

Thermodynamic Theory of the Viscoelasticity and Yield of Glassy Polymers: Internal Time Theory

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ABSTRACT: A nonlinear viscoelastic constitutive equation of glassy polymers has been developed on the basis of the internal time and irreversible thermodynamics of internal variables. The constitutive equation is a generalization of spring–dashpot models and describes the yield behavior of glassy polymers. With this constitutive equation, the rate of entropy production has been determined to show a peak near the yield. We propose a new yield criterion, that yield

occurs at the maximum rate of entropy production. The yield criterion is almost equivalent to that of peak stress and a thermodynamic interpretation of yield. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2400–2411, 2003

Key words: thermodynamics; viscoelastic properties; yielding

INTRODUCTION

As the use of polymers as structural materials increases, it becomes more important to describe the mechanical behavior of solid polymers. Unlike metals, solid polymers show complex mechanical behavior, such as stress dependence on both the strain rate and temperature and the stress at a fixed strain being relaxed. In addition, the yield stress of a polymer cannot be described by a simple criterion of von Mises because the yield stress depends on both the strain rate and temperature.

Various researchers^{1–9} have developed constitutive equations for glassy polymers that can predict the yield. Most theories are based on internal time, which is the rescaling of time for normalizing the effects of deformation and temperature. Some have employed yield models of Eyring or Argon to specify the plastic strain rate.^{5,8} Others have proposed a combination of the concepts of internal time and linear viscoelasticity.^{2–4,6}

The works in this field by Knauss and Emri,⁴ Boyce et al.,⁵ and Schapery⁷ are noteworthy. Although the constitutive formulation developed in this article has a form similar to that of Knauss and Emri, it has been derived from a generalization of spring–dashpot models with both internal time and irreversible thermodynamics. Although our theory shares a common theoretical foundation with that of Schapery, strain is

used as one of the independent thermodynamic variables instead of stress.

Molecular approaches have also been used to describe yield mechanisms.^{10–15} They are not constitutive equations but relations between the yield stress and strain rate. We call them yield equations to distinguish them from constitutive equations. Although Boyce et al.⁵ and Tervoort et al.⁸ developed constitutive equations based on existing yield equations, Bernstein and Shokoh¹ derived a yield equation from the Kaye-Bernstein, Kearsely, Zapas (K-BKZ) constitutive equation modified by the internal time of stress. This article consists of two parts. The first part charts the development of a nonlinear viscoelastic constitutive equation based on irreversible thermodynamics that is a generalization of linear viscoelasticity including the internal time concept.^{1–4,6} The second part suggests a thermodynamic interpretation of yield that results in a yield equation derived from the constitutive equation. The yield equation is expected to predict the yield behavior of glassy polymers from stress–relaxation experiments.

CONSTITUTIVE EQUATION THEORY

Linear viscoelasticity and thermodynamics

It is well known that a linear viscoelastic constitutive equation can be derived from an analogy of the mechanical response of polymers to a combination of mechanical elements such as springs and dashpots. We adopt another methodology¹⁶ based on the irreversible thermodynamics of internal variables. Figure 1 is a schematic expression of the combination of

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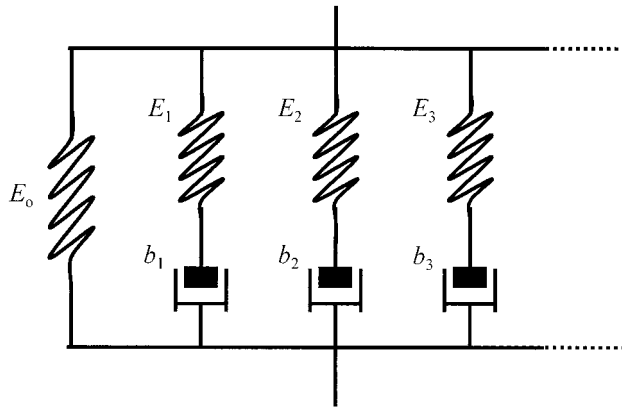


Figure 1 Mechanical model of a linear viscoelastic material.

mechanical elements. We define the free energy as the strain energy stored in the spring elements:

$$f(e, q_i, T) = \frac{1}{2} E_0 e^2 + \frac{1}{2} \sum_{i=1}^N E_i (e - q_i)^2 \quad (1)$$

where T is the temperature, e is the total strain, q_i is the strain of the i th dashpot, E_0 and E_i are the moduli corresponding to the spring elements in Figure 1, and N is the total number of Maxwellian elements. From the irreversible thermodynamics,^{16,17} stress is

$$\sigma = \frac{\partial f}{\partial e} = E_0 e + \sum_{i=1}^N E_i (e - q_i) \quad (2)$$

The evolution equation of q_i is suggested to be

$$\frac{dq_i}{dt} = \frac{E_i}{b_i} (e - q_i) \quad (3)$$

where b_i is the viscosity of the i th dashpot. The methodology gives results identical to those from the conventional methodology with Laplace transform.

The front factor in eq. (3) denotes the inverse of the relaxation time τ_i :

$$\tau_i \equiv \frac{b_i}{E_i} \quad (4)$$

Therefore, the real time t can be rescaled under the assumption that all relaxation times have a common factor τ , that is, $\tau_i = \tau/\alpha_i$. All relaxation times are assumed to have a common temperature dependence, which is equivalent to the principle of time-temperature superpositioning with a shift factor of the Arrhenius type. We define the internal time z as

$$z(t) \equiv \int_0^t \frac{dt'}{\tau} \quad (5)$$

With the help of z , eq. (3) becomes

$$\frac{dq_i}{dz} = \alpha_i \frac{dz}{dz} (e - q_i) \Leftrightarrow \frac{dq_i}{dz} = \alpha_i (e - q_i) \quad (6)$$

where

$$\alpha_i \equiv \frac{\tau}{\tau_i} \quad (\text{assumed to be constant})$$

The introduction of z with the associated assumption gives a mathematical form of the principle of time-temperature superpositioning when the relaxation time τ is a function of temperature.

The basic formulations of irreversible thermodynamics of internal variables¹⁷ state that the rate of entropy production is

$$T \frac{ds_{\text{in}}}{dt} = - \sum_{i=1}^N \frac{\partial f}{\partial q_i} \frac{dq_i}{dt} \geq 0 \quad (7)$$

where s_{in} is the entropy produced by the inherent irreversibility of the system and not by the flux of entropy from the surroundings. A more detailed rendering of eq. (7) is

$$- \sum_{i=1}^N \frac{\partial f}{\partial q_i} \frac{dq_i}{dt} = \sum_{i=1}^N E_i (e - q_i) \frac{dq_i}{dt} \quad (8)$$

The rearrangement of eq. (3) yields

$$e - q_i = \tau_i \frac{dq_i}{dt} \quad (9)$$

The substitution of eq. (9) into eq. (8) and the definition of the relaxation time τ_i in eq. (4) yield

$$- \sum_{i=1}^N \frac{\partial f}{\partial q_i} \frac{dq_i}{dt} = \sum_{i=1}^N b_i \left(\frac{dq_i}{dt} \right)^2 \geq 0 \quad (10)$$

Equation (10) shows that the evolution [eq. (3)] satisfies the second law of irreversible thermodynamics [eq. (7)].

Generalization of linear viscoelasticity

It is well known that the linear viscoelastic model cannot describe the mechanical characteristics of real solid polymers, such as the yield, strain softening, and strain hardening. Therefore, we should generalize the

methodology to describe the mechanical behavior. We generalize the relaxation times as functions of temperature and deformation. Many researchers¹⁻⁹ have used this concept. In the stress-clock model, the relaxation time is a function of stress, whereas strain is a variable for the relaxation time in the strain-clock model. The stress-clock and strain-clock models yield time-stress-temperature and time-strain-temperature superpositioning, respectively.

Because Hookian springs in Figure 1 cannot realistically describe the stress relaxation at a fixed strain larger than the yield strain, nonlinear springs are chosen. Therefore, we suggest a free energy such that

$$f(e, q_i, T) \equiv f_E(e, T) + f_i(e, q_i, T) \quad (11)$$

where

$$f_i(e, q_i, T) = \frac{1}{2} \sum_{i=1}^N B_i q_i^2 - \sum_{i=1}^N C_i q_i e \quad (12)$$

A detailed form of f_E should be determined by experiments (e.g., stress relaxation). We assume that the moduli B_i and C_i are independent of e and q_i and are functions of temperature.

The viscosity of a polymeric fluid depends on the strain rate. It may be reasonable that a possible mathematical form of the viscosity is

$$b_i(e, \dot{e}, T) \equiv \frac{\bar{b}_i(e, T)}{1 + (|\dot{e}|/\bar{\dot{e}}_0)^n} \quad (13)$$

where the dot over e represents differentiation with respect to real time, $\bar{b}_i(e, T)$ is a function of strain and temperature, $\bar{\dot{e}}_0$ and n are material constants. Therefore, a generalized evolution equation corresponding to eq. (6) may be

$$\frac{dq_i}{dt} = \frac{\alpha_i}{\tau(e, T)} (e - q_i) \quad (14)$$

It is noteworthy that α_i need not be assumed to be constant in the generalization. The new version of eq. (8) is

$$-\sum_{i=1}^N \frac{\partial f}{\partial q_i} \frac{dq_i}{dt} = -\sum_{i=1}^N B_i q_i \frac{dq_i}{dt} + \sum_{i=1}^N C_i e \frac{dq_i}{dt} \quad (15)$$

and eq. (9) becomes

$$q_i = e - \frac{\tau(e, T)}{\alpha_i} \frac{dq_i}{dt} \quad (16)$$

In a similar way, we obtain

$$-\sum_{i=1}^N \frac{\partial f}{\partial q_i} \frac{dq_i}{dt} = -\sum_{i=1}^N \left[(B_i - C_i) e \frac{dq_i}{dt} - B_i \frac{\tau(e, \dot{e}, T)}{\alpha_i} \left(\frac{dq_i}{dt} \right)^2 \right] \quad (17)$$

Because the rate of entropy production must not be negative, we assume that $B_i = C_i$ for all i . An analogy to eq. (10) gives

$$\frac{B_i}{\alpha_i} \tau(e, T) = \frac{\bar{b}_i(e, T)}{1 + (|\dot{e}|/\bar{\dot{e}}_0)^n} \quad (18)$$

Because B_i is assumed to be independent of the strain and strain rate, we define α_i as

$$\alpha_i \equiv \bar{\alpha}_i [1 + (|\dot{e}|/\bar{\dot{e}}_0)^n] \quad (19)$$

where $\bar{\alpha}_i$ is constant. We suggest a new internal time:

$$z(t) \equiv \int_0^t [1 + (|\dot{e}|/\bar{\dot{e}}_0)^n] \frac{ds}{\tau(e, T)} \quad (20)$$

Parsimony of material parameters with the Kohlrausch-Williams-Watts (KWW) model

The formulations in the previous section demand the information of the relaxation time distribution, which requires complex procedures of data processing. In addition, the formulations of the multimode model restrict the capability of calculating various quantities in a closed form. For greater mathematical simplicity, we again define another internal time $\zeta(t)$, which includes the information of the relaxation time distribution:

$$\zeta(t) \equiv z^\beta(t) \quad (21)$$

where the exponent β corresponds to that of the KWW model.^{18,19} When we discuss stress relaxation, the meaning of β will appear. By this definition of internal time, we can construct a new and simpler model of a single mode. The free energy in the previous sections becomes

$$f(e, Q, T) = f_E(e, T) + f_I(e, Q, T) \quad (22)$$

where Q is a new internal strain and

$$f_I(e, Q, T) = \frac{1}{2} B Q^2 - B Q e \quad (23)$$

The evolution equation becomes

$$\frac{dQ}{dt} = \alpha \frac{d\zeta}{dt} (e - Q) \quad (24)$$

where α is constant. The viscosity becomes

$$b(e, \dot{e}, T) \equiv \frac{B}{\alpha} \left(\frac{d\zeta}{dt} \right)^{-1} \quad (25)$$

The calculation of stress can be performed in a way similar to that before. If the strain rate is constant and the initial values of the strain and internal strain are zero, then a more detailed expression of stress is

$$\sigma(t) = \Delta\sigma_E[e(t)] + B\dot{e} \int_0^t e^{-\alpha[\zeta(t)-\zeta(s)]} ds \quad (26)$$

where

$$\Delta\sigma_E[e(t)] \equiv \frac{\partial f_E}{\partial e} [e(t), T] - Be(t) \quad (27)$$

is equivalent to the fully relaxed stress at a fixed strain e . In addition, it is noteworthy that

$$Q(t) = e(t) - \int_0^t e^{-\alpha[\zeta(t)-\zeta(s)]} \frac{de}{ds}(s) ds \quad (28)$$

A detailed procedure for obtaining eq. (26) is shown in the appendix.

Determination of the material parameters

To determine the material parameters, we need experimental data for the stress-relaxation and stress-strain curves. Stress-relaxation measurements have to be performed at various strains and temperatures. The measurement of stress-strain curves should be obtained at a constant strain rate with various temperatures and strain rates. To determine the parameters, we used the stress-relaxation values and stress-strain curves of unplasticized poly(vinyl chloride) (PVC) measured by Povolo et al.¹⁹ Because the data are not sufficient for determining the parameters of our model, we introduce some assumptions to compensate for the lack of data.

The formulations for stress relaxation can be obtained by the constitutive equation with appropriate initial conditions. The result is

$$\Xi(t) \equiv \frac{\sigma(t) - \sigma(\infty)}{\sigma(0) - \sigma(\infty)} = \exp[-\alpha\zeta(t)] \quad (29)$$

where $\sigma(t)$ is the stress at time t , $\sigma(\infty)$ is the fully relaxed stress equivalent to $\Delta\sigma_E(\bar{e})$, \bar{e} is a fixed applied strain, and $\sigma(0)$ is the initial stress. We call $\Xi(t)$ the relaxation function. The internal time in the relaxation experiment becomes

$$\zeta(t) = \left[\frac{t}{\tau(\bar{e}, T)} \right]^\beta \quad (30)$$

under the assumption that the applied strain is fixed and the effect of the previous deformation history on the internal variable Q is negligible. Most material parameters are determined with eqs. (29) and (30) and the experimental data measured at various temperatures and applied strains. A procedure for obtaining eq. (29) is given in detail in the appendix. Although most parameters are determined by stress relaxation, we need the data of stress-strain curves to determine B and the dependence of the internal time on the strain rate. The internal time in the tensile experiment at a constant strain rate is

$$\zeta(t) = \varphi^\beta(\dot{e})\lambda^\beta[e(t)] \quad (31)$$

where

$$\varphi(\dot{e}) \equiv \frac{1 + (|\dot{e}|/\bar{\dot{e}}_0)^n}{\dot{e}} \quad (32)$$

$$\lambda(e) \equiv \int_0^e \frac{d\varepsilon}{\tau(\varepsilon, T)} \quad (33)$$

Equation (31) can easily be derived from eqs. (20) and (21). Note that

$$\begin{aligned} z(t) &\equiv [1 + (|\dot{e}|/\bar{\dot{e}}_0)^n] \int_0^t \frac{ds}{\tau(e, T)} \\ &= \frac{1 + (|\dot{e}|/\bar{\dot{e}}_0)^n}{\dot{e}} \int_0^e \frac{d\varepsilon}{\tau(\varepsilon, T)} \quad (\text{at constant strain rate}) \end{aligned}$$

From tensile experiments at various strain rates and eqs. (26) and (32), we can determine the values of $\bar{\dot{e}}_0$, n , and B .

To simplify the problems, we suggest a mathematical form of the relaxation time $\tau(e, T)$. Although there may be various possible forms of relaxation time^{4,6} $\tau(e, T)$, we suggest

$$\ln \tau(e, T) \equiv \frac{\Delta E}{RT + W(e, T)} \quad (34)$$

where

$$W(e, T) \equiv \frac{1}{2} T\Omega e^2 \quad (35)$$

R is the gas constant, ΔE is the activation energy, and Ω is the material constant. Equation (34) means that mechanical perturbation in the disordered structure

TABLE I
Material Parameters

Parameter	Value	Remarks
α	2.870×10^2	Determined by relaxation data
β	4.955×10^{-1}	Determined by relaxation data
$\beta\Delta E/R$	$3.281 \times 10^3 \text{ K}$	Determined by relaxation data
Ω/R	2.055×10^2	Determined by relaxation data
$G_E (273\text{K})$	$1.316 \times 10^3 \text{ MPa}$	Determined by relaxation data
μ	1.579×10^3	Determined by relaxation data
ν	4.017×10^1	Determined by relaxation data
$\alpha \left[\frac{1 + (\dot{e}/\dot{e}_0)^n}{\dot{e}} \right]^\beta$	8.9×10^4	Determined by stress-strain data
$\frac{dB}{dT}$	9.185 MPa K^{-1}	Determined by stress-strain data
$B(T) - \frac{dB}{dT} T$	$-1.881 \times 10^3 \text{ MPa}$	Determined by stress-strain data
n	0.7	Assumed
\dot{e}_0	$1.544 \times 10^{-6} \text{ s}^{-1}$	Calculated by assumed n

physically has an effect similar to that of thermal energy. The values in Table I were determined by the data of Povoletto et al.¹⁹

Because their relaxation data were measured at the strains below the yield point, the following approximation of the fully relaxed stress is introduced to compensate for the lack of data:

$$\Delta\sigma_E(e) \approx G_E e_F \left[1 - \exp\left(-\frac{e}{e_F}\right) \right] \quad (36)$$

where

$$e_F \equiv \frac{\sigma_F}{G_E} \quad (37)$$

σ_F is the plateau stress denoted in Figure 2, and G_E is the initial slope of the fully relaxed stress determined by the data of stress relaxation. σ_F is determined by the average stress over a range of strains for which the

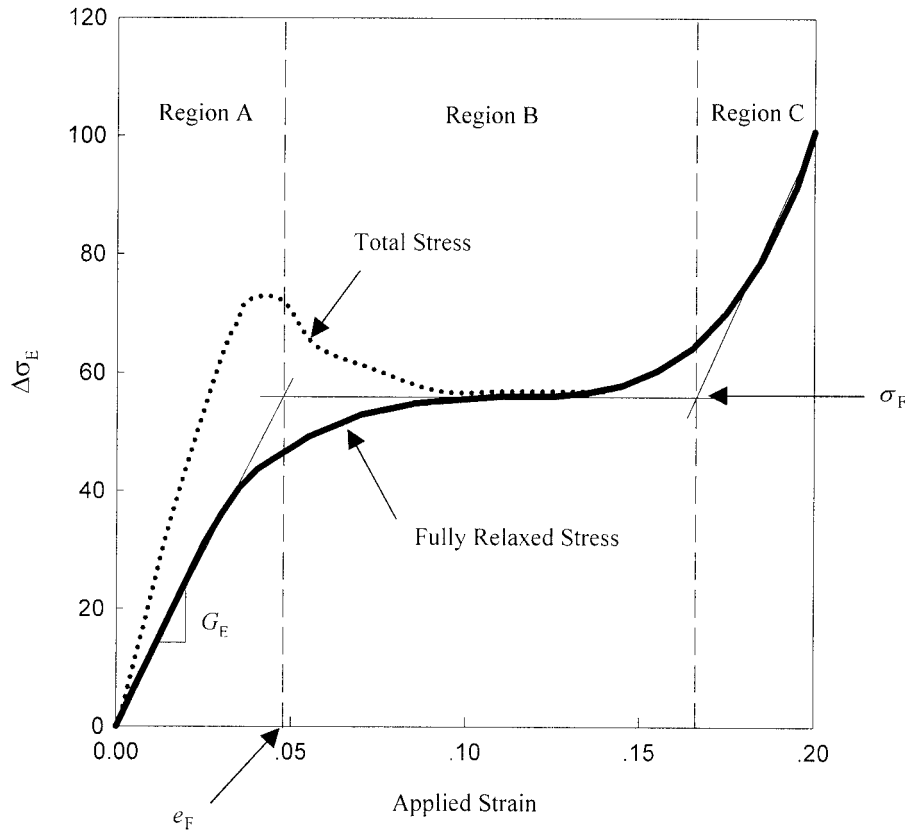


Figure 2 Schematic diagram of the fully relaxed stress: (A) linear viscoelastic behavior, (B) plastic flow, and (C) strain hardening. The total stress reduces to the fully relaxed stress by relaxation when the strain remains constant after loading.

TABLE II
Plateau Stress

Temperature (K)	301	313	324	332	343
σ_F (MPa)	44.0	39.0	31.0	26.7	18.0

variation of stress is small after the yield strain. The values of σ_F determined by the experimental data of Povolo et al.¹⁹ are listed in Table II. The modulus G_E should be a function of temperature, the dependence of which may be described by

$$G_E(T) \approx \frac{\mu + 1}{\mu + (T/T_R)^\nu} G_E(T_R) \quad (38)$$

where T_R is the reference temperature and μ and ν are the parameters to be determined by the fitting of experimental data.

Figure 3 shows the regression results of eq. (29). With the help of the regression, we can determine α , ΔE , β , ω , $\sigma(\infty)$, $\sigma(0)$, μ , ν , and $G_E(T_R)$ at $T_R = 273$ K. Figure 4 shows the initial modulus of the fully relaxed

stress determined by the regression of Figure 3. Figure 5 shows the regression results of eq. (38), which show that eq. (38) is a good approximation. Because our theory is based on the theory of internal time, time-strain-temperature superpositioning is presented (Fig. 6).

Figure 7 shows a comparison between the experimental data of the stress-strain curves¹⁹ and our theory. Some deviations may be due to the insufficient data, the limit of the KWW distribution, and the assumed initial condition of $Q(0) = 0$. Because Povolo et al.¹⁹ did not measure the stress-strain curves at various strain rates, we assume that the exponent n in eq. (32) is equal to 0.7. With this value, the regression results of eq. (32), and the experimental condition of Povolo et al.¹⁹ ($\dot{\epsilon} = 6.6 \times 10^{-4} \text{ s}^{-1}$), we can determine the value of \bar{e}_0 , which is listed in Table I.

From a complete set of determined parameters, we have drawn Figure 8, which shows the effect of the strain rate on the stress-strain curve. Figure 8 shows a realistic behavior of the yield strain varying with the strain rate. The realistic effect of the temperature on

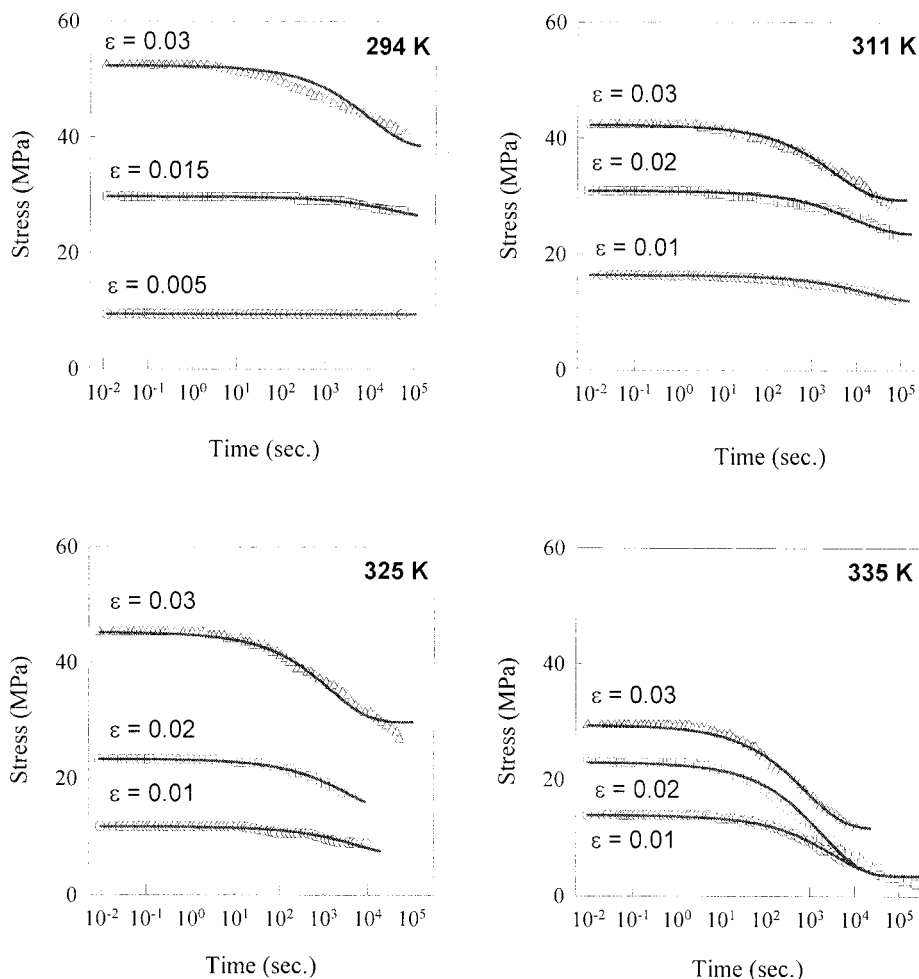


Figure 3 Stress-relaxation curves for unplasticized PVC. The experimental data were obtained from in Povolo et al.¹⁹ The solid curves were calculated with eq. (29).

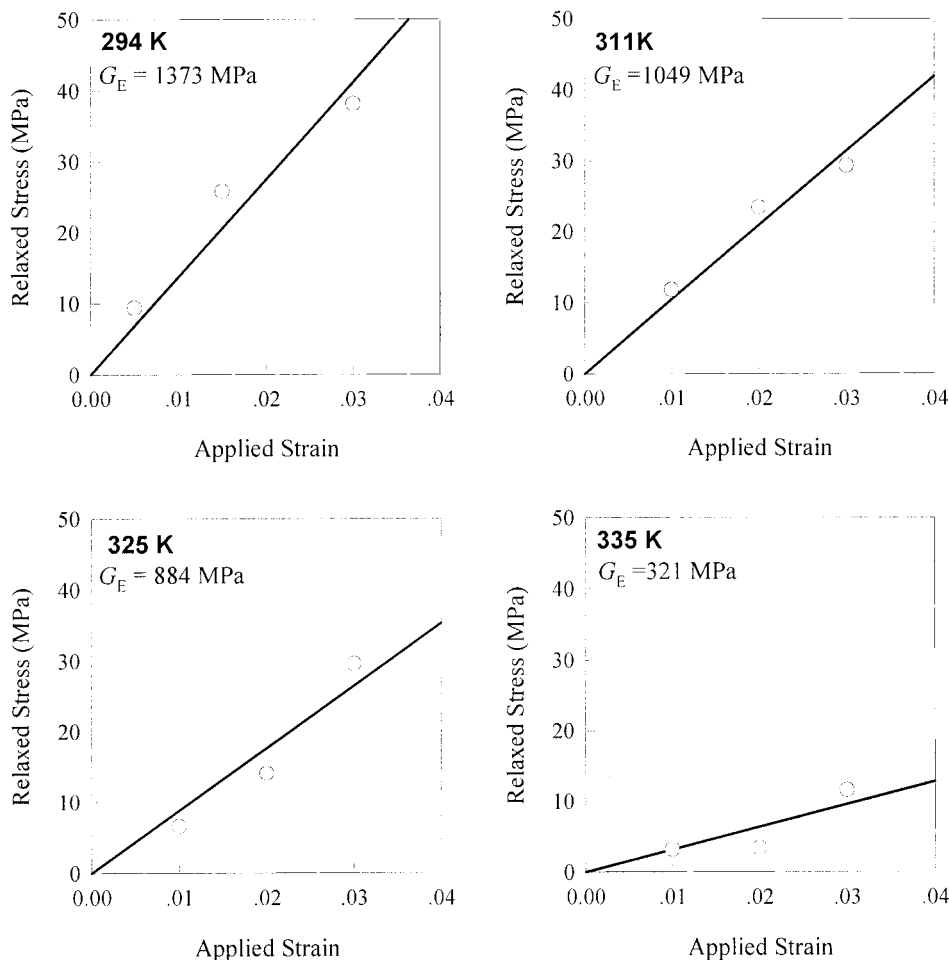


Figure 4 Fully relaxed stress versus the applied strain. The data were obtained from the regression analysis of the initial slopes at various temperatures (G_E) correspond to the relaxed moduli of linear viscoelasticity.

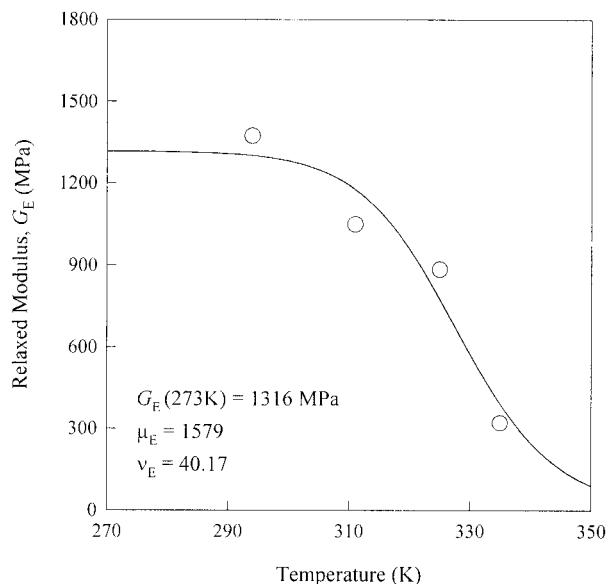


Figure 5 Approximation of G_E as a function of temperature. The regression line was obtained with eq. (38). The reference temperature is 273 K.

the yield strain is also presented in Figure 7. Because the approach in this work allows various modifications, appropriate modifications in the mathematical forms, such as the fully relaxed stress of eq. (36), are expected to reduce the deviation that appears after the yield (Fig. 7). The modulus B is linearly proportional to temperature and is similar to that of the modulus of rubber (Fig. 9). It shows a linear proportionality to temperature. If we interpret the physical meaning of the internal strain Q as a representation of microscopic random motions of polymer segments, the temperature dependence of B seems to be attributable to entropy, and this agrees with the fact that the rate of entropy production is the quadratic function of the rate of Q .

YIELD MECHANISM

Among various theories on the yield,^{10,12,13} our reasoning on the yield mechanism begins with a consideration of Robertson's theory¹² because his theory contains more fluent molecular meaning than others. The theory states that the fraction of high-energy molecu-

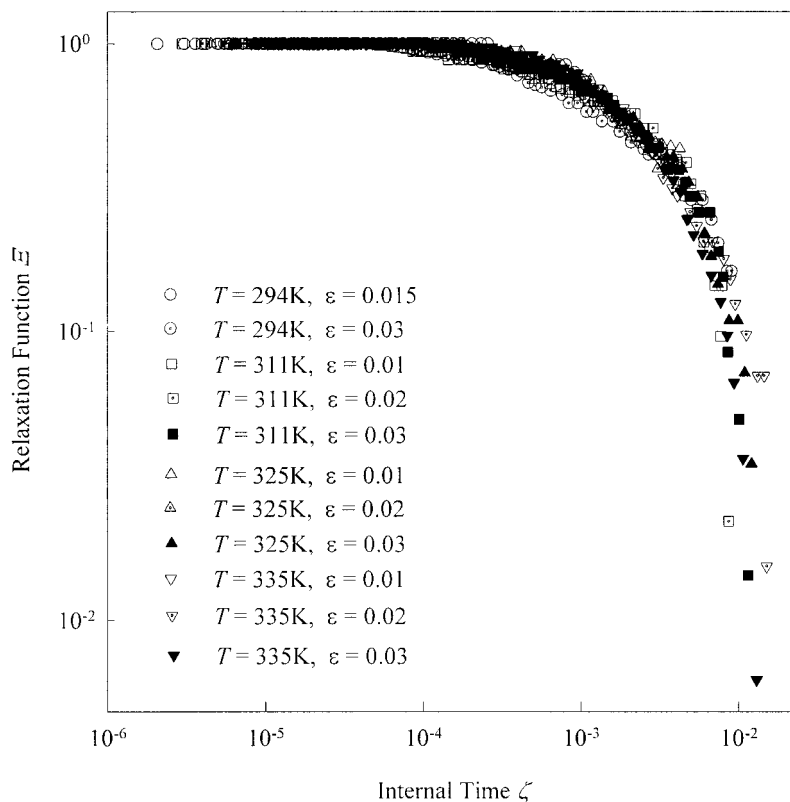


Figure 6 Time-strain-temperature superposition. Relaxation function Ξ of eq. (29) is replotted against internal time ζ .

lar conformation becomes that of the glass transition as the deformation approaches a yield point.

Experimental works^{20,21} have shown evidence of Robertson's theory by measuring the fraction of the

conformation during deformation. IR data show a peak-shaped fraction as a function of strain. The fraction of the high-energy conformation increases before the yield and decreases after the yield. The fraction of the molecular conformation must be related to the segment configuration of polymer chains. Here, we

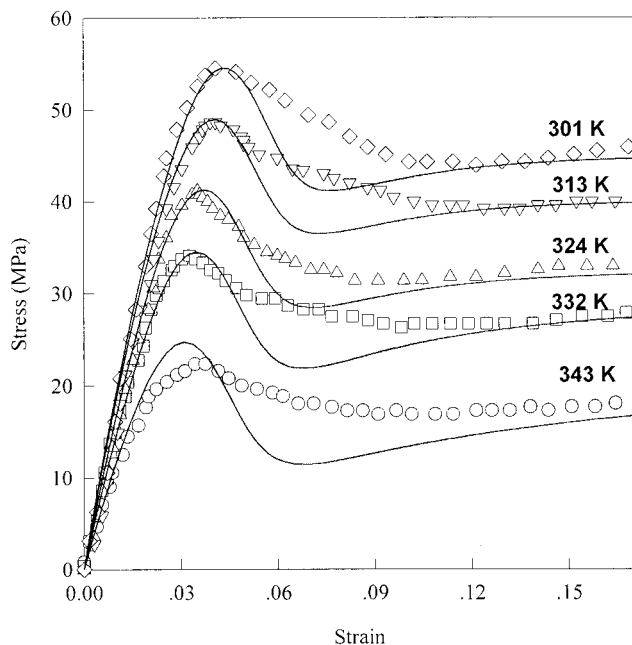


Figure 7 Stress-strain curves for unplasticized PVC at various temperatures. The experimental data were obtained from Povoilo et al.¹⁹ The regression curves were calculated with eq. (26). The strain rate is $6.6 \times 10^{-4} \text{ s}^{-1}$.

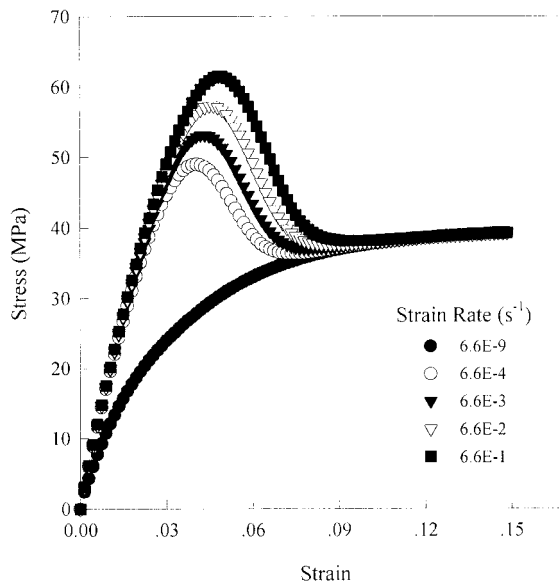


Figure 8 Effect of the strain rate on the stress-strain curve for unplasticized PVC. The data were calculated with eq. (26). The temperature is 313 K.

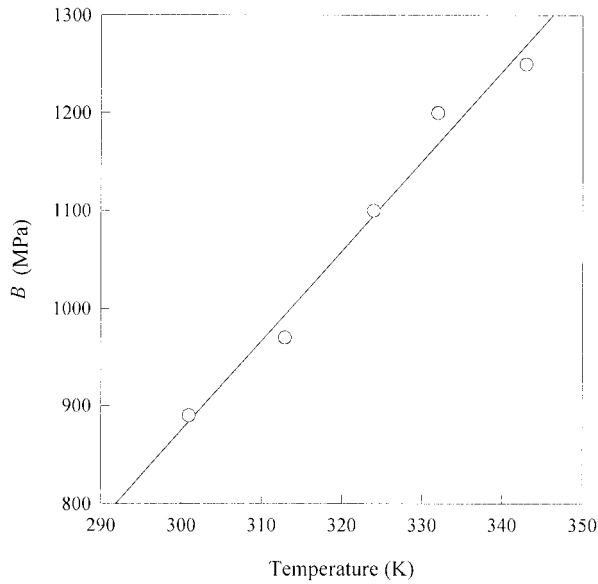


Figure 9 Temperature dependence of inelastic modulus B . The data were obtained from the analysis in Figure 7.

use the word *configuration* to indicate the spatial arrangement of the segments. Changes in the configuration give rise to those in thermodynamic functions, such as entropy and internal energy. Before the yield, the solid polymer behaves elastically because there is no large change in the configuration of the segments. Near the yield point, however, there may be great changes in the configuration. After the yield, a process of alignment of the polymer chains occurs, which increases the order of the structure to reduce microscopic random motions of the segments to some extent.

We can guess that a scalar quantity attributed to the random motions should show a peaklike shape when we plot it against the deformation because the fraction of conformation of polymers shows a peak when it deforms.^{20,21} The entropy must not be the quantity because it monotonically increases as deformation proceeds. A possible candidate may be the rate of entropy production. Jang and Jo²² performed a computer experiment using molecular mechanics in the study of the plasticity of solid polymers. They found that the derivative of the entropy with respect to the strain shows a peak near the yield point. Because the algorithm used in the molecular mechanics does not contain any time effect, the strain represents an internal time induced by deformation. Therefore, the derivative of entropy may correspond to the rate of entropy production in this study. From IR measurements^{20,21} and computer simulation,²² we have tried to determine whether the rate of entropy production of our theory shows a peak near the yield. Figure 10 shows that the rate of entropy production has a peak near the yield point.

Although how to define the yield from a stress-strain curve is controversial, it may be reasonable to

define the yield as the first local maximum of the stress. Because the definition of the yield as a peak stress is widely accepted, we have to compare it with the maximum rate of entropy production, the new definition of the yield. Two yield equations are derived from the two yield conditions, the extremum of stress and the maximum rate of entropy production.

Yield equation from the maximum stress

The yield defined as the maximum stress can be expressed under the constant strain rate as

$$\frac{d\sigma}{dt} = \frac{\partial^2 f_E}{\partial e^2} \dot{e} - B \frac{dQ}{dt} = 0 \quad (\text{at yield}) \quad (39)$$

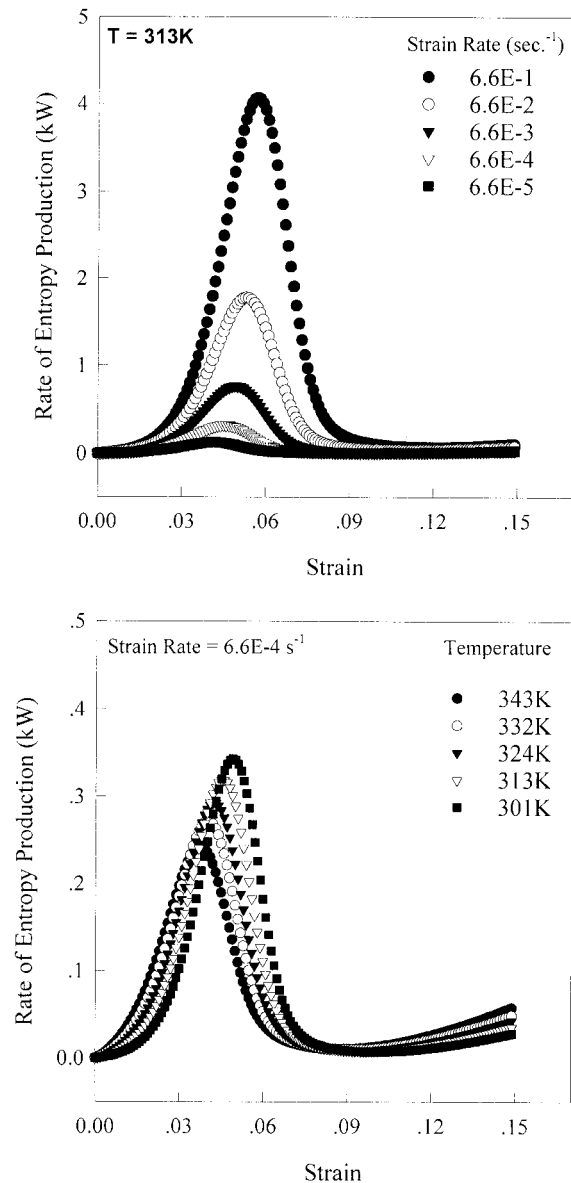


Figure 10 Variation of the rate of entropy production with the strain rate and temperature.

Substituting the evolution into eq. (39) yields

$$\frac{\partial^2 f_E}{\partial e^2} \dot{e} = \alpha B \frac{d\zeta}{dt} (e - Q) \quad (\text{at yield}) \quad (40)$$

Because our constitutive equation is

$$\sigma = \frac{\partial f_E}{\partial e} - BQ \Leftrightarrow Q = \frac{1}{B} \left(\frac{\partial f_E}{\partial e} - \sigma \right) \quad (41)$$

we obtain

$$e - Q = e - \frac{1}{B} \left(\frac{\partial f_E}{\partial e} - \sigma \right) = \frac{1}{B} (\sigma - \Delta\sigma_E) \quad (42)$$

Substituting eq. (42) for the yield point into eq. (40) and rearranging it, we obtain

$$\sigma_Y = \Delta\sigma_E(e_Y) + \frac{(\partial^2 f_E / \partial e^2)_{e_Y}}{\alpha(d\zeta/dt)_{e_Y}} \dot{e} \quad (43)$$

Because we have assumed a constant strain rate, the derivative of the internal time is

$$\frac{d\zeta}{dt} = \beta z^{\beta-1} \frac{dz}{dt} = \beta [\varphi(\dot{e})\lambda(e)]^{\beta-1} \frac{\varphi(\dot{e})\dot{e}}{\tau(e, T)} \quad (44)$$

Substitution of eq. (44) into (43) gives

$$\sigma_Y = \Delta\sigma_E(e_Y) + \frac{(\partial^2 f_E / \partial e^2)_{e_Y} \lambda(e_Y) \tau(e_Y, T)}{\alpha \beta [\varphi(\dot{e})\lambda(e_Y)]^\beta} \quad (45)$$

Yield equation from the maximum rate of entropy production

If we combine eqs. (7), (12), and (42) in an appropriate way, the rate of entropy production is

$$T \frac{ds_{in}}{dt} = \frac{\alpha}{B} \frac{d\zeta}{dt} (\sigma - \Delta\sigma_E)^2 \quad (46)$$

The condition of the maximum rate of entropy production at a constant strain rate can be written as

$$\frac{d}{dt} \left(T \frac{ds_{in}}{dt} \right) = 0 \quad (47)$$

or

$$\frac{d^2 \zeta}{dt^2} (\sigma - \Delta\sigma_E) = 2 \frac{d\zeta}{dt} \left(\frac{d\Delta\sigma_E}{dt} - \frac{d\sigma}{dt} \right) \quad (48)$$

Because

$$\frac{d\sigma}{dt} = \frac{\partial^2 f_E}{\partial e^2} \dot{e} - B \frac{dQ}{dt} = \frac{\partial^2 f_E}{\partial e^2} \dot{e} - \alpha \frac{d\zeta}{dt} (\sigma - \Delta\sigma_E) \quad (49)$$

and

$$\frac{d\Delta\sigma_E}{dt} = \frac{\partial^2 f_E}{\partial e^2} \dot{e} - B\dot{e} \quad (50)$$

we have

$$\frac{d\Delta\sigma_E}{dt} - \frac{d\sigma}{dt} = \alpha \frac{d\zeta}{dt} (\sigma - \Delta\sigma_E) - B\dot{e} \quad (51)$$

The substitution of eq. (51) into (48) and a suitable rearrangement would yield

$$\sigma = \Delta\sigma_E + \frac{2B\dot{\zeta}\dot{e}}{2\alpha\dot{\zeta}^2 - \ddot{\zeta}} \quad (52)$$

With the help of eqs. (21) and (44), we have

$$\frac{d^2 \zeta}{dt^2} = \beta(\beta - 1)z^{\beta-2} \left(\frac{dz}{dt} \right)^2 + \beta z^{\beta-1} \frac{d^2 z}{dt^2} \quad (53)$$

$$\frac{d^2 z}{dt^2} = - \frac{\varphi(\dot{e})\dot{e}^2}{\tau^2(e, T)} \frac{\partial \tau(e, T)}{\partial e} \quad (54)$$

$$\frac{2B\dot{\zeta}\dot{e}}{2\alpha\dot{\zeta}^2 - \ddot{\zeta}} = \frac{2B}{[2\alpha\beta(\varphi(\dot{e})\lambda(e, T))^\beta - (\beta - 1)] \times (\tau(e, T)\lambda(e, T))^{-1} + \frac{\partial \ln \tau(e, T)}{\partial e}} \quad (55)$$

Finally, eq. (52) can be rewritten as

$$\sigma_Y = \Delta\sigma_E(e_Y) + \frac{2B\tau(e_Y, T)\lambda(e_Y, T)}{2\alpha\beta[\varphi(\dot{e})\lambda(e_Y, T)]^\beta - (\beta - 1) + \tau(e_Y, T)\lambda(e_Y, T)(\partial \ln \tau(e, T)/\partial e)_{e_Y}} \quad (56)$$

It is noteworthy that e_Y is the strain at the maximum rate of entropy production in this section.

Comparison of the yield criteria

Figure 11 shows measured and calculated yield stresses of eqs. (45) and (56). The measured yield strain at the peak stress and the strain at the maximum rate of entropy production were used for the calculation of eqs. (45) and (56), respectively. Although both eqs. (45) and (56) give good correlations with the experimental data, there exists an inconsistency between the strain at the maximum rate of entropy production and the measured yield strain. Of course, it is difficult to directly measure the former through experiments. We can determine the strain by an indirect method in which the strain is calculated with the parameters determined by relaxation and stress-strain curves. Figure 12 shows the plot of the measured yield

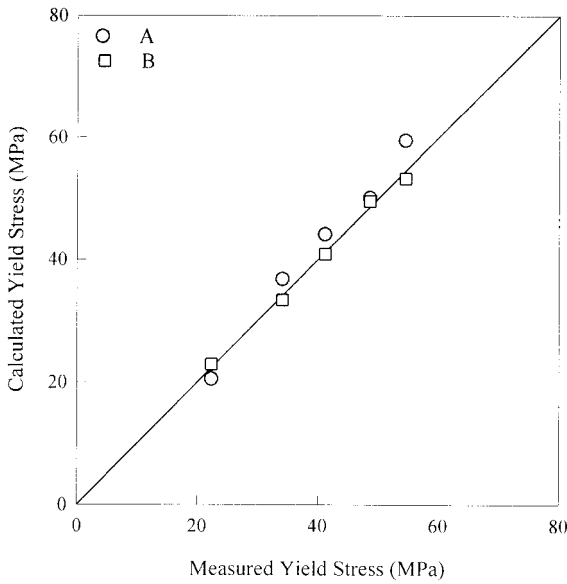


Figure 11 Comparison of the calculated yield stress and the measured yield stress: (A) the calculation of eq. (45), for which the yield strain is used as the strain at maximum stress, and (B) the calculation of eq. (56), for which the yield strain is used as the strain at the maximum rate of entropy production.

strain versus the strain at the maximum rate of entropy production. There is a considerable discrepancy that shows that the two strains are not identical.

From the schematic diagram in Figure 2, we expect an energetic contribution to the yield because the fully relaxed stress changes drastically near the yield. Although a complete set of data is necessary for our theory to analyze the validity of the yield criterion of the entropy production rate in a more detailed form,

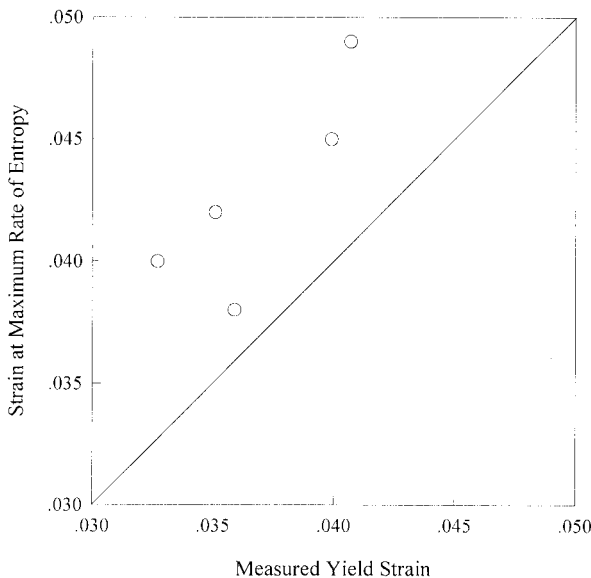


Figure 12 Plot of the measured yield strain versus the strain at the maximum rate of entropy production.

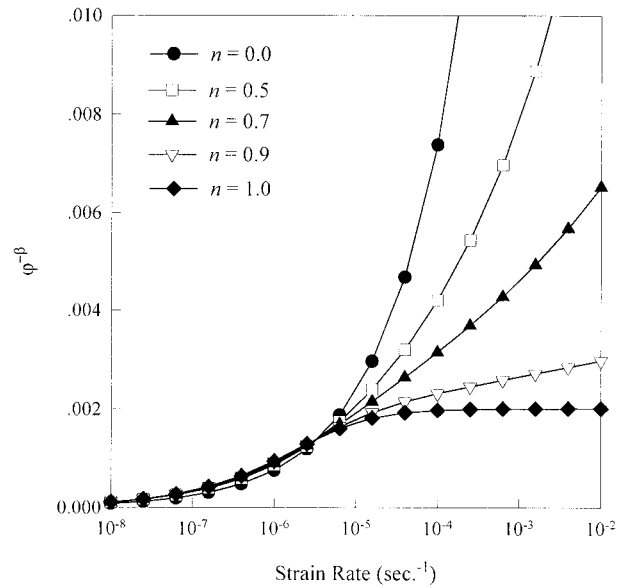


Figure 13 Main effect of the strain rate on the yield stress of eqs. (45) and (56). The parameter n is equivalent to the exponent of the viscosity of the power-law fluid. $n = 0$ means Newtonian dashpot, and $n = 1$ indicates rate-insensitive materials such as metals. We have chosen $n = 0.7$.

Figure 11 suggests a new insight into the yield mechanism.

Equations (45) and (56) contain the term representing the effect of the strain rate, $\phi(\dot{\epsilon})$. The experimental and theoretical results of Rusch and Beck²³ state that the yield strain depends on the strain rate and temperature. Our model can describe such dependencies of the yield strain at the maximum stress.

If $\Delta\sigma_E(\epsilon)$ varies sufficiently little in the neighborhood of the yield strain, the effect of the strain rate on the yield stress depends mainly on $\phi^{-\beta}(\dot{\epsilon})$. Figure 13 shows the plot of $\phi^{-\beta}(\dot{\epsilon})$ versus the strain rate. The behavior of $\phi^{-\beta}(\dot{\epsilon})$ can be seen as a modified Eyring equation.¹¹

CONCLUSIONS

We have developed a nonlinear viscoelastic constitutive equation by the generalization of linear viscoelasticity based on the internal time and irreversible thermodynamics. The constitutive equation gives new insight into the yield mechanism, indicating that the yield occurs when the rate of entropy production becomes maximum. The yield of glassy polymers contains both the energetic contribution represented by fully relaxed stress and the entropic one represented by internal strain Q and internal time. Our model shows that the new yield condition is equivalent to the conventional one in many respects and is confirmed by a comparison with the experimental data.

APPENDIX

Derivation of eq. (26)

We define the initial conditions as follows:

$$e(0) = 0, \quad Q(0) = 0 \quad (A.1)$$

The evolution of eq. (24) in terms of the internal time is

$$\frac{dQ}{d\zeta} = \alpha(e - Q) \quad (A.2)$$

The integration of eq. (A.2) with the initial conditions of eq. (A.1) yields

$$Q(\zeta) = \int_0^\zeta e^{-\alpha(\zeta-x)} e(x) dx \quad (A.3)$$

The application of integration by parts gives eq. (28):

$$Q[\zeta(t)] = e[\zeta(t)] - \int_0^{\zeta(t)} e^{-\alpha[\zeta(t)-\zeta(s)]} \frac{de[\zeta(s)]}{d\zeta(s)} d\zeta(s) \quad (28)$$

Because irreversible thermodynamics states that

$$\sigma \equiv \frac{\partial f}{\partial e} = \frac{\partial f_E}{\partial e} - BQ \quad (A.4)$$

the substitution of eq. (24) into eq. (A.4) yields eq. (26) under the assumption of a constant strain rate.

Derivation of eq. (29)

In the stress-relaxation experiment, the initial value of Q is not zero because of previous loading. If we maintain a fixed strain after stopping the loading process, the initial conditions will be

$$e(0) = e_0 \text{ (constant)}, \quad Q(0) = Q_0 \neq 0 \quad (A.5)$$

where we set time $t = 0$ when we stop the loading and begin observation. The integration of eq. (A.2) with the initial conditions of eq. (A.5) and a zero strain rate yield

$$\begin{aligned} Q[\zeta(t)] &= e^{-\alpha\zeta(t)} Q_0 + \alpha \int_0^{\zeta(t)} e^{-\alpha[\zeta(t)-\zeta(s)]} e_0 d\zeta(s) \\ &= e^{-\alpha\zeta(t)} Q_0 + e_0 [1 - e^{-\alpha\zeta(t)}] \end{aligned} \quad (A.6)$$

The substitution of eq. (A.7) into eq. (A.4) gives

$$\sigma[\zeta(t)] = \frac{\partial f_E}{\partial e}(e_0) - B e^{-\alpha\zeta(t)} Q_0 - B e_0 [1 - e^{-\alpha\zeta(t)}] \quad (A.7)$$

Note that the initial stress is

$$\sigma[\zeta(0)] = \sigma(0) = \frac{\partial f_E}{\partial e}(e_0) - BQ_0 \quad (A.8)$$

because $\zeta(0)$ is 0. At infinite time, the stress becomes

$$\sigma[\zeta(\infty)] = \sigma(\infty) = \frac{\partial f_E}{\partial e}(e_0) - B e_0 \quad (A.9)$$

because the internal time is a monotonically increasing function of the real time. The rearrangement of eq. (A.7) gives eq. (29).

References

1. Bernstein, B.; Shokooh, A. *J Rheol* 1980, 24, 189.
2. Shay, R. M., Jr.; Caruthers, J. M. *J Rheol* 1986, 30, 781.
3. Rendel, R. W.; Ngai, K. L.; Fong, G. R.; Yee, A. F.; Bankert, R. J. *Polym Eng Sci* 1987, 27, 2.
4. Knauss, W. G.; Emri, I. *Polym Eng Sci* 1987, 27, 86.
5. Boyce, M. C.; Parks, D. M.; Argon, A. S. *Mech Mater* 1988, 7, 15.
6. Spathis, G.; Maggana, C. *Polymer* 1997, 38, 2371.
7. Schapery, R. A. *Mech Time-Dependent Mater* 1997, 1, 209.
8. Tervoort, T. A.; Klompen, E. T. J.; Govaert, L. E. *J Rheol* 1996, 40, 779.
9. Drozdov, A. D. *Int J Solids Struct* 1998, 35, 2315.
10. Eyring, H. *J Chem Phys* 1936, 4, 283.
11. Ree, T.; Eyring, H. *J Appl Phys* 1955, 26, 793.
12. Robertson, R. E. *J Chem Phys* 1966, 44, 3950.
13. Argon, A. S. *Philos Mag* 1973, 28, 839.
14. Bowden, P. B.; Raha, S. *Philos Mag* 1974, 29, 149.
15. Brereton, M. G.; Duckett, R. A.; Joseph, S. H.; Spence, P. J. *J Mech Phys Solids* 1977, 25, 127.
16. Haupt, P. In *Non-Equilibrium Thermodynamics with Application to Solids*; Muschik W., Ed.; Springer-Verlag: Vienna, 1993; Chapter 3, pp 77.
17. Valanis, K. C. *Irreversible Thermodynamics of Continuous Media: Internal Variable Theory*; Springer-Verlag: Vienna, 1971.
18. Williams, G.; Watts, D. C. *Trans Faraday Soc* 1970, 66, 80.
19. Povolo, F.; Schwartz, G.; Hermida, E. B. *J Polym Sci Part B: Polym Phys* 1996, 34, 1257.
20. Theodorou, M.; Jasse, B.; Monnerie, L. *J Polym Sci Polym Phys Ed* 1985, 23, 445.
21. Xu, Z.; Jasse, B.; Monnerie, L. *J Polym Sci Part B: Polym Phys* 1989, 27, 355.
22. Jang, S. S.; Jo, W. H. *Macromol Theory Simul* 1999, 8, 1.
23. Rusch, K. C.; Beck, R. H., Jr. *J Macromol Sci Phys* 1969, 3, 365.