THE NONLINEAR VISCOELASTIC BEHAVIOR OF ADHESIVES AND CHOPPED FIBER COMPOSITES

by

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NOMENCLATURE

a_σ	Stress-dependent time scale factor
a_T	Temperature-dependent time scale factor
g_0, g_1, g_2	Stress-dependent material properties
t, t_1, t', t_f, τ	Time
A,B,D	Failure material properties
A(o)	Initial linear viscoelastic creep compliance
$A_{ijk\ell}$	Creep compliance
ΔA	Transient component of linear viscoelastic creep compliance
$\hat{A}$	Nonlinear viscoelastic creep compliance
$\Delta\hat{A}$	Transient component of nonlinear viscoelastic creep compliance
C, C', C_1, C_2	Material properties
$E_{ijk\ell}$	Relaxation moduli
H(t)	Unit-step function
N	Creep power law exponent
T, T_θ, T_R	Temperature
ΔT	Change in temperature
Y(t)	Time dependent yield stress
α_{ij}	Thermal strain expansion coefficient
β_{ij}	Thermal stress expansion coefficient
$\beta = C \frac{g_1 g_2}{a_\sigma^N} (1 + 2\nu^2)^{1/2}$	Material property

$\delta(t)$	Dirac delta function
ϵ, ϵ_{ij}	Viscoelastic strain component
ϵ_{ij}^E	Elastic strain component
ϵ_{ij}^V	Viscoelastic strain component
$\Delta\epsilon_1 = \epsilon(t_1) - \epsilon_0$	Transient component of strain
ϵ_0	Initial component of elastic strain
ϵ_r, ϵ_r'	Recovery strain
$\bar{\epsilon}_r = \epsilon_r - \frac{\Delta\epsilon_1}{g_1}$	Shifted recovery strain
$\zeta, \zeta', \psi, \psi'$	Reduced time parameters
λ	Reduced recovery time
ν	Poisson's ratio
ρ, ρ_0	Density
σ_{ij}, σ	Stress
$\sigma_f(t)$	Uniaxial failure stress
χ	Time dependent material property

I. INTRODUCTION

In recent years a great deal of attention has been given to the characterization of lightweight but strong polymeric and composite materials. Chopped glass/fiber polyester composites such as sheet molding compound (SMC), filament wound glass fiber/polyester composites and polymeric structural adhesives, as with all polymeric materials, have properties which are sensitive to time and temperature as well as many other environmental parameters. The measurement, analytical calculation or prediction and understanding of temperature dependent viscoelastic processes are needed for the proper design of structural components. There is special need for knowledge of time dependent failure and fracture processes such that meaningful advance predictions can be made in order to avoid delayed catastrophic failures within the design lifetime of a particular structural component.

The application of reinforced composite materials has made the reliable design of adhesively bonded joints extremely desirable. Adhesive bonding techniques would eliminate bolting and riveting, which result in the cutting of fibers as well as the introduction of stress concentrations, thus allowing a more efficient stress distribution and permitting greater design stresses.

Several attempts have been made to determine whether the mechanical properties of an adhesive in a joint can be correlated with the properties of the bulk adhesive [1-3]. It is felt that adhesives do not exhibit the same material properties in a joint as they do in the bulk, even though attempts are made to cure the adhesive identically for both tests. Significant and often complex effects of parameters such as thickness, and the mode and rate of loading have been reported [4]. Also, constraint by the adherend surface must play a major role in determining at least some of these effects. It is felt, however, that behavior in a joint should in some way resemble bulk behavior. Before any differences can be expressed quantitatively material parameters and the effect of composition, history, specimen thickness, stress distribution, and environment must be understood with assurance. Only then would the prediction of joint behavior, from properties obtained on the resin in bulk form, be possible. To date this has not been accomplished.

The purpose of this investigation was to study the time dependent or viscoelastic behavior of a chopped glass fiber/polyester sheet molding compound (SMC-25) and a commonly used epoxy structural adhesive, Metlbond 1113-2, in bulk form. Time dependent properties such as moduli and strength were to be obtained. A nonlinear viscoelastic characterization procedure of Schapery [5-8] was to be applied to uniaxial creep and creep recovery data. A procedure was to be developed such that the Schapery method could be used in conjunction with a viscoplastic or time dependent failure law of Crochet [9] to characterize and predict delayed failures. Further, creep data at elevated temperatures was to be presented and the feasibility of a temperature-stress-time property surface was discussed. This involved applying the previously mentioned method of Schapery in conjunction with the time-temperature superposition principle of Williams, Landel and Ferry [10,11].

The principles of linear viscoelasticity have been widely used to characterize the mechanical behavior of polymers [10,11]. However, such concepts are usually only valid, if at all, for low levels of stress and strain. That is, the Boltzmann superposition integral is not an adequate or accurate description of the relations between the stress and strain at a material point from initial loading to incipient failure; i.e., yielding and/or separation. For this reason numerous efforts have been made to develop a nonlinear viscoelastic theory which could accurately represent the constitutive behavior of a polymer over its total response regime [12,13]. Many of these techniques, such as the modified superposition principle or the multiple integral representation are theoretically attractive but quite difficult to apply to the quantification of measured material parameters. Schapery has developed a procedure using thermodynamic concepts which appears to lack some of these limitations [8]. As will be shown subsequently, his integral equation approach has the same form as the familiar Boltzmann equation and the time parameters involved are the same as those from the linear theory.

The nonlinear procedures mentioned above are only for the purpose of mathematically describing the relation between stress and strain; i.e., modulus properties.

Failure, which may be defined in terms of either yielding and/or separation, is often a time dependent process for many polymers.

Nagdi and Murch have developed a general viscoplasticity theory which accounts for a time dependent yield process [14]. Crochet used their method to determine yielded regions in a bar under torsion [9]. In so doing he gave specific form to several failure parameters as well as postulating a time dependent yield law for uniaxial tension. Brinson demonstrated that a modified Bingham model and Crochet's postulate could be used to characterize the stress-strain and delayed yielding behavior of polycarbonate [15]. Later the same procedures, i.e., Bingham model and Crochet's postulate, were shown to be applicable to an epoxy adhesive [2]. It was shown that the procedures worked for separation, i.e., fracture, as well as for yielding.

Polymer based fiber reinforced composites have time dependent material properties for all stress situations where the polymer matrix is the primary load bearing component [16-19]. For graphite/epoxy laminated composites Brinson et al. have shown that fiber dominated properties are time dependent and that matrix dominated properties display a similar time dependence to that of the neat resin [18]. Additionally, they have demonstrated that the time temperature superposition principle and associated accelerated characterization procedures are applicable and can be used in conjunction with lamination theory to predict long-term properties of a laminate [17,18].

Because of attractive processing and fabrication characteristics, composites containing short fibers in a polymeric or metallic matrix have been studied extensively [20]. More recently, effort has been expended to determine the mechanical properties of a chopped glass fiber/polyester material, SCM-25 [21-25]. Adhesives to be used in uniting one structural component to another have also received considerable attention [1-3].

II. ANALYTICAL METHODOLOGY

As previously mentioned, polymeric materials have properties which are sensitive to time and temperature as well as other effects such as moisture and vibration. The linear viscoelastic relations between stress and strain for a thermorheologically simple material may be written by means of the Boltzmann integral [11] as,

$$\epsilon_{ij} = \int_{-\infty}^{t} A_{ijk\ell}(\zeta - \zeta') \frac{d\sigma_{k\ell}}{d\zeta'} d\zeta' - \int_{-\infty}^{t} \beta_{ij}(\zeta - \zeta') \frac{d\Delta T}{d\zeta'} d\zeta' \qquad (1)$$

and the inverse form as

$$\sigma_{ij} = \int_{-\infty}^{t} E_{ijk\ell}(\zeta - \zeta') \frac{d\epsilon_{k\ell}}{d\zeta'} - \int_{-\infty}^{t} \alpha_{ij}(\zeta - \zeta') \frac{d\Delta T}{d\zeta} d\zeta \qquad (2)$$

where ϵ_{ij} and σ_{ij} represent the strain and stress, respectively; $A_{ijk\ell}$ $E_{ijk\ell}$ are the creep compliance and relaxation moduli, respectively, and α_{ij} and β_{ij} are the thermal strain and stress expansion coefficients, respectively. Also,

ΔT = change in temperature, T

$$\zeta = \int_{-\infty}^{t} \frac{dt}{a_T} = \text{reduced time}$$

$$\zeta' = \int_{-\infty}^{\tau} \frac{dt}{a_T} = \text{reduced time}$$

and

$$a_T = a_T(t) = \text{shift factor} .$$

Note that the lower integral limit (-∞) is used to account for any past loading history of the material.

The Boltzmann superposition integral is valid, however, only for the linear range of the material. There are two checks on linearity which must be met. The first criterion is that of proportionality, and the second that of superposition. The first condition requires that a proportional change in input causes the same proportional change in output. The second requirement states that the response due to two given inputs acting together must be equivalent to the sum of the two responses acting separately. For all practical purposes, these two conditions are seldom met over the entire response range of a material.

Nonlinear Viscoelastic Theory

Schapery's nonlinear constitutive equations developed in [5,6] allows one to express material properties in terms of strain or stress by using the linear viscoelastic creep compliance or relaxation moduli, respectively. When stress is treated as the independent state variable Schapery's nonlinear constitutive equation for uniaxial loading, may be written as [6],

$$\epsilon = g_0 A(o)\sigma + g_1 \int_{0^-}^{t} \Delta A(\psi - \psi') \frac{dg_2\sigma}{d\tau} d\tau \qquad (3)$$

where $A(o)$ is the initial value of the linear viscoelastic creep compliance and $\Delta A(\psi)$ is the transient component. The quantities,

$$\psi = \psi(t) = \int_0^t \frac{dt'}{a_\sigma} \quad ; \quad \psi' = \psi(\tau) = \int_0^\tau \frac{dt'}{a_\sigma} \tag{4}$$

are reduced time parameters which are a function of the stress dependent shift function a_σ. That is, equations (4) are descriptive of a stress dependent method of reduced variables analogous to the well-known temperature dependent method of reduced variables [11]. The variables g_0, g_1 and g_2 are stress-dependent material properties that represent the nonlinear nature of the material which must be determined experimentally. It should be noted that when $g_0 = g_1 = a_\sigma = 1$ equation (3) reduces to the modified superposition principle (MSP) proposed by Leaderman [26]. When all stress dependent properties, g_0, g_1, g_2 and a_σ are taken to be equal to one, equation (3) reduces to the Boltzmann superposition integral.

The stress dependent properties in equation (3) have a thermodynamic origin [6]. Schapery has shown that changes in g_0, g_1, and g_2 reflect dependence of the Gibbs' free energy on the applied stress, and changes in a_σ arise due to dependence of both entropy production and free energy changes.

When strain is taken as the independent state variable, a constitutive equation may be derived similar in form to equation (3). The strain dependent properties are h_e, h_1, h_2 and a_ϵ and can be shown to be linked to changes in the Helmholtz free energy [5]. Relaxation (constant strain) tests may be used to evaluate the strain dependent properties mentioned above.

With stress as the dependent variable, creep and creep recovery data are sufficient to evaluate the stress-dependent properties of Equation (3).

Stepwise Stress Loading

When the stress is applied in a stepwise manner, such as in a creep test, Equation (3) reduces to an algebraic expression. Consider the loading.

$$\sigma = \begin{cases} \sigma_a \quad , & 0 < t < t_1 \\ \sigma_b \quad , & t_1 < t < t_2 \end{cases} \tag{5}$$

where the material is in a virgin state prior to the application of load at $t = 0^+$, and σ_a and σ_b are constants. The step-stress input given by (3) may be written as,

$$\sigma_a[H(t) - H(t - t_1)] + \sigma_b[H(t - t_1) - H(t - t_2)] \tag{6}$$

Substituting equation (6) into equation (3) we may write (see Appendix A) for $0 < t < t_1$:

$$\epsilon = \left[g_o{}^a \, A(o) + g_1{}^a g_2{}^a \, \Delta A\left(\frac{t}{a_\sigma{}^a}\right)\right]\sigma_a \tag{7}$$

and for $t_1 < t < t_2$:

$$\begin{aligned} \epsilon = g_o{}^b \, A(o)\sigma_b + g_1{}^b\Bigg[\int_{o^-}^{t_a{}^-} \Delta A(\psi - \psi') \, \frac{dg_2\sigma}{d\tau} \, d\tau \\ + \int_{t_a{}^-}^{t} \Delta A(\psi - \psi') \, \frac{dg_2\sigma}{d\tau} \, d\tau\Bigg] \end{aligned} \tag{8}$$

where t_a^- represents the time immediately prior to the application of the load σ_b. The superscript on the material properties indicate the particular stress at which they are to be evaluated. Realizing that $dg_2\sigma/d\tau$ is zero except at $\tau = 0$ and $\tau = t_a$ we may integrate equation (8); so that,

$$\epsilon = g_o{}^b\ A(o)\sigma_b + g_1{}^b\left[g_2{}^a\ \sigma_a\ \Delta A\left(\frac{t_a}{a_\sigma{}^a} + \frac{t - t_a}{a_\sigma{}^b}\right) + \left(g_2{}^b\ \sigma_b - g_2{}^a\ \sigma_a\right)\Delta A\left(\frac{t - t_a}{a_\sigma{}^b}\right)\right] \tag{9}$$

Creep and Creep Recovery

For creep and creep recovery tests a step-stress input is applied at $t = 0$ and removed at $t = t_1$ as shown in Figure 1. From equation (7) we see then that the expression for the creep strain may be written as,

$$\epsilon = \left[g_o{}^a\ A(o) + g_1{}^a\ g_2{}^a\ \Delta A\left(\frac{t}{a_\sigma{}^a}\right)\right]\sigma_a \quad ; \quad 0 < t < t_1\ . \tag{10}$$

Likewise from equation (9) setting $\sigma_b = 0$ and noting that all nonlinear material properties with a "b" superscript approach one, we may write the recovery strain, ϵ_r, as,

$$\epsilon_r = \left[\Delta A\left(\frac{t_a}{a_\sigma{}^a} + t - t_a\right) - \Delta A(t - t_a)\right] g_2{}^a\ \sigma_a \quad ; \quad t > t_1\ . \tag{11}$$

Notice that for a linear viscoelastic material $g_2 = a_\sigma = 1$ such that,

$$\epsilon_r = [\Delta A(t) - \Delta A(t - t_a)]\sigma \tag{12}$$

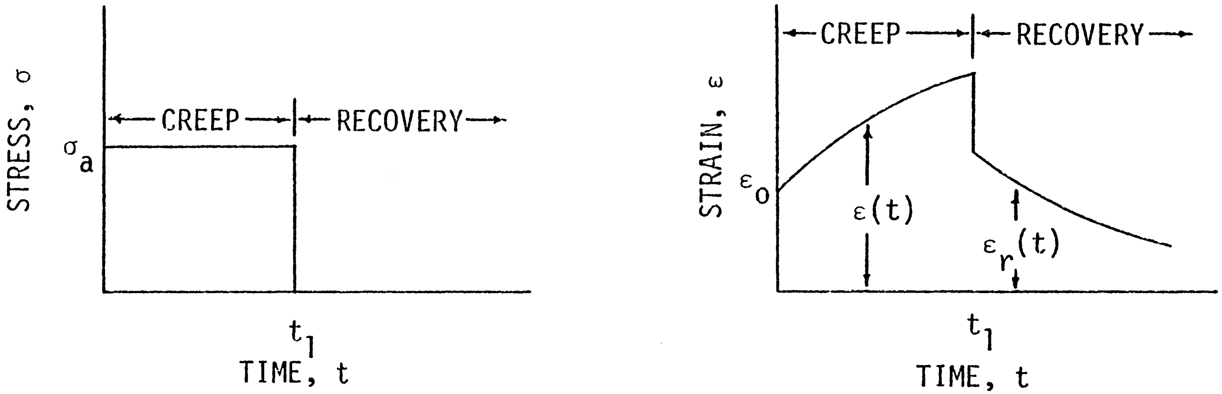


Figure 1. Typical stress-strain response for creep and creep recovery test.

as expected. Notice that $\epsilon = \epsilon_c = g_0 A(o)\sigma + g_1 g_2\, \Delta A\left(\frac{t_1}{a_\sigma}\right)$ immediately before the load is removed at t_1 and $\epsilon_r = \epsilon_r' = g_2\, \Delta A\left(\frac{t_1}{a_\sigma}\right)\sigma$ immediately after the load is removed at $t = t_1$. The jump in strain at $t = t_1$ may be written then as,

$$\epsilon = \epsilon_c - \epsilon_r' = g_0 A(o)\sigma + (g_1 - 1)g_2\, \Delta A\left(\frac{t}{a_\sigma}\right) \tag{13}$$

where for brevity the superscripts have been dropped. Notice that for a linear viscoelastic material with g_0, g_1, g_2 and a_σ equal to one, we have the expected result that the jump in strain at t_1 is equal to the initial jump at $t = 0$.

The nonlinear creep compliance, $\hat{A}$, is defined in the same way as the linear creep compliance, and is the ratio of strain-to-stress in a creep test,

$$\hat{A} = \epsilon/\sigma\ . \tag{14}$$

If it is assumed that the compliance follows a power law in time, as do many plastics, the transient portion may be written as,

$$\Delta A(\psi) = C\psi^{N}\ . \tag{15}$$

Equations (10), (14) and (15) combine to define the nonlinear creep compliance as,

$$\hat{A} = \frac{\epsilon}{\sigma} = \left[g_0\ A(o) + C\ g_1 g_2 (t/a_\sigma)^N\right] \tag{16}$$

and the recovery strain of equation (12) becomes,

$$\epsilon_r = \frac{\Delta\epsilon_1}{g_1}\left[(1 + a_\sigma\,\lambda)^N - (a_\sigma\,\lambda)^N\right] \tag{17}$$

where

$$\lambda = \frac{t - t_1}{t_1} \tag{18}$$

and

$$\Delta e_1 = \epsilon(t_1) - \epsilon_0 = g_1 g_2\, C\psi_1{}^N\sigma\ . \tag{19}$$

In equation (19) $\Delta\epsilon_1$ represents the transient component of strain just prior to removal of the stress at $t = t_1$.

Delayed Failure Analysis

The previous sections of this chapter were devoted mainly to the discussion of Schapery's nonlinear constitutive theory. To completely characterize a material also requires a criterion to be used to define time dependent failure or more specifically time-dependent separation or rupture.

A possible mathematical model for the characterization of a delayed yield phenomenon was proposed by Crochet [9]. He assumed the yield stress to be a monotonically increasing function for increasing strain rate which implies that a faster loading rate produces a higher yield stress, as shown in Figure 2. The yield stress was given the specific form such that,

$$Y(t) = A + B\exp(-D\chi) \tag{20}$$

where Y(t) is a time dependent yield stress and A, B and D are material

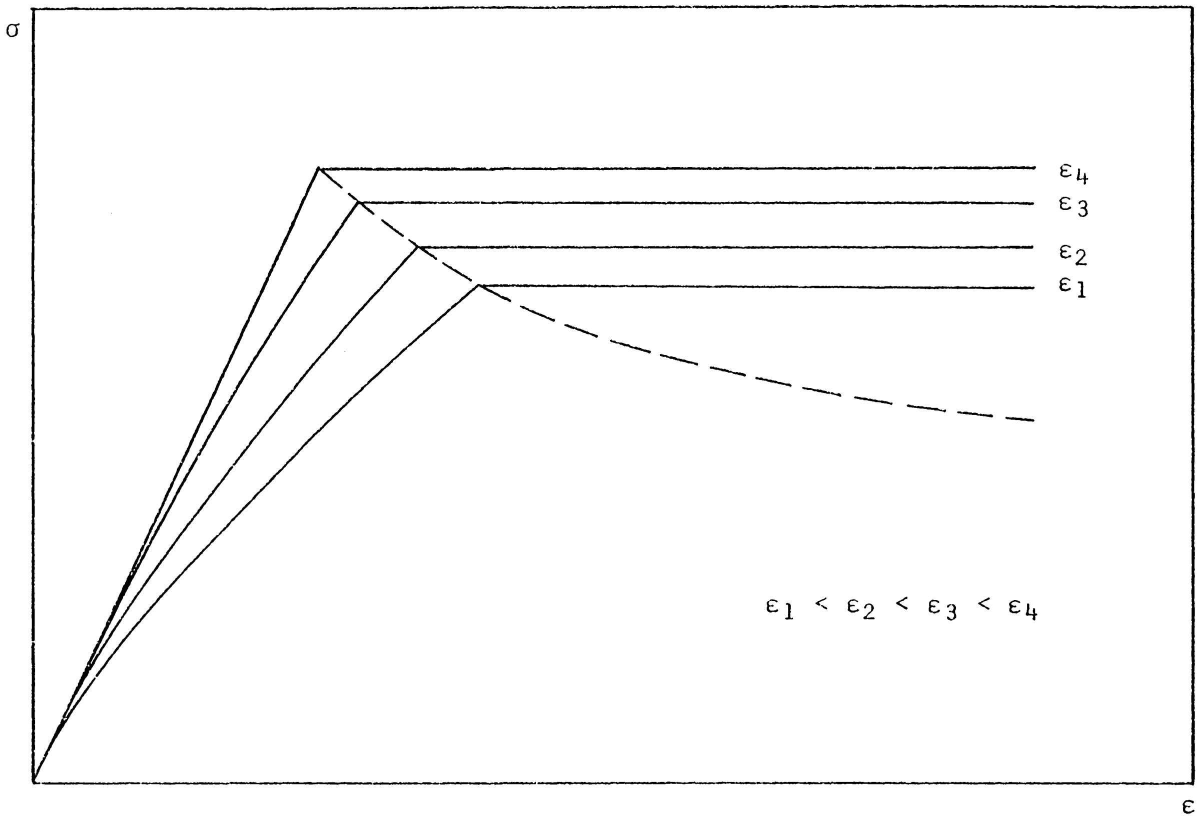


Figure 2. One-dimensional stress-strain curves for different rates of loading

constants. The time dependent material function, χ, was defined by Crochet as,

$$\chi = \left[\left(\epsilon_{ij}^{V} - \epsilon_{ij}^{E}\right)\left(\epsilon_{ij}^{V} - \epsilon_{ij}^{E}\right)\right]^{1/2} \tag{21}$$

where ϵ_{ij}^{V} and ϵ_{ij}^{E} refer to the viscoelastic and elastic strains respectively.

Brinson et al. have demonstrated that a modified Bingham model and Crochet's postulate could be used to characterize the stress-strain and delayed yielding behavior of Metlbond 1113 [2]. For uniaxial tension, equation (21) may be written as,

$$\chi = \left[\left(\epsilon_{11}^{V} - \epsilon_{11}^{E}\right)^2 + \left(\epsilon_{22}^{V} - \epsilon_{22}^{E}\right)^2 + \left(\epsilon_{33}^{V} - \epsilon_{33}^{E}\right)^2\right]^{1/2} . \tag{22}$$

Substitution of the creep strain from equation (16) into equation (22) gives,

$$\chi = C \frac{g_1 g_2}{a_\sigma^N} \sigma\, t^N (1 + 2\nu^2)^{1/2} \tag{23}$$

where a constant Poisson's ratio, ν, has been assumed. It should be noted that in equation (16) the term $g_0 A(o)\sigma$ represents the elastic strain behavior.

Assuming that the rupture stress has the same form as equation (20), and realizing that for a creep to rupture test, the applied stress is the rupture stress, then we may write,

$$\sigma_f(t_f) = A + B \exp(-D\chi) \tag{24}$$

where $\sigma_f(t)$ represents the stress at rupture. (Note: The χ function of equation (23) also contains the rupture stress $\sigma_f(t)$ for a creep to rupture test.) Substitution of equation (23) into (24) and solving for t_f gives,

$$t_f = \left[\frac{1}{D\beta\sigma_f} \ell n \frac{\sigma_f - A}{B}\right]^{1/N} \qquad (a)$$

where (25)

$$\beta = C \frac{g_1 g_2}{a_\sigma^N} (1 + 2\nu^2)^{1/2} \qquad (b)$$

Equation (25) represents the time necessary for creep to rupture to occur under the constant applied stress σ_f.

Time-Temperature-Superposition Principle (TTSP)

The TTSP or method of reduced variables [10,11] is a method by which long-term time-dependence may be determined by short-term response at various elevated temperatures. The relation which is based on a temperature dependent shift function, a_T, may be written as,

$$A_{ij}(t',T_o) = \frac{T\rho}{T_o\rho_o} A_{ij}(t,T) \qquad (26)$$

where A_{ij} are the isothermal values of the creep compliance taken at temperatures T_o and T, respectively. The temperatures, T and T_o, represent the temperature of testing and the reference temperature, respectively, and ρ and ρ_o are the densities at temperature T and T_o, respectively. For polymeric materials the ratio ρ/ρ_o is very small and is often neglected. The time parameters t' and t are related to the shift factor, a_T, in much the same manner as a_σ is related to the reduced time parameter ψ previously discussed. That is;

$$t = \int_0^{t'} \frac{dt}{a_T} . \qquad (27)$$

By applying equations (26) and (27) the time dependence of a viscoelastic material over a short time range at various temperatures may be extended by the use of the shift function, a_T, to predict behavior at long times at some reference temperature, T_o. That is, by conducting short-term tests at various temperatures the data may be shifted horizontally to form a single continuous master curve for extended time.

Generally, the TTSP may be applied with good correlations using only a horizontal shift of the data. However, due to morphological changes associated with changes in temperature and load, [27,28] poor correlations between theory and experiment may occur. As a result, shifting the deformation versus log time curves vertically, in addition to the horizontal shifts is sometimes required [29,30]. When this procedure is necessary the material is referred to as thermorheologically complex. The only verification of the deformation curves obtained by the shifting procedure is made by performing long-term tests.

III. EXPERIMENTAL CONSIDERATIONS

The two materials investigated in this study were SMC-25 and Metlbond 1113-2. Metlbond 1113-2 is a 100% solid, modified epoxy film produced by Narmco Whittaker, Corp. of Costa Mesa, California. All tests were conducted on bulk dog bone specimens such as shown in Figure 3.

SMC-25 is a fiber reinforced material reinforced with 25% E-glass fiber by weight embedded in a polyester matrix. Fiber lengths were ∿ 2.54 cm (∿ 1.0 in). Manufacturing details can be found in reference [24] while Table 1 shows the detailed composition of SMC-25.

The Metlbond 1113-2 panel from which the specimens were cut was cured at 50 psi. Narmoco Whittaker also produces a modified epoxy film adhesive, labeled Metlbond 1113, with a synthetic carrier cloth. Metlbond 1113-2 is the identical film without the carrier cloth. For a comparison of the behavior of both materials see [3].

Dog bone shaped specimens with a cross section of ∿ 1.27 cm (∿ 0.5 in) x ∿ .05 cm (∿ .1259 in) were used for tensile testing of both the SMC and Metlbond materials. Creep tests were performed using a pneumatic testing machine manufactured by Allied Research Associates. The constant load level was monitored using a Baldwin SR-4 (Type U-1) load cell with a Vishay (Model 2160) strain amplifier. The load was found to be constant throughout the test. The specimens were instrumented using electrical strain gages of 350 ohms to minimize heating effects. A full bridge setup was chosen to compensate for bending

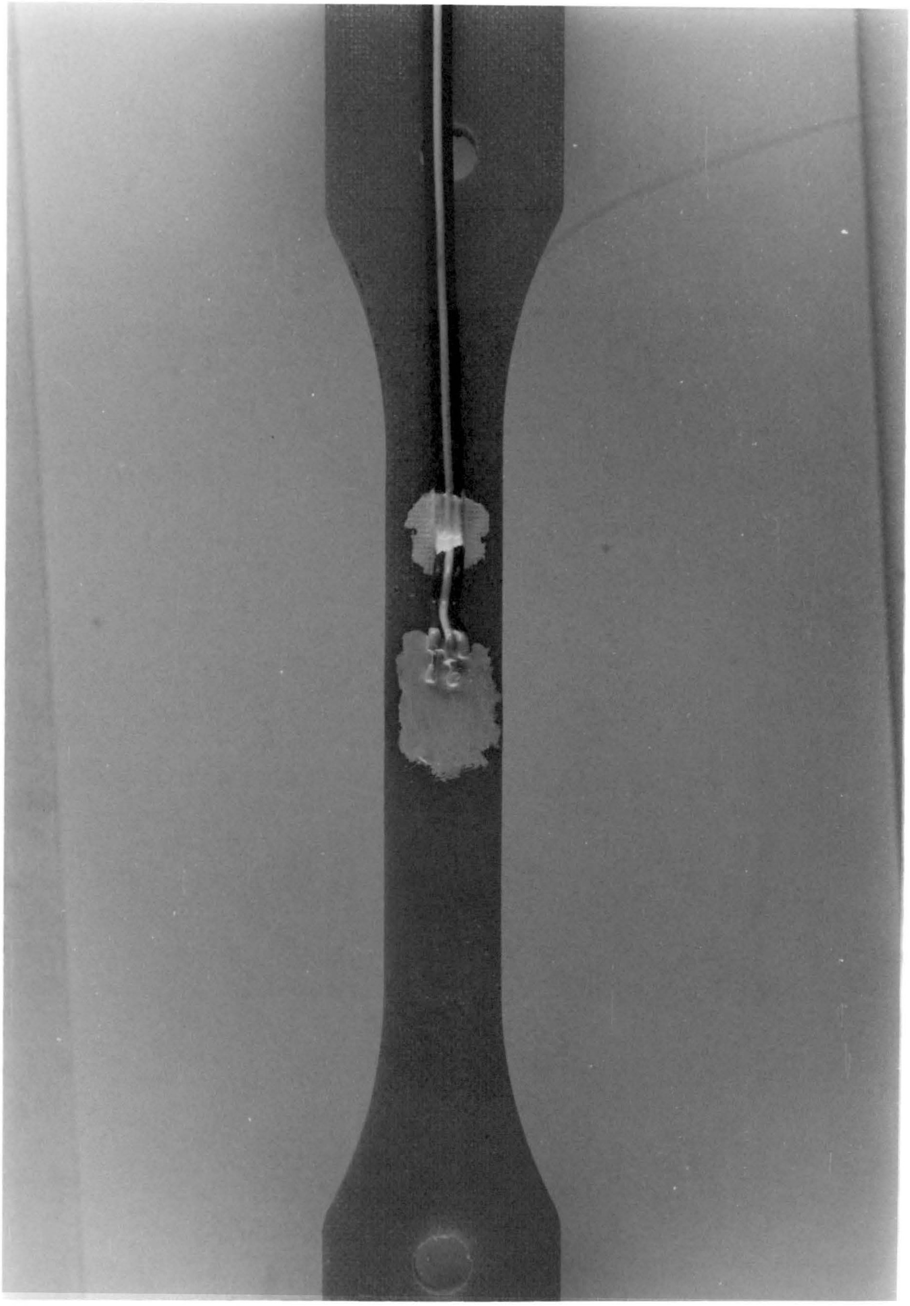


Figure 3a. Metlbond 1113-2 specimen before testing.

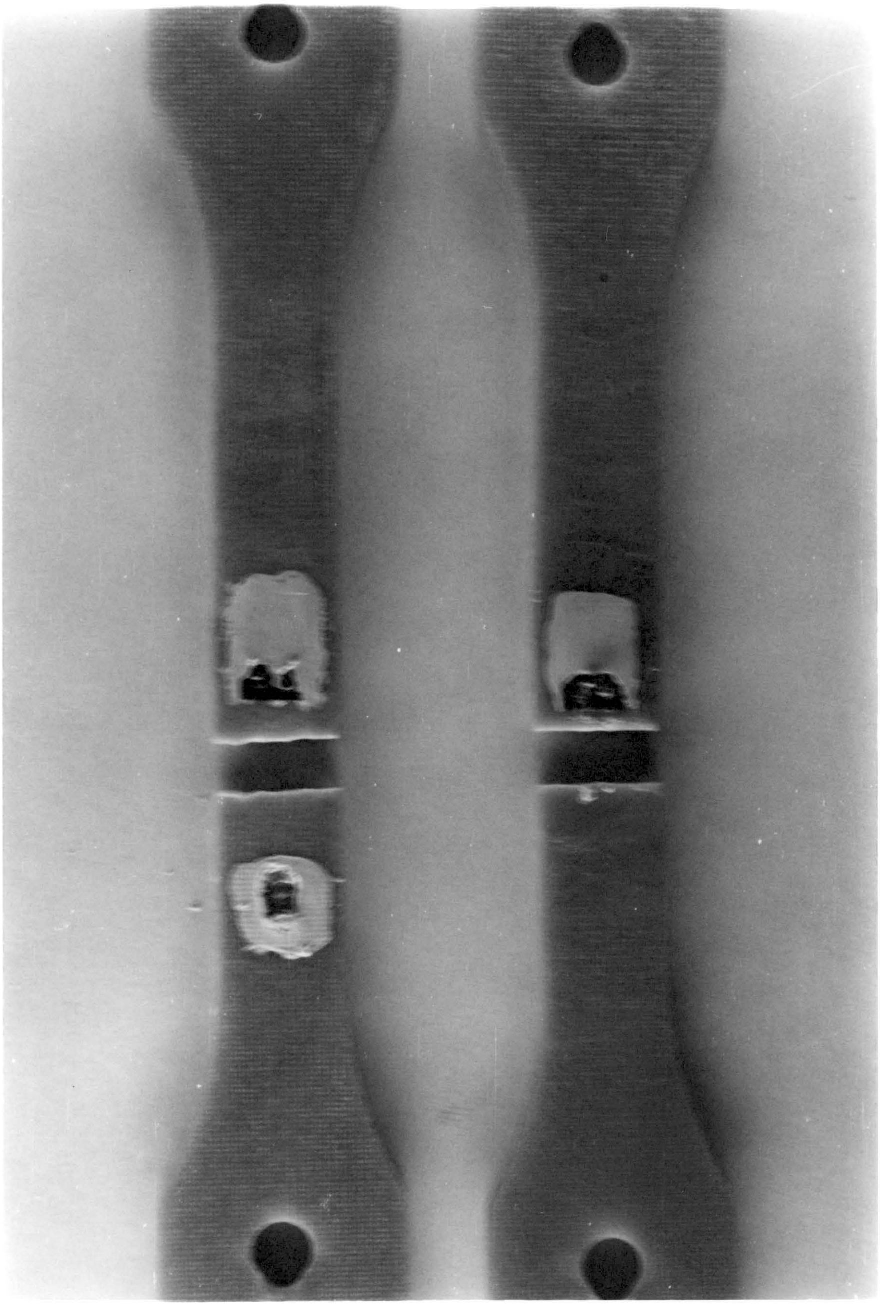


Figure 3b. Metlbond 1113-2 specimen following creep to rupture.

TABLE 1: SMC-25 MATERIAL FORMULATIONS

INGREDIENT	TYPE	WEIGHT %
Polyester (OCF* E-920-1)	Resin	29.4
Calcium Carbonate	Filler	41.8
Zinc Stearate	Internal Release	1.1
Tertiary Butyl Perbenzoate	Catalyst	0.3
Magnesium Hydroxide	Thickener	1.5
Mapico Black	Pigment	0.8
E-Glass (OCF 951 AB)	2.54 cm Chopped	25.

and to increase the sensitivity. All data were recorded on a Hewlett Packard (7100 B) dual channel strip chart recorder. The experimental setup is shown in Figure 4. The load was introduced through steel plates bolted to the specimen.

Elevated Temperature Tests

Creep tests at various temperatures above and below the glass transition temperature of the materials were conducted on an Instron machine (Model 1125) with an Instron environmental chamber. The apparatus used is shown in Figure 5. Test fixtures were fabricated to position the specimen inside the chamber. A copper cooling coil was affixed to the top fixture to dissipate heat away from the load cell. The strain data were amplified and recorded using the same equipment as described previously. The load was held constant and monitored by use of instrumentation on the Instron.

Mechanical Conditioning

Uniaxial tensile properties of SMC have been studied extensively by General Motors under a variety of conditions [21-25]. They have shown that considerable experimental scatter does occur from panel to panel and with the location and direction of a specimen taken from within a single panel. This is understandable when the method of fabrication is considered. SMC is made up into a "baker's dough" type compound and then compression molded into the desirable form. As a result the fibers have preferred directions depending upon flow. As a result, a series of tests were performed on a single specimen at

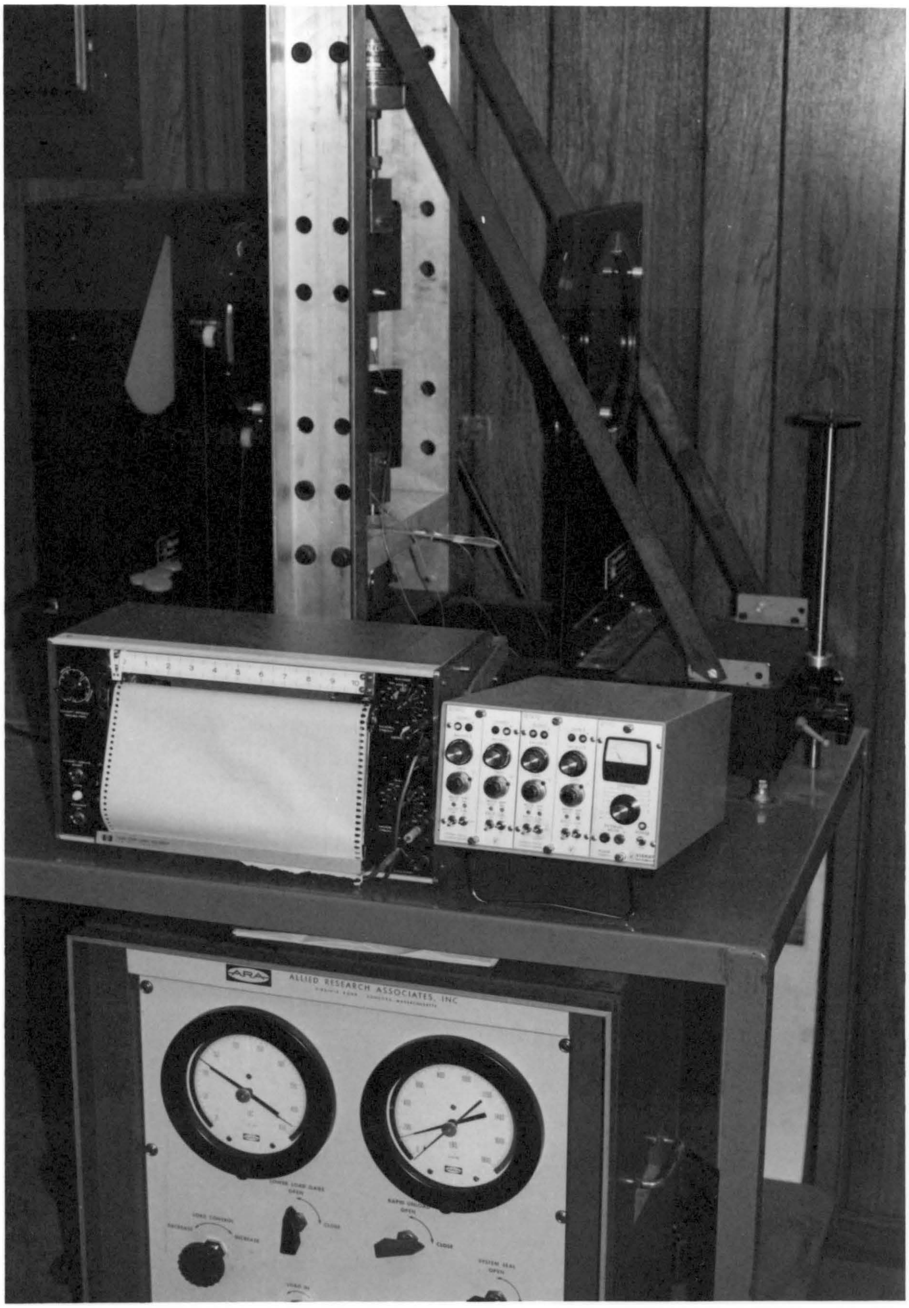


Figure 4. Creep testing apparatus.

Figure 5. Elevated temperature testing apparatus.

a single strain rate up to about 50% of the ultimate stress to ascertain if a mechanical conditioning process, as proposed by Schapery [8], was necessary. It was found that changes in the stress-strain diagram did occur with cycling up to about the 20th cycle but thereafter the loading and unloading behavior were unchanged as seen in Figure 6. It was further learned that all changes were recoverable; i.e., repeatable stress-strain data could be obtained after allowing the specimen to recover a few hours.

Inasmuch as the purpose of the present effort was to determine the feasibility of using Schapery's nonlinear viscoelastic characterization procedures for SMC-25 and Metlbond and not to determine statistically valid properties, the testing program needed to determine the nonlinear parameters described in the preceding chapter was conducted on a single specimen. That is, we were interested in studying phenomenology rather than variations arising due to fabrication.

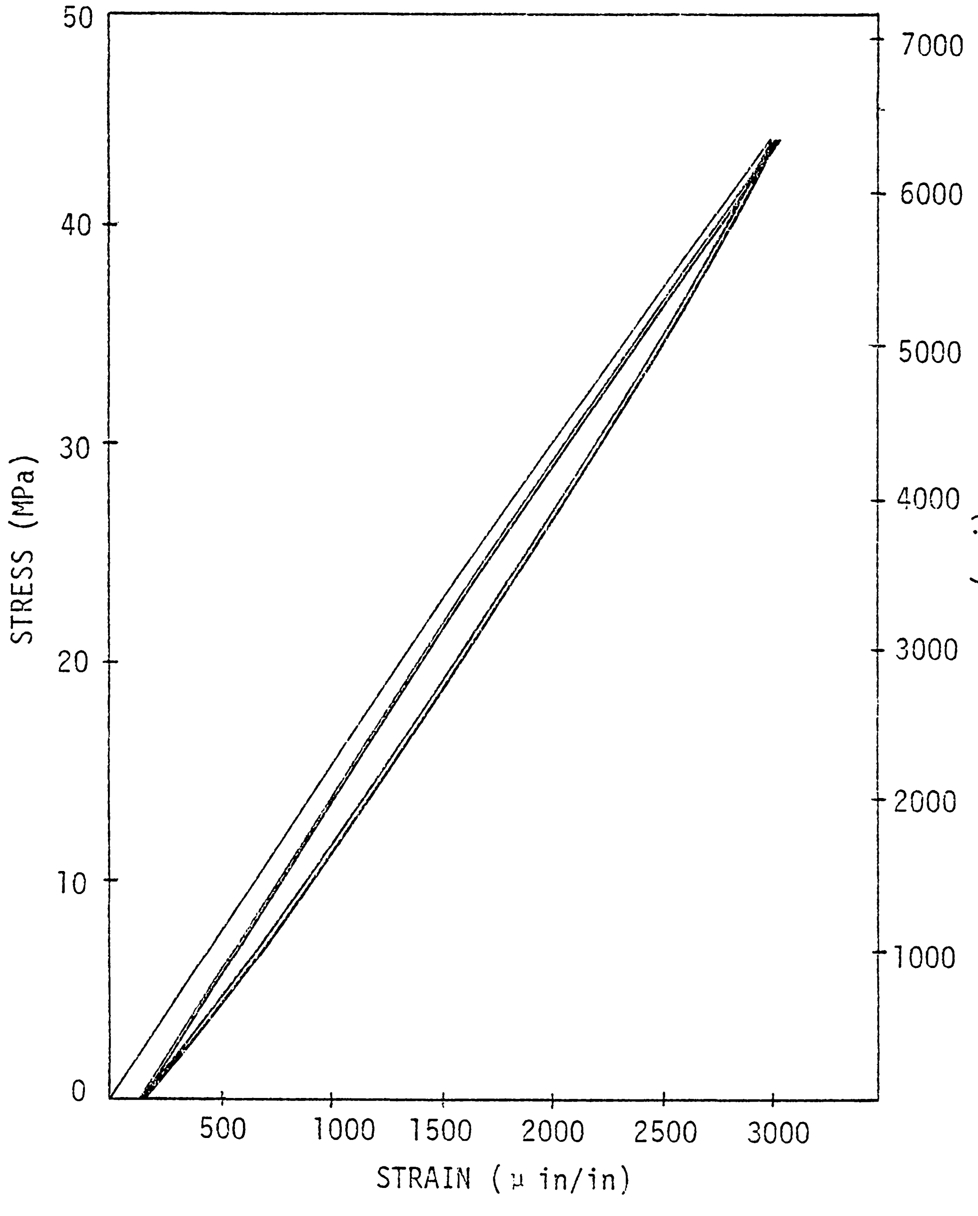


Figure 6. Mechanical conditioning of SMC-25.

IV. REDUCTION OF EXPERIMENTAL CREEP AND CREEP RECOVERY DATA

As previously discussed creep and creep recovery data provide ample information for the characterization of the nonlinear viscoelastic properties. Creep recovery data alone provides information for the evaluation of $\Delta\epsilon_1/g_1$ and a_σ. Taking $\log_{10}$ of equation (17) yields,

$$\log \epsilon_r = \log \frac{\Delta\epsilon_1}{g_1} + \log\left[(1 + a_\sigma\,\lambda)^N - (a_\sigma\,\lambda)^N\right] \tag{28}$$

Providing that the fundamental material descriptions given by the constitutive law of equation (3) and the power law of equation (15) are correct, equation (28) can be interpreted as the defining equation for determining $\frac{\Delta\epsilon_1}{g_1}$ and a_σ.

The creep recovery data determined from the testing program at different stress levels are shown in Figures 7 and 8, plotted on a log-log plot, for the SMC-25 and Metlbond 1113-2 materials, respectively. The curves for the lowest stress level, 1540 psi for the SMC specimen and 795 psi for the Metlbond specimen, were assumed to be in the linear viscoelastic range of the materials. Recalling that $a_\sigma = g_1 = 1$ for the linear range, examination of equation (28) reveals that the only unknown is N. Therefore we may rewrite equation (28) as,

$$\log \bar{\epsilon}_r = \log \frac{\epsilon_r}{\Delta\epsilon_1} = \log\left[(1 + \lambda)^N - (\lambda)^N\right] . \tag{29}$$

From equation (29) we see that for a plot of $\bar{\epsilon}_r$ versus λ, a family of

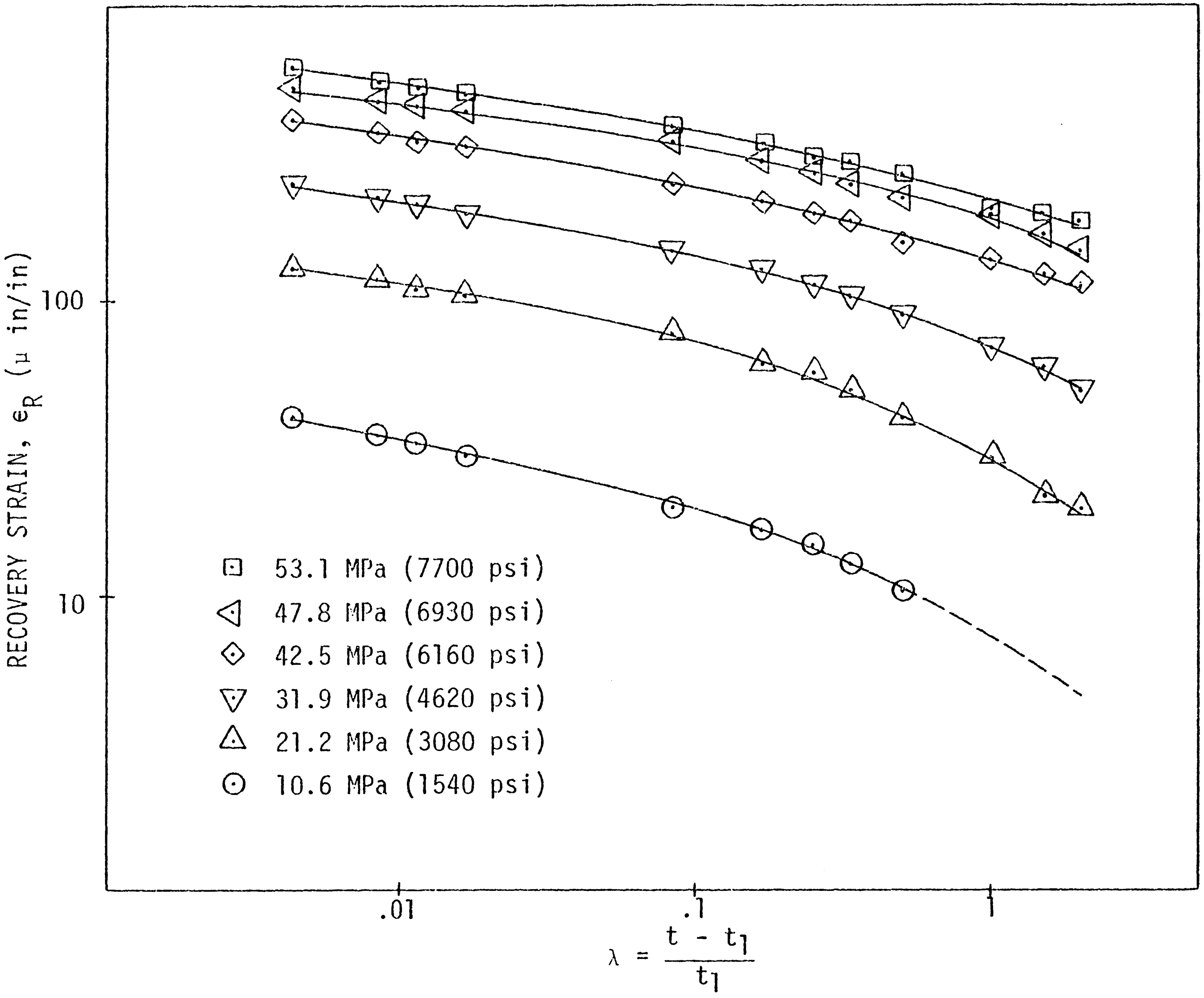


Figure 7. Recovery strains for various stress levels, SMC-25.

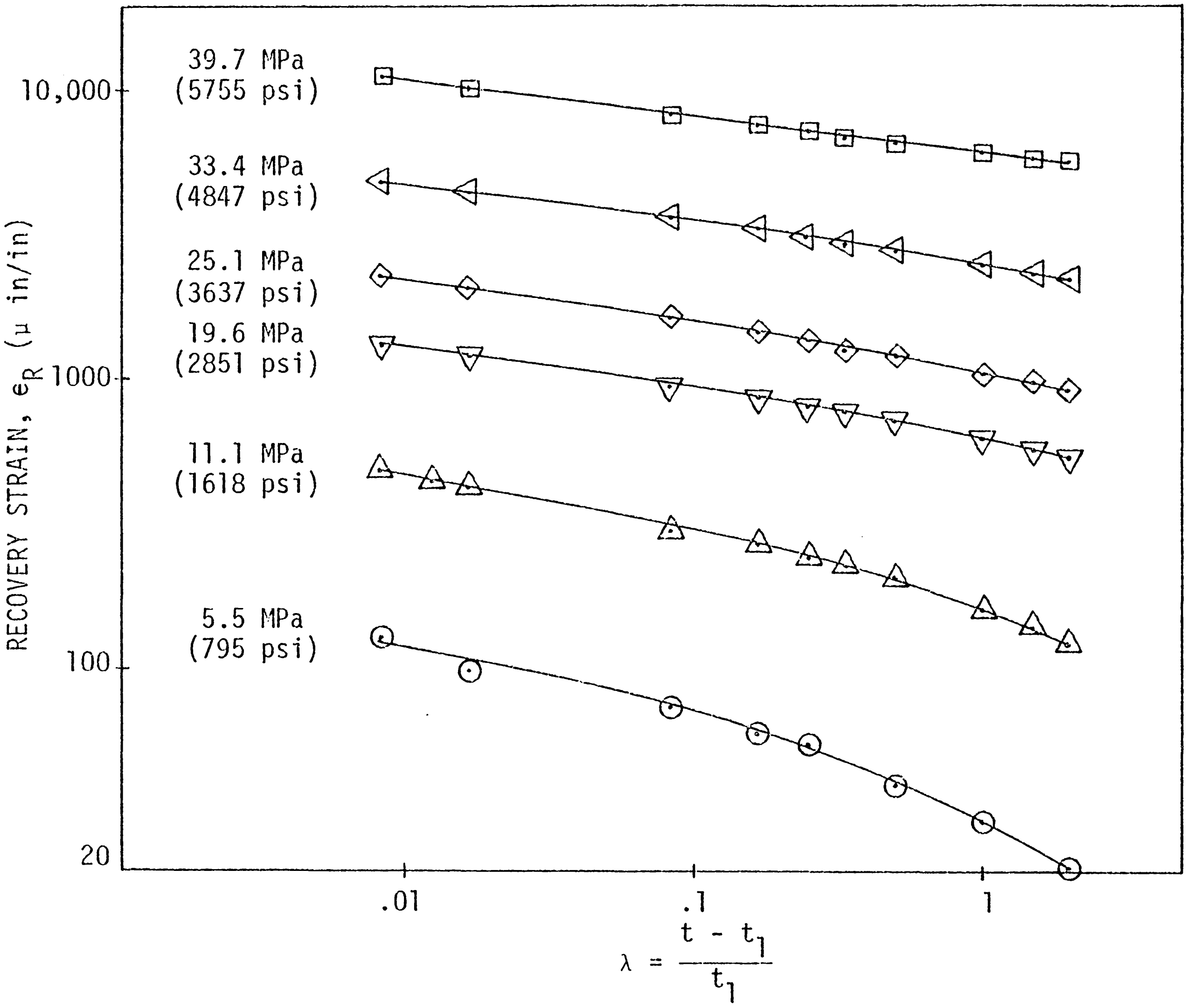


Figure 8. Recovery strains for various stress levels, Metlbond 113-2.

curves exist for different values of the power law exponent N as seen in Figure 9. Examination of equation (29) indicates that if the proposed constitutive law is valid, the recovery curve for low stress levels may be shifted vertically to coincide with one of the reference curves as shown in Figure 9. Thus by this method the best fit for the power law exponent, N, may be obtained.

Schapery's method now assumes that the same power law can be used to describe the recovery curves at all other stress levels. This implies that the same sequence of events will occur at a higher stress level as at a lower stress level--only faster. Therefore, a master creep recovery curve can be obtained by shifting each recovery curve horizontally and vertically to coincide with a reference curve for which $a_\sigma = g_1 = 1$.

The creep recovery curves were shifted vertically and horizontally to obtain the master curves as shown for the two materials in Figures 10 and 11. The amount of horizontal and vertical shift defined the quantities a_σ and $\frac{\Delta\epsilon_1}{g_1}$, respectively, as a function of stress level. These are shown plotted in Figures 12 and 13.

Using equation (16), the total creep strain can be written as,

$$\epsilon = g_0 A(o)\sigma + C\, g_1 g_2 \left(\frac{t}{a_\sigma}\right)^N \sigma \,. \tag{30}$$

The initial compliance, A(o), is easily found as it is simply the ratio of the initial strain to applied stress for creep curves within the linear range of the material. If we now rewrite equation (30) in the form

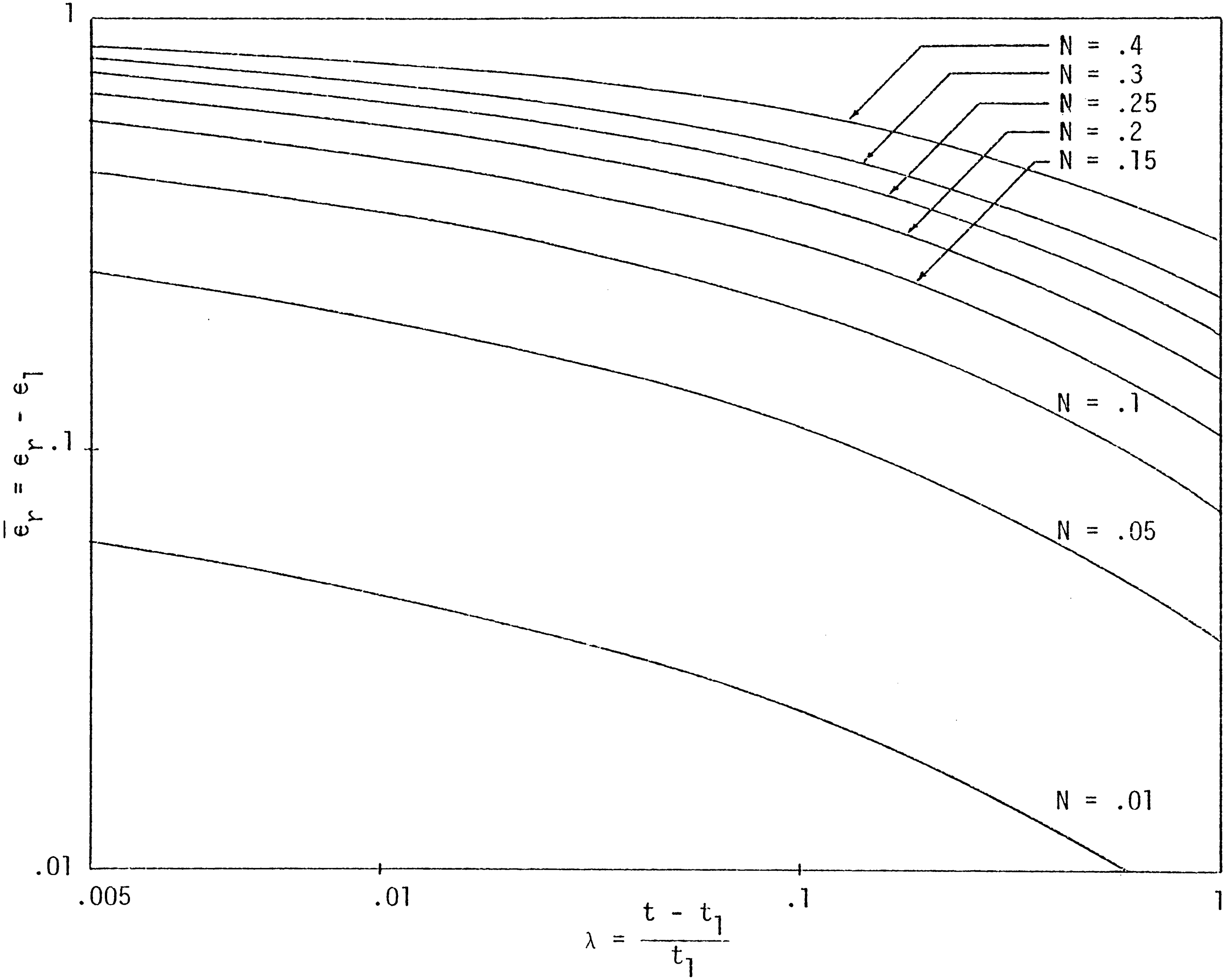


Figure 9. Normalized recovery curves, $\bar{\epsilon}_r = \epsilon_r - e_1$ for various values of the power law exponent, N.

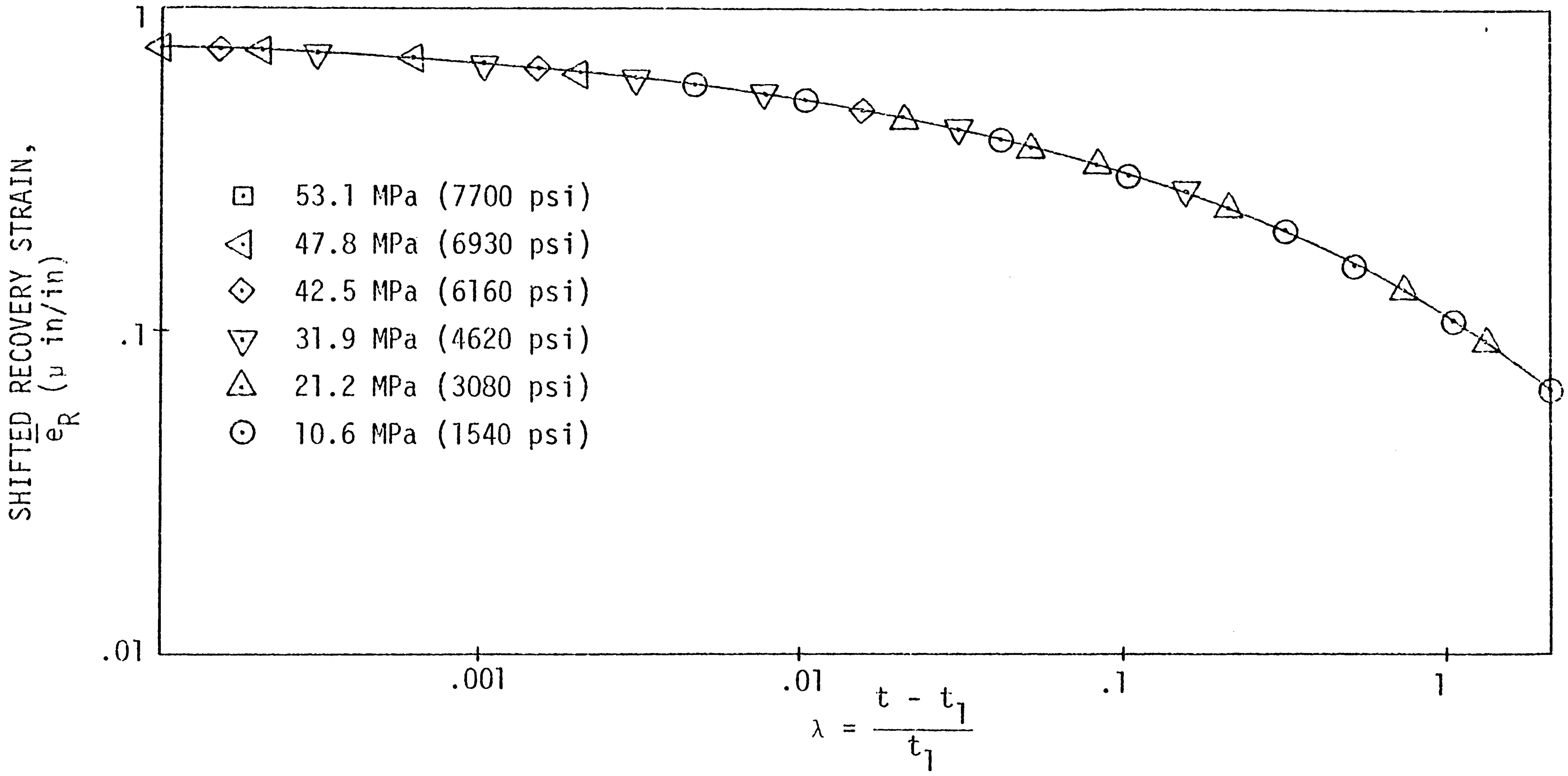


Figure 10. Master recovery curve, SMC-25.

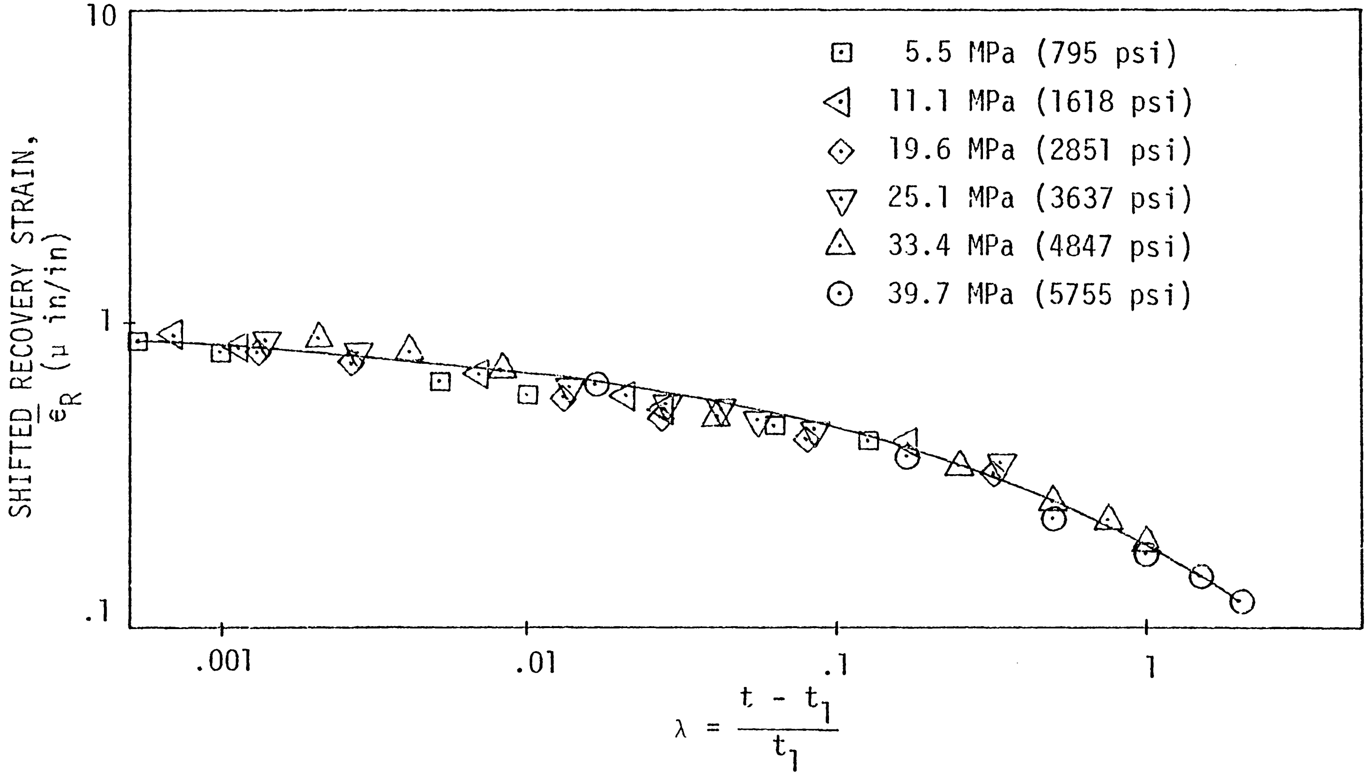


Figure 11. Master recovery curve, Metlbond 1113-2.

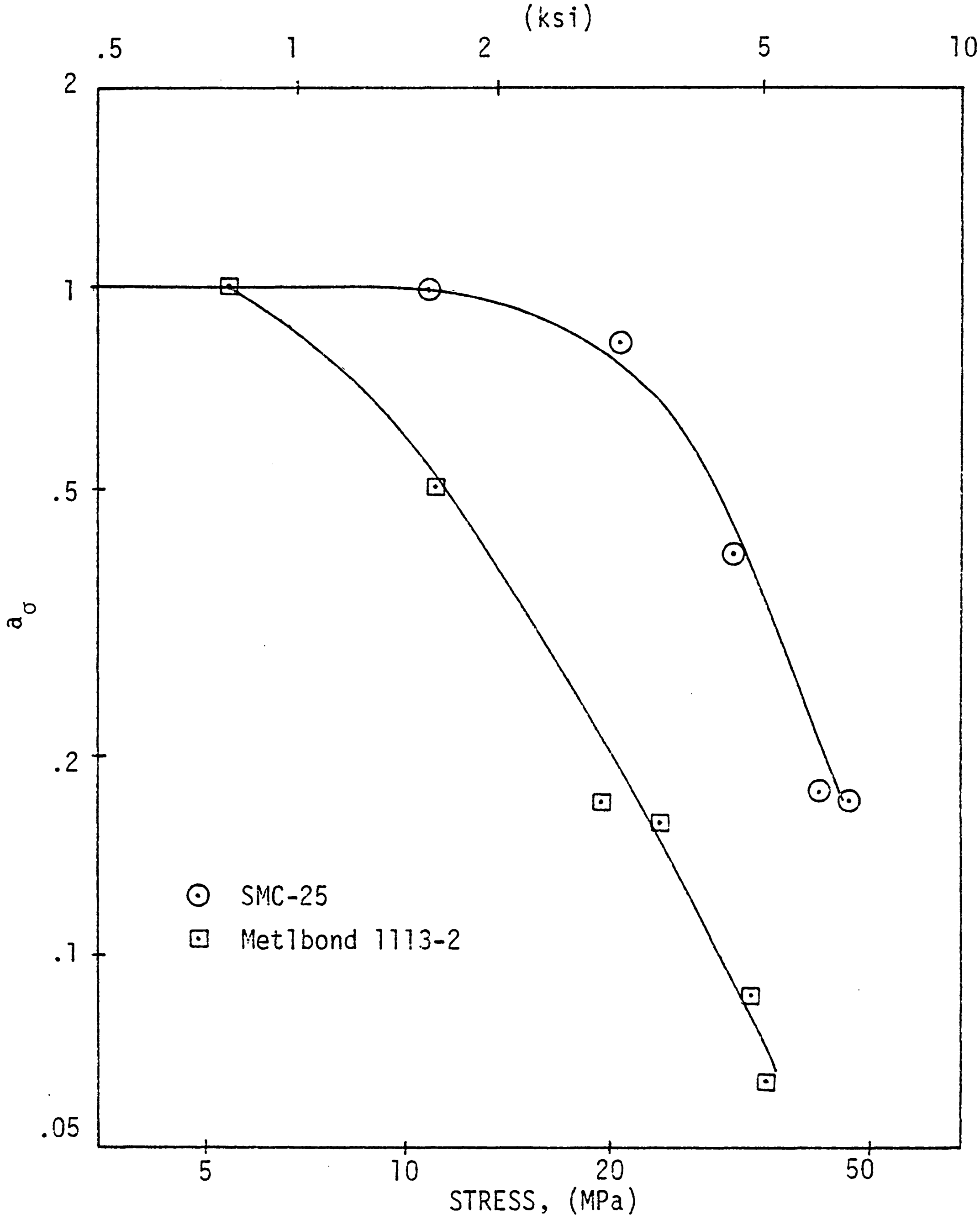


Figure 12. Shift function a_σ as a function of stress level.

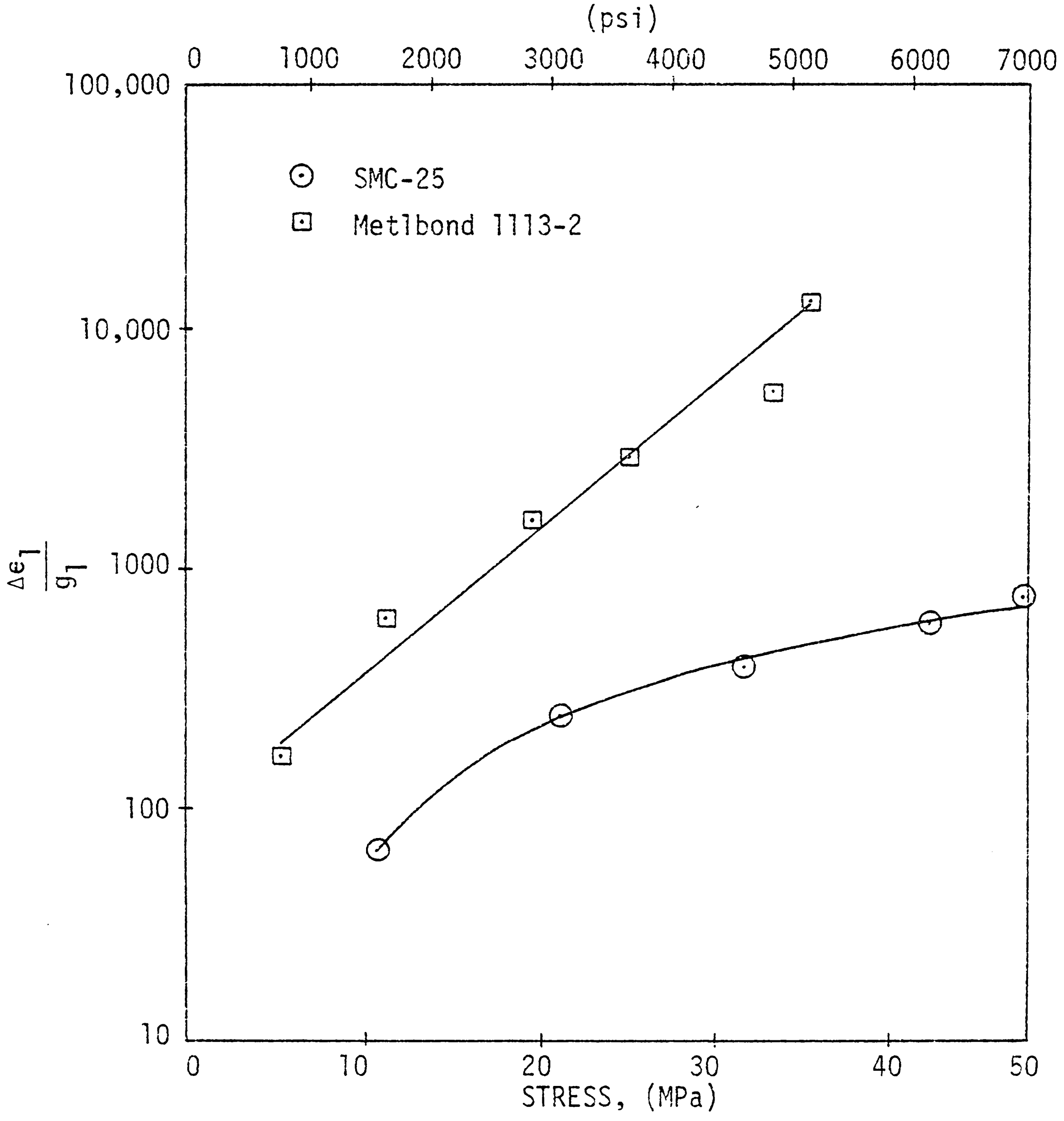


Figure 13. $\frac{\Delta\epsilon_1}{g_1}$ as a function of stress level.

$$\epsilon = \epsilon_0 + C't^N \tag{31}$$

where $\epsilon_0 = g_0\ A(o)\sigma$ is the initial strain at time $t = 0$, and

$$C' = \frac{g_1 g_2}{a_\sigma{}^N} C\sigma \ . \tag{32}$$

then we may solve for ϵ_0 and C' by considering two points on the experimental creep curves shown in Figures 14 and 15. The property g_0 may now be calculated from the equation,

$$g_0 = \frac{\epsilon_0}{\sigma\ A(o)} \tag{33}$$

Having ϵ_0, the transient component of the nonlinear creep compliance may be obtained as,

$$\hat{A} = \frac{(\epsilon - \epsilon_0)}{\sigma} \tag{34}$$

and is shown plotted against t on log-log paper in Figures 16 and 17. The creep compliance, in terms of material properties is,

$$\Delta\hat{A} = C\ \frac{g_1 g_2}{a_\sigma{}^N}\ t^N \qquad \text{(a)}$$

or (35)

$$\log \frac{g_1 g_2 t^N}{a_\sigma{}^N} = \log \Delta\hat{A} - \log C \qquad \text{(b)}$$

All remaining unknown nonlinear material parameters may now be obtained from the values of the nonlinear creep compliance found by equation (34). The "creep coefficient", $g_1 g_2/a_\sigma{}^N$ is shown plotted as a function of stress in Figure 18.

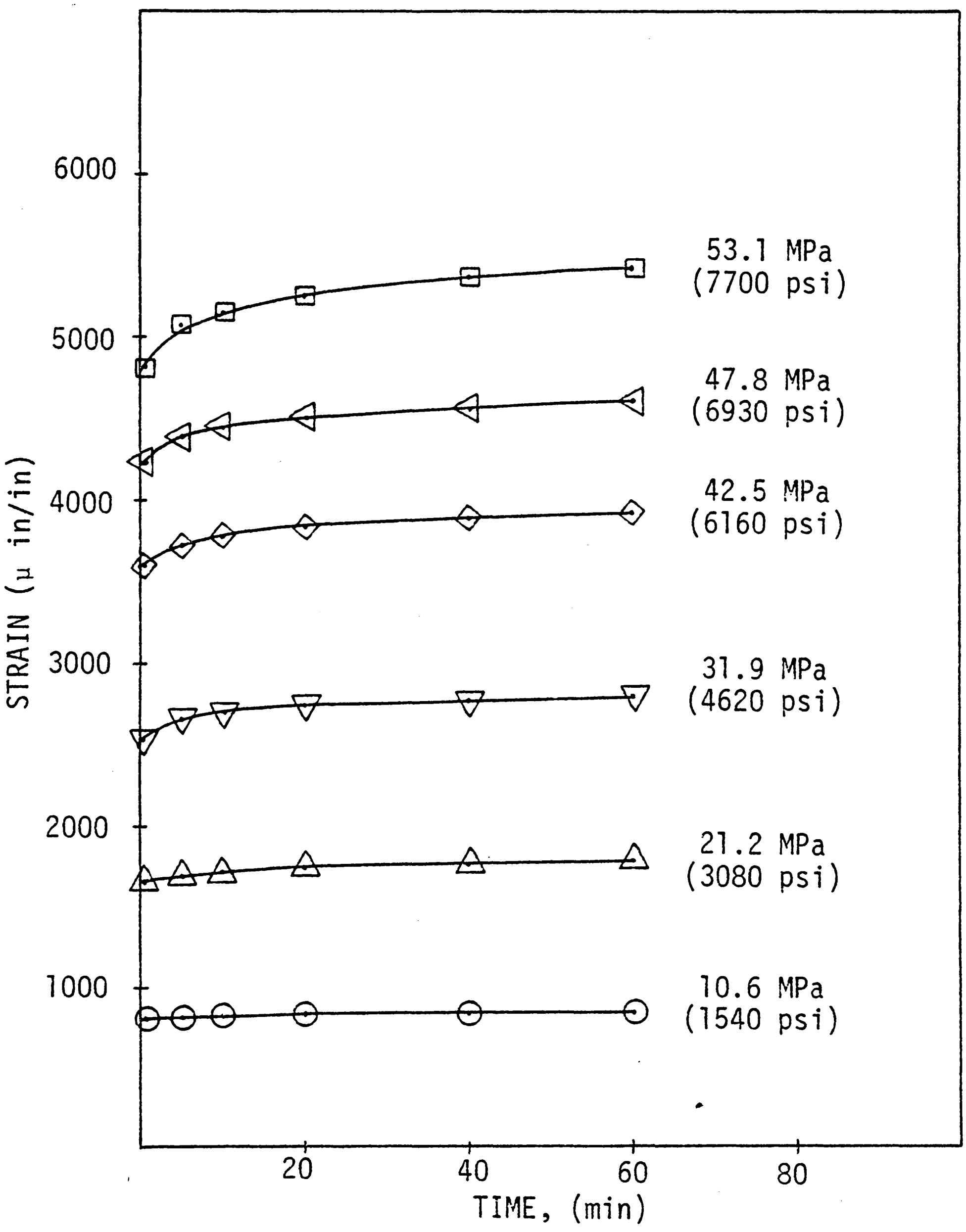


Figure 14. Experimental creep curve, SMC-25.

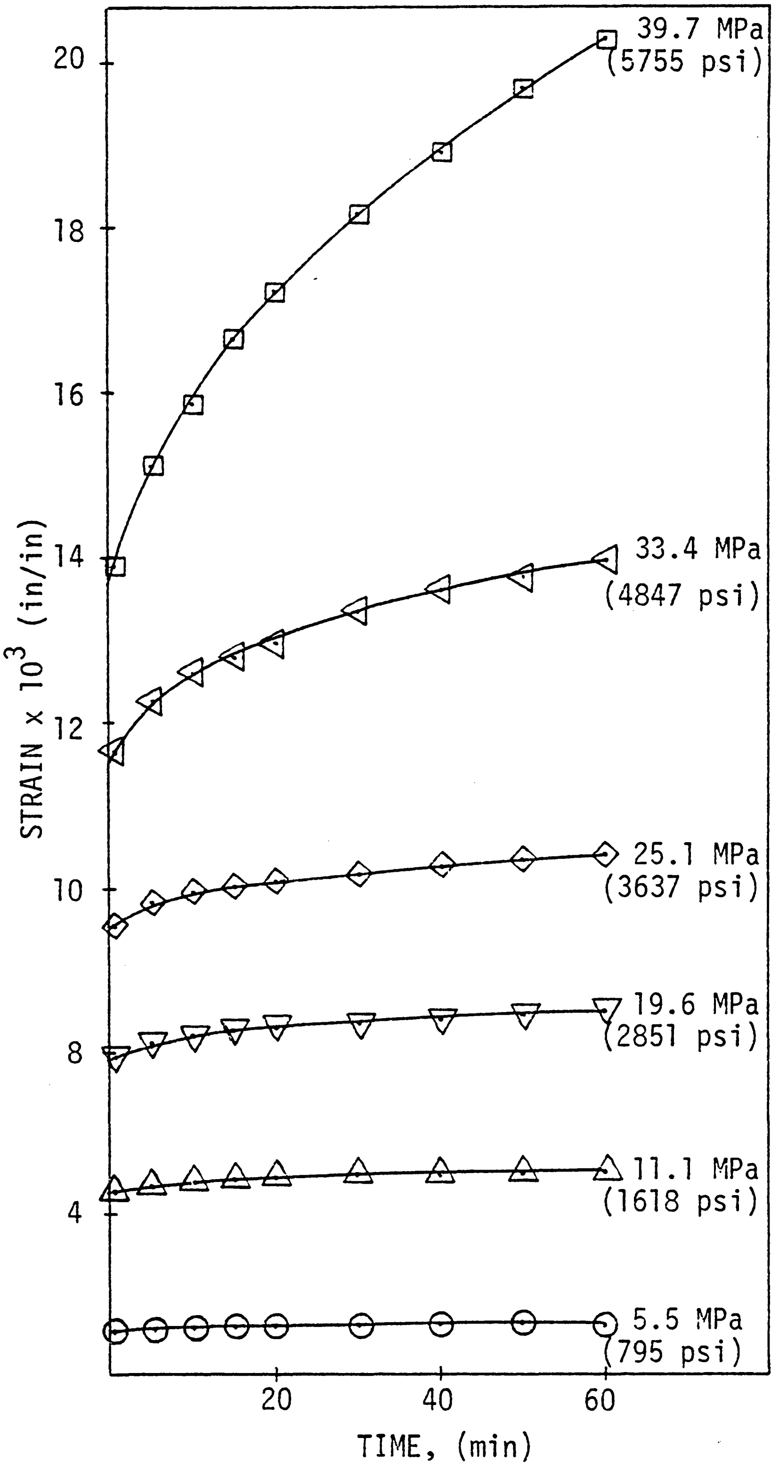


Figure 15. Experimental creep curve, Metlbond 1113-2.

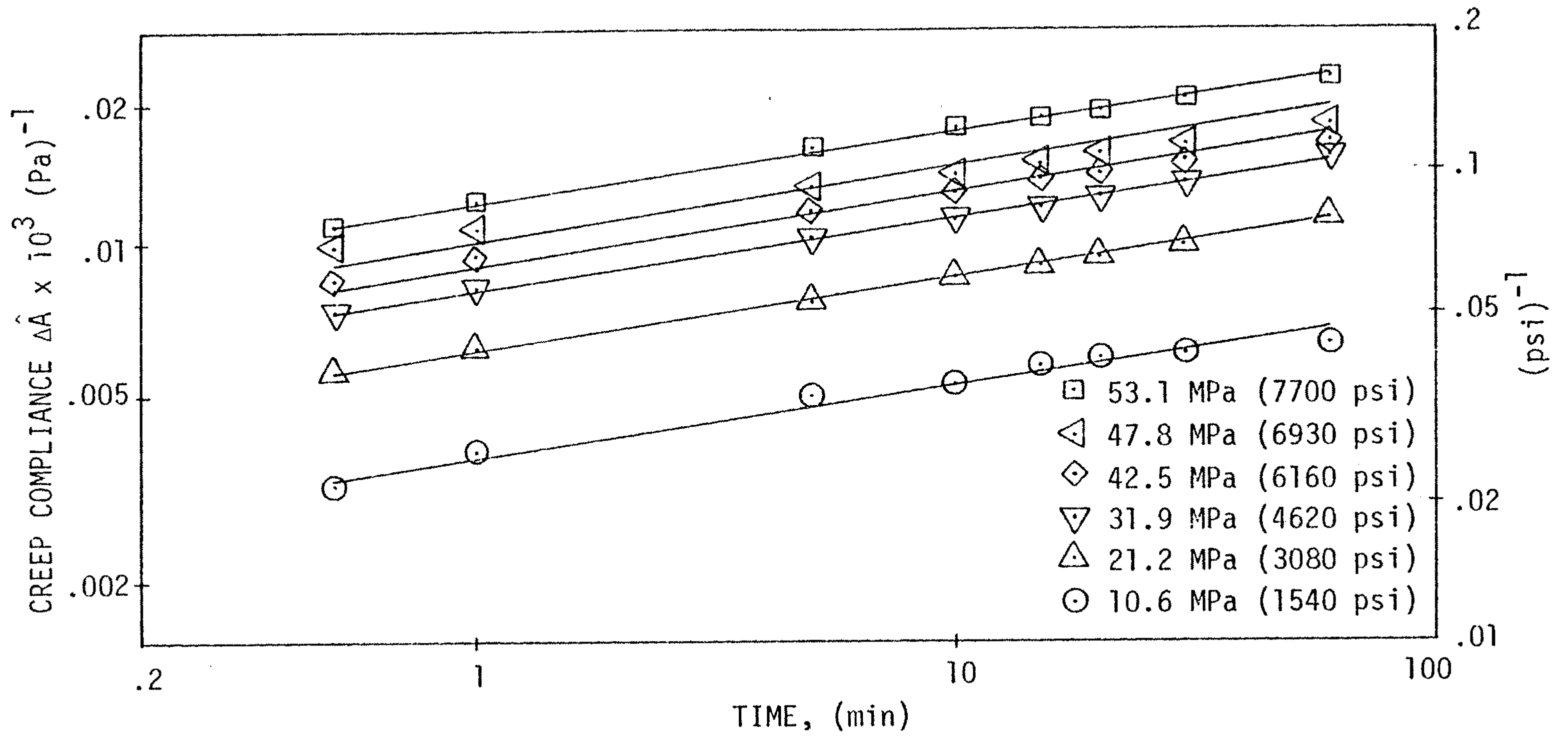


Figure 16. Transient creep compliance for different stress levels, SMC-25.

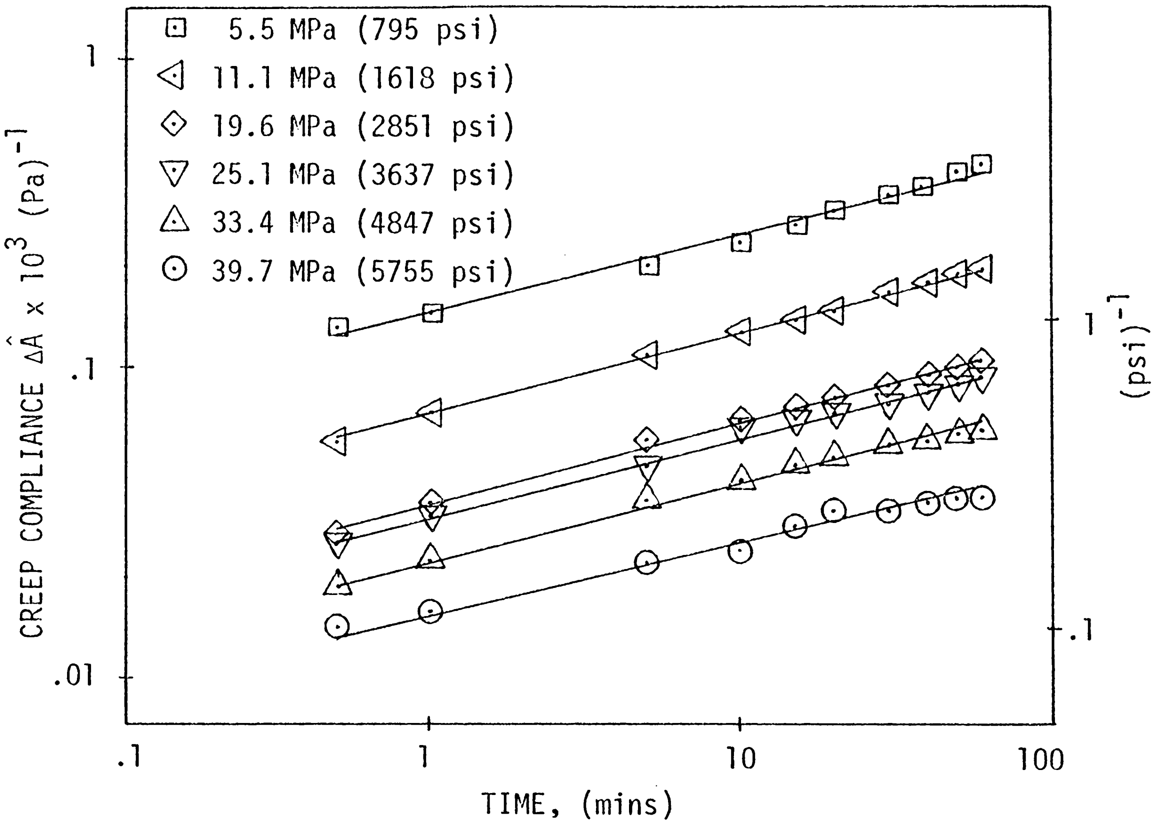


Figure 17. Transient creep compliance for different stress levels, Metlbond 1113-2.

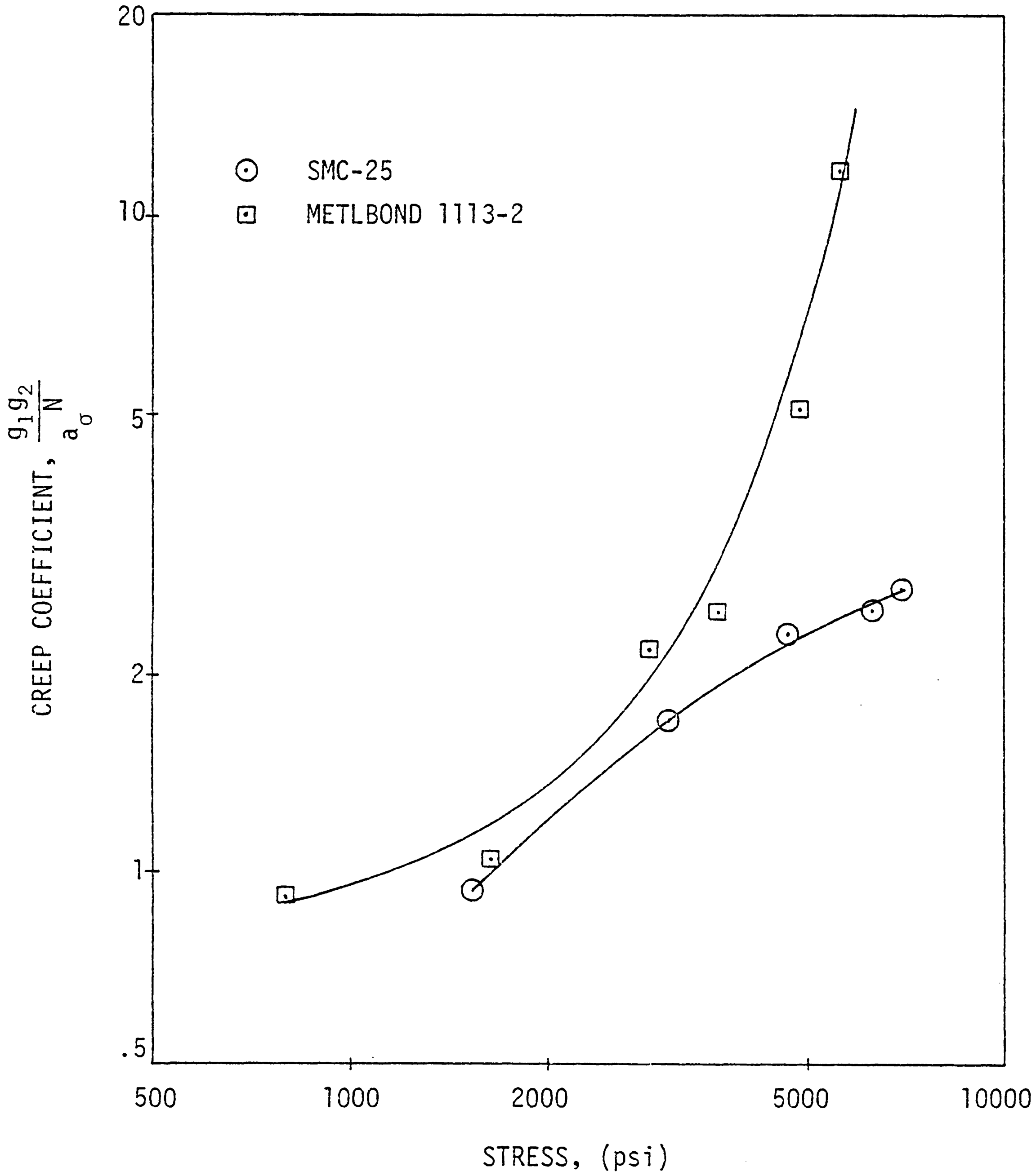


Figure 18. Creep coefficient, $\frac{g_1 g_2}{a_\sigma N}$, as a function of stress

A complete compilation of the material parameters for SMC-25 and Metlbond 1113-2 obtained in the foregoing manner are shown in Tables 2 and 3, respectively. These values allow the prediction of the nonlinear creep response.

Equation (30) was used together with the calculated values of C, N, a_σ, g_0, g_1 and g_2 to obtain the creep curves shown in Figures 19 and 20.

TABLE 2: MATERIAL PARAMETERS FOR SMC-25 (N = .15)

STRESS LEVEL MPa (psi)	a_σ	$\log \frac{\Delta\epsilon_1}{g_1}$	ϵ_o, μ cm/cm	g_o	g_1	g_2	$\frac{g_1 g_2}{a_\sigma^{.15}}$
10.6 (1540)	1.0	1.81	769	1.0	1.02	.91	.928
21.2 (3080)	.83	2.37	1538	1.0	1.02	1.62	1.70
31.9 (4620)	.39	2.58	2320	1.0	1.27	1.58	2.30
42.5 (6160)	.17	2.77	3272	1.06	1.12	1.70	2.47
47.8 (6930)	.17	2.89	3865	1.12	.947	2.16	2.67

TABLE 3: MATERIAL PROPERTIES FOR METLBOND 1113-2 (N = .25)

STRESS LEVEL MPa (psi)	a_σ	$\log \frac{\Delta \epsilon_1}{g_1}$	ϵ_o, μ cm/cm	g_o	g_1	g_2	$\frac{g_1 g_2}{a_\sigma^{.25}}$
5.48 (795)	1.0	2.21	940	1	1.20	.765	.918
11.2 (1620)	.50	2.78	4256	1.44	1.15	1.09	1.05
19.6 (2850)	.170	3.18	7165	1.38	1.17	1.19	2.17
25.1 (3640)	.160	3.45	10,152	1.53	.922	1.70	2.48
33.4 (4850)	.085	3.73	12,873	1.45	1.30	2.09	5.03
39.6 (5750)	.063	4.11	13,784	1.31	1.45	3.91	11.32

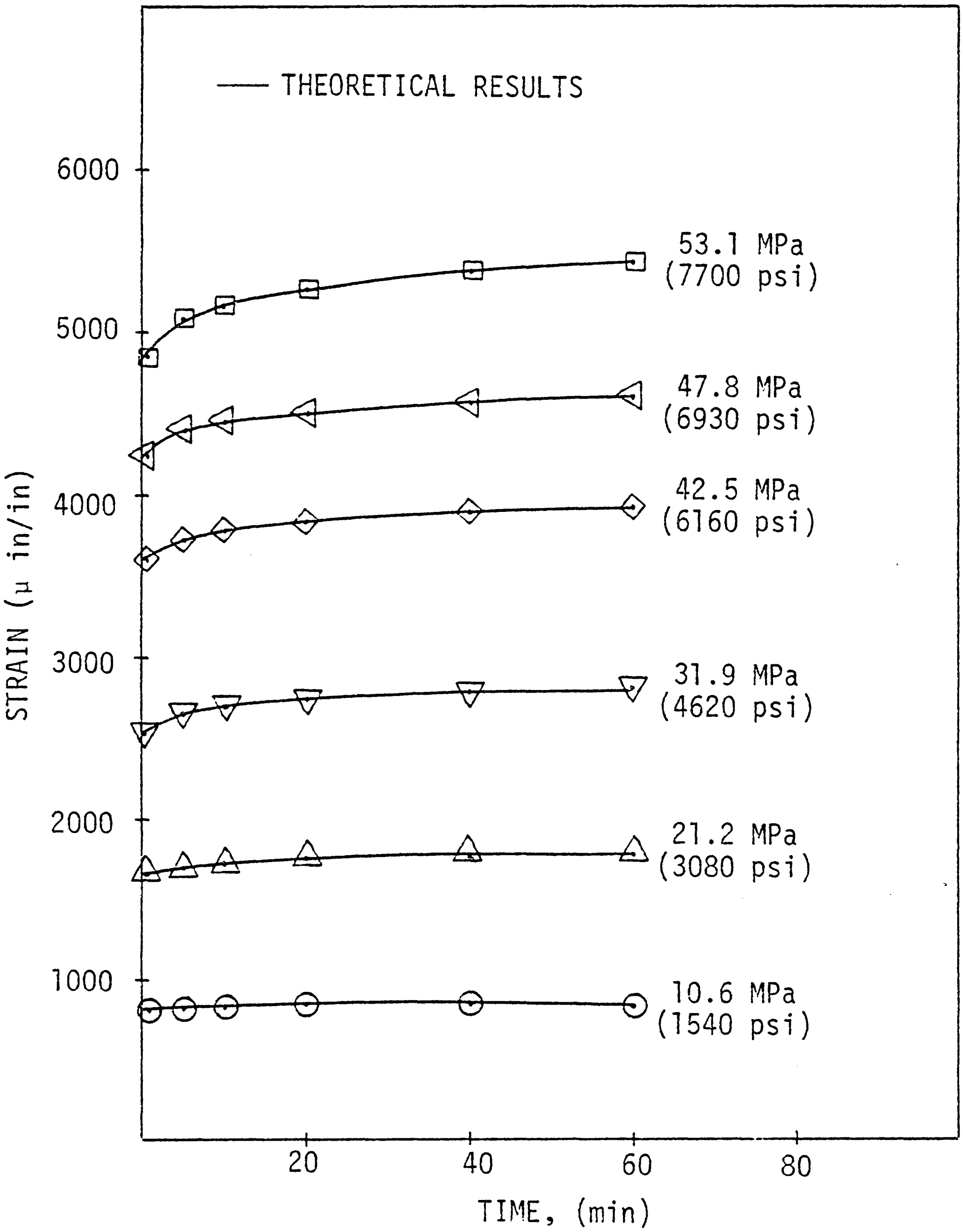


Figure 19. Experimental creep data versus theoretical results, SMC-25.

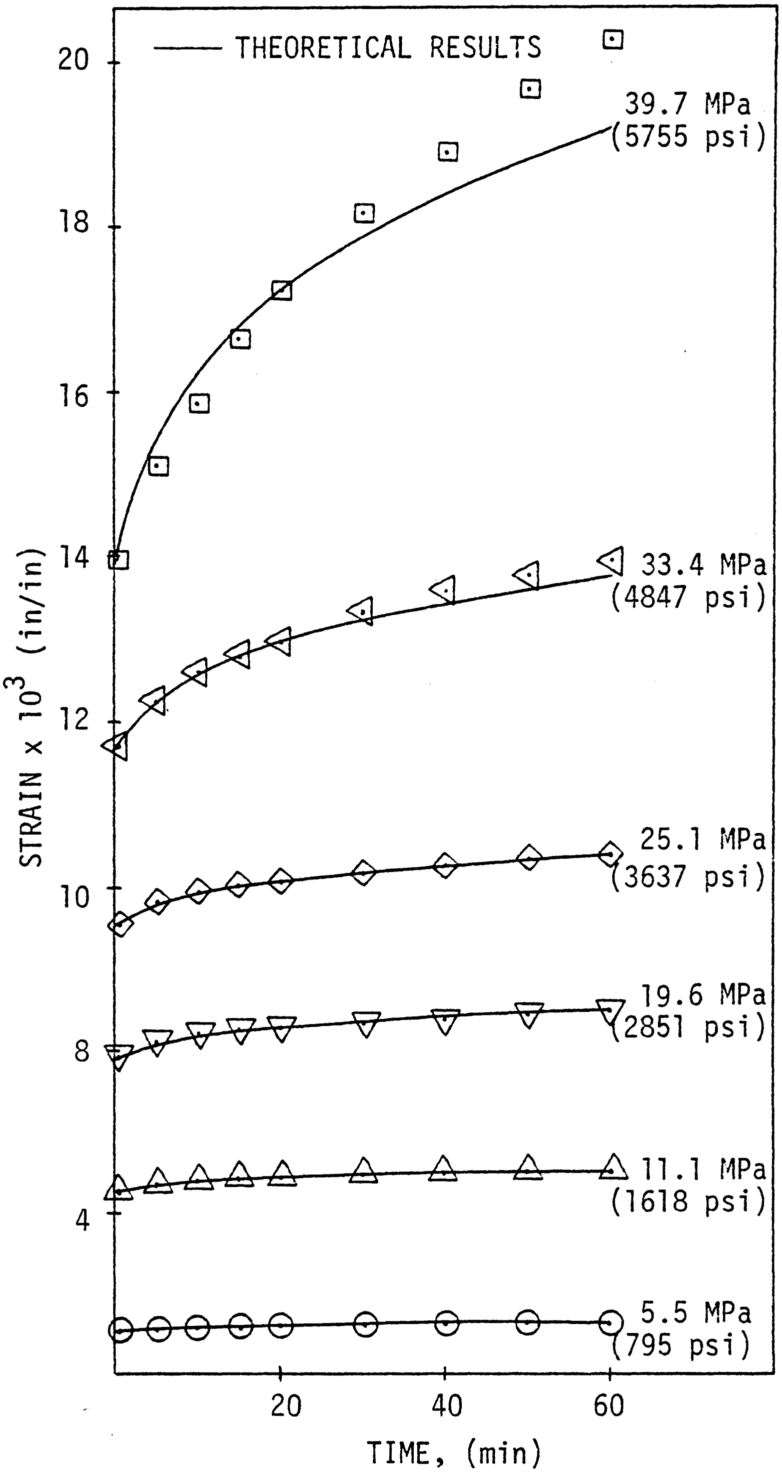


Figure 20. Experimental creep data versus theoretical results, Metlbond 1113-2.

VI. RESULTS AND DISCUSSION

The nonlinear viscoelastic constitutive equation developed by Schapery was used to characterize creep and creep recovery data. Schapery's theory was then used in conjunction with a delayed failure postulate of Crochet. The combination allows the calculation or prediction of delayed failure times in a uniaxial creep to rupture test. A discussion of the results follows.

SMC-25

The chopped glass fiber/polyester material, SMC-25, examined herein exhibited viscoelastic creep and creep recovery phenomena which could be characterized using Schapery's theory. The master recovery curve for SMC-25 is shown in Figure 10. As may be seen the master curve formed represents a single continuous curve over an extended time scale longer than for which testing was actually performed. Very good agreement between the shifted experimental points and the curve for $N = .15$ is found. Also, the agreement found between experiment and theory for creep was very good as seen in Figure 19.

Specific nonlinear properties needed for Schapery's theory were determined and reported in Table 2. However, as the data for the SMC-25 material was taken only from a single specimen, no particular emphasis should be placed upon the specific numbers for SMC-25. That is, to develop appropriate numbers to use for design, an adequate statistical data base needs to be generated. The author is convinced however, that this could be done and that the approach of Schapery could be used to describe the viscoelastic nature of SMC-25.

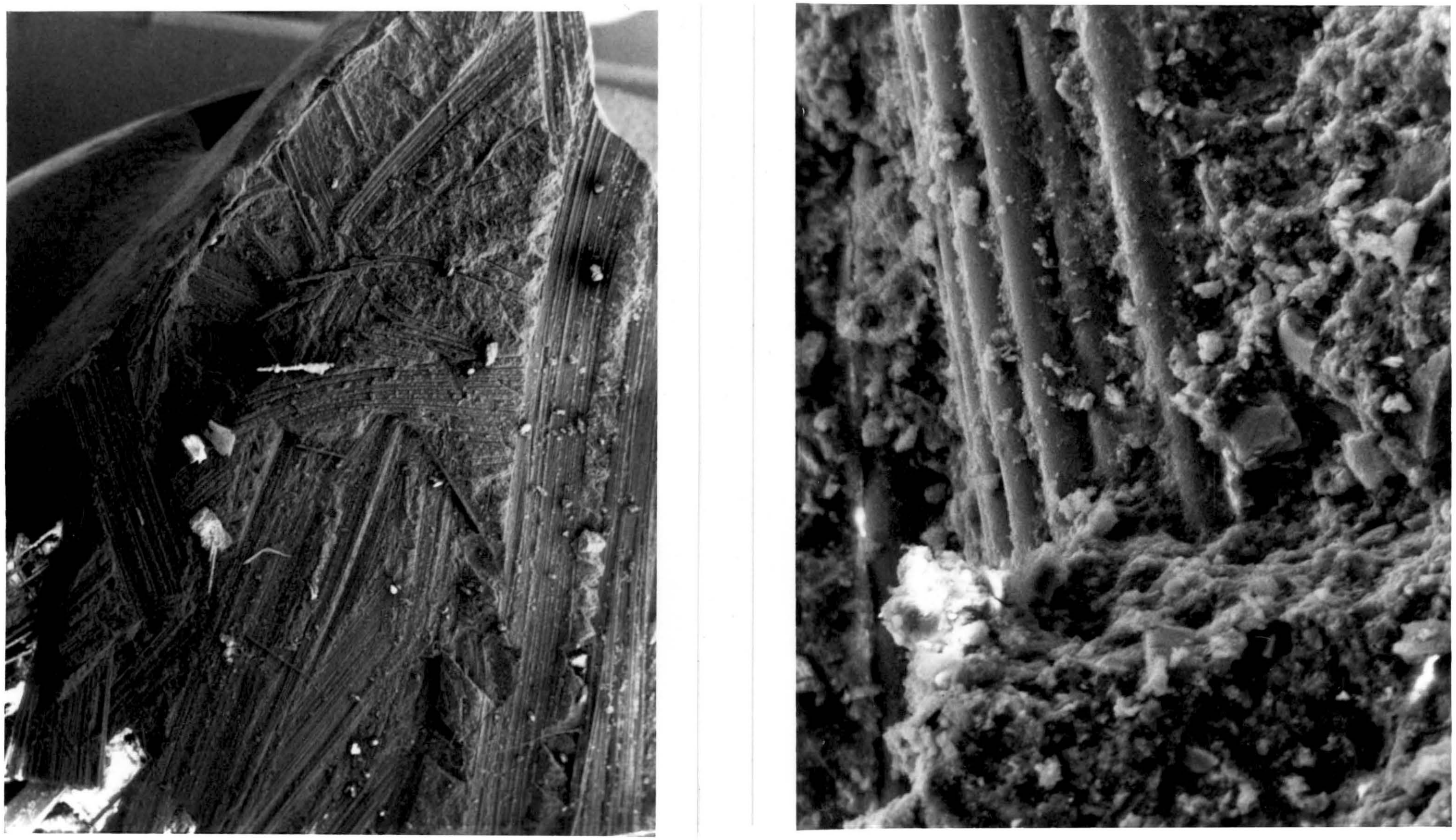
It should be noted that preliminary testing of SMC-25 indicated a linear response up to a stress level of approximately 13.8 MPa (2000 psi). The tangent modulus up to this stress level was found to be 12.4 x 10^3 MPa (1.8 x 10^6 psi). Comparison of these results with the results of shear modulus tests now in progress shows that for a Poisson's ratio of .25, good agreement is obtained up to 15.2 MPa (2200 psi). The value of .25 for Poisson's ratio was obtained in preliminary testing at low stress levels. Over the time scale involved no variation in Poisson's ratio was observed. The time dependent variation in Poisson's ratio over an extended time range has not yet been examined.

It is concluded from the above observations that a threshold value of stress seems to exist. Brinson [15] in previous work has suggested material behavior which is elastic at low stress levels and then goes through a transition into a region of linear viscoelastic response at higher stress levels. Since even at these lower stress levels, SMC-25, exhibits creep and stress relaxation an assumption of transition from a linear viscoelastic state to a nonlinear viscoelastic response is probably more realistic. Such a conclusion is consistent with the values of the nonlinear properties obtained by the analysis presented herein. That is, the nonlinear coefficients g_0, g_1, g_2 and a_σ are essentially one up to a stress level of 13.8 MPa (2000 psi).

A fractured SMC-25 specimen was examined microscopically and photomicrographs of the fracture surface were taken. As may be seen in Figure 21, the fibers within the specimen were in bundles rather than discrete fibers. That is, in the fabrication process fibers, apparently, tended to flow in such a way that resin rich regions and fiber rich regions exist. Observations taken by C-scan seem to indicate this may be the case. C-scans seem to indicate a fiber rich region in the center of a charged panel with the amount of fibers falling off in radial directions away from the position of the original charge.

Examination of the fracture surface indicates that excessive "fiber bundle" pullout occurred which is believed to have served as a fracture initiation site. The presence of large voids between fibers within a bundle, as reported by McGarry, et al. [31] were noted and may be seen in Figure 21. It is interesting to note that McGarry and others have found similar results for sheet molding compounds. They have further found for such materials containing high percentages of glass fibers and calcium carbonate filler, microcracking could be greatly reduced by the addition of small amounts of a rubber to the polyester matrix.

The nonlinear creep response equation developed from the Schapery method together with a delayed failure law by Crochet was used to obtain a prediction of rupture times. Data taken from the literature suggested that the delayed failure times so predicted were appropriate. The creep to failure prediction for SMC-25 is shown in



(a) 20X (b) 500X

Figure 21. Photomicrographs of the fracture surface of an SMC-25 specimen.

Figure 22a. As found with polycarbonate and epoxy previously, it does appear that a stress level does exist below which few delayed failures will occur [2,13,15].

The predictions found for SMC-25 are encouraging. Again however, an adequate statistical sampling is necessary to verify the use of the method described herein to predict failures. It is worth noting that the nonlinear viscoelastic stress-strain data taken in our laboratory for a single specimen could be used to approximate the delayed failure times reported in the literature [22-24] for several specimens tested at values of stress and time outside the range of our data. This implies that the mathematical form of the procedures used herein are appropriate.

Metlbond 1113-2

The modified epoxy adhesive, Metlbond 1113-2 examined was found to exhibit creep, creep recovery, and delayed failures as with the SMC-25. The master recovery curve for Metlbond 1113-2 is shown in Figure 11. The comparison between theory and experiment showed an error of approximately 6% at high stress levels while good agreement was found for stress levels below $\sim$ 33.4 MPa ($\sim$ 4850 psi). The value of the power law exponent was N = .25. The agreement found between experiments and theory for creep is shown in Figure 20. Again, the error obtained was approximately 6%.

One possible reason for this error may be the choice of the power law exponent. However, since good agreement was found at low

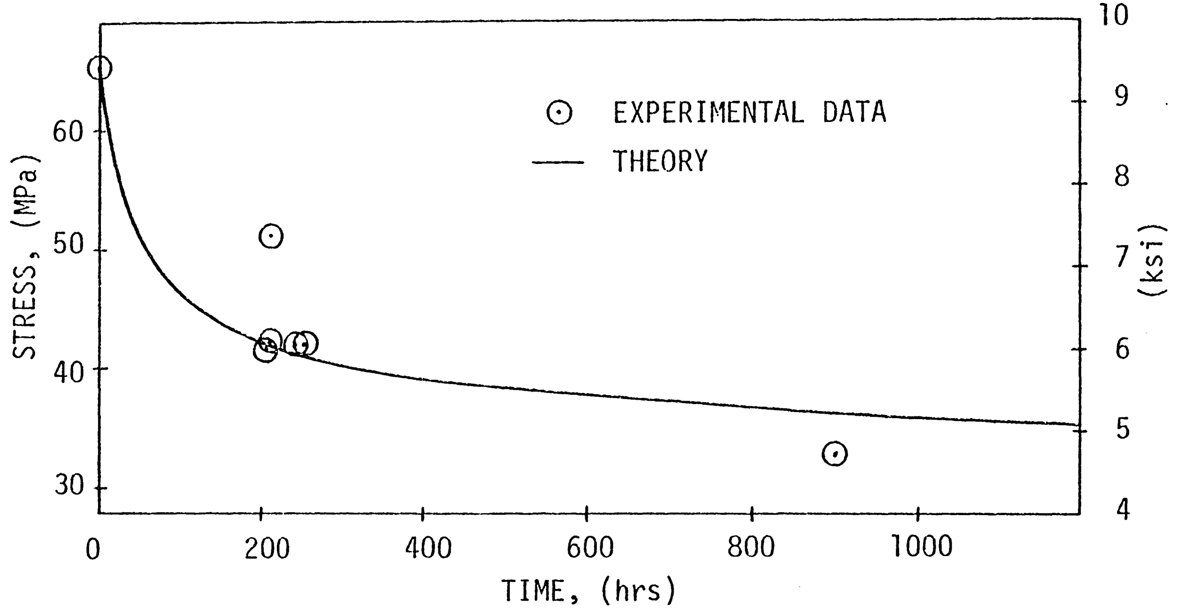


Figure 22(a). Delayed failure prediction, SMC-25.

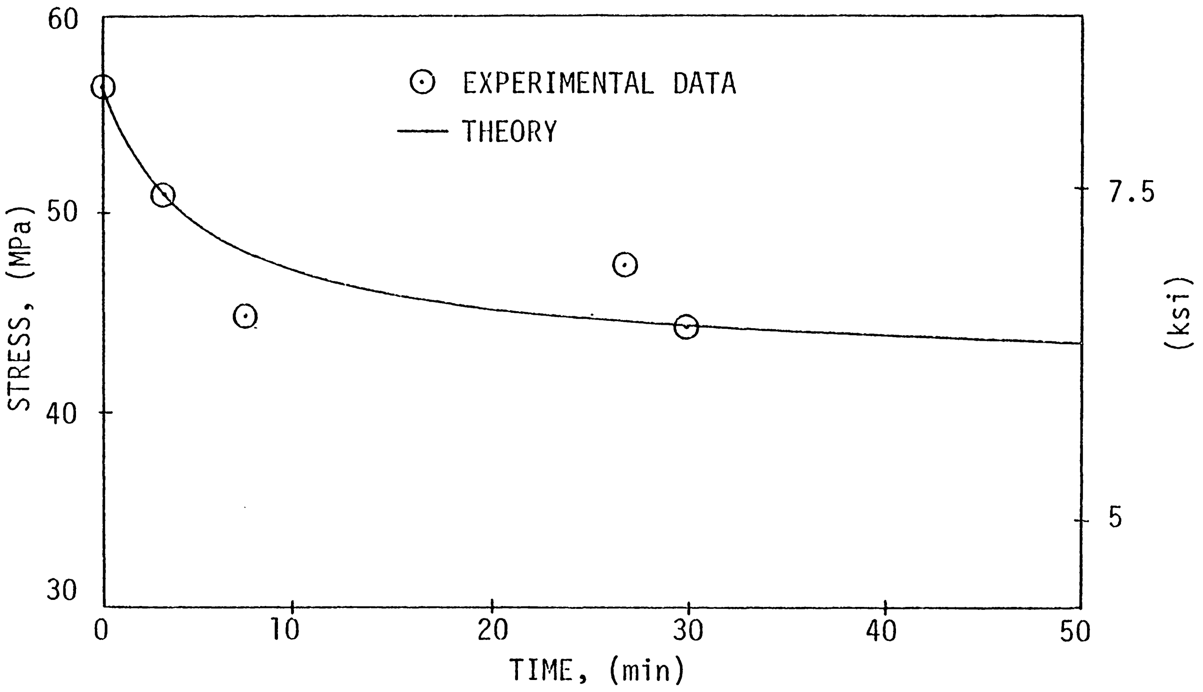


Figure 22(b). Delayed failure prediction, Metlbond 1113-2.

stress levels it is felt that $\dot{N} = .25$ was probably a valid choice. Another possible reason lies in the assumption that the creep strain follows a power law in time. Another form of the equation for creep strain may be valid.

It is felt, however, that the primary reason for this error may arise due to a stress-whitening, or crazing phenomenon which was observed at higher stress levels. Schapery's theory was developed for homogeneous materials. However, when crazes are present within a material the density may vary greatly on a local level. This phenomenon is discussed below.

The prediction of delayed failure times for Metlbond 1113-2 is shown in Figure 22b. Note that good agreement is found with the experimental failure times. Since the Crochet model is of an exponential form this should not be surprising. That is, even though error was found in the prediction of creep strains at high stress levels a good fit could still be obtained. It should be realized that the method proposed by Crochet is based upon an assumption of the form of χ and represents only a convenient mathematical tool. Before accurate predictions of delayed failure times can be made a greater understanding of the physical significance of the nonlinear variables of Schapery's theory must be obtained. Only after extensive observation of the various phenomena can meaningful advanced predictions be made.

The Metlbond 1113-2 adhesive exhibited a stress whitening, or crazing phenomenon at higher levels of creep stress. These craze marks are evident on the tested specimen shown in Figure 3. Since the crazed material has an index of refraction different from the bulk material, crazes appear as small shiny cracks. This phonomenon was also observed by Renieri [3] during his investigation of epoxy adhesives. Crazing in a material may be defined as the occurrence of localized highly elongated regions (crazes) whose density may vary from zero (true crack) to that of the virgin material [32]. Hull [11] states that crazes formed in a uniaxial tensile stress field have a shape similar to a crack, and the plane of the craze is at right angles to the stress axis. Hull also points out that in a complex stress field, the plane of a craze is normal to the maximum principal tensile stress. Further, Wunk, et al. [33] states that crazes are regions of highly deformed material which form at the tip of advancing microcracks and serve as an energy "sink."

It is believed that the crazing process is evidence that a local damage or failure mechanism begins well in advance of rupture, thus causing regions of high stress concentrations. As such, it is an important characteristic of this material which may be a contributing cause of the error previously discussed.

Elevated Temperature Behavior

The mechanical properties of both polymeric materials examined herein have a strong dependence upon temperature. Depending upon the temperature level, a polymer may display one of five types of response [10,11]. These five temperature regions are referred to as glassy, transition, rubbery, rubbery flow or liquid flow. Of these five regions, cross-linked polymers almost without exception exhibit at least three. These are, the glassy region, the transition region, and the rubbery plateau. Two temperatures, the glass-transition (T_g) or 2^{nd} order transition temperature and the melt temperatures or 1^{st} order transition temperature (T_M) are of special interest as they identify the thermal levels which separate the above regions. The T_g essentially separates the glassy and transition regions while the T_M separates the rubbery flow and liquid flow regions. The region which is of most concern in viscoelasticity is the transition zone. In the glassy state, the time response of a viscoelastic material varies only over several decades of time, whereas within the rubbery range they occur so fast they are difficult to observe experimentally.

It is clear that the behavior of SMC and Metlbond are greatly affected by the T_g and T_M. For this reason results of DSC and TGA measurements are included (results from Brinson, et al. [23]) in Figures 23 and 24. Figure 25 shows the T_g for Metlbond 1113-2 (from Renieri, et al. [3]).

Time-Temperature Superposition Principle

It is well known that high temperature short-time behavior is essentially equivalent to low temperature response at longer times. Williams, Landel, and Ferry [34] have established experimentally that viscoelastic behavior above the T_g can be correlated by using a transformed or reduced rate or time variable. This reduced rate ("WLF") variable, as previously discussed, is the product of the physical rate or time parameter and a temperature shift factor a_T, such that;

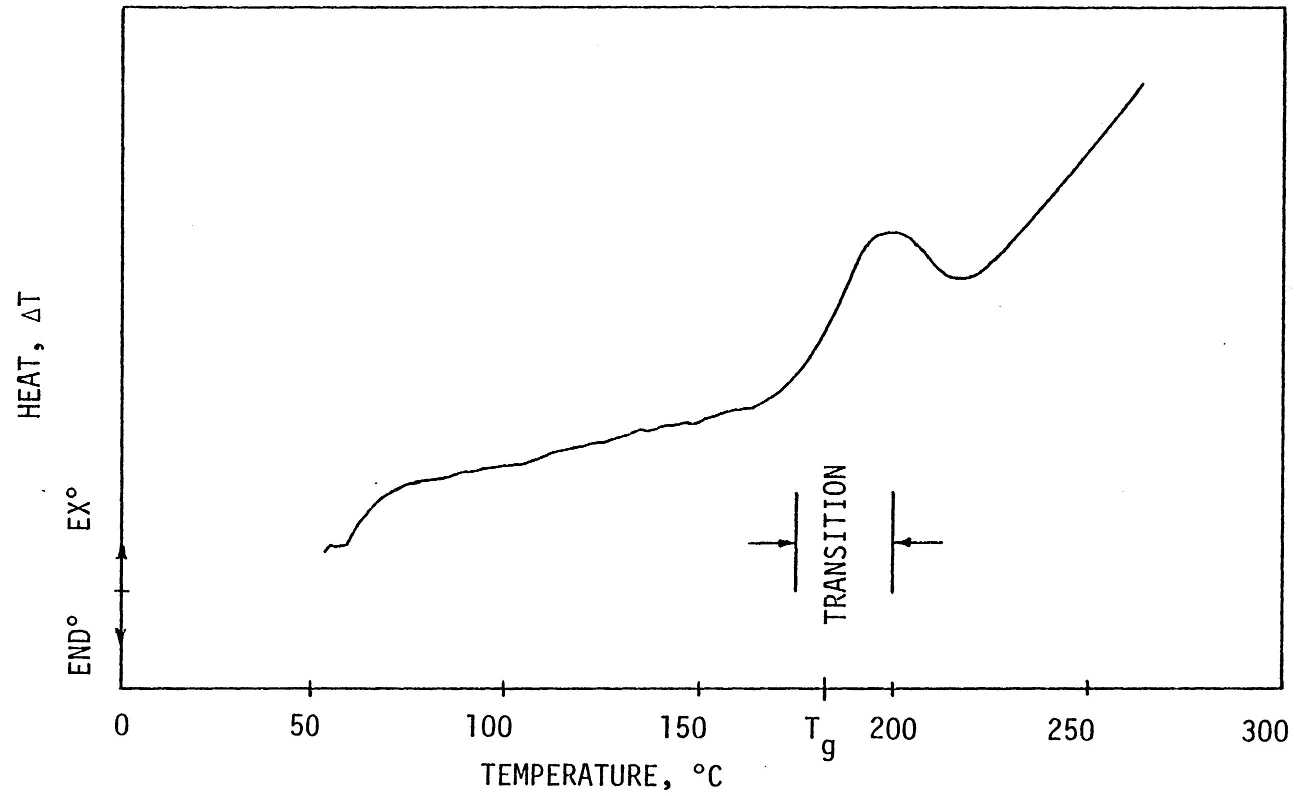


Figure 23. DSC measurement indicating the T_g for SMC-25 [23]

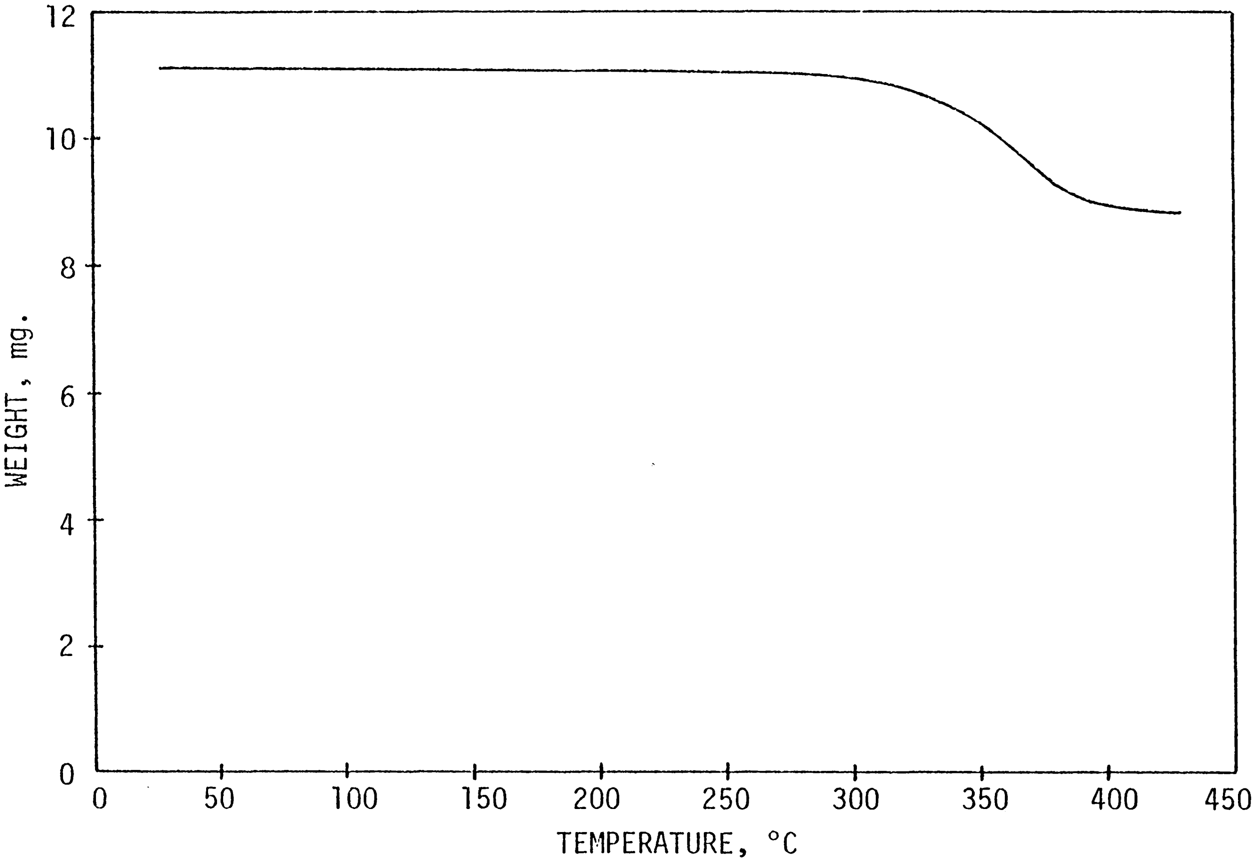


Figure 24. TGA measurement indicating the T_M for SMC-25 [23].

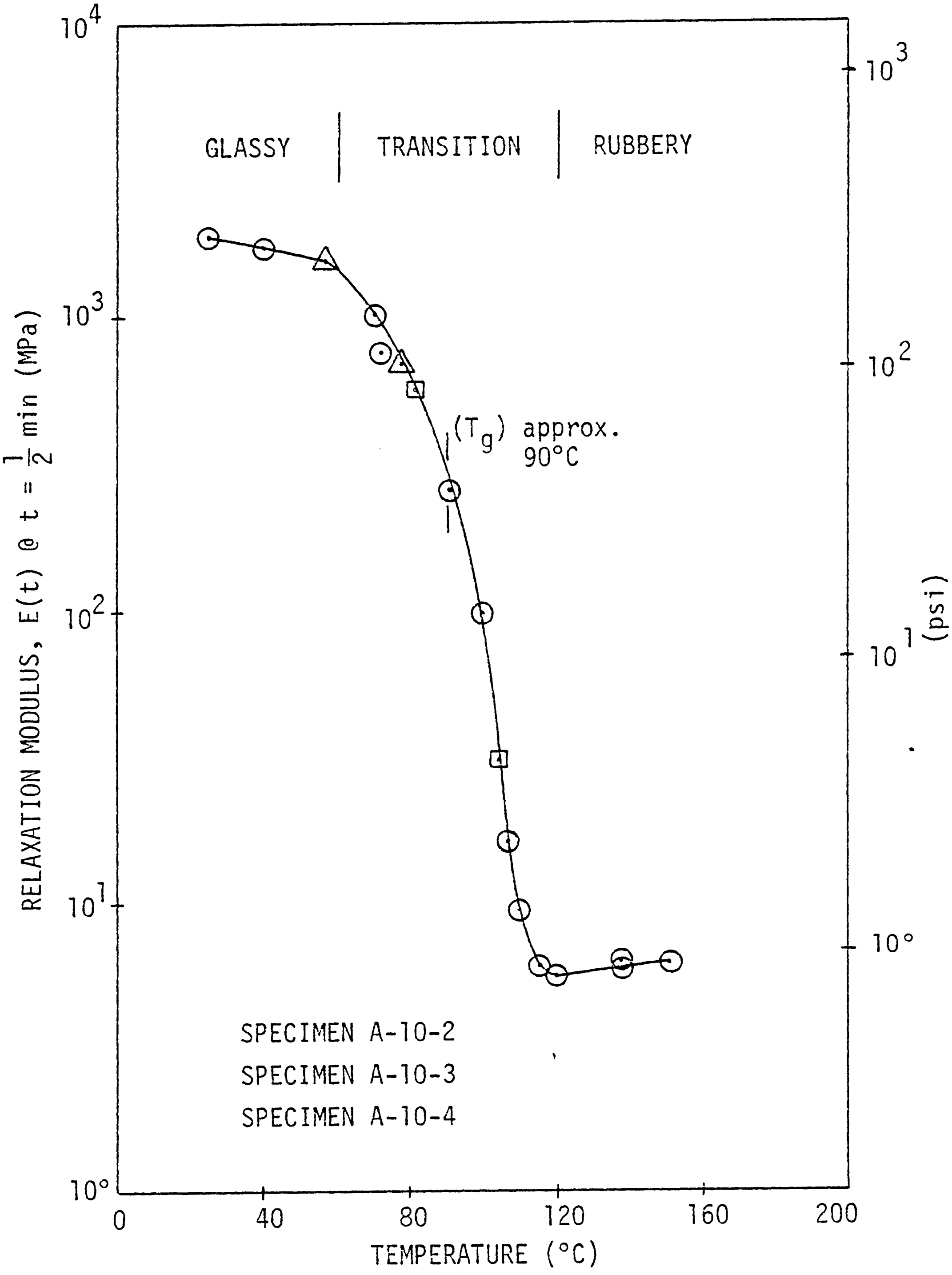


Figure 25. Variation in relaxation modulus with temperature for Metlbond 1113-2 [3].

$$\log_{10} a_T = - C_1(T - T_R)/(C_2 + T - T_R) \tag{36}$$

where T_R is the reference temperature and C_1 and C_2 are constants. Figure 26 shows the master curves for the adhesive material under consideration. Figure 27 shows the comparison between experimental data and the WLF equation.

Schapery [35] has shown that if the shift principle holds for one property of an isothermal viscoelastic body, then it holds for all continuum properties. Additional efforts to include temperature into the analysis procedures of Schapery presented herein are underway. Studies are being conducted to determine the feasibility of combining the stress shifting procedures of Schapery in conjunction with the WLF equation. This would involve the determination of a shift function which would be a function of both stress and temperature. It is suggested [36] that such an analysis is possible provided that all testing is carried out isothermally. That is, the theory at present would not allow for transient temperature effects.

Rupture depends on many parameters simultaneously, and until their interactive as well as their separate effects are known, our understanding of the fracture process will be incomplete. The determination of a shift function as described above is one possible mathematical method by which the experimental results may be synthesized into a more coherent whole. This would allow the determination of a physical property surface, as suggested by Landel and Feders [37]. If the properties are considered as a three-dimensional surface, then rupture represents some limiting value to or boundary of the surface.

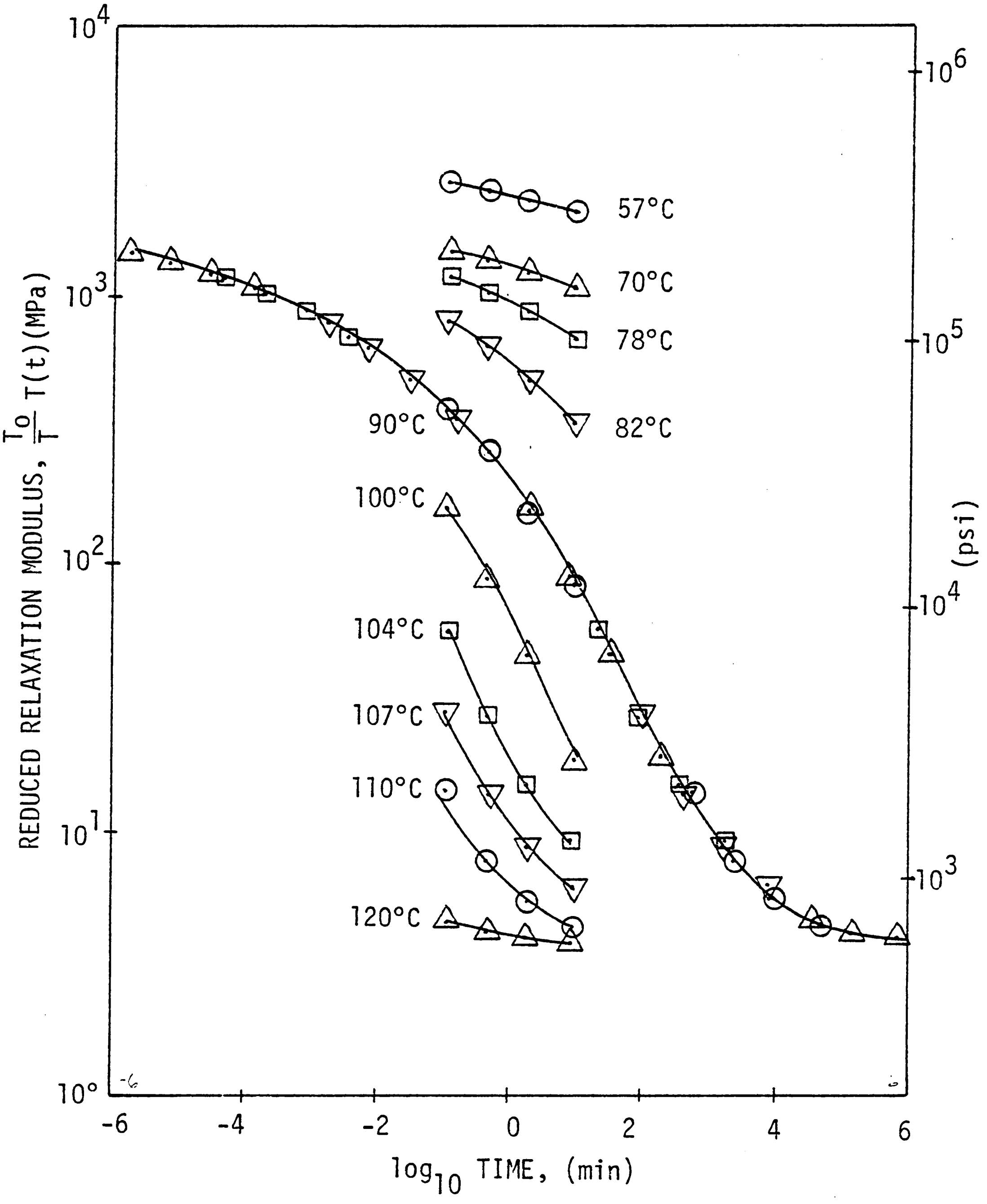


Figure 26. Master curve Metlbond 1113-2 [3].

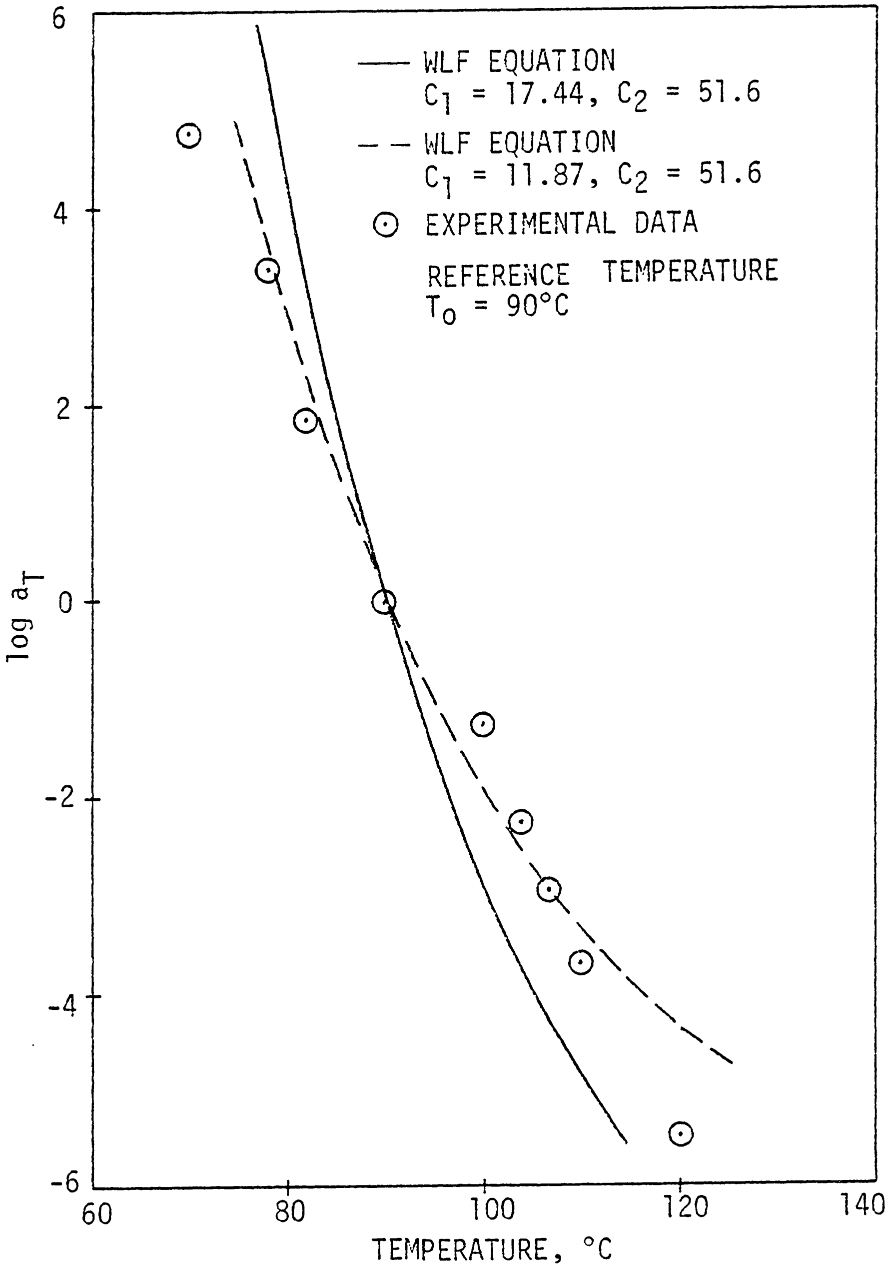


Figure 27. Comparison between experimental data and WLF equation, Metlbond 1113-2 [3].

It should be noted however that the surface would imply a particular type of stress- or strain-loading and that the surface would be non-conservative. That is, the values of stress or strain at any given time will depend upon the path or experiment performed, due to the viscoelastic nature of polymers and consequent energy dissipation [37].

VI. CONCLUSIONS AND FURTHER CONSIDERATIONS

The present investigation has been concerned with the nonlinear viscoelastic characterization of two materials, SMC-25 and Metlbond 1113-2. The investigation may be summarized as follows:

- The nonlinear viscoelastic procedure proposed by Schapery was found to be a useful mathematical tool for the characterization of the materials studied herein. Good agreement was found between creep predictions and experiment at all stress levels for SMC-25. For Metlbond 1113-2 agreement was good up to a stress level of 25 MPa (3640 psi).
- A threshold value of stress seems to exist for SMC-25 below which the material exhibits essentially linear viscoelastic behavior. Preliminary tests show this level to be about 13.8 MPa (2000 psi). This agrees well with the result from Schapery's theory.
- Fibers within the SMC-25 material existed in "fiber bundles" rather than discrete fibers. It is believed that large areas of void; i.e., regions of very little matrix, exist within these bundles of fibers.
- Mechanical conditioning of SMC-25 specimens prior to testing was found to be unnecessary.
- A stress-whitening or crazing phenomenon was observed in the 1113-2 adhesive at high stress levels. It was felt that the less dense material within the crazed area is one reason for

the error seen in the nonlinear characterization procedure for Metlbond 1113-2.

- A delayed failure phenomenon was observed for both materials studied. Crochet's method combined with Schapery's constitutive equation was shown to be appropriate.

Overall, the agreement between analyses and experiments were satisfactory in all cases, i.e., creep and creep to rupture. The investigation however represents only a preliminary portion of the work which needs to be done in order to completely forecast the effects of time, temperature, vibration and moisture. Recommendations for further work include:

(1) Further testing to ascertain the time-temperature behavior through the use of the WLF shift function.

(2) Further verification of the nonlinear properties obtained herein by an adequate statistical sampling.

(3) Develop a methodology to include the effects of both stress and temperature by developing a shift function dependent on both stress and temperature.

(4) Explore the possibilities of an effective time-temperature-stress failure or rupture surface.

(5) Examine the effects of vibration, i.e., dynamic effects at various isothermal states.

(6) Investigate the feasibility of using nondestructive test techniques to identify void and/or damage zones within the material.

The above items would provide for a coherent picture of the response of a material due to complex interactive effects. A symbiosis between analysis and experiment must exist, however, if the resulting methodology is to be meaningful.

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APPENDIX A

The purpose of this section is to present the derivation of the equations referred to within the text. Beginning with the nonlinear constitutive equation proposed by Schapery [8], stepwise stress loading will first be considered and then creep and creep recovery loading. As before, we may write the constitutive equation as,

$$e = g_0 A(o)\sigma + g_1 + g_1 \int_{0^-}^{t} \Delta A(\psi - \psi') \frac{dg_2\sigma}{d\tau}\, d\tau \qquad \text{(A-1)}$$

and the reduced time parameters as,

$$\psi = \psi(t) = \int_0^t \frac{dt'}{a_\sigma} \quad ; \quad \psi' = \psi(\tau) = \int_0^\tau \frac{dt'}{a_\sigma} \qquad \text{(A-2)}$$

where A(o) is the initial value of the linear viscoelastic creep compliance and $\Delta A(\psi)$ is the transient component.

Stepwise Stress Loading

Consider the stepwise stress loading as given by,

$$\sigma = \begin{cases} \sigma_a \quad , & 0 < t < t_1 \\ \sigma_b \quad , & t_1 < t < t_2 \end{cases} \qquad \text{(A-3)}$$

The step-stress input given by (A-3) may be written as,

$$\sigma_a[H(t) - H(t - t_1)] + \sigma_b[H(t - t_1) - H(t - t_2)] \qquad \text{(A-4)}$$

where H(t) represents the symmetrical unit step function such that,

$$H(t) = \begin{cases} 0 < \text{ for } t \quad 0 \\ 1/2 \quad \text{for } t = 0 \\ 1 > \text{ for } t \quad 0 \end{cases} \tag{A-5}$$

Substituting equation (A-4) into equation (A-1) we write;

$$\begin{aligned} \epsilon = {} & g_0 A(o)\{\sigma_a[H(t) - H(t-t_1)] + \sigma_b[H(t-t_1) - H(t-t_2)]\} \\ & + g_1 \int_{0^-}^{t} \Delta A(\psi-\psi') \frac{dg_2\{\sigma_a[H(\tau) - H(\tau-t_1)] + \sigma_b[H(\tau-t_1) - H(\tau-t_2)]\}}{d\tau} d\tau \end{aligned} \tag{A-6}$$

Realizing that the integrals above are in the form of Stieltjes integrals and using the relationship,

$$\delta(\tau) = \frac{d}{d\tau} H(\tau) \tag{A-7}$$

where $\delta(\tau)$ represents the Dirac delta function we may write (A-6) as,

$$\begin{aligned} \epsilon = {} & g_0{}^a A(o)\sigma_a[H(t) - H(t-t_1)] + g_0{}^b \sigma_b A(o)[H(t) - H(t-t_1)] \\ & + g_1 \int_{0^-}^{t} \Delta A(\psi-\psi') g_2\{\sigma_a[\delta(\tau) - \delta(\tau-t_1)] \\ & + \sigma_b[\delta(\tau-t_1) - \delta(\tau-t_2)]\}d\tau \end{aligned} \tag{A-8}$$

where the superscript denotes the stress at which the nonlinear properties are to be evaluated. The above integrals are now defined explicitly by definition of the Dirac delta function.

Considering (A-8) for times such that $0 < t < t_1$ we see,

$$\epsilon = [g_0{}^a \, A(o) + g_1{}^a \, g_2{}^a \, \Delta A(\psi)^a]\sigma_a \tag{A-9a}$$

or by definition of ψ,

$$\epsilon = \left[g_o{}^a\ A(o) + g_1{}^a\ g_2{}^a\ \Delta A\left(\frac{t}{a_\sigma{}^a}\right)\right]\sigma a \tag{A-9b}$$

If we now consider equation (A-8) for times such that $t_1 < t < t_2$ we may write,

$$\epsilon = g_o{}^b\ A(o)\sigma_b + g_1{}^b\left[\int_{o^-}^{t} \Delta A(\psi-\psi')g_2\{\sigma_a[\delta(\tau) - \delta(\tau-t_1)] + \sigma_b[\delta(\tau-t_1) - \delta(\tau-t_2)]\}\right] \tag{A-10}$$

or separating,

$$\epsilon = g_o{}^b\ A(o)\sigma_b + g_1{}^b\left[\int_{o^-}^{t_a^-} \Delta A(\psi-\psi')g_2\{\sigma_a[\delta(\tau) - \delta(\tau-t_1)]\}d\tau + \int_{t_a^-}^{t} \Delta A(\psi-\psi')g_2\{\sigma_a[\delta(\tau) - \delta(\tau-t_1)] + \sigma_b[\delta(\tau-t_1) - \delta(\tau-t_2)]\}d\tau\right] \tag{A-11}$$

where t_a^- is the time just prior to the application of the second stress σ_b. Performing these integrations then we may write,

$$\epsilon = g_o{}^b\ A(o)\sigma_b + g_1{}^b[g_2{}^a\ \sigma_a\ \Delta A(\psi - \psi')]\Big|_{o}^{t_a^-} + (g_2{}^b - g_2{}^a\ \sigma_a)\Delta A(\psi - \psi')]\Big|_{t_a^-}^{t} \tag{A-12}$$

where for $\Delta A(\psi - \psi')$ over the range of $0 < t < t_a^-$

$$(\psi - \psi') = \frac{t_a}{a_\sigma{}^a} + \frac{t - t_a}{a_\sigma{}^b} \qquad \text{(a)}$$

and for $t > t_1$, (A-13)

$$\begin{aligned}(\psi - \psi') &= \frac{t_a}{a_\sigma{}^a} + \frac{t - t_a}{a_\sigma{}^b} - \frac{t_a}{a_\sigma{}^a} \\ &= \frac{t - t_a}{a_\sigma{}^b}\end{aligned} \qquad \text{(b)}$$

from the definition of ψ. So then we may write the strain for times $t_1 < t < t_2$ as,

$$\begin{aligned}\epsilon = g_0{}^b\, A(o)\sigma_b + g_1{}^b \Bigg[g_2{}^a \sigma_a\, \Delta A\left(\frac{t_a}{a_\sigma{}^a} + \frac{t - t_a}{a_\sigma{}^b}\right) \\ + (g_2{}^b\, \sigma_b - g_a{}^a\, \sigma_a)\Delta A\left(\frac{t - t_a}{a_\sigma{}^b}\right)\Bigg]\end{aligned} \qquad \text{(A-14)}$$

Creep and Creep Recovery

Now consider the equations for creep and creep recovery where a creep load is applied at $t = 0$ and removed at $t = t_1$. From equation (A-9b) the creep strain may be written as,

$$\epsilon = \left[g_0\, A(o) + g_1 g_2\, \Delta A\left(\frac{t}{a_\sigma}\right)\right]\sigma_a \qquad \text{(A-15)}$$

where the superscripts have been dropped for brevity.

From equation (A-14) we may write the recovery strain by setting $\sigma_b = 0$ such that,

$$\epsilon_r = g_2\left[\Delta A\left(\frac{t_1}{a_\sigma} + t - t_1\right) - \Delta A(t - t_1)\right]\sigma \qquad \text{(A-16)}$$

where for $\sigma_b = 0$ the values of the nonlinear properties are one. The creep and creep recovery strain are now completely defined by equations (A-15) and (A-16).

THE NONLINEAR VISCOELASTIC BEHAVIOR OF ADHESIVES AND CHOPPED FIBER COMPOSITES

by

James Smoot Cartner, Jr.

(ABSTRACT)

The viscoelastic behavior of a chopped glass fiber/polyester sheet molding compound (SMC-25) and of a modified epoxy adhesive (Metlbond 1113-2) as determined by creep and creep recovery tests is presented. A nonlinear viscoelastic characterization method of Schapery is presented and applied to the data for both materials. The nonlinear constitutive equation so obtained is used together with a delayed failure law postulated by Crochet to describe creep rupture data for both materials. Discussion is also given on the feasibility of applying the nonlinear viscoelastic procedures of Schapery in conjunction with the time-temperature superposition principle to obtain a time-stress-temperature surface to define failure.