Modeling the Elastic Modulus of HDPE in Terms of Stress-Dependent Thermally Activated Rate Process

F. DAVER* and B. W. CHERRY

Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia

SYNOPSIS

If a three-element mechanical model incorporating a stress-dependent thermally activated rate process is used to predict the instantaneous and anelastic components of elastic modulus of high density polyethylene, it is suggested that the measured elastic modulus determines the anelastic response rather than an instantaneous response and, furthermore, it is related to an interlamellar shear rather than a slip process in the crystalline region. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The response of polymers to an external force consists of three parts: the instantaneous elastic response, the noninstantanous elastic response, and the permanent plastic response. The instantaneous elastic response is characterised by all of the mechanical energy put into the polymer being recovered instantaneously upon the release of the external force.[1] The noninstantaneous elastic response or anelastic response[2] is characterised by all of the mechanical energy put into the system being recovered upon the release of the external force, but the response is not an instantaneous but a time-dependent one. Finally there is the permanent, plastic response that does not change significantly with time, and leaves the polymer permanently deformed upon the release of the external force. The mechanical energy that results in a permanent plastic response is dissipated through various permanent rearrangements or structural changes occuring within the polymer.[3] Mechanical analogs are commonly used to analyze the stress-deformation behavior of polymers.[4-6] However, the relationship between the elements of the model and the mechanical properties measured by standard methods is not always entirely obvious, and it is the aim of this article to relate the modulus

of elasticity as determined in a standard constant strain rate test to the appropriate portion of the three-element mechanical model.[7]

MODELING

Figure 1 shows a model that is widely used to represent stress relaxation results. The Eyring dashpot in the model represents a stress-dependent thermally activated process (SDTAP) associated with slip in the crystalline and/or interfacial regions. Anelasticity is provided in the model by a linear spring in series with the dashpot, and this spring may be associated with amorphous chains linking portions of deforming crystallites. The stress acting on this branch of the three-element mechanical model is termed the effective stress and given the symbol σ^*. The instantaneous deformation that stems from the entropic elasticity of amorphous regions is represented by another linear spring in parallel with the anelastic component. An internal stress, which is associated with the stretched tie molecules, is assumed to act on this branch of the model and given the symbol σ_i. In a stress relaxation experiment the internal stress is the stress level reached when all the relaxation processes have been exhausted.

If the stress relaxation arises as a result of internal deformation, that is, the flow in the Eyring dashpot, SDTAP theory can be applied to this process and the variation of the effective stress with time cal-
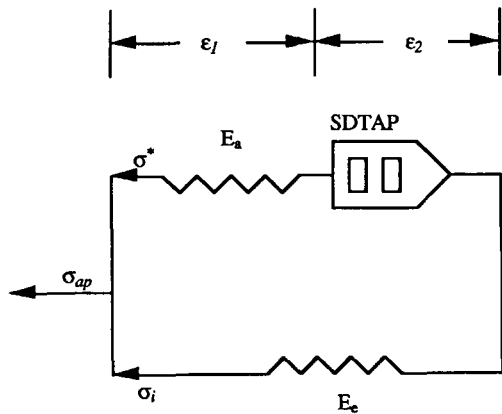
Figure 1   Three-element model.

culated.[8,9] When, as in a stress relaxation experiment the total rate of change of strain can be equated to zero, the effective stress can be calculated as shown below in terms of the initial applied stress, activation energy, activation volume, temperature, time, and the elastic and anelastic components of elastic modulus.

The total applied strain is equivalent to the sum of the strain on the spring and the dashpot

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

and

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt}$$

Now

$$\frac{d\varepsilon_1}{dt} = \frac{1}{E_a} \frac{d\sigma^*}{dt} \, ,$$

and according to stress-dependent thermal activation theory

$$\frac{d\varepsilon_2}{dt} = K \sinh (\alpha\sigma^*)$$

Here, $\alpha = (V)/(2KT)$, where V is the activation volume, k is Boltzmann's constant, and K is a function of activation energy.[6]

In a stress relaxation experiment, the total applied strain is held at a constant level, and so:

$$\dot{\varepsilon}_1 + \dot{\varepsilon}_2 = \frac{\dot{\sigma}^*}{E_a} + K \sinh(\alpha\sigma^*) = 0;$$

hence

$$-\dot{\sigma}^* = E_a K \sinh(\alpha\sigma^*), \tag{1}$$

which is equivalent at high stresses to

$$-\dot{\sigma}^* = \frac{E_a K}{2} \exp(\alpha\sigma^*).$$

Hence,

$$\ln(-\dot{\sigma}^*) = \ln\left(\frac{E_a K}{2}\right) + \alpha\sigma^* \tag{2}$$

(since $\dot{\sigma}^* < 0$ in a stress relaxation experiment, $-\dot{\sigma}^* > 0$).

α and $(E_a K)$ can be calculated from eq. (2) for each individual stress relaxation experiment. In a stress relaxation experiment, the internal stress is the stress level reached when all the relaxation processes have been exhausted. Similarly, the effective stress is the difference between the applied stress and the internal stress. Hence, the effective stress can be calculated at any instant, and if this is plotted against the natural logarithm of the decay rate of the effective stress $\ln(-\dot{\sigma}^*)$ for each stress relaxation data point, the slope of the line obtained gives α, which is equal to $(V)/(2kT)$ and the intercept of the line gives $(E_a K)/(2)$.

From eq. (1)

$$\frac{d\sigma^*}{E_a} = -K \sinh(\alpha\sigma^*)dt \text{ and } \sinh(\alpha\sigma^*)$$

$$= \frac{\exp(\alpha\sigma^*) - \exp(-\alpha\sigma^*)}{2};$$
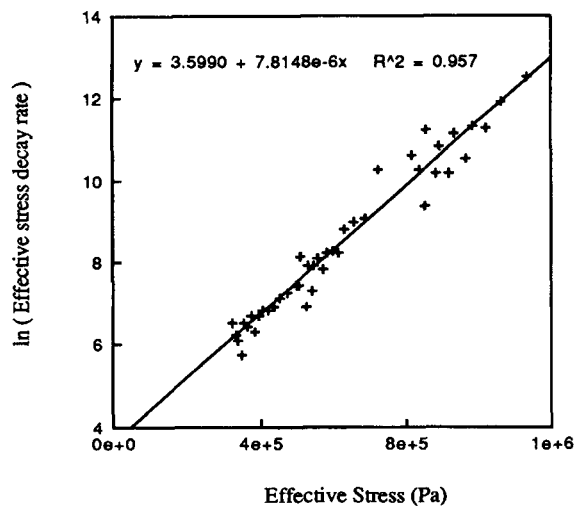

Figure 2   Natural logarithm of stress decay vs. effective stress.

hence,

$$\frac{d\sigma^*}{\exp(\alpha\sigma^*) - \exp(-\alpha\sigma^*)} = -\frac{KE_a}{2}\,dt,$$

which can be integrated to yield

$$\tanh^{-1}[\exp(\alpha\sigma^*)] - \tanh^{-1}$$

$$\times [\exp(\alpha\sigma_o^*)] = \frac{\alpha KE_a}{2}\,t. \quad (3)$$

At $t = 0$, dashpot does not move; therefore, $\varepsilon_2 = 0$ and the applied stress is distributed between the two linear springs so that

$$\frac{(\sigma_i)_o}{E_e} = \frac{\sigma_o^*}{E_a} = \frac{(\sigma_{app})_o}{E_e + E_a},$$

where $(\sigma_i)_o$ is the internal stress, σ_o^* is the effective stress, and $(\sigma_{app})_o$ is the applied stress at $t = 0$. Hence,

$$\sigma_o^* = \frac{(\sigma_{app})_o E_a}{E_e + E_a}. \quad (4)$$

Inserting eq. (4) into eq. (3) after some mathematical manipulations gives the effective stress as a function of the initial applied stress, activation energy, activation volume, temperature, time, elastic, and anelastic components of elastic modulus.
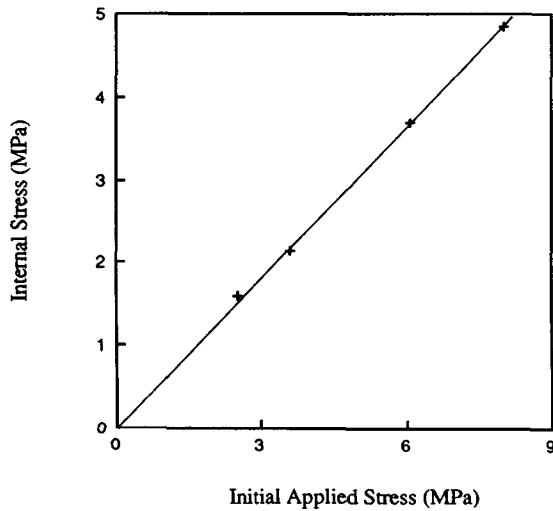
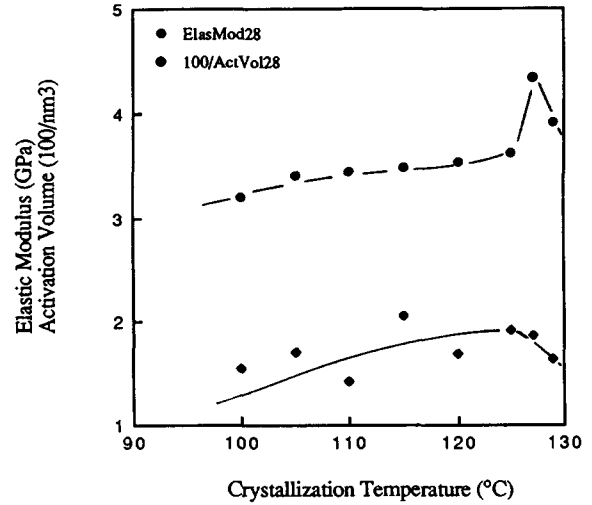**Figure 3** Internal stress vs. initial applied stress.

Figure 4 The relationship between elastic modulus and activation volume at $T = 28°C$.

$$\sigma^* = \frac{1}{\alpha}\ln\left\{\frac{\exp\left(\alpha\frac{(\sigma_{app})_o E_a}{E_e + E_a}\right) + \tanh\left(\frac{\alpha KE_a}{2}t\right)}{1 + \exp\left(\alpha\frac{(\sigma_{app})_o E_a}{E_e + E_a}\right)\tanh\left(\frac{\alpha KE_a}{2}t\right)}\right\}.$$

$$(5)$$

If the α and $(E_a K)$ have been calculated from eq. (3) for each stress relaxation experiment and inserted into eq. (5), for a set of stress elaxation experiments carried out with different initial stresses then the resulting expression gives effective stress as a function of initial applied stress, time, and instantaneous (E_e) and anelastic (E_a) component of elastic modulus. Consequently, if eq. (5) is fitted into the stress relaxation curves, instantaneous (E_e) and the anelastic (E_a) component of elastic modulus can be obtained.

In order to compare the magnitudes of instantaneous (E_e) and anelastic (E_a) components of elastic modulus with the measured elastic modulus that might be obtained by standard methods and the magnitudes of the activation volume with the expected magnitudes of various activation processes, it is necessary to refer to the specific experimental data.

EXPERIMENTAL

The polymer used was high-density polyethylene supplied in powder form without additives by Hoechst Pty Ltd and designated GA7260 (M_w = 97,900 and M_n = 10,000). The polymer was sub-

jected to a number of heat treatments in order to produce a series of samples with a range of structures. Samples 0.5 × 6.4 × 45.7 mm were used for subsequent experiments. Both elastic modulus and stress relaxation experiments were performed using a dual cantilever bending fixture on a Rheometrics Solid Analyser (RSAII) at two different temperatures, T = 28°C and T = 48°C. The sample extension at elevated temperatures was compensated by the spring-loaded clamps in the fixture. The elastic modulus was recorded for both groups at static strain sweep mode at a strain of 0.1%. Stress relaxation experiments were conducted at a strain of 0.1%. The strain was held for a sum of four time zones over a duration of 4164 s. In each time zone, 16 equally timed measurements were taken. The existence of four different time zones enabled the recording of sufficient data over a narrow range of time when the sample was undergoing a great deal of change at the beginning of the experiment and the recording of less frequent data points over a longer period of time when the sample was undergoing considerably less change.[10]

σ^* was equated to the difference between the instantaneous applied stress at any time and the equilibrium stress at long times, and then α and (E_aK) were calculated by determining the instantaneous decay rate at every point as shown in Figure 2. Using the values of V and E_aK, thus, obtained the values of the other constants and were calculated through a least squares minimization program utilizing the Marquardt-Levenberg algorithm to fit eq. (5) to the obtained stress relaxation curves.

RESULTS AND DISCUSSION

Internal stress calculations

In order to distinguish between the two types of internal stresses, stress relaxation experiments were conducted at four different strains (0.6, 0.1, 1.5, and 2%) by using samples made from the same microstructure. The internal stress values were calculated for each stress relaxation experiment. It can be seen that as initial applied stress approaches zero, internal stress also approaches zero. The disappearance of internal stress with zero initial applied stress suggests that the samples that were used for the stress relaxation experiments were virtually free of any residual internal stresses and all the internal stresses present in the samples were due to the deformation preceding the stress relaxation experiments (Fig. 3).
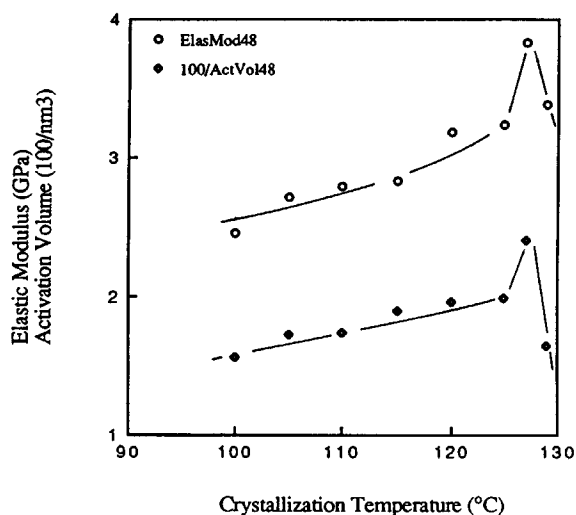

Figure 5 The relationship between elastic modulus and activation volume at T = 48°C.

Elastic Modulus, Instantaneous, and Anelastic Modulus Results

Typical values obtained from one series of experiments were as follows:

At T = 28°C, Elastic modulus = 4.1 GPa,

$$E_e = 2.4 \text{ MPa}, E_a = 3.4 \text{ GPa}.$$

At T = 48°C, Elastic modulus = 3.4 GPa,

$$E_e = 4.8 \text{ MPa}, E_a = 5.2 \text{ GPa}.$$

It can be seen from the relative magnitudes of the instantaneous elastic modulus and the anelastic modulus that the anelastic modulus is very much closer to the elastic modulus, as measured in a conventional mechanical test. This implies that in an elastic modulus measurement what is measured is probably related to the anelastic component of the elastic modulus rather than the instantaneous component. The elastic component, which may be associated with the rubber-like elesticity of the intercrystalline regions, is very much smaller, and it can be seen that it increases with temperature as might be expected for entropic elasticity. These results suggest that the elastic modulus as measured in a conventional mechanical test is not controlled by E_e or E_a, but is controlled by the slip in the interfacial region.

The Relationship between the Elastic Modulus and Activation Volume

If the elastic modulus as measured in a constant strain rate experiment is, in fact, a function of the

slip processes occurring in the body of the polymer, then the "elastic" modulus should be a function of the activation volume for that slip process. According to the SDTAP theory, in a constant strain deformation for which $\sigma = K_2 t$,

$$\dot{\varepsilon} = K_1 \exp\left(\frac{V\sigma}{2kT}\right) \qquad (6)$$

the elastic modulus, E is given as

$$E = \frac{K_2}{K_1}\left[1 + \frac{K_1 2kT}{V K_2 \varepsilon}\right]$$

or

$$E \approx \frac{1}{V}. \qquad (7)$$

Equation (7) suggests an inverse relationship between the measured elastic modulus values and the calculated activation volume results.

Samples were prepared in which the structure was modified by a range of heat treatments.[11] The activation volume and the measured modulus of elasticity were determined. The inverse relationship between the elastic modulus and the activation volume is observed very clearly if the elastic modulus and the inverse of the activation volume are plotted together. Figures 4 and 5 show this inverse relationship at $T = 28°C$ and at $T = 48°C$, respectively. It seems likely, therefore, that the measured value of the

elastic modulus in experiments carried out in a constant strain rate experiment should be related, not to the elastic processes that take place within the body of the polymer, but to the reversible plastic processes associated with slip.

REFERENCES

1. S. Matsuoka and T. K. Kwei, in *Macromolecules: An Introduction to Polymer Science*, F. A. Bovey and F. H. Winslow, Eds., Academic Press, New York, 1979, p. 340.
2. W. N. Findley, J. S. Lai, and K. Onaran, *Creep and Relaxation of Non-Linear Viscoelastic Materials*, Chap. 5, North-Holland Publishing Co., Amsterdam, 1976.
3. A. Peterlin, *J. Polym. Sci.*, **C18**, 123, 1967.
4. H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).
5. D. G. Fotheringham and B. W. Cherry, *J. Mater. Sci.*, **13**, 231 (1978).
6. B. W. Cherry and S. H. Teoh, *Polymer*, **24**, 1067 (1983).
7. W. R. Krigbaum, R. J. Roe, and K. J. Smith, Jr., *Polymer*, **5**, 533 (1964).
8. J. Kubat, J. Petermann, and M. Rigdahl, *Mater. Sci. Eng.*, **19**, 185 (1975).
9. J. Kubat, M. Rigdahl, and R. Selden, *J. Appl. Polym. Sci.*, **20**, 2799 (1976).
10. F. Daver, Ph.D. Thesis, Department of Materials Engineering, Monash University, Clayton, Victoria, Australia, 1992.
11. F. Daver and B. W. Cherry, *Appl. Polym. Sci.*, to appear.