used since the precise analytical interconversion is
cumbersome. In this assumption the inverse of the creep compliance
tensor is assumed equal to the relaxation modulus tensor, which is
similar to assuming the relaxation modulus is equal to the reciprocal
of creep compliance for an isotropic material.

All of the equations used thus far are only rigorously valid for
a nonaging material. An aging material exhibits changes in behavior
that cannot be accounted for within the treatment here since these
changes often preclude use of the convolution integral. Such changes
may accompany high temperature, UV radiation, ozone and damage due to
high stress, or may be due to nonequilibrium amounts of free volume
as in the case of physical aging. Some of these effects will be dis-
cussed subsequently.

A more detailed treatment of viscoelasticity may be found in
Flügge (1975), Ferry (1970) or Christensen (1971). An excellent treat-
ment of anisotropic linear viscoelasticity is given by Schapery (1974).

IV. TIME TEMPERATURE SUPERPOSITION IN LINEAR VISCOELASTICITY

The Time Temperature Superposition Principle (TTSP) is central to the work described in this paper, so a detailed description of its history, use, and implications is merited. The TTSP is referred to by a number of different names including Time Temperature Analogy, Method of Reduced Variables, Time Translation Equivalence and others. TTSP was preferred here because it is the most prevalent name that is best descriptive of the process.

The TTSP provides a method by which long-term behavior can be predicted from short-term tests (accelerated characterization). Initially the technique was applied to the relaxation modulus and the creep compliance. Subsequently, it has been applied to a number of other properties including failure. In the TTSP procedure, temperature shift factors and master curves are generated as will be described in detail later.

History of TTSP

The history of TTSP has been recently summarized by Markovitz (1975) in some detail. In his description he points out that the knowledge of the general effects of temperature on creep and relaxation were known by a number of investigators in Russia, Europe and the United States. Markovitz, however, finds no explicit reference to TTSP prior to Leaderman's 1943 report where Leaderman states in his discussion of creep compliance vs. log time curves, "It appears reasonable to assume that the curves for different temperatures are

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of the same shape, but that increase of temperature displaces the creep curve for constant load to the left; we can then say that increase of temperature has the effect of contracting the time scale." Leaderman did not suggest that a vertical shift would be required for superposition and according to Markovitz no master curves were actually formed by Leaderman at that time. Markovitz reports that Tobolsky and Andrews in 1945 were the first to make use of Leaderman's observations to form what are now known as master curves. However, Tobolsky also introduced a vertical shift in his relaxation curves so that the individual short-time curves would superpose at long times.

Since 1945 many investigators have studied the effects of temperature on creep and relaxation utilizing TTSP. The method has met with such success that the influence of other factors such as humidity and stress level have also been investigated in a similar manner. Most of this work has been performed on amorphous polymers and only more recently have Brinson et al (1978), Morris et al (1979), Yeow et al (1979), Crossman et al (1978), Kibler (1979), and others applied TTSP to composites. This chapter will utilize the homogeneous isotropic relationships used for amorphous polymers because of their inherent simplicity. TTSP is often associated with linear viscoelasticity but this is not a requirement as will be discussed later.

Thermorheological Simple Behavior

Central to the study of TTSP is a concept known as thermorheological simplicity. Consider the isothermal creep compliance of a homogeneous linearly viscoelastic solid at temperature, T_o, in terms

of its retardation spectrum (see for example Ferry (1970))

$$D(T_0, t) = D_0 + \int_{-\infty}^{\infty} L(T_0, \ln \tau)[1 - e^{-t/\tau}] \, d \ln \tau \qquad (4\text{-}1)$$

where D = creep compliance for uniaxial tension

D_0 = initial compliance

L = a continuous weighting function or retardation spectrum

T_0 = an arbitrary temperature

τ = retardation time

For a thermorheologically simple material (TSM) it is possible to cal-culate the creep compliance for other temperatures using the same retardation spectrum. For this purpose a temperature dependent time scale shift factor, a_T, is introduced as was shown by Urzhumtsev and Maksimov (1970) and others.

$$D(T, t) = D_0 + \int_{-\infty}^{\infty} L(T_0, \ln \tau)\left[1 - e^{-\frac{t}{a_T \tau}}\right] \, d \ln \tau \qquad (4\text{-}2)$$

Thus the compliance time and temperature dependencies are functions of the spectrum L and the shift factor a_T respectively. The effect of a_T in log time is to merely translate the spectrum distribution left or right.

Additional insight can be gained by the introduction of a reduced time variable ξ which is defined below.

$$\xi = \frac{t}{a_T} \qquad (4\text{-}3)$$

By simple substitution into the previous equation we have

$$D(T,t) = D_0 + \int_{-\infty}^{\infty} L(T_0, \ln \tau)\left[1 - e^{-\frac{\xi}{\tau}}\right] d \ln \tau \qquad (4\text{-}4)$$

or simply

$$D(T,t) = D_0 + \Delta D(\xi) \qquad (4\text{-}5)$$

where $\Delta D(\xi)$ is the transient component of compliance in reduced time. It is worth noting that once $\Delta D(\xi)$ is known, the compliance for any temperature may easily be calculated. This is particularly obvious when one takes the log of both sides of equation (4-3).

$$\log \xi = \log t - \log a_T \qquad (4\text{-}6)$$

Thus the $\log \xi$ scale may be transformed into the $\log t$ scale by adding the log of the shift factor a_T. It should be kept in mind that the initial component of compliance, D_0, may be a function of temperature. If so, then the assumptions necessary for a TSM do not apply.

Master Curve Formation for a TSM

Thus far the phenomenon of TSM behavior has been described; however, the actual procedure for the formation of master curves has not been discussed. The TTSP formation process is compactly shown in the example of Rosen (1971), shown in Figure 4-1. In this instance the log of short term relaxation data was first plotted versus log time. Due to the drastic change in modulus over the range of temperature studied, the log of the modulus was plotted. However, as explained later in this paper it is sometimes desirable to plot the viscoelastic function on a linear scale. Before shifting can be accomplished, a reference temperature must be selected as indicated in Figure 4-1.
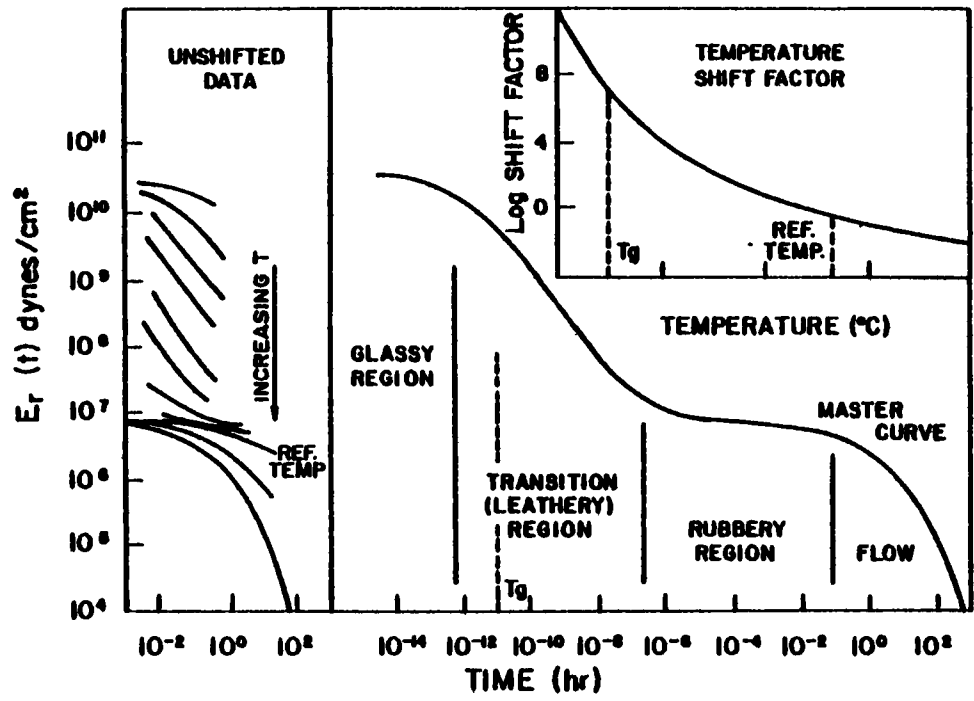
Figure 4-1. TTSP formation process as given by Rosen (1971).

The unshifted short-term data shown on the left of Figure 4-1 was translated horizontally with respect to the reference temperature to form the smooth master curve shown on the right. The amount each curve was shifted represents the log of the previously described shift factor. Naturally, log a_T for the reference temperature is zero. The relationship between log a_T and temperature for these data is also shown in Figure 4-1. Consistent with the use of the shift factor thus far, a shift to the left represents a positive shift. This convention is not accepted universally and it should be noted that in Russian literature a shift to the right is considered positive. For the latter case, equation (4-3) must be modified to be,

$$\xi = t\, a_T' \qquad (4\text{-}7)$$

where

$$a_T' = \frac{1}{a_T} \qquad (4\text{-}8)$$

and a_T' is the alternate shift factor. There seems to be no advantage of either convention.

Thermorheologically Complex Materials

Often the pure translation or horizontal shifting procedure described above fails to provide a smooth master curve for all of the data. It is not uncommon to experience difficulty at either end of the temperature range, i.e., the glassy range or the rubbery range. For these situations an additional vertical shift may be required for a smooth master curve. In the event that a vertical as well as a horizontal shift is required to produce a smooth master curve, the

material is said to be thermorheologically complex. Vertical shifting is often associated with environmental (temperature, humidity, etc.) effects and may also be associated with the stress dependent effects of nonlinear viscoelasticity. The present discussion will be confined to the linear range and vertical shifts required are other than those associated with stress. Schapery (1974) describes several thermorheologically complex materials (TCM) he derived from thermodynamic considerations which he refers to as types 1 and 2.

Type 1: A type one material is made up of two or more viscoelastic components which have different shift factors. This type is not of interest at present since graphite/epoxy contains only one viscoelastic component.

Type 2: A type two material has the following creep compliance in reduced time,

$$D(T,t) = D_0(T) + \Delta D(\xi)/a_g(T) \qquad (4-9)$$

where $D_0(T)$ = initial component of compliance now a function of temperature

$a_g(T)$ = a new (vertical) shift factor, also a function of temperature

$\Delta D(\xi)$ = transient component of compliance in reduced time.

Master curves can easily be formed for this latter type material when the initial value of compliance $D_0(T)$ can be subtracted from the total. For these cases the transient compliance should be plotted using both vertical and horizontal log scales. The data can then be shifted horizontally and vertically for the best fit. When a vertical

log scale is used the amount of vertical shift required represents
log a_g and the horizontal shift log a_T. Of course, after master curve
formation both shift factors would be required to position the master
curve relative to the reference temperature for use at any other
temperature.

The measurement of the initial creep compliance, $D_0(T)$ in the
transition and rubbery regions is often experimentally difficult.
One reason that $D_0(T)$ is difficult to measure is that practical creep
testing requires the application of the load over a small interval of
time instead of instantaneously. (An instantaneously applied load
would lead to undesirable impact or dynamic effects.) For these condi-
tions, the first data point used for the estimation of $D_0(T)$ should be
obtained at a time large compared to the duration of load application.

When $D_0(T)$ is not known accurately, it may be desirable to plot
$D(T,t)$ on a linear scale. If a good or smooth master curve can be
formed by first vertical shifting $D(T,t)$ on a linear scale, the effects
of $a_g(T)$ are likely small and the master curve may be used for predic-
tion of medium or long-term results. On the other hand, if a smooth
master curve is unattainable in this manner, the effects of $a_g(T)$ are
likely quite large.

Schapery (1974) mentions a special type 2 TCM behavior when
$D_0(T)$ is defined as

$$D_0(T) = D_0(T_R)/a_g(T) \qquad (4\text{-}10)$$

where T_R = reference temperature.

A simplified form of the compliance is now obtained where

$$D(T,t) = [D_o(T_R) + \Delta D(\xi)]/a_g(T) \qquad (4\text{-}11)$$

The total compliance may again be plotted on a log scale. Vertical shifting is still required, however, the master curve in these situations represents the total compliance and not just the transient component. Unfortunately, the functional nature of the compliance is usually not known a priori. This necessitates trying several methods to obtain the smoothest master curve.

Normalization Procedures

As might be expected, a number of different manipulations appear in the literature for the formation of master curves. They involve vertical adjustments to the data prior to horizontal shifting similar to those described in the preceding section. This procedure is called normalization. In this paper we have elected to refer to all materials requiring normalization as TCM. A number of investigators including Markovitz (1975) and Urzhumtsev (1975) have referred to materials requiring certain types of normalization as TSM.

A number of normalization procedures have been tried on various polymeric and metallic materials. Most of these procedures are reviewed in a paper by McCrum and Pogany (1970). In their paper the creep compliance in shear of an epoxy resin was studied at temperatures varying from the glassy to the rubbery range. The need for vertical shifting has already been described in the preceding discussion of TCM. In general, the greatest problems in forming master curves are encountered in the low temperature glassy region and the high temperature rubbery region and in these areas proper

normalization can have the most significant impact. A normalization procedure is intended to account for all required vertical correction. Thus, the raw short-term data is adjusted (normalized) prior to horizontal shifting, and master curves are subsequently formed by horizontal movement only.

McCrum and Pogany (1970) report that the first normalization is due to Tobolsky and Ferry who independently applied the procedure. The basis of the technique comes from the theory of rubber elasticity and is described in some detail by Ferry (1970). Rubber in general and polymeric materials in their rubbery range (above the T_g) become stiffer at higher temperatures. As expected, higher temperatures are associated with faster viscoelastic response (shorter retardation and relaxation times). However, the limiting values of creep compliance and relaxation modulus at long times surprisingly decrease and increase respectively with increasing temperature. For this reason, without a vertical correction (normalization), short term curves in the transition (leathery) and rubbery temperature range cannot be shifted to form a smooth master curve.

For the sake of reference, McCrum and Pogany (1970) first attempted to shift their experimental data horizontally as Leaderman had suggested without any vertical normalization (a vertical log compliance scale was used). Had the material been of the TSM type, the horizontal shifting would have provided a smooth master curve. However, McCrum and Pogany found a rather poor master curve was obtained at both temperature extremes.

In order to test the Tobolsky-Ferry method of normalization the compliance data was first shifted vertically by a factor of $\frac{T \, \rho}{T_o \, \rho_o}$. Thus the plotted data was prepared as follows

$$D_p(T,t) = \frac{T \, \rho}{T_o \, \rho_o} D(T,t) \qquad (4\text{-}12)$$

where $D_p(T,t)$ = the plotted data prior to horizontal shifting

T = absolute temperature of test

ρ = density at test temperature T

T_o = absolute reference temperature

ρ_o = reference density at temperature T_o

The effects of density change are small for most polymer systems and are often neglected. After shifting, McCrum and Pogany found that the high temperature data did indeed form a good master curve as one would expect due to the theory of rubber elasticity. However, they found the fit in the glassy region to be worsened by the normalization. Ferry (1970) and others have also witnessed this behavior. The lack of fit in the glassy region was attributed to the temperature dependence of the initial value of compliance, $D_o(T)$, which in the glassy region increases with increasing temperature. The correction for rubbery behavior, $\frac{T \, \rho}{T_o \, \rho_o}$, has the opposite sense, so one would expect divergent curves in the glassy region when working with the total compliance.

McCrum and Pogany (1970) also investigated what they termed the Ferry-Fitzgerald approach due to Ferry and Fitzgerald (1953). With this normalization technique the Tobolsky-Ferry procedure is retained, however, it is only applied to the transient component of compliance. Thus we have

$$D_p(T,t) = D_0(T) + (D(T,t) - D_0(T))\,\frac{T\,\rho}{T_0\,\rho_0} \qquad (4\text{-}13)$$

where all variables have been previously defined. Intuitively one can see from equation (4-13) that the effect of normalization is now minimal at low temperatures where the transient component is small. At high temperatures the initial compliance is small relative to the transient component and the procedure approaches the Tobolsky-Ferry technique. Thus, this technique would provide a smooth master curve in the rubbery range, but still very little assistance in the glassy range. McCrum and Pogany did not actually apply this technique to their data.

Kê (according to McCrum and Pogany) performed a number of creep experiments on aluminum and successfully formed master curves by first dividing the total compliance by the initial compliance at each temperature. Thus the plotted data took the form

$$D_p(T,t) = D(T,t)/D_0(T,t) \qquad (4\text{-}14)$$

where all variables are previously defined. McCrum and Pogany found this procedure to give a smooth master curve in the glassy region; however, the resulting master curve in the transition and rubbery range was poor.

Thus far all of the techniques described have had certain limitations. The unnormalized Leaderman approach incorrectly assumed no temperature dependent effects at either end of the spectrum. The Tobolsky-Ferry approach incorrectly assumed that both extremities were similarly affected. The Ferry-Fitzgerald technique ignored any

temperature dependence in the glassy region, and the Kê procedure assumed some common form of dependence at both temperature extremes. It should be restated that these procedures failed to work for McCrum and Pogany (1970) on a particular cross linked eposy over a wide range of temperatures. This is not to say these normalization techniques are inapplicable for other polymer systems or smaller temperature ranges as previously discussed.

In order to remove some of the above restrictions McCrum and Morris (1964) proposed a normalization technique that could account for the opposite type of temperature dependence in the glassy and rubbery range. McCrum and Pogany (1970) also applied this technique to their experimental data. To apply the McCrum-Morris method of normalization the data is adjusted as shown below

$$D_p(T,t) = \alpha \frac{D_0(T_0)}{D_0(T)} D(T,t) + (1 - \alpha) D_0(T_0) \qquad (4\text{-}15)$$

where

$$\alpha = \frac{(D_\infty(T_0)/D_0(T_0)) - 1}{(D_\infty(T)/D_0(T)) - 1}$$

where $D_\infty(T)$ = the limiting value of compliance at long time. This type of normalization has the proper type of correction at both temperature extremes. McCrum and Pogany (1970) not surprisingly were able to get a smooth master curve over the entire temperature range using the McCrum-Morris technique. The method has the distinct disadvantage of requiring both values of limiting compliance $D_0(T)$ and $D_\infty(T)$; except in rare cases these data are not easily attainable. In the case of McCrum and Pogany, $D_0(T)$ was estimated from the first data

point at ten seconds. However, this estimate becomes increasingly discrepant at higher temperatures. McCrum and Pogany further assumed that the long time dependence of $D_\infty(T)$ on temperature would be of the Tobolsky-Ferry type. There is little reason to believe this to be so in the glassy region. Nonetheless, the master curve provided by McCrum-Morris normalization was relatively smooth. Of primary interest here is McCrum and Pogany's observation that all the techniques yielded similar shift factors as a function of temperature. They do not show a comparison of results--and our opinion is that their contention would be doubtful in the glassy region. It should be kept in mind that, in all normalizations applied by McCrum and Pogany, the vertical scale was the log of the compliance. This provides a decided advantage when the master curve is used to provide a compliance curve for an arbitrary temperature. With such a scale a multiplicative correction can be made through a vertical translation. When a linear scale is used a multiplicative adjustment must be made point by point. Thus, when a normalization technique is being applied, and the data will be used graphically, it is easier to use a vertical log scale.

In the process of gathering the above information on the TTSP the authors were left in a state of wonder as to the best procedure for making master curves. In general, normalization in the glassy and rubbery regions would be difficult due to the previously mentioned inability of applying an instantaneous load and measuring a valid instantaneous compliance, $D_0(T)$. It was realized this problem would be especially true for graphite/epoxy laminates. An alternate procedure which would overcome the above difficulty would be to <u>shift the</u>

short term data both vertically and horizontally for a visual best fit.
This process will be referred to as "graphical normalization." It
will be recalled by the reader that such a procedure was alluded to in
the discussion of TCM. Furthermore, such a technique was also tried
by McCrum and Pogany (1970). While it did not give identical results
to the McCrum-Morris approach they comment, "There is little to choose
between the temperature dependence of log a_T determined using the
critique of vertical shift (graphical normalization) on the one hand,
and the McCrum-Morris normalization, on the other." Furthermore,
Schapery (1974) comments in his review, "It is believed that the
graphical shift methods usually will provide the best average material
properties and be easier to apply, especially when the experimental data
are insufficient to determine the limiting values of compliance."

Graphical Normalization

Initially the graphical normalization technique was thought to
be undesirable because too many shifting possibilities would likely be
present over the desired temperature range spanning portions of the
glassy, transition and rubbery regions for the graphite/epoxy material
to be tested. However, it eventually became apparent that smooth
master curves could not be obtained any other way.

Ordinarily, the TTSP is performed on short term experimental
data to form master curves and to determine the accompanying shift
factors as described previously. In the event a smooth master curve
can be formed, the procedure is often assumed valid. Whether or not
the procedure is truly valid can only be ascertained by appropriate

long term testing. The exact vertical and horizontal shifting procedures used in the TTSP method can significantly affect the shape of the resulting master curve. Therefore it was felt appropriate to learn as much as possible about shifting parameters and scaling procedures by performing a graphical experiment.

Consider the hypothetical case where the master curve and shift factors are known a priori. In such a case one can simulate short term experimental data for different temperatures using the master curve and corresponding shift factors. Bear in mind that such a situation is purely hypothetical. The different TTSP procedures can now be applied to the simulated short term data. If a particular procedure flawlessly produced the original master curve and shift factors used to simulate the short term data, then it would be fair to assume the procedure to be correct. On the other hand, in the event a procedure produced a master curve and shift factors at variance with their original hypothetical counterparts, the procedure would have failed. Of course one could not expect perfect agreement, but it seems reasonable to expect agreement within 10-15%. In order to learn the maximum amount from the graphical experiment the effects of initial compliance, a_T, and a_g were studied individually and in combination.

The experiment was also designed to study the effects of linear vs. log scales for plotting the viscoelastic functions. Schapery's type two TCM was chosen at the material model, and is restated below.

$$D(T,t) = D_o(T) + \Delta D(\xi = t/a_T)/a_g(T) \qquad (4-9)$$

As a first step, values and functions had to be selected for the various unknowns on the right hand side. A range of three temperatures was selected for the initial compliance, $D_0(T)$, horizontal shift, $a_T(T)$ and vertical shift and $a_g(T)$ distributions. Additional temperatures could have been used; however, it was thought that the superposition of three curves would provide adequate insight. The relative magnitudes and variations of each function was guided by experimental data and judgment to prevent domination by any one term. Very little was known about $a_g(T)$ so its variation was chosen to be of the same order as the variation in $D_0(T)$. A transient creep function $\Delta D(\xi)$ was also required. Schapery (1969) and Lou and Schapery (1971) have shown the transient component of creep compliance for composites to be a power law in reduced time. A power law dependence has also been observed by many others for amorphous polymers and appears valid for graphite/epoxy. The form shown below was selected for $\Delta D(\xi)$.

$$\Delta D(\xi) = C\ \xi^n \tag{4-16}$$

The constants that were used were not chosen to be representative of any given material but merely to display typical behavior. The following values were used:

	T_0	T_1	T_2
D_0	2.0×10^{-6}	2.1×10^{-6}	2.2×10^{-6}
a_g	1.00	1.05	1.10
a_T	1.0	.5	.25

with $C = .2 \times 10^{-6}$ and $n = .25$.

A number of different cases were run in order to extract the most information. Each case was tested using a vertical log scale, a vertical linear scale, graphical normalization, and, if possible, horizontal translation only. The following list enumerates the cases considered:

Case 1. $D_p(T,t) = D_0(T) + \Delta D(\xi)$

Here a_g was assumed equal to 1.0 for all temperatures.

Case 2. $D_p(T,t) = D_0 + \Delta D(\xi)/a_g(T)$

D_0 was assumed equal to 2.0 for all temperatures.

Case 3. $D_p(T,t) = D(T,t) - D_0(T) = \Delta D(\xi)/a_g(T)$

In this case it was assumed that $D_0(T)$ was known and hence the transient compliance could be studied directly.

Case 4. $D_p(T,t) = D_0(T) + \Delta D(\xi)/a_g(T)$

In this case all the distributions were used.

Case one was conducted to determine the effects of initial compliance. Both linear and log scale representations gave excellent master curves using graphical normalization. However, the linear scale representation provided the exact shift factors while the log scale provided somewhat reduced shift factors as shown in Figure 4-2. The vertical shifts required were very nearly identical (for comparison's sake the antilog was used for the log scale case). It was completely impossible to obtain a master curve using pure horizontal translation of the curves. This would lead one to believe that effects of initial compliance are best handled by graphical normalization, preferably with a linear scale where vertical movement represents
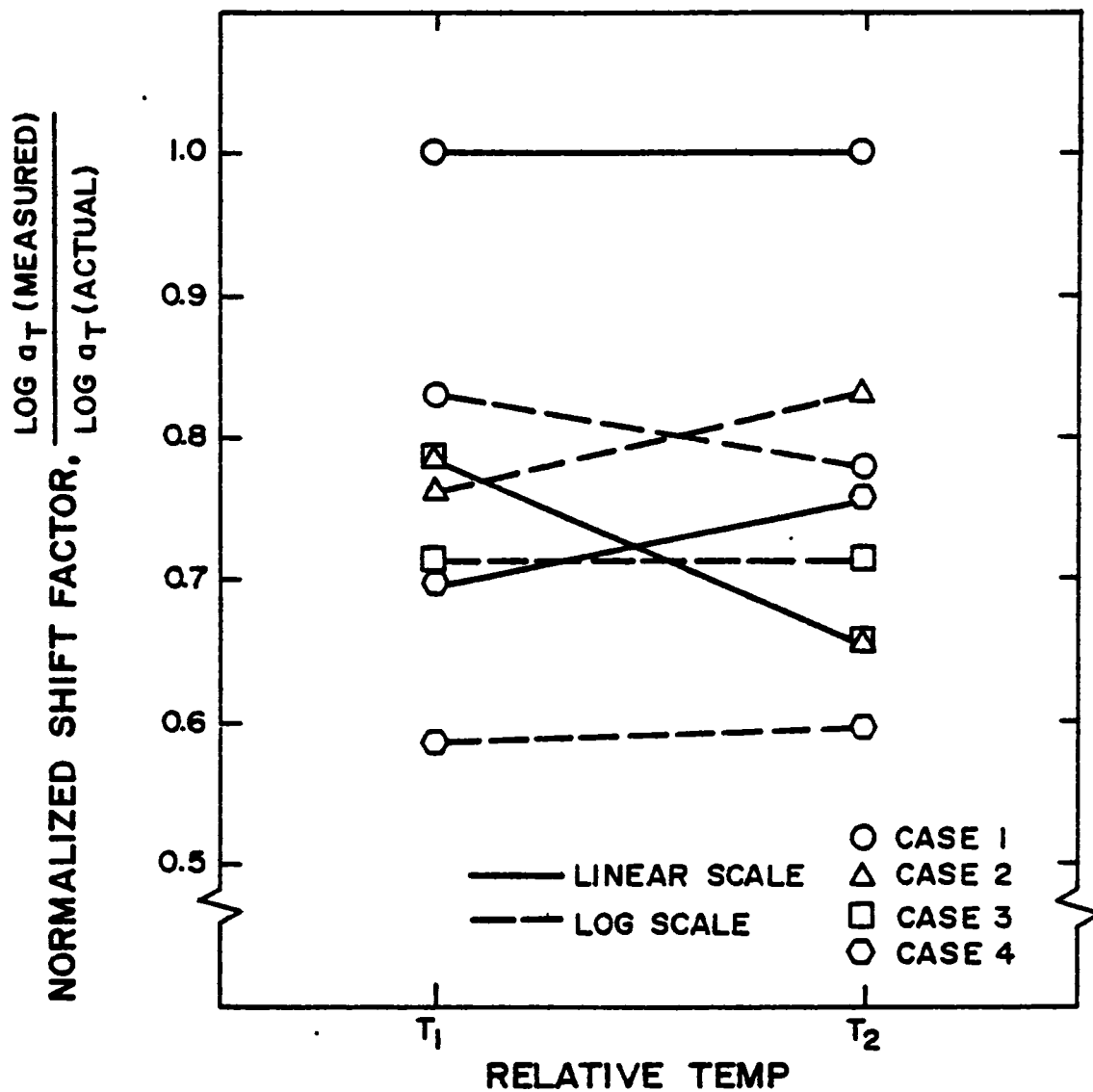
Figure 4-2. Comparison of normalized temperature shift factors
obtained from graphical experiment.

subtraction or addition. The problems encountered when dealing with variations in initial compliance can best be shown by Figure 4-3. Shown in the figure is a portion of a hypothetical master curve and a single hypothetical short term test which was used to form the master curve. When a horizontal translation, log a_T, is applied to the short term curve (moving it from AB to CD) it can be seen that perfect alignment is not attained. However, when a somewhat smaller horizontal shift, log a_T', to EF is applied, a small vertical shift, Δ, to GH may be used to attain a perfect fit.

Case two was conducted to determine the effects, if any, of the $a_g(T)$ shift factor. Master curves of good quality were obtained for both vertical scales with and without graphical normalization. As was anticipated, graphical normalization with a vertical log scale gave the best shift factors. However, the amount of vertical shifting was very small. The shift factors obtained are again shown in Figure 4-2. It was somewhat perplexing that all four master curves (cases 1 and 2, linear and log) were nearly identical; however, the shift factors were somewhat different. This is in direct contradiction to McCrum's and Pogany's (1970) observations.

Case three was investigated to determine the effects of working with net compliance. As one would expect, the linear scale provided the same information as in case two since the subtraction of D_0 just moved all the curves vertically. However, the log scale results were somewhat surprising and can best be described by examination of the equations. Rewriting equation (4-9) in terms of net or transient compliance gives
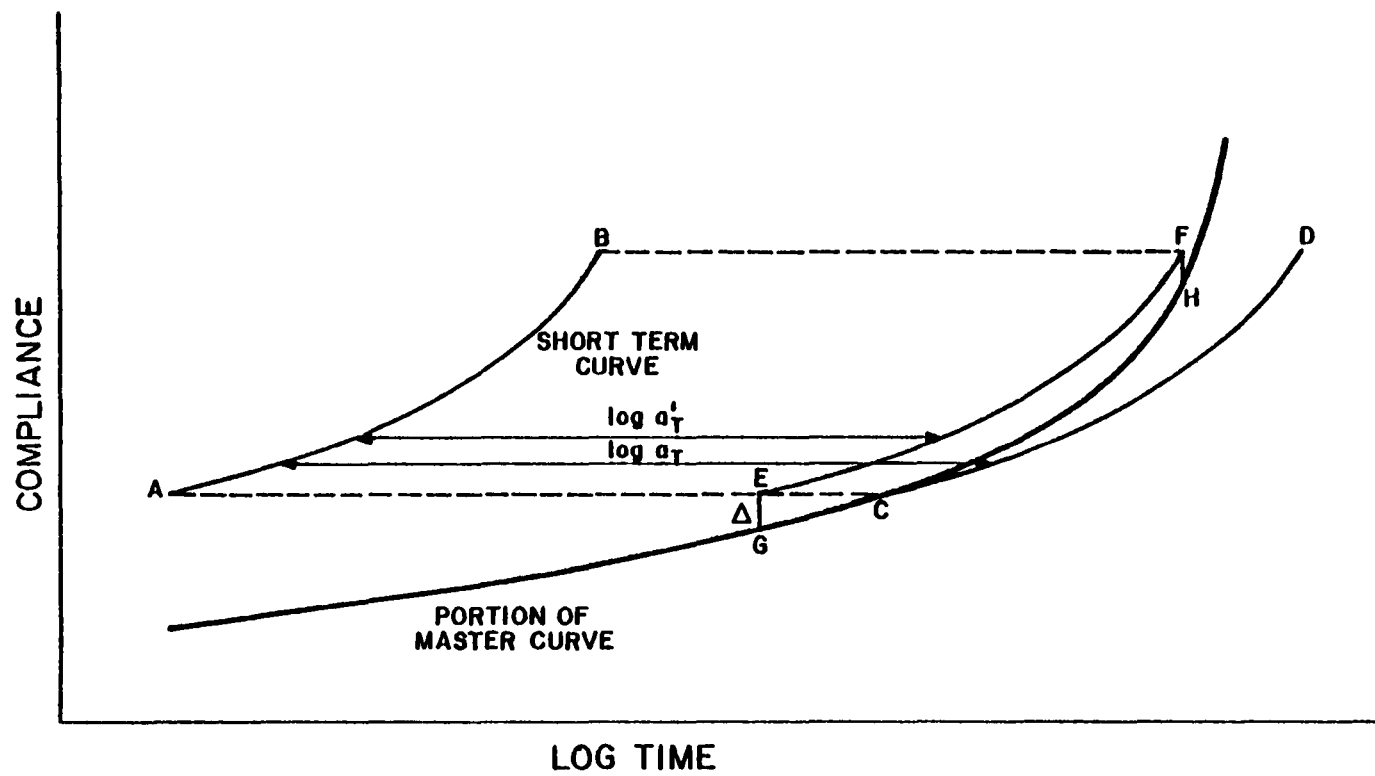
Figure 4-3. The nature of vertical shifting to compensate for change in initial compliance.

$$D(T,t) - D_0(T) = \Delta D(\xi)/a_g(T) \tag{4-9}$$

Inserting the assumed power law in reduced time into (4-9) yields

$$D(T,t) - D_0(T) = C\left(\frac{t}{a_T}\right)^n /a_g(T) \tag{4-16}$$

Taking the log of both sides yields

$$\log \text{(net compliance)} = n \log t + \log C - n \log a_T - \log a_g \tag{4-17}$$

It can be seen from equation (4-17) that the log of net compliance can be plotted as a straight line vs. log t with slope n. Further, all temperatures will plot as a family of parallel lines, whose vertical separation is due to both a_g and a_T. The problem arises when one attempts to isolate a_g and a_T. A master curve can easily be obtained since there is no difficulty shifting parallel straight lines to form a single straight line. However, the effects of a_T and a_g are indistinguishable from one another. Closer examination of this feature reveals that no error is introduced by such an ambiguity and that a_g should be considered equal to one for all temperatures for maximum extrapolation power. As before, the shift factors are shown in Figure 4-2.

Case four was investigated to determine the usefulness of the shifting techniques for a general TCM. It was found that graphical normalization gave good master curves on both linear and log scales. Due to the effect of $D_0(T)$, master curves could not be formed by pure translation with either scale. Results of the shift factors are shown in Figure 4-2. As can be seen both methods underpredict the true values. The vertical shift factors were again nearly identical.

For Case 1 it was concluded from the above investigation that graphical normalization is indeed required for master curve formation when one is dealing with changes in initial compliance. For the other cases and for the range of $a_g(T)$ studied it can also be concluded that graphical normalization is not required for master curve formation, however pure translation gives slightly different results and both techniques yield a_T shift factors at variance with those in the equation used to generate the creep curves. In fact, in only one case were shift factors exactly determined. This is probably not as serious as it sounds however, since the actual master curves generated in all the procedures were quite similar. This may indicate greater difficulty in using a master curve to estimate short times at high temperature than long times at low temperatures.

The difficulties surrounding the formation of master curves points to the need of at least partial validation through long-term experiments. Unfortunately, many master curves in the literature have not undergone the rigors of long-term testing. A long-term test need not cover as many decades as the master curve for reasonable validity. Furthermore, according to Krokosky (1967) within the linear range of viscoelasticity all viscoelastic functions are said to have the same shift factor. Thus, when the shift factor is verified for one function it might not need to be checked for another.

The Nature of Log a_T
_____

Before discussing other types of superposition the nature of log a_T as a function of temperature should be discussed. In a very

important paper, Williams, Landel and Ferry (1955) introduced what is commonly known as the WLF equation.

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + T - T_0} \qquad (4\text{-}18)$$

It was noticed by these investigators that nearly all materials had a similar temperature dependence of $\log a_T$. Furthermore, when a reference temperature, T_r, was selected 50°C above the primary glass transition temperature, T_g, the constants C_1 and C_2 had universal values of 8.86 and 101.6 respectively for many materials. In general these values of C_1 and C_2 have not been found valid for the various composite systems studied. Furthermore, the WLF equation is generally only valid above the T_g (generally to T_g + 100°C). For a further description of the WLF equation and derivation of its form see Ferry (1970) or Arridge (1975). Below the T_g creep is said to be a rate activated process and hence subject to kinetic rate theory. In this region relaxation and retardation times, τ, are governed by the Arrhenius equation shown in equation (4-19).

$$\tau = \tau_0 \, e^{\frac{\Delta H}{RT}} \qquad (4\text{-}19)$$

where

    τ = relaxation time

    τ_0 = a constant

    ΔH = an activation energy (often assumed to be a constant for a given material)

R = universal gas constant

T = absolute temperature

As shown by Arridge (1975) and Ferry (1970) this results in a different
form for the shift factor as given by,

$$\log a_T = \frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_R}\right] \tag{4-20}$$

where T_R = a reference temperature often chosen as the T_g.
Regardless of whether one is working above or below the glass transi-
tion, one is well advised to determine the shift factor, a_T, empirical-
ly by curve shifting in lieu of using equations (4-19) and (4-20).

Combined Superposition in Linear Viscoelasticity

Temperature is not the only variable that speeds up viscoelastic
response. Other common accelerating effects include moisture,
oscillating load, and stress level. The presence of solvents may also
cause a similar effect by plasticizing the matrix material. Stress
effects will not be considered here since they are nonlinear by nature.

The effects of humidity on the superposition principle have
been studied by many people including Maksimov et al. (1972),
Urzhumtsev et al. (1970), and Wang and Liu (1975). In addition the
combined effects of temperature and humidity have been studied by
Crossman and Flaggs (1978), Maksimov et al. (1975, 1976), Renton and
Ho (1978) and Kibler (1979). Often times a composite is subjected to
two or more accelerating factors simultaneously. Temperature and
humidity are of particular interest because both effects can occur
within the regime of linear viscoelasticity.

For hygrothermalrheologically simple materials, HTSM, the creep compliance should have a functional dependence as given below.

$$D(T,H,t) = D_0 + \Delta D(\xi) \qquad (4-21)$$

where reduced time ξ is now

$$\xi = \frac{t}{a_T\, a_H} = \frac{t}{a_{TH}} \qquad (4-22)$$

and is a function of the product of shift factors for temperature and humidity which may be thought of as a combined shift factor, a_{TH}. Master curves for such materials may be formed in several ways. For the sake of discussion assume that the collection of data is complete and that a family of creep compliance curves have been plotted vs. log time as shown in Figure 4-3. Each curve has a particular temperature and humidity level associated with it. A reference temperature and humidity level must be selected for curve formation. All the remaining curves would then be moved horizontally (as will be recalled no vertical shift is required for simple materials) to form a master curve. The amount of shift in each case represents log a_{TH}. The individual values of log a_{TH} for all values of temperature and humidity can easily be shown as a shift surface. Such a surface produced by Crossman and Flaggs (1978) for stress relaxation of a ± 45° laminate is shown in Figure 4-4.

Master curves for HTSM's could also be formed in other ways as well. It seems that with sufficient data one could form master curves for humidity at constant temperature and for temperature at constant humidity. This procedure would provide log a_H and log a_T as functions
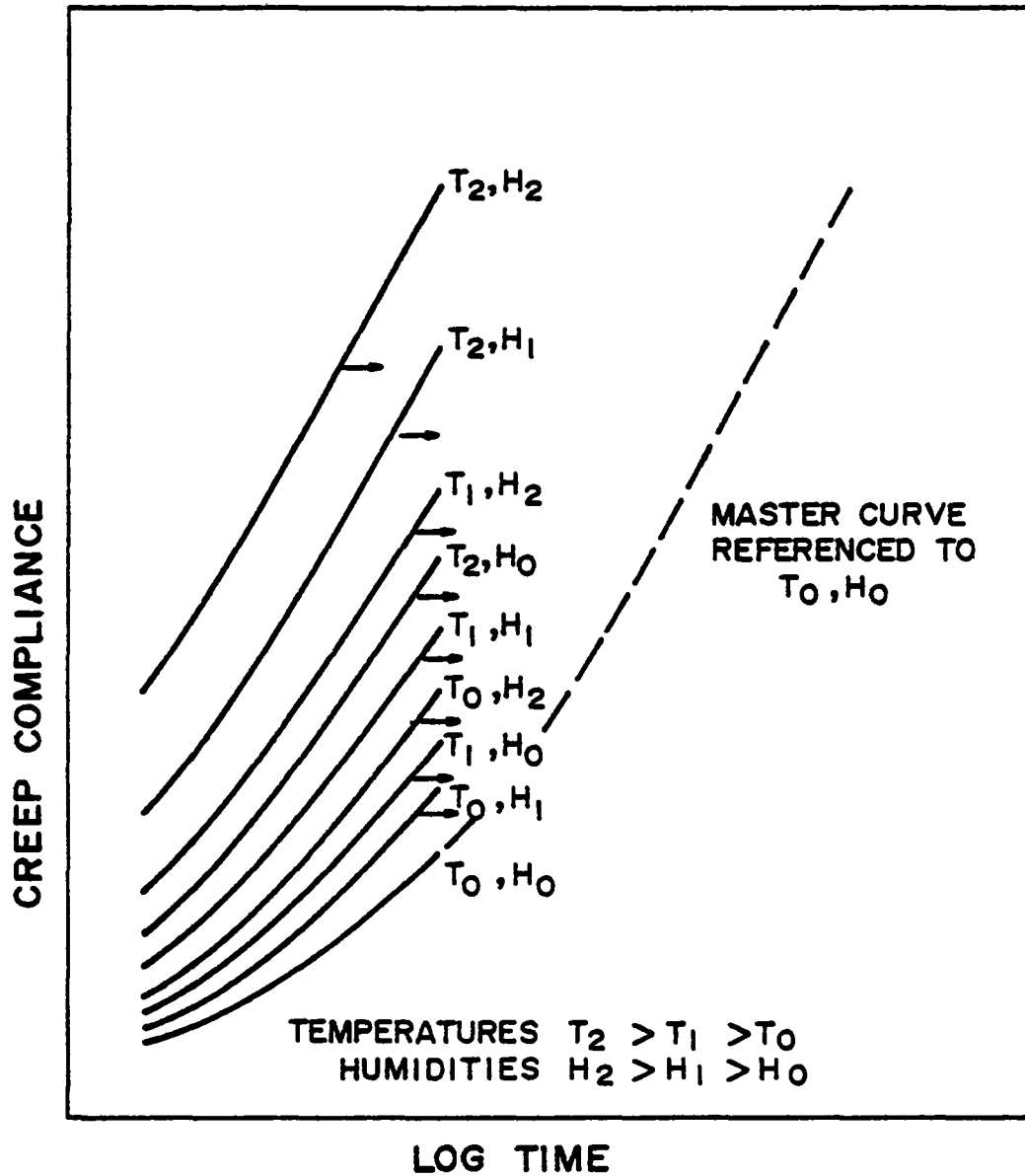
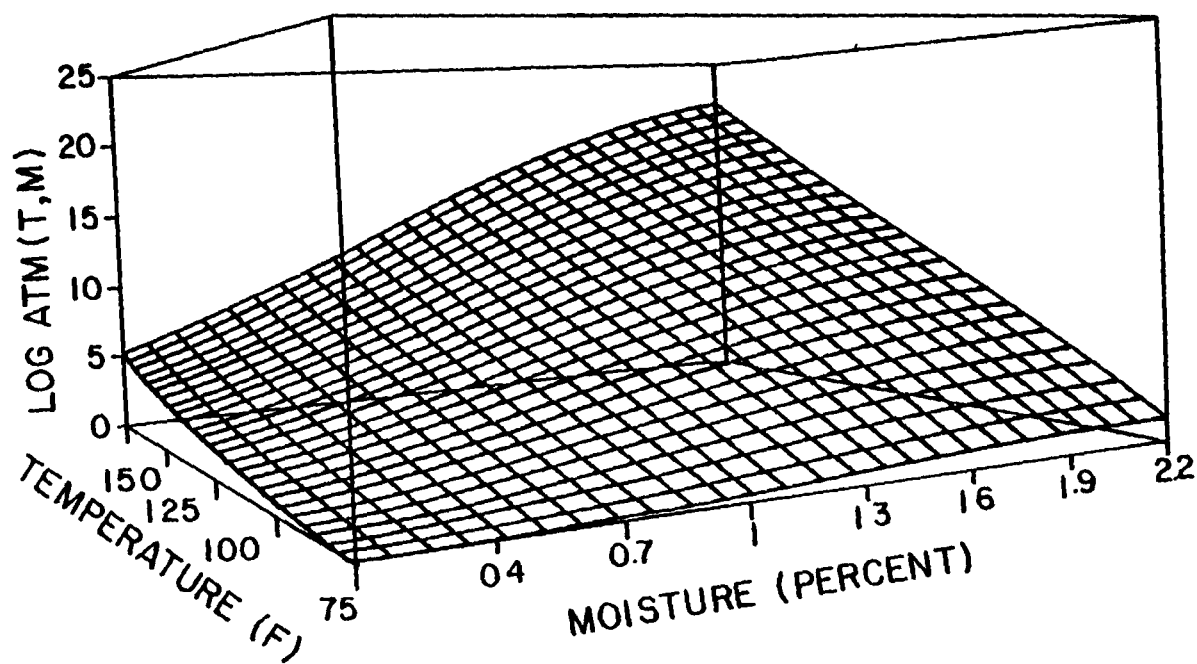Figure 4-4. Combined temperature-humidity creep compliance master curve formation referenced to T_o, H_o.

Figure 4-5. Combined temperature-humidity shift surface of Crossman and Flaggs (1978) obtained for stress relaxation of a ± 45° cross ply laminate.

of temperature and humidity. The combined shift factor could then be found by adding the appropriate shift factors as shown.

$$\log a_{TH}(T_i, H_i) = \log a_T(T_i, H=const) + \log a_H(H_i, T=const) \quad (4-23)$$

where the subscripted values are used to imply the dependencies. Obviously, the _primary_ dependencies of a_T and a_H remain temperature and humidity respectively. A combined master curve, sometimes called a unified curve, could then be formed by applying the shift factor $\log a_{TH}$ to the individual creep curves. The combined master curve obtained in such a way should carry with it greater credibility in the event it was smooth. Alternatively, one could create master curves at constant humidity as previously described, and then shift the entire master curves for superposition. Of course, this procedure could also be done with the family of constant temperature master curves.

Four ways of combining the effects of temperature and humidity have been described. The authors believe that all these techniques are equivalent for a HTSM. The shifting procedure is much less obvious for a hygrothermalrheologically complex material (HTCM). In these cases the following form for compliance is proposed.

$$D(H,T,t) = D_0(H,T) + \Delta D(\xi)/a_g(H,T) \quad (4-24)$$

It is obvious that vertical shifting would be required in this case to form a master curve since $D_0 = f(H,T)$. In such cases the method first given for use on HTSM may be the only appropriate method (individual shifting of each curve). If the effects of a_g are small, a linear vertical scale can be used for best results. In the unlikely event the combined dependence of the initial compliance is

$$D_0(H,T) = D_1(H) + D_2(T) , \qquad (4-25)$$

it would seem that any of the other procedures described could be used.

It should be made clear that even when one is not particularly interested in the effects of an accelerating factor, such as humidity, use of the factor for master curve formation may still be desirable. Let us assume that one is attempting to form a predictive master curve for use at 150°C and near dry conditions. Further, suppose that some form of aging, oxidation, or other degradation becomes activated at 200°C. The TTSP is thus limited to a temperature range of only 50°C above the desired temperature, which will probably curtail any extrapolative power of the method. In order to extend the master curve one can introduce humidity as an additional variable. Assuming that the individual curves are shiftable to form a master curve, one need not even measure the shift factors due to humidity, or temperature for that matter. The master curve is all that would be required since it is valid for the reference temperature without shifting. While this procedure is not recommended, it could prove useful for making quick estimates.

Linear Viscoelasticity with Changing Environment

In Chapter III the constitutive equations for isothermal linear viscoelasticity were presented. These equations can be further modified to account for various states of constant temperature by the introduction of reduced time as shown below.

$$\varepsilon_{ij}(t) = \int_0^t S_{ijk\ell}(\xi - \xi') \frac{d\sigma_{k\ell}}{d\tau} d\tau \tag{4-26}$$

where

$$\xi = \frac{t}{a_T} \quad \text{and} \quad \xi' = \frac{\tau}{a_T} \quad \text{and} \quad T = \text{const.} \tag{4-27}$$

Morland and Lee (1960) extended these equations to the transient case for a TSM by merely changing the form of reduced time to

$$\xi = \int_0^t \frac{d\eta}{a_T} \quad \text{and} \quad \xi' = \int_0^\tau \frac{d\eta}{a_T} \tag{4-28}$$

which provides an averaging effect on reduced time. In the same manner other accelerating factors can be introduced in the linear theory by merely modifying reduced time appropriately. Thus, in general the reduced time will take on a generalized form utilizing all the accelerating factors required.

$$\xi = \int_0^t \frac{d\eta}{a_T \, a_H \, \cdots} \quad \text{and} \quad \xi' = \int_0^\tau \frac{d\eta}{a_T \, a_H \, \cdots} \tag{4-29}$$

Equations (4-26) and (4-29) thus provide constitutive laws for any TSM with varying environment. In this paper e_{ij} has consistently been reserved for mechanical strain, i.e., strain due to stress. For completeness, the following equation gives the constitutive law for the total strain, i.e., mechanical plus thermal strain

$$E_{ij} = \int_0^t S_{ijk\ell}(\xi - \xi') \frac{d\sigma_{k\ell}}{d\tau} d\tau + \int_0^t \alpha_{ij}(\xi - \xi') \frac{d\Delta T}{d\tau} d\tau \tag{4-30}$$

where E_{ij} = total strain

α_{ij} = thermal expansion coefficients

ΔT = temperature change from the initial state

Of course the inverse relationships to equations (4-26) and (4-30) exist. It is unlikely that these equations have ever been experimentally verified for the transient case.

Corresponding equations for a HTCM have been suggested by Crossman and Flaggs (1978). In terms of our variables the mechanical strain can be written as

$$\varepsilon_{ij} = S_{ijk\ell}\,\sigma_{k\ell} + \int_0^t \Delta S_{ijk\ell}(\xi - \xi')\,\frac{d}{d\tau}\left[\frac{\sigma_{k\ell}}{a_g}\right]\,d\tau \qquad (4\text{-}31)$$

Crossman and Flaggs (1978) have used an analogous form which includes thermal and moisture expansion strains. Of course similar equations can be written in terms of the contracted notation that is often used in plane stress analysis of laminated composites.

Although equations (4-26) and (4-31) appear formidable, they are relatively simple compared with some of the equations used in nonlinear viscoelasticity. It is important that the user of such equations be cognizant of their range of applicability. Such equations are only rigorously applicable when the effects of stress level are insignificant and the material is nonaging as described in Section III.

V. STRESS EFFECTS AND NONLINEAR VISCOELASTICITY

Materials for which properties are stress dependent are nonlinear
and for such materials the superposition integral of linear visco-
elasticity is not applicable. Stress dependent effects may occur with
or without damage where the latter are often associated with some form
of plasticity, failure or fracture mechanism. In many materials nearly
all nonlinear effects are associated with irreversible damage. However,
for many nonlinearly viscoelastic materials (e.g., elastomers and/or
crosslinked polymers in the rubbery range) the effects of stress may
not induce damage. For this reason only stress dependent effects
which produce no damage will be considered herein.

It is of interest to note that TTSP seems to work well in the non-
linear range. Most references to master curves in the nonlinear range
appear in the Russian literature where Maksimov et al. (1974),
Urzhumtsev et al. (1974a) and Daugste (1974) show similar results.
In all cases examined, the initial response had to be deducted from the
total compliance prior to shifting, due to the stress and temperature
dependence of the former.

Time temperature equivalence in nonlinear viscoelasticity has
also been observed by Morgan and Ward (1971) and Foot and Ward (1972).
In this case reduced time was used in a nonlinear viscoelastic multiple
integral approach. It was found that the same reduced time could be
used in all the integrals and hence the material was said to have been
a TSM even in the nonlinear range of viscoelasticity. It was further

noted that the shift factor for temperature, a_T, was not affected appreciably by stress level over the ranges studied. On the other hand, all the Russian work indicates very definite coupling between stress and temperature. Stress, as will be discussed shortly, may also be regarded as an accelerating factor. Furthermore, the stress level at which nonlinear creep behavior occurs becomes smaller as temperature increases. Thus, as demonstrated by Efimova and Maksimov (1977), one may begin testing in the linear viscoelastic region using TTSP and finish testing with increasingly nonlinear behavior at the higher temperatures. Therefore, the initial accelerating factor may be temperature, while at higher temperatures both accelerating factors are acting simultaneously even though the stress level is held constant. Nevertheless, all of the published Russian master curves are accompanied by long-term tests that for the most part are in good quantitative agreement with the master curves.

Stress Time Superposition

The effects of stress have been studied as an accelerating factor and used to form master curves for nonlinearly viscoelastic materials by a number of investigators. This effect is usually known as stress time superposition or stress time analogy. In the Russian literature, Urzhumtsev and Maksimov (1970) or Daugste (1974) for example, the net creep compliance is used for curve formation. Thus, only horizontal shifting on a log time scale was required, and a linear vertical compliance scale was used. Cessna (1971) also formed master curves of creep compliance with a vertical linear scale.

In this case he shifted the individual curves both vertically and horizontally. Cessna attributed the vertical shift as a correction for stress effects on initial response which is exactly the same as that discussed earlier for temperature dependence due to the use of a linear vertical scale. Brody (1969) used only horizontal shifts with a linear vertical scale. However, he generated his creep data from isochronous stress strain curves, so it seems that vertical shifting may have been unnecessary. Bergen (1967) has also introduced stress as an accelerating factor, however his master curve formation was guided by assumed forms for the compliance master curves

The basis for stress time superposition can be viewed in a similar manner to the effects of temperature. As stated by Urzhumtsev (1970), "Time-stress superposition postulates the experimentally verified fact that an increase in stresses in the presence of non-linear viscoelasticity leads to an acceleration of the relaxation processes and a shift of the relaxation spectrum into the region of shorter times." In this vein let us assume a relationship somehwat like that given for a TSM relating compliance to the retardation spectrum.

$$D(T_0,\sigma,t) = D_0(T_0,\sigma) + b_\sigma \int_{-\infty}^{\infty} L(T_0,\sigma_0,\ell n\ \tau)\left[1 - e^{\frac{t}{a_\sigma\tau}}\right] d\ \ell n\ \tau \quad (5\text{-}1)$$

where a_σ = time scale shift factor for stress

b_σ = vertical shift factor for stress

Introducing reduced time

$$\xi = \frac{t}{a_\sigma} \qquad (5\text{-}2)$$

yields

$$D(T_0,\sigma,t) = D_0(T_0,\sigma) + b_\sigma \int_{-\infty}^{\infty} L(T_0,\sigma_0,\ell n\ \tau)[1 - e^{\xi/\tau}]\ d\ \ell n\ \tau \qquad (5\text{-}3)$$

This equation does not appear explicitly in the literature but it can be concluded as reasonable from the work of Urzhumtsev et al. (1968, 1970, 1974a,b). Equation (5-3) suggests that the creep compliance can be written as

$$D(\sigma,t) = D_0(\sigma) + b_\sigma\ \Delta D(\xi)\ . \qquad (5\text{-}4)$$

where all terms are considered at the reference temperature T_0. This equation is analogous to the TCM type II behavior given earlier except now stress has replaced the role of temperature. All of the previously made statements relative to horizontal and vertical shifting and the use of linear and log scales with respect to master curve formation for TCM-2 are still valid. Equation (5-4) may be regarded as a form of isothermal nonlinear constitutive equation for creep compliance. Such an equation is not useful for evaluating other load histories such as ramp loading, multistep, etc., because interrelations among properties for different loading conditions are not generally developed for nonlinear materials.

Schapery's Nonlinear Theory

It is of interest to compare equation (5-4) with at least one
other form of nonlinear characterization. For this purpose we will
use the nonlinear theory of Schapery (1969, 1971). This theory
utilizes a single integral and incorporates the linear transient creep
compliance as the only time dependent function. The theory is
derivable from thermodynamic principles, and its simplicity is a
result of assuming special forms for Gibbs free energy and other thermo-
dynamic concepts. The isothermal stress strain equation for uniaxial
loading is

$$e(t) = g_0 \, D_0 + g_1 \int_0^t \Delta D(\xi - \xi') \, \frac{d(g_2\sigma)}{d\tau} \, d\tau \qquad (5\text{-}5)$$

where $\quad D_0 \qquad$ = initial compliance from linear theory

$\quad \Delta D(\xi) \qquad$ = transient compliance from linear theory

$\quad g_0, g_1, g_2, a_\sigma$ = functions of stress

with

$$\xi = \int_0^t \frac{d\eta}{a_\sigma} \quad \text{and} \quad \xi' = \int_0^\tau \frac{d\eta}{a_\sigma} \qquad (5\text{-}6)$$

being reduced time variables for varying stress similar to that of
Morland and Lee (1960) for variable temperature. Thus all of the
material nonlinearity is introduced by the four functions of stress,
g_0, g_1, g_2, and a_σ. In order to evaluate equation (5-5) for the case of
uniaxial creep we let

$$\sigma = \sigma_0 \, H(t) \qquad (5\text{-}7)$$

and introduce (5-7) into (5-5). Making use of the properties of the Dirac delta function one obtains,

$$e = g_0 \, D_0 \, \sigma_0 + g_1 \, g_2 \, \Delta D(\xi) \, \sigma_0 \tag{5-8}$$

It can easily be seen that (5-8) is in exactly the same form as (5-4) with

$$D_0(\sigma) = g_0 \, D_0 \tag{5-9}$$

and

$$b_\sigma \Delta(\xi) = g_1 \, g_2 \, \Delta D(\xi) \ . \tag{5-10}$$

Thus stress time superposition can be viewed as a special case of Schapery's nonlinear theory. In the event that $\Delta D(\xi)$ is in the form of a power law, which according to Lou and Schapery (1971) is very typical, other observations can be made. Assume that $\Delta D(\xi)$ has the form

$$\Delta D(\xi) = C \, \xi^n \tag{5-11}$$

Upon substitution of (5-11) into (5-8) one obtains

$$e = g_0 \, D_0 \, \sigma_0 + \frac{g_1 \, g_2}{a_\sigma^n} \, C \, t^n \tag{5-12}$$

Equation (5-12) emphasizes the fact that g_1, g_2, and a_σ are not unique functions for uniaxial creep with a power law. Obviously, additional testing is required for unique determination of all the stress dependent functions. Lou and Schapery (1971) show that the easiest approach to define all the functions is to use both creep and creep recovery data. The principal advantage of Schapery's technique is that it is based upon the use of the linear creep compliance which results in a single integral expression.

Schapery's procedure has been successfully used by Cartner, et al. (1978) to model the nonlinear viscoelastic response of an SMC chopped glass fiber/polyester composite.

Combined Effects of Stress and Temperature

Of primary interest here are the combined effects of temperature and stress level. Thus far it has been shown that TTSP is valid within nonlinear viscoelasticity and that stress may be considered an accelerating factor at constant temperature. Why then cannot one use a combined superposition technique to reflect stress level and temperature? One could, for example, add temperature effects to Schapery's nonlinear approach. However, all of the stress dependent functions are also functions of temperature. It is somewhat unclear as to how temperature can be most consistently introduced into Schapery's theory. It is far more convenient for a first attempt to study a much simpler constitutive law. The joint application of TTSP and stress time superposition provides just such a law. We will refer to this procedure as the time temperature stress superposition principle (TTSSP). TTSSP can be thought of in much the same way as the combined superposition of temperature and moisture. The major difference is that the compliance relation obtained in temperature-humidity super-position may in turn be used in the convolution integral to make predictions for varying loads and environmental conditions. To the contrary, the compliance relation generated in the TTSSP may only be used to predict creep behavior under constant load and environment, a very major difference.

The joint application of temperature and stress superposition techniques or the TTSSP method are illustrated schematically in Figure 5-1. It is important to note that the combined procedure has the same inherent shifting difficulties as the TTSP and insight needs to be established for a particular material on the need for vertical shifting procedures as well as whether to use linear or logarithmic vertical scales.

Daugste (1974) appears to be the first in the literature to apply TTSSP. His work was done on 45° off-axis specimens of fiberglass reinforced plastic. Daugste produced master curves for temperature at each stress level, stress at each temperature, and a combined curve for all stresses and temperatures. He found it necessary to work with the net compliance due to the stress/temperature dependence of the initial response. His master curves are reasonable, but they are far from being perfectly smooth. A long time verification test is in good agreement with the master curve. Daugste also documented the cross-sensitivity of temperature on a_σ and stress level on a_T.

In the present work, combined master curves were formed directly without intermediate steps. Vertical translations were used on a linear scale to account for initial compliance variations. Thus, the combined shift factors log $a_{T,\sigma}$ were determined from the amount of horizontal shift required. This method implicitly assumes that the nonlinear creep compliance is of the form

$$D(T,\sigma,t) = D_0(T,\sigma) + \Delta D(\xi) \qquad (5\text{-}13)$$

where $\xi = \dfrac{t}{a_{T,\sigma}}$

a) Data Needed for TTSP

b) Data Needed for TSSP

c) TTSP Master Curves for T_1 at Different Stress Levels

d) TSSP Master Curves for σ_1 at Different Temperature Levels

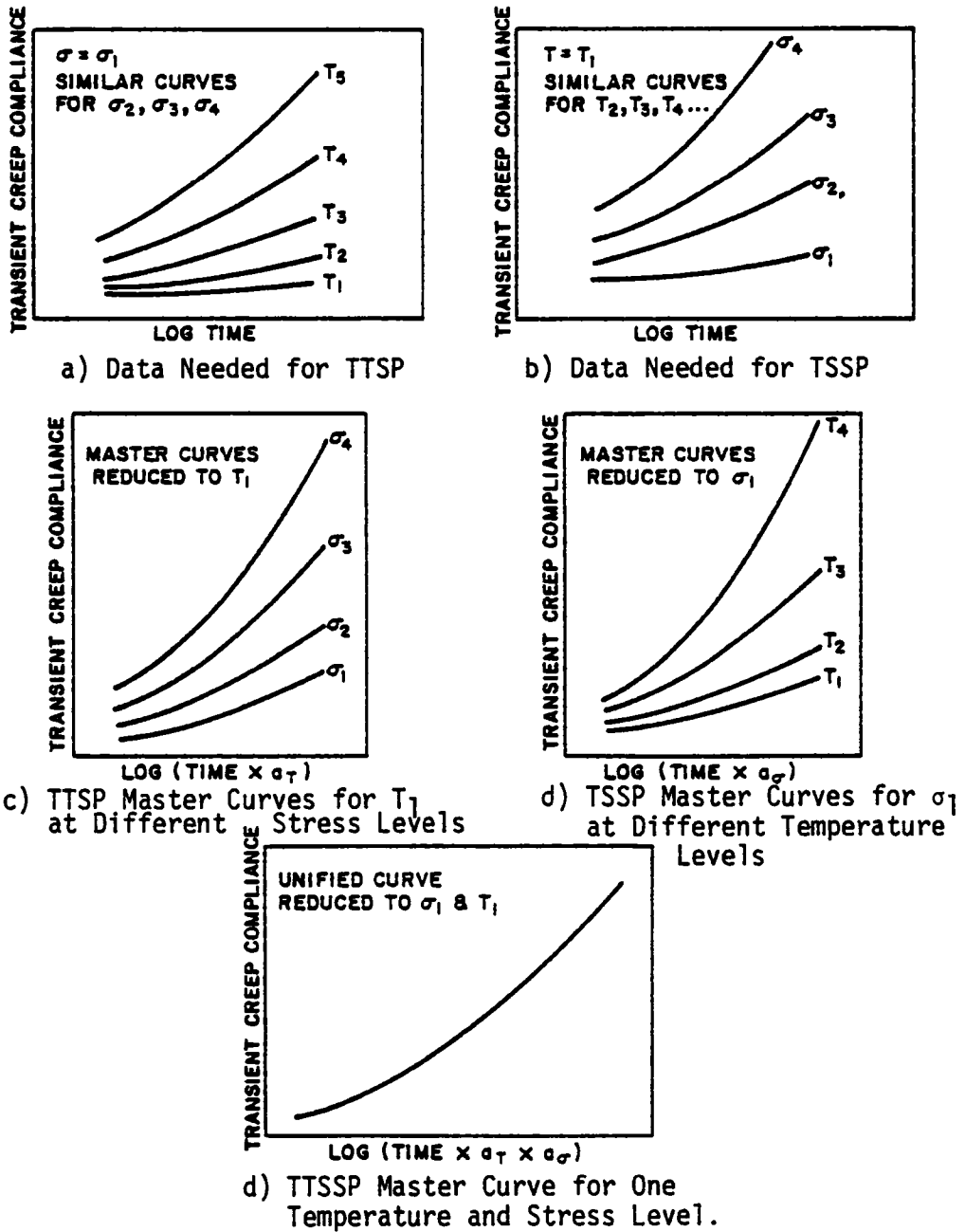d) TTSSP Master Curve for One Temperature and Stress Level.

Figure 5-1. Schematic diagram to illustrate the time-temperature-stress superposition principle (TTSSP).

The absence of a multiplier on $\Delta D(\xi)$, as will be shown, is assumed valid due to the quality of agreement with long term tests and the smoothness of the master curves. In accordance with previous discussion, it was found that a linear vertical scale was best to eliminate the effects of initial response.

In the previous work at VPI & SU the Tobolsky-Ferry normalization procedure was used with a linear vertical scale to produce TTSP master curves for small stress and strain levels such that linear viscoelasticity was not violated.

VI. TIME DEPENDENT FAILURE OF POLYMERS AND COMPOSITES

A time dependent failure is one in which failure does not occur at the time of load application but after the passage of time. Time dependent failures due to mechanical or other loads may be complicated or affected by conditions of environment. Due to the complexity of the effects of a changing environment only a constant environment will be considered herein. Two types of constant environment time dependent failure tests are available to the experimentalist, creep to rupture and relaxation to rupture. The relaxation test has several disadvantages as already mentioned in a previous section. Furthermore, rupture in a relaxation test of the material of interest here is difficult to attain. Therefore, the creep rupture* test was selected for use with graphite epoxy.

Over the years the creep rupture phenomenon has received considerable attention. Until recently much of this work has centered around the phenomena in metals at elevated temperature. More recently polymers have received increasing attention. The literature in the mechanics of polymer fracture has been exhaustively reviewed by Knauss (1973), Regel and Tamuzh (1977) and Maksimov and Urzhumtsev

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*There is no general agreement in the literature on the use of the terms creep rupture and stress rupture. It appears that creep rupture implies measurement of creep strain until rupture, and stress rupture implies measurement of only the rupture time. However, creep rupture is often used to mean stress rupture. Due to the popularity of the term creep rupture it will be used here even though creep strain was not generally measured.

(1977). Due to the viscoelastic nature of polymers, any study of polymer fracture (except at possibly high rates of failure or low temperature) necessarily includes time dependent effects. Time dependent studies of continuous fiber unidirectional composites have been reviewed by Lifshitz (1974). He indicates that the majority of such work has been done on 0° laminates. In such laminates a delayed failure can occur when the fiber itself exhibits time dependent behavior (as in the case of aramid fibers) or if there are sufficient discontinuous fibers, in which case the matrix comes into play. Experimental data for the creep rupture of off axis unidirectional and general laminates is rather sparse at present.

Types of Delayed Failure Investigations

Delayed failures in composites may be studied from several different viewpoints including microfailure, phenomenological, and deformational. Microfailure investigations can include the study of the microscopic or small scale failure mechanisms that progress in delayed failures. Such phenomena as fiber-matrix interfacial failure, matrix crazing, delamination, or other damage formation, are potential areas of study. Microfailure investigations are normally in support of, or to provide insight into, other predictive methods. Phenomenological approaches simply attempt to correlate the measured data with some form of failure law. These techniques are often used to extrapolate into the future so in this sense they may be viewed as accelerated characterization. History has provided a number of such approaches from the study of metals such as the Larson-Miller, Dorn, or

Manson-Haferd parametric methods. In the foreign literature Zhurkov's modified Arrhenius equation also is of the phenomenological type. Such techniques have the disadvantage that tests are required to determine empirical constants prior to prediction even for new orientations of a laminate that has already been studied. Subsequently, the phenomenological approach of Wu (1974,1975) will be discussed which does not suffer from this last requirement. Deformational approaches utilize knowledge of the material response and some criterion for failure. Such theories may consider the macroscopic deformation of the laminate or deformation within the matrix itself via micromechanics theory.

All of the approaches just described have been used here to study the delayed failure of off axis unidirectional and, in some cases, general laminates. Microfailure studies were most limited and consisted of several photomicrographs. The other approaches are described below in greater detail.

Phenomenological Approaches

Of primary interest here is the method that seems to be most often associated with Zhurkov sometimes known as kinetic rate theory. This exclusive association, however, may not be entirely merited. According to several sources (Kargin and Slonimsky (1971) and Stepanov (1975) 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

(1965), Zhurkov first used the relationship to predict rupture times
in 1953. The most common form of the equation is given as

$$t_r = t_o \, e^{\frac{u_o - \gamma\sigma}{KT}} \qquad (6\text{-}1)$$

where

t_r = rupture time

t_o = a constant normally about 10^{-12}

u_o = a constant activation energy

γ = a constant

σ = applied uniaxial <u>true</u> stress

K = Boltzman's constant

T = absolute temperature

In the form originally used by Alexandrov, t_r, represented the relaxation time at stress and temperature levels σ 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. (1976) have even suggested the existence of something called the "kinetic rule of mixtures." Such a relation would seem to be of very dubious merit for a fibrous composite. Outside the USSR the method has received some attention. Chiao et al. (1976, 1977) at Lawrence Livermore 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 (6-1) 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 (1965), Bartenev and Zuyev (1968), or Chiao (1976). A detailed description of the procedure for constant determination will not be given here. However, a description of the character that the data must have is worthwhile. One notices that for a certain stress level, the exponential term in equation (6-1) tends toward one when the quantity $\gamma\sigma$ is equivalent to the activation energy u_0, i.e.,

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

This implies the existence of a so-called pole (common intersection) when log t_r is plotted vs. stress as shown in Figure 6-1. 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 γ, 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 γ by taking the natural log of both sides of equation (6-1) and rearranging terms.
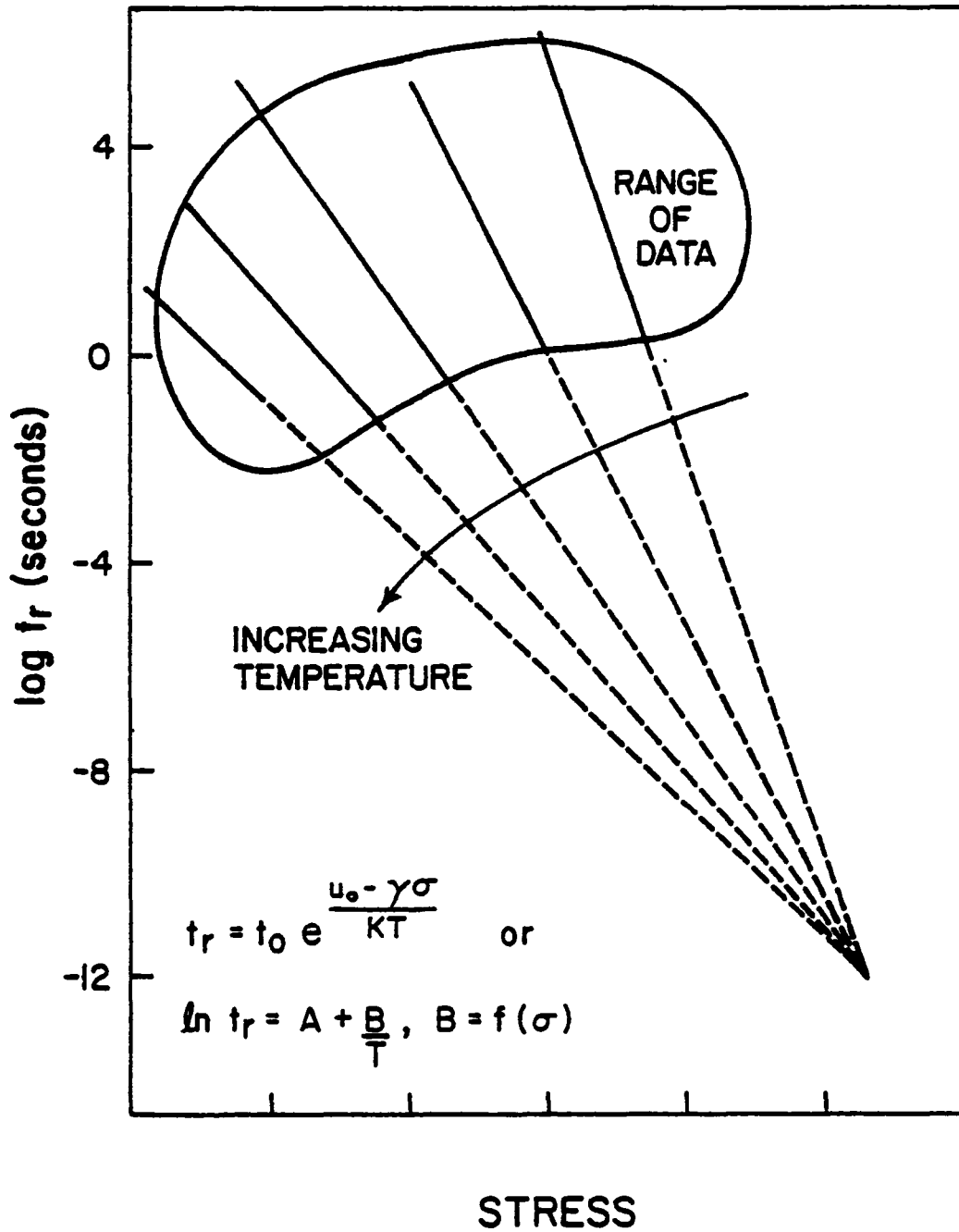
Figure 6-1. Typical data obeying Zhurkov's equation.

The universal nature of equation (6-1) is not automatically
assumed in the Western scientific community. For example, after
several paragraphs of discussion Knauss (1973) states, "Zhurkov's
impressive findings appear thus to be the somewhat fortuitous result
of a particular test method." Notwithstanding Knauss' view, it does
seem reasonable to conclude that equation (6-1) does predict delayed
failures in creep for many materials. However, it is believed to be
founded on no greater scientific basis than other classical parametric
methods described subsequently. Close scrutiny of equation (6-1)
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. (1977) found that

$$t_r = t_o \, e^{\left(\frac{u_o}{RT} - \gamma\sigma\right)} \tag{6-2}$$

worked for some materials and Ratner and Yartsev (1974) have used

$$t_r = t_o \, e^{\left(\frac{u_o - \gamma\sigma}{RT}\right)\left(1 - \frac{T}{T_p}\right)} \tag{6-3}$$

where T_p is the pole temperature.

Other phenomenological methods are surveyed by Conway (1969)
and Goldhoff (1959). The most popular of these are the Larson-Miller,
Dorn, and Manson-Haferd methods. The details of these methods will
not be given here but necessary equations are briefly presented in
Appendix A. 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

$$\log t_r = A + \frac{B}{T} \qquad (6-4)$$

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

$$\log t_r = A - BT \qquad (6-5)$$

for constant stress. For typical values of $\log t_r$ and absolute temperature, T, equations (6-4) and (6-5) 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 $[\pm 45°]_{4s}$ laminates, described elsewhere in this paper, it is noted that failure at high stress levels involves little delamination, while the 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 (1976) for one example). Therefore, there is little reason to believe that the parameters for one orientation are the same as those for another. The possibility of unifying the parameters for several orientations will be discussed later.

There is one phenomenological approach specifically tailored to the time dependent fracture of composites. Wu and Ruhmann (1975) have extended the original work of Wu (1974) 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 inplane normal and shear stresses, $\sigma_1, \sigma_2, \tau_{12}$, relative to the principal material axes. Wu postulated that the failure surface shrank 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 (1974) has demonstrated that a minimum number of tests is required for the time independent case. To date, very little experimental evidence to support this theory is available but the method should work. It should be added that in previous work done by Yeow et al. (1978), the time independent failure law of Puppo and

Evensen (1972) was also adopted for the time dependent case by replacing time independent strengths with their time dependent counterparts.

The phenomenological theories cannot be extended to transient loading or environment without some form of cumulative damage law. The very existence of such a law for some systems is somewhat in question due to the nature of the data given subsequently in the results sections and the residual strength data of Chiao (1976).* Nevertheless one such hypothesis has been proposed for kinetic rate theory by Kargin and Slonimsky (1971). They suggest that rupture under varying loads can be determined by the equation,

$$\int_0^t \frac{dt}{t_r[\sigma(t);T(t)]} = 1 \tag{6-6}$$

It is recognized that equation (6-6) is similar in concept to an integral form of Miner's rule.

Deformational Approaches to Failure

Deformational approaches utilize knowledge of the state of stress, strain and time. The classic approach to this phenomenon is given by Landel and Fedors (1964). In this classic 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.

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*Chiao observed no loss in residual strength for specimens which were tested prior to failure in creep.

Thus, the property surface uniquely establishes the stress-strain-time relationship for <u>any load path</u>, and the surface will also give the stress and strain at the time of failure. Their visualization was only for the case of uniaxial stress or pure shear. For a polymer matrix composite this means that such a surface could be established for the macromechanical behavior of a given unidirectional off axis orientation. As in the case of the phenomenological approaches, a different surface would be required for each orientation. Landel suggests that the uniaxial limitation can be overcome with a geometric rupture surface and, indeed, this concept for isotropic materials is identical to Wu's tensor polynomial surface for anisotropic materials described earlier. Landel indicates that the surface may be made in stress or strain space but how time dependence would be incorporated is not discussed.

In previous work at VPI, Brinson et al. (1978) assumed that the shape of the creep rupture strength master curve was the same as the reciprocal of linear viscoelastic compliance master curve. This rupture master curve is similar to the ones already discussed except it relates rupture stress to rupture time. Different temperatures can be accommodated by merely translating the master curve in accordance with the same shift factors used for compliance. It was not recognized until recently that such an assumption is indeed a deformational theory of failure. Let us presume that an off axis linear viscoelastic compliance master curve, $S_{xx}(t)$ is known at a reference temperature T_o. It would be an easy operation to form the reciprocal of compliance, $1/S_{xx}(t)$, master curve. Now presume that one failure point is known,

say σ_1 and t_1. We now must adjust the vertical scale by some multiplicative constant, A, so that

$$A/S_{xx}(t_1) = \sigma_1 \qquad (6-7)$$

It can easily be seen by rearrangement of (6-7) that

$$A = \sigma_1 \, S_{xx}(t_1) \qquad (6-8)$$

Furthermore, it is assumed that all other rupture times and stresses are given by,

$$A = \sigma_i \, S_{xx}(t_i) \qquad (6-9)$$

The right hand side of (6-9) represents the creep strain at failure. The left hand side is of course constant for all σ_i and t_i. There-fore, 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 (1975)). 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.

In a series of recent papers Brüller (1978a,1978b,1979) has established a creep energy criterion that he found useful in correlating the onset of crazing and the limits of linear viscoelasticity in polymethylmethacralate, polycarbonate, and epoxy. Brüller correlated the Reiner-Weisenberg criterion for stored energy to the onset of crazing. This criterion states that failure (crazing in this case) will occur when the conserved energy density reaches a maximum value.

Brüller found, however, that the transient component of stored energy correlated better with the initiation of crazing for creep loading. Splitting the transient creep energy into its stored and dissipated components is a nontrivial task, and Brüller noticed that since the proportions of stored and dissipated energy remained approximately constant, the same correlation could be made with the total transient creep energy. In terms of the symbols already used for isotropic behavior Brüller found that crazing could be predicted by the equation,

$$W_c = \sigma_0^2 \, \Delta D(t) \tag{6-10}$$

where

W_c = critical crazing energy

σ_0 = creep stress

$\Delta D(t)$ = transient component of creep compliance

Brüller also found that W_c remained relatively constant for a range of temperatures. Thus (6-10) may be rewritten

$$W_c = \sigma_0^2 \, \Delta D(\xi) \tag{6-11}$$

for materials whose transient component is a function of reduced time only.

Brüller does not comment on the applicability of this concept to variable loading states. However, he did determine that W_c was constant for both creep and relaxation loading. Since these two loadings are so different, it stands to reason that W_c may be considered approximately constant for any type of loading. Needless to say, the calculation of stored strain energy is nontrivial particularly when load reversals are permitted, however, such a theory offers a

method of predicting crazing or possible failure for transient loads and temperatures.

The usefulness of the Reiner-Weisenberg criteria in multiaxial loading cases is unknown. When such a criterion is applied to a composite the additional problem of elastic energy being stored in the fibers is present. It seems reasonable that the stored energy in the fibers will not change significantly in a creep test, hence all of the transient creep energy will be stored or dissipated in the matrix. Of course, this matrix energy will be due to a multiaxial set of stresses. The beauty of the method is that it is quite general and can be applied to any composite system for which the constitutive law is known. Realistically one could not expect W_c to be a constant when different failure processes dominate for different types of loading. In other words, one would expect that the W_c for interfacial failure would be different from that for matrix failure.

VII. EXPERIMENTAL PROCEDURE

Materials Used in Testing

All materials tested were T300/934 graphite/epoxy prepared by Lockheed Missiles and Space Company (LMSC) of Sunnyvale, California. Specimens were prepared from two orders of the material. The first order was procured during the 1977-1978 contract year, and it will henceforth be referred to as the "old" material. In the subsequent contract year another order was placed for the identical material. This batch will be referred to as the "new" material.

The "new" material was received in February of 1979 and consisted of one 66" x 30" sheet each of the following lay-ups $[0°]_{8s}$, $[0°,90°]_{4s}$ and $[0°,\pm45°,0°]_{2s}$. Upon receipt of the material a brief investigation was initiated so that a comparison of the "new" material could be made with the "old" material. Two $[0°]_{8s}$ and two $[90°]_{8s}$ tensile specimens were instrumented with strain gages in usual fashion such that bending effects were eliminated (more will be said about specimen preparation later). Each specimen was cycled four or five times at a constant cross head rate of 0.05 in/min for modulus determination and then taken to failure. These room temperature results were consistent and somewhat surprising as shown in Table 7-1.

The preliminary investigation revealed that the room temperature properties for the fiber direction of the "new" material were nominally those of the "old" material. However, it can be seen that the properties transverse to the fibers of the "new" are a factor of

Table 7-1. A Comparison of the "Old" and "New" Batches of Material.

Specimen #	Axial Modulus		Fracture Stress		Fracture Strain	
	1978*	1979	1978*	1979	1978*	1979
$[0°]_{8s}$ #1	19.88×10^6 psi	20.74×10^6 psi	207.9 ksi	195.6 ksi	.95%	.87%
$[0°]_{8s}$ #2**	19.88×10^6 psi	20.79×10^6 psi	-	-	-	-
$[90°]_{8s}$ #1	2.17×10^6 psi	1.47×10^6 psi	5.80 ksi	11.60 ksi	.43%	.83%
$[90°]_{8s}$ #2	2.17×10^6 psi	1.50×10^6 psi	5.80 ksi	12.40 ksi	.43%	.90%
$[90°]_{8s}$ #3***	-	-	5.80 ksi	13.28 ksi	-	-

*As reported in Yeow, Y. T. and Brinson, H. F., "A Comparison of Simple Shear Characterization Methods for Composite Laminates," Composites, Jan. 1978.

**Slipped in grip.

***For strength measurement only.

two greater than those of the "old". In the work described here the properties of the matrix are highly important since they are the sole contributors to the viscoelastic response of the composite. It is particularly noteworthy that the transverse strength of the "new" material was a factor of two greater than that obtained earlier. In certain respects such a variation may be considered fortuituous because it dramatically demonstrates the kind of variation one can experience in properties between two different batches of the same material. The reader should bear in mind that all the composite panels were fabricated by the same vendor using materials and procedures that were intended to be identical.

Thickness Variation

One additional problem with the "new" unidirectional material was thickness variation. When traversing the panel transverse to the fibers the thickness was found to periodically vary from 0.078-in to 0.092-in which is a ±8% variation from the average thickness. This proposed a considerable problem in the preparation of creep rupture specimens since failure ordinarily occurs at the location of highest stress. The thin places did not appear randomly but on six inch centers. Because of this periodicity, it is believed that some form of lay-up error resulted in the variation. For example, if twelve inch wide prepreg was used in the fabrication of the material one would obtain prepreg joints on six inch centers by staggering the overlap as one does laying bricks. These joints could then contribute to thickness variation. The precise cause of this variation as of

yet has not been determined. However, after several discussions with LMSC personnel a possible explanation was suggested. It was determined that the twelve inch prepreg used by the vendor in fabricating the panels was thinner at the outer edges. Thus when two prepreg edges were butted together a thin area would result. In a sixteen ply laminate eight such joints would fall at the same location. LMSC reported that such problems have never occurred in general laminates.

The thickness variations were further investigated to determine if the material in the various regions of thickness differed significantly. It was postulated that if the volume fraction was similar throughout the panel, the properties would also be similar. Thus the unidirectional panel was checked for fiber volume fraction at nine locations of various thickness using the ASTM D3171-73 revised test method. With this technique the composite specimen is first weighed and then heated in concentrated sulfuric acid. Hydrogen peroxide is occasionally added until all of the matrix material is leached away leaving only the fibers. The fibers may then be rinsed, dried, and weighed. Using this procedure the average fiber volume fraction was determined to be 72.4% by weight. Furthermore, only minor variations of several percent were observed in the data and the data that was obtained after the first few attempts was very consistent. It was therefore concluded that the assumption of material uniformity was reasonable. Variations in thickness in the "old" material were much less severe.

Specimen Preparation

The full impact of the thickness variation of the "new" uni-directional material was not at first appreciated. Initially speci-mens were removed from the sheet without regard for this variation. However, it was quickly determined that many of these specimens were breaking at or near the loading grips. This occurred because the smallest cross sectional area (thinnest point) was frequently at the extremities of the specimens. Later specimens were removed from the parent panel such that the thinnest point fell near the center of the specimen eliminating this problem. However, this procedure increased the amount of material waste drastically.

Groups of specimens were first "roughed out" using a table saw with a diamond blade and a mister for coolant. Manageable pieces approximately 9.5" x 12" were obtained in this manner. These pieces were then cut into individual specimens using a more precise diamond saw with a carriage and automatic cross feed. The standard size of the finished specimens was 9.5" x 0.5". The specimens unavoidably came into contact with the saw coolant during fabrication, so all specimens were subsequently heated for several hours at 250°F to drive off absorbed moisture and stored in a dessicator until the time of testing. Weight measurements made on several specimens verified that this procedure would be adequate. Well into the testing program it became obvious that the material would need to be conserved as much as possible. Therefore, some $[90°]_{8s}$ and $[60°]_{8s}$ specimens were made of a shorter length in a manner which nearly eliminated waste of the parent material. However, at all times specimens were made of

sufficient length such that end effects were of negligible importance.

End Tabs

Initially 2 in. long end tabs were attached to the ends of all specimens using high temperature epoxies. The end tab material was a glass/epoxy cross ply laminate known as Scotchply. Micromeasurements M-Bond 610 (a solvent thinned epoxy) or Epoxylite 5403 (a 100% filled epoxy) were used to attach the end tabs. With the end tabs in place the aspect ratio of the remaining test section was 10:1 which was considered adequate.

The proper sizing of composite specimens is a nontrivial subject that warrants additional discussion. The aspect ratio of the test section must be sufficient to allow for the effects of clamped ends. Additionally, the width of the specimen should be such that interply shears and out-of-plane normal stresses (in the case of general laminates) do not significantly affect the intraply response. Finally, the material cost in testing programs is a significant factor leading to the conservation of material which of course runs contrary to the other factors already discussed. These factors must all be considered. For our unidirectional specimen size it is believed that a reasonable compromise was struck, however a wider specimen would have been desirable for the general laminates.

After considerable testing with specimen end tabs it became apparent that they should be avoided if possible. It was concluded that end tabs did not significantly reduce grip failures in off axis unidirectional specimens with angles greater than 30° (if anything,

end tabs seemed to increase grip failures). Furthermore their fabrication and installation took considerable time and effort. Therefore, the use of end tabs was eliminated on most specimens without ill effects.

Strain Gage Installation

Several techniques for strain gage installation were employed. It was at first believed that any technique used should modify the specimen surface to the least degree possible. With many composites very little preparation would be required because of a naturally smooth surface finish. Unfortunately, the material fabricated by LMSC is covered on both sides with a scrim cloth. When removed, this scrim cloth leaves a corrugated surface much like cloth in texture. As a first attempt, strain gages were mounted directly on this rough surface for use at room temperature with Micromeasurements M-Bond 200 (equivalent to Eastman 910). This type of installation worked fine for room temperature work. The same preparation was also used with Micromeasurements M-Bond 610 for use at higher temperatures. In the latter instance the installation proved unsatisfactory for high temperatures due to adhesive failure. Regardless of how the adhesive was applied the low spots were left unadhered. To correct this problem Epoxylite 5403 was used to fill the surface irregularities prior to gage installation. This procedure provided a smooth surface for gage installation, however the resulting bond line was so thick that excessive gage adhesive creep was unavoidable at high temperatures. As a final resort the gage installation area was sanded prior to gage

installation. This procedure seems less desirable than the others mentioned, however, it gave the best overall performance. To achieve a smooth surface on both sides of the specimen approximately .003 - .005 in. must be removed from the specimen thickness. Since the cross sectional area at the gage location is used for the calculation of stress, this would not seem to be a problem. However, most of the thickness which was removed was a resin rich outer layer which would generally tend to slightly decrease modulus or strength measurements due to the lack of fiber reinforcement. Nevertheless, the sanding procedure gave the best installation so it was used throughout the course of this study. The procedure which was finally adopted consisted of the following steps:

1. Light sanding of the specimen surface using 220, 320, and 400 grit paper.

2. Cleaning of the sanded surface with propanol until a clean tissue can be wiped over the area without picking up graphite.

3. Baking of the specimen for one hour at 250°F to drive out any absorbed propanol.

4. Installation of the gage using recommended Micromeasurements procedure for M-Bond 610.

5. Curing of the gage installation for two hours at 250°F (this reduces bubble formation) followed by one hour at 350°F.

6. Installation of lead wires, tabs, etc.

7. Post cure for two hours at 430°F.

8. Application of GE RTV 3140 over the gage area for protection.

The above procedure worked adequately, however, it is likely that it could be improved upon. Care should be exercised to avoid the use of any plasticizing solvents such as acetone in the surface preparation.

350 Ω gages and low excitation levels (1 to 2 V) were used throughout the study to minimize any localized heating due to gage heat dissipation. Even with all the above precautions it appeared that a modest amount of gage adhesive creep occurred with $[0°]_{8s}$ specimens at elevated temperatures, thus further fine-tuning of the installation procedure or adhesive system is warranted.

The gage installations were tedious and time-consuming. In the future it might be desirable to avoid strain gages altogether for measurement of axial elongation through the use of a clip gage. Of course, strain gages will still be necessary in cases where multiaxial data is required.

Test Equipment

Tests were conducted in several testing machines. Initially an Instron 1125 was used for all testing. This piece of equipment is screw driven and is primarily useful for constant strain rate testing. Unfortunately an Instron is unsuited and too expensive to use for long term creep tests. It became apparent that additional machines would be required to conduct the number of tests described here, so two additional lever arm creep machines were obtained. A new machine was obtained from Applied Test Systems (ATS) and an additional Budd creep machine was obtained from storage and renovated for use on the project. Both creep machines had the load capacity to conduct any

of the tests described here except $[0°]_{8s}$. All the equipment was fitted with environmental chambers for use at elevated temperatures, however, humidity could not be directly controlled.

Temperatures were measured with iron-constantan thermocouples and a Leeds and Northrup thermocouple potentiometer. Prior to use, the potentiometer was checked at the ice point and steam point and found to be in good calibration. A laboratory thermometer was often situated in a visible position adjacent to thermocouples for a double check. During testing the temperature was monitored at the center of the specimen test section. Initially all of the test ovens were checked for temperature variations with a special specimen which contained five embedded thermocouples. The worst temperature variation occurred in the renovated Budd creep machine (which was fitted with a new ATS oven) where a symmetric 3°F variation was measured with the grip ends of the specimen being cooler. The variation is believed to be due to conduction through the load train and hence largely unavoidable. Prior to test all specimens were allowed to soak for a minimum of 30 minutes.

Strains were measured with a variety of Micro-Measurements strain gages which were installed as previously described in this section. Most often Vishay 2120 strain gage amplifiers were used in conjunction with Hewlet Packard strip chart recorders or x-y plotters. Due to the lack of significant viscoelastic effect at lower test temperatures extreme care was taken to get the very best experimental data. The instrumentation was continually checked via external shunt calibration. Temperature compensation was continually

maintained with dummy gages mounted on geometrically similar specimens and care was exercised to maintain lead wires of constant length. Even with the above precautions experimental error was not minimized to the degree desired. Additional accuracy could have been obtained with a more sophisticated strain recording device. Furthermore, the local power was found to be full of transients and unreliable. A constant voltage isolation supply was obtained to power all instrumentation, however, even this precaution did not eliminate the periodic signal injected to energize the University bell system. The use of shielded lead wires did not significantly reduce the above mentioned problems.

As may be discerned from the foregoing, accepted procedures were followed for material handling and storage, machining specimens and instrumenting specimens and collecting data. While the absolute accuracy of the data is not known, it was likely within tolerable limits to the extent that the phenomena observed was real and not artificial.

VIII. EXPERIMENTAL RESULTS AND DISCUSSION - MATERIAL CHARACTERIZATION

At the onset of the experimental program many aspects of the problem were not well understood, particularly those subjects discussed in sections IV - VI. As a result, much time was spent pursuing unfruitful approaches and improving the experimental technique. At the conclusion of initial testing over 25 specimens had been instrumented and tested in an effort to characterize the material. Only a fraction of these results are presented here.

Secondary Transition

Initially, specimens were prepared from the new material precisely as described in section VII, stored in a dessicator, and tested as required. The characterization work began with $[90°]_{8s}$ specimens because it was felt that these specimens would best reflect matrix behavior. Ramp loaded rupture strengths were first determined to gain a general idea of what stresses would be allowable in characterization studies, and these results (and others) are shown in Table 8-1. With this information a series of tests were begun using five stress levels at numerous temperatures. The stress levels were chosen such that nonlinear behavior would be observed while minimizing the likelihood of specimen rupture during test. The room temperature test specimens exhibited only slight viscoelastic behavior as expected. However, the effect of stress was generally of opposite sense or inconsistent at best. Figure 8-1 shows the S_{22} creep compliance at room temperature for various values of stress. Ordinarily one would expect increasing

Table 8-1. Miscellaneous Strain Rate Tests.

Spec. No.	Orientation	Old/New	Test Temp °F	350° Post Cure, Hours	Head Rate In/Min	Strength psi
H-1	$[90°,\pm60°,90°]_{2s}$	Old	356	-	.002	6,142
H-2	$[90°,\pm60°,90°]_{2s}$	Old	356	-	.02	6,128
H-3	$[90°,\pm60°,90°]_{2s}$	Old	356	-	.2	6,726
H-4	$[90°,\pm60°,90°]_{2s}$	Old	356	-	2.	7,403
Y60-1	$[60°]_{8s}$	Old	320	-	.05	6,046
Y60-4	$[60°]_{8s}$	Old	320	-	.05	5,744
Y30-2	$[30°]_{8s}$	Old	320	-	.05	9,287
Y30-3	$[30°]_{8s}$	Old	320	-	.05	9,186
90-12	$[90°]_{8s}$	New	RT	-	.05	12,840
90-27	$[90°]_{8s}$	New	320	-	.05	6,608
90-28	$[90°]_{8s}$	New	365	-	.05	5,050
90-13	$[90°]_{8s}$	New	386	-	.05	2,758
10-1	$[10°]_{8s}$	New	RT	-	.05	51,021
10-2	$[10°]_{8s}$	New	310	-	.05	46,069
10-3	$[10°]_{8s}$	New	357	-	.05	32,313
10-4	$[10°]_{8s}$	New	386	-	.05	22,316
45-10	$[45°]_{8s}$	New	350	24	.05	8,551
45-10	$[45°]_{8s}$	New	350	12	.05	7,315
45-7	$[45°]_{8s}$	New	350	6	.05	7,246
45-4	$[45°]_{8s}$	New	350	2	.05	6,758
45-1	$[45°]_{8s}$	New	350	0	.05	6,191
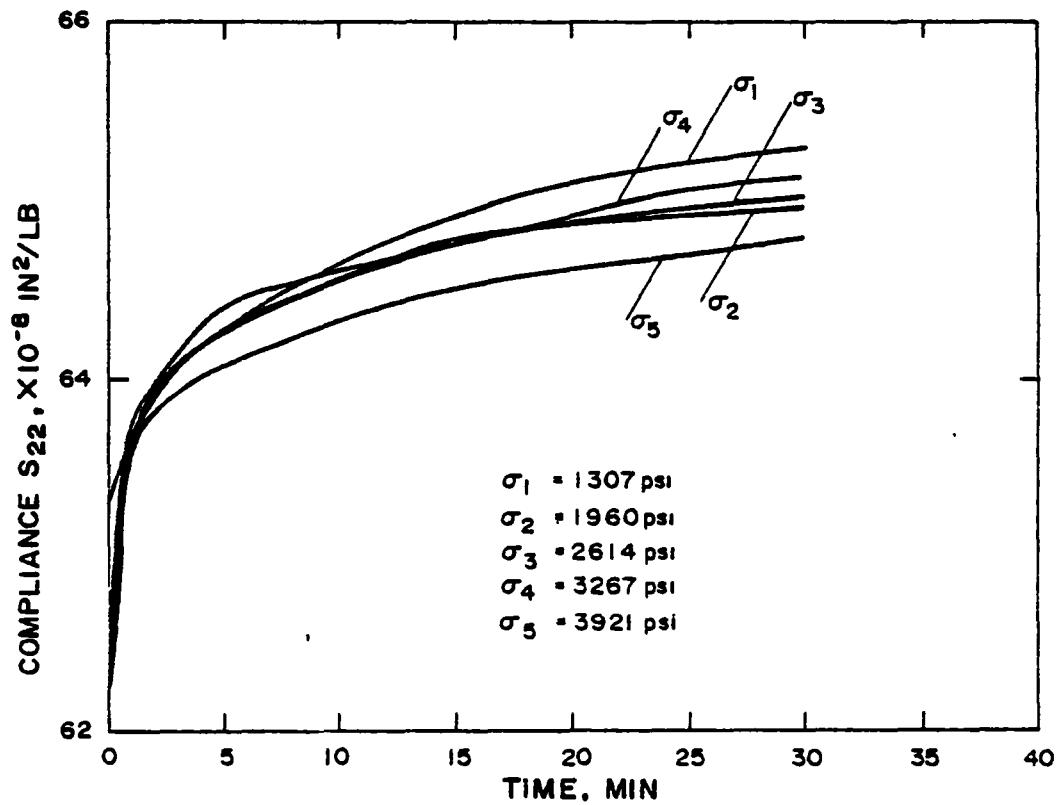
Figure 8-1. Original results obtained at 79°F on a [90°]$_{8s}$ specimen showing inconsistent or lack of stress effect.

values of compliance at higher values of stress. Of course the vertical scale in Figure 8-1 has been greatly exaggerated so one could possibly argue that there was no stress effect at all. Upon further increase in temperature the material entered a region of near elastic like behavior as shown in Figure 8-2. This effect began at about 200°F and seemed to continue until 250°F with the maximum effect being at 220°F. It is believed that this behavior is a direct result of a secondary transition temperature occurring at approximately 200°F. This behavior has also been noticed by Schapery (1979). The presence of the plateau region coupled with the inconsistent effects of stress level made formation of a combined stress-temperature master curve impossible. These difficulties suggested that some form of mechanical, thermal, or thermomechanical conditioning or aging process was occurring in the material during testing.

Stress Independent Studies

The initial experiments clouded the whole characterization effort to such a degree that an effort to characterize the material at low stress levels was made. Several $[90°]_{8s}$ specimens were used to create S_{22} master curves, one of which is shown in Figure 8-3. The corresponding shift factor, a_T, is given in Figure 8-4. In order to minimize problems experienced around the 200°-250°F quasi elastic region, creep tests were conducted from 290°F to 410°F for 16-minute durations. This, unfortunately, prohibits the use of the master curve below 290°F. The S_{22} master curve was formed by horizontal movement of the individual creep curves without normalization.
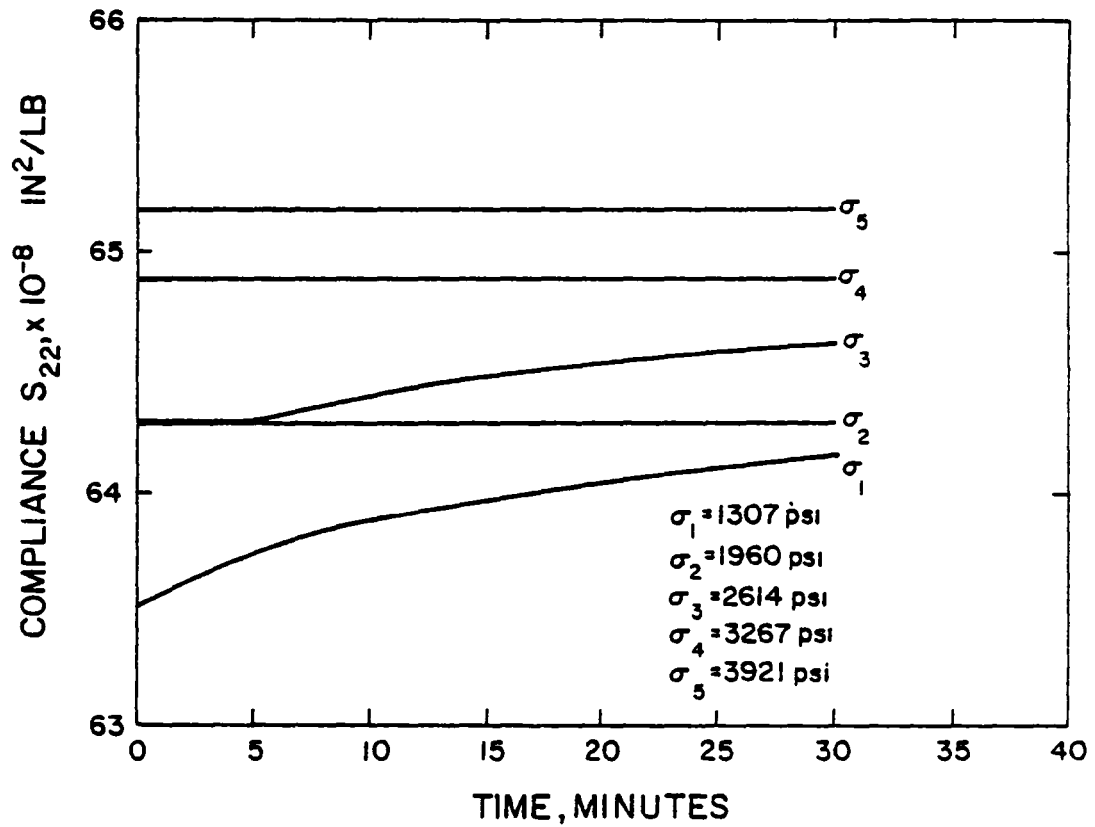
Figure 8-2. Original results obtained at 220°F on a $[90°]_{8s}$ specimen showing "elastic-like" behavior.
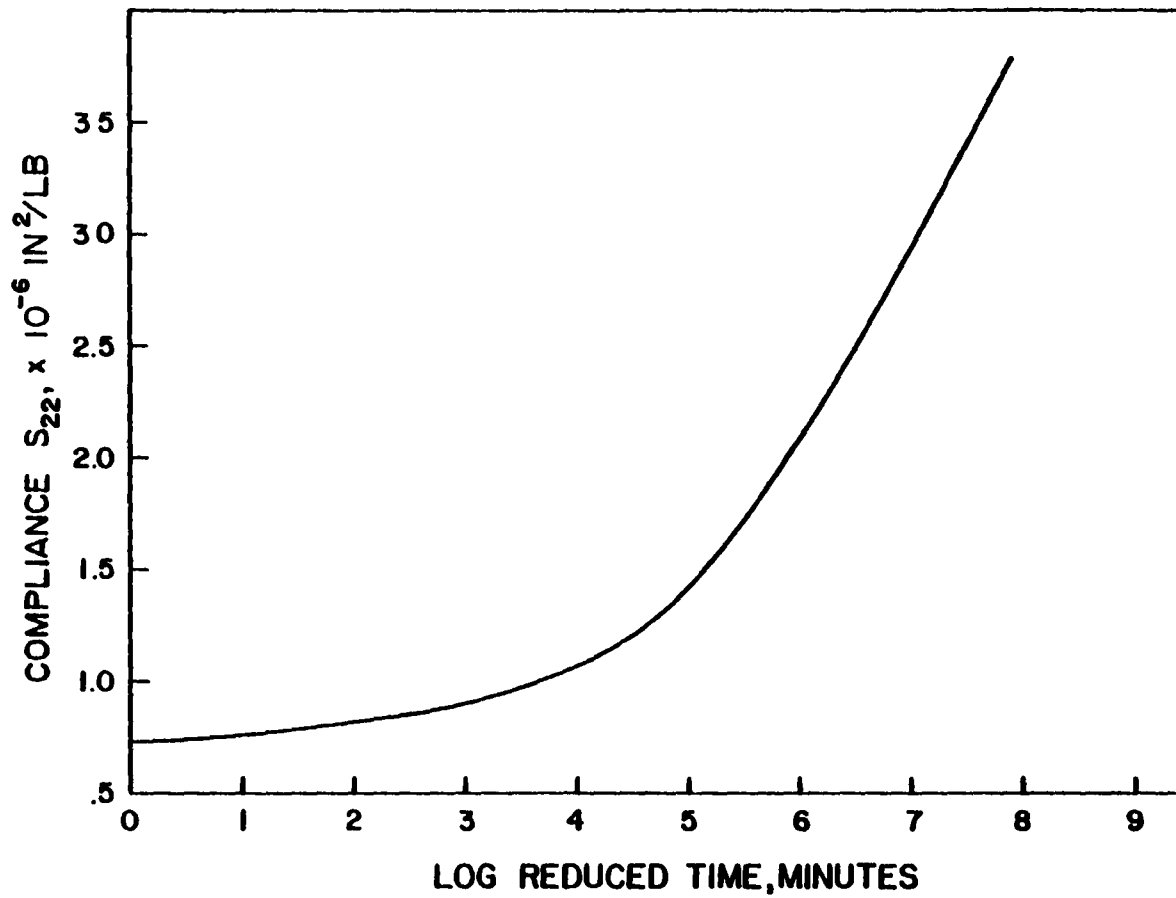
Figure 8-3. S_{22} master curve reduced at 290°F obtained by horizontal shifting only with an unconditioned specimen.
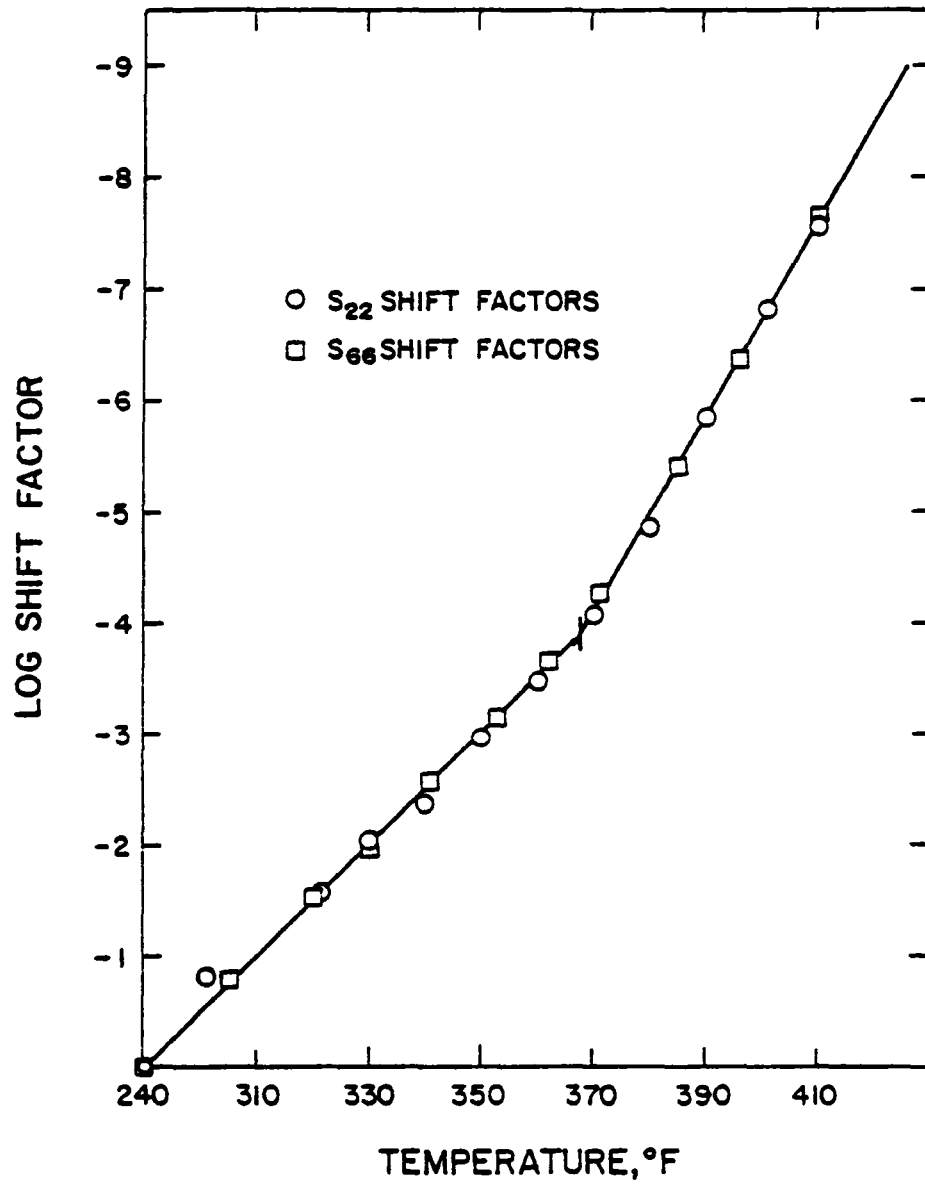
Figure 8-4. Shift factors for unconditioned specimens with horizontal shifting only.

The short term curves for different temperatures were not in perfect alignment when shifted but a smooth master curve was obtained.

A similar master curve was formed for the creep compliance in shear, S_{66}. There are a variety of ways to measure creep compliance in shear, and some of these are summarized by Yeow and Brinson (1978b) who found the 10° off-axis test to be superior. In light of their findings and those of C. C. Chamis (1977) the 10° off-axis test was selected for use in this study. To perform this test a 10° off-axis specimen is first instrumented with a full strain gage rosette. This permits the shear strain to be calculated relative to the principal material axes. The shearing stress relative to the same axes is calculated using tensorial transformation. A family of 16-minute $S_{66}(t)$ compliance curves were generated over the same temperature interval used with the 90° specimens, 290°-410°F. The resulting master curve is shown in Figure 8-5 and the shift factor, a_T, is again shown in Figure 8-4. It is interesting to note that the shift factors for both compliance functions, S_{22} and S_{66}, are nearly identical. Furthermore, log a_T is a bilinear function with a slope discontinuity occurring at 368°F. It is generally accepted in the linear theory that one shift factor, a_T, will superpose all viscoelastic functions, Krokosky (1967). However, the bilinear form of the curve is not generally expected. The WLF equation can model this behavior in only a very crude manner. The Arrhenius form gives a nearly straight line below the T_g so it could possibly be used to model the lower portion. This bilinear form has also been noticed recently by Kibbler (1979). As can be seen from Figures 8-3 and 8-5, the shapes of the S_{22} and S_{66} compliance master curves
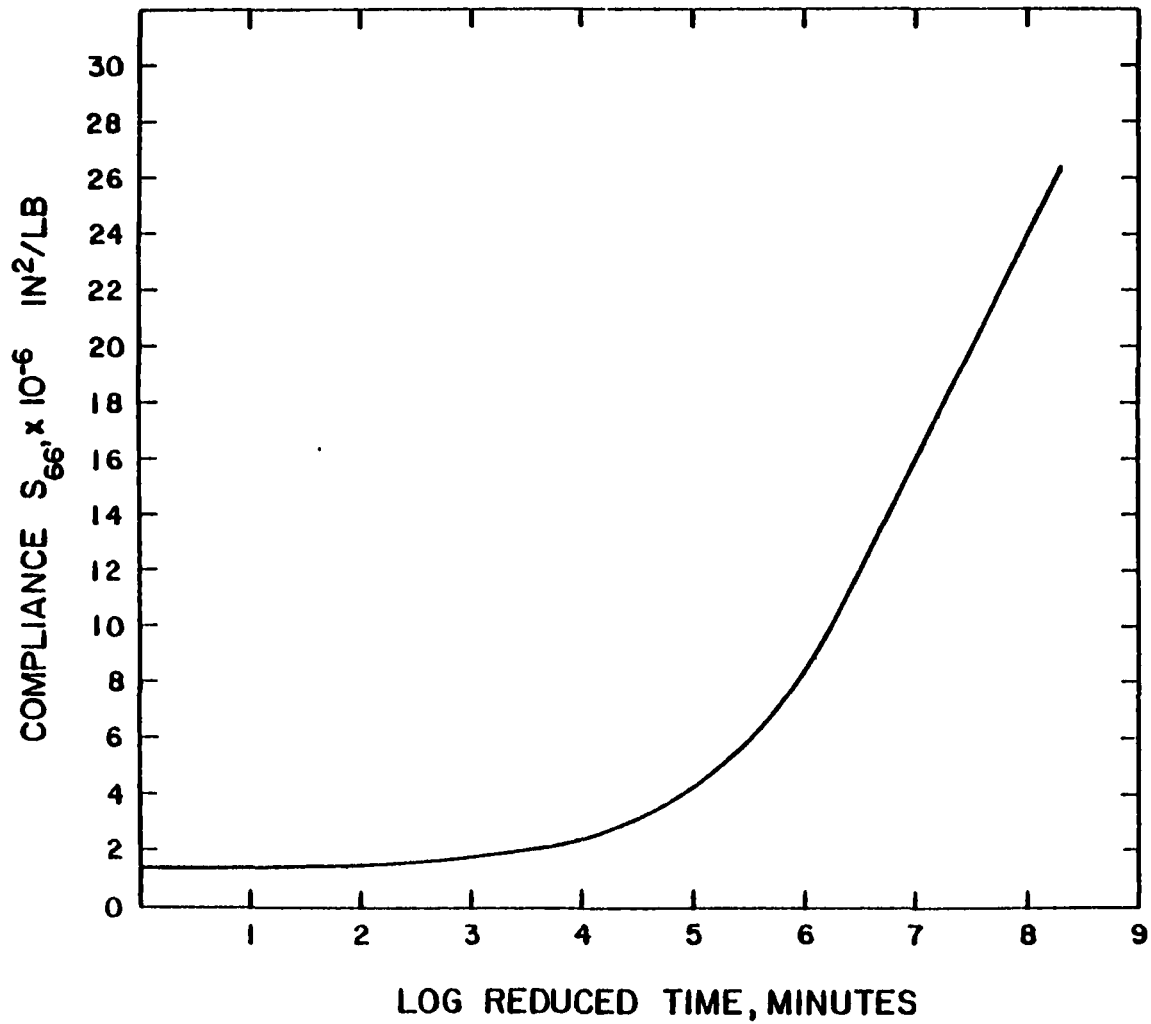
Figure 8-5. S_{66} master curve reduced at 290°F obtained by horizontal shifting only with an unconditioned specimen.

appear quite similar, however, the normalized S_{66} compliance increases at a more rapid rate. This is thought to be an artifact of the additional constraint present in the $[90°]_{8s}$ case where the matrix is likely in a state of biaxial tension due to the high stiffness of the fibers.

Effects of Stress Level

As previously discussed, a great deal of difficulty was encountered when a single specimen was used to obtain the temperature and stress dependent nature of creep compliance. At first it was thought that the primary difficulty was some form of mechanical conditioning that progressed during testing. Ten new specimens were instrumented to circumvent this problem. It was intended that each specimen would be used at multiple load levels at a single temperature, thereby reducing the number of load applications on a given specimen and perhaps minimizing any conditioning taking place. Preconditioning was avoided at that time since the characterization was desired on the virgin material and not its conditioned counterpart. This use of multiple specimens did not provide consistent data for the effect of stress level, however.

Eventually, by the process of elimination it was determined that some form of postcuring was taking place in the specimens during testing. This behavior will be described in detail subsequently.*

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*In the earlier work of Yeow et al (1978), it was ascertained that no thermal conditioning of specimens was necessary. However, this was for the "old" material referred to earlier at low levels of stress only. It was discovered that the manufacturer eliminated a post-curing procedure on the "new" material which was performed on the "old" material.

It was determined that a period of 36 hours of postcure at 380°F all but eliminated the postcuring effect with respect to creep compliance. After this postcure reasonably consistent effects due to temperature and stress were obtained. Furthermore, it was found that horizontal and vertical shifting were required in master curve formation to eliminate the temperature and/or stress effects of initial compliance. Master curves for the creep compliances S_{22}, S_{66} and S_{10° are shown in Figures 8-6, 8-7, and 8-8 respectively. These master curves were obtained using the methods described in section V. In this case the S_{66} master curve was generated through use of the S_{22} and S_{10° master curves and equation 2-4 (transformation equation). Perhaps it should be noted that the smoothness of the resulting master curves was extremely good. The corresponding shift surfaces for S_{22} and S_{10° are shown in Figures 8-9 and 8-10, and the necessary vertical shifts are given in Table 8-2.

The individual S_{10° creep compliance curves for 290°, 320°, 350°, and 380°F are given in Figures 8-11, 8-12, 8-13, and 8-14 respectively. The validity of these master curves has undergone the rigors of comparison with long term tests in excess of 150 hours. These comparisons are shown in Figures 8-15 and 8-16 for a test temperature of 320°F. It appears that at extremely long times the master curves may tend to over-predict the compliance. The reason for this may be due to additional curing or more likely some other form of aging of the material. Nevertheless, the agreement between predictions and experiment is reasonable.
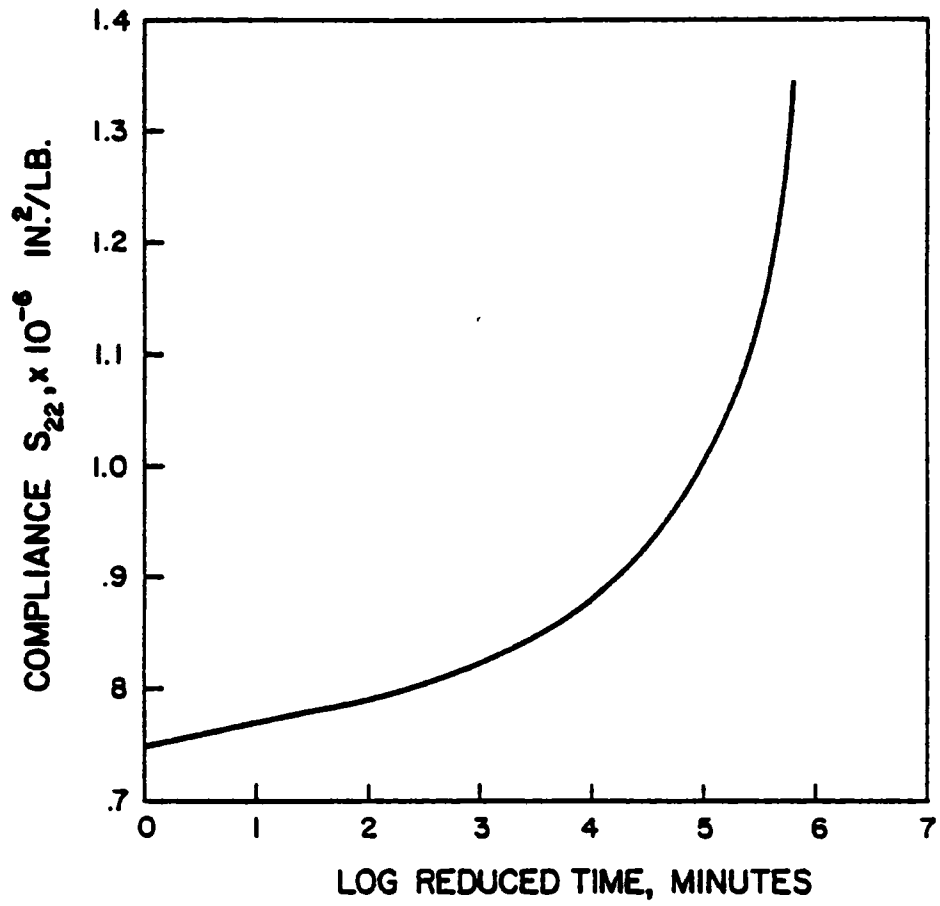
Figure 8-6. S_{22} master curve reduced at $T_0 = 290°F$ and $\sigma_0 = 1400$ psi.
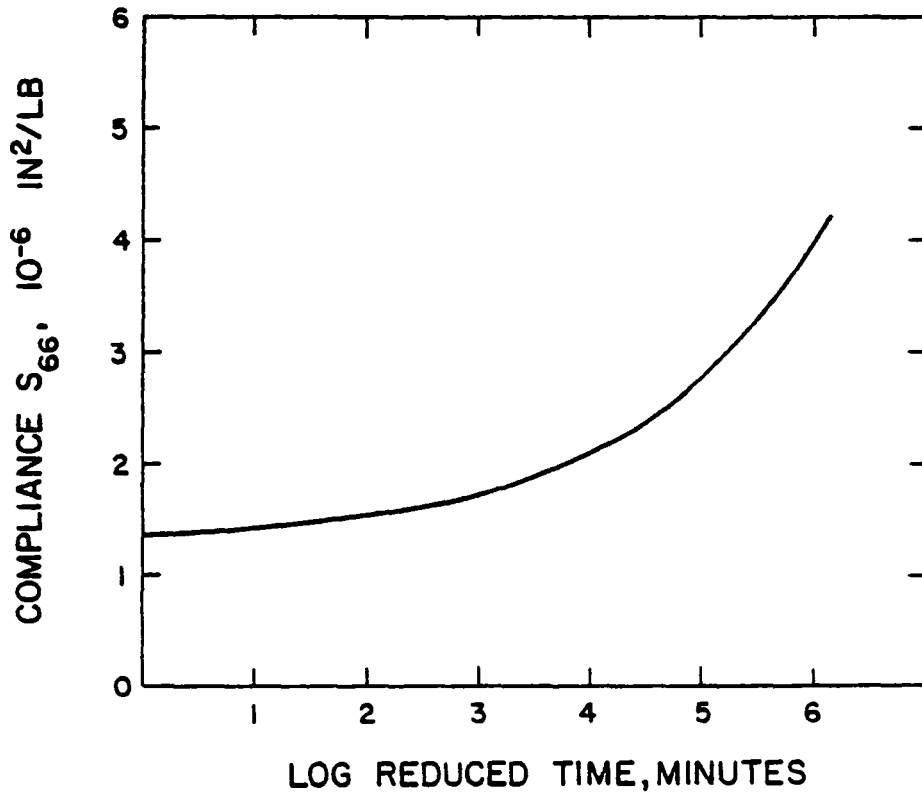
Figure 8-7. S_{66} master curve reduced at $T_0 = 290°$ and $\tau_0 = 810$ psi.
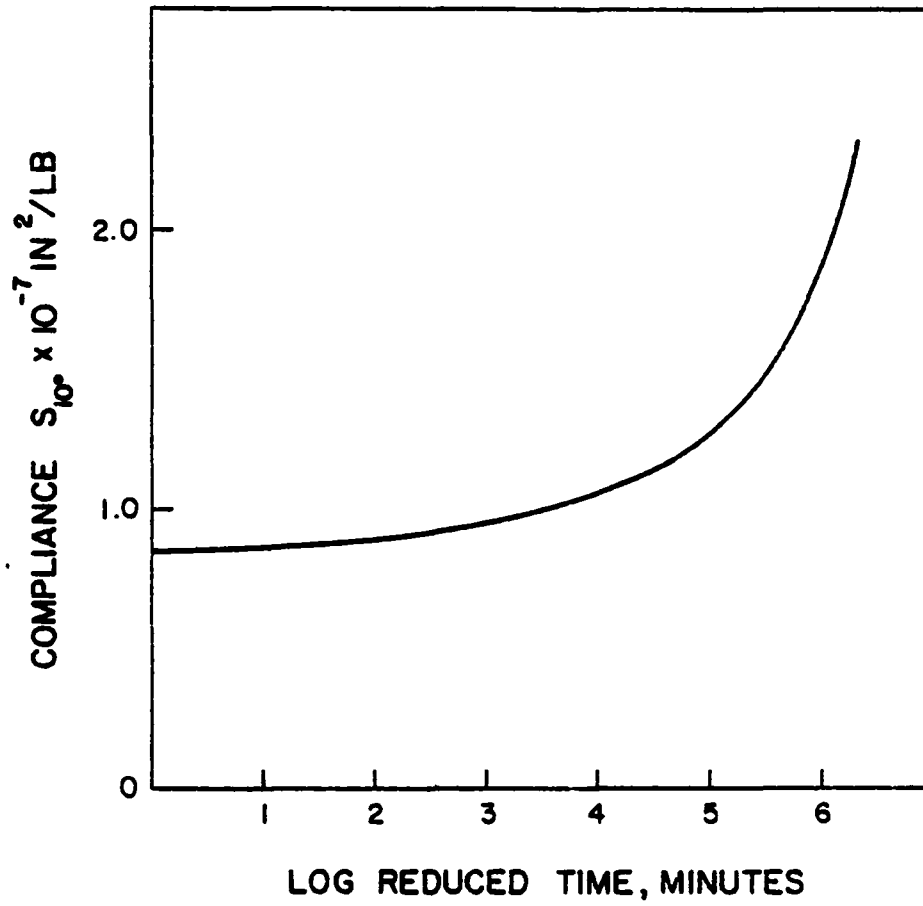
Figure 8-8. S_{10° master curve reduced at T_0 = 290°F and σ_0 = 4,750 psi.
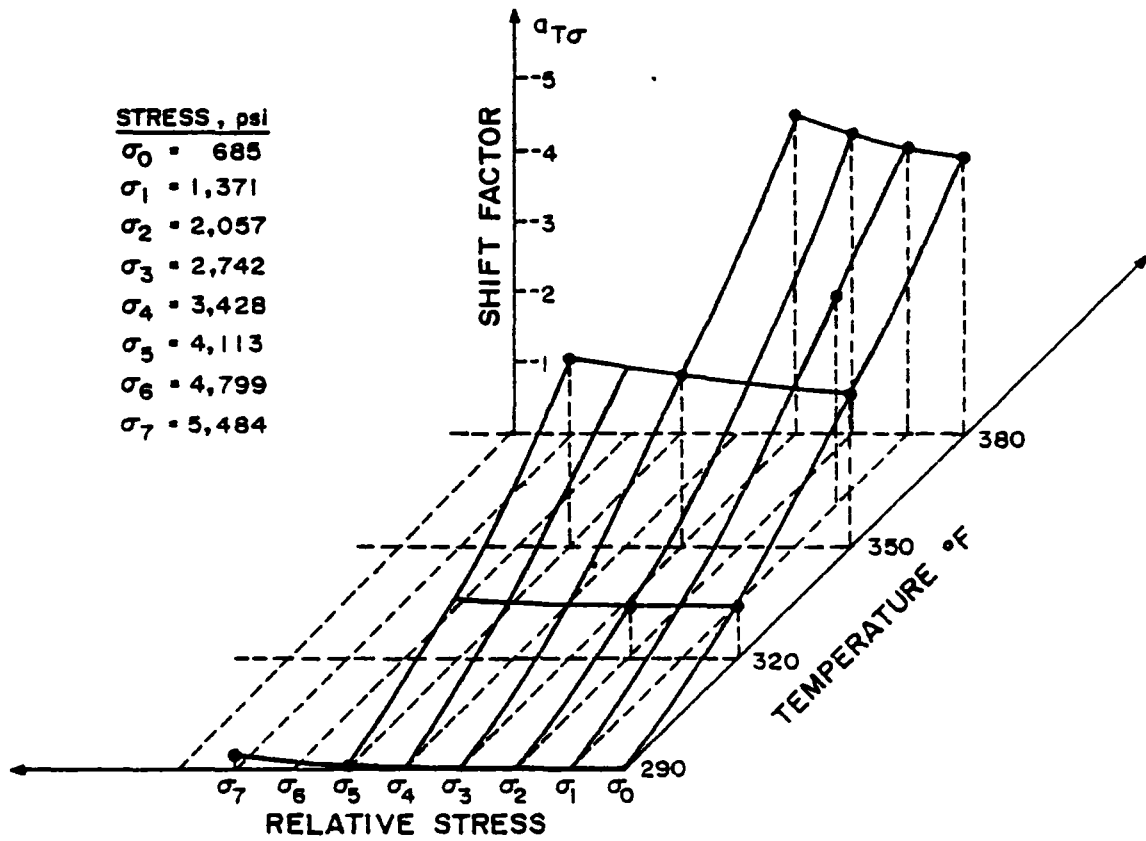
Figure 8-9. Shift surface for combined shift factor, $a_{T\sigma}$, for S_{22} taken from a thermally conditioned specimen.
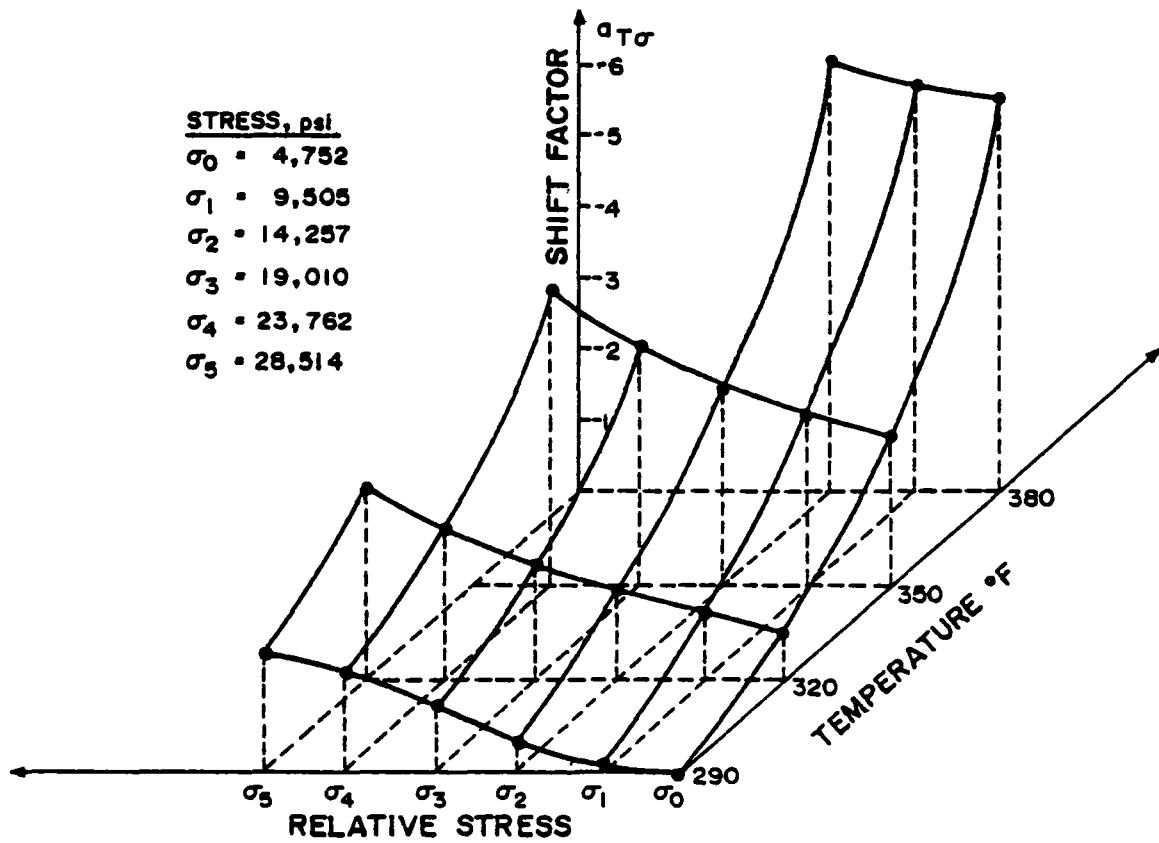
Figure 8-10. Shift surface for combined shift factor, $a_{T\sigma}$, for $S_{10°}$ taken from a thermally conditioned specimen.

Table 8-2. Vertical Shifts for S_{22} and $S_{10°}$.

Temp, °F	Stress, psi	Shift, ΔS
	Vertical Shifts for $S_{10°}$	$\Delta S_{10°} \times 10^{-7}$
290	4,752	0.0
290	9,505	.004
290	14,257	.002
290	19,010	-.012
290	23,762	-.015
290	28,514	-.045
320	4,752	-.007
320	9,505	-.014
320	14,257	-.012
320	19,010	-.025
320	23,762	-.043
320	28,514	-.064
350	4,752	-.023
350	9,505	-.025
350	14,257	-.047
350	19,010	-.045
350	23,762	-.040
380	4,752	-.005
380	9,505	-.010
380	14,257	-.045
	Vertical Shifts for S_{22}	$\Delta S_{22} \times 10^{-6}$
290	685	0.0
290	4,113	-.0091
290	5,484	-.0110
320	685	-.0149
320	2,057	-.0201
350	685	-.0285
350	2,742	-.0159
350	4,113	-.0176
362	1,371	-.0170
380	685	-.0547
380	1,371	-.0686
380	2,057	-.0610
380	2,742	-.0575
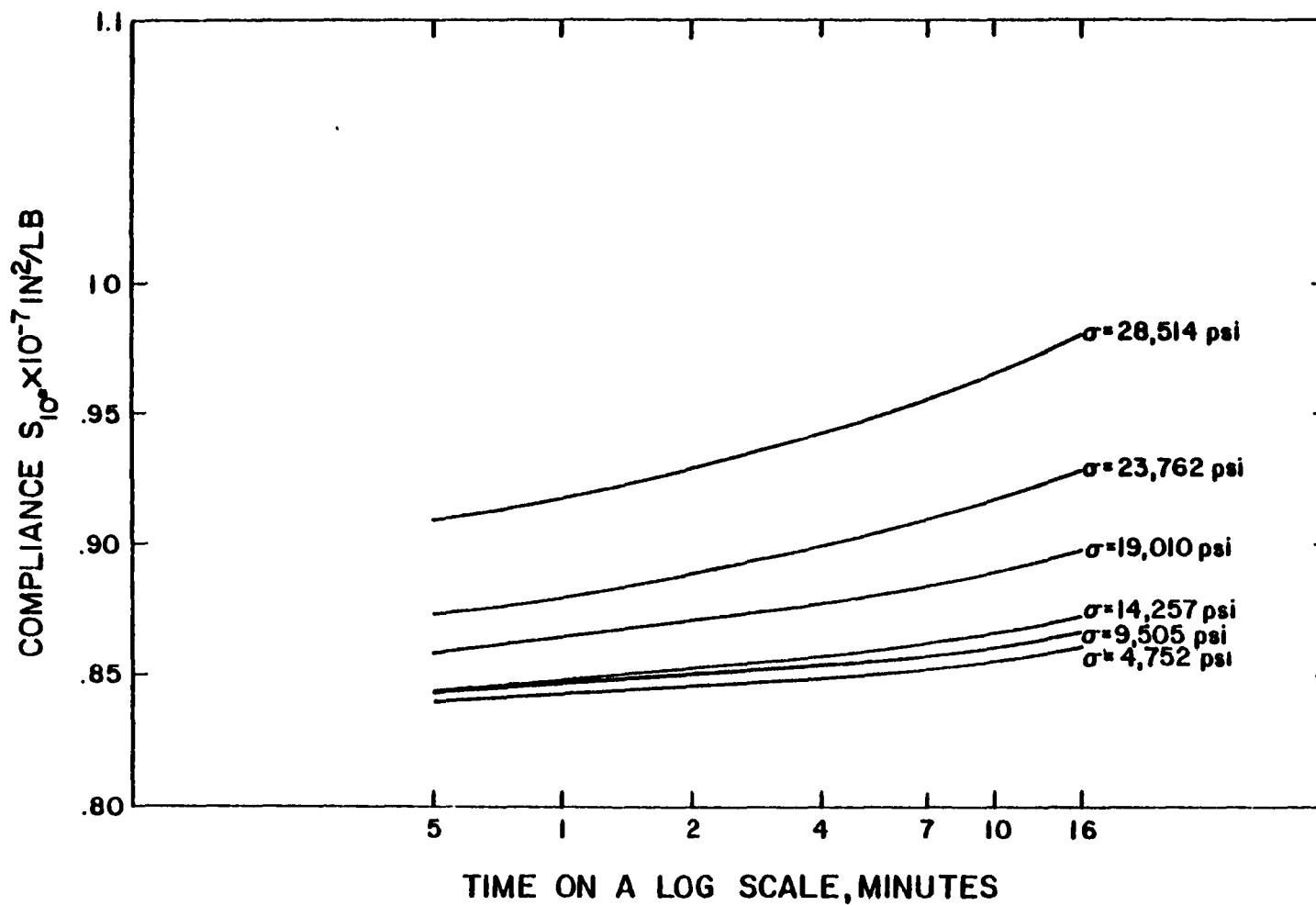
Figure 8-11. S_{10° compliance at 290°F as a function of stress level.
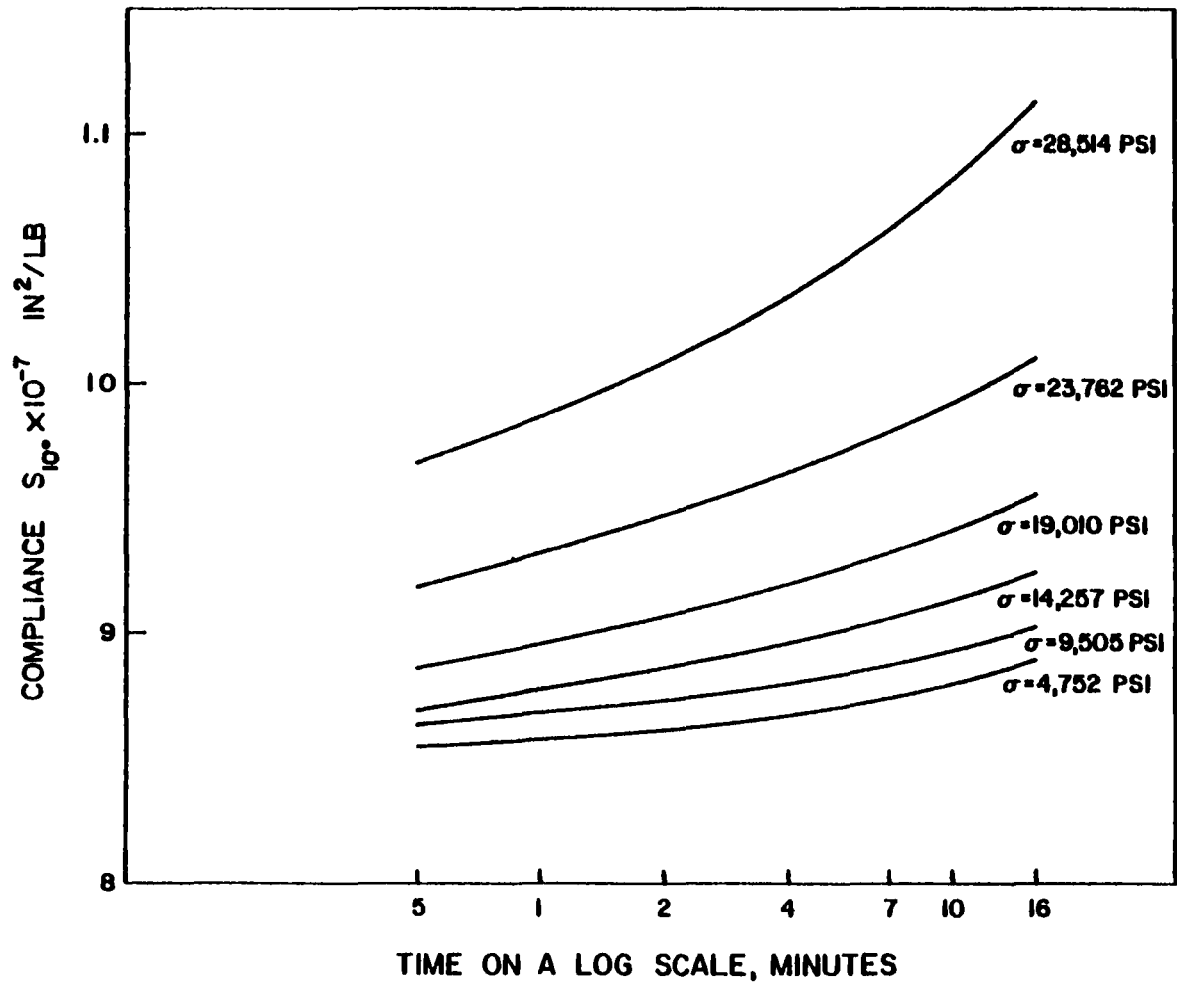
Figure 8-12. S_{10° compliance at 320°F as a function of stress level.
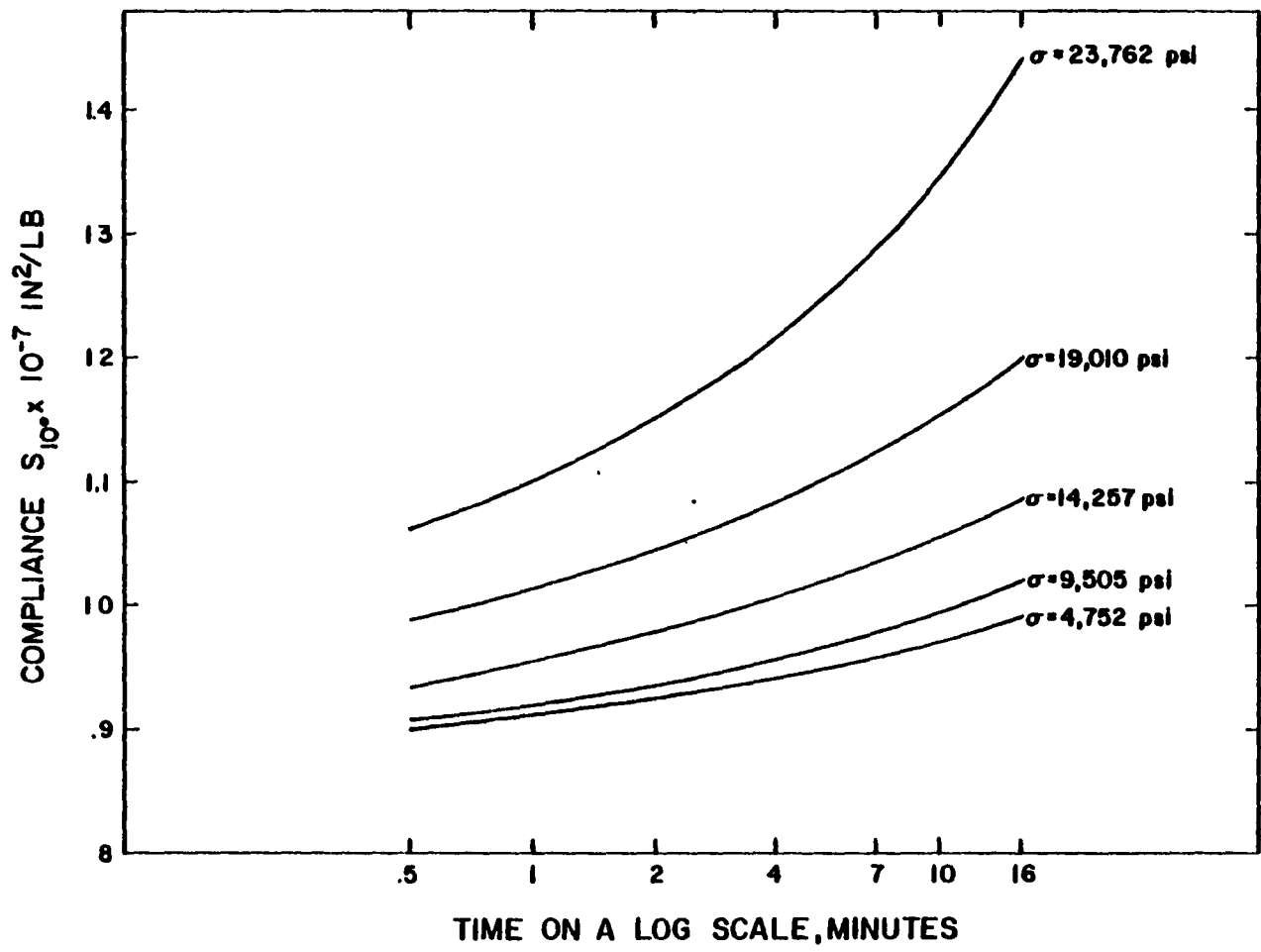
Figure 8-13. S_{10° compliance at 350°F as a function of stress level.
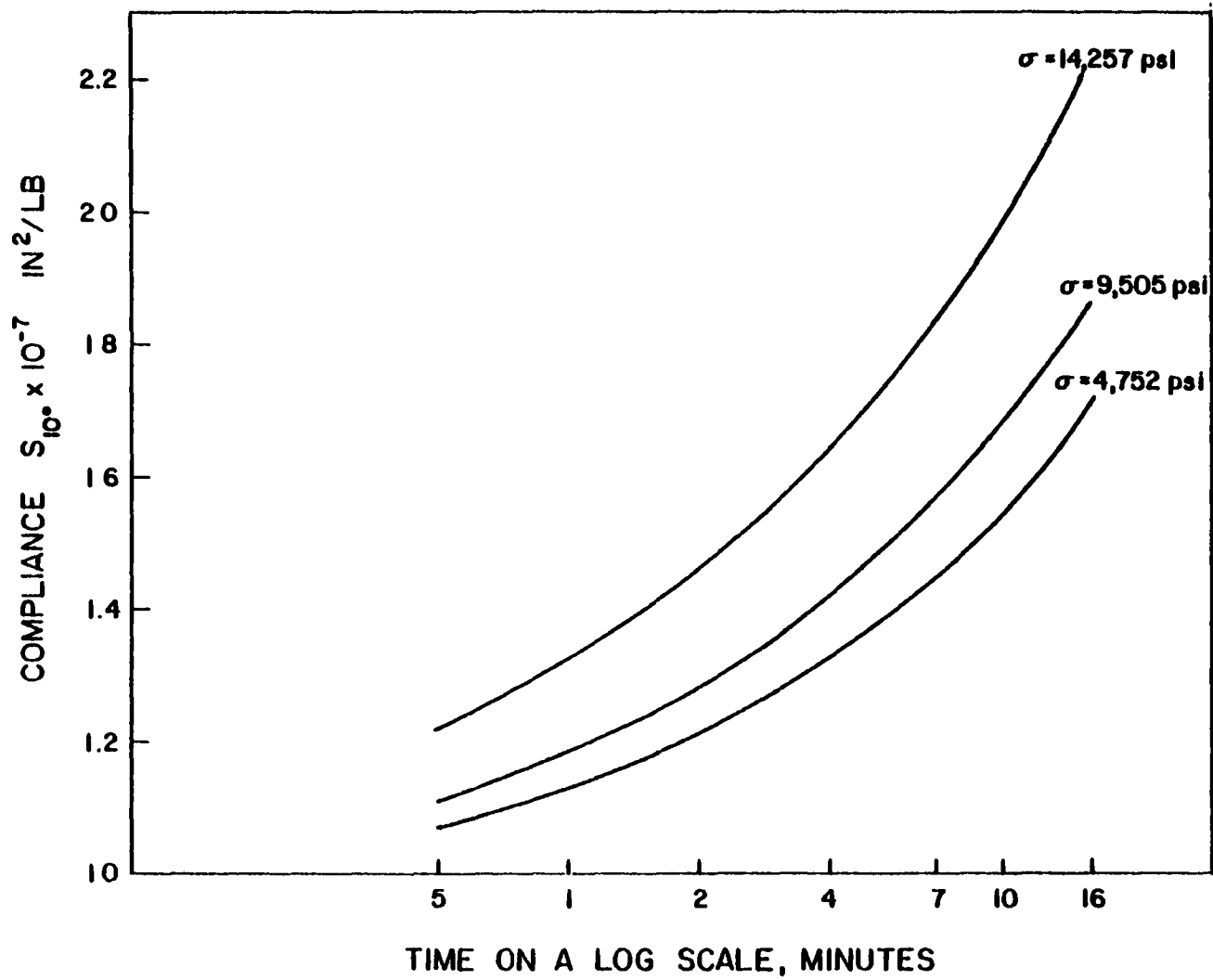
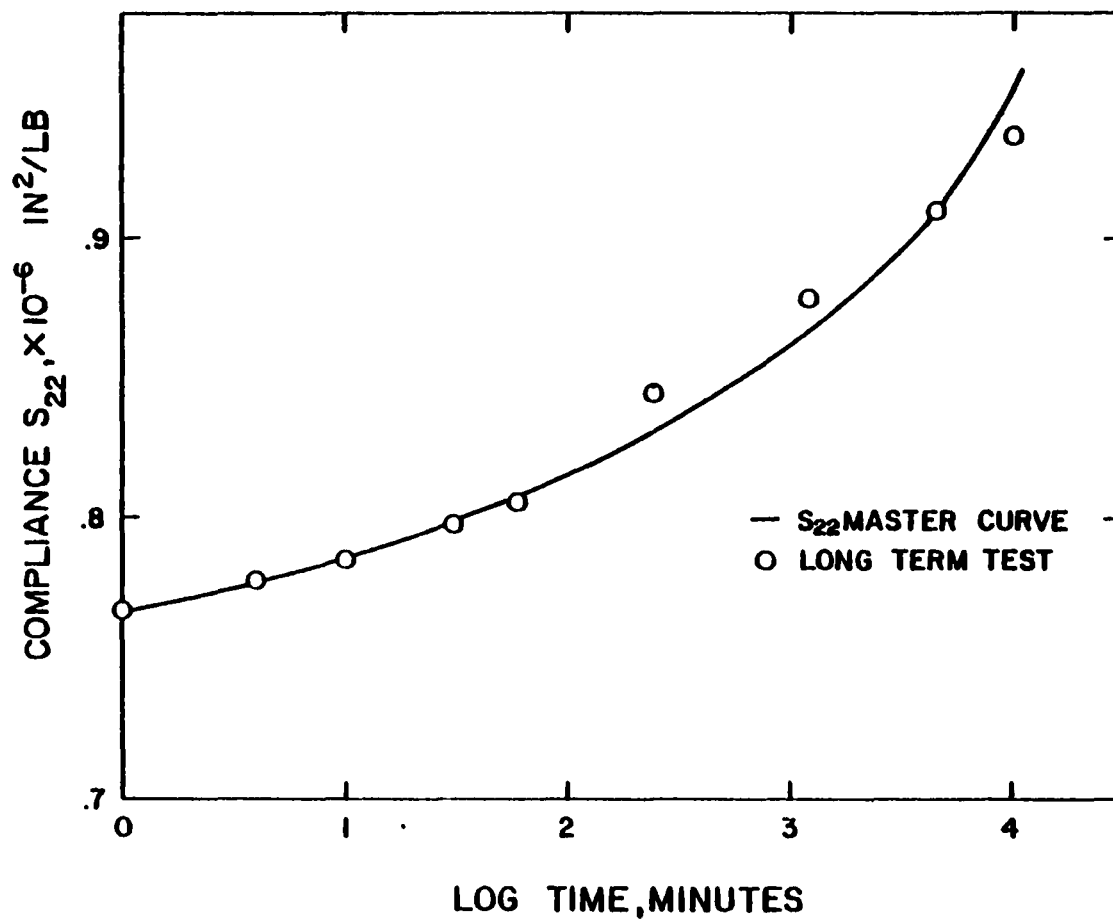Figure 8-14. $S_{10°}$ compliance at 380°F as a function of stress level.

Figure 8-15. Comparison of S_{22} master curve with a long term test at 320°F and σ = 2,750 psi.
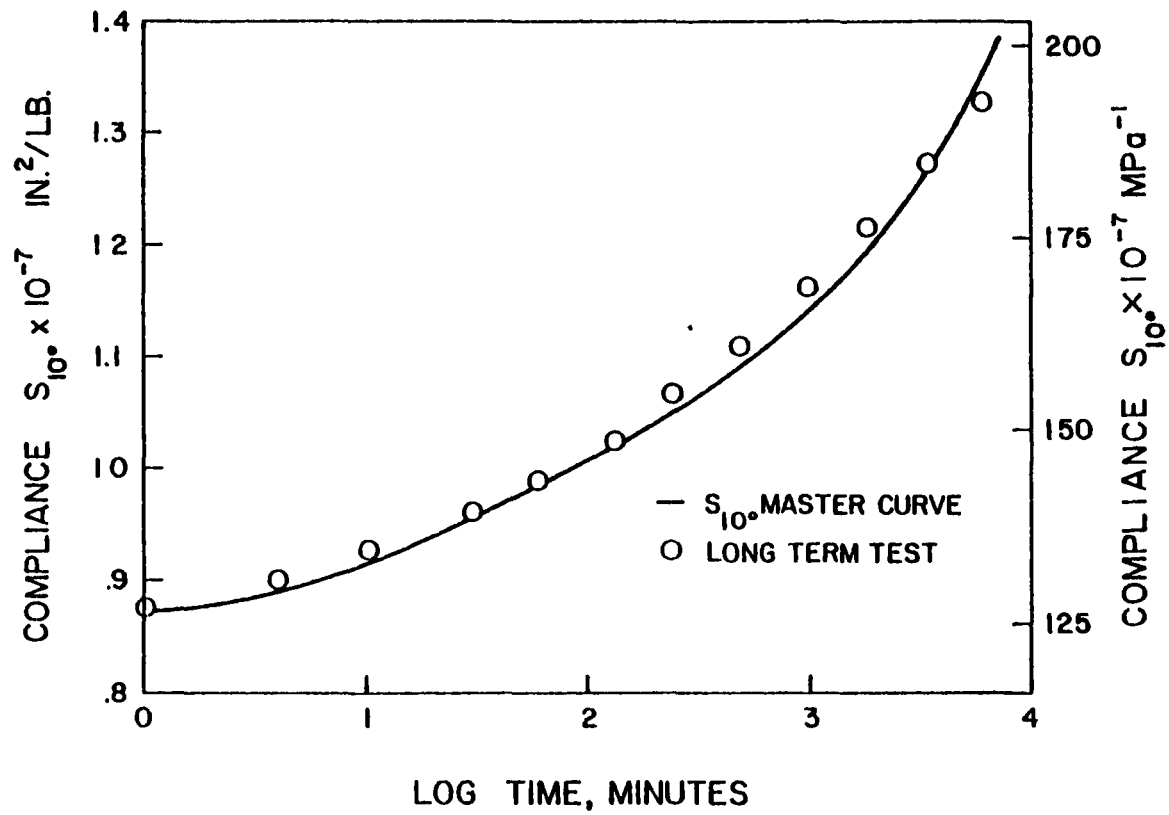
Figure 8-16. Comparison of S_{10° master curve with a long term test at 320°F and σ = 19,500 psi.

The S_{22} and S_{66} stress dependent master curves were also used in conjunction with equation 2-4 (the transformation equation) to predict the long term compliance of $[30°]_{8s}$ and $[60°]_{8s}$ specimens at 320°F. These predictions are compared with long term tests in Figures 8-17 and 8-18. Agreement is seen to be fair to good.

By way of explanation, the 320°F temperature was selected to result in a creep test of reasonable duration, i.e., about one week in length or a time interval of 10^4 min. Lower temperatures such as 290°F would have required a very long creep test to achieve significant changes in compliance. On the other hand, a higher temperature of about 350°F would have produced significant changes in transient creep strain in too short a time period with the possibility of premature creep ruptures and undesirable scatter.

When an off-axis prediction is made, the stress must be broken into components associated with the principal material axes. Further, vertical and horizontal shifting is required of the master curves to match the conditions of the test. Of course, the precise amounts of shift due to temperature and stress are not known individually but only in aggregate.

When equation 2-4 (transformation equation) is used to make a prediction, S_{11} and S_{12} must be known. Separate tests using biaxial gages were run on $[0°]$ specimens to determine these values over a range of temperatures. It was anticipated that neither S_{11} or S_{12} would be temperature dependent. However, S_{11} was noticed to decrease slightly with increasing temperature. Changes in gage factor with temperature cannot account for this effect. Nor does any specific
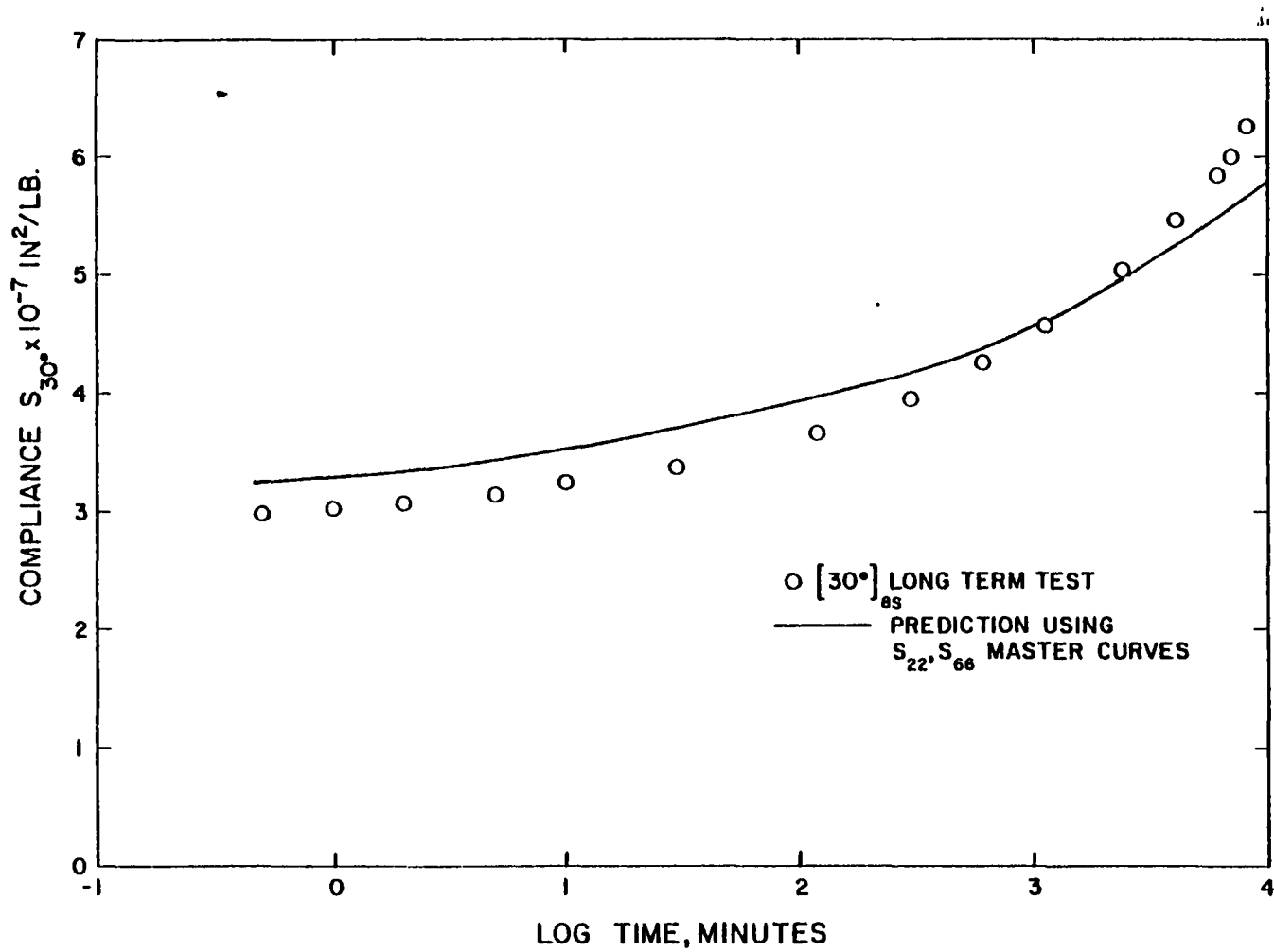
Figure 8-17. Comparison of predicted long term compliance, $S_{30°}$, with that measured in a long term test at 320°F.
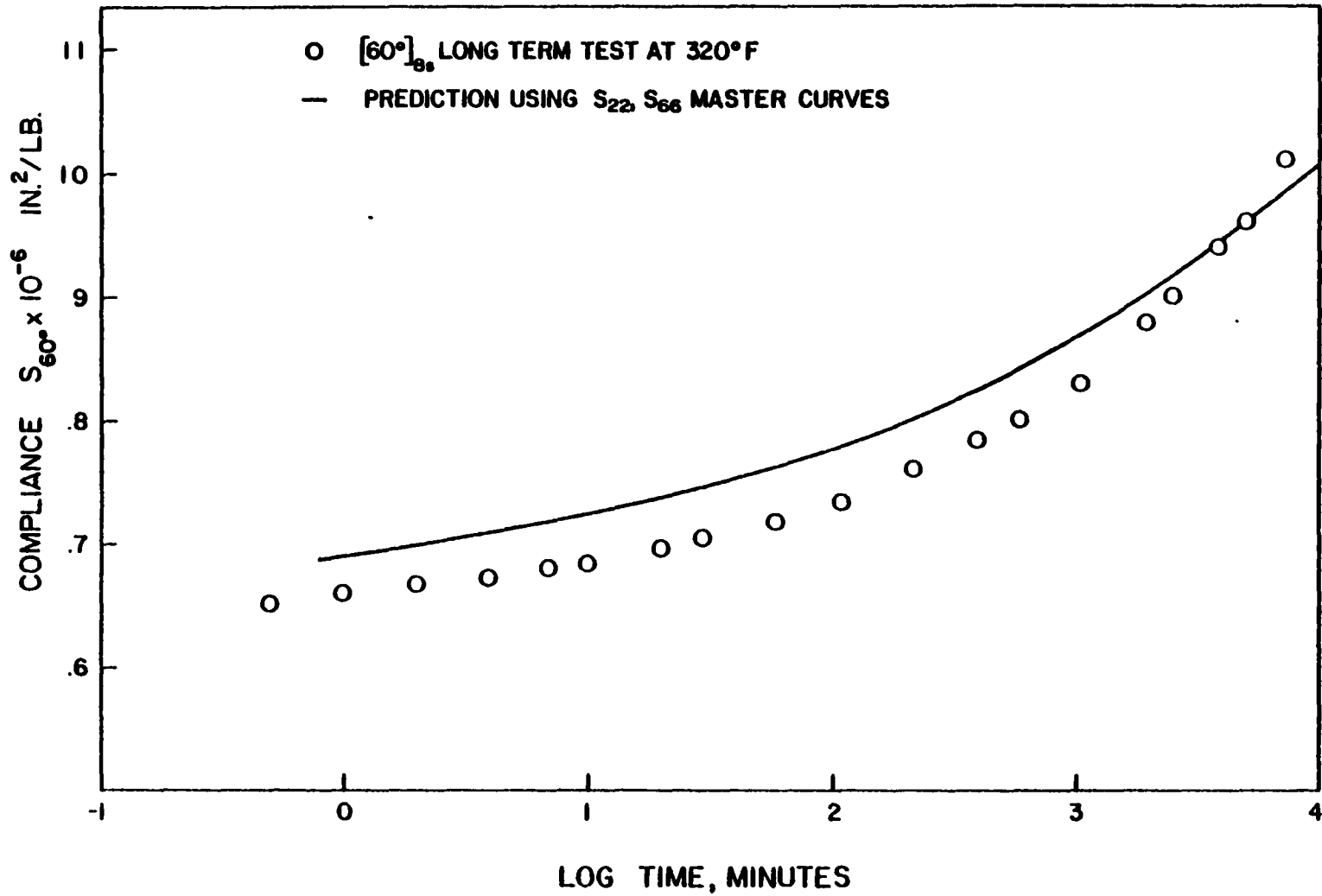
Figure 8-18. Comparison of predicted long term compliance, $S_{60°}$, with that measured in a long term test at 320°F.

reference of such behavior appear in the literature, however, in the work of Yeow (1978a) this author noticed that the S_{11} compliance used at elevated temperature differed from that reported for room temperature. Also, a slight negative time dependence (i.e., contraction under tension) was noticed in S_{11} at elevated temperatures. The viscoelastic nature of the gage adhesive was thought to be the cause of the above two phenomena. The gage installations in question were prepared as previously described with a postcure. It is possible that an alternative adhesive, such as a ceramic cement, may be warranted if greater precision is required. Alternatively, an entirely different type of strain transducer, such as a high temperature LVDT extensometer, could be employed to alleviate any adhesive problem.

The conditions for which S_{12} is equal to S_{21} were given previously. The measured values of these compliances were not identical, however, they were close enough to be considered equal in the work described here. Yeow (1978a), in independent tests, also verified this assumption after forming master curves for $v_{12}(t)$. In the work presented here the following average values were used for S_{11} and S_{12}.

$$S_{11} = 4.587 \times 10^{-8} \text{ in}^2/\text{lb}$$
$$S_{12} = -1.514 \times 10^{-8} \text{ in}^2/\text{lb}$$

Curing Phenomena

Previously described anomolies in the mechanical behavior of the specimens led to the idea that the specimens could indeed be experiencing additional curing (postcuring) during testing. Additional curing could in turn lead to changes in compliance and strength.

In order to test this hypothesis a small test program was initiated.

Initially the T300/934 graphite/epoxy prepared by LMSC was cured at 350°F for 90 minutes. The effects of cure time and temperature on thermosetting epoxy resins have been extensively studied by Gillham (1974,1977). He demonstrated that cure temperature and length of cure can drastically affect the glass transition temperature and mechanical properties. Of particular importance is the relationship between the cure temperature, the glass transition at the gel point, and the maximum glass transition of the fully cured resin. A full discussion cannot be given here, however, the important point appears to be whether vitrification of the resin occurs before, simultaneously, or after gelation. The susceptibility of the resin to postcuring phenomena also depends on the length of cure. For a complete understanding of the curing process a series of tests with the neat resin would be required.

The measurement of the T_g may be done in a number of ways. Several of the more popular techniques involve measurement of thermal expansion or damping ratio. It is well known that the coefficient of thermal expansion undergoes a slope discontinuity at the primary (alpha) transition and that the damping coefficient peaks at primary and secondary (alpha, beta, etc.) transitions. Alternatively, a Differential Scanning Calorimeter (DSC) may be used. In the present study only thermal expansion and DSC methods were used. The DCS provided the least definitive results and hence will not be discussed further.

No specialized equipment was available for measurement of thermal expansion so strain gages were employed. A piece of low expansion

glass was procured locally from the Corning Glass Works for use in bridge completion. Two strain gages were mounted on opposite sides of a $[90°]_{8s}$ specimen and two gages were mounted on the glass. Gages on the specimen were wired into opposite arms of a full bridge. Small amounts of "apparent" strain effect not eliminated did not hinder the determination of the T_g as absolute measurements are not required. A more important consideration was the installation and curing of the gages. In order to reduce postcuring in the composite during curing of the strain gage installation, a low cure temperature was utilized.

The thermal expansion was measured with a strain indicator while the specimen was heated in an oven. The temperature was monitored with a thermometer whose sensing element was in contact with the specimen. At each test temperature at least five minutes was allowed for stabilization. When the specimen was first heated the thermal expansion showed a discontinuity in slope at 356°F as shown in Figure 8-19. The specimen was subsequently cooled to room temperature and reheated to 420°F. The specimen was again cooled to room temperature while measurements were made. In this instance the T_g was again determined to be 356°F. However, the slope of the thermal strain curve obtained during cooling was considerably steeper than the curve obtained during heating. The reason for this phenomenon is not known, but it could be an important point since in analytical and numerical thermal stress analysis the same coefficients are used for heating and cooling. After several heating cycles the specimen was heated for twelve hours at 420°F, cooled slowly to room temperature (to eliminate physical aging), and slowly reheated to 420°F while measurements were taken. This data
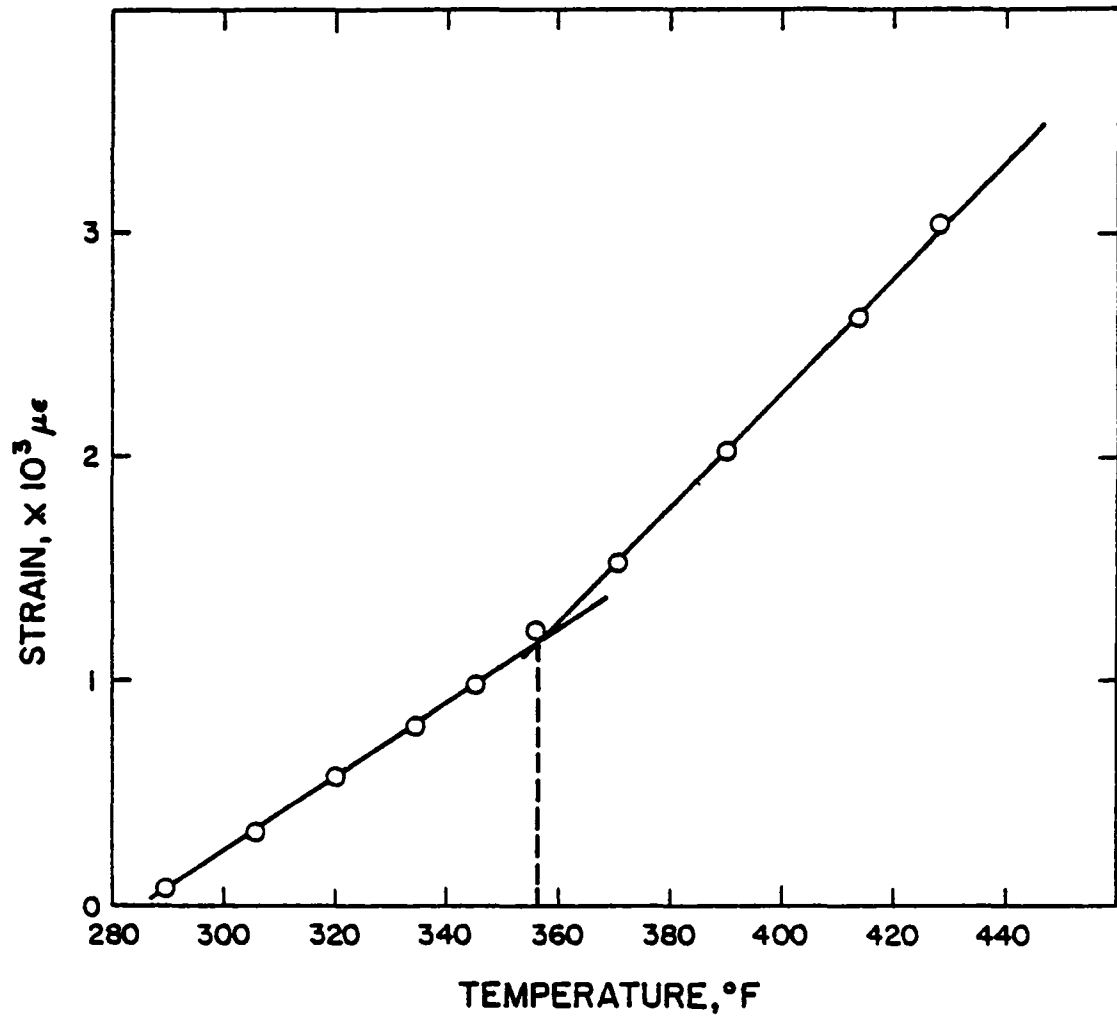
Figure 8-19. Thermal expansion prior to post cure.

is shown in Figure 8-20 where it can be seen that the slope discontinuity is now at 381°F. In a similar type of postcuring experiment Blaine and Lofthouse (1979) increased the T_g of an epoxy by 100°C with a three-hour postcure after 45 minutes of initial curing.

Within the reliability of the data, the thermal expansion experiments prove that some form of material postcuring occurred. Also, these results demonstrate the need to ascertain if specimen preconditioning prior to testing is necessary, as was true in this case.

A testing program to quantify the effects of postcuring or thermal conditioning was undertaken. The creep response of a typical $[10°]_{8s}$ specimen and S_{66} master curves before and after postcuring are shown in Figures 8-21 and 8-22 respectively. As may be observed, large differences between compliances of postcured and unpostcured specimens were found. Additional curing of the composite was also accompanied by increases in strength. The effects of postcure time on the ramp loaded strength of $[45°]_{8s}$ tensile specimens are shown in Table 8-1. As can be seen, these effects are indeed significant. Furthermore, this phenomena made the evaluation of creep rupture test results much more difficult. Just recently it was learned that T300/934 often received a lengthy postcure several years ago.* Such was not the case with any of the material discussed here.

Physical Aging

Physical aging is known to cause severe problems of data interpretation similar to the postcuring phenomenon just discussed and
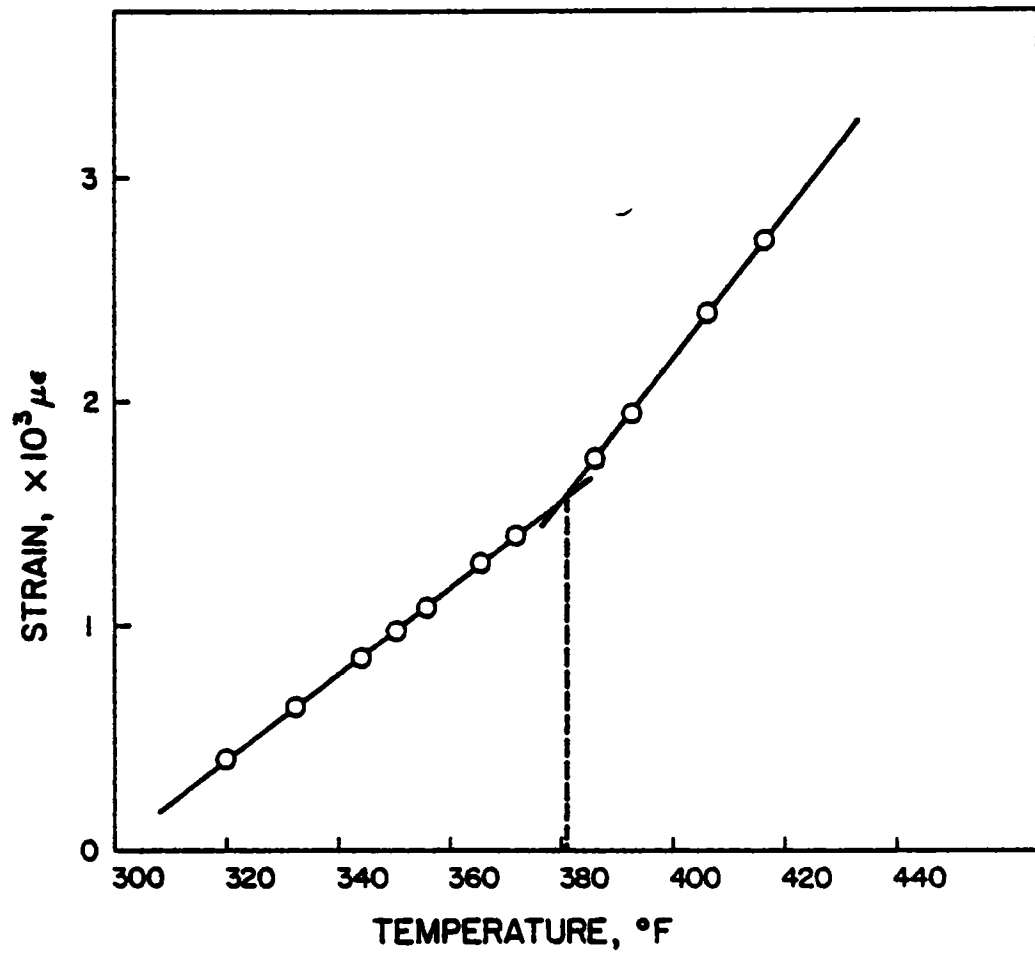
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*See note on page 97.

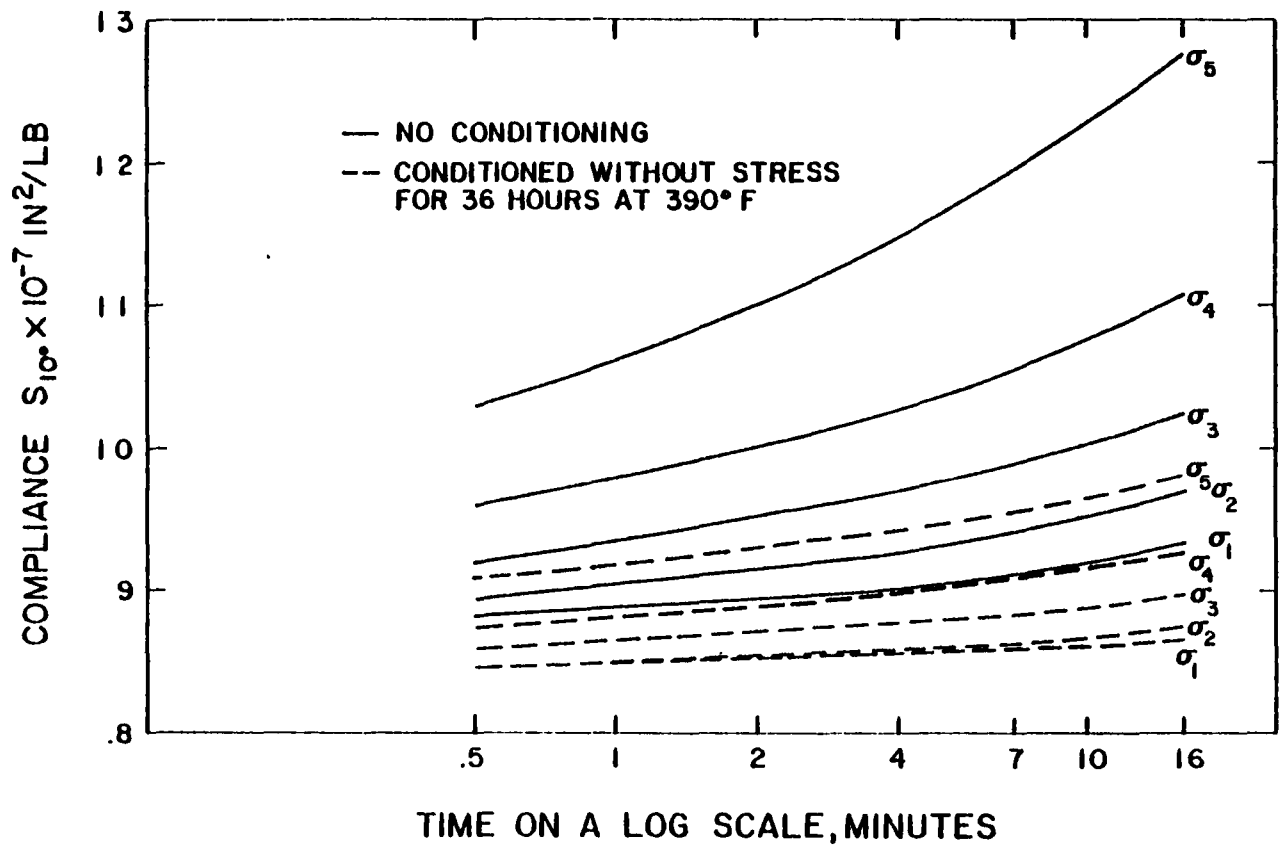Figure 8-20. Thermal expansion subsequent to post cure.

Figure 8-21. Comparison of S_{10° compliance at 290°F with and without thermal conditioning.
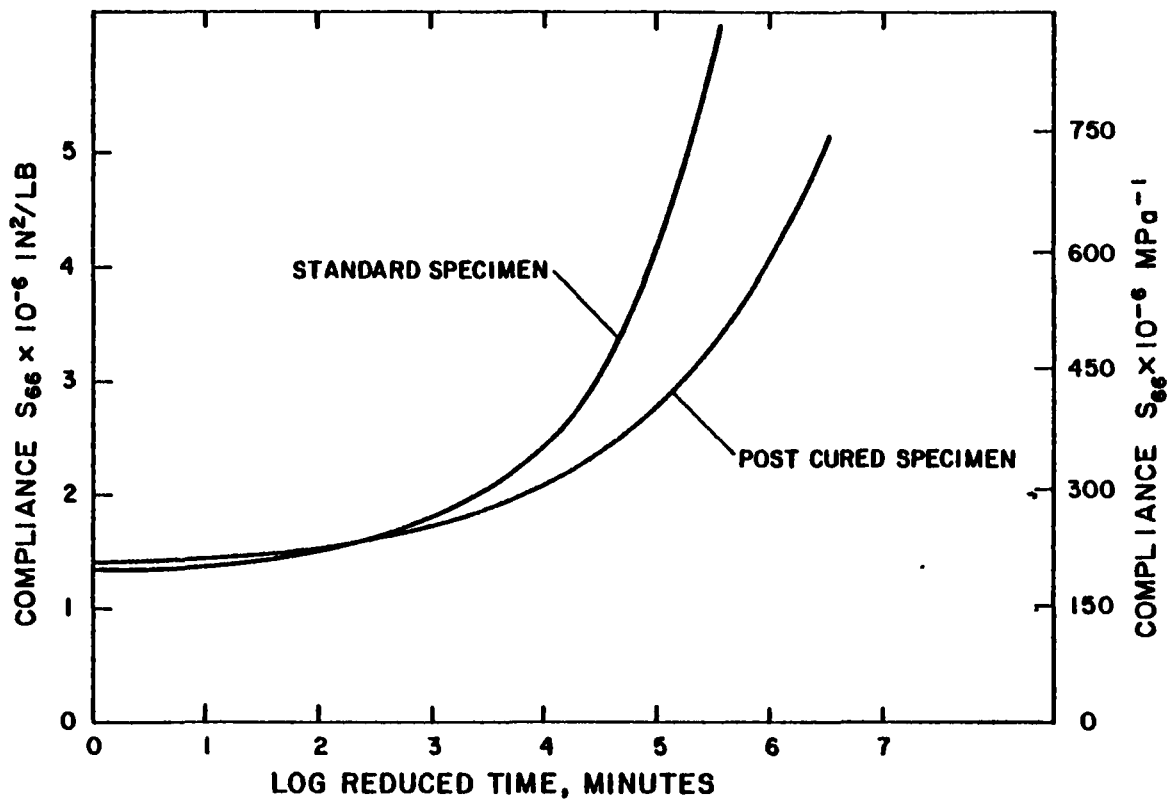
Figure 8-22. A comparison of S_{66} obtained from specimens with and without post cure.

is potentially equally important to the experimentalist. Aging was originally investigated in an attempt to understand the erratic nature of the original experimental results and certain aspects of the material behavior which were unexplainable as was described earlier. While the concept does not directly account for many of the phenomena observed, anyone doing testing of polymeric composites is well advised to be aware of the physical aging process for polymer based materials.

In a polymeric material, such as epoxy, the molecules are very long and intertwine in a manner similar to spaghetti. Some of the volume contained within the material is occupied by the molecular chains themselves, however, a good deal of volume is unoccupied and hence is termed free volume, V_f. Many investigators postulated long ago (see Ferry (1970) for example) that free volume plays an important role in molecular segment mobility. The greater the free volume the greater the molecular freedom and hence the larger the deformations. For each temperature a unique amount of free volume is required for thermodynamic equilibrium. Generally, most polymers have equilibrium free volume vs. temperature relationships similar to the one shown in Figure 8-23. The similarity between Figure 8-23 and the thermal expansion data given earlier for T300/934 graphite/epoxy is apparent. That free volume and thermal expansion are closely related is well known and is to be expected. Excess amounts of free volume may be trapped in a material when temperature change is not quasi-static. For example, Figure 8-23 shows what might occur when a polymer is rapidly cooled from a temperature, T_o, above the T_g to a temperature, T_1, below the T_g. Obviously an extra amount of free volume, ΔV_f, is
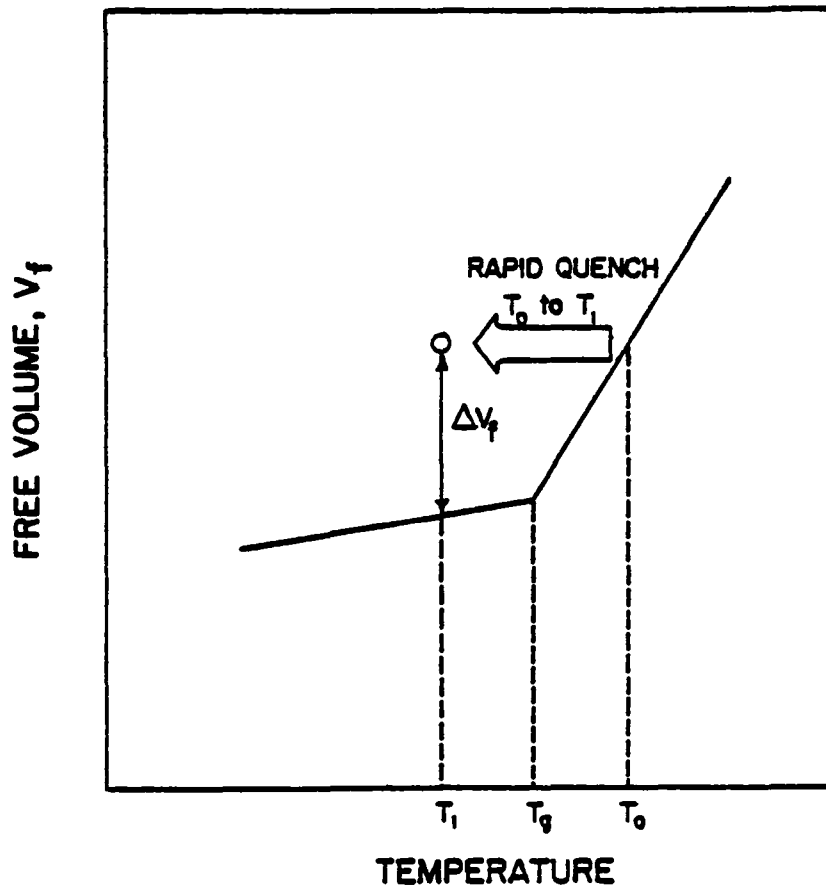
Figure 8-23.   Relation between free volume and
temperature.

quenched into the material beyond the amount normally present upon cooling slowly. The more rapid the cooling rate the larger ΔV_f will be, however, some extra free volume will generally be present whenever the temperature change is not quasi-static. Depending on the temperature, T_1, the free volume will gradually assume its equilibrium value. Struik (1978) has suggested that when T_1 is below the highest secondary transition temperature, T_β, the excess free volume will likely be permanent (at least for all practical purposes). However, when T_1 falls between T_β and T_g, ΔV_f may change significantly over periods of time comparable to or shorter than the duration of testing programs. The variation in free volume with time and the relation between this variation and subsequent effects on virtually all material properties is termed "physical aging." As would be expected, the rate of change of free volume is affected by the aging temperature and is also proportional to the magnitude of the instantaneous value of ΔV_f. Thus, the equilibrium value of free volume is approached asymptotically, and the effects of the aging may persist for long periods of time.

Recently, Struik (1978) has written a monograph on this subject and additional details on most of the aspects of physical aging may be found there. Of primary importance here are the effects of physical aging on creep compliance (particularly short term creep compliance used in preparing master curves) and rupture strength. Struik (1978) has shown that the short term creep compliance may be strongly affected by physical aging as shown in Figure 8-24. Here, the aging time, t_e, represents the elapsed time between quenching and the time of each test. As can be seen from the figure, the aging time
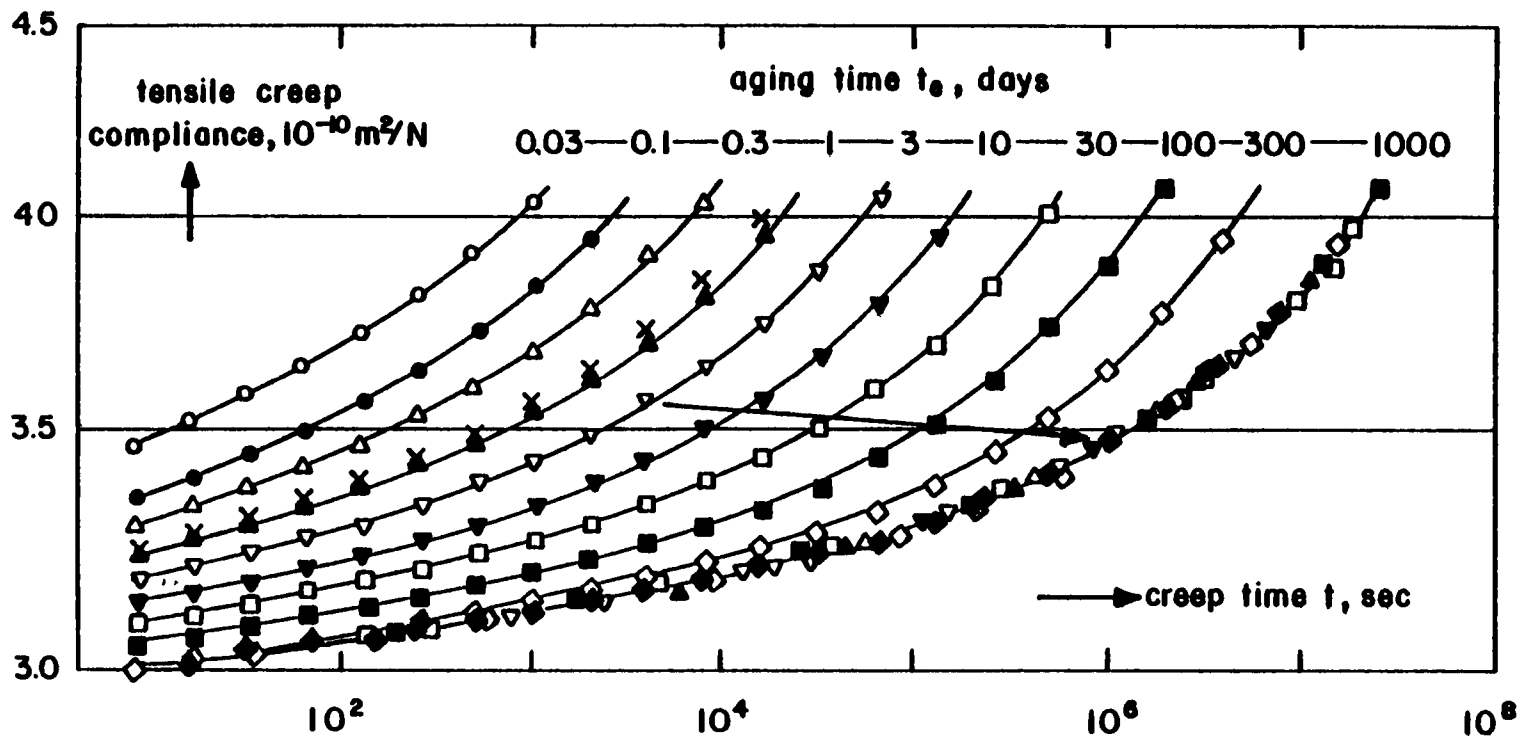
Figure 8-24. The results of Struik (1978) showing physical aging of creep compliance for PVC quenched from 90 to 20°C. The X's show the results to be thermoreversible when the specimen was requenched.

can introduce changes in the compliance curves of up to four orders of magnitude. Furthermore, the shape of the individual compliance curves is such that a master curve may be formed by translation of the individual curves. Of primary importance, however, is the result that the aging process is thermoreversible. As seen from the figure, at the conclusion of the testing the specimen was requenched and tested after one day of aging. Nearly identical results were obtained. Thus, whenever a polymer is taken above its T_g there is a possibility for reinitiation of the aging process.

One might ask how physical aging could affect the results presented here. There are several considerations. As previously described the material was cured by the manufacturer for 1-1/2 hours at 350°F. This was shown to be at or about the T_g. If, for example, the material received a temperature excursion or for some reason the curing temperature and time was insufficient for complete curing, the aging process could be activated upon specimen cool-down. Aging would then continue indefinitely for temperatures above T_β, which is thus far unknown. (Hassel (1979) has shown T_β to be -70°C for one epoxy laminate.) More likely, activation of aging would be due to rapid cooling from the temperatures required for curing or postcuring gages or end tabs. Fortunately, the specimens used here were allowed to cool slowly in the oven, because it was thought at the time that undue thermal shock would be harmful to the specimen. However, the possibility of some physical aging is still a definite possibility.

When creep data is taken from an individual specimen for master curve creation while aging is taking place, an erroneous master curve

will be obtained. Struik describes a number of predictive methodologies that may be used in the presence of aging. However, it seems most appropriate that a better solution is to avoid the aging phenomenon all together. To do this the specimen need only be heated above its T_g at any reasonable rate, and then subsequently cooled at a very slow rate (several degrees F per hour should be more than adequate) to a point reasonably below the T_g. The specimen could subsequently be cooled more rapidly to ambient. This procedure is quite similar to the "freezing" cycle used in the frozen stress technique of photoelasticity. Once annealed in this way the specimen would contain the equilibrium amount of free volume and hence ΔV_f would be zero. The temperature could be subsequently raised and the specimen tested without fear of physical aging effects.

Much less has been written about the effects of physical aging on the strength of polymers. One would expect the decrease in free volume during aging to produce a decrease in ductility. This has been verified by Ophir et al. (1978). Furthermore, the reduction in ductility has been shown by Ophir to give somewhat lower rupture strains. Unfortunately, the corresponding rupture stresses are not given.

Also, virtually no information is available about aging effects on composite moduli or strengths. Quite obviously, as most composites are effectively quenched, aging and postcuring effects may be quite significant and need to be carefully investigated. In fact, almost all matrix dominated data for composites in the literature could be suspect due to these effects. Thus, aging and postcuring may be prime

reasons for the large amount of data scatter found in composites. Variations in delayed fracture times of over 4 orders of magnitude have been found for chopped fiber composites (Brinson et al. (1977) and Heimbuch and Sanders (1978)) and may have been the result of aging and/or postcuring behavior.

IX. EXPERIMENTAL RESULTS AND DISCUSSION -- CREEP RUPTURE

In the course of this study creep rupture results were obtained on both the "old" and "new" materials. Tests on the "old" material included off axis unidirectional laminate tests on $[30°]_{8s}$ and $[60°]_{8s}$ specimens and general laminate tests on $[90°/±60°/90°]_{2s}$ and $[±45°]_{4s}$ specimens. Tests conducted on the "new" material were all unidirectional and included $[90°]_{8s}$, $[60°]_{8s}$, and $[45°]_{8s}$ geometries.

The tests conducted on the "old" material were done primarily to ascertain the validity of the previously discussed assumption that a strength master curve exists and has the same shape as the reciprocal of compliance master curve. On the other hand, creep rupture tests conducted on the "new" material were evaluated with respect to several of the other criteria discussed in section VI. Tests on the "old" material were limited to a single temperature due to lack of material. On the other hand, the "new" unidirectional material was tested at multiple temperatures for a more complete study of the time dependent strength.

General Laminate Tests on the Old Material

The first series of creep rupture tests conducted were performed at 356°F on $[90°/±60°/90°]_{2s}$ and $[±45°]_{4s}$ specimens made from the "old" material. These tests were primarily conducted so that a comparison could be made with previous predictions made by Brinson (1979). These predictions incorporated the previously discussed assumption of similarity between the strength and reciprocal of

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compliance master curves and lamination theory. The raw data obtained in these tests is shown in Tables 9-1 and 9-2. Comparisons between the data and the predictions of Brinson (1979) are shown in Figures 9-1 and 9-2. Several observations can be made from the tables and figures. First, it is noted that there was a great deal of difficulty in obtaining a creep rupture failure, particularly in the case of $[\pm45°]_{4s}$ specimens, in which case only four creep ruptures occurred. As can be seen from the figure, there is only marginal agreement between the predicted strength and the data. Of particular concern is that the predicted strength drops off rapidly while the data seems to be nearly time independent. One encouraging aspect is that the predicted strength at short times is not grossly in error, particularly in the $[\pm45°]_{4s}$ case. This is of interest because room temperature strengths were used to scale the prediction in a manner consistent with that discussed in section VI.

In the case of the $[\pm45°]_{4s}$ specimens, rather large deformations were present at failure. Failure strains of nearly 20% were not uncommon. These large deformations can be directly attributed to a "latticing" of the plies. In these cases the fiber angle can make significant changes in orientation. Simple calculations indicate that a fiber initially at 45° would rotate to 38° under an elongation of this magnitude. Clearly, such a rotation would be accompanied by significant changes in properties. The large axial deformations were also accompanied by significant delamination. Figure 9-3 shows several photographs of a $[\pm45°]_{4s}$ specimen after 3-1/2 days of creep. It was estimated that fully one third of the specimen was damaged, which

Table 9-1. Summary of T300/934 G/E [±45°]$_{4s}$ Creep Rupture Testing.

Spec. No.	Stress* (psi)	Max. Nom. Strain** (%)	Time to Max. Strain hr:min:sec.	Creep Rupture?	Remarks
G-1	11,000 23,300	7.7 -	22:30:00 00:10:00	No Yes	Test discontinued. Load nearly doubled by step increase and creep rupture did occur.
G-2	17,000	-	00:01:30	Yes	-
G-3	15,000	12.5	-	No	Failed during loading.
G-4	12,100	13	-	No	Failed during loading.
G-5	11,300	-	-	No	Failed during loading.
G-6	13,100	-	-	No	Failed during loading.
G-7	11,400	18.8	72:11:30	No	No failure. Specimen micrographed.
G-8	11,400	13.0	-	No	Failed during loading.
G-9	10,800	12.8	-	No	Failed during loading.
G-10	11,100	20.0	00:04:00	Yes	-
G-11	11,200	17.0	00:02:00	Yes	-
G-12	11,000	15.8	-	No	Failed during loading.
G-13	9,800 18,700	17.5 21.8	96:18:00 110:00:00	No Yes	Test discontinued. Load nearly doubled and creep rupture did occur.
G-14	10,900	12.5	-	No	Failed during loading.

*Specimen initially ramp loaded at 1"/min. All testing at 356°F.

**Elongation divided by specimen length.

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Table 9-2. Summary of T300/934 G/E $[90°/±60°/90°]_{2s}$ Creep Rupture Testing.

Spec. No.	Stress* (psi)	Max. Nom. Strain** (%)	Time to Max. Strain hr:min:sec.	Creep Rupture?	Remarks
H-1	6140	1.48	-	No	Failed during loading (rate = .002"/min)
H-2	6130	1.53	-	No	Failed during loading (rate = .02"/min)
H-3	6730	1.62	-	No	Failed during loading (rate = .2"/min)
H-4	7400	1.68	-	No	Failed during loading (rate = 2"/min)
	5350	1.07	18:53:00	No	Test discontinued. Load step increased
H-5	6240	1.22	20:59:00	No	until creep rupture did occur.
	6680	1.35	23:23:00	Yes	
H-6	6210	1.63	00:04:20	Yes	-
H-7	6030	1.24	00:01:07	Yes	-
H-8	5760	1.33	00:02:17	Yes	-
H-9	5590	1.99	29:38:00	Yes	-
H-10	5760	1.47	00:05:56	Yes	-
H-11	5760	1.35	00:37:30	Yes	-
H-12	5670	1.73	00:15:48	Yes	-
H-13	5670	1.87	15:02:00	Yes	-
H-14[1]	5960	1.55	00:07:25	Yes	-
H-15[1]	5870	1.25	-	No	Failed during loading (rate = .5"/min)
H-16[1]	6140	1.41	-	No	Failed during loading (rate = .5 and .2"/min)

*Specimen initially ramp loaded at 1"/min (unless otherwise noted). All testing at 356°F.

**Elongation divided by specimen length.
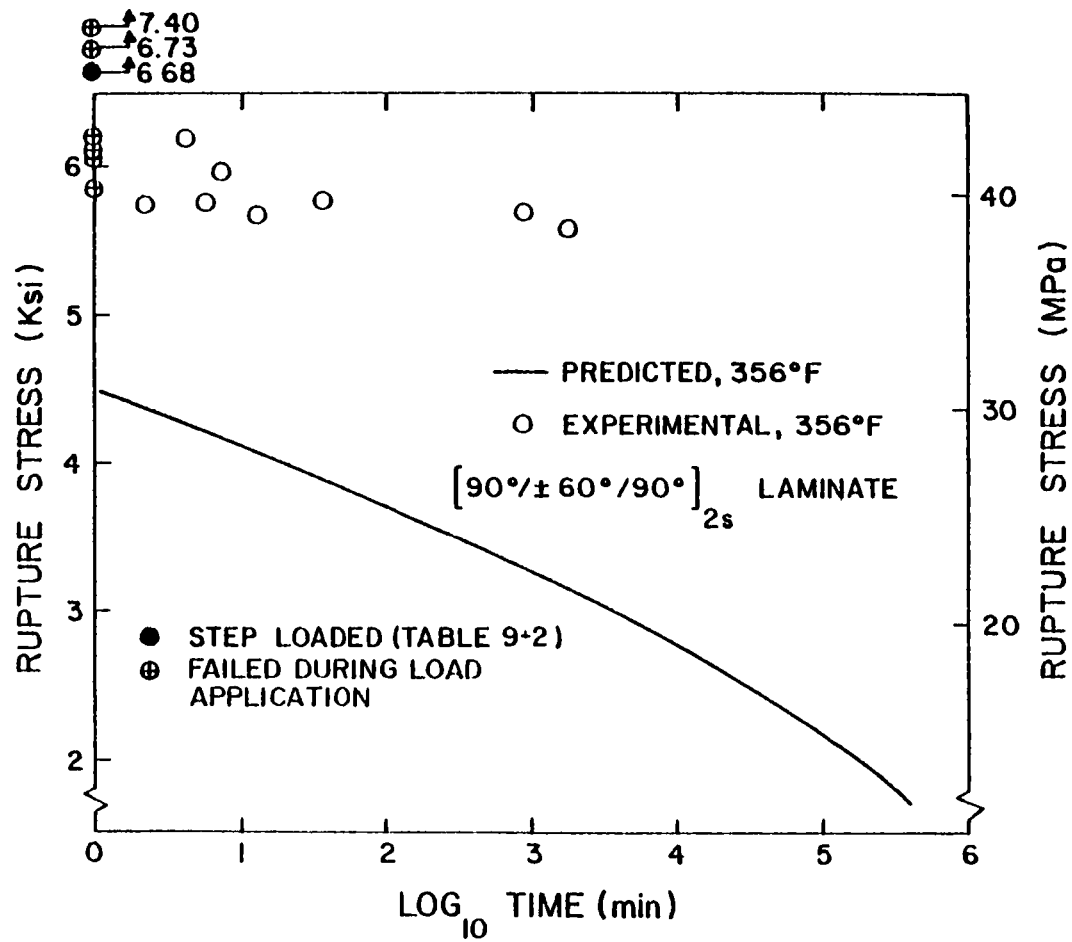
[1]Sharp knee in load-deflection curve.

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Figure 9-1. Comparison of [±45°]₄ₛ creep rupture predictions and experimental results.

Figure 9-2. Comparison of $[90°/\pm60°/90°]_{2s}$ creep rupture predictions and experimental results.
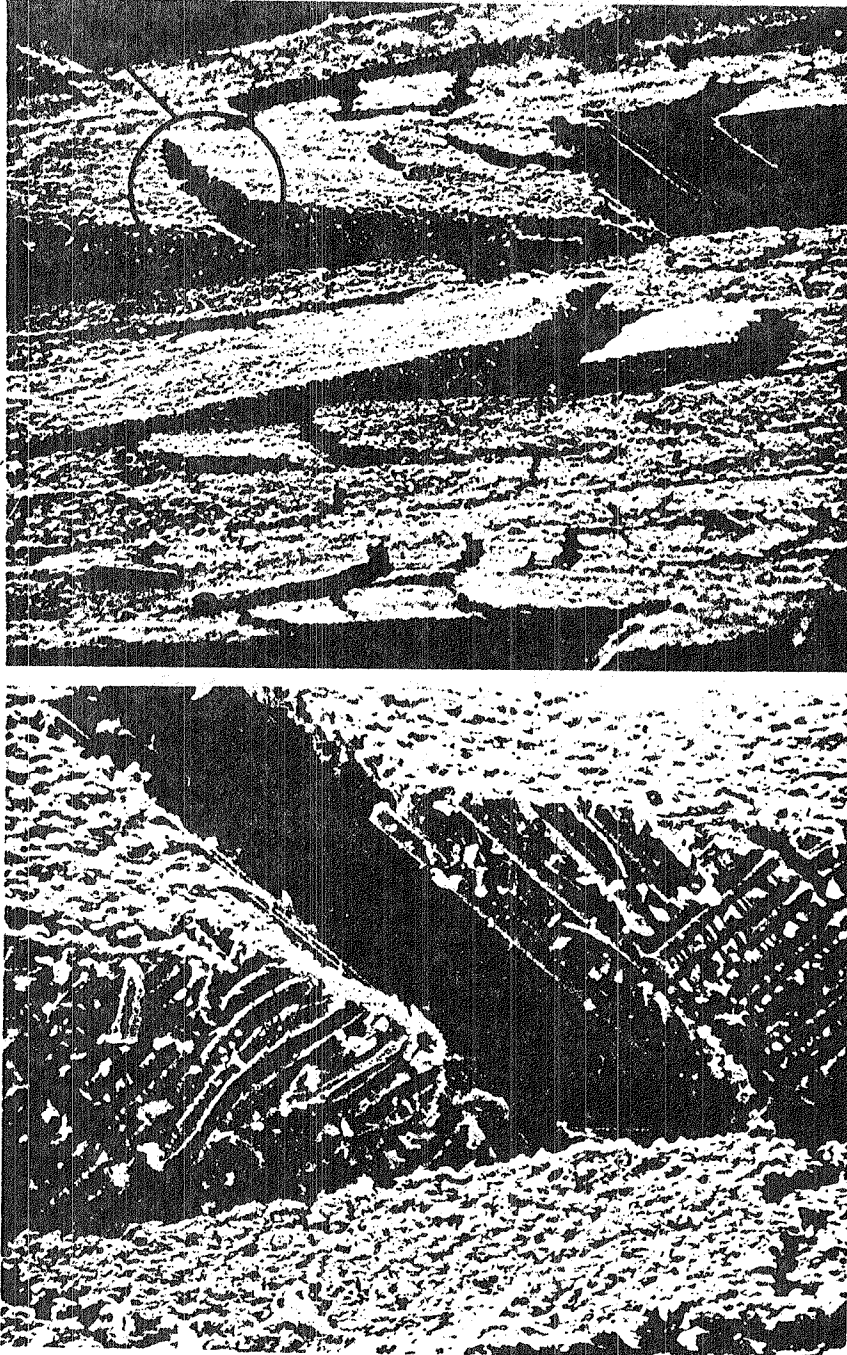
Area enlarged below

Figure 9-3. Photographs of edge delaminations in a $[\pm45°]_{4s}$ creep
specimen.

would indicate that the true rupture strength is in excess of the nominal values reported here.

The deformations in the $[90°/\pm60°/90°]_{2s}$ specimens were of much smaller magnitude probably due to the constraint provided by the 90° plies. When these specimens were loaded a number of them showed pronounced "knees" in their load deflection curves which was likely due to failure of 90° plies. The fact that nearly all the $[90°/\pm60°/90°]_{2s}$ specimens failed at or about the same stress was somewhat surprising. Perhaps the same postcuring phenomenon noticed in the new material was a contributing factor.

Unidirectional Laminate Tests of the Old Material

Creep rupture tests were performed on unidirectional $[30°]_{8s}$ and $[60°]_{8s}$ specimens fabricated from the "old" material at a test temperature of 320°F as shown in Figures 9-4 and 9-5. The test temperature used in the general laminate tests was purposely reduced for these tests in the hope of eliminating scatter in the data. Small errors in temperature control and measurement were believed to be much less critical at 320°F since this temperature was considerably below the T_g. In the vicinity of the T_g it is well known that small variations in temperature can produce large changes in properties in some polymers. As may be observed, the unidirectional creep strength data agrees reasonably well with predictions using the compliance master curve and the assumption of similar compliance and creep rupture master curves. The room temperature strengths were used to scale the reciprocal of compliance master curves to produce the strength
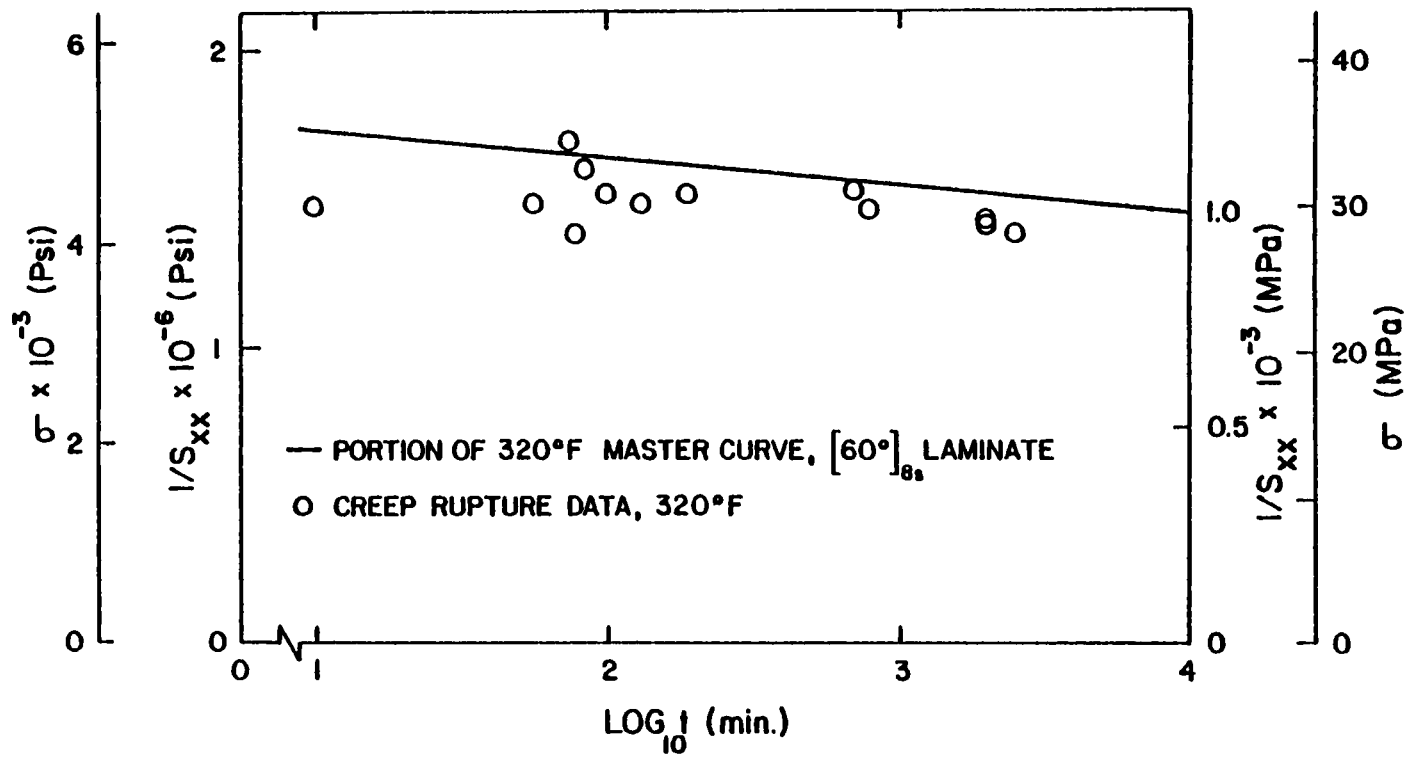
Figure 9-4. Comparison of [60°]$_{8s}$ creep rupture predictions and experimental results. Predictions assume strength and modulus master curves have the same shape.
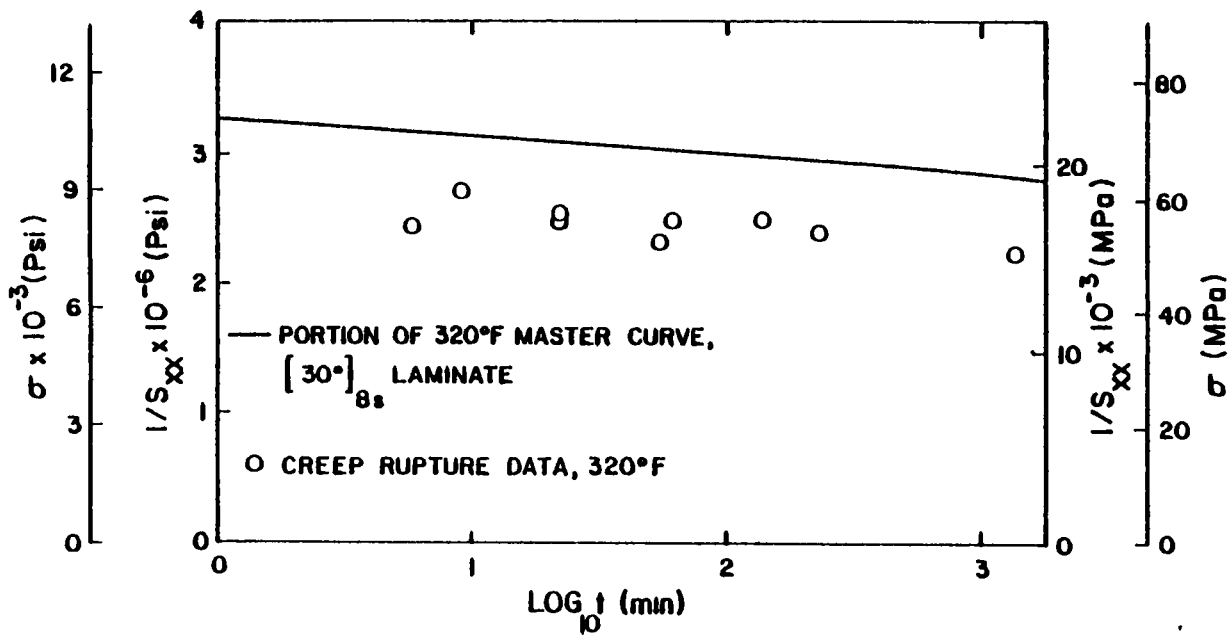
Figure 9-5. Comparison of [30°]_{8s} creep rupture predictions and experimental results. Predictions assume strength and modulus master curves have the same shape.

predictions shown in Figures 9.4 and 9.5. Had the 320°F short term strengths been used to scale the prediction instead, the agreement would have been better since the slopes of the data and the prediction are similar. Unfortunately, adequate supplies of the "old" unidirectional material were unavailable for additional testing at other temperatures. Thus, these data are inadequate to prove or disprove the strength master curve assumption.

Unidirectional Tests on the New Material

With an adequate supply of "new" material available, a more extensive creep rupture program was begun with $[90°]_{8s}$, $[60°]_{8s}$, and $[45°]_{8s}$ specimens. Each orientation was tested at 290°F, 320°F, 350°F, and 380°F. These data are shown in Figures 9-6, 9-7, and 9-8. The solid lines drawn through the data points in the figures represent "best fit" lines obtained through linear regression. In addition, an effort was made to correlate the creep rupture data with the theories of Zhurkov, the modified rate equations 6-2 and 6-3, and the Larson-Miller and Manson-Haferd equations given in Appendix A. In general the classical behavior of rupture times emanating from a pole as discussed in Chapter VI were not observed. It is appropriate to note that the reciprocal of compliance-strength master curve assumption discussed in the preceding section is in general agreement with the various classical theories of creep rupture.

A computer program was written to determine the statistically most correct parameters for the Larson-Miller method. The Manson-Haferd method was also tried using cross plotting techniques.
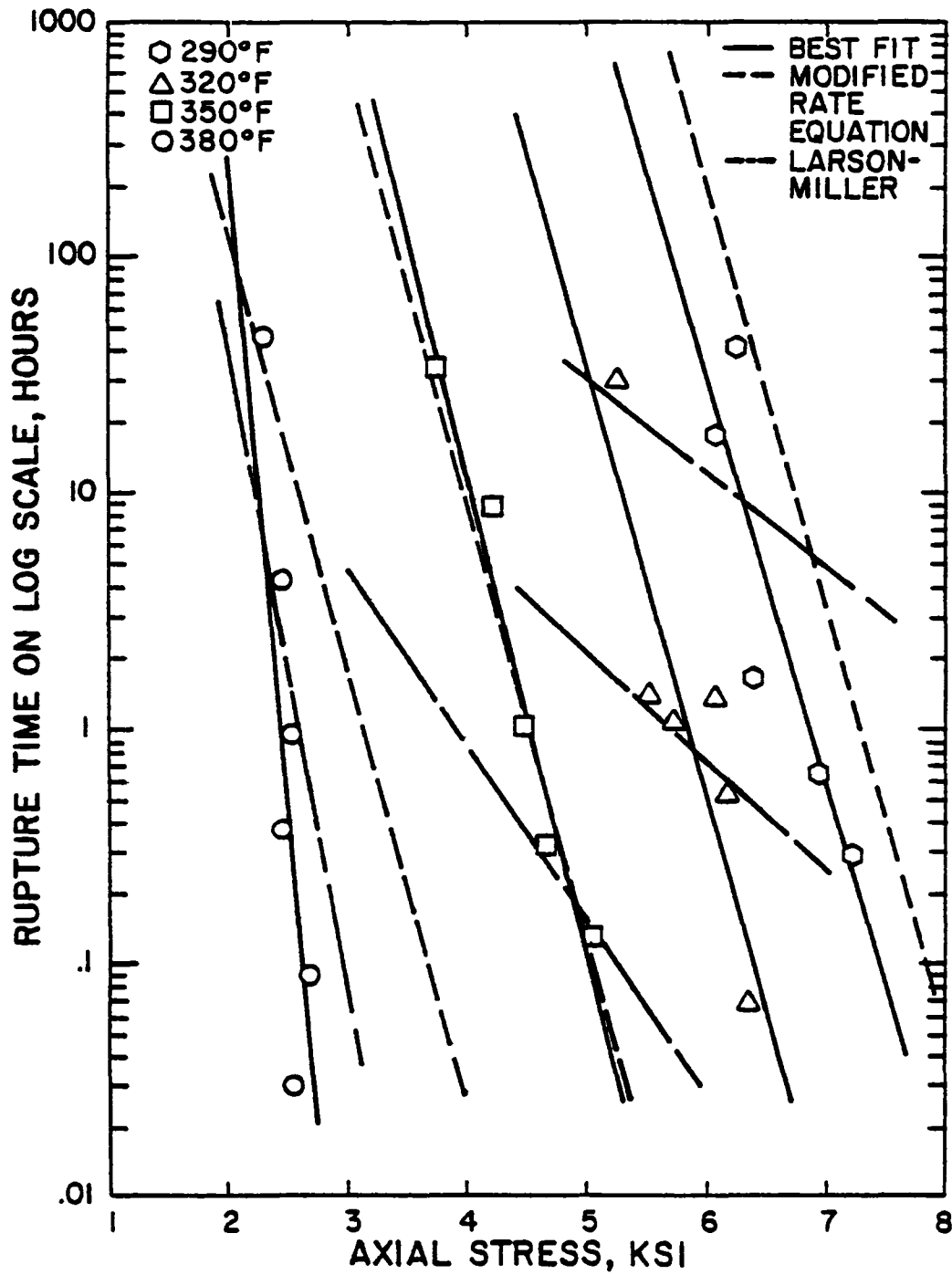
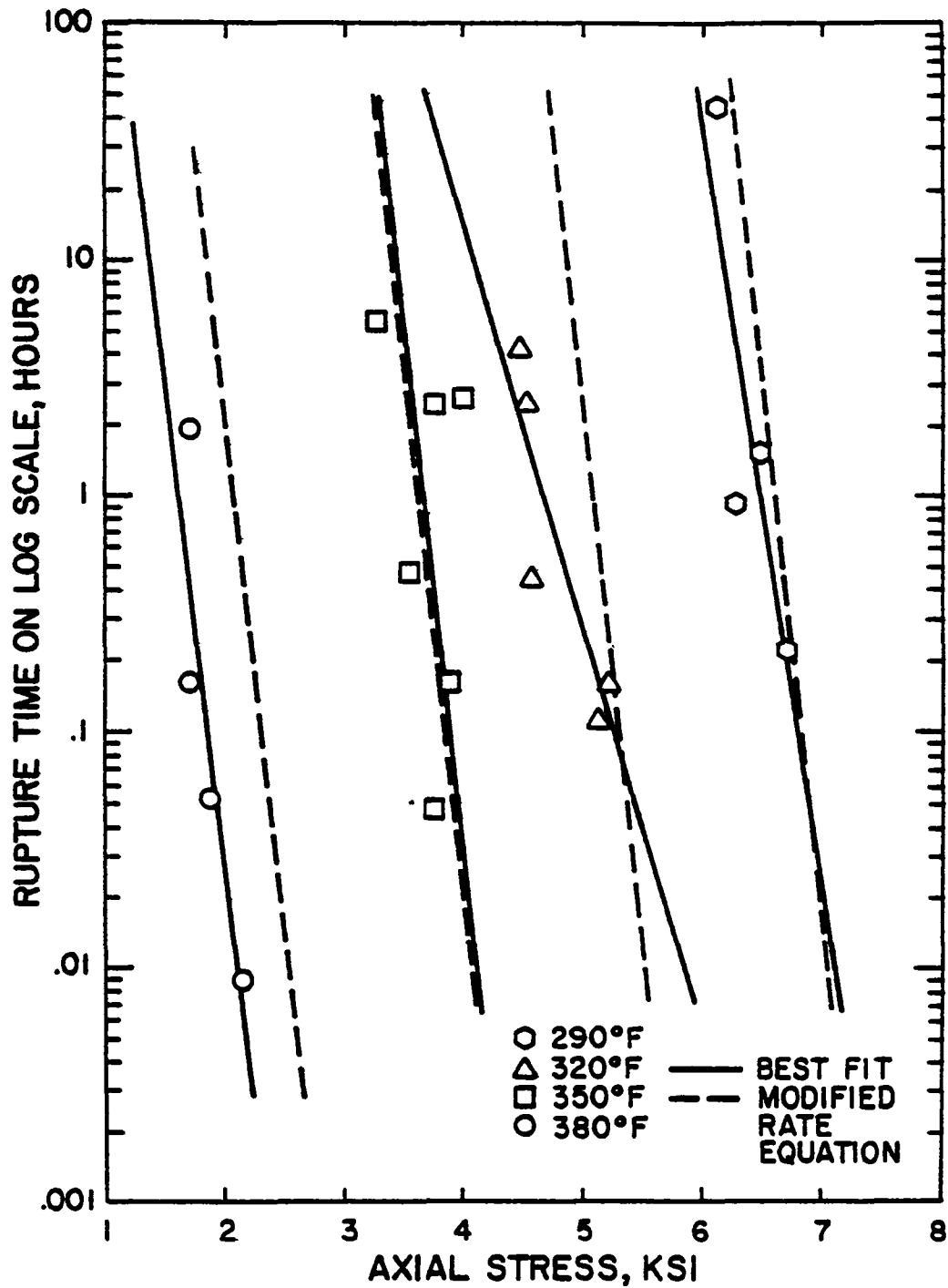Figure 9-6. Summary of creep rupture data obtained on $[90°]_{8s}$ specimens, lines are best fit.

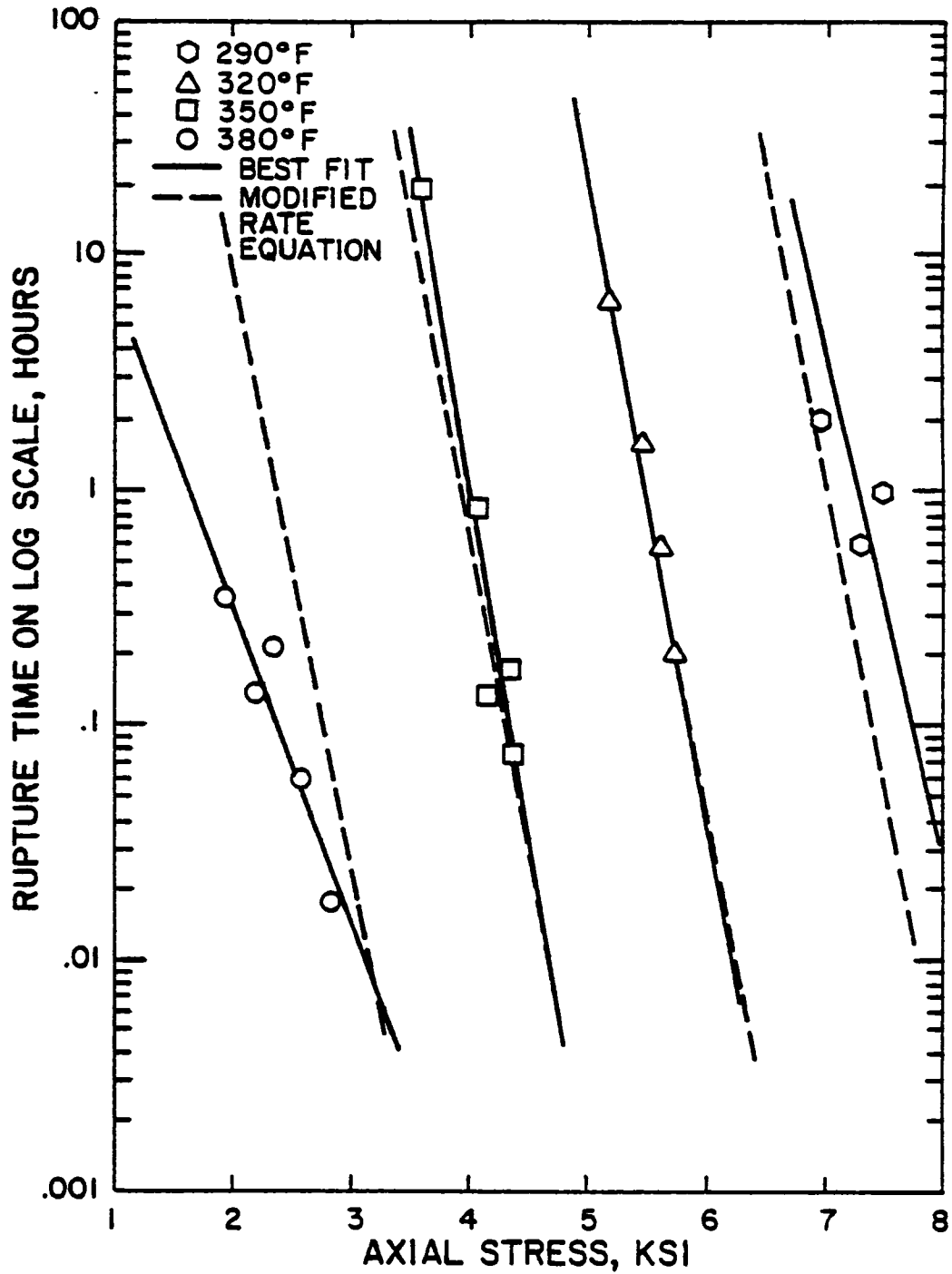Figure 9-7. Summary of creep rupture data obtained on $[60°]_{8s}$ specimens, lines are best fit.

Figure 9-8. Summary of creep rupture data obtained on $[45°]_{8s}$ specimens, lines are best fit.

Neither of these techniques proved capable of modeling behavior similar to that shown in the figures. For example, the Larson-Miller results are shown in Figure 9-6.

Initial attempts to apply Brüller's energy criterion also failed to give the proper creep rupture response. However, the theory was applied as if the composite were homogeneous. No attempt was made to apply a micromechanics approach which would have separated the energy in the matrix from that in the fiber. In a unidirectional creep specimen it would seem that the energy stored in the fiber would be nearly constant. This being the case, a micromechanics treatment would not seem to be required. The validity of Brüller's theory or other deformational theories would have been much easier to test if creep measurements via a clip gage or extensometer had been made on all specimens during each creep rupture test.

The most successful fit of the data was made with equation 6-2 of Slonimskii et al. (1977). The dashed lines in Figures 9-6, 9-7, and 9-8 show the results of using equation 6-2 to fit the data. The fit is not considered excellent, but in most cases it is good or fair. Slonimskii et al. (1977) attribute the difference between equation 6-2 and the classical Zhurkov equation 6-1 to the type of bond breakage. They believe that equation 6-1 is valid when chemical bonds are being broken and that equation 6-2 is more appropriate when some kind of intermolecular unraveling is taking place. The validity or applicablity equation 6-2 to composite laminates is unknown.

The true reason for the creep rupture results not agreeing with classical creep rupture theories may be related to the postcuring

phenomenon. The material may be continually strengthening due to curing while at the same time it is being weakened by the creep rupture process. Using this argument, the data of Figures 9-6, 9-7, and 9-8 would indicate that at high temperature the strengthening progresses faster than the weakening for all but the highest stress levels.

One may wonder what, if any, connection might exist between the $[90°]_{8s}$, $[60°]_{8s}$, and $[45°]_{8s}$ data. One possible relation is the octahedral shear stress. Lou and Schapery (1971) found that octahedral shear stress in the matrix could be used as a normalizing factor in the nonlinear viscoelastic characterization of unidirectional composites of various angles. According to their analysis the normalized octahedral shear stress, $\frac{\tau_0}{\sigma}$ (where τ_0 = octahedral shear stress and σ = remote applied stress), is nearly constant for the unidirectional orientations studied here. When figures 9-6, 9-7, and 9-8 are overlayed enough similarity is found to lend credibility to the idea that octahedral shear stress in the matrix may well be the most significant factor in creep rupture or fracture of unidirectional composites. For more complete verification smaller fiber angles, such as $[30°]_{8s}$ and $[15°]_{8s}$, would be required. These orientations have significantly different values of normalized octahedral shear.

X. SUMMARY AND CONCLUSIONS

The present study was intended to complement and supplement previous VPI efforts to develop analytical and experimental procedures for the prediction of long term moduli and strengths of graphite/epoxy laminates (T300/934) from short term test results (accelerated characterization). Where previous efforts were based upon the TTSP and linear viscoelasticity, it was intended that the current work would be directed toward nonlinear viscoelasticity as would be appropriate for rupture or fracture events. A major feature was to search the literature for information relative to master curve formation where nonlinearities would naturally be included.

In the course of the literature survey it was ascertained that the TTSP principle for TSM (simple) materials usually incorporates only horizontal shifting or a time scale change for compliance (modulus) master curve formation. On the other hand, often TCM materials require vertical as well as horizontal shifting. The type of shifting necessary to form master curves may be different in the glassy, transition and rubbery regions, it was learned. This fact is of great importance inasmuch as earlier VPI work used only a Tobolsky-Ferry normalization (vertical shifting) procedure for all temperature levels including the glassy region. As a result, earlier data may have been partially responsible for the discrepancies in the predictions of lamina and laminate strengths shown earlier in Figures 9-1, 9-2, 9-4 and 9-5.

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The compliance (modulus) process of TTSP master curve formation was also found to be a function of the type of vertical scale used, i.e., linear or logarithmic. A linear vertical scale is justified when the initial and transient components have the same temperature dependencies. T300/934 seems to be this kind of material as vertical shifting on a linear scale was appropriate in previous and current efforts.

Procedures to incorporate the nonlinear effects of stress level into master curve formation were also studied. Due to apparent inherent difficulties in the analytical procedures studied, a graphical time stress superposition method (TSSP) was used. The method, when coupled with TTSP, gave rise to a combined time temperature stress superposition principle (TTSSP). Vertical and horizontal shifting was a function of both stress and temperature giving rise to a combined shift factor, $a_{T\sigma}$.

Similar procedures for introducing humidity were discussed together with the concept of a property surface in n-dimensional space where n would represent the number of accelerating parameters.

Perhaps, the single most important feature of all the super-position procedures whether temperature, stress, humidity, etc., or combinations thereof is to recognize that they tacitly assume deformation mechanisms are the same from zero load and time until rupture occurs. That is, an accelerating parameter only serves to speed up a deformation process. For example, for a given value of an accelerating parameter a sequence of deformation events occur over a

certain time interval. For a larger value of the same parameter, the same events occur, only faster.

This does not mean that changing mechanisms could not be incorporated, only that the current continuum experimental and mathematical models we have investigated do not do so.

Vertical shifting procedures and considerations of the type of vertical scale was noted to be important in stress and humidity master curve formations as was the case for TTSP.

Aging and postcuring effects were discussed and noted to have a potentially serious effect on master curve formation. Experimental evidence was given to the effect of postcuring on T300/934. It was noted that the manufacturer eliminated a crucial postcuring operation on T300/934 between our receipt of "old" and "new" batches of material. Other manufacturing deficiencies led to thickness variations. "Old" and "new" batches had significantly different matrix dominated properties.

Creep and creep rupture data was presented. The TTSSP was used to form master curves for 10° and 90° laminates. This information together with the orthotropic transformation equation was used to predict 30° and 60° laminate compliances over 10^4 minutes. Creep tests were performed over 10^4 minutes and comparisons were made with all master curves. Reasonable agreement was obtained.

Unidirectional creep rupture data for the "old" material was presented and was compared to creep rupture predictions. The creep rupture predictions were made on the assumption that the creep rupture curve had the same form as the reciprocal of compliance master curve.

Reasonable agreement was obtained.

The unidirectional creep rupture predictions were used as dis-
cussed in an earlier publication, Brinson et al. (1978), to predict
creep rupture of $[90°/\pm60°/90°]_{2s}$ and $[\pm45°]_{4s}$ laminates. Creep
rupture results were presented and compared with predictions. Poor
agreement was obtained.

Unidirectional creep rupture data for "new" T300/934 material
was presented and compared to various analytical predictions. Only
the modified rate equation among those discussed gave reasonable
agreement.

The work described here represents the first known application
of an accelerated characterization technique utilizing both tempera-
ture and stress as accelerating factors on an advanced reinforced
composite such as graphite/epoxy. The method can easily be extended
to include the effects of humidity as described earlier. Due to the
many pitfalls likely to be encountered when applying the TTSSP tech-
nique, long or at least medium term tests are absolutely necessary
for master curve credibility. If long term tests cannot be conducted,
then several medium term tests should be performed. At least one
test should be used in the lower temperature area where properties
vary slowly with time.

The creep rupture data acquired during this investigation
represents the largest body of graphite/epoxy off-axis data presently
available. Unfortunately, none of the predictive methods tried thus
far accurately represents the data. At present, the reasonable agree-
ment between the reciprocal of compliance-strength similarity

assumption found in the "old" $[30°]_{8s}$ and $[60°]_{8s}$ specimens is still unresolved particularly in view of possible postcuring and aging effects and the fact that the creep rupture results with the "new" material were inconclusive in this regard. However, one must bear in mind that the "old" material was only tested at a single temperature and therefore not put to a rigorous test. To obtain consistent and accurate results future test programs would of necessity need to eliminate any aging/curing phenomena present in the material. At high temperatures the curing process is undoubtedly greatly accelerated. Additionally, all specimens should be exposed to as consistent a preparation and test environment as possible. This includes baking and storing specimens identically and carefully monitoring elapsed time for thermal stabilization prior to test. All specimens should be tested in as short a time frame as possible to reduce other unavoidable aging phenomena to a minimum.

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APPENDIX A

The following sections briefly describe several of the more common parameteric approaches to the creep rupture phenomenon.

Larson-Miller Parameter

The Larson-Miller method of predicting creep rupture assumes that the following equation is valid for a given stress level.

$$T (C + \log t_r) = \text{constant} \tag{A-1}$$

where T = the absolute temperature

t_r = the time to rupture

C = Larson-Miller constant

The entire left hand side of equation (A-1) is referred to as the Larson-Miller parameter which takes on different values for various levels of applied stress. For many materials the Larson-Miller constant, C, is said to be twenty. In principle C and the Larson-Miller parameter for a given stress may be determined from only two data points obtained at the same stress level. The best approach, however, is to collect many sets of data and determine C and the stress dependence of the Larson-Miller parameter in the least squares sense. In the study previously described this was done. However, the method was incapable of describing the creep rupture behavior of the experimental data.

In actual practice, C and the Larson-Miller parameter are often calculated from short term data and then used to predict much longer

rupture times.

Manson-Haferd Parameter

The Manson-Haferd method of predicting creep rupture assumes the validity of the following equation:

$$\frac{T - t_a}{\log t_r - \log t_a} = \phi \qquad \text{(A-2)}$$

where

T = the absolute temperature

t_r = the time to rupture

T_a and $\log t_a$ = material constants

ϕ = the Manson-Haferd parameter (a function of applied stress)

The Manson-Haferd parameter, ϕ, may be calculated for a given stress level by solving equation A-2 simultaneously with the results of two data sets at constant stress, σ_0, but at different temperatures. ϕ may similarly be calculated for another stress level, σ_1. The material constants T_a and $\log t_a$ may then be calculated by simultaneous solution of equation A-2. A better approach is to plot sets of data obtained at several stress levels on a graph of $\log t_r$ vs. T. Straight lines drawn through the data at each stress level are made to intersect at a point. The stress dependence of ϕ may be calculated from the slope of the line through each set of constant stress data. The material constants T_a and $\log t_a$ may be calculated from the point of common intersection. This procedure was used on the creep rupture data given previously, however, the data could not be forced to intersect at a common point so the method could not be applied.

16 Abstract

A brief review of necessary fundamentals relative to composite materials and viscoelasticity is proveded. Subsequently the accelerated characterization techniques of Time-Temperature-Superposition and Time-Temperature-Stress-Superposition are treated in detail. An experimental procedure for applying the latter to composites is given along with results obtained on a particular T300/934 graphite/epoxy. The accelerated characterization predictions are found in good agreement with actual long term tests. A postcuring phenomenon is discussed that necessitates thermal conditioning of the specimen prior to testing. A closely related phenomenon of physical aging is described. The effect of each on the glass transition temperature and strength is discussed.

Creep rupture results are provided for a variety of geometries and temperatures for T300/934 graphite/epoxy. The results are found to compare reasonably with a modified kinetic rate theory.

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