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On the Use of Accelerated Test Methods for Characterization of Advanced Composite Materials

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Abstract

A rational approach to the problem of accelerated testing for material characterization of advanced polymer matrix composites is discussed. The experimental and analytical methods provided should be viewed as a set of tools useful in the screening of material systems for long-term engineering properties in aerospace applications. Consideration is given to long-term exposure in extreme environments that include elevated temperature, reduced temperature, moisture, oxygen, and mechanical load. Analytical formulations useful for predictive models that are based on the principles of time-based superposition are presented. The need for reproducible mechanisms, indicator properties, and real-time data are outlined as well as the methodologies for determining specific aging mechanisms.

Nomenclature

ε	Strain
γ_{xy}	Shear strain in a lamina
σ	Stress
$\Delta\sigma$	Stress jump
τ_{xy}	Shear stress in a lamina
D	Generalized compliance
S	Compliance
S_o	Initial compliance
$[S]$	Compliance matrix for a lamina
$[\bar{S}]$	Transformed compliance matrix for a lamina
S_{ij}	Compliance terms in $[S]$
E	Generalized stiffness or modulus
t	time
τ	Relaxation time
t_e	Aging time
t_{eref}	Reference aging time
t_e^o	Initial aging time
ξ, λ	Effective time
c_1, c_2	Constants used in WLF equation
T	Temperature

T_o	Reference temperature
T_g	Glass transition temperature
a_{te}	Aging shift factor
a_T	Temperature shift factor
$\bar{a}_T$	Temperature shift factor that includes aging effects
$\bar{a}^{t_{e1}}_{T_1/T_2}$	Temperature shift factor at aging time and temperature
ΔH	Activation enthalpy
R	Gas constant
β	Shape parameter
μ	Aging shift rate
$[T]$	Transformation matrix
H	Heaviside unit function

1 Background

Accelerated testing of materials has been a goal of many small-scale and large-scale material characterization programs. Proposed test methods for accelerating material degradation can be found in the literature for application to a wide range of materials including those found in aerospace, civil infrastructure, automotive and transportation, and materials for electronic applications. For advanced polymer matrix composite (PMC) materials, some of the earliest published work on accelerated testing was performed by Brinson and his co-workers [1], [2], [3]. They focused on response at elevated temperature and the use of the time-temperature superposition principle to predict long-term mechanical performance from short-term tests. The analysis approach was to consider the composite to be a viscoelastic material and to use creep testing to generate material constants. For the more general problem of long-term exposure of polymers to a range of environmental conditions, several accelerated test schemes, largely empirical, have been proposed, a number of which can be found in refs. [4] and [5]. More recently, due to the significant number of polymer-based commercial and industrial products, the long-term, or aging behavior of polymers and polymeric composites has been a subject of renewed interest [6], [7] [8], [9], [10] and most recently was the topic of a series of grants sponsored by the National Science Foundation [11]. The accelerated aging philosophy developed by many of these research programs has promoted the use of individual test methods combined in an integrated scheme to provide an accurate method for understanding the different contributions of various degradation mechanisms to durability of PMC materials.

Perhaps the most demanding and critical applications for accelerated testing of materials have involved structural materials for aerospace vehicles. The NASA Super Sonic Transport (SST) program (ca. 1970's) was the first large program designed to explore the use of polymeric composites for structural materials in supersonic commercial transports. During the course of the program, both real-time, and accelerated test methods were developed [12]. Results from this program suggested that singular effects such as load or elevated temperature could be addressed in an accelerated test program if the external variables such as test machine failures, material variability, and laboratory environment could be quantified. During the early 1990's, NASA again started a research program on commercial supersonic flight that included a significant effort to develop primary composite airframe structure [13], [14]. To support this effort and at the request of NASA, the National Research Council's National Materials Advisory Board (NMAB) published a report in 1996 ([15]) on accelerated aging of advanced materials for future aircraft structures. The NMAB study committee was established to (1) provide an overview of long-term exposure effects; (2) recommend improvements to analytical methods and approaches to accelerate laboratory testing; and (3) identify research needed to develop and verify the required testing, predictive analytical capabilities, and evaluation criteria. The NMAB report identified issues related to the aging of aluminum, titanium, polymer matrix composites, and ceramic matrix composites. Suggestions were outlined for accelerated evaluation approaches and analytical methods to characterize the durability of future aircraft materials throughout their service life.

Accelerated testing and long-term durability of polymeric composites continues to be a challenging topic and the point of emphasis for many research programs that cut across several disciplines and applications [16], [17], [18]. The current work draws on this wealth of experience and focuses on specific details associated with accelerated testing, durability, and aging of polymer matrix composite (PMC) structural materials suitable for aerospace applications.

The objective of this report therefore is to provide a rational approach to the problem of accelerated testing for mechanical material properties of advanced polymer matrix composites.

The methods provided herein should be considered as a set of tools that the practicing engineer could use in the screening of material systems for long-term engineering properties in aerospace applications. Requirements for accelerated testing are provided and details of both semi-empirical and analytical based methods are discussed. Consideration is given to long-term exposure in extreme environments that include elevated temperature, reduced temperature, moisture, oxygen, and mechanical load.

2 Introduction

In aerospace vehicles, the durability of a material is ultimately an issue that directly relates to the operational cost of the vehicle. By taking into account durability during the lifetime of the vehicle one can minimize these operational costs. Cost issues aside; studying and understanding the processes related to durability in high performance aerospace materials are critical to the safe design, construction and operation of the vehicle. Unfortunately, despite close attention to details and using the best design methods, the long-term exposure of advanced PMC materials to the use-environment will eventually result in irreversible change(s) in the original properties of the material.

This process of change over time is loosely referred to as "aging". Aging may be broadly categorized by three primary mechanisms: chemical, physical, and mechanical. The interaction (if any) between these three areas is dependent on two variables: material characteristics, and aging environment. Material aging may translate to structural changes in mission-critical components that for an aerospace vehicle can have a potentially catastrophic effect on both the vehicle and its payload [19], [20], [21].

In order to address the primary issue, reduced vehicle lifetime costs, verified accelerated test methods for aging are needed to provide guidance for materials development, and to screen materials, or accurately assess aging tendencies of new and candidate materials. The concept of accelerated testing can be interpreted many different ways and it is therefore important that a common definition of some important terms be established before going into further detail. Three terms are of particular importance: environmental degradation factor, critical degradation mechanism, and accelerated aging.

Environmental degradation factor is the general term for specific use-environment conditions. Heat, moisture, mechanical load, etc. are all environmental degradation factors. Critical degradation mechanism refers to the fact that polymer materials are susceptible to attack by a specific set of environmental degradation factors that include influences due to chemical, physical, and mechanical processes. The critical degradation mechanism is the mechanism that occurs due to this attack and results in a significant loss in any important bulk physical property of the material system. It is assumed that the critical degradation mechanism occurs when the environmental degradation factors are inside the boundaries of the use-environment. For example, critical degradation due to moisture would be assumed to occur only in environments where the relative humidity is typical of operating conditions. Accelerated aging is defined as the process or processes required to accelerate a specific critical degradation mechanism or mechanisms relative to a baseline aging condition; thereby resulting in the material reaching the same aged end-state as a real-time aged material, but in less time.

Only by understanding how aging affects a given material system can it be determined if that aging mechanism can be properly accelerated. In the simplest case, aging is associated with a single mechanism, in which case acceleration of this mechanism will allow meaningful accelerated aging methods to be developed. More likely, the actual aging process involves several different mechanisms that may or may not act synergistically, complicating the problem significantly. Irrespective of these difficulties, it is critical that the mechanisms underlying aging in PMC material systems be studied and explored. Without an understanding of these underlying mechanisms, there is little hope that accelerated aging studies will be of much use in the materials science community. For example, the worst-case scenario is that without the scientific underpinnings, all aging studies would be reduced to costly, trial-and-error, empirical test programs.

In general, material testing is a costly process that often involves many materials-related disciplines and a wide variety of laboratory equipment. It is recognized that while long-term, real-time testing is required to fully assess the durability of materials, accelerated aging may reduce the expense and time involved by significantly narrowing or screening the field of acceptable candidate materials which would go into long-term qualification tests. In addition to materials screening, accelerated testing may help determine residual service life of existing structures and suggest directions for product improvements. This type of information may then lead to changes in the standard practice for materials selection and provide quantitative rationale for manufacturers and fabricators to follow new and improved specific procedures. Typically, a largely empirical approach is used for accelerated aging studies.

The empirical methods for accelerated testing may address the concerns for specific applications and environments, but the need for predicting performance in broader service conditions will require the development of empirical techniques coupled with analytical methods. Overlying this process is the development of accelerated aging methods that define critical environmental degradation factors and their interactions. It is a goal, therefore, that all of the testing that is undertaken should provide insight into how a material behaves and establish input for the development of analysis methods to predict material performance under various conditions of load, temperature, and environment. Validation of accelerated aging methods takes place through a comparison of mechanical properties, damage mechanisms, and physical parameters (e.g. weight loss, changes in glass transition or fracture toughness) from accelerated testing with those from real-time testing.

3 Requirements for Accelerated Testing

Material structure-property relationships can be used to further the understanding of the requirements for accelerated testing. Whether or not we totally understand the relationship between the molecular and morphological structures of a polymer system and its bulk mechanical properties, the fact remains that those bulk properties are determined by features at the molecular and microscopic level. And while the details of the aging process in any given PMC system can be quite complicated, it is worth pausing to consider that the general process of aging is fairly straightforward.

As an illustrative example, during aging of PMC's, one or more environmental degradation factors may act on the polymer matrix. The effects of these degradation factors are then translated down to the microscopic/molecular level where a specific molecular mechanism affects change in the polymer network or chain. This modification of structure is then translated back to the macroscopic level and observed as a change in bulk mechanical performance. Without accurate comparisons to baseline data during real-time aging, this continual evolution of bulk properties may be gradual and largely unnoticeable. It is the challenge of an accelerated test program to speed up the effects of exposure to environmental degradation factors without forcing a departure from the underlying mechanisms that give rise to molecular property modification and hence bulk property changes. Ideally, test conditions can be chosen to accelerate material aging to a sufficient degree that one can establish the rate associated with acceleration.

3.1 Reproducible Mechanisms

This somewhat generalized understanding of structure-property relationships and the influence on the aging process can be expanded further. The most important requirement to keep in mind during the development of an accelerated test method is that it must replicate those changes that occur in the real-time, long-term application. Thus emphasis must be put on the need to understand and reproduce degradation mechanisms associated with each accelerated aging condition. A mechanistic approach to this requirement would require complete knowledge of all relevant degradation mechanisms and the recognition that competing mechanisms may proceed at different rates as well as interact synergistically. This mechanistic approach is beyond the scope of most test programs. Therefore, an approach is proposed that relies on determination of primary degradation mechanisms that are easy to measure.

3.2 Indicator Properties

Another key requirement for accelerated testing is to establish a list of indicator properties that will be measured during test. Examples of these indicator properties include weight, glass transition temperature, and damage state (e.g. crack density). These material indicator properties form the basis for development of more economical accelerated aging schemes for screening new materials and for evaluating the status of materials in long-term aging. To develop this list of indicator properties, exploratory tests should be run with a wide range of properties investigated using in-situ and/or post-test evaluation. Indicator properties should be easy to measure and reliably correlate to changes in residual mechanical properties. Absolute changes and rates of change should be measurable and easily tracked against a firm baseline.

3.3 Real-Time Data

Perhaps the most significant requirement for accelerated testing is coupling mechanical property data from accelerated aging of materials with real-time aging data. The comparison of the accelerated data with real-time data will determine the accelerating factor for any given degradation mechanism. This correlation between real-time and accelerated implies the need to clearly define all environmental degradation factors and determine sensitivity of the factors to variations in parameters (e.g., temperature, humidity). For most commercial, PMC material systems, the cost of developing an extensive real-time database will force laboratories to collaborate and develop national databases. This type of coordinated effort will rely on the use of standardized test methods and data reporting.

For typical environmental degradation factors such as temperature, load, and moisture, it is normal for one or two environmental degradation factors to dominate the aging of a material system. Therefore, when possible each aging mechanism should be investigated by separate real-time, long-term tests in order to determine the dominant environmental degradation factors and provide the critical degradation mechanism of a given material system.

4 Accelerated Test Methodologies for Polymer Matrix Composites

The three basic constituents of advanced polymer matrix composites (PMC's) are fiber, fiber-matrix interface, and polymer matrix. During long-term aging, changes in most of the design properties such as composite stiffness, strength, and fatigue life can be related to changes in the mechanical properties of the polymer matrix constituent. Therefore, in many circumstances the polymer matrix can be considered the key constituent that contributes to degradation or changes in durability of PMC's and will be the point of emphasis in the following discussion.

4.1 Three Primary Degradation Mechanisms

As mentioned in the Introduction section, degradation (aging) mechanisms for PMC's are divided into three broad yet distinct mechanisms: chemical, physical, and mechanical. These three mechanisms may be additive or subtractive depending on material type, the environment, and the mechanical loads. Because so much of the accelerated testing is dependent on temperature and an understanding of temperature related behavior, a short description of the glass transition temperature is provided prior to the discussion of the three primary degradation mechanisms.

Polymers have a second order transition temperature below the melting temperature called the glass transition temperature, T_g. This temperature marks the division between rubbery and glassy behavior for the material and it is a measure of the ease of torsion of the backbone of the polymer. At the glass transition temperature, discontinuities exist in the values of heat capacity and thermal coefficient of expansion. Correspondingly, there is a change in slope of the specific volume versus temperature: at temperatures above T_g, Brownian motion of the molecules is rapid such that an increase/decrease of temperature causes an increase/decrease of volume in the time scale of the temperature change. At lower temperatures, however, the slow molecular motion is such that a change in temperature is not immediately reflected by a corresponding change in volume of the material. Experimentally T_g is often measured using dynamic mechanical analysis (DMA) and characterized as the temperature corresponding to the peak in the $\tan\delta$ value where $\tan\delta$ is defined as the ratio between the loss and storage modulus [22]. These measurements are sensitive to heating rate, sample preparation, and loading mode.

4.1.1 Chemical Aging

Chemical aging refers to an irreversible change in the polymer chain/network through mechanisms such as cross-linking or chain scission. Chemical degradation mechanisms include thermo-oxidative, thermal, and hydrolytic aging. At typical PMC operating temperatures (75° F – 350° F), cross-linking and oxidation are the dominant chemical aging mechanisms. Thermo-oxidative degradation becomes increasingly important as the exposure temperature and time increase. Frequently, such aging results in an increase in cross-linking density that can severely affect the mechanical properties by densification and increasing the glass transition temperature (T_g).

4.1.2 Physical Aging

Physical aging will occur when a polymer is cooled below its T_g, and the material evolves toward thermodynamic equilibrium. This evolution is characterized by changes in the free volume, enthalpy, and entropy of the polymer and will produce measurable changes in the mechanical properties ([23], [24]). As an example, the volume evolution as a function of temperature is shown in Figure 1.

Referring to Figure 1, the slope of the volume-temperature curve is dependent upon the rate of cooling of the material. A material held isothermally below T_g will experience a slow continuous decrease in volume associated with aging of the material. This response occurs as the material evolves towards the desired equilibrium volume state, an evolution that occurs instantaneously for $T>T_g$. This type of aging is referred to as physical aging and is responsible for substantial changes over time of modulus, strength, and ductility for polymers in the glassy range. Since most polymer composite structures are used in the glassy range of the polymeric matrix, physical aging has an important impact on long-term durability of composites used in applications. Physical aging is thermo-reversible for all amorphous polymers by heating the polymer above its T_g and subsequently rapidly quenching the material. It is assumed that this thermo-reversible behavior does not occur in thermoset materials due to the tendency for elevated temperature to affect their extent of cross-linking and/or influence chain scission. Operational mean temperature and lifetime thermal history have a strong influence on the rate of physical aging.

4.1.3 Mechanical Degradation

Mechanical degradation mechanisms are irreversible processes that are observable on the macroscopic scale. These degradation mechanisms include matrix cracking, delamination, interface degradation, fiber breaks, and inelastic deformation; and thus have a direct effect on engineering properties such as stiffness and strength. If the stress in a material is too high its response is no longer elastic, i.e. plastic. This limiting stress level is called the elastic limit. The strain that remains after removal of the stress is called the inelastic strain or the plastic strain. Plastic strain is defined as time-independent although some time-dependent strain is often observed to accompany plastic strain.

Creep is the continuous time-dependent deformation of a material under constant stress. For small strains, constant load and constant stress experiments are the same. The first stage in which creep occurs at a decreasing rate is called primary creep; the second, called secondary stage, proceeds at a nearly constant rate; and the third or tertiary stage occurs at an increasing rate and terminates at fracture. Stress relaxation is the gradual decrease in stress of a material subjected to a constant strain. This stress may asymptotically reach a limiting value slowly over time.

In some cases, mechanical degradation mechanisms dominate only after chemical or physical aging mechanisms have altered the polymer properties. For example, thermo-oxidative stability is a problem with many thermoset materials that often leads to matrix cracks along exposed surfaces and edges. Once these cracks occur, they then serve as initiation sites for extensive crack growth from subsequent mechanical loading. Once the cracks start to grow, the longer cracks provide additional surface area for thermo-oxidative degradation and hence additional sites for new crack growth.

4.2 Superposition and Accelerated Testing

One of the major analytical approaches to accelerated testing is to utilize elevated temperature and apply the principles of superposition. Accelerated testing based on superposition is best examined using concepts of linear viscoelasticity and laboratory experiments at multiple temperatures where in each test; the experimental time range is relatively short. Long-term response is obtained by use of superposition using both temperature and time based superposition principles. Evaluation of time-dependent properties such as creep compliance is typically used in conjunction with superposition as a metric or measure of acceleration. The use of accelerated testing methods based on superposition has also been used with other properties such as damage or fatigue life wherein testing over reasonable (short) time scales is performed at multiple elevated temperatures, where the material responses occur quickly, and results are extrapolated to lower use temperatures and longer times. Examples of this can be found in work by Miyano et.al. [25], [26], [27] and Brinson [28].

4.2.1 Stress Based Superposition

Superposition principles occur in several domains in viscoelasticity, but the first to consider is stress based superposition. For linear viscoelastic materials, the strain responses to two different stress inputs applied separately can be simply superposed to provide the strain response for a combined loading of the two stress inputs. This naturally implies the modulus and compliance

(E(t) and D(t)) are not functions of stress. This concept is the basis of the Boltzman superposition principle [29] that is used to create a hereditary integral form for a viscoelastic constitutive law.

To illustrate this concept, consider a series of stress steps applied to a viscoelastic material as in Figure 2, where at time zero an initial stress of σ_0 is applied and at subsequent times, t_i, a stress jump, $\Delta\sigma_i$, (either positive or negative) is applied. Considering each individual stress jump as the applied load in equation (1) and applying the principle of superposition, we can obtain the strain response as

$$\varepsilon(t) = \sigma_0 D(t) H(t) + \sum_i \Delta\sigma_i D(t - t_i) H(t - t_i) \tag{1}$$

Where H(t) is the Heaviside unit function. If we now take the limit as $\Delta t_i \rightarrow 0$, we obtain a constitutive law for a viscoelastic material that can be applied to any loading, not limited to discrete step loading:

$$\varepsilon(t) = \sigma_0 D(t) H(t) + \int_0^t D(t - t') \frac{d\sigma(t')}{dt'} dt' \tag{2}$$

Expression (2) is a Riemann convolution integral and in practice is often written as

$$\varepsilon(t) = \int_0^t D(t - t') \frac{d\sigma(t')}{dt'} dt' \tag{3}$$

where it is assumed that the lower limit really represents $t = 0^-$ and the stress is understood to be expressed with a step function at the origin, $\sigma(t) = \sigma(t)H(t)$, in which case (3) reduces to (2) identically. By a similar approach, the constitutive law relating a stress output to a strain input may be obtained as

$$\sigma(t) = \int_{0^-}^t E(t - t') \frac{d\varepsilon(t')}{dt'} dt' \tag{4}$$

Clearly, from (3) and (4), the relationship between compliance and modulus is not a simple mathematical inverse. It can easily be shown that compliance and modulus are related to each other in a convolution

$$\int_0^t E(t-\zeta)D(\zeta)d\zeta = t \tag{5}$$

The mathematical representation for linear viscoelastic materials also provides a means to easily test whether one is in the linear range of a given material. To sufficiently ensure material linearity, two common techniques are used: the first method is to perform short-term creep tests on the material at several load levels. In the linear viscoelastic range, the compliances, $D(t) = \frac{\varepsilon(t)}{\sigma_0}$, obtained from each creep test will superpose on top of one another. At a certain load level, the compliance response will begin to differ and for successively higher load levels the discrepancies will increase. This increase defines the nonlinear region of loading for the given material. The second method to verify linearity of a material is to perform a creep and recovery test. The creep portion of the experiment is used to obtain the creep compliance of the material, D(t). This creep compliance is then used to predict the recovery portion of the data via Boltzman's superposition principle. See Figure 3. Note that the stress in Figure 3 can be written

$$\sigma(t) = \sigma_0 H(t) - \sigma_0 H(t-t_0) \tag{6}$$

Substitution into equation (3) yields the prediction for the strain

$$\varepsilon(t) = \sigma_0 D(t) H(t) - \sigma_0 D(t-t_0) H(t-t_0) \tag{7}$$

and the portion evaluated after time t_0 is checked against the experimental data. For a linear viscoelastic material, the prediction and the data should be superposed as illustrated in figure 4 with data for tension test on a $[90]_{12}$ IM7/K3B laminate.

4.2.2 Time-Temperature Superposition

In a polymer, higher temperatures relate to easier rearrangements of the polymer chain backbones and thus to higher compliance (lower moduli). The measured effect of temperature on the time-dependent creep compliance of a $[\pm 45]_{2s}$, matrix-dominated polymer composite is shown in Figure 5a. For most polymeric materials, the quantitative impact of temperature on mechanical properties is embodied in the time-temperature superposition principle (TTSP). TTSP, illustrated graphically in Figure 6, indicates that the compliance curves at different temperatures are related to one another by a simple shift on the log time scale. This result implies that the relaxation times for a material, which represent the ease of motion of different segments of the polymer chain, are all scaled by temperature in an identical manner. The relaxation times for a given material are short at high temperatures, long at low temperatures, and can be calculated relative to those at a reference temperature by a simple temperature shift factor, a_T. As an example, the individual compliance curves in figure 5a have been time shifted to a reference temperature and the superposed or master curve is shown in figure 5b.

Above the T_g, the method of reduced variables can be used to arrive at the WLF (Williams, Landel, Ferry) equation [30] for temperature shift factor

$$\log a_T = \frac{-c_1\left(T-T_o\right)}{c_2+\left(T-T_o\right)} \tag{8}$$

while below the T_g the Arrhenius equation [31]

$$a_T = \exp\frac{\Delta H}{R}\left[\frac{1}{T}-\frac{1}{T_o}\right] \tag{9}$$

can be used where T is the temperature, T_o is the reference temperature, c_1 and c_2 are constants, and ΔH and R are the activation enthalpy and gas constant respectively. Note that $a_T=1$ for $T=T_0$ and T_g is often used as the reference temperature, T_0. If free volume considerations are not of concern, a_T below the glass transition temperature can simply be found directly through shifting of the experimental data in the time domain.

4.2.3 Effective Time

For linear viscoelastic materials, the effect of many factors on material response can be expressed as a simple time shift, as we saw for temperature earlier. The effects of aging, moisture and stress levels can all be captured by use of the shift factor concept and associated method of reduced variables. This result gives rise to a powerful tool called the *effective time* concept. Considering temperature effects as the example, and referring to concepts illustrated in Figure 6 we see that the modulus E_T at any temperature T can be defined relative to the modulus E_{T_R} at the reference temperature, T_R by

$$E_T(t) = E_{T_R}(a_T t) \tag{10}$$

The "reduced time" or "effective time", ξ, is defined by noting that all relaxation mechanisms in time increment dt at temperature T are a_T times slower/faster than those in a time increment $d\xi$ at T_R so that:

$$d\xi = a_T dt \rightarrow \xi(t) = \int_0^t a_T(\zeta)d\zeta \tag{11}$$

Note that if the temperature T is constant, a_T is also constant and therefore $\xi = a_T\, t$ and we have as before that

$$E_T(t) = E_{T_R}(\xi(t)) = E_{T_R}(a_T t) \tag{12}$$

Thus the constitutive law (4) for the material at temperature T can be written in the time domain as

$$\sigma(t) = \int_{0^-}^{t} E_{T_R}(\xi(t) - \xi(t'))\frac{d\varepsilon(t')}{dt'}dt' \tag{13}$$

or in the effective time domain as

$$\sigma(\xi) = \int_{0^-}^{\xi} E_{T_R}(\xi - \xi')\frac{d\varepsilon(\xi')}{d\xi'}d\xi' \tag{14}$$

For constant temperatures this notation is perhaps cumbersome, but the power of the technique becomes apparent when considering a loading during a variable temperature history, T(t). In this case, again the reduced time can be defined in the same manner as equation (11) and the constitutive law by equations (13) and (14) but now a_T is no longer constant (and could be given in a form like equations (8) and (9)). Note that equation (14) is still a convolution integral, which has advantages in calculations over the form in (13) which is no longer a convolution. In calculations with (14) the strain $\varepsilon(t)$ is mapped to $\varepsilon(\xi)$ by use of (11); however, the modulus $E_{T_R}(\xi)$ is simply $E_{T_R}(t)$ with t replaced by ξ. Effective time is used in viscoelasticity to perform calculations of material response in conditions of variable temperature, moisture, aging and/or damage by using different forms of equation (11).

4.2.4 Time-aging-Time Superposition

To accurately account for material aging, a time-aging-time superposition (TASP) procedure must be developed. To illustrate this concept, the case of isothermal physical aging will be considered using creep compliance as the viscoelastic behavior of interest. Assume a polymer based material is quenched from above the T_g to a temperature below it's T_g. The time the material exists below the T_g is referred to as the aging time *(t_e)*. As aging time progresses, a series of short (in comparison to the elapsed aging time) creep tests are run to measure the momentary creep compliance of the material. This test procedure is described by Struik [23] and illustrated schematically in figure 7.

A simple model of momentary creep compliance is the Kohlrausch three parameter model as described in ref. [32] is given by

$$S(t) = S_o e^{(t/\tau)^\beta} \tag{15}$$

where S_o is the initial compliance, β is the shape parameter, t is the time and τ is the relaxation time. As illustrated in [33], and [34], it is possible to shift a series of these momentary curves into a momentary master curve using the aging shift rate

$$\mu = \frac{-d\log a_{te}}{d\log t_e} \tag{16}$$

where a_{te} is the aging shift factor found through test and given as

$$a_{te} = \left(\frac{t_{eref}}{t_e}\right)^\mu \tag{17}$$

where t_{eref} is the reference aging time. This allows the relaxation time in (15) to be given as

$$\tau(t_e) = \tau(t_{eref})/a_{te}\,. \tag{18}$$

Therefore, the momentary creep compliance at any aging time can be found by knowing the initial creep compliance, the shape parameter, the shift rate and the relaxation time at a reference aging time. For physical aging, the shift rate is a function of temperature and will approach zero as test temperature approaches the glass transition temperature (T_g).

Taking the initial aging time t_e^o to be the reference aging time $(t_{e_{ref}} = t_e^o)$, the shift factor at any instant in time can be defined based on the shift rate μ

$$a_{t_e^o}(t) = \left(\frac{t_e^o}{t_e^o + t} \right)^{\mu}. \tag{19}$$

Using the previously introduced concepts of effective time, the effective time increment can then be defined [23]

$$d\lambda = a_{t_e^o}(t)dt \tag{20}$$

and the total test time can be reduced to the effective time λ

$$\lambda = \int_0^t a_{t_e^o}(\xi)d\xi. \tag{21}$$

Integration of (21) using (19) gives two distinct expressions for effective time

$$\begin{aligned} \lambda &= t_e^0 \ln(\tfrac{t}{t_e^0} + 1) \quad for\ \mu = 1 \\ \lambda &= \frac{t_e^0}{1-\mu}\left[(1 + \tfrac{t}{t_e^0})^{1-\mu} - 1 \right] \quad for\ \mu \neq 1 \end{aligned} \tag{22}$$

Therefore, using effective time in place of real time, equation (15) gives

$$S(t) = S^o e^{(\lambda / \tau(t_e^0))^{\beta}} \tag{23}$$

that allows the prediction of long-term behavior based solely on the material parameters determined from short-term or momentary tests. This procedure, along with various enhancements to account for laminated composite plates and automated data reduction schemes, have been used successfully by a number of PMC test programs, details of which can be found in [32], [33], [34], [35], [36].

4.2.5 Time-temperature-aging-time Superposition

To account for both temperature and aging time effects simultaneously, a combined approach or time-temperature-aging-time superposition can be used. In most cases, this is most easily accomplished by performing isothermal viscoelastic testing (eg. creep or relaxation) at definite temperature levels below the glass transition temperature. A general form of the time-temperature-aging-time shift factor is given by Sullivan [37]

$$\log a = \log a_{te} + \log \bar{a}_T \tag{24}$$

where a_{te} is the aging time shift factor defined by (17) and $\bar{a}_T$ is the time-temperature shift factor that depends on aging. If aging is to be considered, for temperatures below T_g equation (9) may not be used because it neglects aging effects. However some investigators [38] have had success finding $\bar{a}_T$ using a linear fit for the shift factor data below T_g. As derived in [32], given the aging shift rate as a function of temperature and the time-temperature shift factor at a single aging time, $\bar{a}_T$ can be calculated at any aging time using

$$\frac{\bar{a}_{T_1/T_2}^{t_{e2}}}{\bar{a}_{T_1/T_2}^{t_{e1}}} = \left(\frac{t_{e2}}{t_{e1}}\right)^{\mu(T_2)-\mu(T_1)} \tag{25}$$

where T_1 and T_2 are two different temperatures and t_{e1} and t_{e2} are two different aging times.

4.2.6 Application to Composite Materials

Time-temperature and time-aging-time superposition have been coupled with classical laminated plate (CLT) theory [39] to provide a framework for analysis of laminated composite materials and details can be found in [40], [32] and [41]. The complete description of this analysis framework is beyond the scope of this text, however the fundamental equations can be easily illustrated.

For a single lamina or ply under plane stress conditions, the stress-strain relations, as given by CLT, are

$$\begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \gamma_{xy} \end{Bmatrix} = \left[\bar{S}\right] \begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy} \end{Bmatrix} \tag{26}$$

where ε_{ij} and σ_{ij} represent the strain and stress in the body axis directions. The transformed compliance matrix $\left[\bar{S}\right]$ is given by

$$\left[\bar{S}\right] = [T]^{-1}[S][T] \tag{27}$$

where $[T]$ is the transformation matrix and $[S]$ is the compliance matrix referenced to the material coordinate axis and given by

$$[S] = \begin{bmatrix} S_{11} & S_{12} & 0 \\ S_{12} & S_{22} & 0 \\ 0 & 0 & S_{66} \end{bmatrix}. \tag{28}$$

As demonstrated by Sullivan [35] and Hastie [42], the only time-dependent compliance terms in equation (28) are the transverse (S_{22}) and shear (S_{66}) terms that are associated with matrix dominated deformation of a ply. Therefore, based on a compliance expression such as given in equation (23), the time-dependent compliance terms can be written in a general form as

$$S_{22}(t) = f\left(S_{22}^{0}, \beta_{22}, \tau_{22}(t_{eref}), \mu_{22}; t\right) \tag{29}$$

$$S_{66}(t) = f\left(S_{66}^{0}, \beta_{66}, \tau_{66}(t_{eref}), \mu_{66}; t\right) \tag{30}$$

where t_{eref} is the reference aging time.

For a laminated composite plate, the laminate compliance are found using CLT. Due to the time dependence of equations (29) and (30), the laminate compliance will also be time-dependent. The amount of time dependence and the effects of aging will depend on the layup and therefore the relative contributions of equations (29) and (30) to the total laminate compliance. As an example, if it is assumed that the fiber is linear-elastic, a unidirectional laminate (e.g. $[0]_n$) loaded in the fiber direction will not exhibit viscoelastic behavior. Conversely, the same unidirectional laminate loaded transverse to the fiber direction will have a compliance governed by equation (29), and exhibit both viscoelastic and aging behaviors. Most laminates will have a range of ply and load orientations and consequently considered to exhibit some aspects of time-dependent behavior.

4.3 General Procedures for Accelerated Testing

Prior to performing data reduction and analysis using procedures and methods such as outlined in section 4.2, the beginning of an accelerated aging program for PMC's attention should be focused on the determination of critical degradation mechanism(s). The key to this task is to determine the material performance after systematic exposure to one or more environmental degradation factors. This section will provide the details necessary to construct a test program considering a wide variety of environmental degradation factors.

4.3.1 Identify Material Type

The first step requires material identification. For this purpose, a thermoset is defined as a cross-linked polymer network that hardens to final shape after cool down from the forming temperature and is incapable of being reshaped. A thermoplastic material is a linear polymer of amorphous, semi-crystalline, or mixed morphology. A thermoplastic softens on heating to a state where the shape may be changed by physical forces and resolidifies on cooling. In principle, the process of softening and solidifying may be repeated indefinitely.

4.3.2 Establish Critical Degradation Mechanisms

Material performance is defined by a set of indicators that measure a specific property for the material. The indicators will be dependent upon the mechanism of interest. The suggested procedure is as follows:

1. Identify material by class (i.e. thermoplastic, thermoset).

2. Identify mechanism to evaluate (e.g. thermal stability, matrix cracking, etc.).

3. Choose an environmental degradation factor for aging. (e.g. elevated temperature, moisture, etc.)
4. Conduct aging experiment within limits of the chosen environmental degradation factor using established methods.
5. Perform in-situ or post-aging measurements with indicators sensitive to changes in material performance and compare results to unaged values.

The results of such a study will allow one to evaluate whether this particular degradation mechanism will be critical for the given application. This procedure can be repeated for all degradation mechanisms of interest for that material. It should not introduce extraneous damage/degradation mechanisms nor should it omit any known degradation mechanisms. Additionally, the set of mechanical properties or indicators chosen for screening should be those most critical from the structural performance viewpoint and those most sensitive to degradation. Examples that highlight these criteria are provided in the following sections.

4.3.3 Establish Geometry or Size Effects

The rate and magnitude of most transport processes can be related to the volume and surface area of the material. Therefore, it is worthwhile considering that the geometry of a composite laminate may be used to accelerate the effects of aging. It is known, for instance, that thermo-oxidative degradation of many materials occurs from the surface inward. Therefore, thinner samples (low volume) should reflect the effects of thermo-oxidative degradation more rapidly than thicker samples (high volume). For continuous fiber composites, these effects are complicated by the transversely isotropic nature of the material, which can lead to degradation rates that vary according to the differences in the laminate surfaces.

To illustrate this behavior, consider Figure 8 that shows a typical uniaxial test sample with the fibers running along the transverse direction (90^{o}). We define the surfaces with the most exposed area (top and bottom in Figure 8) as the major surfaces and the thin exposed edges as the minor surfaces. In this case the minor surfaces contain fiber ends that provide an advantageous site for moisture uptake. Therefore, it would be expected that due to capillary action, transport properties such as moisture diffusion would be more significant on these minor surfaces. This behavior along with the differences due to geometry (i.e. exposed area) could then be taken advantage of in order to accelerate the degradation process by selectively sealing exposed surfaces and/or choosing laminates with more or less fibers terminating on minor surfaces.

4.3.4 Assess Aging by Thermo-Oxidative Degradation

In the polyimide material systems, the oxidation reaction occurs through a radical chain process ([4], [5], [8]) and is referred to as autoxidation. Experimentally, thermal methods such as thermogravimetric analysis (TGA) have been used to obtain data related to thermo-oxidative degradation [14]. The TGA relies on weight loss data as a measure of thermo-oxidative stability (TOS) [22]. The experimentalist can utilize several measurements to quantify TOS including the temperature at onset of TOS, the temperature at which half the sample has decomposed, or the apparent activation energy of the reaction from the weight loss data. This latter approach has been used to provide a 'kinetic map' of the reaction as a means of comparing the TOS of similar materials [14]. It should be noted that in a TGA experiment, the reactions are temperature driven and thus occur sequentially as temperature is increased.

It is possible to model the chemical kinetics on a limited basis by coupling the oxygen diffusion to the chemical reaction [43]. This approach assumes a classical diffusion model such as Fick's law along with a reaction equation that provides the rate of oxygen consumption. The chemical reactions proceed more rapidly at higher temperatures. For the simple case of single activation energy, the reaction may be modeled by the Arrhenius equation [44]. The absolute effects of oxygen exposure during aging can only be determined if compared against aging in an inert environment. For example, as shown in Figure 9, samples were aged at temperatures above the upper use-environment temperature, but below the glass transition temperature in both the presence and absence of oxygen. Some indicators that monitor thermo-oxidative degradation are:

1) *Weight*: Initial weight loss of a polymer exposed to thermo-oxidative environment may occur due to loss of moisture and residual volatiles and is not related to polymer breakdown. Usually, after several hundred hours of exposure, the sample weight

stabilizes and any additional weight loss is indicative of thermo-oxidative degradation [43], [14]. This is shown in Figure 9 by comparing weight loss for three different exposure environments. Once polymer degradation occurs, the evolution of gaseous degradation products accompanies weight loss.

2) *Physical Changes*: Optical measurements of changes in color, surface texture, and crack density can be indicators of thermo-oxidative degradation. An example of observable physical changes can been seen in the photographs in Figure 10.

3) *Glass Transition Temperature:* Changes in the glass transition temperature are frequently observed by dynamic mechanical analysis (DMA). Usually, an increase in T_g suggests chain extension or network cross-linking. Figure 11 shows an example how the T_g can increase due to long-term exposure. A decrease is normally associated with chain scission.

4) *Mechanical Properties:* Most residual properties such as tension strength, compression strength, and stiffness do not make good indicators of thermo-oxidative degradation early in the aging process. However, more subtle mechanical properties such as fracture toughness and plasticity are sensitive indicators of short-term aging due to their dependence on matrix-dominated behavior [44].

4.3.5 Assess Aging by Thermal Degradation (Elevated Temperature)

Elevated temperature aging in polymers in the absence of oxygen can also lead to changes in material properties due to additional cross-linking and/or chain scission. These changes make an analytical approach based on principles of viscoelasticity and aging-based-superposition quite complicated. For example, if the glass transition temperature increases during aging due (as in the case with most thermoset materials), then the aging shift rate is not a constant during aging and would have to be fully characterized as a function of both time and temperature, unlike physical aging where the shift rate is strictly a function of temperature. Schematically, this dependence of shift rate on time and temperature is illustrated in Figure 12.

As a consequence of the difficulties associated with chemical aging, analytical models capable of predicting the long-term changes due to chemical aging are rare. An example of a model which correlates change in mechanical properties due to additional cross-linking is given in [45]. Generally, thermoset systems initially tend to embrittle during purely thermal aging. Depending upon thermoset chemistry, these systems may either continue to embrittle or start to degrade significantly. Indicators that are useful for tracking thermal degradation are given below and are similar to those for thermo-oxidative degradation. As an example, Figure 10 shows a comparison between properties measured for room temperature and elevated temperature fatigue of a graphite/bismaleimide composite ([46]). As shown, the changes incurred during the elevated temperature fatigue (case B) included loss in weight, increase in glass transition temperature, and increase in crack density.

1) *Weight*: Initial weight loss of a polymer exposed to a purely thermal environment may occur due to loss of moisture and residual volatiles, just as in thermo-oxidative degradation. However, the magnitude of weight loss for equal exposure times and temperatures is generally much less in purely thermal degradation than it is in thermo-oxidative degradation.

2) *Physical Changes*: Optical measurements of changes in color, surface texture, and crack density can be indicators of thermo-oxidative degradation. Frequently, these changes are less noticeable in thermally aged samples compared to those aged under the same conditions with oxygen present.

3) *Glass Transition Temperature:* Changes in the glass transition temperature are frequently observed by dynamic mechanical analysis. These changes are considerably smaller for equivalent aging conditions than for samples aged in the presence of oxygen.

4) *Mechanical Properties*: Most residual properties such as tension strength, compression strength, and stiffness do not make good indicators of thermal degradation early in the aging process. However, more subtle mechanical properties such as fracture toughness are sensitive indicators of short-term aging.

4.3.6 Assess Aging by Thermal Degradation (Cryogenic Temperature)

Unlike elevated temperature, cryogenic temperature aging in polymers will not lead to changes in material properties due to additional cross-linking and/or chain scission. It is expected that most changes in material properties at cryogenic temperatures are due to a loss in molecular mobility of the polymer chains [47]. Generally, polymeric systems tend to embrittle at cryogenic temperatures and viscoelastic or time-dependent behavior decreases significantly [48], [49]. Although most engineering properties will continue to change as the temperature is lowered, there is no assurance that the response is linear and can be accelerated strictly by testing at a temperature lower than the use temperature [50]. It is advisable to have a comprehensive set of thermal-related properties such as coefficient of thermal expansion and specific heat capacity before using reduced temperature to effectively accelerate degradation. Thermally induced strains due to cool down from the stress-free condition may be significant and cause extensive microcracking. The levels of these induced strains will be dependent on the material type and laminate configuration. Indicators that are useful for tracking reduced temperature thermal degradation are given below.

1. *Physical Changes*: Optical measurements of changes in color, surface texture, and crack density can be indicators of degradation induced by exposure to cryogenic temperatures and cryogenic fluids such as liquid nitrogen or liquid helium.

2. *Mechanical Properties*: Residual mechanical properties such as tension, compression strength, and stiffness are good indicators of degradation due to cracking while aging at cryogenic temperatures. However, in the absence of damage, these tests may not provide data directly related to aging [51], [52].

4.3.7 Assess Aging by Hydrolytic Degradation

Hydrolytic degradation in PMC's is due to diffusion of water into the material leading to moisture uptake and possible plasticization of the polymer matrix. Most mechanical properties are sensitive to hydrolytic degradation. For example, a decrease in fracture toughness has been observed when a PMC was simultaneously exposed to water and mechanical stress [53]. Viscoelastic properties such as creep may also be responsive to moisture-induced degradation and can provide a good method for determining long-term influence on stiffness related degradation. For example, Figure 13 shows the predicted long-term creep behavior of a $[\pm45]_{3s}$ laminate of IM7/K3B at 225°C subjected to 2 hygrothermal exposure conditions and compared to the baseline or as-received condition. In this case, the two hygrothermal exposure conditions were (45°C, 45%RH) and (90°C, 90%RH) for 1700 hours. The test sequence used to generate the inputs for the predictive model was the isothermal creep-recovery, momentary tests as described in the previous sections on superposition and aging. The long-term predictions were then made using the physical aging model in conjunction with TTSP. Degradation in the form of plasticization and matrix-cracks induced during the hygrothermal exposure is reflected in the long-term predictions in the form of increases in compliance and creep rate with respect to the baseline curve.

The diffusivity of a PMC is found to be a function of specimen geometry, moisture concentration, temperature, and time and is often modeled using the standard Fick's law as described in [54]. The activation energy for water diffusion may be determined from the slope of the natural log of the diffusion coefficient versus the reciprocal immersion temperature. Moisture concentration may reach a plateau level within the PMC, however the plasticization in a polymer may increase over time. For an inhomogeneous material, diffusion into the polymer can vary which may result in significant differences in water concentration from one region of the sample to the next. This nonuniform concentration or non-Fickian behavior can impose stresses on the material. In a composite laminate at constant temperature, this stress can give rise to internal damage in the form of matrix cracks [55].

Damage in the form of microcracks may also develop due to the general process of hydrolytic degradation, as shown by Bao [56]. Occurrence of microcracking will subsequently affect the rates of moisture absorption/desorption during repeated hygro-thermal cycling. An example of this is provided in Figure 14, which shows the moisture absorption, desorption curves for a graphite thermoplastic polyimide. This is a good example of a critical degradation mode. With internal stresses, microcracks that formed in the laminate subsequently allowed for new pathways for moisture uptake. In this case, the environmental degradation factors were elevated temperature, moisture, and mechanical load.

Indicators that are useful for tracking hydrolytic degradation are:

1) *Weight*: Exposure to a wet environment will result in weight gain over time. For Fickian behavior, the rate of weight gain and saturation level is proportional to relative humidity while the time required to reach saturation is a function of temperature. This behavior is illustrated in Figure 15 for $[\pm 45]_{2s}$, IM7/K3B composite test data.

2) *Physical Changes*: An increase in crack density may be observed after exposure. As shown in Figure 14, anomalous weight change behavior may be noted during cyclic exposure with the time to saturation and drying shortened by orders of magnitude following microcrack formation.

3) *Mechanical Properties*: Fracture toughness, fatigue life, and linear viscoelastic creep are particularly sensitive to hygro-thermal degradation [57], [58]. Other engineering properties such as residual tension and compression strength, and stiffness, are also affected to a lesser extent.

4.3.8 Assess Physical Aging

As noted earlier, physical aging involves subtle changes in thermodynamic properties of the polymer matrix. A measure of the rate and hence acceleration of physical aging using isothermal creep tests has been well documented on a number of polymer systems with low glass transition temperatures ([35], [59], [60], [61], [62], [63]). Physical aging of polymers and polymer composites usually employs a method that relies on short-term tests and the concept of an aging-induced shift factor. This test method provides an approach to obtain quantitative relationships among the short-term, time-dependent experimental data, aging-free creep master curves, and the long-term behavior. For PMC's, details of these test procedures are provided in [33], [64]. All of the experimental and analytical procedures described in these documents make use of the principles of time-temperature superposition (TTSP) [30] and time-aging time superposition (TASP) [23]. The fundamental assumption in both cases is that the time-based response can be accelerated. For the case of TTSP, an increase in temperature will accelerate the time-dependent response (e.g. creep, relaxation), however changes in the aging behavior are not accounted for. To accelerate the aging effects, both TTSP and TASP must be utilized. The TTSP and TASP shift factors and the associated material master curves are found through test. Shift factors and other parameters then form the basis of the material related inputs to the predictive models.

Models for prediction of long-term viscoelastic behavior in PMC's that include the effects of physical aging are outlined in section 4.2. Most of these models use an integral expression where the effect of physical aging is normally accounted for by modifying the expression for the viscoelastic compliance. The indicator used to characterize the physical aging of polymer composites is as follows:

1) *Mechanical Properties*: Time-dependent tests, which can be used to assess the degree of physical aging, include creep and stress relaxation. These tests should be made so that the material remains within the linear viscoelastic range. Static residual properties, which indicate a change in behavior due to physical aging, include tension and compression strength and stiffness of notched and unnotched specimens.

For the physical aging mechanism, it was suggested [23] that loading a material to a nonlinear stress level will apparently "deage" or reverse age the material. The explanation proposed was that large deformation processes caused by high stress, generate free volume and rejuvenate the sample, partially erasing the previous aging. An alternative explanation for the reduction of shift rate with high stresses has also been proposed [65], in which it was stated that an increase in the amplitude of the stress applied in the physical aging experiment resulted in a decrease in the shift rate simply because the changes in structure accompanying volume recovery affect the nonlinear response differently at large stresses than at small ones. Investigations on the effects of stress during physical aging of PMC's have also been performed [66].

4.3.9 Assess Aging by Mechanical Degradation

Mechanical degradation mechanisms are those associated with the initiation of damage or the growth of pre-existing damage due to the application of load or deformation. Often these mechanisms are the result of prior or concurrent physical or chemical aging that change the constituent mechanical properties [10], [67], [68]. Mechanical degradation is also aided by other factors such as initial defects or flaws in the materials. The dominant mechanical mechanisms include matrix cracking, delamination, fiber breaks, and inelastic deformation [28].

4.3.9.1 Matrix Cracking

Given a sufficient mechanical load, matrix cracking will occur in PMC's. Cracks that initiate due to localized stress concentrations typically act as a stress relieving mechanism. These cracks have the same effect as lowering the stress concentration factor and allowing more load to be carried by the laminate and, therefore, increase the gross strength. Conversely, matrix cracks that initiate in off-axis plies will result in a loss of laminate stiffness. The magnitude of the load and the extent of the environmental degradation factors determine the degree of matrix cracks [68]. An example of the effects of load and temperature are shown in Figure 16 ([46]). In this figure, the matrix crack density data from the composite laminate shows that at most test temperatures, crack density will increase with an increase in the mechanical load and that even in the absence of mechanical load, high temperature exposure alone may be sufficient to generate substantial micro-cracks.

In general, crack density increases as the exposure time increases. Therefore, long-term exposure increases the probability of subsequent delamination and eventually fiber breakage. Preferred methods of accelerating this mechanism are increasing the rate and magnitude at which the mechanical and thermal spectra are applied. The indicators used to characterize the matrix cracking of polymer composites are as follows:

1) *Physical Changes*: An increase in crack density may be observed after static or fatigue loading. Crack density can be measured using both optical and radiographic methods. Typically, the data is normalized over a given length or volume. Examples of these measurements can be found in [46].

2) *Mechanical Properties*: Static residual properties, which indicate a change in stiffness and strength, include tension and compression of notched and unnotched specimens. Matrix dominated laminates should be used to provide a clear indication of the failure mechanisms.

4.3.9.2 Delamination

Polymer composite laminates delaminate when through-the-thickness strain energy release rate exceeds interlaminar fracture toughness ([69], [70], [71], [72]). This type of damage mechanism can significantly reduce the compressive strength of the laminate by reducing the stability in the region where the delamination occurs thereby increasing the likelihood of a buckling failure mode. The level of applied stress directly influences the incidence and rate of delamination. Preferred methods of accelerating this mechanism are by increasing the rate at which the mechanical and thermal spectra are applied. The indicators used to characterize the delamination of polymer composites are as follows:

1) *Physical Changes*: Void formation detected by non-destructive evaluation of laminate integrity using ultrasonic C-scans.

2) *Mechanical Properties*: Static residual properties, which indicate a change in stiffness and strength, include tension and compression of notched and unnotched specimens, and interlaminar fracture toughness.

4.3.9.3 Fiber Failure

Fiber failure in PMC's occurs when mechanical loads exceed fiber tensile or compressive strength or from shear-induced failure during out-of-plane loads. Environmental degradation factors such as temperature or moisture may decrease fiber strength as well as modify the matrix response to externally applied loads. Preferred methods of accelerating this mechanism are by increasing the frequency at which mechanical fatigue loads and thermal cycles are applied. The indicators used to characterize the fiber failure of polymer composites are as follows:

1) *Physical Changes*: Failure surfaces can be evaluated evaluation using optical microscopy or through transmission x-ray radiography.

2) *Mechanical Properties:* Static residual properties, which indicate a change in stiffness and strength, include tension and compression of notched and unnotched specimens.

4.3.9.4 Inelastic Deformation

Mechanical damage can occur in a PMC due to inelastic deformation associated with plasticity, creep or stress relaxation. However, the dominant affect on a laminate would be observed as a change in its matrix dominated properties such as shear and transverse stiffness. This mechanism can be accelerated by exposure to higher stresses and higher temperatures.

The indicators used to characterize inelastic deformation of polymer composites are as follows:

1) *Physical Changes*: There is generally little physical evidence of inelastic deformation. Optical photomicrographs of a failure surface may provide indications of inelastic deformation.

2) *Mechanical Properties:* Static and time-dependent residual properties, which indicate inelastic deformation would include: stiffness reduction or yielding, strength reduction, non-proportional stress-strain behavior, and violation of Boltzman's superposition principle [29].

4.3.10 Assess Aging by Solvent Exposure

Degradation in PMC's due to exposure to solvents can take several forms. It is generally assumed that the solvent will do irreversible damage to the polymer material and the rate and extent of damage will be proportional to solvent concentration and exposed surface area.

Most mechanical properties are sensitive to solvent induced degradation. Damage may occur due to chemical changes in the polymer and loss of polymer material over time and can lead to matrix cracks or delamination. As with hydrolytic degradation, matrix cracking will subsequently affect the rates of solvent absorption/desorption during repeated solvent cycling.

Typical soak times for solvent exposure tests may be up to 250 hours. Indicators that are useful for tracking solvent degradation are:

1. *Weight*: Exposure to a solvent environment may result in weight gain or loss over time depending on the material system and the chemical nature of the solvent.

2. *Physical Changes*: A decrease in surface quality, increase in crack density and increases in delamination may be observed after exposure.

3. *Mechanical Properties*: Stiffness loss during fatigue is a good indicator of solvent

sensitivity. Crossply laminates such as $[0/90/0]_{2s}$ have been found useful for this type of test. Typical fatigue test parameters are up to $1\text{x}10^6$ cycles at a R-ratio of 0.05. After removal from the soaking environment, specimens are wrapped in several layers of a non-porous barrier (such as aluminum foil) to help eliminate solvent evaporation prior to fatigue testing. Modulus changes during fatigue approaching 5% are probably due to damage accumulation in the form of matrix microcracking. Moreover, changes approaching (and beyond) 10% are probably due to the onset and growth of delamination zones. These large stiffness changes forcast specimen failure. Other engineering properties such as residual tension and compression strength, and stiffness, are also affected to a lesser extent.

4.3.11 ***Real-time Testing***

The requirements for real-time testing are that the material should be exposed to loads and environmental degradation factors that reproduce the critical aspects of the service environment. The methodology for real-time testing of a durable composite over the service life of typical applications has been detailed in several standards documents such as provided by MIL-HDBK-17 and ASTM standard test methods. These standards provide guidance on the selection of methods to assess degradation due to a variety of mechanical factors. When considering the effects of environmental degradation factors on durability, these standard test methods form a starting point for the development of new accelerated test methods.

Essentially, the real-time testing provides the baseline data against which all accelerated work must be validated. This testing should include individual and combined effects of specific environmental degradation factors on the degradation process. For example, environmental degradation factors under consideration may include aging at temperature, aging in different gaseous environments, aging under load, and exposure to moisture. Data from aging under real-time exposure is used to determine which environmental degradation factors that dominate the degradation process and hence which degradation modes should be tracked closely in the accelerated test study. Once an understanding of the material behavior is obtained, models can be developed to predict material performance under different exposure and loading conditions.

These models can be used to simulate the effects of different aging profiles to help formulate an accelerated aging scenario.

5 Summary and Concluding Remarks

Accelerated testing can reduce time and cost of durability-based material characterization by facilitating material screening and suggesting key degradation mechanisms associated with long-term durability. Accelerated testing can speed up the aging behavior of the material by influencing the process of mechanical degradation, chemical aging, and physical aging. The rates and degree of interaction of these three processes are dependent on material type, environmental degradation factors, and test methods.

Time-temperature superposition and time-aging time superposition are proven methods for assessing long-term aging performance from short-term data. These methods have shown a great deal of utility in test programs that rely on elevated temperature (sub-Tg) as the accelerant. Less is known about the validity of the methods for other types of accelerated environments (e.g. moisture, solvents). However, some key studies have indicated that the methods may have great utility. Combining the time-based superposition methods with the correct experimental program can lead to tremendous time savings when screening materials for long-term performance.

Historically, the two dominant test environments for accelerating aging in PMC's are the use of increased levels of mechanical stress and temperature. Increasing mechanical stress has several effects at the molecular level: diffusion of gases and liquids into the polymer matrix is enhanced and some population of chemical bonds in the polymer chain will be loaded to a higher level, thereby reducing the energy needed to rupture the bond. In turn, at the macroscopic level the time to achieve a characteristic damage state will be reduced.

Increasing the temperature accelerates all thermally activated rate processes and will also reduce the activation energy of chemical bond rupture in the polymer. Elevated temperature (sub-Tg) will also increase the free volume in the polymer, hence decreasing the time needed to age to thermodynamic equilibrium. Increased temperature is also usually associated with decreases in both strength and stiffness in PMC's and will lead to increased ductility and strain to failure.

Unfortunately, the use of elevated temperature for acceleration of the aging mechanism(s) may promote degradation mechanisms that do not occur at use-environment temperatures or alter the rates so that degradation may not be accelerated proportionally.

For chemical aging mechanisms, mechanical load, or stress, may increase the probability of bond rupture within the polymer. Residual stress or the externally applied stress on the chemical bond can accelerate chain scission caused by chemical reaction. It has also been found that stress can alter the effective activation energy for a chemical reaction. The use of stress to accelerate physical aging is not recommended due to a lack of clear understanding of the possibility to de-age a material. Increased stress has been traditionally used as the primary means for accelerating mechanical degradation. The occurrence of microcracks, fiber breaks, and delamination will all be accelerated through the application of increased static or fatigue stress.

Aside from elevated temperature and stress, secondary accelerators such as moisture, partial pressure of oxygen, geometry, and layup should be considered for PMC's. The application of a particular accelerator or set of accelerators will be dictated by the dominant degradation mechanism for each use-environment. One must also consider that aging performed in the standard environment may actually represent an accelerated aging case for material systems that don't operate in the standard environment. As an example, consider real-time isothermal aging used to establish baseline conditions. For this example, the level of oxygen concentration in laboratory air in aging ovens exceeds by several orders of magnitude the concentration of oxygen that a laminate on a supersonic aircraft would see when it is at altitude undergoing operational load.

Prior to the development of accelerated test methods, several limiting factors should be recognized. Perhaps the most important limiting factor is that the "short-term test" can actually take several years to develop and validate. Hence, time available for methods development may control the final outcome of the test program. Other limiting factors to consider include:

- Lack of in-situ NDE methods.
- Some property behavior cannot be accelerated.
- Scaling or size effects may play a significant role.

- Synergistic mechanisms can confound data analysis.
- Lack of integration of field data and lab data.
- Site specific environmental factors must be addressed.
- Introduction of new materials may make some data obsolete.
- Lack of standards for data collection.

Clearly, the study of aging, accelerated aging, and the effects of aging on high performance laminated materials is a challenging and difficult task. Nevertheless, it is imperative that a scientific knowledge base is built up as the demands on material systems increase on all fronts. Only through long-term, dedicated perseverance in addressing the difficult and complex issues surrounding this area of research can we expect to extend the use of modern materials systems safely and reliably to the most demanding, challenging and rewarding applications.

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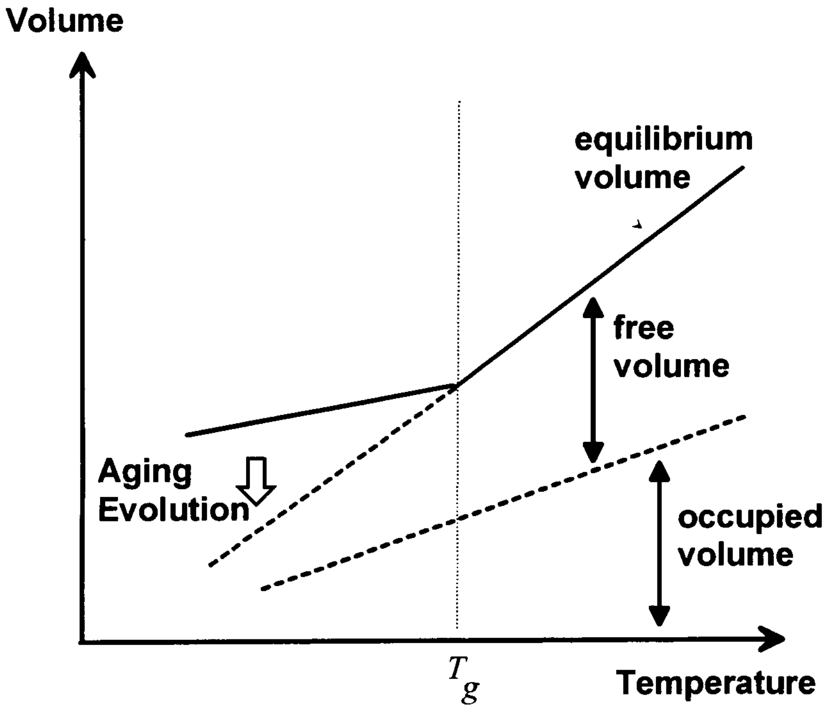


Figure 1. Illustration of the relationship between volume and temperature in a polymer in both the glassy (sub – Tg) and rubbery (above – Tg).

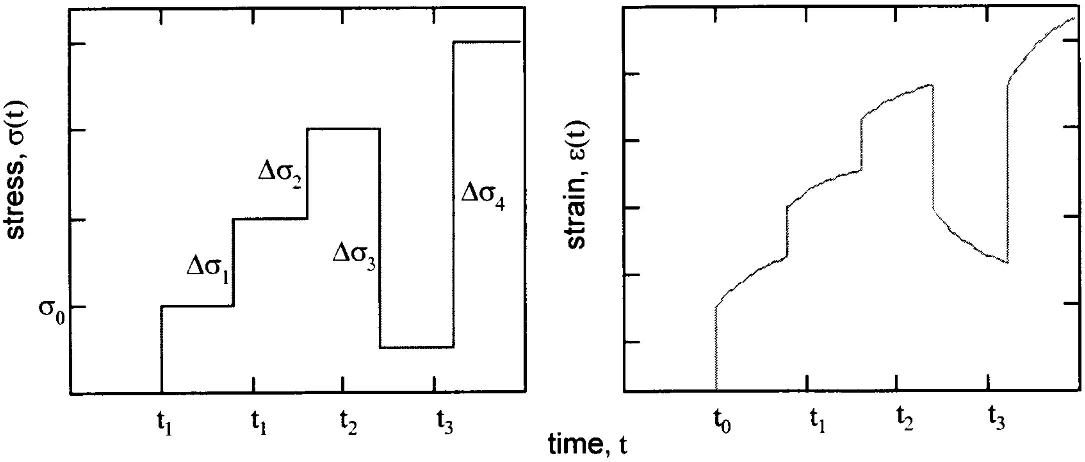


Figure 2. Schematic representation of the relationship between stress and strain for a linear viscoelastic material.

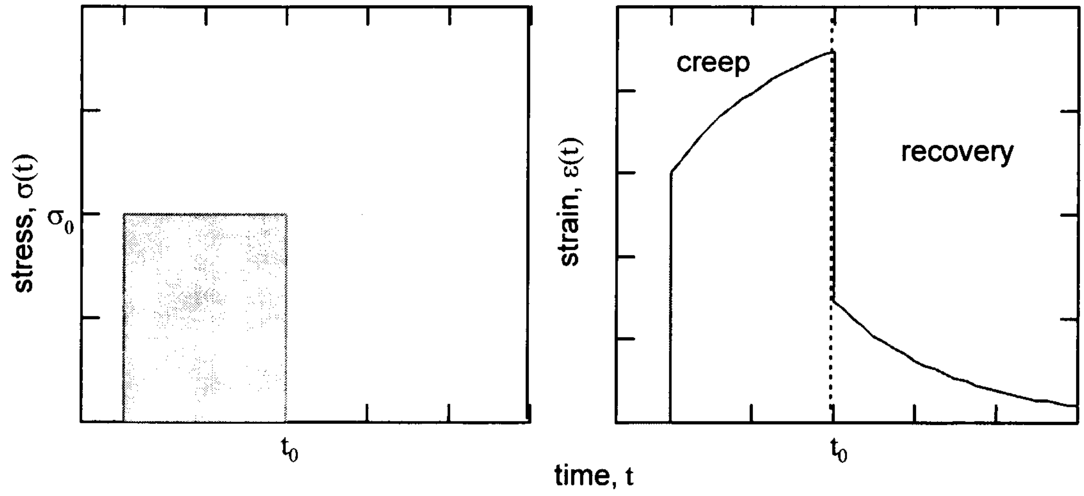


Figure 3. Schematic representation of the relationship between stress and strain for a linear viscoelastic material exhibiting creep and recovery.

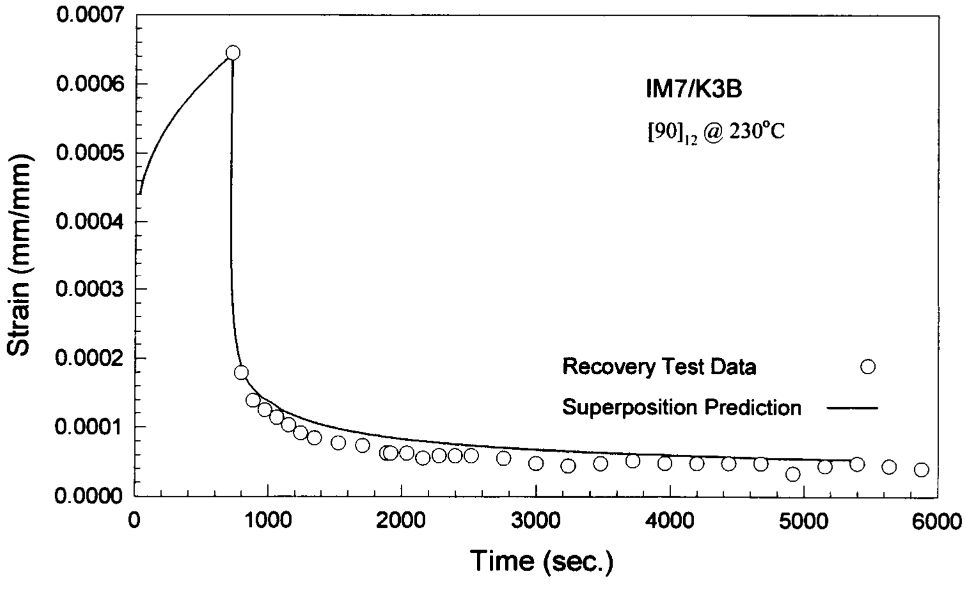


Figure 4. A check for Boltzman superposition. Comparison between test and prediction for creep and recovery of a composite material.

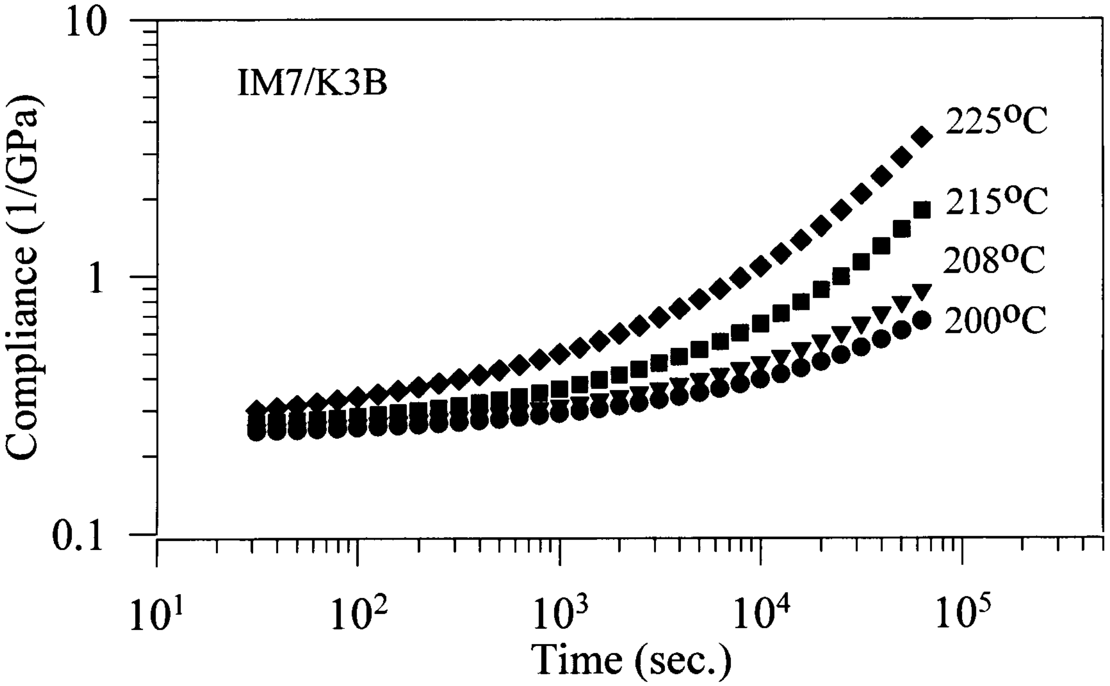


Figure 5a. Isothermal, shear creep compliance data for a $[\pm45]_{2s}$ composite material.

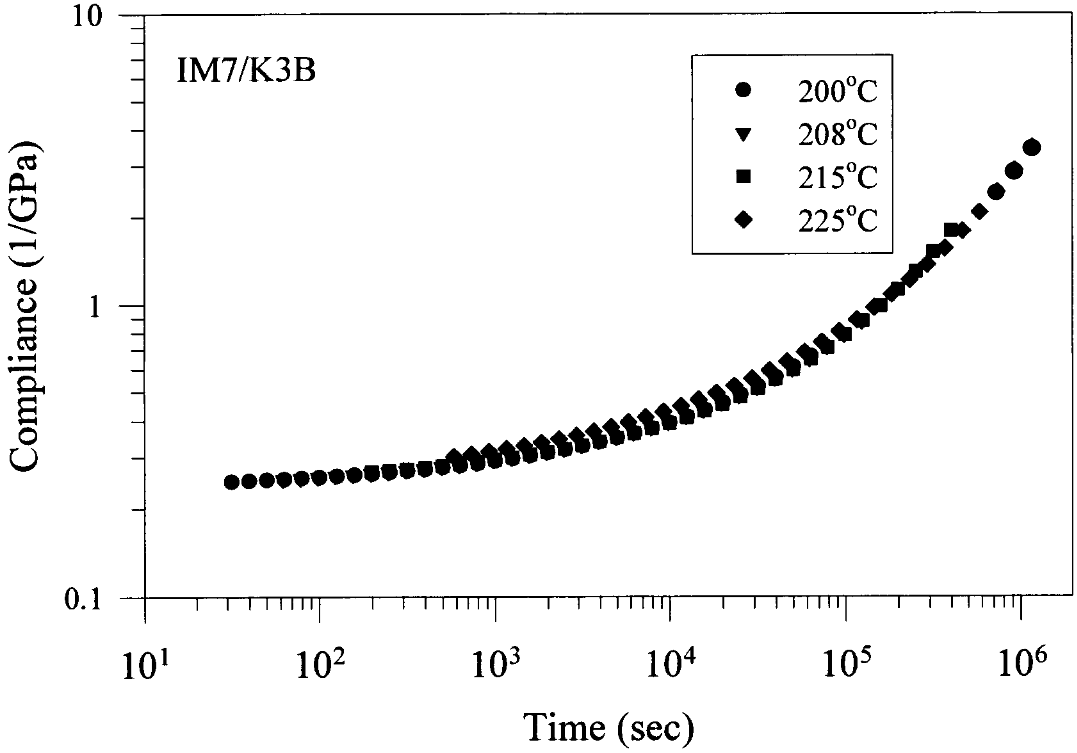


Figure 5b. Shear creep compliance master curve for data in Figure 5a. after applying time-temperature superposition.

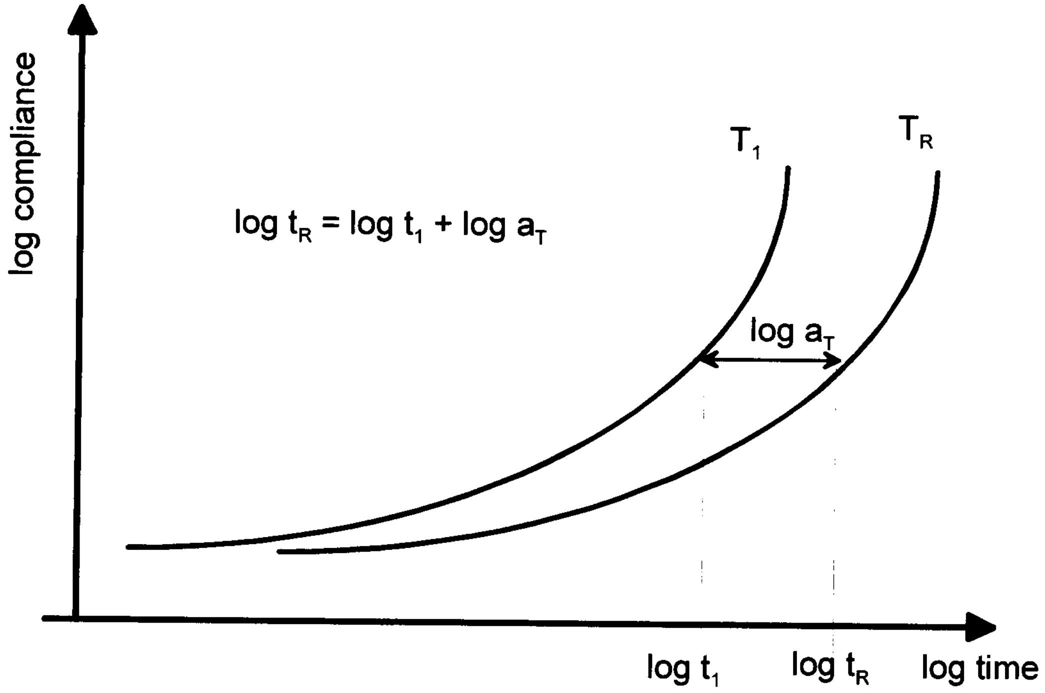


Figure 6. Illustration of time-temperature superposition for isothermal creep compliance curves where t_R and T_R are the reference time and temperature respectively.

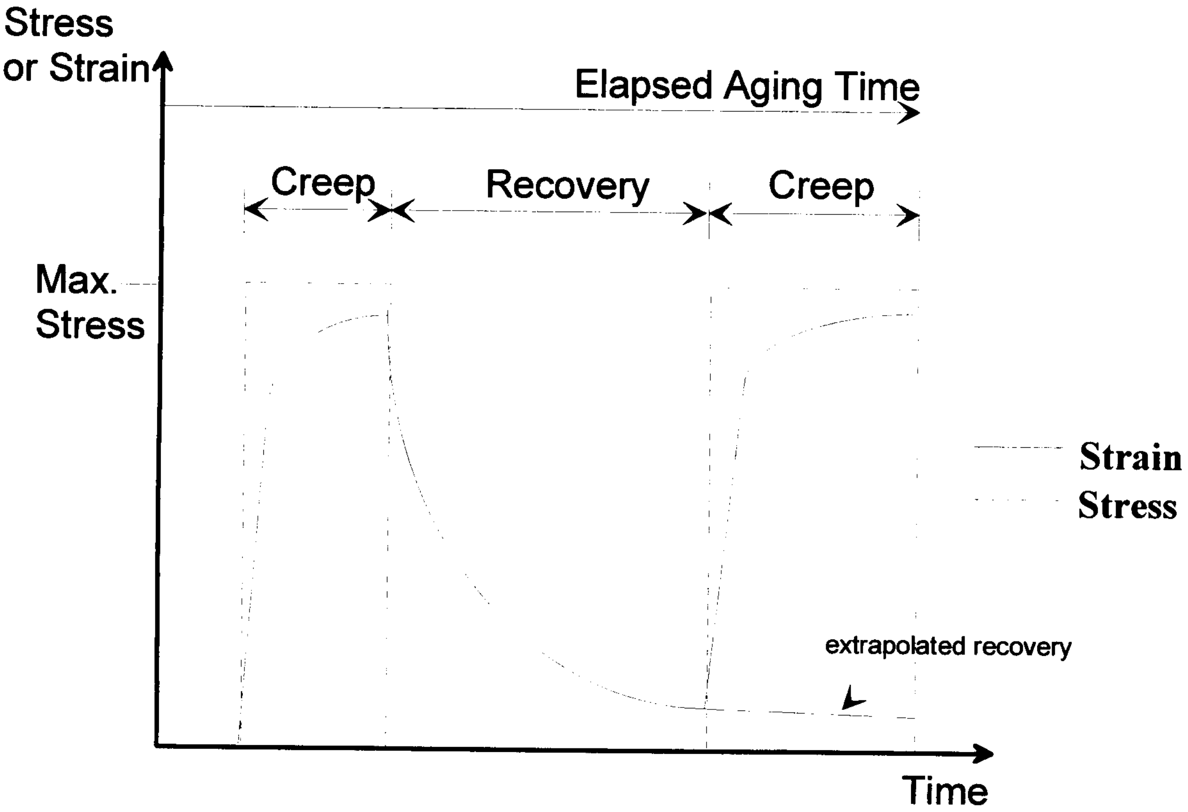


Figure 7. Illustration of sequenced test procedures used to establish time-aging time superposition for isothermal creep compliance.

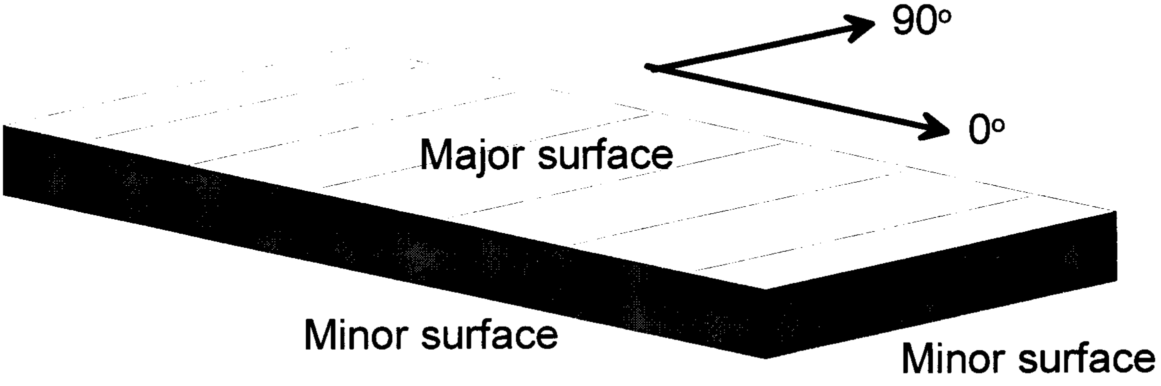


Figure 8. Schematic of typical unidirectional composite laminate illustrating the minor and major surfaces.

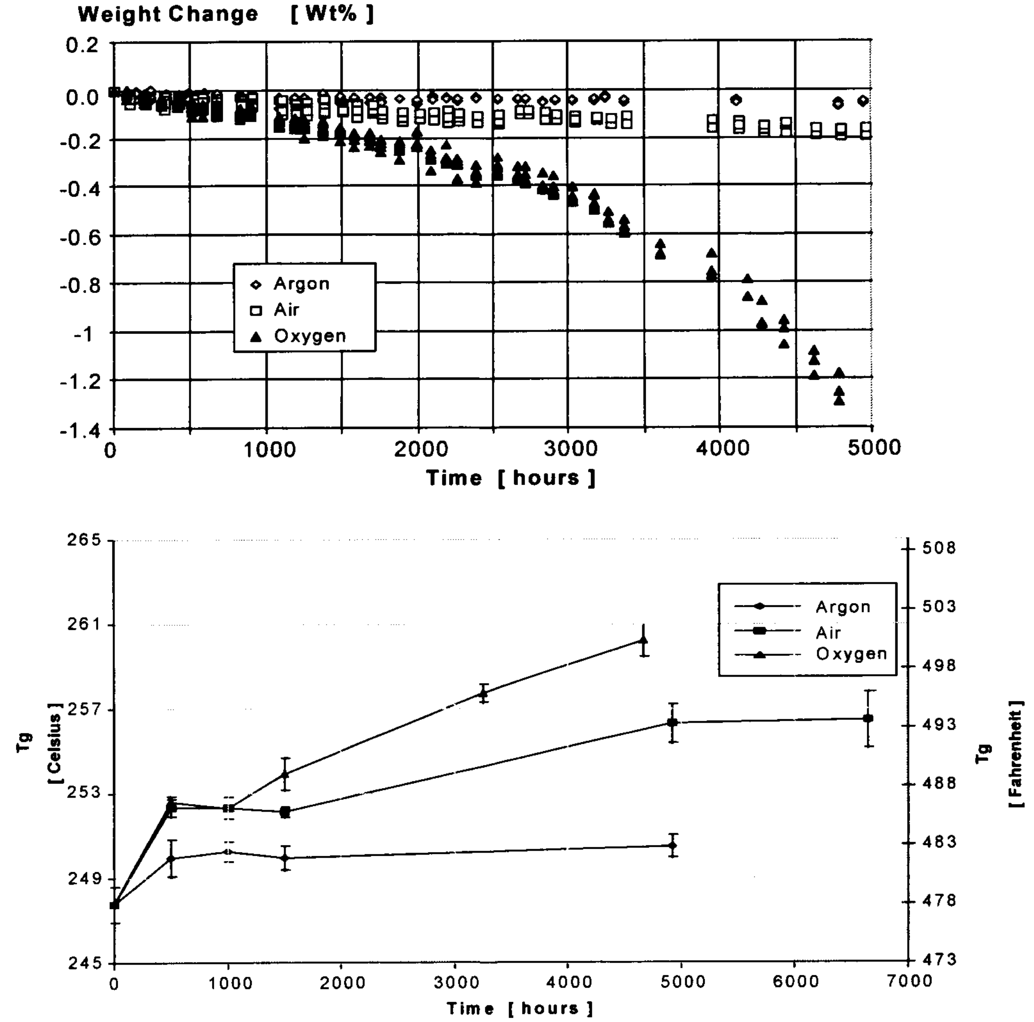
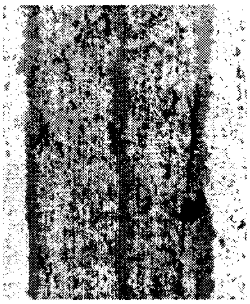


Figure 9. Effects of oxygen content on the measured change in weight and glass transition temperature of a graphite/thermoplastic.

A

Fatigue Conditions:
σ_{max}= **238 MPa.**
Temperature =**23°C**

Measurements:
$\Delta_{\text{weight loss}}$= None
ΔTg= None

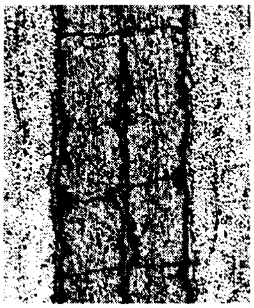


Photomicrograph (25x) of laminate edge showing absence of damage

B

Fatigue Conditions:
σ_{max}= **238 MPa.**
Temperature =**218°C**

Measurements:
$\Delta_{\text{weight loss}}$= 0.2 %
ΔTg= 40 °C



Photomicrograph (25x) of laminate edge showing microcrack damage

Figure 10. Effects of temperature during isothermal fatigue on the residual weight, glass transition, and damage state of a graphite/bismaleimide composite.

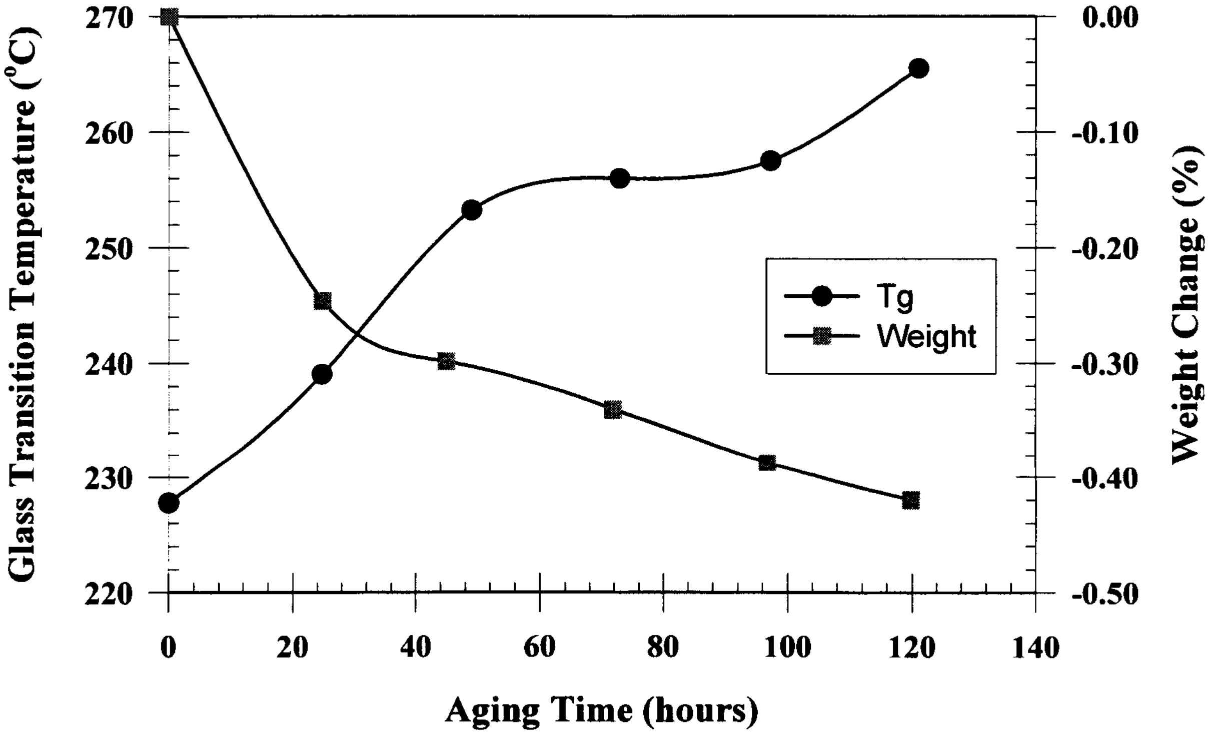


Figure 11. Measured change in weight and glass transition temperature during isothermal aging of a graphite/bismaleimide composite.

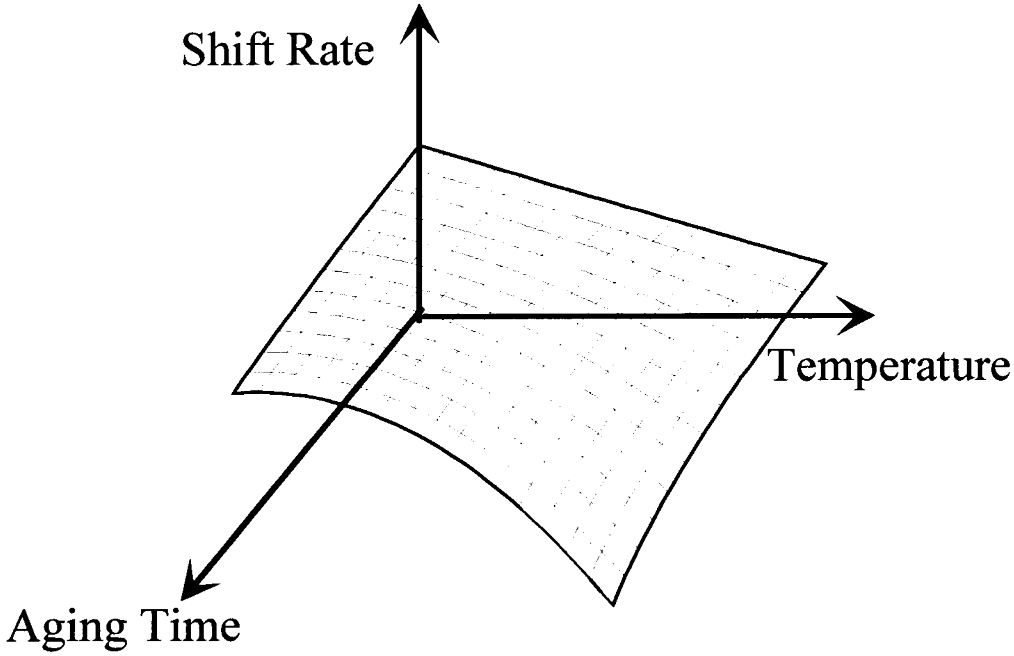


Figure 12. Illustration of the complex dependence of shift rate on temperature and aging time for a polymeric material during chemical aging.

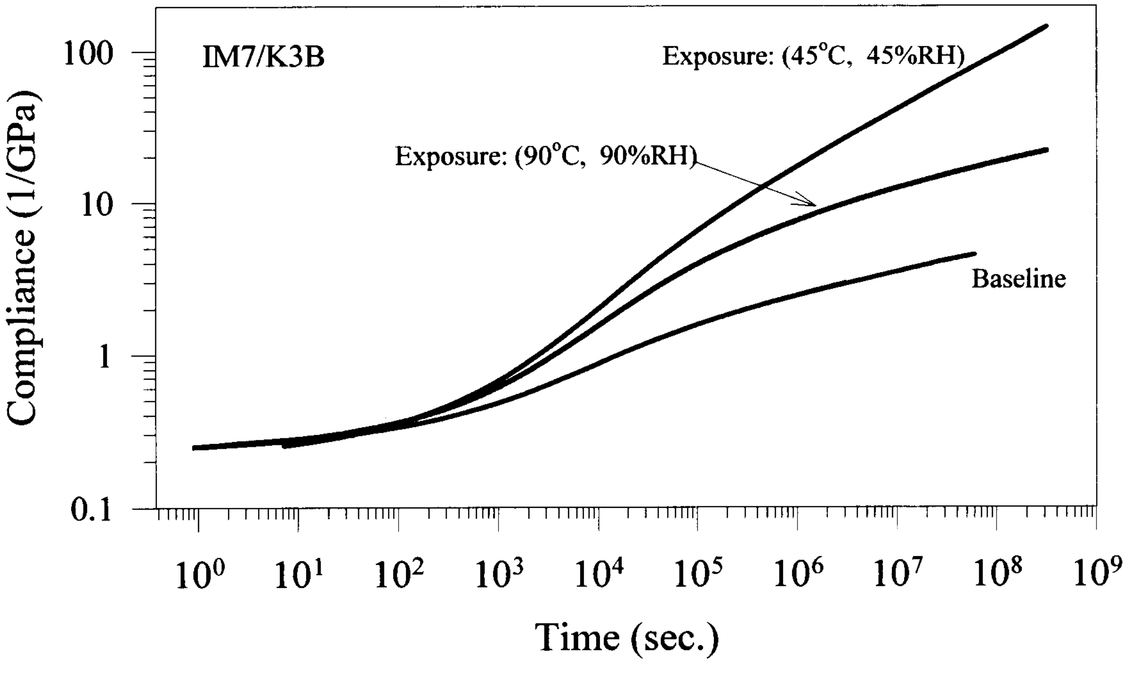


Figure 13. Predicted long-term creep compliance of a $[\pm 45]_{3s}$ composite material based on the measured short-term viscoelastic properties. Effects of prior hygrothermal exposure at two different conditions are illustrated.

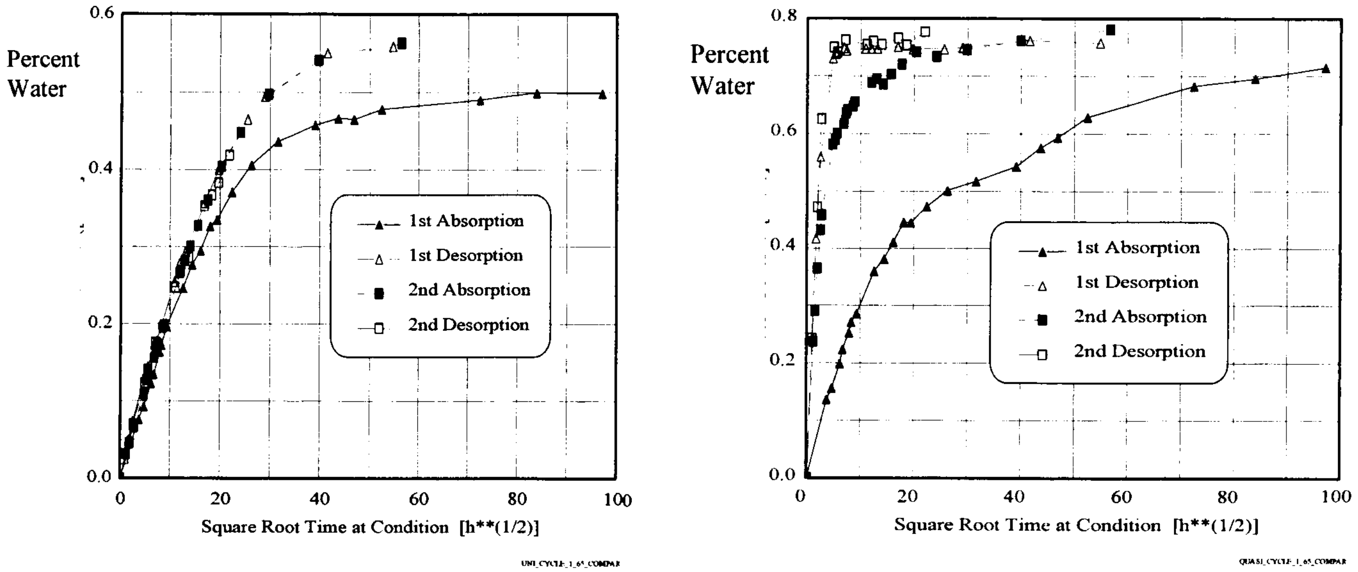


Figure 14. Fickian curves showing effects of internal stress on the measured water uptake of a graphite/thermoplastic.

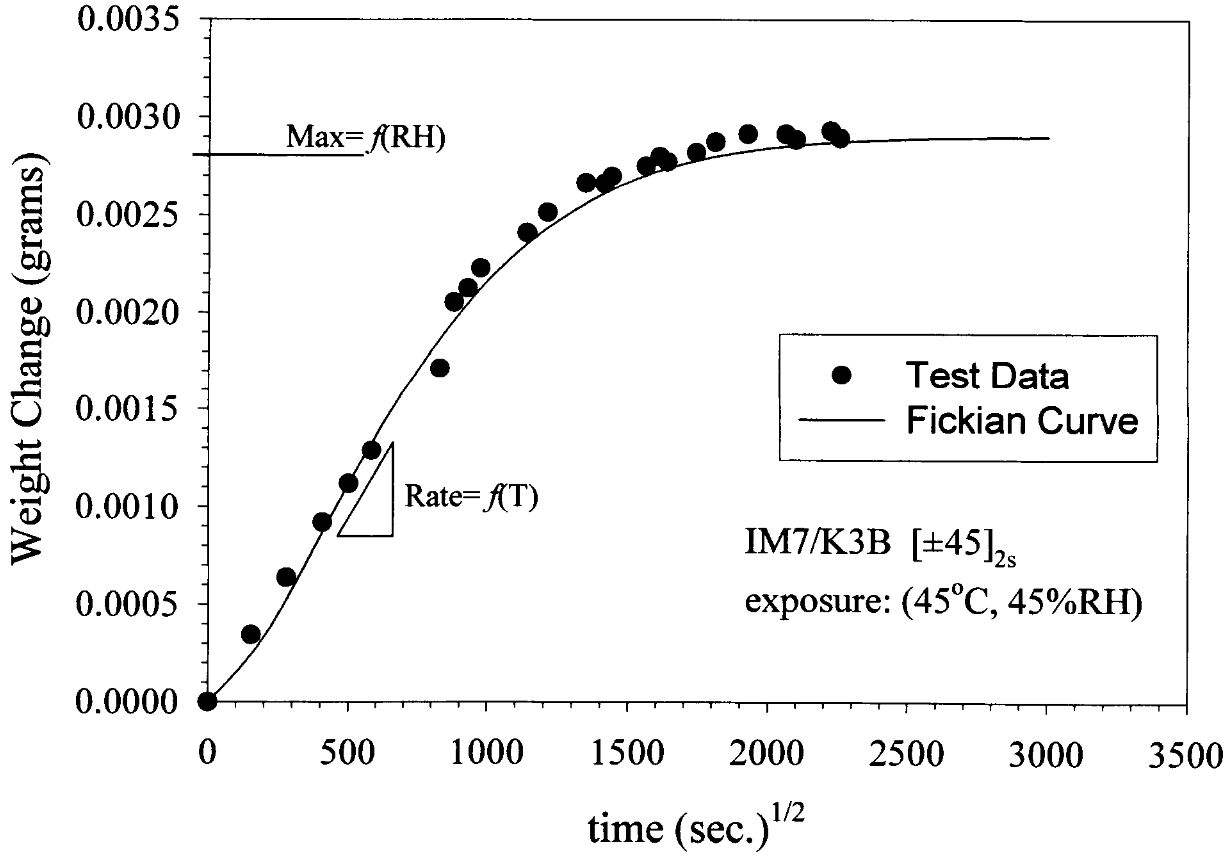


Figure 15. Test data and Fickian curve showing the measured water uptake of a graphite/thermoplastic composite and the determination of absorption rate and maximum uptake.

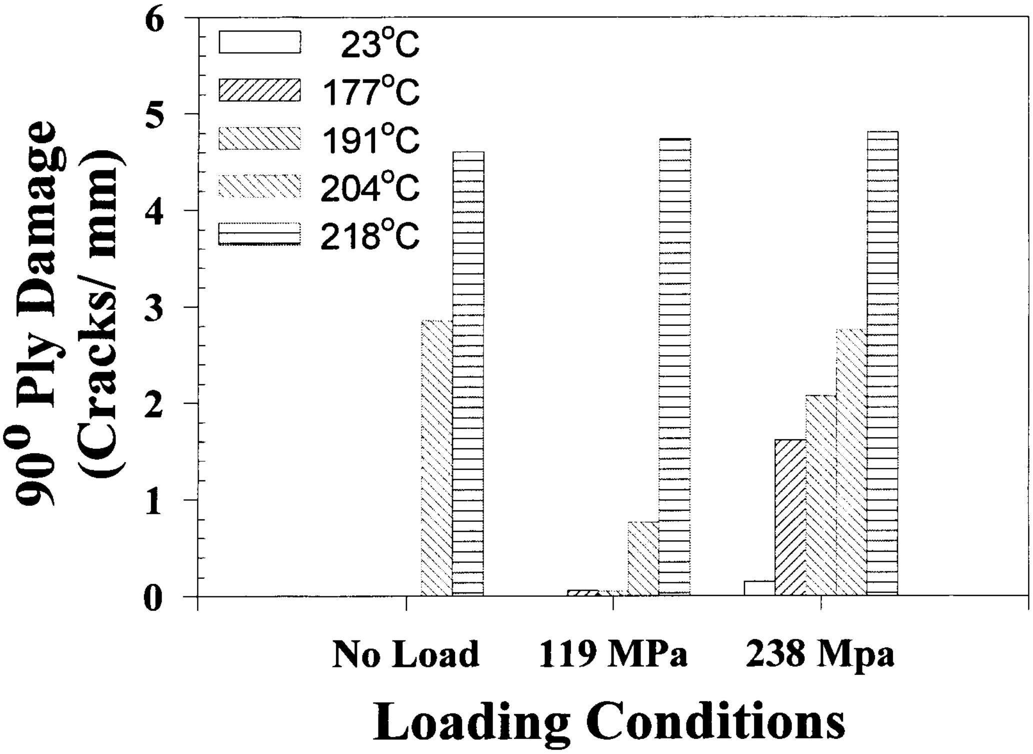


Figure 16. Effects of test temperature and fatigue stress level on the development of matrix cracks of a graphite/bismaleimide composite.

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13. ABSTRACT *(Maximum 200 words)*

A rational approach to the problem of accelerated testing for material characterization of advanced polymer matrix composites is discussed. The experimental and analytical methods provided should be viewed as a set of tools useful in the screening of material systems for long-term engineering properties in aerospace applications. Consideration is given to long-term exposure in extreme environments that include elevated temperature, reduced temperature, moisture, oxygen, and mechanical load. Analtical formulations useful for predictive models that are based on the principles of time-based superposition are presented. The need for repoducible mechanisms, indicator properties, and real-time date are outlined as well as methodologies for determining specific aging mechanisms.

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