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Rate-Dependent Stress–Strain Behavior of Polymeric Materials

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Synopsis

The investigation characterizes the rate-dependent uniaxial stress–strain behavior of several polymeric materials. The characterization is done using both a mechanical model with rate-dependent elements and a general nonlinear theory of viscoelasticity. Experimental data were gathered on a Laminac polyester resin, and further data on polycarbonate and PMMA were collected from the work of Brinson. The mechanical model could be called a modified Bingham type, while the nonlinear viscoelastic theory was the single integral constitutive model proposed by Bernstein, Kearsley, and Zapas. Results from the mechanical model gave good agreement with the experimental data, the maximum difference being about 10%. The BKZ theory predictions modeled the data to within 5–12% average error.

INTRODUCTION

A review of the literature indicates that there have been many theoretical studies pertaining to the linear viscoelastic behavior of polymeric materials. The linear infinitesimal theory of viscoelasticity is well formulated and has been successfully used with experimental data for the determination of needed theoretical material parameters. In comparison, however, nonlinear viscoelastic behavior at finite strains, being more difficult to model, has had relatively few successful characterization studies. The difficulty with nonlinear viscoelastic modeling lies in finding a suitable constitutive model which will allow a straightforward experimental determination of the model material parameters.

McLellan[1] used a phenomenological constitutive equation to describe conventional stress–strain behavior for several metallic and nonmetallic materials. His constitutive equation is based on the Ramberg-Osgood equation for describing stress–strain curves.

Soden and Sowerby[2] were able to predict all the important features of tensile stress–strain curves of commercially pure lead and cellulose nitrate, using creep test data. Their description included the dependence of the stress–strain curve upon extension rate.

A spring-dashpot model proposed by Haward and Thackray[3] has been used to describe the isothermal stress–strain curves of certain high polymers. Chase and Goldsmith[4] considered a nonlinear, four-parameter, elastic-viscoplastic model to describe the mechanical behavior of a polyester–styrene co-

polymer. Their model covers a range of seven decades of strain rate and strains up to 40%.

Brinson and DasGupta[5] used a mechanical model of the Bingham type to predict the stress–strain–strain rate behavior of polycarbonate for any individual strain rate. The same type of model was used by Chander[6] to characterize the stress–strain behavior of a polyester material for arbitrary strain rates. More recently, the same results as those of Chander have been found by Brinson, Renieri, and Herakovich.[7] Both Chander[6] and Brinson et al.[7] show that the Bingham model elements follow a semilog relationship.

Fitzgerald and Vakili[8] demonstrate that Pth order Lebesgue norms may be used for the nonlinear characterization of sand–asphalt concrete. Agreement between theory and experiment is very good for relaxation tests, constant strain-rate tests, and interrupted- and reverse-ramp strain tests.

Several nonlinear integral constitutive models have been used to predict uniaxial behavior of polymers, e.g., Ward and Onat,[9] Pipkin and Rodgers,[10] and Bernstein, Kearsley, and Zapas.[11,12] Of primary importance in using nonlinear constitutive relations is the experimental determination of the material constants and/or functions used in the particular theory. For nonlinear materials with memory, such a determination can often be quite complex. Because of its relative simplicity and past success, the single integral model proposed by Bernstein, Kearsley, and Zapas (hereinafter referred to as BKZ) will be one of the constitutive relations used in the present analysis. Experimental verification[13,14] and productive mathematical analyses have proven this theory to be very worthwhile.

The purpose, then, of this investigation is to characterize the rate-dependent uniaxial stress–strain behavior of several polymeric materials. Characterization is done using both a mechanical model with rate-dependent elements as originally developed by Chander[6] and Brinson[7] and the nonlinear BKZ theory of viscoelasticity. Modeling success is measured by the ability of the model to predict experimental stress–strain data at various strain rates.

EXPERIMENTAL PROGRAM

The experimental program consisted of constant head-(strain)-rate and relaxation tests on a polyester polymeric material marketed in the United States by American Cyanamid under the trade name Laminac. The material tested consists of 60% flexible (Laminac EPX-126-3) and 40% rigid (Laminac 4116) resins. All tests were performed under controlled environmental conditions of approximately 70°F and 50% relative humidity.

Constant strain-rate tests were performed with a tensile machine capable of controlled head rates. Load measurements were made with a load cell and recorded on one channel of a dual-channel recorder.

Strain measurements were made by recording cross-head position of the testing machine on the second channel of the recorder, as a function of time. The relationship between strain and cross-head position was determined by calibration. The calibration procedure consisted of measuring the distance between finely scribed transverse lines on a tensile specimen as a function of screw rotation. A traveling microscope was used for distance measurements. By employing the definition of strain, it was possible to relate rotation to

strain. Numerous tests were run, and it was established that a linear relationship existed between strain and rotation for the long, slender, tensile specimens being used.

Since strain and load were recorded simultaneously as a function of time, it was possible to eliminate time as a factor in the mechanical characterization tests.

Relaxation tests were conducted using the same machine as previously discussed, with a slight modification. Load was applied to the tensile specimen by means of a lever and weight. Different values of constant deformation were attained by adjusting the vertical screw of the testing machine. Practically instantaneous deformation was attained by lowering weights on a pan attached to the lever. A load cell and digital voltmeter gave load as a function of time. Strain measurements were made using a traveling microscope to measure the distance between finely scribed transverse lines on a tensile specimen, both before and after application of weights.

The one-dimensional stress–strain data[6] shown in Figure 1 indicate that the mechanical behavior is initially linear, followed by a region of nonlinear viscoelastic behavior, and finally extends to a region of almost perfectly plastic flow. This particular type of behavior motivates the selection of the mathematical mechanical model shown in Figure 2.

Typical relaxation results are shown in Figure 3. Relaxation tests consisted of strains ranging from the linear portion of the stress–strain curves (0.5%) to the region of almost perfectly plastic flow (6%). Subjecting the tensile specimens to larger strains resulted in brittle fracture. This relaxation data

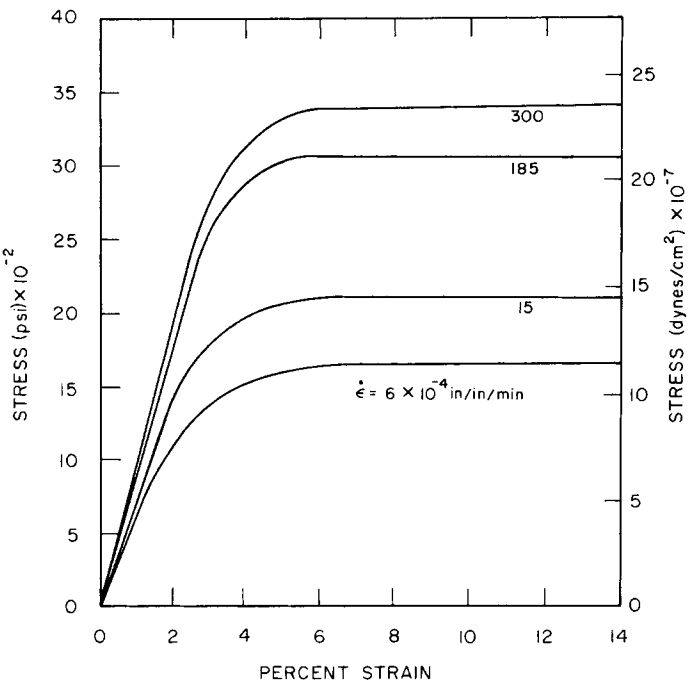

Fig. 1. Experimental stress–strain data of polyester resin.

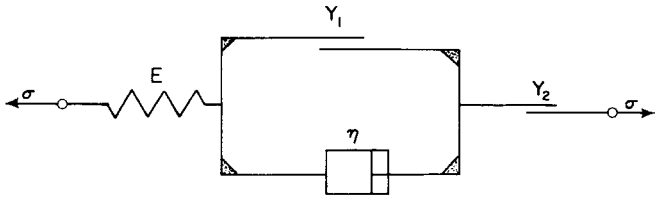

Fig. 2. Mechanical model of Bingham type

is to be used in determining material parameters needed in the BKZ theory of viscoelasticity.

MODIFIED BINGHAM MODEL

The first of two analytical techniques used to match the experimental data employs the use of the mechanical model shown in Figure 2. The model, which would be called a modified Bingham type, is composed of an elastic element with modulus E, a viscous element with viscosity η, and rigid, perfectly plastic elements with yield values Y_1 and Y_2. This model qualitatively gives the elastic, viscoelastic, and perfectly plastic behavior found in the experimental data in Figure 1. Brinson and DasGupta[5] employed this model for fixed element parameters E, η, Y_1, and Y_2 to predict the behavior of polycarbonate. Chander[6] and Brinson et al.[7] also employed this model with rate-dependent elements. In addition, Chase and Goldsmith[4] have used a similar model with rate-dependent element parameters to model polyester copolymer data.

The stress–strain relationship predicted by this model is given by

$$\sigma = E\epsilon;\ \sigma < Y_1$$

$$\frac{\eta}{E}\dot{\sigma} + \sigma = Y_1 + \eta\dot{\epsilon};\ Y_1 \leq \sigma < Y_2 \tag{1}$$

$$\sigma = Y_2;\ \epsilon > \epsilon_y$$

where ϵ_y is the yield strain at the initiation of perfectly plastic flow. The solution of eq. $(1)_2$ for the constant strain rate case is

$$\sigma = Y_1 + \eta R\left\{1 - \exp\left[-\frac{E}{\eta R}(\epsilon - \epsilon_0)\right]\right\} \tag{2}$$

where $\dot{\epsilon} = R$ = constant, and $\epsilon_0 = Y_1/E$.

In order to adequately predict the stress–strain behavior shown in Figure 1, the parameters E, η, Y_1, and Y_2 must be taken to be rate dependent, i.e., they must be functions of the strain rate R. The elastic modulus E, the two yield stresses Y_1 and Y_2, and the yield strain ϵ_y were empirically determined as functions of the strain rate from the stress–strain data. With these parameters known, eq. (2) may be employed at the perfectly plastic point ($\sigma = Y_2$ when $\epsilon = \epsilon_y$) to generate an expression which can be solved numerically to determine η as a function of R. The results are

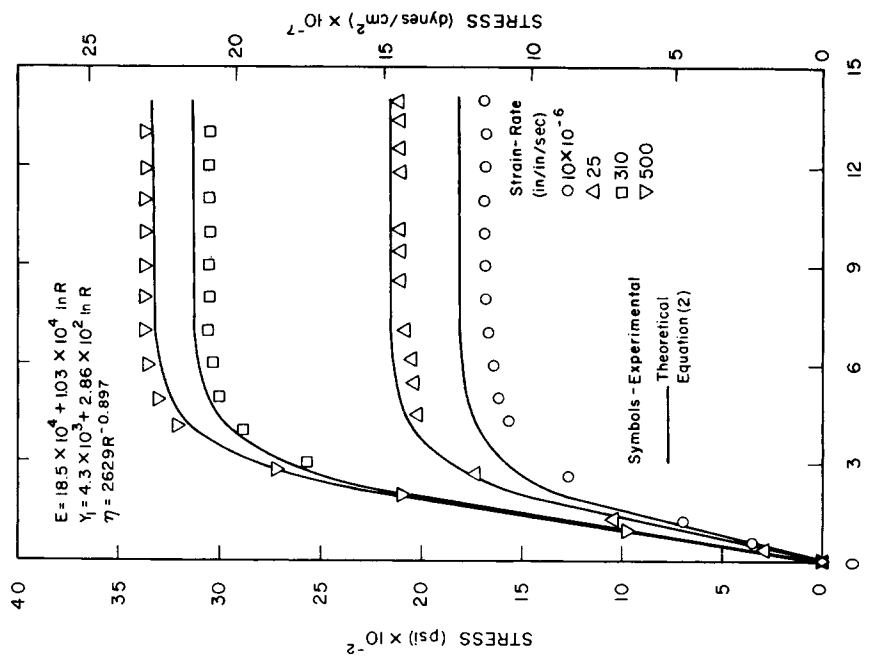

Fig. 4. Comparison between mechanical model and experimental data for polyester: E in psi, Y_1 in psi, and η in psi/sec.

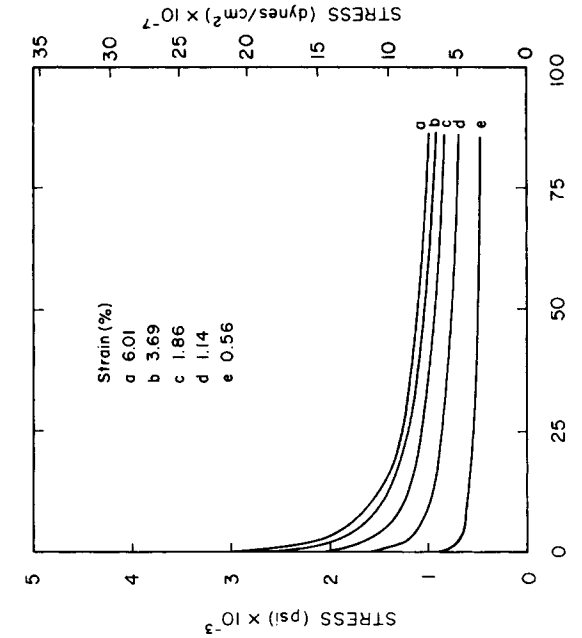

Fig. 3. Stress relaxation data of polyester resin.

$$E = E_0 \ln R + E_{00}$$
$$Y_1 = Y_{10} \ln R + Y_{100} \tag{3}$$
$$Y_2 = Y_{20} \ln R + Y_{200}$$
$$\eta = \eta_0 R^m$$

where E_0, E_{00}, Y_{10}, Y_{100}, Y_{20}, Y_{200}, η_0, and m are constants whose numerical values will be given in subsequent figures.

It turns out that eq. (2) models the data even for $\epsilon > \epsilon_y$, since $\exp [- E/\eta R (\epsilon - \epsilon_0)] \ll 1$ for $\epsilon > \epsilon_y$. Hence, eq, (1c) is actually not used for the present study. A comparison between the experimental polyester data and the analytical model is shown in Figure 4. Good agreement between theory and experiment is found, with the maximum error being about 10%.

The constitutive eqs. (1) and (2) were also used to predict the stress–strain behavior of polycarbonate and poly(methyl methacrylate) (PMMA). Experimental data from Brinson[5] were used to determine the empirical relation-

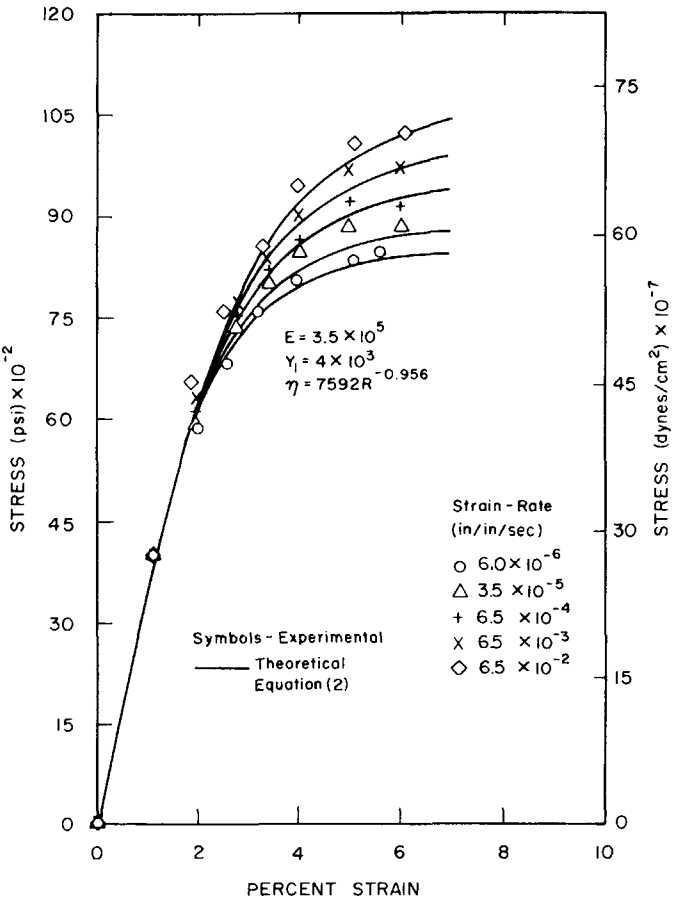

Fig. 5. Comparison between mechanical model and experimental data for polycarbonate: E in psi, Y_1 in psi, and η in psi/sec.

ships for E, Y_1, Y_2, and η. The correlation between theory and experiment for these two materials is shown in Figures 5 and 6. Again, it can be seen that good agreement is obtained, indicating that the nonlinear mechanical model is also valid for other polymeric materials.

NONLINEAR BKZ MODEL

Realizing the limitations and short comings of a mechanical model, the stress–strain data were also modeled using a nonlinear theory of viscoelasticity. The particular theory which was used is the single integral constitutive model proposed by Bernstein, Kearsley, and Zapas.[11,12] This BKZ theory, in addition to modeling non-Newtonian solutions and melts, can also model bulk polymers.

The incompressible, isotropic, and isothermal form of this theory relates the stress σ at time t to the past history of the strain through the expression

$$\sigma = -pI + 2\int_{-\infty}^{t}\left[\frac{\partial U}{\partial I_1}\mathbf{C}_t^{-1}(\tau) - \frac{\partial U}{\partial I_2}\mathbf{C}_t(\tau)\right]d\tau \tag{4}$$

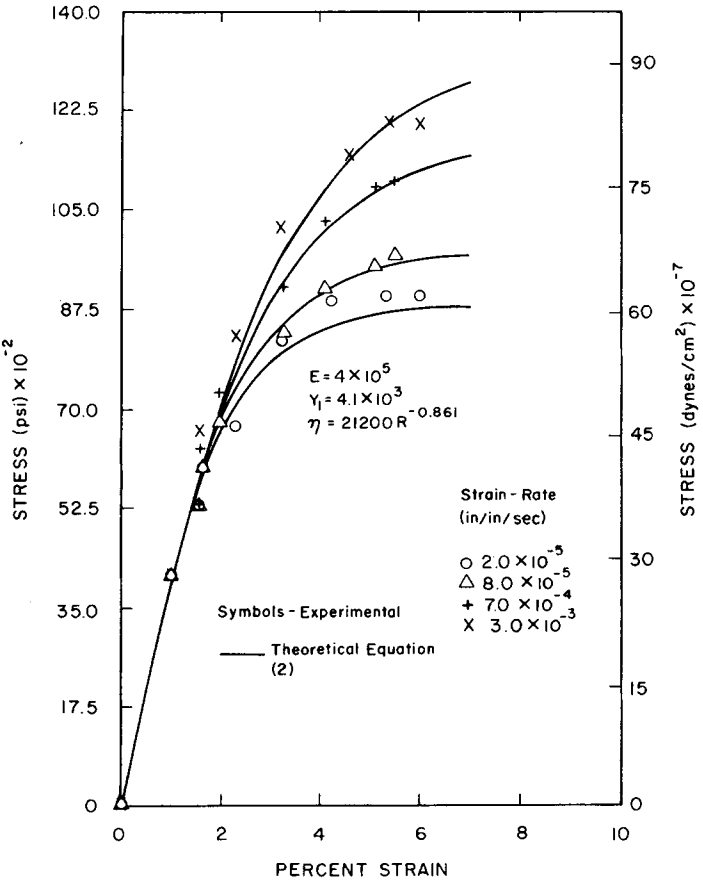

Fig. 6. Comparison between mechanical model and experimental data for PMMA: E in psi, Y_1 in psi, and η in psi/sec.

where p is the hydrostatic pressure, $\boldsymbol{I}$ is the unit tensor, $\boldsymbol{C}_t$ is the relative right Cauchy-Green strain tensor, $(\,)^{-1}$ indicates the inverse, and U is a material function which depends on the time τ and the two invariants of the strain tensor I_1 and I_2, with

$$I_1 = \text{tr } \boldsymbol{C}_t^{-1}(\tau)$$
$$I_2 = \text{tr } \boldsymbol{C}_t(\tau) \tag{5}$$

where tr is the trace operation.

For the uniaxial strain case under consideration, the stress along the direction of stretch follows from eq. (4) to be[12]

$$\sigma(t) = \int_{-\infty}^{t} \left[\frac{\lambda^2(t)}{\lambda^2(\tau)} - \frac{\lambda(\tau)}{\lambda(t)}\right] h\left(\frac{\lambda(t)}{\lambda(\tau)}, t-\tau\right) d\tau \tag{6}$$

where λ is the principal extension ratio and is related to the infinitesimal strain by $\lambda = 1 + \epsilon$, and h is a material function defined by

$$h\left(\frac{\lambda(t)}{\lambda(\tau)}, t-\tau\right) = 2\left[\frac{\partial U}{\partial I_1} + \frac{\lambda(\tau)}{\lambda(t)}\frac{\partial U}{\partial I_2}\right]. \tag{7}$$

An important, useful result concerning this theory is found in the single-step stress relaxation situation, i.e.,

$$\lambda(t) = \begin{cases} 1; t < 0 \\ \lambda; t > 0 \end{cases}. \tag{8}$$

For this case, the stress is given by

$$\sigma(t) = \left(\lambda^2 - \frac{1}{\lambda}\right) H(\lambda,t) \tag{9}$$

where

$$H(\lambda,t) = \int_t^{\infty} h(\lambda,\xi)d\xi$$

and so

$$h(\lambda,t) = -\frac{\partial H(\lambda,t)}{\partial t}. \tag{10}$$

Equations (9) and (10), then, imply the important result that data from a stress relaxation experiment allow the determination of the material function h and hence allow the calculation of the stress response to any other deformation history in the same uniaxial geometry.

Using the preceding characterization concept, stress relaxation data were gathered on the polyester resin under study (see Fig. 3). These data are replotted in Figure 7 using the reduced stress, $\sigma_R = \sigma/(\lambda^2 - 1/\lambda)$, as the ordinate; hence, by eq. (9) the material function $H(\lambda,t)$ is actually plotted. An empirical curve was fitted to the data by a least-squares computer routine using the form

$$H(\lambda,t) = \frac{1}{a(\lambda) + b(\lambda)t^n} \tag{11}$$

where $a(\lambda)$ and $b(\lambda)$ are functions of the strain alone, and n is a constant.

For each relaxation curve, the best a and b were determined for n = constant. Then, by plotting a and b versus λ, the functional dependence of the strain was found. The results are

$$a(\lambda) = A_1 e^{-A_2(\lambda-1)} + A_3$$
$$b(\lambda) = B_1\lambda + B_2 \tag{12}$$
$$n = .23$$

where A_1, A_2, A_3, B_1, and B_2 are constants. The curve fitting was done with a maximum error of about 1.5%. Since the determination of $h(\lambda,t)$ requires the differentiation of $H(\lambda,t)$, it is important to fit the data as close as possible.

With the material function $h(\lambda,t)$ now determined, attention is directed toward predicting the stress–strain curves. These curves correspond to the situation of constant rate of strain following rest history, i.e.,

$$\lambda(t) = \begin{cases} 1; t < 0 \\ 1 + Rt; t > 0 \end{cases} \tag{13}$$

For this case, eq. (6) gives the stress response as

$$\sigma(t) = \left[(1+Rt)^2 - \frac{1}{1+Rt}\right] H(1+Rt,t) + \frac{1}{R(1+Rt)} \int_1^{1+Rt} \left(1 - \frac{1}{\xi^3}\right) h\left[\xi, \frac{1+Rt}{R}\left(1 - \frac{1}{\xi}\right)\right] d\xi. \tag{14}$$

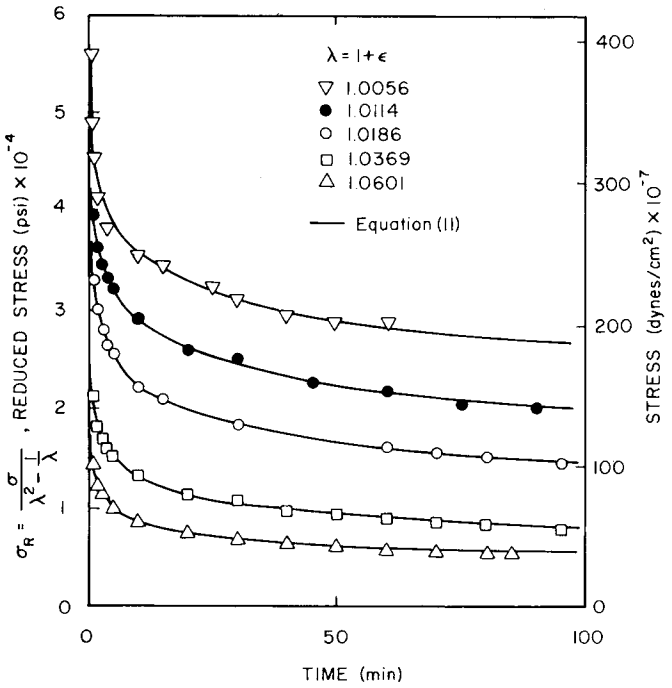

Fig. 7. Reduced stress relaxation data of polyester. Solid line corresponds to empirical curve fit.

The material functions h and H given by eqs. (10)–(12) are then substituted in eq. (14) to generate the BKZ theoretical results. It was not possible to evaluate the integral appearing in eq. (14) in closed form; consequently, use was made of a numerical integration scheme. A comparison between the experimental polyester data and the analytical BKZ model is shown in Figure 8. Agreement for this case can only be classified as fair, with an average error of about 5–12%. It appears from the figure that, in the initial and final portions of the curve, the BKZ model is not correctly predicting the data. Reasons which suggest an explanation for this are given in the concluding section.

DISCUSSION

The previous study has attempted to characterize the one-dimensional, rate-dependent stress–strain behavior of certain polymeric materials. The characterization was done using both a mechanical model (modified Bingham type) and a general nonlinear theory of viscoelasticity (BKZ single integral model). Characterization success was measured by the ability of the particular model to accurately predict the experimental data in a constant strain rate situation.

The question remains, will the characterization for this particular test be adequate to predict the material's response to other loading situations? For the case of the mechanical model, the answer to the question is no. Because

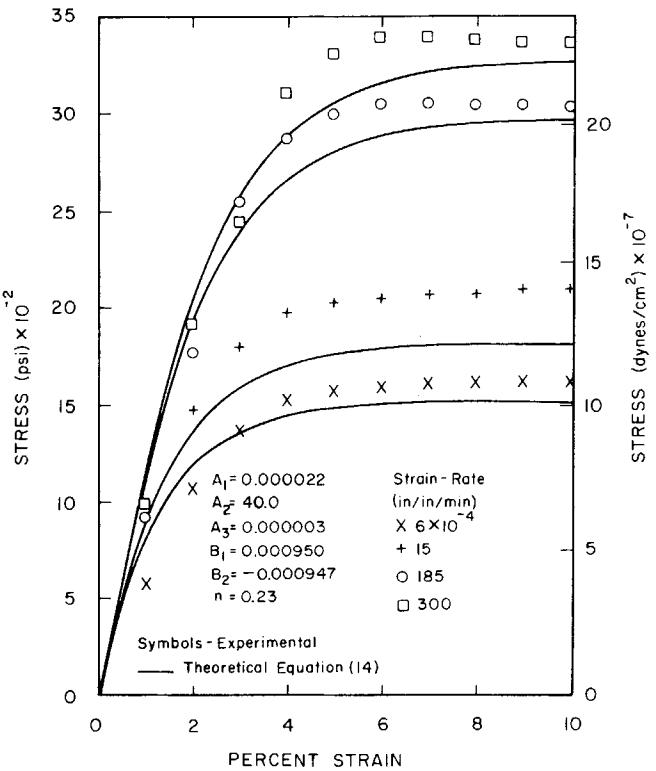

Fig. 8. Comparison between BKZ model and experimental data for polyester: A_1 in $(\text{psi})^{-1}$, A_2 nondimensional, A_3 in $(\text{psi})^{-1}$, B_1 in $(\text{psi/min}^n)^{-1}$, B_2 in $(\text{psi/min}^n)^{-1}$, n nondimensional.

of the high degree of empiricism, the mechanical model with rate-dependent elements cannot be expected to give adequate results for, say, nonconstant strain-rate tests. On the other hand, the BKZ model, as pointed out previously, will predict material behavior for any loading history. Specifically, for the uniaxial case, once the material function $h(\lambda,t)$ is found (i.e., the material is characterized), then, according to the theory, the behavior to any uniaxial loading situation can be computed. The work by Zapas[13,14] experimentally confirms this fact.

Although mechanical modeling suffers because of its empiricism, it can be useful with rate-dependent elements in a given geometric deformation configuration. It has been shown that one model with a fixed form for the element rate dependence can give very good results for more than one particular polymeric material.

With regard to the BKZ theory, its marginal comparison with the data in the initial and final portions of the stress–strain curve can be traced to the determination of the material functions $h(\lambda,t)$ and $H(\lambda,t)$. The function $H(\lambda,t)$ was found by curve-fitting stress relaxation data. It was very difficult experimentally to gather accurate small time data in this type of test because the stress is changing very rapidly. Furthermore, in the determination of the strain dependence of $H(\lambda,t)$, i.e., the determination of $a(\lambda)$ and $b(\lambda)$ in eq. (12), it was experimentally difficult to run stress relaxation tests at large strains with the particular polyester. And for the case of $h(\lambda,t)$, which requires the differentiation of $H(\lambda,t)$, these errors become amplified.

In light of this initial modeling problem with the BKZ theory, it is interesting to investigate the initial slope of the stress–strain curve according to the theory. The slope follows from differentiation of eq. (14):

$$\begin{aligned}\frac{d\sigma}{d\epsilon} = \frac{1}{R}\frac{d\sigma}{dt} = &\left[2(1+Rt) + \frac{1}{(1+Rt)^2}\right] H(1+Rt,t) \\ &+ \left[(1+Rt)^2 - \frac{1}{1+Rt}\right]\frac{1}{R}\frac{dH}{dt}(1+Rt,t) \\ &- \frac{1}{R(1+Rt)^2}\int_1^{1+Rt}\left(1-\frac{1}{\xi^3}\right) h\left[\xi, \frac{1+Rt}{R}\left(1-\frac{1}{\xi}\right)\right] d\xi \\ &+ \frac{(1+Rt)^3-1}{R(1+Rt)^4} h(1+Rt,t) \\ &+ \frac{1}{R^2(1+Rt)}\int_1^{1+Rt}\left(1-\frac{1}{\xi^3}\right)\frac{\partial}{\partial t} h\left[\xi, \frac{1+Rt}{R}\left(1-\frac{1}{\xi}\right)\right] d\xi. \end{aligned} \quad (15)$$

Considering the initial slope at $t = 0$ gives

$$\begin{aligned}\left.\frac{d\sigma}{d\epsilon}\right|_{t=0} = &\ 3H(1,0) \\ &+ \lim_{t\to 0}\left\{\frac{3t\left(1+Rt+\frac{1}{3}R^2t^2\right)}{1+Rt}\left[\frac{dH}{dt}(1+Rt,t) + \frac{h(1+Rt,t)}{(1+Rt)^3}\right]\right\}. \end{aligned} \quad (16)$$

It appears from the functional dependence in the limit term in eq. (16) that, although this term may be nonzero, it will be independent of the strain rate R regardless of the choice of material function $H(\lambda,t)$. Consequently, the initial slope itself would be independent of the strain rate. This result is contrary to the polyester experimental data shown in Figure 1. Note that for the mechanical model, the modulus E was rate dependent as given in eq. (3a).

For the particular material function chosen in this study, defined by eqs. (11) and (12), the limit term in (16) is zero and

$$\left.\frac{d\sigma}{d\epsilon}\right|_{t=0} = 3H(1,0) = \frac{3}{A_1 + A_3}. \tag{17}$$

Furthermore, Zapas and Craft[13] used the form

$$H(\lambda,t) = \alpha(t)\ (\lambda^2 - 1) + \frac{1}{\lambda}\beta(t) + \gamma(t) \tag{18}$$

for the material function, with α, β, and γ being arbitrary functions of time alone. They found excellent agreement between theory and experiment, but only presented one curve at a single strain rate. For their case, if α, β, and γ along with their derivatives are assumed to be finite for $0 \leq t < \infty$, then, from eq. (16),

$$\left.\frac{d\sigma}{d\epsilon}\right|_{t=0} = 3H(1,0) = 3[\beta(0) + \gamma(0)] \tag{19}$$

which is rate independent.

This work is intended only to be preliminary in establishing theoretical constitutive models capable of predicting uniaxial rate-dependent behavior of polymers subjected to finite strains. Further data on other polymers over a wider range of strain rates are needed to test the validity of the two models proposed in this study. In addition, further nonlinear theories such as those proposed by Pipkin and Rogers[10] and Green and Rivlin[15] should be characterized and compared with data.

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