Quantitative relation between the relaxation time and the strain rate for polymeric solids under quasi-static conditions

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ABSTRACT: Relaxation time is an essential physical quantity reflecting the hysteresis of the microstructure of materials. To associate the relaxation time with the strain rate, the stress–strain curves of six types of polymers at low strain rate were normalized, and a nondimensional generalized Maxwell model incorporating strain-rate-dependent relaxation times was obtained by the internal variable theory of irreversible thermodynamics. The results indicate that the constitutive equation may capture well the normalized stress–strain behaviors that are not related to the strain rate. The ratio of the initial modulus to the secant modulus at the maximum stress was also found to not rely on the strain rate anymore. Furthermore, strain-rate independence occurred only when the relaxation time was proportional to the time interval for stress from zero to the maximum stress. The relaxation time varied in a power law with the strain rate. The explicit relation is helpful for providing a concise and promising solution for predicting the quasi-static mechanical response of viscoelastic solids. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44114.

INTRODUCTION

Polymers are usually considered a random packing of low-density and high-density nanoscale domains bound together by intramolecular and intermolecular forces; the deformation-induced segmental mobility correlates with the strain rate.[1,2] Therefore, the stress of polymers not only depends on the current strain but also on the strain rate and the deformation history.[3] As a reduced mobility during strain hardening is coupled with an increase in the rate of nonaffine segmental displacements,[4] both the strength and stiffness (including the tangential modulus and secant modulus) of polymers increase with the strain rate. Therefore, a number of efforts have been made to investigate the strain-rate-dependent mechanical properties of polymers and their composites. Most researchers have concentrated on the high-strain-rate deformation and failure behavior of these viscoelastic solids with split-Hopkinson pressure bar (SHPB); a relatively limited number of works has addressed the strain-rate effects under quasi-static loading. For example, Kara et al.[5] reported that the modulus and maximum stress of a symmetric E-glass/polyester composite increased with increasing strain rate, whereas the strain-rate sensitivity in the in-plane direction was higher than that in the through-thickness direction. From the one-dimensional stress–strain curves of polycarbonate (PC) under different strain rates, van Breemen et al.[6]

observed a great effect of the strain rate on the true stress. Qiao and Wu[7] evaluated the rate dependence of the mechanical behavior of polyurea in a strain-rate region from 5.3×10^{-4} to 5.1×10^{-2} s^{-1} and compared it with results at intermediate strain rates.

To quantitatively describe the dependence of the strain rate, Nemat-Nasser and Hori[8] thought that two classes of constitutive models could be identified within the phenomenological framework: (1) fully rate-dependent plasticity and (2) viscoplasticity. Usually, the latter is applied for metal materials. For the former, Nemat-Nasser and Hori further pointed out the deformation rate consists of an elastic constituent and an inelastic constituent throughout the entire deformation history. If such an inelastic deformation is considered a viscous deformation, this model will degenerate into a viscoelastic case. As the yield surface does not exist in the deformation of polymers, the viscoelastic model is suitable for describing the strain-rate effects.

The relaxation time is an essential physical quantity in the viscoelastic constitutive model; it reflects the hysteresis of the microstructure of polymeric materials under external loading.[9–16] The dependence of the relaxation times on the shear (or strain rate) has been studied extensively for viscoelastic fluids in the past. For instance, in polymer melts, nonequilibrium molecular dynamic simulations have shown that the relaxation

Table I. Material Parameters and Testing Conditions for the Polymeric Solids

Polymer	Classification	Experimental temperature (°C)	Glass-transition temperature (°C)	Weight-average molecular weight (g/mol)	Specimen type
PC	Thermoplastic	Room temperature	150	30,500	ASTM D 638
PA6	Thermoplastic	25	53	18,000–52,000	ASTM D 638
Hot-mix asphalt	Thermoplastic	20	263	—	ASTM D 638
HTPB	Thermosetting	50	−76	100,000	PRC QJ 924
HDPE	Thermoplastic	18	−68	274,000	ASTM D 638M
PP	Thermoplastic	5	−10	386,648	ASTM D 638M

times of polymer chains are shear-rate dependent, especially in high values of shear rate (nonlinear regime); general discussions were given in the seminal work by Evans and Morriss[17] and in reports by Baig and coworkers.[18,19] Nonetheless, the relaxation time has normally been treated as an inherent characteristic constant for polymeric solids that would not be affected by the loading conditions; the result of this may be the overstatement of the material properties. To overcome this drawback, a strain-dependent relaxation time perspective was proposed for a visco-hyperelastic constitutive equation to track the large compressive and tensile deformation response of incompressible elastomeric materials at high strain rates.[20] Similarly, with respect to the strain dependence of the relaxation time, Khajehsaeid et al.[21] developed a three-dimensional viscohyperelastic constitutive model for describing the rate-dependent behavior of rubberlike materials at large deformations. These results are of great importance for modeling the stress–strain curve of elastomeric materials in a wide range of strains. However, because the number of required material parameters is still relatively large, it appears that these viscohyperelastic models are not conveniently applied in the design of polymeric products. In addition, there is very little known about whether the strain rate has a substantial influence on the relaxation time of a glassy polymer subjected to quasi-static stress and how to quantitatively describe the rate sensitive effect. Nevertheless, this issue is crucial for adequately and efficiently evaluating the mechanical behaviors of viscoelastic solids in service life.

Because of their good physical and mechanical properties, resistance to chemical corrosion, and easy processing, PC, polyamide 6 (PA6), high-density polyethylene (HDPE), propene (PP), and hot-mix asphalt have played significant roles in a wide number of areas, including in electrical and electronics components, the aerospace industry, and the automotive and construction industries. Therefore, these typical polymers, including not only glassy solids (PC, PA6, and hot-mix asphalt) but also elastomers [hydroxyl-terminated polybutadiene (HTPB), HDPE, and PP] were used in this investigation on the strain-rate dependence of the relaxation time. The published experimental tension data from previous thermoplastic polymers (PC,[6] PA6,[22] hot-mix asphalt,[23] HDPE,[24] and PP[9] and thermosetting elastomers (HTPB[15]) under low strain rates were normalized by a coordinate scaling transformation method, and we noted that the processed stress–strain relations were strain-rate independent. According to internal variables, the theory of irreversible

thermodynamics, and Onsager's principle, a nondimensional general Maxwell model incorporating strain-rate-dependent relaxation times, was obtained. The experimental results indicate that the constitute equation with a single relaxation time is able to capture the quasi-static tensile behavior of the previous six types of viscoelastic solids. Furthermore, the association between the relaxation time and strain rate was analyzed in detail. We observed that the relaxation time of polymers varied as a power law function of the strain rate. Finally, we attempted to qualitatively explain this relationship by virtue of the molecular network model of polymers.

NORMALIZED STRESS–STRAIN RELATION UNDER COORDINATE SCALING TRANSFORMATION

With the purpose of discussing the impacts of the strain rate on the relaxation time, we first analyzed the one-dimensional experimental constitute behaviors of typical polymers, the glass-transition temperature, weight-average molecular weight, and testing conditions of which are listed in Table I. Figure 1(a–f) shows the stress–strain curves at different strain-rate values for PC,[6] PA6,[22] hot-mix asphalt,[23] HTPB,[15] HDPE,[24] and PP,[9] respectively. We readily observed that all of the stress–strain curves were rate sensitive.

For convenience, coordinate scaling transformation[25] was adopted, where the following equalities were assumed:

$$\sigma^* = \sigma/\sigma_0, \quad \varepsilon^* = \varepsilon/\varepsilon_0, \quad t^* = t/t_0, \qquad (1)$$

where σ^* is the normalized stress, σ is the stress, σ_0 is the maximum stress on the stress–strain curve, ε^* is the normalized strain, ε is the strain, ε_0 is the strain at σ_0, t^* is normalized time, t is time and t_0 is the time interval for stress increases from 0 to σ_0.

Equation (1) was applied to normalize the constitute curves for the mentioned polymers, as shown in Figure 2. We observed that for the same material, the normalized stress–strain data for different strain rates were almost located on a single curve. Therefore, we could regard the normalized stress–strain relation as strain-rate independent.

NONDIMENSIONAL GENERALIZED MAXWELL MODEL WITH THE STRAIN-RATE-DEPENDENT RELAXATION TIME

For the glassy polymeric solid under quasi-static loading, it was rational to presume that the deformation in material was small, and the thermodynamic process of the system was treated as an
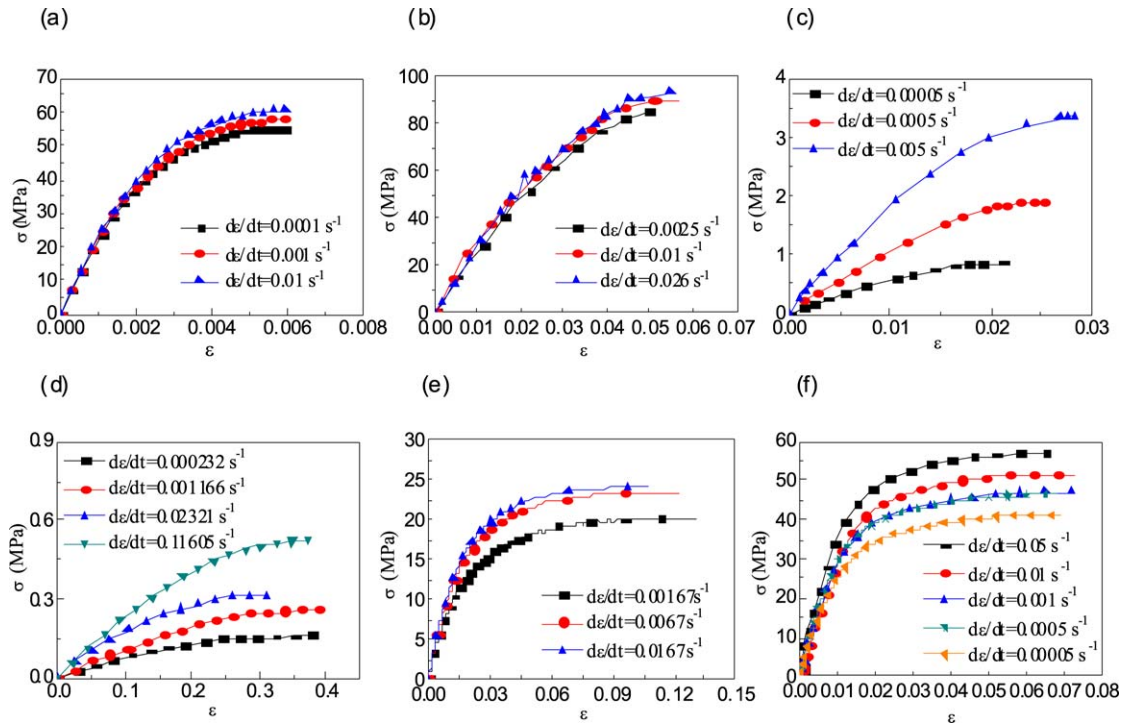
Figure 1. Stress–strain curves of (a) PC, (b) PA6, (c) hot-mix asphalt, (d) HTPB, (e) HDPE, and (f) PP under uniaxial stress at different strain rates ($d\varepsilon/dt$ values). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

isothermal process, where free-energy density functions no longer contained temperature. The Helmholtz free-energy density function (ψ) can be expressed as follows:

$$\psi = \sum_{i=1}^{n} \psi_i$$

$$\psi_i = \frac{1}{2} E_i (\varepsilon - \xi_i)^2 \quad (i=1, \ldots, n) \tag{2}$$

where ξ_i ($i=1, \ldots, n$) is an internal variable indicating the inelastic strain and E_i ($i=1, \ldots, n$) is the modulus. Thus, the relation between the stress and strain can be treated as follows:

$$\sigma = \frac{\partial \psi}{\partial \varepsilon} = \sum_{i=1}^{n} \frac{\partial \psi_i}{\partial \varepsilon} = \sum_{i=1}^{n} E_i (\varepsilon - \xi_i) \tag{3}$$

Generally, the evolution equation of an internal variable may be assumed to obey Onsager's principle, namely

$$\eta_i \dot{\xi}_i = \frac{\partial \psi}{\partial \xi_i} = E_i (\varepsilon - \xi_i) \tag{4}$$

where η_i ($i=1, \ldots, n$) is the viscosity coefficient. The change rate of the internal variable with respect to time $\dot{\xi}_i$ can be calculated as follows:

$$\dot{\xi}_i = \frac{1}{\tau_{Mi}} (\varepsilon - \xi_i) \tag{5}$$

where $\tau_{Mi} = \eta_i / E_i$ ($i=1, \ldots, n$) represents the relaxation time spectrum.

Let

$$\varepsilon_{(e)i} = \varepsilon - \xi_i \tag{6}$$

where $\varepsilon_{(e)i}$ ($i=1, \ldots, n$) is the ith normalized elastic strain. With the derivation of time taken to eq. (6), this yields

$$\dot{\varepsilon}_{(e)i} = \dot{\varepsilon} - \dot{\xi}_i \tag{7}$$

The solution of eqs. (5) and (6) can be expressed as follows:

$$\varepsilon_{(e)i} = \int_{-\infty}^{t} \exp\left[-\left(\frac{t-\tau}{\tau_{Mi}}\right)\right] \dot{\varepsilon}(\tau) d\tau \tag{8}$$

where, τ is an independent variable, which represents a random time point before the time point of t. The substitution of eq. (8) into eq. (3) gives

$$\sigma = \sum_{i=1}^{n} E_i \int_{-\infty}^{t} \exp\left[-\left(\frac{t-\tau}{\tau_{Mi}}\right)\right] \dot{\varepsilon}(\tau) d\tau \tag{9}$$

Set

$$\tau_M^* = \tau_M / t_0 \quad \text{and} \quad E^{(s)} = \sigma_0 / \varepsilon_0 \tag{10}$$

where τ_M^* is the normalized relaxation time, τ_M is the relaxation time. Dividing the maximum stress with respect to both sides of eq. (9), and considering eqs. (1) and (10), we obtain

$$\sigma^* = \sum_{i=1}^{n} \frac{E_i}{E^{(s)}} \int_{-\infty}^{t^*} \exp\left[-\left(\frac{t^*-\tau^*}{\tau_{Mi}^*}\right)\right] \dot{\varepsilon}^*(\tau^*) d\tau^* \tag{11a}$$

Equation (11a) is the nondimensional constitute relation, which is an extension of the generalized Maxwell model incorporating strain-rate-dependent relaxation times, and it can be also expressed by the following formula, that is
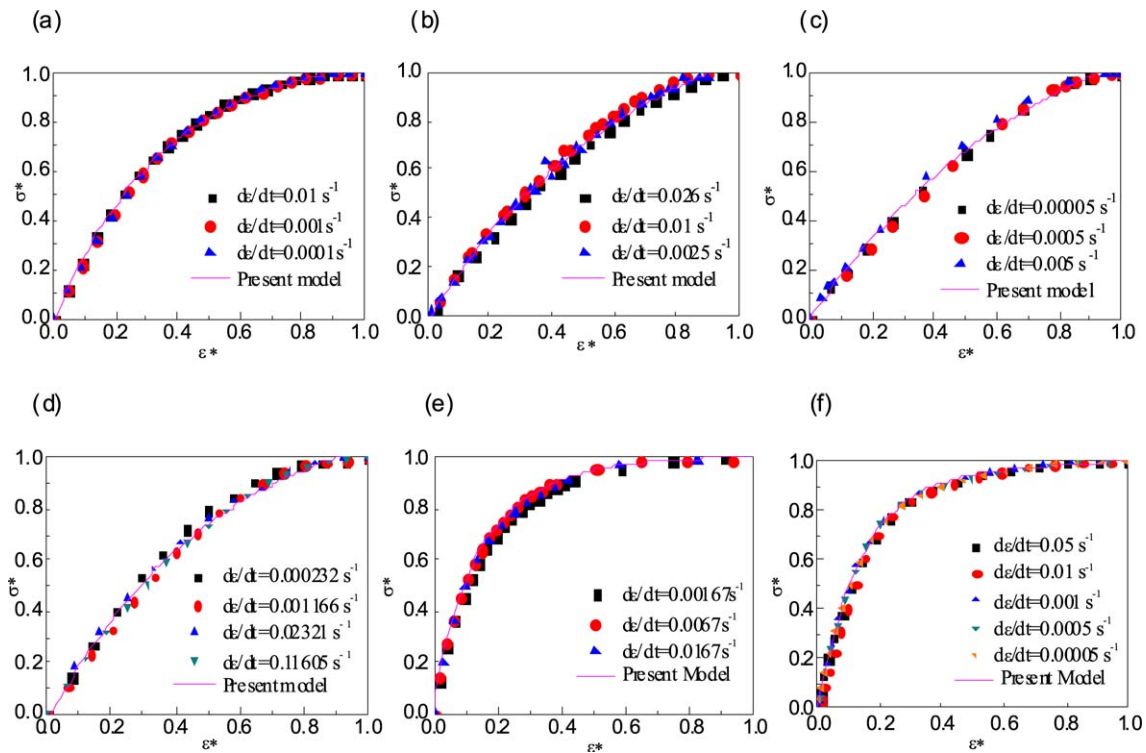
Figure 2. Normalized stress–strain curves of (a) PC, (b) PA6, (c) hot-mix asphalt, (d) HTPB, (e) HDPE, and (f) PP under coordinate scaling transformation at different strain rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\sigma^* = \sum_{i=1}^{n} A_i \int_{0}^{\varepsilon^*(t^*)} \exp - \left[\frac{\varepsilon^*(t^*) - \varepsilon^*(\tau^*)}{\tau_M^*} \right] \right\} d\varepsilon^*(\tau^*), A_i = \frac{E_i}{E^{(s)}} \quad \text{(11b)}$$

RESULTS AND DISCUSSION

An important question is how many terms used in eq. (11) could perfectly describe the normalized experimental stress–strain curves of the PC, PA6, hot-mix asphalt, HTPB, HDPE, and PP under uniaxial tension at a low strain rate. As shown in

Figure 2, the simplified constituted equation ($n = 1$), that is, only the use of a single relaxation time [see eq. (12)] tracked the tensile behavior of the six types viscoelastic solids well in the strain-rate region from 1.0×10^{-5} to 1.2×10^{-1} s^{-1}. We noticed that the multiple relaxation times ($n > 1$) would be a much better choice for other polymeric materials in higher systems. In future work, we envisage that the tensile and compressive deformation responses of epoxy and its composites in different rate ranges will be investigated to further verify eq. (11).
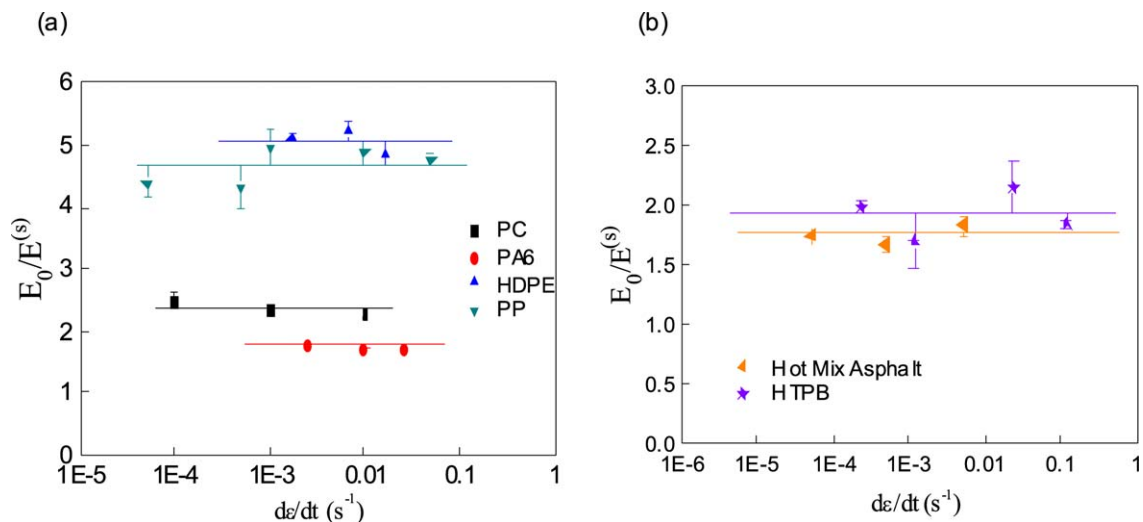
Figure 3. Values of $E_0/E^{(s)}$ at different strain rates for (a) PC, PA6, HDPE, and PP and (b) hot-mix asphalt and HTPB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
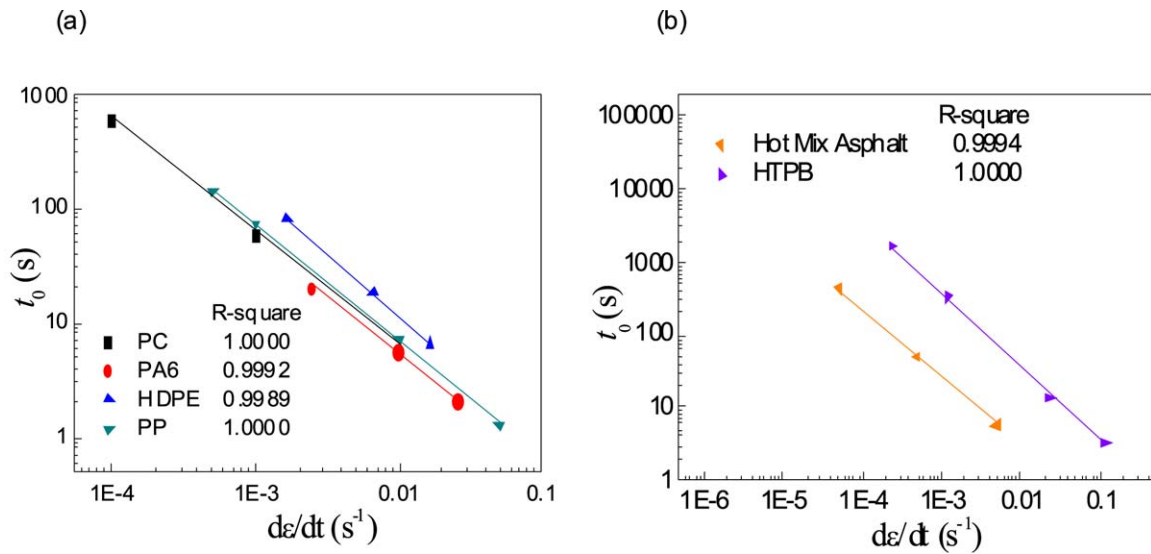
Figure 4. Magnitude of t_0 values at different strain rates for (a) PC, PA6, HDPE, and PP and (b) hot-mix asphalt and HTPB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\sigma^* = \frac{E_0}{E^{(s)}} \int_0^{\varepsilon^*(t^*)} \exp\left\{-\left[\frac{\varepsilon^*(t^*)-\varepsilon^*(\tau^*)}{\tau_{Mi}^*}\right]\right\} d\varepsilon^*(\tau^*) \quad (12)$$

Figure 2 indicates that the normalized stress–strain curves were strain-rate independent, which implies that

$$E_0/E^{(s)} = \text{Constant} \quad (13)$$

$$\tau_M^* = \text{Constant} \quad (14)$$

The values of $E_0/E^{(s)}$ at different strain rates are shown in Figure 1 and plotted in Figure 3. From these figures, $E_0/E^{(s)}$ could be regarded as a strain-rate-independent parameter.

According to eq. (14), the normalized relaxation time is a constant, and this leads to the following equation:

$$\tau_M^* = \tau_M/t_0 = \alpha \quad (15)$$

where α is a constant.

Thus

$$\tau_M = \alpha t_0 \quad (16)$$

Equation (16) indicates that the relaxation time is directly proportional to t_0.

The magnitudes of t_0 at different strain rates are shown in Figure 1 and plotted in Figure 4. We observed that log t_0 was directly proportional to $\log\dot{\varepsilon}$, namely

$$\log t_0 = b\log\dot{\varepsilon} + \log c \quad (17)$$

where b is the effect factor of strain rate, c is the value of t_0 at a reference strain rate. Thus

$$t_0 = c(\dot{\varepsilon}/\dot{\varepsilon}_r)^b \quad (18)$$

where $\dot{\varepsilon}_r = 1 s^{-1}$ is a reference strain rate.

To check the power law relation between t_0 and $\dot{\varepsilon}$, a numerical fitting method was adopted. The calculated results were in agreement with the data of $t_0 - \dot{\varepsilon}$ (see Figure 4); the correlation

coefficient close to 1 indicated that $\dot{\varepsilon}$ following power law dependence with t_0 was believable. The numerical fitting values of c and b for the six mentioned polymeric solid materials are listed in Table II.

From eqs. (16) and (18), we obtained

$$\tau_M = a(\dot{\varepsilon}/\dot{\varepsilon}_r)^b \quad (19)$$

where $a = \alpha c$ is a parameter of the materials.

It can be concluded from eq. (19) that the relaxation time is not a constant but a function of the strain rate. Furthermore, the relaxation time varies in a power law with strain rate.

The time-dependent or viscoelastic behavior of the polymeric system is linked to complicated molecular adjustments that result from macroscopic mechanical deformations.[26] Alfrey[27] described the morphology of a polymer in terms of convolutions, curls, and kinks. Each molecular bond has a rotational freedom that allows the direction of the chain molecule to change at every bond. Thus, the entire molecular chain can twist, spiral, and tangle with itself or with adjacent chains. In view of molecular network models,[28–30] polymers are composed by a network of molecular chains with different lengths, for example, in localized regions with relatively short chains and in long convolutions that span larger areas. Molecules in polymers

Table II. Magnitudes of c and b

Viscoelastic solid	c (s)	b
PC	0.05737	−1.003
PA6	0.06768	−0.9579
Hot-mix asphalt	0.04355	−0.9272
HTPB	0.4335	−0.9836
HDPE	0.09101	−1.057
PP	0.06835	−1.001

subjected to stress slide except at the entanglements and cross-links. Relaxation, intermolecular slippage accompanied by some reversible breaking or swapping of bonds, takes place during this time. A molecular chain may be considered approximately as a nonlinear spring, and it possesses characteristics of relaxation because of readjustments of the kink in the chains. At a greater strain rate, the kinks of a chain with shorter length corresponding to a lesser mass may easily slide, and this will lead to a decrease in the relaxation time; under a lower strain rate, however, the kinks of chains with both lesser mass and larger mass are all induced to slide, and this results in a longer relaxation time. This is why the time for relaxation processes decreases with increasing strain rate.

CONCLUSIONS

In this study, we normalized the stress–strain curves of PC, PA6, hot-mix asphalt, HTPB, HDPE, and PP under quasi-static loading according to the coordinate scaling transformation method. The normalized tension behaviors of the six types of polymeric materials were found to not be sensitive to the strain rate. Moreover, this behavior may be described well by the constitute equation based on a nondimensional Maxwell model incorporating the strain-rate-dependent relaxation time.

From the experimental results at a low strain rate, the ratio of the initial modulus and secant modulus at the maximum stress did not rely on the strain rate, and the correlation between t_0 and strain rate obeyed the power law relation. We further inferred that the power law relation existed between the relaxation time and strain rate. This concise and explicit formulation provides a potential approach for accurately obtaining the relaxation time of polymer glass, and it would help to efficiently track the mechanical response of viscoelastic solids in a quasi-static case.

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