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(Progress Report to the NSWC, Carderock for the Period September, 1996 to December, 1997)

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ABSTRACT

A viscoelastic model is developed to describe the behavior of a polyurethane rubber provided to NIST by NSWC, Carderock. The model is based on concepts of time-dependent rubber elasticity and single integral models of viscoelasticity. The strain energy density function is assumed to be of a Valanis-Landel form, while its time-dependence is analyzed using the "perfect elastic fluid" model of Bernstein, Kearsley and Zapas. In addition, time-strain separability and time-temperature superposition are assumed to apply to the polyurethane in the temperature range of interest. Single step stress relaxation experiments in uniaxial extension are used to determine the model parameters. From these, multiple step stress relaxation and creep histories are applied to the material and it is found that the model can describe the nonlinear time-dependent viscoelastic response of the polyurethane resin to these cyclic histories to within approximately ±10 % of the load or deformation value applied.

I. INTRODUCTION

The isothermal, nonlinear viscoelastic response of polymeric materials above the glass transition temperature has been relatively well described using the perfect elastic fluid model of Bernstein, Kearsley and Zapas (BKZ)[1,2]. This is particularly true when one considers loading histories in which the deformations or loads of interest are monotone increasing [3]. In addition to giving a reasonable representation of the nonlinear viscoelastic response of polymer melts, the BKZ model has some advantages of simplicity. The response functions are determined from single step stress relaxation experiments [4] and the formalism looks much like a "time-dependent" elasticity. One drawback to the BKZ model, however, has been the fact that it is formulated in terms of the invariants of the (relative) deformation tensor with the result that the material parameters for each geometry of deformation must be obtained experimentally from stress relaxation experiments in that geometry. The result is a need for a large number of experiments to make a full three-dimensional model of material behavior.

Recently, however, there has been work carried out in this laboratory [5,6] in which a hybrid Valanis-Landel (VL)[7]-BKZ model was developed and used to predict the response of a poly(vinyl chloride) melt to multiaxial, constant rate of deformation experiments from single step stress relaxation experiments in uniaxial extension. It is the goal here to further develop this approach with the aim of describing the long term creep response of polyurethane materials in use by the U.S. Navy from single step stress relaxation experiments in uniaxial extension. The work described in this progress report is that performed during the period from September, 1996 through April, 1998 with the purpose of evaluating the utility of the hybrid VL-BKZ model as a tool for estimating the long term creep performance of polyurethane rubber samples provided by

the NSWC, Carderock to NIST. Subsequent work will consider and model moisture effects on the resin behavior.

II. METHODS OF ANALYSIS

Large Deformations

The states of strain in large deformations are commonly described by the principal extension ratios, λ_1, λ_2, λ_3 or by three strain invariants whose values are independent of the coordinate system [8].

$$I_1 = \sum_{i=1}^{3} \lambda_i^2 \ , \quad I_2 = \sum_{i,j=1, i \neq j}^{3} \lambda_i^2 \lambda_j^2 \ , \quad I_3 = \lambda_1 \lambda_2 \lambda_3 \qquad \textbf{(1)}$$

The polyurethane material studied here is assumed to be incompressible, which introduces the further relation:

$$I_3 = \lambda_1 \lambda_2 \lambda_3 = 1 \qquad \textbf{(2)}$$

The Valanis-Landel Strain Energy Function for an Elastic Material

For an incompressible material, Valanis and Landel [7] postulated the existence of a strain energy function $W(I_1, I_2, I_3) = W(\lambda_1, \lambda_2, \lambda_3)$ that is separable in the principal stretches λ_1, λ_2, λ_3.

$$W(\lambda_1,\lambda_2,\lambda_3) = w(\lambda_1) + w(\lambda_2) + w(\lambda_3) + a\ln(\lambda_1\lambda_2\lambda_3) \tag{3}$$

where $w(\lambda_i)$ will be referred to as the VL function and a is an arbitrary constant that can be set to 0 for an incompressible material.

The principal stress differences can be written in terms of the derivative $w'(\lambda)$ of the VL function:

$$w'(\lambda) = \frac{\partial W(\lambda)}{\partial \lambda}$$
$$\sigma_i - \sigma_j = \lambda_i w'(\lambda_i) - \lambda_j w'(\lambda_j) \tag{4}$$

For a uniaxial deformation, the above equation can be reduced to:

$$\lambda_1 = \lambda_2 = \frac{1}{\sqrt{\lambda}} \quad (\textit{incompressibility})$$
$$\textit{with } \Delta\sigma = \sigma_{11} - \sigma_{22} : \qquad \Delta\sigma(\lambda) = \lambda w'(\lambda) - \frac{1}{\sqrt{\lambda}} w'\left(\frac{1}{\sqrt{\lambda}}\right) \tag{5}$$

$w'(\lambda)$ can be obtained from a combination of data from tension and compression measurements using the approach of Kearsley and Zapas [9] using a recursive set of equations. By forming the sequence of equations of the form of equation 5 , replacing λ by λ_k , and by summing them, one finds:

$$
\begin{aligned}
&\textit{with} \quad \lambda_k = \lambda^{(-1/2)^k} \\
&\Delta\sigma(\lambda_k) = \lambda_k w'(\lambda_k) - \frac{1}{\sqrt{\lambda_k}} w'\left(\frac{1}{\sqrt{\lambda_k}}\right) \\
&\qquad\qquad \vdots \\
&\qquad\qquad \vdots \\
&\Delta\sigma(\lambda_{k+j}) = \lambda_{k+j} w'(\lambda_{k+j}) - \frac{1}{\sqrt{\lambda_{k+j}}} w'\left(\frac{1}{\sqrt{\lambda_{k+j}}}\right) \\
&\text{----------} \\
&\sum_{k=0}^{\infty} \Delta\sigma(\lambda_k) = \lambda w'(\lambda)
\end{aligned}
\tag{6}
$$

Since the left hand side of the equation can be obtained from data in simple extension and compression experiments, the function $w'(\lambda)$ is readily obtained and equation 6 gives a solution to the separation problem.

Here, because we have only limited compressive data and substantial extensional data, we chose to describe the stress-strain response of the rubber with the semi-empirical equation of Martin, Roth and Stiehler (referred to as the MRS equation [10]), which is known to fit adequately data of cross-linked polymers [8,11] for stretches up to λ=3.5 and for compressions down to λ=0.5 . The MRS equation can be written as:

$$
\Delta\sigma(\lambda) = M\left(1-\frac{1}{\lambda}\right)e^{A\left(\lambda-\frac{1}{\lambda}\right)} \tag{7}
$$

The two adjustable parameters M and A (nominally material constants) can be found by

fitting the tension data and the compressive response is estimated by extrapolation of the function. (Note, in future work, direct compressive experiments will be performed to better determine the MRS parameters.)

The Viscoelastic Description and Bernstein, Kearsly and Zapas Theory

In 1963, Bernstein, Kearsley and Zapas [1,2,4] proposed a model known as the BKZ theory which describes the time-dependent behavior of non-linear viscoelastic "perfect elastic fluid"-like materials. For an incompressible material, the stress $\sigma_{ij}(t)$ can be calculated for any deformation history, using the BKZ constitutive equation:

$$\sigma_{ij}(t,T) = -p\delta_{ij} + \int_{t}^{-\infty} [U_1(I_1,I_2,t-\tau,T)B_{ij}(t,\tau) - U_2(I_1,I_2,t-\tau,T)B_{ij}^{-1}(t,\tau)]\,d\tau \qquad (8)$$

$$with \quad U_i = \frac{\partial U}{\partial I_i}$$

where:

t is the time,

T is the temperature,

p is the hydrostatic pressure,

δ is the Kroneker symbol,

$B_{ij}(t, \tau)$ is the relative left Cauchy-Green deformation tensor,

U is the strain potential function.

In the case of uniaxial deformations, the relative, left Cauchy-Green tensor is written as:

$$B_{i,j}(t,\tau) = \begin{bmatrix} \frac{\lambda(t)^2}{\lambda(\tau)^2} & 0 & 0 \\ 0 & \frac{\lambda(\tau)}{\lambda(t)} & 0 \\ 0 & 0 & \frac{\lambda(\tau)}{\lambda(t)} \end{bmatrix}, \qquad B_{i,j}^{-1}(t,\tau) = \begin{bmatrix} \frac{\lambda(\tau)^2}{\lambda(t)^2} & 0 & 0 \\ 0 & \frac{\lambda(t)}{\lambda(\tau)} & 0 \\ 0 & 0 & \frac{\lambda(t)}{\lambda(\tau)} \end{bmatrix} \tag{9}$$

and the deformation invariants are:

$$\begin{aligned} I_1(t,\tau) &= \frac{\lambda(t)^2}{\lambda(\tau)^2} + 2\frac{\lambda(\tau)}{\lambda(t)} \\ I_2(t,\tau) &= \frac{\lambda(\tau)^2}{\lambda(t)^2} + 2\frac{\lambda(t)}{\lambda(\tau)} \end{aligned} \tag{10}$$

$\Delta\sigma(t)$ for uniaxial strain is obtained by the equation:

$$\Delta\sigma(t) = 2\int_t^{-\infty}\left[\frac{\lambda(t)^2}{\lambda(\tau)^2} - \frac{\lambda(\tau)}{\lambda(t)}\right]\left[\frac{\partial U}{\partial I_1} + \frac{\lambda(t)}{\lambda(\tau)}\frac{\partial U}{\partial I_2}\right]d\tau \tag{11}$$

Single-step deformation history: stress relation

Let us define the following function:

$$W(I_1,\ I_2,\ t)\ =\ \int_t^{\infty} U(I_1,I_2,s)\,ds$$

$$\textit{then} \qquad W_{I_1}(t)\ =\ \frac{\partial W}{\partial I_1}\ =\ \int_t^{\infty} U_1(I_1,I_2,s)\,ds\ , \qquad W_{I_2}(t)\ =\ \frac{\partial W}{\partial I_2}\ =\ \int_t^{\infty} U_2(I_1,I_2,s)\,ds \tag{12}$$

We now represent the single step stress relaxation in simple extension :

$$\Delta\sigma(t)\ =\ 2(\lambda^2-\frac{1}{\lambda})(W_{I_1}(t)+\frac{1}{\lambda}W_{I_2}(t)) \tag{13}$$

And we note that the above equation resembles the Rivlin and Saunders [12] finite elasticity equations, except that $W_{I1}(t)$ and $W_{I2}(t)$ are time dependent as are I_1 and I_2. Moreover, this equation applies to a material which is not assumed to be in its equilibium state, since the stress may be relaxing. That is, it applies to viscoelastic materials.

Determination of responses to other histories from single-step stress relaxation data:

Let us define the function $G(\lambda,t,T)$ as the value of $\Delta\sigma(t,T)$ in a single step stress relaxation experiment carried out at a given temperature:

$$G(\lambda,t,T)=\Delta\sigma(\lambda,t,T) \tag{14}$$

and its partial derivative by:

$$G_{*}(\lambda,t,T)\ =\ \frac{\partial G(\lambda,t,T)}{\partial t} \tag{15}$$

We can then predict the stress history in any uniaxial deformation, using the constitutive

equation:

$$\Delta\sigma(\lambda,t,T) = -\int_{-\infty}^{t} G_*\left(\frac{\lambda(t)}{\lambda(\tau)}, t-\tau, T\right) d\tau \qquad \textbf{(16)}$$

If one considers deformations for which the material is at rest at times prior to $\tau = 0$ (motion following the rest history), equation (16) becomes:

$$\Delta\sigma(\lambda,t,T) = G(\lambda(t),t,T) - \int_{0}^{t} G_*\left(\frac{\lambda(t)}{\lambda(\tau)}, t-\tau, T\right) d\tau \qquad \textbf{(17)}$$

Validity of the time-dependent BKZ theory model

In order to test the validity of the VL-BKZ approach for a given material and stress or deformation histories one follows the sequence:

1. Perform single step stress relaxation experiments over a range of deformations and times, at a given temperature.

2. From the relaxation measurements, determine $G_*(\lambda, t)$.

3. Perform tests in arbitrary deformation or stress histories and compare the results calculated from the BKZ model with the observed responses;

   i. In multiple step stress relaxation or constant rate of deformation histories, one needs to simply calculate the expected response from equation 17 for the imposed deformation history.

   i.i. In creep experiments, one measures the deformation and inserts the experimental $\lambda(t)$ into the right-hand side of the single integral equation, and checks if the calculated stress fits the experimental stress. For example, in a constant stress experiment does one calculate a constant stress from the observed deformations?

III. EXPERIMENTAL METHODS[13a]

Materials

The results presented in the subsequent sections were obtained for a polyurethane rubber designated 506 KW7 and provided by the NSWC, Carderock in the form of approximately 8 cm wide and 2 m long strips of 4 mm thickness. The material was not otherwise specified. Rectangular samples for testing in uniaxial extension were prepared by cutting the samples with a guillotine-type cutter. The samples are roughly 50 mm long, between 2 and 3 mm wide and 2 mm thick. The width was chosen to avoid grip effects. That is, the samples, upon testing, were found to have the same deformation within a 1 cm gage section as that determined by measuring the grip displacement and dividing by the original grip separation.

Apparatus

Environmental testing chamber

In order to validate the model over a range of experimental conditions, a PC controlled humidity and temperature chamber was designed and built. It is depicted schematically in Figure 1. The temperature is controlled by an integrated circuit which receives analog signals from the computer. The temperature probe output voltage is compared to the computer analog signal. The differential voltage is amplified by a series of operational amplifiers. The corresponding amplified signal triggers on or off a heating device. An extra cold air source enables the chamber to be cooled to 0 °C. The useful temperature range for the apparatus is from 0 °C to 80 °C with a measured stability of ±0.2 °C.

In a similar manner, a personal computer controls the relative humidity in the inner box. Two humidity sensor signals give a spatial average value of the moisture content in the inner chamber. The signal is then compared to that which is proportional to the desired relative humidity. Amplified, the differential voltage regulates a proportional integral differential (PID) electronics system which activates two valves to provide either wet or dry air flow. The relative humidity range goes from 5 % to 90 %, with a measured stability of ± 2 %.

Tension and compression tests

The uniaxial tension and compression tests were performed using a load frame moved symmetrically about the center using a stepper-motor (Daedal, Inc) monitored by a personal computer for command and acquisition of input signals. The system is described in Figure 2. Commands are sent to the motor through an indexer and a board coupled together. Both the velocity and the acceleration of the motor screw are calculated to reach the desired displacement or stress with the minimum of overshoot. The sample length is measured by a miniature Linear Variable Transformer (LVDT type MHR-100 or MHR-500, Schaevitz, Inc.) connected to an Analog Transducer Amplifier (ATA 101, Schaevitz, Inc.). The signal is then converted into a digital one. The uncertainty of the extension ratio is less than 0.1 %. The force applied is measured using a load cell (MB-10 or MB-100 type, Interface, Inc.). The range of forces studied goes from 5 lbs (25 N) to 250 lbs (1250 N) , depending on the load cell features.

The true stress in the deformed sample is calculated assuming that the material is incompressible. The PC reads both the specimen length and the applied force through an AD/DA converter card (RTI-815, Analog Devices, Inc). The extensometer (respectively load cell) signal

is used as a feedback to control the strain (respectively the stress) in stress relaxation (respectively creep) experiments.

A program was written in a Turbo Pascal code to control the apparatus in order to perform single or multiple step stress relaxation or creep tests. Constant strain or stress rate experiments can be carried out as well.

IV. RESULTS

Single-step Stress Relaxation Experiments

Typical results for a single step stress relaxation experiment are shown in Figure 3a. The uncertainty of the experimental stress data was determined to be approximately 5 % as a single standard deviation by replicate measurements at 10 °C with samples taken from arbitrary positions within a single strip of material provided to NIST. An F-test [13b] showed that the standard errors obtained at three different strains (20 %, 50 %, 80 %; 0.20, 0.50, 0.80) at 10 °C are not significantly different within a probability of 95 %.

In order to compensate the time that the motor takes to reach the desired strain, a systematic shift of half of the loading time is applied to the experimental data [14].

Variable Separation Assumption

We assume that the response is time-temperature and strain separable and use separable functions to describe the stress history:

$$\sigma(\lambda, t, T, r_h) = g_{MRS}(\lambda).f(t,T).h(r_h)$$
with:
t: *time,*
T: *temperature,*
r_h: *relative humidity.* **(18)**

Relative Humidity Effect

Both mass up-take and mass loss experiments are currently being carried out on the polyurethane to study the absorption and desorption of water. Further experiments performed in temperature and relative humidity controlled conditions will enable us to analyze the impact of the moisture content on the material response. The relative humidity parameter will then be included in the model developed to describe the polyurethane resin behavior.

Time-temperature Dependence

The time-temperature dependent function $f(t,T)$ was obtained using data from stress relaxation experiments of 3000 seconds duration. The range of temperatures considered was from 10 °C to 65 °C. The reference temperature T_0 was taken as 10 °C. The horizontal shift factors were calculated from a WLF-type equation (Eq. 19), while the vertical shift is given by $b_{To}(T) = T_0 / T$. An uncertainty of ±10 % was allowed on $b_{To}(T)$ to optimize the curve fit to the master curve.

$$Log(a_T) = -\frac{c_1(T-T_0)}{c_2+(T-T_0)} \qquad \textbf{(19)}$$
with $c_1 = 9.57 \pm 0.11$, $c_2 = (123.7 \pm 0.9)\ ^oC$, $T_0 = 10\ ^oC$

The uncertainties on the parameters c_1 and c_2 represent a single standard error of estimate from the curve fitting procedure.

The master curve equation for the stress relaxation response was then fitted to a modified stretched exponential function:

$$f(t,T) = e^{\left(\frac{t/a_T}{t_c}\right)^{-\beta}} \tag{20}$$

Figure 3b depicts the experimental master curve and predictions from the fits to equation 20 extrapolated to 20 years ($7x10^8$ s). To give an idea of the possible uncertainties in such extrapolations, we have chosen to also present the bounds assuming that there is a ±10 % variability in the magnitude of the modulus (i.e., $g_{MRS}(\lambda)$). This represents approximately 2 standard deviations on the mean of such measurements (see first paragraph under Results). We ascribe no obvious physical significance to the two parameters t_c and β [15]. Furthermore, we note that, to our knowledge, a value of the stretching exponent ($-\beta$) that is less than 0 has not been used previously to describe stress relaxation data.

For infinite times, the right-hand side of equation 20 approaches 1 and captures the network behavior:

$$\lim_{t_r \to \infty} f(t_r) = 1 \quad , \quad with \; t_r = \frac{t}{a_T} \tag{21}$$

The parameters t_c and β are determined by fitting the curve using the Fletcher and Reeves Conjugate Gradient method [16] and are depicted in Table 1.

Table 1. Curve Fitting Parameters for Equation 20. (See Text for Discussion).

parameter	value	standard error
t_c	$2.14\ 10^5$ s	-
β	0.026	5 %

Moreover, single step stress relaxation experiments performed on the 506 KW7 elastomer at 10 °C and for strains up to 100 % showed that the time-temperature function $f(t,T)$ does not depend on the stretch ratio λ (for $1 \le \lambda \le 2$).

Figure 4 depicts the stress relaxation data recorded over a time scale of 4 decades along with the fit using the modified stretched exponential function (Eq. 19). The experiment was carried out at 10 °C. For times greater than 10 seconds, the function $f(t,T)$ captures reasonably well the time dependent process.

Strain Dependence:

The semi-empirical Martin, Roth and Stiehler (MRS) equation was used to fit the stress-strain behavior of the rubber. The MRS equation is:

$$g_{MRS}(\lambda) = \Delta\sigma(\lambda) = M(1-\frac{1}{\lambda})e^{A(\lambda-\frac{1}{\lambda})} \qquad \textbf{(22)}$$

To determine the parameters M and A, uniaxial deformation experiments were performed at 10 °C, using the resin type D506 KW7. Tension results are depicted in Figure 5 as the normalized true stress versus the applied stretch ratio. The true stress was normalized by dividing

the experimental values by the reduced time function (Eq. 20) $f(t_r, T)$. Hence, at each λ, three stress points are plotted, one for each isochronal time value (10 s, 100 s, 1000 s). Also shown in Figure 5 is the least squares fit of the MRS function to the isochronal data (10 s, 100 s, 1000 s). Note that the fit seems to deviate somewhat from the data at the highest stretches. This error may be due to a breakdown of the time-strain separability assumption or to the time (resp. strain) dependent power law (resp. MRS) function. The results of fitting the data to equation 22 are presented in Table 2. Further work is to be done to examine other possible material models than the MRS model. However, for the current purposes the MRS function is adequate to proceed to calculate the material response in other deformation histories. {As an aside we add that preliminary experiments in the compression mode ($0.8<\lambda<1$) were conducted on cylindrical samples of the type 506 KW7 polyurethane, but the results could not be used due to technical problems. A new compression apparatus has been built and this will allow us to perform tests in the compression region down to a stretch ratio of approximately 0.75. Hence, the results reported here include only MRS estimates determined from tensile data alone.} Also, we remind the reader that the purpose of using the MRS equation is that a means to extrapolate into compression is required to predict complicated strain histories because the equations in the hybrid VL-BKZ-type model require relative deformations, which become compressive when the deformation becomes non-monotone and for the lateral strains in, e.g., uniaxial deformations.

Table 2. Results from Fitting Tensile Data to Equation 22. (See Text for Discussion).

parameter	value	standard error
M	4.33 MPa	9 %
A	0.07	2 %

The parameter A in equation 22 was found to be +0.07 which differs somewhat from the range 0.3 - 0.4 reported in the literature for cross-linked rubbers [17]. In addition to the visual quality of fit observed in Figure 5, one can get a quantitative estimate by examination of the normalized residual plot shown in Figure 6. While the maximum relative deviation between the fitted curve and the data can be estimated to be approximately ± 6 %, although there is some structure to the residuals, there is little systematic deviation for the different times.

Valanis Landel Function Calculations

Having established the time and strain dependent functions in the MRS equation, the calculation of $w'(\lambda,t,T)$ is now possible. For a given stretch ratio λ_0 , $w'(\lambda_0,t,T)$ is given by:

$$\frac{\lambda_0 w'(\lambda_0,t,T)}{f(t_r)} = \sum_{k=0}^{\infty} M\left(\frac{\lambda_k - 1}{\lambda_k}\right) e^{A\left(\frac{\lambda_k^2 - 1}{\lambda_k}\right)} \qquad \textbf{(23)}$$

$$with \quad \lambda_k = \lambda_0^{(-1/2)^k}$$

A Turbo Pascal program was written to make this calculation. In practice, only 10 terms are necessary to obtain convergence.

VL-BKZ Function Calculations

One can now determine the Kernel function $G_*(\lambda,t,T)$ used to calculate the BKZ single integral for a uniaxial motion following the rest history.

$$with\ G_*(\lambda,t,T)=\frac{\partial G(\lambda,t,T)}{\partial t}\ =\ \frac{\partial}{\partial t}\left[\lambda w'(\lambda,t,T)-\frac{1}{\sqrt{\lambda}}w'(\frac{1}{\sqrt{\lambda}},t,T)\right] \tag{25}$$

The Kernel function becomes:

$$G_*(\lambda,t,T)=\lambda\frac{\partial w'(\lambda,t,T)}{\partial t}-\frac{1}{\sqrt{\lambda}}\frac{\partial w'(1/\sqrt{\lambda},t,T)}{\partial t}$$

$$with\quad \frac{\partial w'(\lambda_0,t,T)}{\partial t}=\frac{1}{\lambda_0}\left[\sum_{k=0}^{\infty}g_{MRS}(\lambda_k)\right]\left[\frac{\partial f(t,T)}{\partial t}\right] \tag{26}$$

This gives the stress history, using the single integral:

$$\Delta\sigma(\lambda,t,T)=G(\lambda(t),t,T)-\int_0^t\left[\frac{\lambda(t)}{\lambda(\tau)}\frac{\partial w'(\lambda(t)/\lambda(\tau),t-\tau,T)}{\partial t}-\sqrt{\frac{\lambda(\tau)}{\lambda(t)}}\frac{\partial w'\left(\sqrt{\lambda(\tau)/\lambda(t)},t-\tau,T\right)}{\partial t}\right]d\tau \tag{27}$$

Prediction of The Stress History For a Multiple-step Uniaxial Motion Following The Rest History

Using the experimentally determined single-step stress relaxation response function (equation 18), one can predict the stress (respectively strain) response to multiple step strain (respectively stress) histories. These are examined in the next paragraphs.

Stress Relaxation Experiment

Multiple step-up stress relaxation experiment

A triple step-up strain history was applied to the rubber sample (D 506 KW7) at a

constant temperature of 50 °C. The strain and the true stress signals were recorded during 3000 s after each deformation. The strain history (Figure 7) is summarized by:

$$\begin{aligned} \lambda(\tau) &= 1 \qquad \tau<0 \\ \lambda(\tau) &= \lambda_1 \qquad 0<\tau<t_1 \\ \lambda(\tau) &= \lambda_2 \qquad t_1<\tau<\tau_2 \\ \lambda(\tau) &= \lambda_3 \qquad t_2<\tau \end{aligned} \tag{28}$$

here

λ_1=1.3 λ_2=1.4 λ_3=1.5
t_1=3000 *s* t_2=6000 *s*

The BKZ single integral (Eq. 27) can be explicitly calculated and the triple step-up stress relaxation response is given by:

$$\begin{aligned} &0<t<t_1: \quad \Delta\sigma(t,T) = G(\lambda_1,t,T) \\ &t_1<t<t_2: \quad \Delta\sigma(t,T) = G\left(\frac{\lambda_2}{\lambda_1},t-t_1,T\right) + G(\lambda_2,t,T) - G\left(\frac{\lambda_2}{\lambda_1},t,T\right) \\ &t_2<t: \quad \Delta\sigma(t,T) = G\left(\frac{\lambda_3}{\lambda_2},t-t_2,T\right) + G\left(\frac{\lambda_3}{\lambda_1},t-t_1,T\right) - G\left(\frac{\lambda_3}{\lambda_2},t-t_1,T\right) + G(\lambda_3,t,T) - G\left(\frac{\lambda_3}{\lambda_1},t,T\right) \end{aligned} \tag{29}$$

We remark that Equation 29 applies to ideal steps. In Figure 8 we depict the material response to the three step deformation history along with the BKZ computation based on Equation 29. The agreement between model and experiment shown in Figure 8 is reasonable. In Figures 9-11 a comparison between the calculated values and the measured values is shown for the individual steps with the time reset to the beginning of each step. These figures show that the BKZ calculation from Equation 29 is reasonable, though the calculated short time response deviates systematically from the measured response. The first reason for this is the finite rate of

deformation effect that is seen in the measured responses. As mentioned previously, this could be corrected by taking away half of the loading time (several seconds) from the experimental results [14]. This is not done here since the purpose is to illustrate that the simple BKZ-step calculation provides a reasonable estimate of the multiple step history. In all subsequent calculations we integrate numerically the full strain history (Equation 27) rather than use Equation 29.

Multiple cycle stress relaxation experiment:

The 506 KW7 material stress response to a quadruple cycle strain history (Figure 12) is shown in Figure 13 along with the hybrid VL-BKZ simulation. The experiment was performed at 10 °C. The stress relaxation computation was made using Equation 27. While the calculation does not fit the stress response for the unloading steps, it does describe reasonably well the relaxation process corresponding to the loading step of the four cycles. This is as anticipated because the BKZ-type constitutive models are known to provide less good predictions when the sample is unloaded or the load is reversed [3].

A point to be made here is that the 'unload' portions of the deformation history were not fully unloaded. This is because a full return of the sample to a nominal zero deformation caused sample buckling (due to compression). Therefore, the deformation was cycled between the maximum extension and a small positive stress to avoid the buckling phenomenon.

Creep Experiments

Multiple step-up stress history

A creep experiment was performed by applying a four step-up stress history, at a temperature of 10 °C. The stress levels were chosen to cover the deformation range of λ=1.2 to λ=1.7 as seen in Figure 14. Each step lasted 2500 seconds. The measured strain history $\lambda(t)$ observed during the multiple creep steps and shown in Figure 14 was used in Equation 27 to compute the stress history. Figure 15 compares the applied stress history with that calculated from the hybrid VL-BKZ model. The model gives a relatively good fit to the experimental data corresponding to the four stress steps (Figures 15 through 19). We do note that, while the deviations between the model calculations and the data are less than about 10 % of the applied stress, the model exhibits a somewhat softer response that approaches the experimental value at long times.

Trapezoidal stress history:

Figures 20 (respectively 21) show the material response (resp. the deformation) to a 2 trapezoidal-shaped step stress history. The experiment was performed at 23 °C, using a sample type 506 KW7. The model is within reasonable agreement (less than 10 % difference) with the experimental data recorded during the increasing stress ramps. As observed for the four cycle stress relaxation experiment, the model does not describe the unloading sections of the history as well as it does the loading ones.

V. CONCLUSIONS AND FURTHER WORK

A time dependent Valanis - Landel strain energy function has been used to describe the non-linear response of a polyurethane rubber. The time dependent VL function was determined

by performing uniaxial single step stress relaxation experiments, assuming that the incompressible material response is time and strain separable. Experiments were performed over a temperature range of 5 °C to 70 °C for strains from 5 % to 100 %. The time - temperature superposition function was established using data obtained at λ=1.5 and for temperatures ranging from 10 °C to 65 °C. The time-temperature dependent strain energy function was then used in the framework of the BKZ single integral viscoelastic constitutive equation. The model developed predicts the non-linear viscoelastic material response to multiple cyclic or step-up stress or strain, and constant rate of deformation histories in uniaxial extension within an error of less than 10 % for the range of parameters examined.

Ongoing experiments to investigate the impact of moisture on the material response will help in the prediction of the behavior of the polyurethane rubber under various environmental conditions. Initial modeling will include the relative humidity variable in the time-temperature-strain function for the rubber as a moisture shift factor, similar to that used in the time-temperature superposition.

In addition, new experiments to obtain reliable data in compression will enable us to describe both the tension and compression isochronal stress-strain results with a better agreement. Other models than the Martin, Roth and Stiehller equation will be investigated to fit the stress-strain isochrone curves, such as the Gaylord-Douglas model [18]. Furthermore, other constitutive equations describing solid-like material responses found in the literature will be compared to the Bernstein, Kearsley and Zapas model.

VI. REFERENCES

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13a. Certain Commercial Materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily the best available for the purpose.

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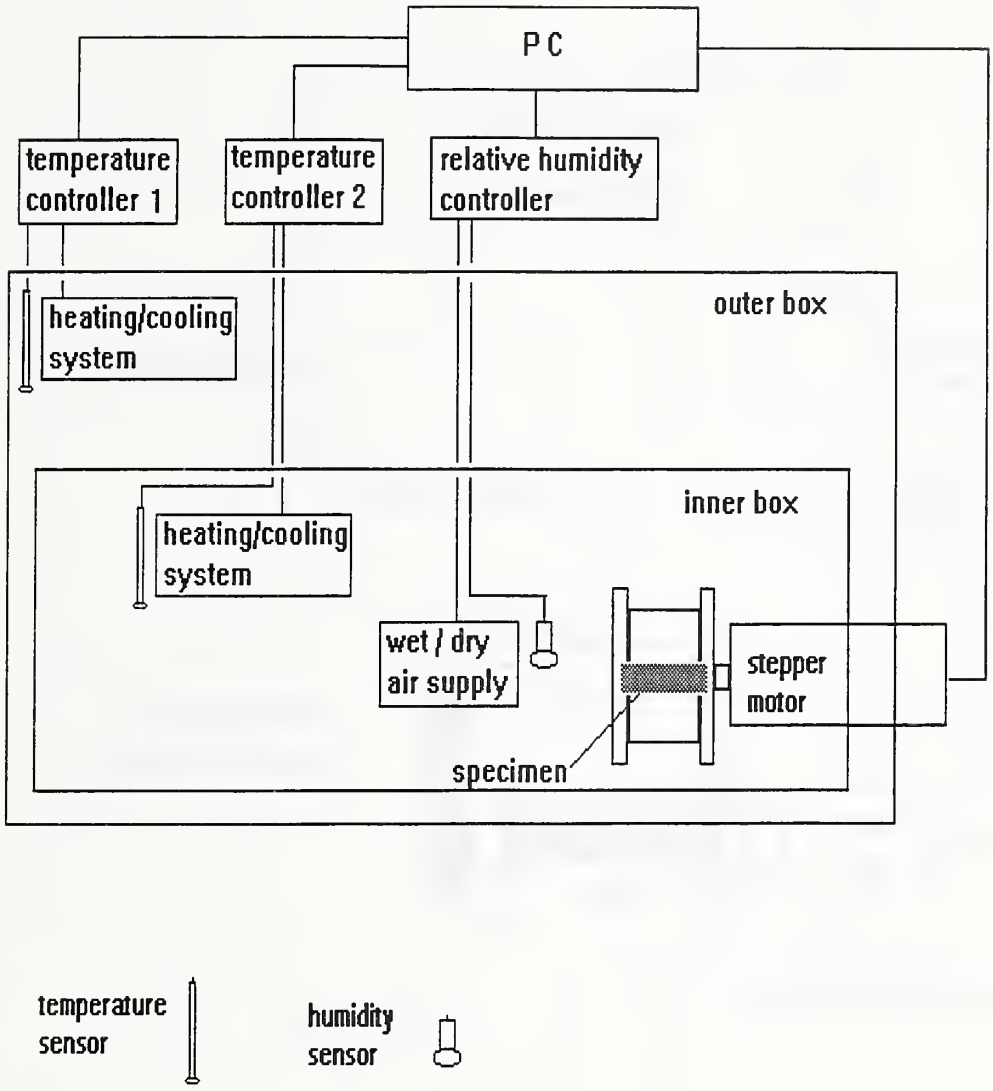

Figure 1. Schematic of Environmental Testing Chamber (See text).

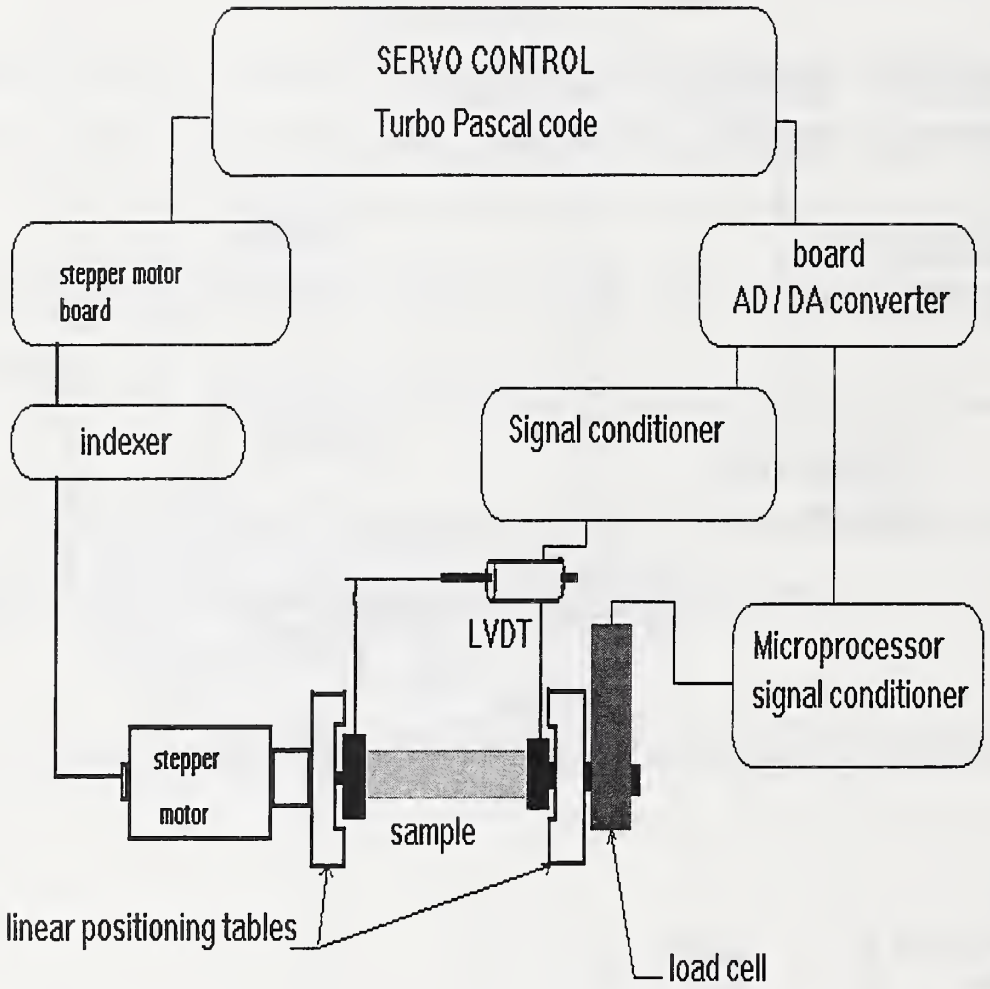

Figure 2. Schematic of Control System for Stepper Motor. (See text.)

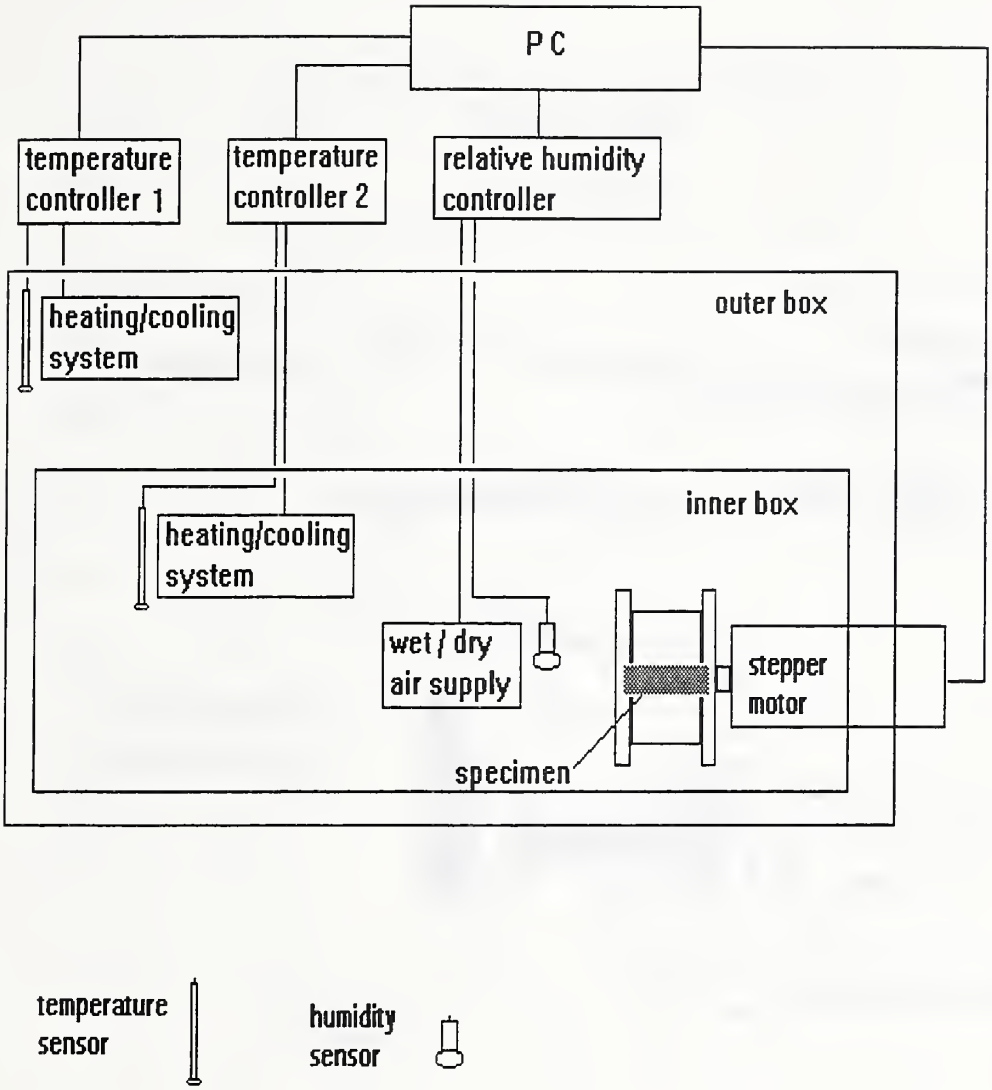

Figure 1. Schematic of Environmental Testing Chamber (See text).

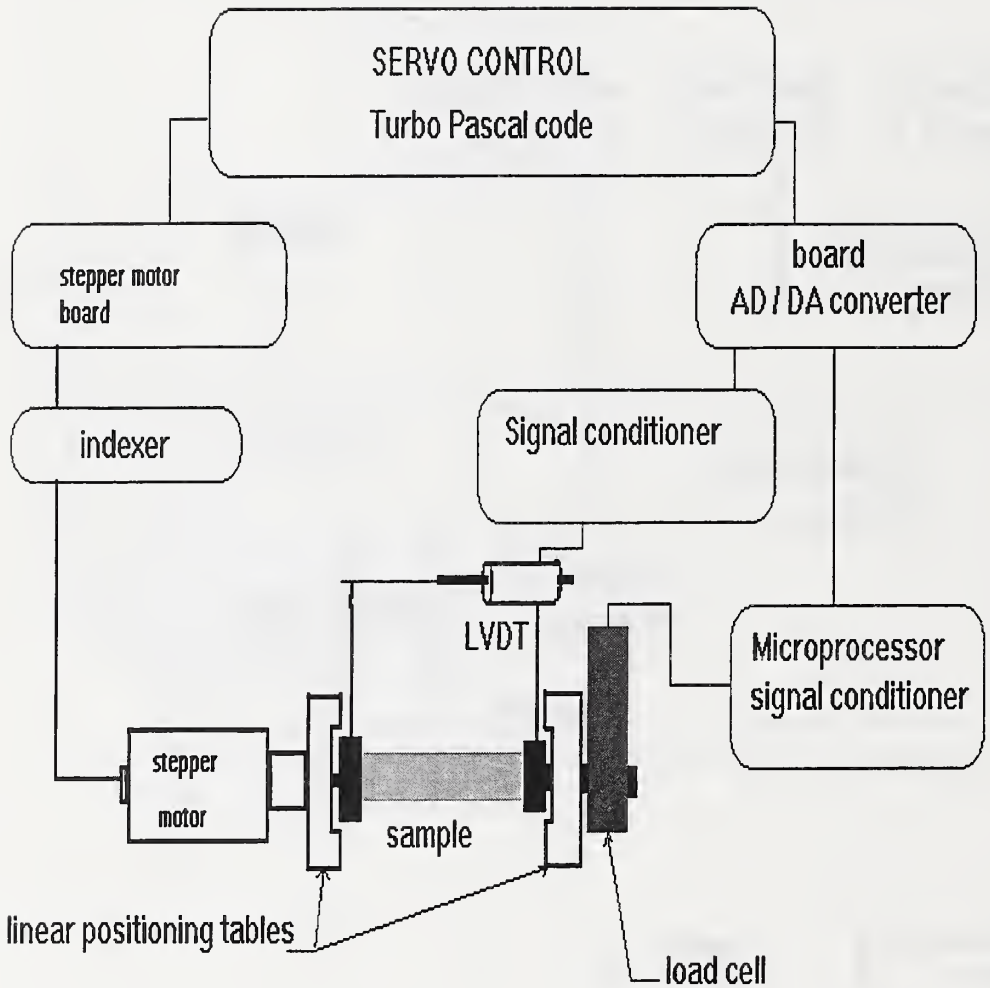

Figure 2. Schematic of Control System for Stepper Motor. (See text.)

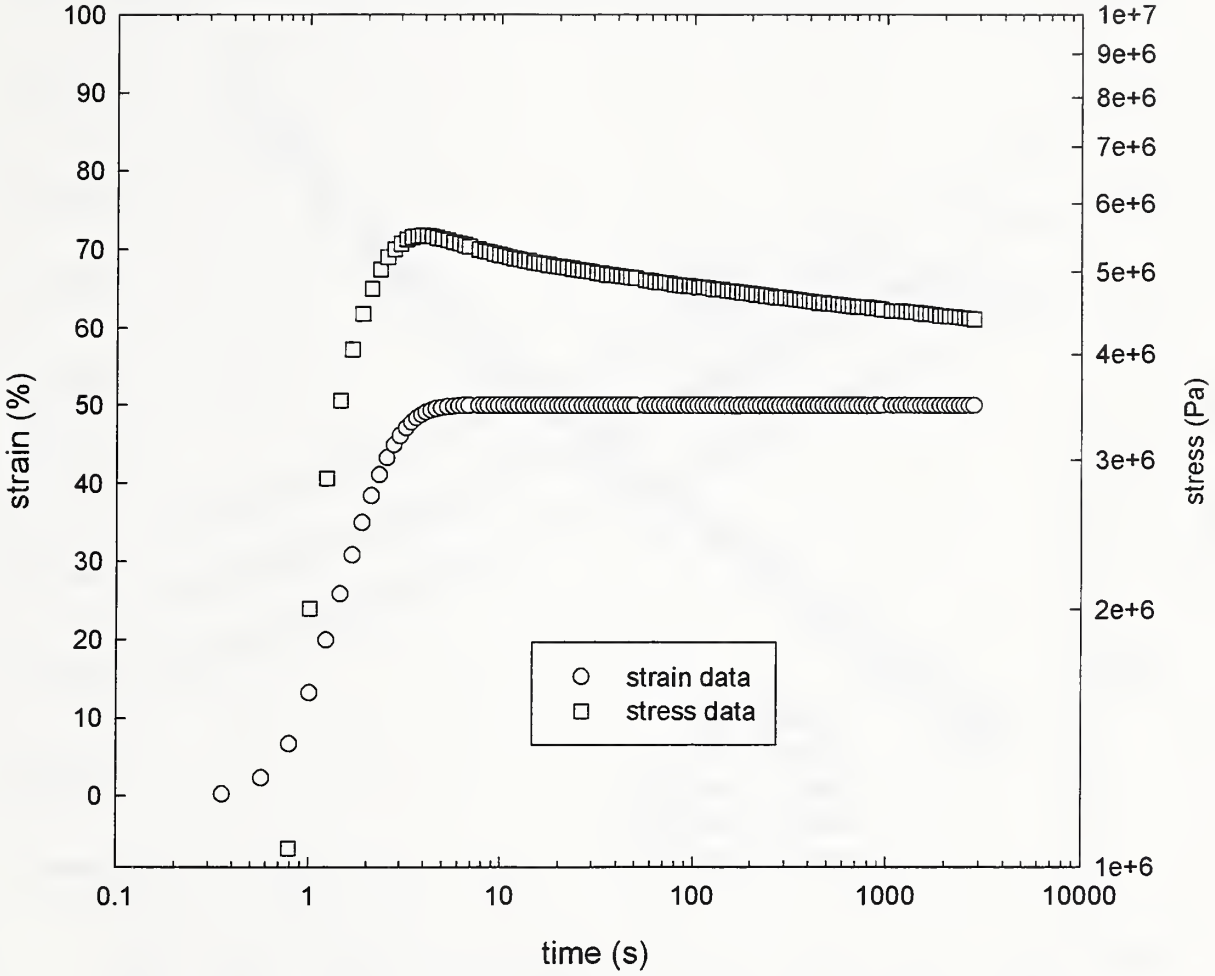

Figure 3a: Typical strain (left) and stress (right) versus time curves for a single step stress relaxation test on a polyurethane elastomer.

Peak strain = 50% ; T = 10°C.

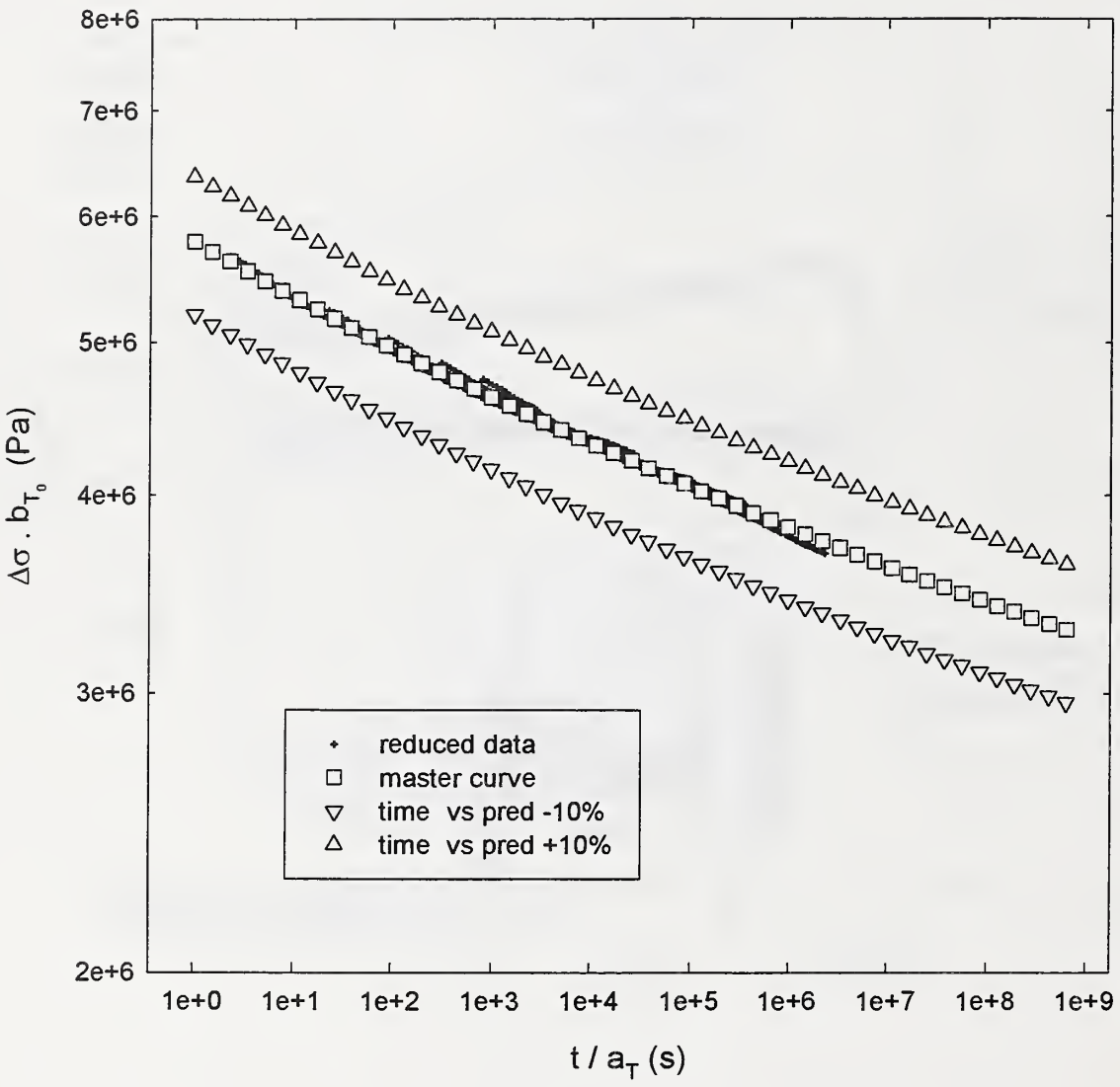

Figure 3b: time - temperature superposition master curve
$\lambda = 1.5$.

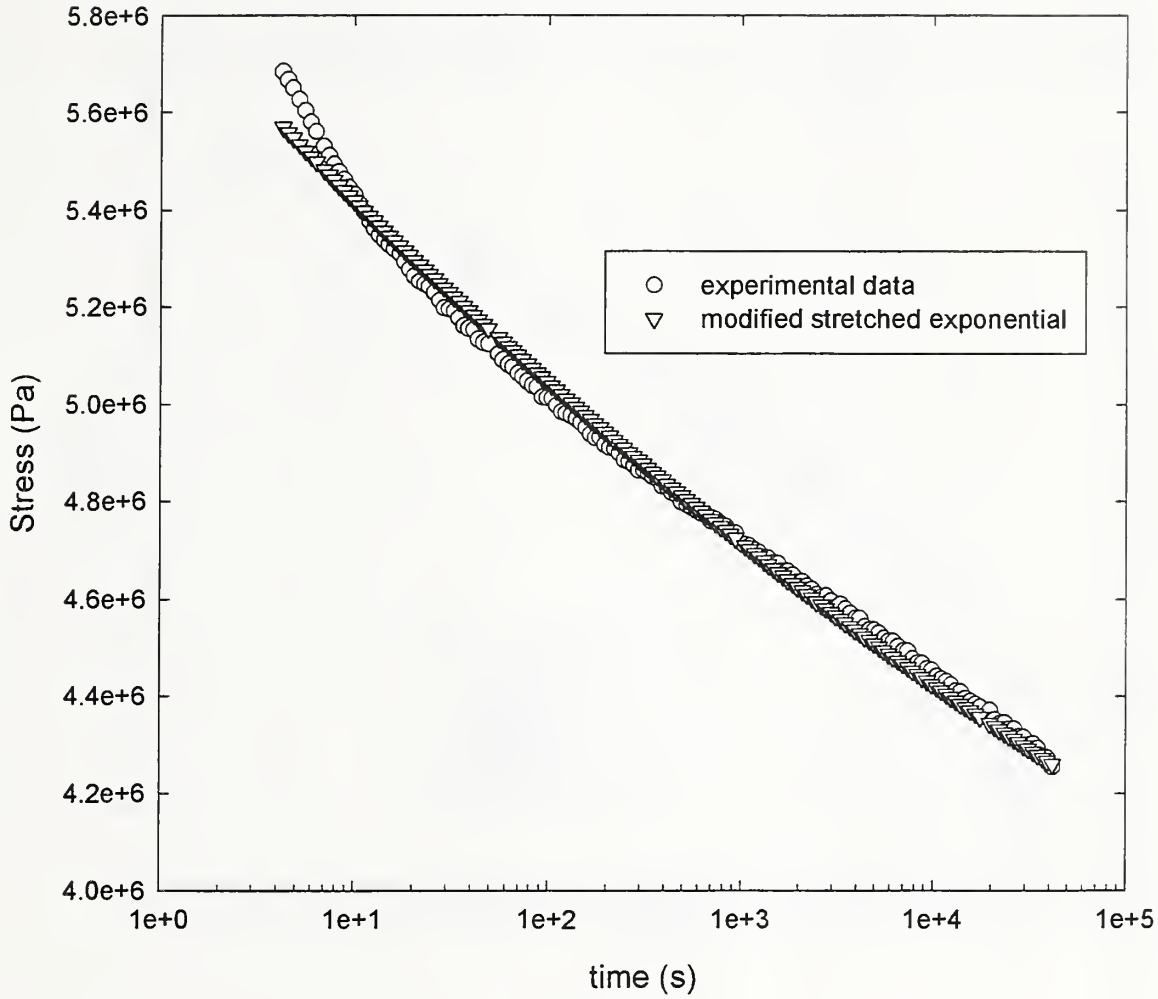

Figure 4: Stress versus Log(time) in stress relaxation test at λ=1.5 and T=10°C. The modified stretched exponential is given by Eq. (19).

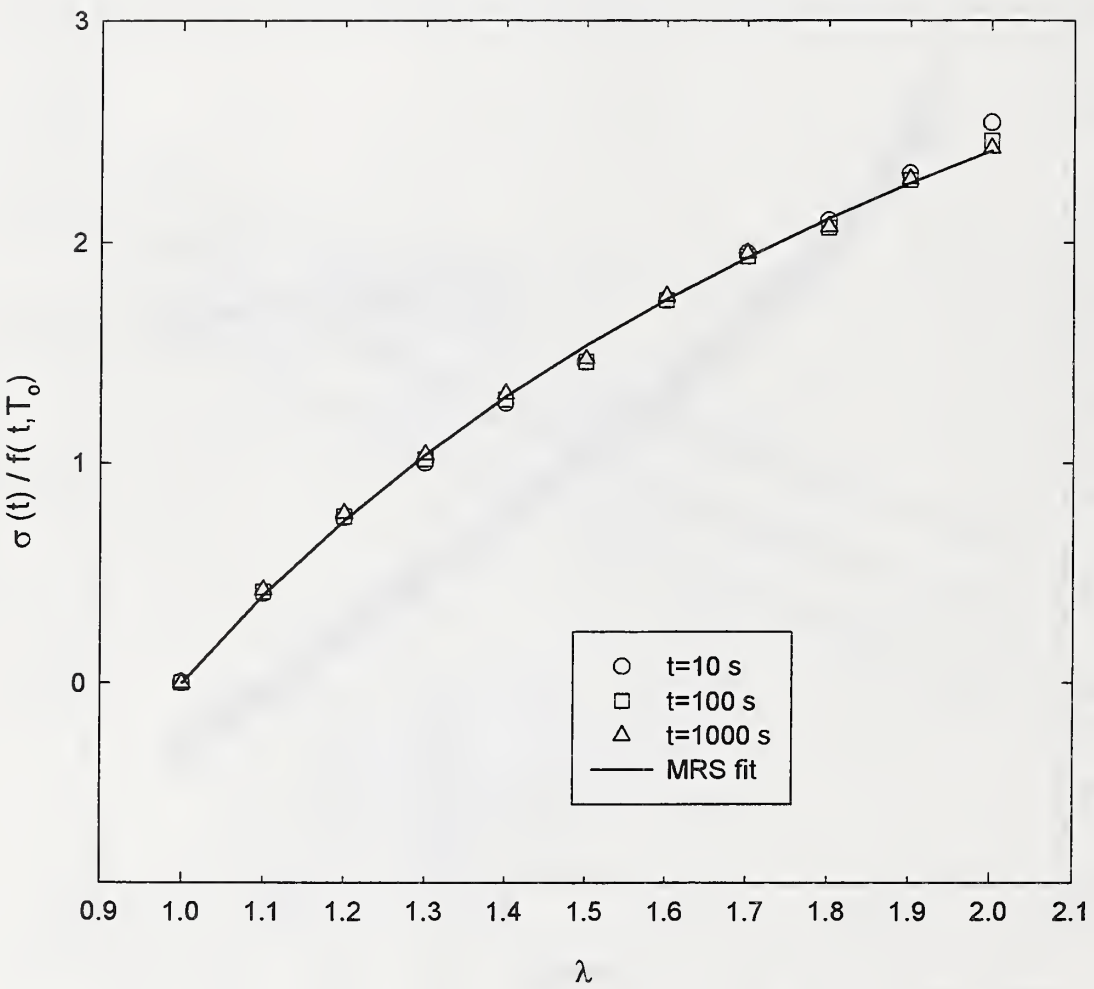

Figure 5: Comparison of normalized stress function vs deformation in tension with curve fit response given for the MRS equation. T_o=10°C.

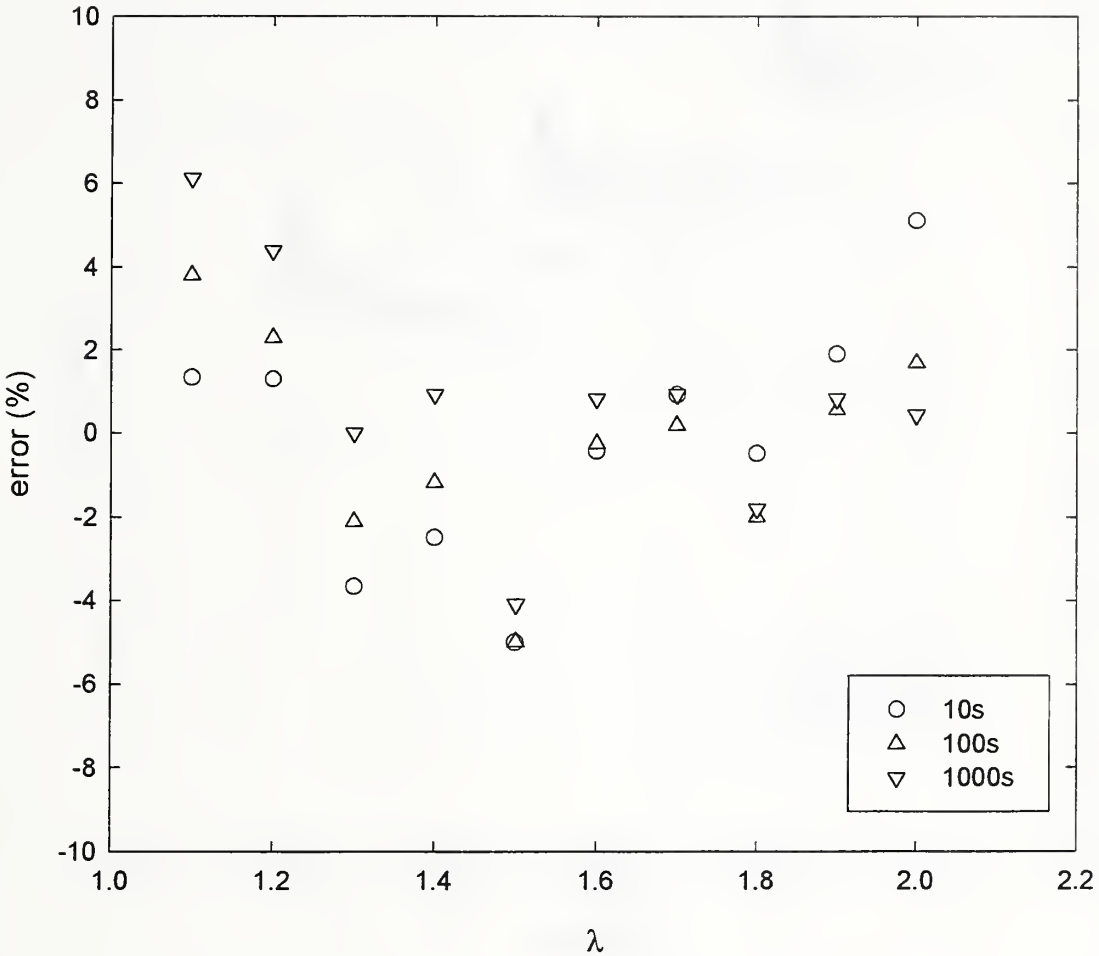

Figure 6: Residuals between normalized stress function (see text) and the MRS curve fit. Data are from Figure 5.

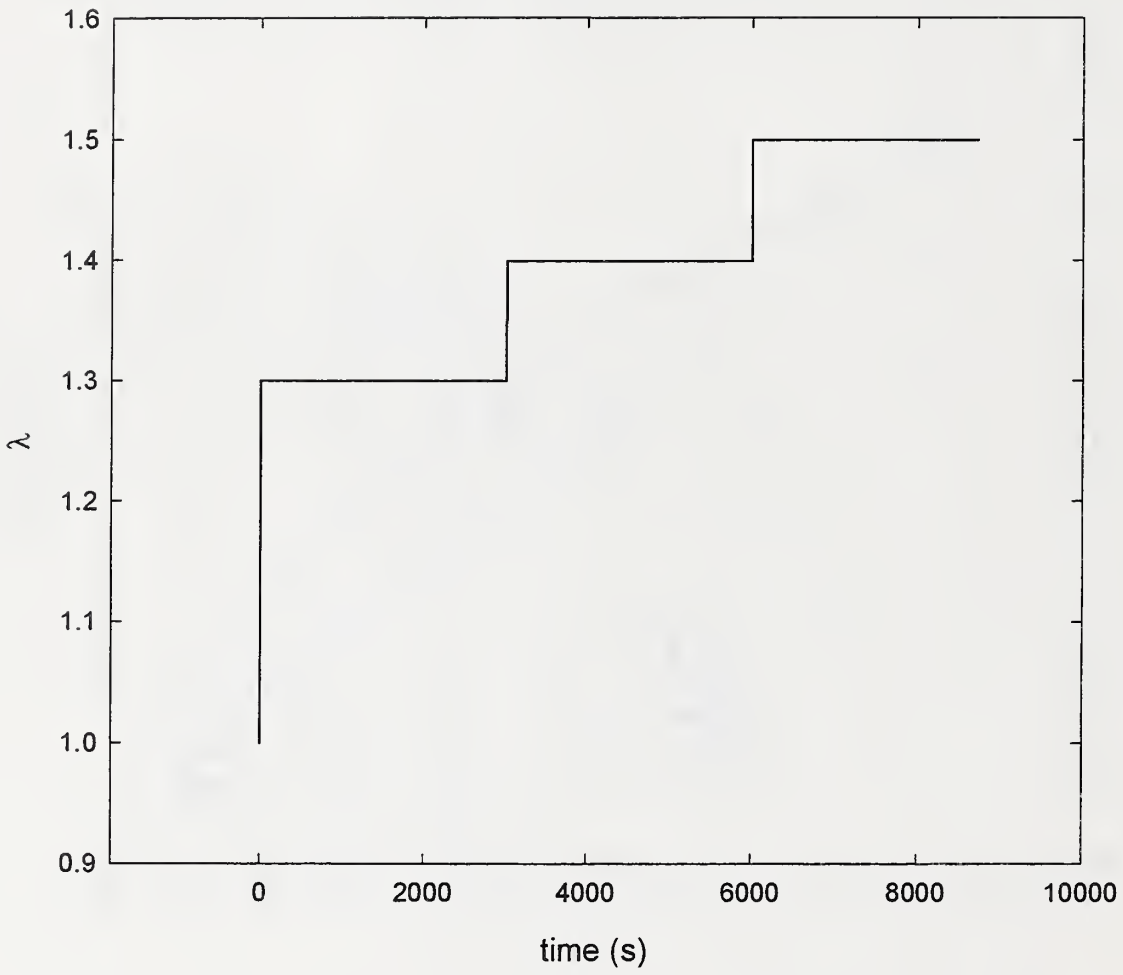

Figure 7: Strain versus time curve for a multiple step-up stress relaxation experiment. T=50°C.

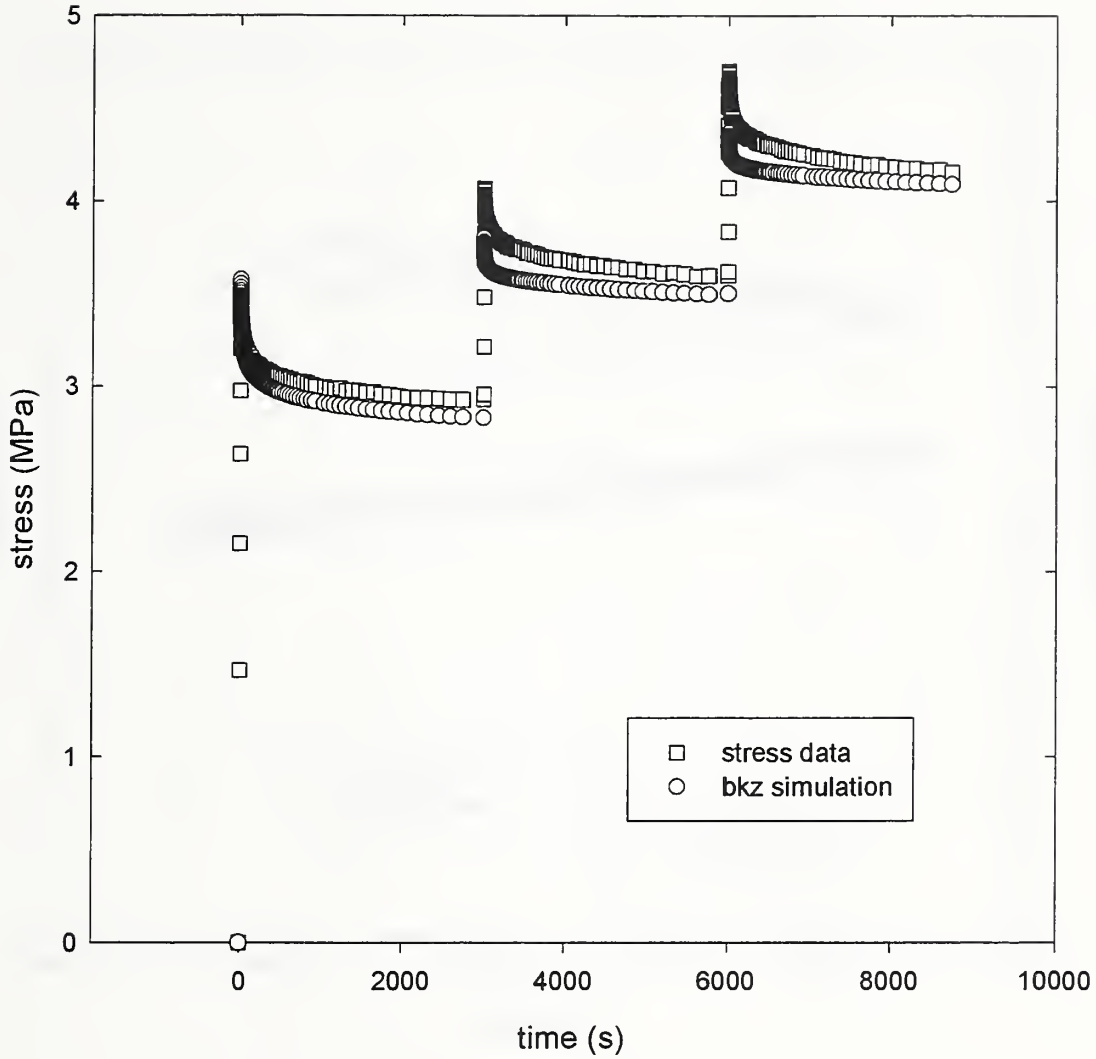

Figure 8: Stress versus time curve for a multiple step-up stress relaxation experiment T=50°C.

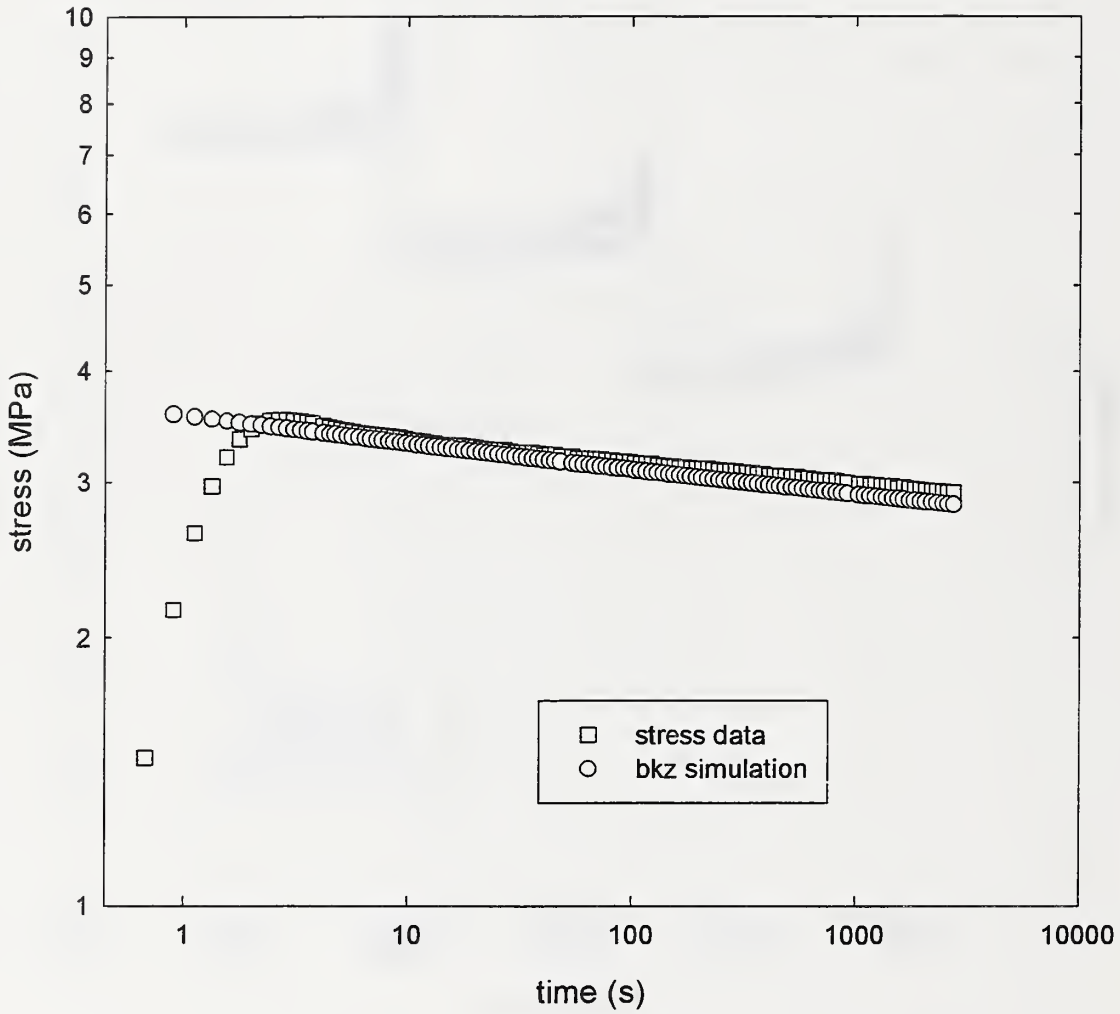

Figure 9: Log(stress) vs Log(time) curve for a multiple step stress relaxation experiment.
T=50°C.
STEP 1.

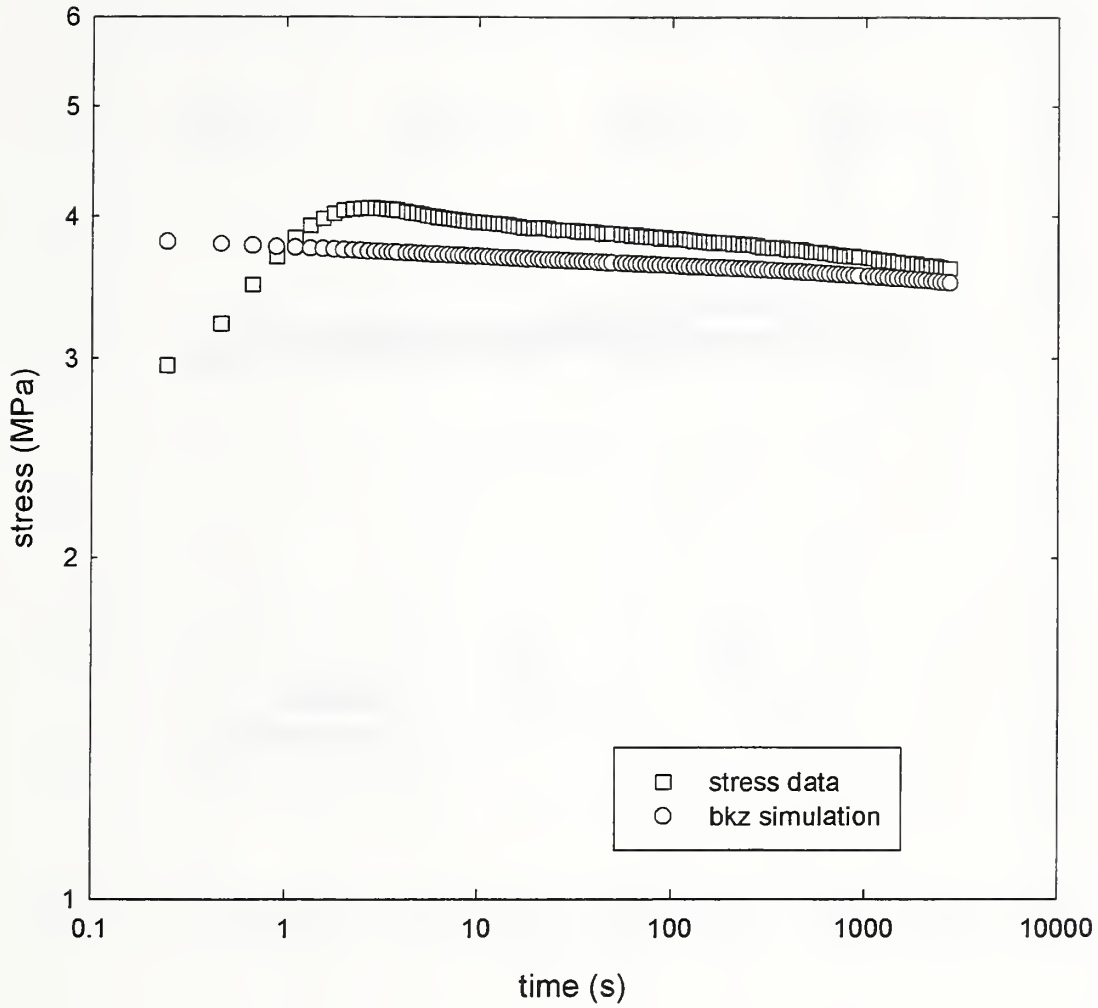

Figure 10: Log(stress) vs Log(time) curve for a multiple step-up stress relaxation experiment.
T=50°C.
STEP 2.

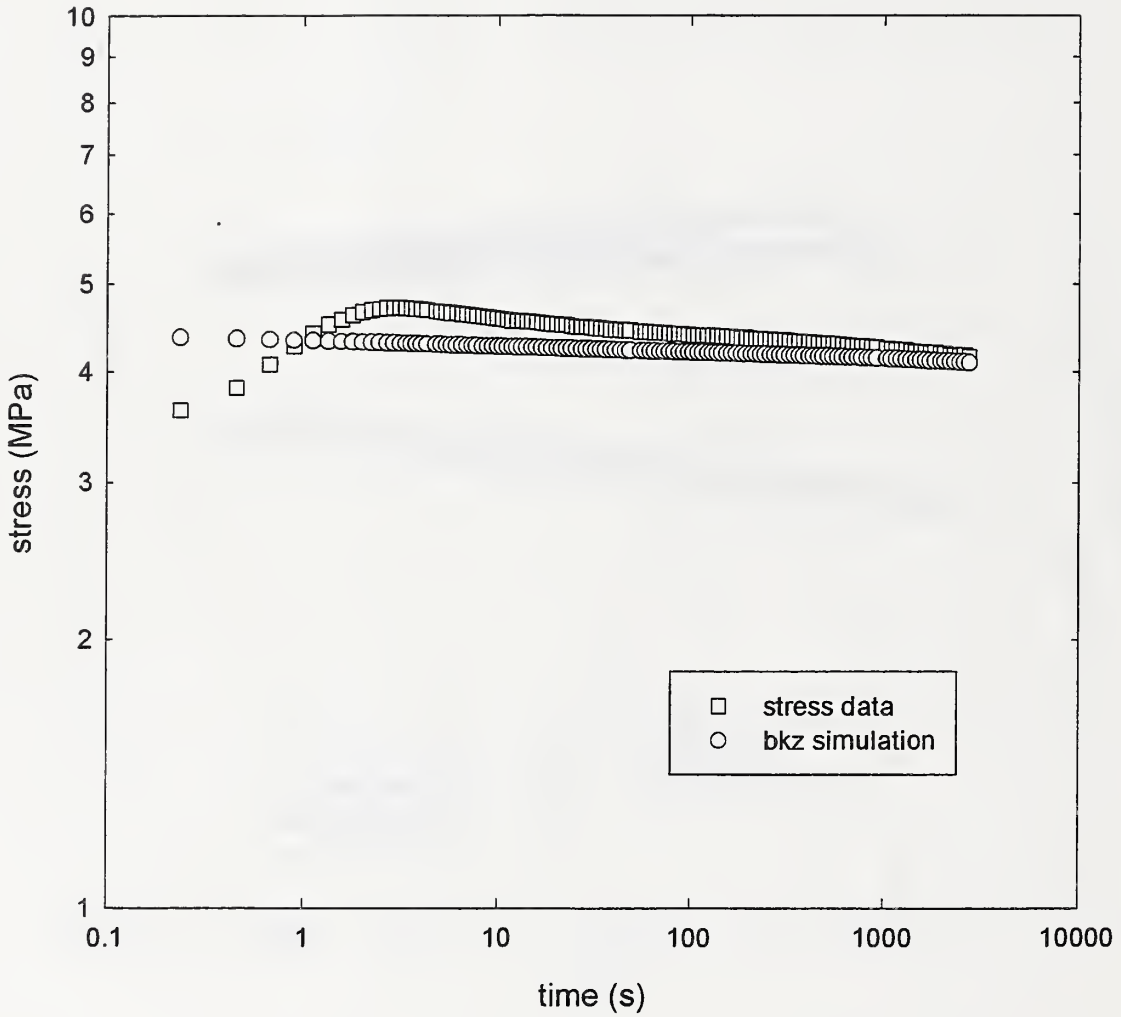

Figure 11: Log(stress) vs Log(time) curve for a multiple step-up stress relaxation experiment.
T=50°C.
STEP 3.

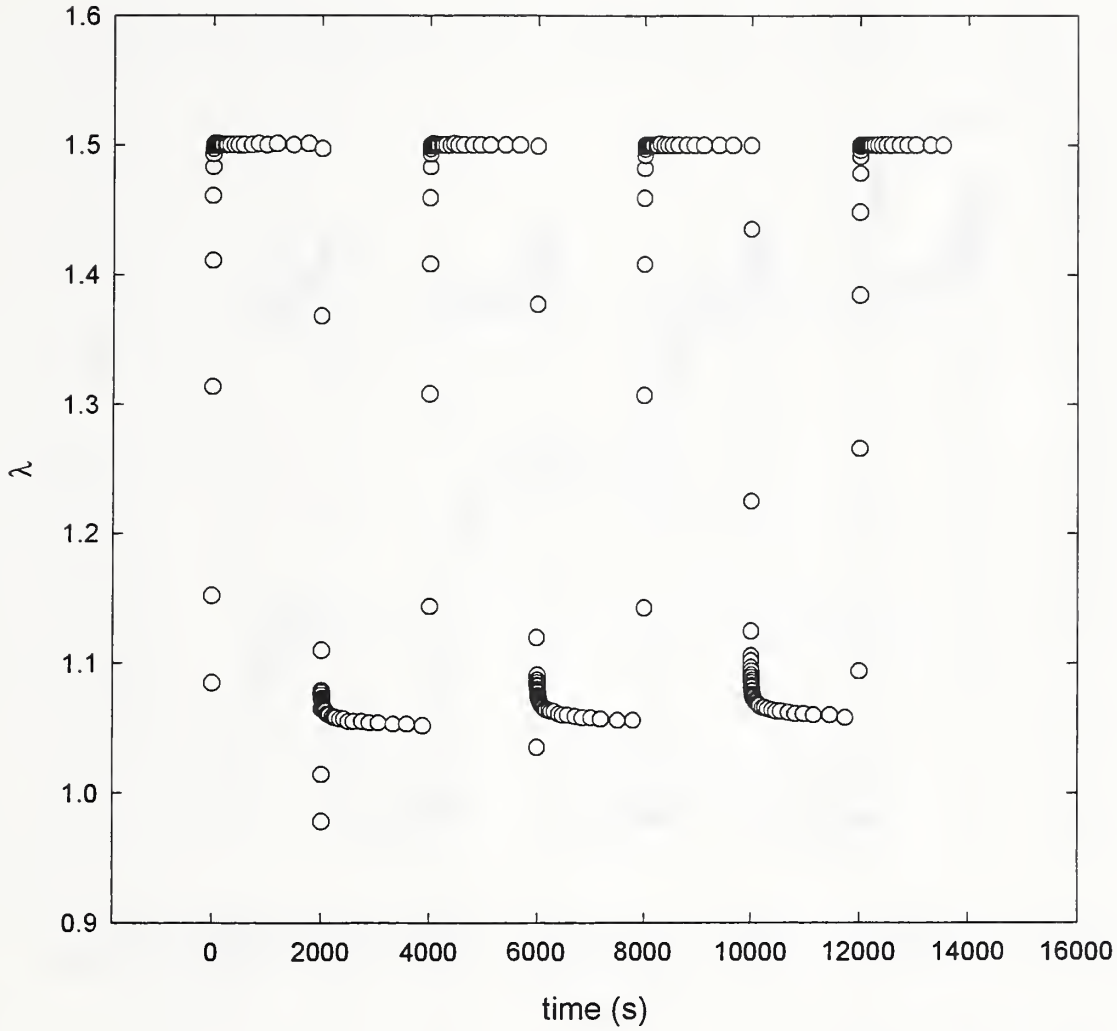

Figure 12: Strain versus time curve for a multiple stress relaxation cyle history. T=10°C.

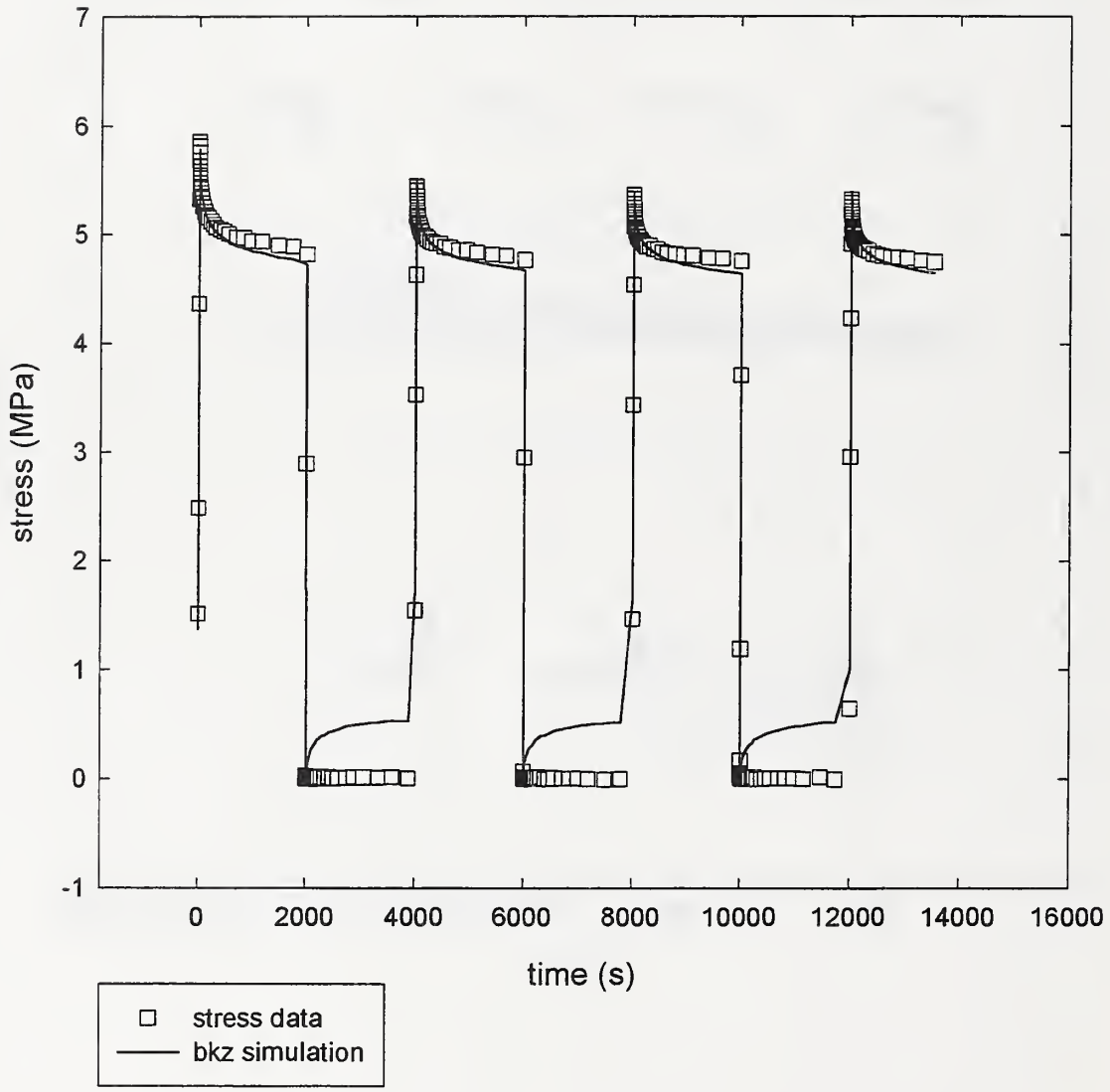

Figure 13: Stress versus time curve for the material response to multiple stress relaxation cycles.
T=10°C.

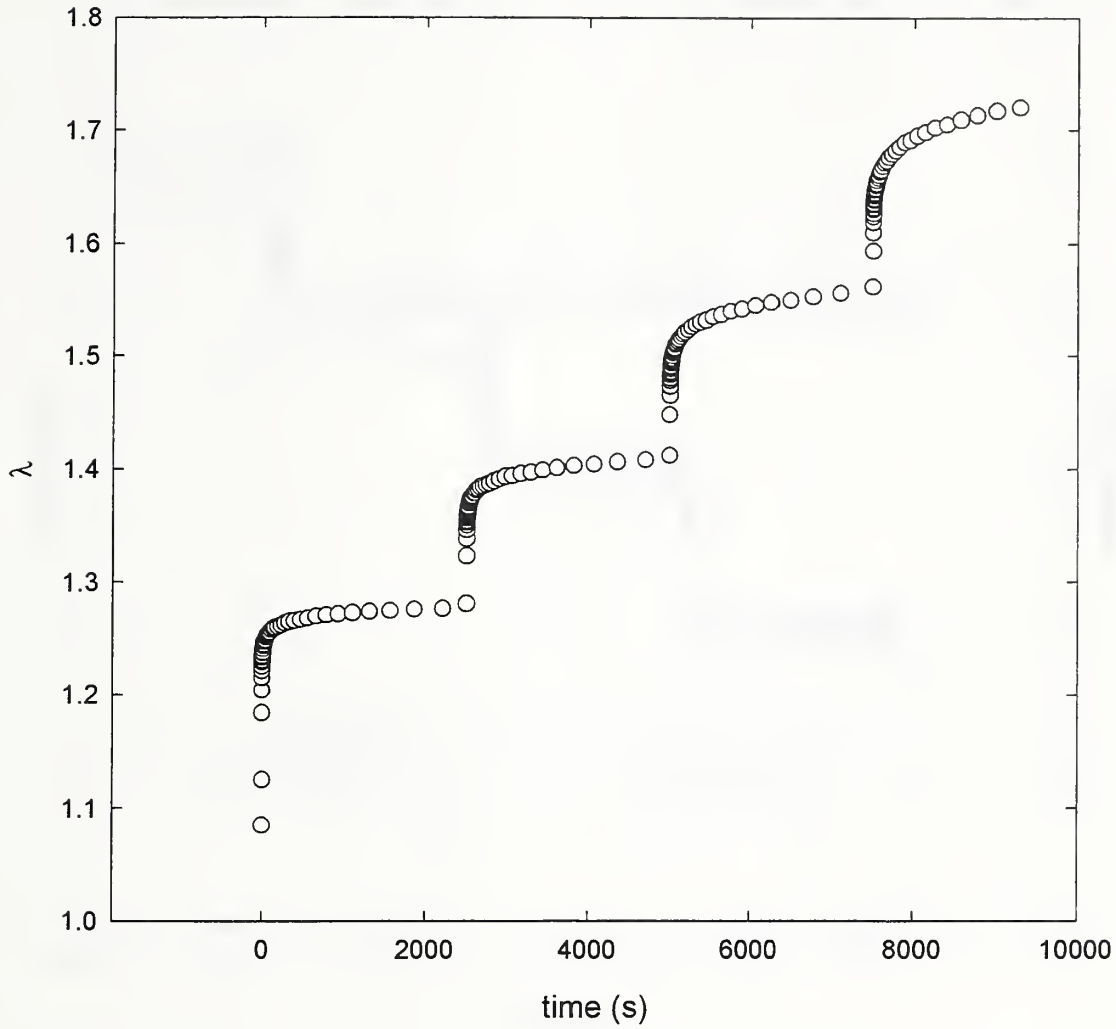

Figure 14: Strain versus time curve for a multiple step-up creep experiment. T=10°C.

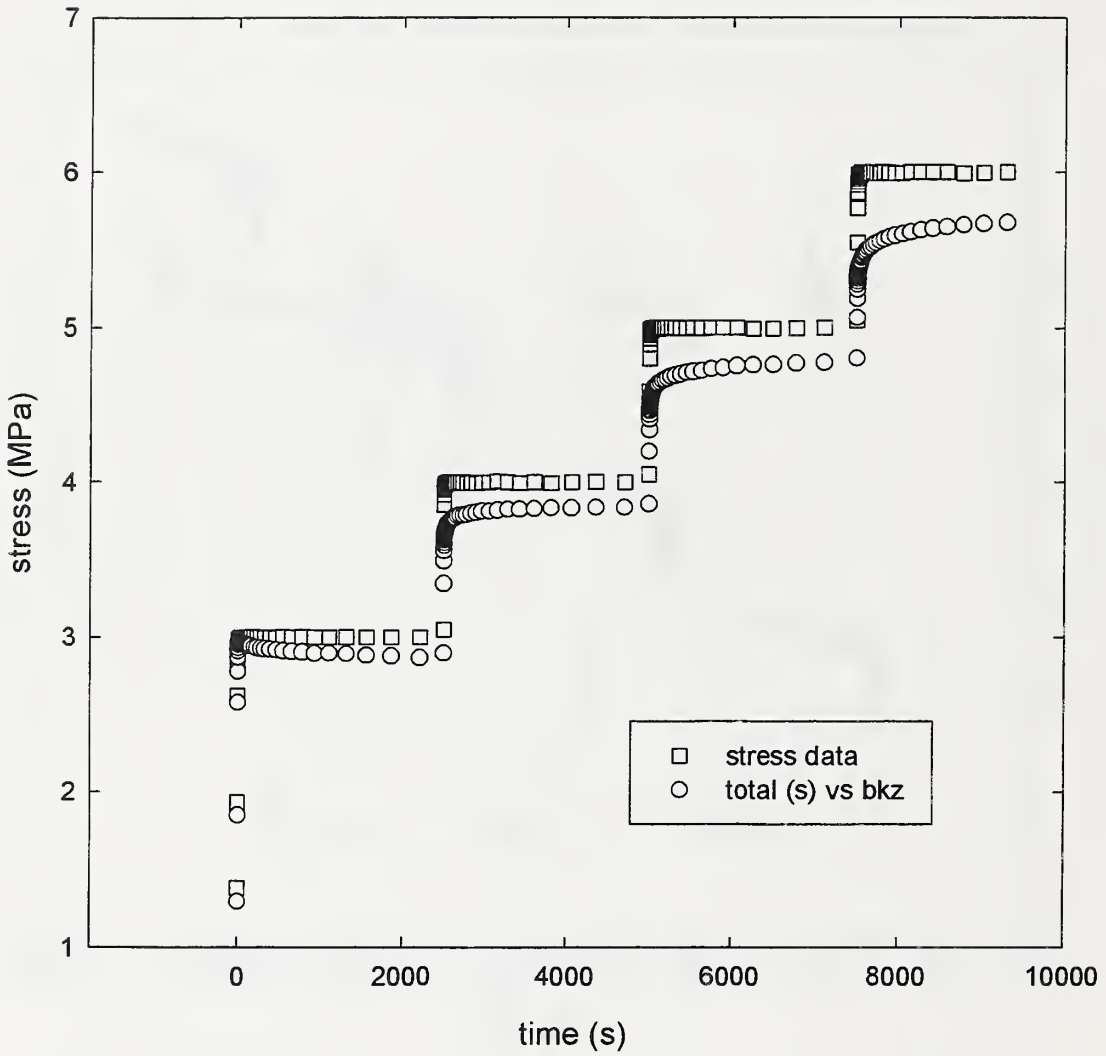

Figure 15: Stress versus time curve for a multiple step-up creep experiment T=10°C.

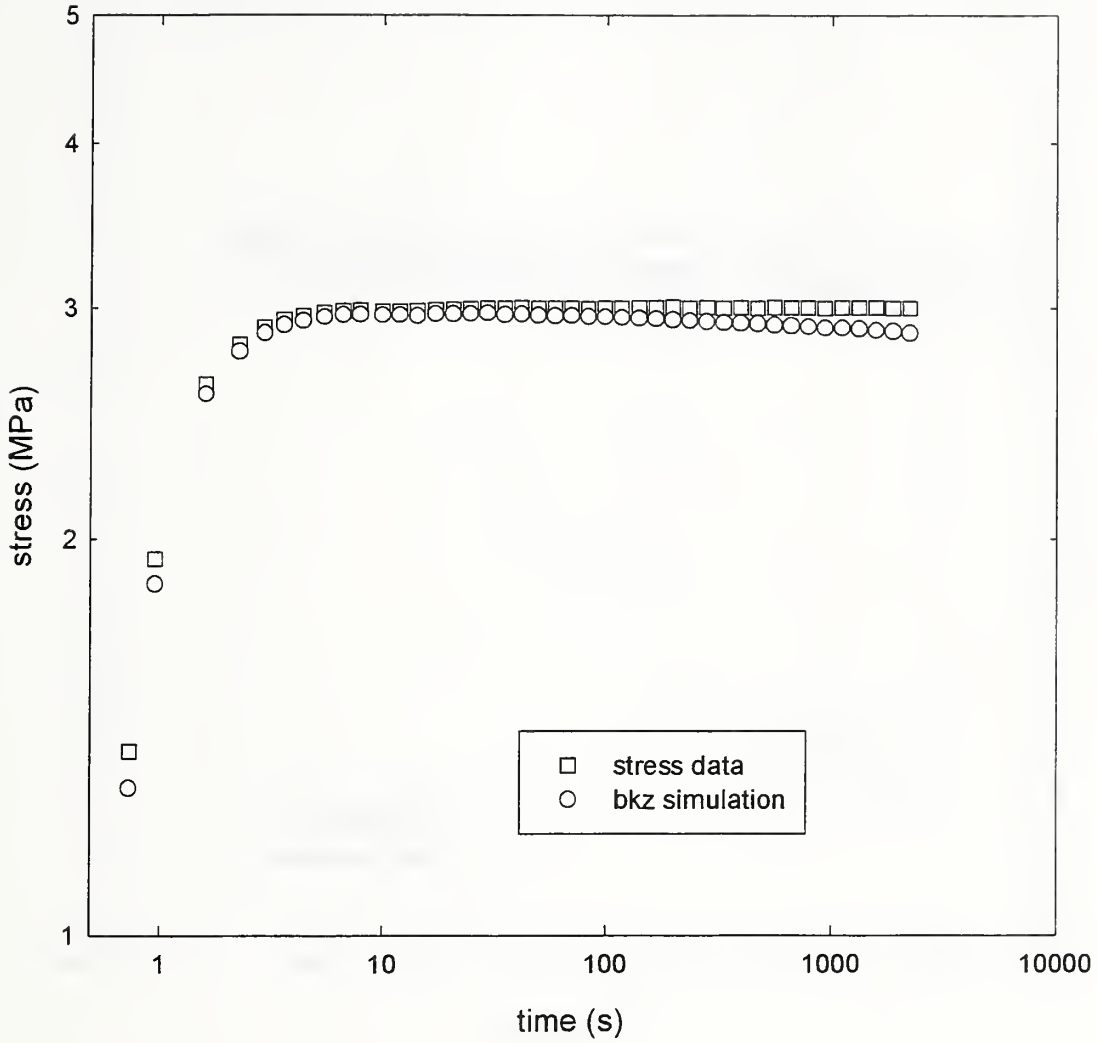

Figure 16: Log(stress) vs Log(time) curve for a multiple step-up creep experiment.
T=10°C.
STEP 1.

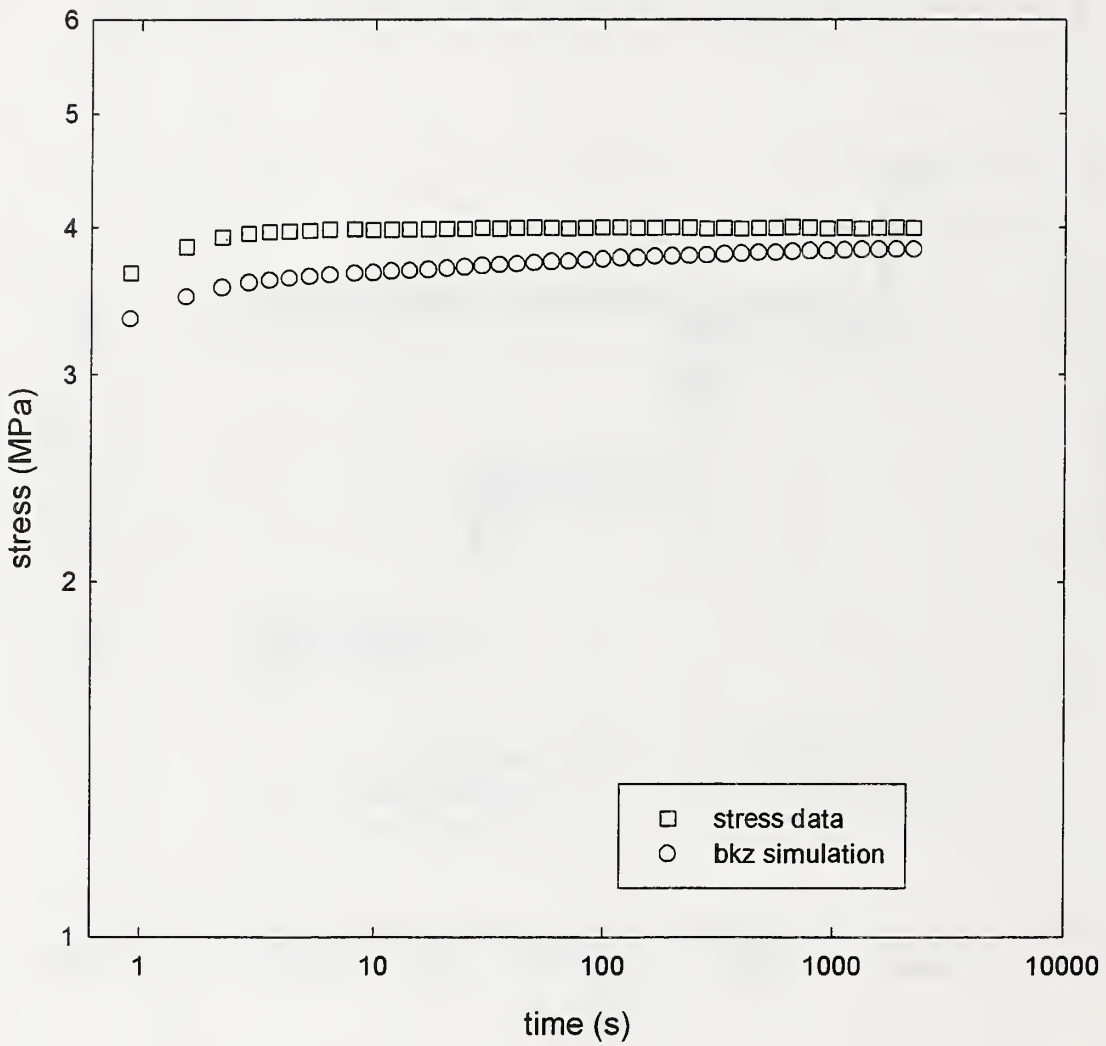

Figure 17: Log(stress) vs Log(time) curve for a multiple step-up creep experiment.
T=10°C.
STEP 2.

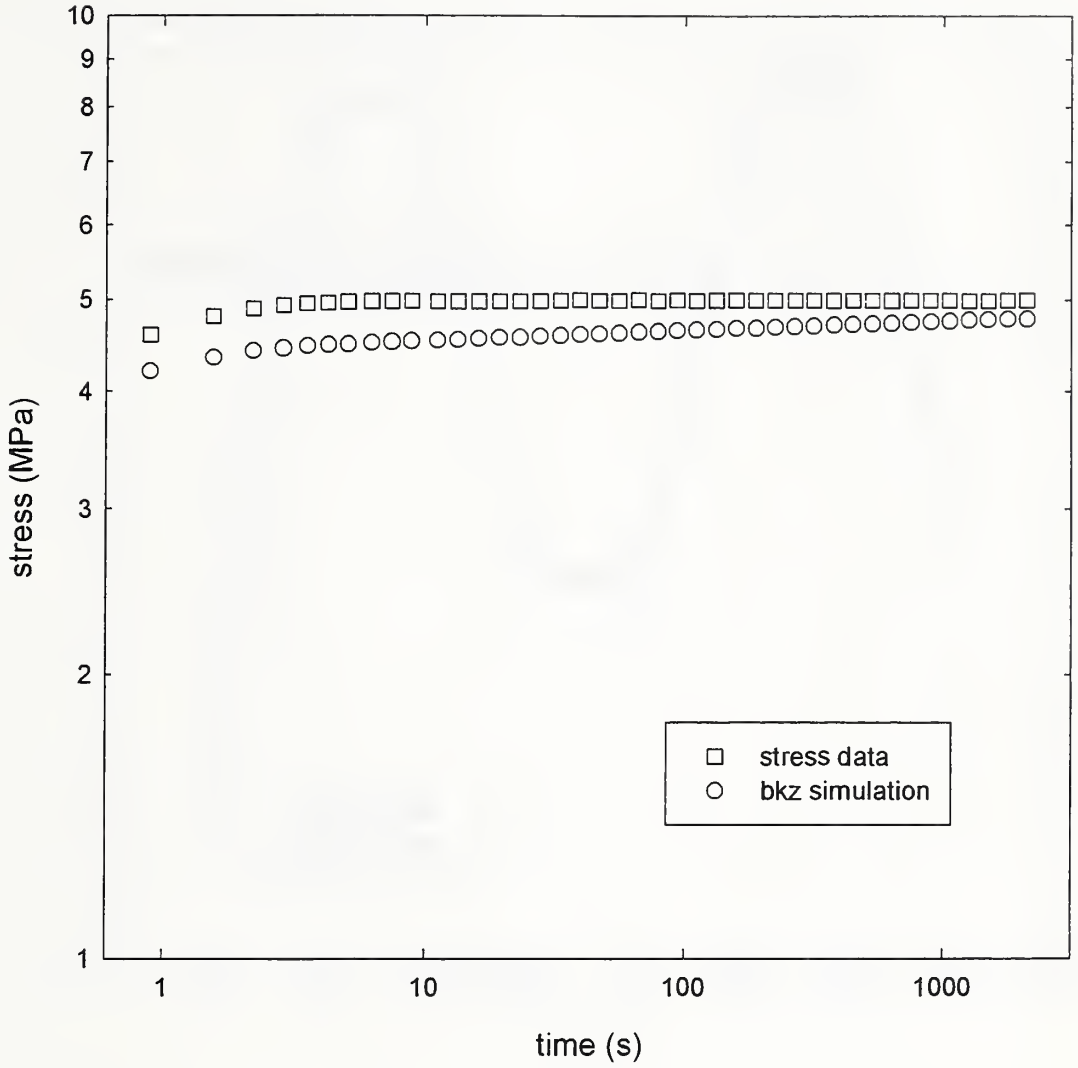

Figure 18: Log(stress) vs Log(time) curve for a multiple step-up creep experiment.
T=10°C.
STEP 3.

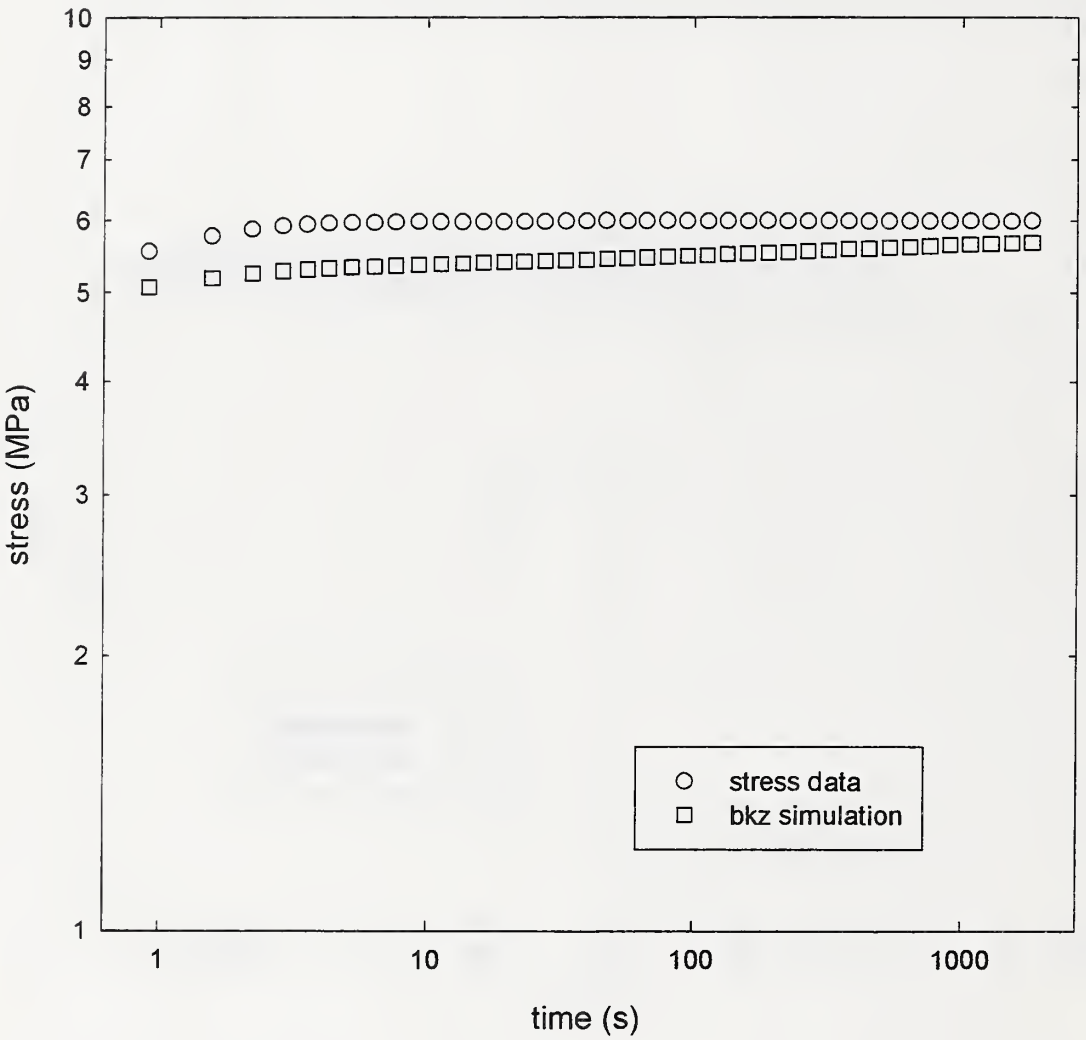

Figure 19: Log(stress) vs Log(time) curve for a multiple step-up creep experiment T=10°C.
STEP 4.

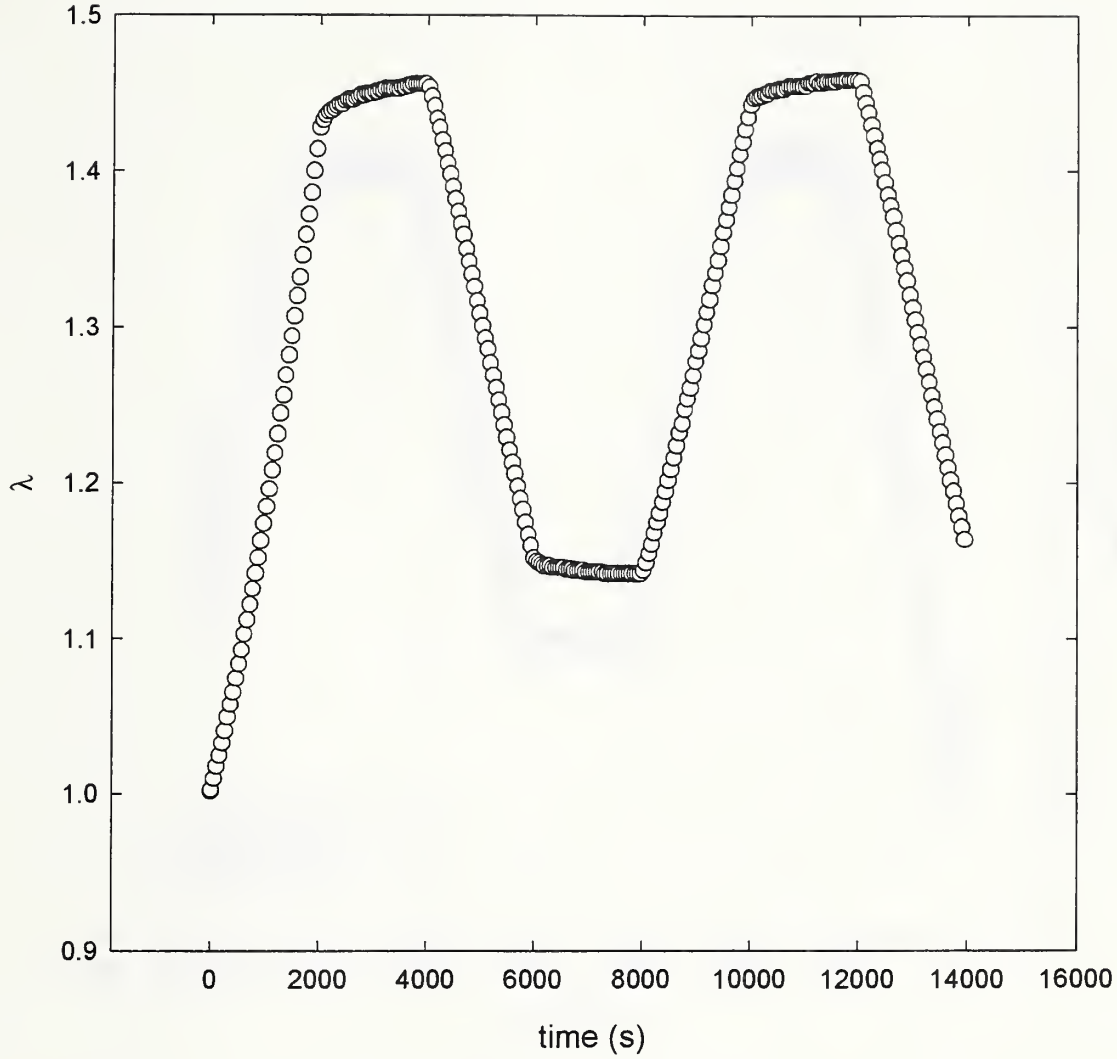

Figure 20: strain versus time vurve for a material response
to a trapezoidal-shaped stress history.
T=23°C

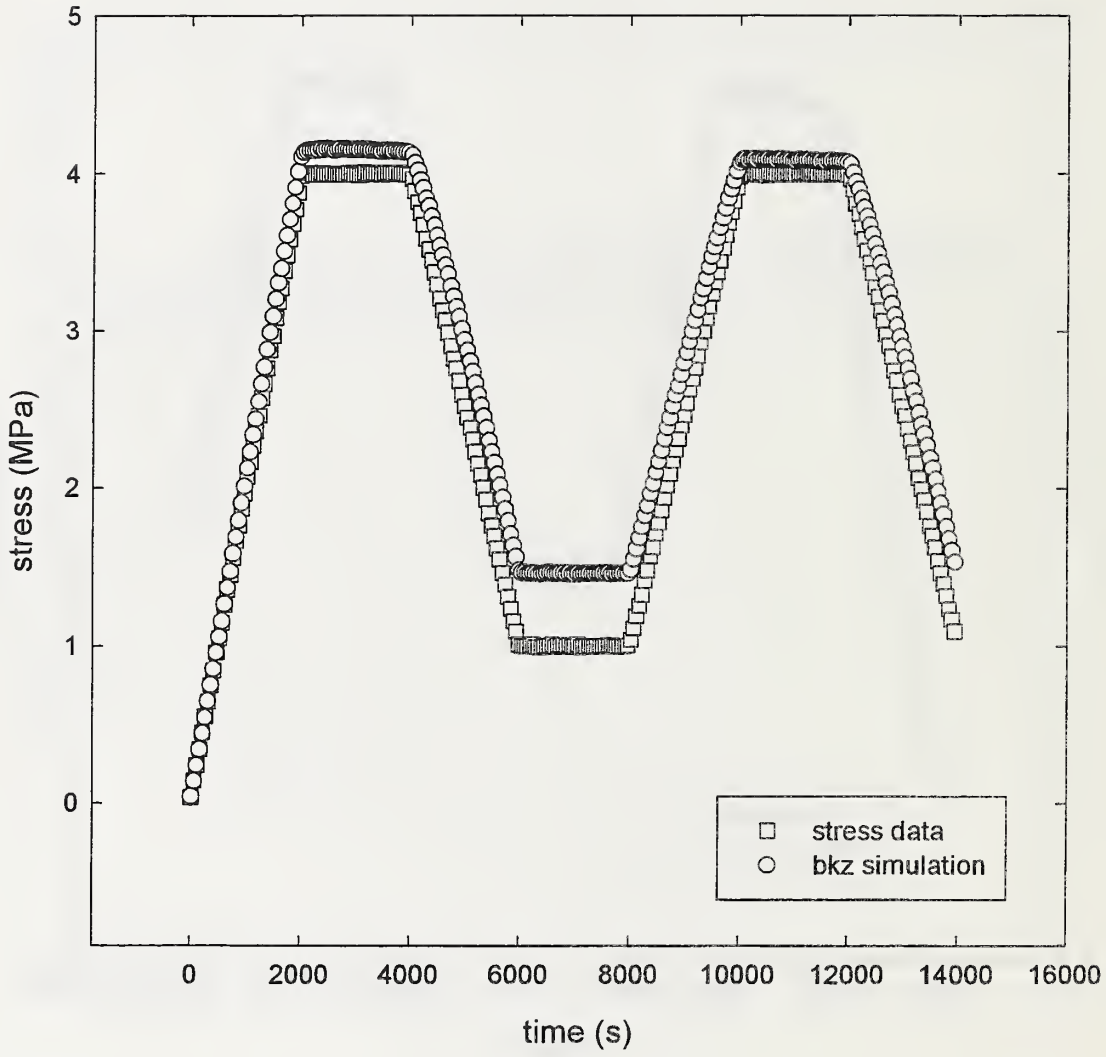

Figure 21: stress versus time curve for a material response to a trapezoidal-shaped stress history.
T=23°C.