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A constitutive equation for nonlinear stress–strain curves of crystalline polymers

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We present a new method for the analysis of stress–strain curves for crystalline polymers such as polypropylene and polyethylene. A nonlinear constitutive equation that includes terms that cover the plastic deformation and anharmonicity of the spring is developed. In order to quantitatively characterize the nonlinear viscoelasticity using this equation, data on the transient moduli during elongation at a constant rate of strain are required. Hence, the simultaneous measurements of linear oscillatory viscoelastic moduli during a constant rate of elongation were investigated. It was found that the present method makes possible the evaluation of the plastic deformation fraction and the Grüneisen constant for crystalline polymers. © *1998 Chapman & Hall*

1. Introduction

The mechanical properties of polymer solids exhibit a marked deviation from linear viscoelastic behaviour even at small strains [1]. This nonlinear viscoelastic behaviour is an important property that has to be considered in the application of these plastic materials. The mechanical properties of polymers are generally treated in terms of phenomenological models [2–8]. A considerable effort has been expanded in order to develop constitutive equations based on modifications of the Boltzmann superposition principle following the pioneering work of Leaderman [2].

Crystalline polymers have a more complicated mechanical behaviour compared to amorphous polymers due to their complicated structures that are composed of both crystalline and amorphous phases [9, 10]. In addition it is well known that polymers containing a high crystalline fraction show strong nonlinearity in their elongation deformation behaviour. It has been observed that plastic deformation [11–13], such as dislocation, the formation of microvoids, and the slippage of crystallites, can arise from any applied strain or stress and that a nonlinear intermolecular interaction [14, 15] can be caused by thermal excitation and strains. Thus, the currently available nonlinear viscoelastic constitutive models, that do not consider these effects, are insufficient to fully describe the nonlinear mechanical properties of crystalline polymers. The plastic deformation and anharmonic interaction need to be considered if fully representative nonlinear constitutive models are to be produced.

The aim of this work is to develop a nonlinear constitutive model that includes the plastic deformation and also to demonstrate a new analytical method which makes it possible to characterize the nonlinear stress–strain behaviour of crystalline polymers such as polypropylene and polyethylene.

2. Constitutive equation

A nonlinear Maxwell element consisting of a nonlinear spring, E_i, and a linear dashpot with a tensile viscosity, η_i, connected in series is the basis for the present theory as is shown in Fig. 1. The following assumptions have been applied: (1) the nonlinear response is assumed to be caused by anharmonicity (or nonlinearity) of the elastic elements; (2) the anharmonicity is independent of the time-scale of the excitation when a time-dependent excitation is applied; and (3) the cross-sectional area remains constant during the elongational deformation.

The anharmonicity will be developed using the experimental facts that the crystal lattice exhibits a thermal expansion, particularly in the α-dispersion regions [16–18], and also that the vibrational frequencies of the crystalline bands in the infrared and Raman spectra are shifted by applied stresses or strains [14, 19]. These frequency shifts largely depend on the magnitude of the applied stresses or strains.

If assumption 3 is valid, the stress can be defined as the load per unit area of undeformed cross-section. This may be achieved by deforming an isotropic film with a small strain. Then, the constitutive equation can be treated by a one dimensional representation.

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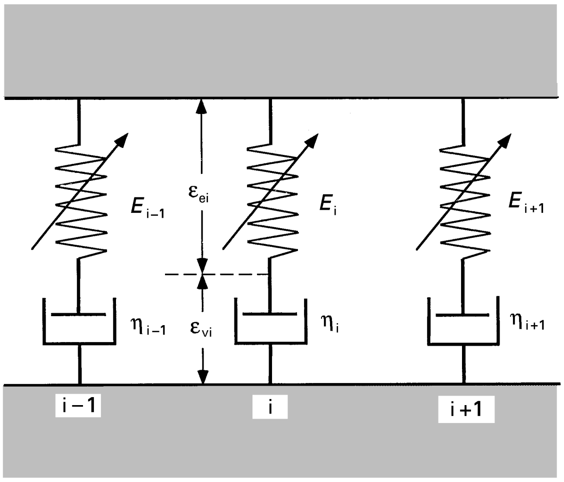

Figure 1 Nonlinear Maxwell element. Nonlinear modulus: $E_i = E_{0i}\,e^{-2\gamma_G \varepsilon_{ei}}$ and relaxation time: $\lambda_i = \eta_i/E_{0i}$.

In this work, for the sake of simplicity, the anharmonic spring introduced by Toda is adopted. The anharmonic potential function, $\phi(\varepsilon)$, is expressed by a closed form [20, 21]:

$$\phi(\varepsilon) = a\varepsilon - \frac{a}{b}(1 - e^{-b\varepsilon}) \tag{1}$$

where a and b are positive constants, and ε is the strain. Differentiating Equation 1 with respect to the strain, we obtain the equation for the stress–strain relation:

$$\sigma(\varepsilon) = a(1 - e^{-b\varepsilon}) \tag{2}$$

Again, differentiating Equation 2 with respect to the strain, we obtain the transient elastic modulus:

$$E(\varepsilon) = ab\,e^{-b\varepsilon} \tag{3}$$

Thus, the Young's modulus E_0 and the Grüneisen constant γ_G, which determines the degree of anharmonicity [22], can be obtained by:

$$E_0 = \lim_{\varepsilon \to 0}\left(\frac{d\sigma}{d\varepsilon}\right) \tag{4}$$

and

$$\gamma_G = -\frac{1}{2}\frac{d\ln E}{d\varepsilon} \tag{5}$$

Substituting Equations 2 and 3 into Equations 4 and 5, respectively, we obtain:

$$E_0 = ab \tag{6}$$

and

$$\gamma_G = \frac{b}{2} \tag{7}$$

Consequently, the stress–strain relation of a nonlinear spring can be rewritten as:

$$\sigma(\varepsilon) = \frac{E_0}{2\gamma_G}(1 - e^{-2\gamma_G \varepsilon}) \tag{8a}$$

If we expand the stress function in terms of a power series of ε, then:

$$\begin{aligned}\sigma(\varepsilon) = {} & E_0\varepsilon - E_0\gamma_G\varepsilon^2 + \tfrac{2}{3}E_0\gamma_G^2\varepsilon^3 \\ & - \tfrac{1}{3}E_0\gamma_G^3\varepsilon^4 + \cdots \end{aligned} \tag{8b}$$

It is found that the high-order strain effects in the stress response can be related to the magnitude of γ_G.

According to assumption 2, the Young's modulus of ith element, E_{0i}, in the generalized nonlinear Maxwell model can be written as:

$$E_{0i} = a_i b \tag{9}$$

Using Equation 6, we have:

$$a_i = \frac{E_{0i}}{2\gamma_G} \tag{10}$$

As a consequence, the differential equation for a nonlinear Maxwell element can be given by:

$$\left(1 + \frac{\lambda_i}{1 - \sigma_i/a_i}\frac{d}{dt}\right)\sigma_i = \lambda_i E_{0i}\dot{\varepsilon} \tag{11}$$

where λ_i ($= \eta_i/a_i b = \eta_i/E_{0i}$) is the characteristic time of each element. If a strain ε is instantaneously applied, the nonlinear Maxwell model gives:

$$\frac{\sigma_i}{a_i - \sigma_i} = \frac{\sigma_{0i}}{a_i - \sigma_{0i}}\,e^{-t/\lambda_i} \tag{12}$$

where σ_{0i} is the stress at $t = 0$. Details of the deviation are presented in the Appendix. Since the dashpot can not be deformed by the sudden strain ε, the initial stress σ_{0i} can be shown, using Equation 2, to be:

$$\sigma_{0i} = a_i(1 - e^{-2\gamma_G\varepsilon}) \tag{13}$$

The substitution of Equation 13 into Equation 12 gives:

$$\sigma_i = \frac{a_i(1 - e^{-2\gamma_G\varepsilon})\,e^{-t/\lambda_i}}{1 - (1 - e^{-2\gamma_G\varepsilon})(1 - e^{-t/\lambda_i})} \tag{14}$$

The kernel (or response function) of the integral constitutive equation is given by differentiating Equation 14 with respect to the strain ε:

$$E_i(t;\varepsilon) = \left(\frac{\partial\sigma_i}{\partial\varepsilon}\right)_t \tag{15}$$

Therefore,

$$E_i(t;\varepsilon) = \frac{E_{0i}e^{-2\gamma_G\varepsilon}e^{-t/\lambda_i}}{[1 - (1 - e^{-2\gamma_G\varepsilon})(1 - e^{-t/\lambda_i})]^2} \tag{16}$$

The sum of Equation 16 becomes the relaxation modulus of the nonlinear model. If ε is sufficiently small or the denominator of Equation 16 is approximately equal to unity, Equation 16 can be rewritten as:

$$E_i(t;\varepsilon) = E_{0i}\,e^{-2\gamma_G\varepsilon}\,e^{-t/\lambda_i} \tag{17}$$

If the linear relaxation modulus $E(t)$ can be defined by:

$$E(t) = \sum_i E_{0i}\,e^{-t/\lambda_i} \tag{18}$$

then we have

$$E(t;\varepsilon) = \sum_i E_i(t;\varepsilon) = E(t)h(\varepsilon) \tag{19}$$

where

$$h(\varepsilon) \equiv e^{-2\gamma_G\varepsilon} \tag{20}$$

As a result, the kernel can be divided into two terms one containing the strain-dependent terms whilst other term contains the time dependent terms. The validity of Equation 19 has been experimentally proved for various crystalline polymers such as polyethylene and polypropylene [23–26].

When a time-dependent excitation, e.g., elongational deformation at constant rate, is applied, the mechanical history effects can be linearly additive as is demonstrated in Equation 18. Thus, the stress can be expressed by the sum of the contributions of all the previous step strains, i.e., the Boltzmann superposition principle.

When the step strain is applied between t' and $t' + \Delta t'$, it will create the following stress at a later time t:

$$\Delta\sigma(t) = E(t - t')\exp\left[-2\gamma_G \sum_{t'} \Delta\varepsilon(t')\right]\Delta\varepsilon(t') \quad (21)$$

According to the Boltzmann principle, the stress at time t can be obtained in the continuous limit as:

$$\sigma(t) = \int_{-\infty}^{t} E(t - t')\,e^{-2\gamma_G\varepsilon}\left(\frac{d\varepsilon}{dt'}\right)dt' \quad (22)$$

When a crystalline polymer is deformed, the plastic deformation will be generated as previously described. The plastic deformation will induce the overestimation of the applied strain γ which is defined as the ratio of the increment of the length to the initial length of the film specimen. A deformation applied to a material is partially consumed as the plastic deformation and the remainder of the deformation effectively strains the material. Hereafter, we referred the strain ε as the "effective strain" and the strain γ as the "apparent strain". Here, a transient effective strain fraction $\Psi(t)$ is introduced as defined by the following equation:

$$d\varepsilon = \Psi(t)d\gamma = \dot{\gamma}\Psi(t)dt \quad (23)$$

where $\dot{\gamma}$ is the apparent strain rate. The function $\Psi(t)$ indicates the contribution of the effective deformation to the total deformation. Consequently, we have:

$$\sigma(t) = \int_{-\infty}^{t} E(t - t')h(\varepsilon)\dot{\gamma}\Psi(t')dt' \quad (24)$$

Equation 24 is the basic equation in the nonlinear Maxwell model.

3. Calculation of parameters

Considering the case in which a crystalline polymer is deformed at a constant rate $\dot{\gamma} = R$ and the deformation is applied at $t = 0$. In this case Equation 24 can be expressed as the Volterra integral equation:

$$\sigma(t)/R = \int_{0}^{t} E(t - t'; \varepsilon)\Psi(t')dt' \quad (25)$$

The solution for $\Psi(t)$ is given by:

$$\Psi(t) = \frac{1}{R}L^{-1}\left[\frac{L[\sigma(t)]}{L[E(t;\varepsilon)]}\right] \quad (26)$$

where the operators of L and L^{-1} denote the Laplace transform and the inverse Laplace transform.

The Fourier transformation of Equation 19 gives:

$$F[E(t;\varepsilon)] = F[E(t)h(\varepsilon)] \quad (27)$$

where F is the Fourier transform operator. If $E^*(i\omega)$ is the complex modulus at each instant of elongational deformation, we have

$$F[E(t)] = i\omega E^*(i\omega) \quad (28)$$

Assuming that $h(\varepsilon)$ is almost independent of time in the case that the frequency of the oscillatory deformation is much higher than the elongational strain rate, $h(\varepsilon)$ can be calculated from the dynamic modulus of the undeformed state $E^*(i\omega)_{t=0}$ as follows:

$$h(\varepsilon) = \frac{|E^*(i\omega)|_{t=t}}{|E^*(i\omega)|_{t=0}} \quad (29)$$

The value of $h(\varepsilon)$ at any elongation time t can be calculated from the transient modulus during elongation. Therefore, the values of $\Psi(t)$ can be calculated from Equation 26 using $E(t)$ obtained from linear stress relaxation data. Moreover, the effective strain ε at any elongation time t can be calculated by:

$$\varepsilon = R\int_{0}^{t}\Psi(t')dt' \quad (30)$$

Also, the fraction of apparent plastic strain $\phi_{pl}(t)$ can be obtained by:

$$\phi_{pl}(t) \equiv \frac{\gamma - \varepsilon}{\gamma} = 1 - \frac{1}{t}\int_{0}^{t}\Psi(t')dt' \quad (31)$$

The $\phi_{pl}(t)$ indicates the accumulated plastic strain when current deformation is applied.

4. Experimental

4.1. Sample characterization

In this work, the tensile properties of isotactic polypropylene (i-PP) and low density polyethylene (LDPE) in the small strain region are analysed using the nonlinear constitutive equation. The samples were of commercial origin. The i-PP has weight- and number-average molecular weights of 2.1×10^5 and 4.3×10^4, respectively, and the LDPE has values of 4.2×10^5 and 5.0×10^4, respectively. The LDPE contains long chain branches of about 8.9 per 1000 carbon atoms, a value that was estimated from simultaneous measurements using intrinsic viscosity and gel permeation chromatography. The film specimens used in this study were quenched. The densities of the i-PP and LDPE films thus obtained were 909 and 919 ($kg\,m^{-3}$), giving a degree of crystallinity of 0.69 and 0.48, respectively.

4.2. Measurements

In order to characterize the nonlinear viscoelastic behaviour of the crystalline polymers, we measured the oscillatory tensile modulus during uniaxial elongation using a dynamic mechanical analyser (DVE-V4, Rheology Co. Ltd.). The apparatus was modified by the authors so that one clamp oscillates sinusoidally whilst the other one moves with a constant rate. The strain and stress waves were analysed using Fourier expansions.

The applied strain γ was determined from the ratio of the increment of the length to the initial length between the clamps. The tensile stress was estimated from the load divided by initial cross-section using assumption 3.

Consider a sinusoidal strain superimposed onto an elongational strain:

$$\gamma(t) = \gamma_{\mathrm{el}}(t) + \gamma_{\mathrm{os}}(t)\sin\omega t \quad (32)$$

and

$$\gamma_{\mathrm{el}}(t) = Rt \quad (33)$$

$$\gamma_{\mathrm{os}}(t) = \frac{\gamma_{\mathrm{os}}}{1 + Rt} \quad (34)$$

where ω is the angular frequency of the oscillatory deformation, γ_{os} is the amplitude of initial oscillatory strain, and R is the strain rate. If the following condition can be attained, then the fundamental component in the Fourier expansion of the applied strain is identical with Equation 32

$$R\frac{2\pi}{\omega} \ll 1 \quad \text{or} \quad \frac{R}{f} \ll 1 \quad (35)$$

where $f\ (=\omega/2\pi)$ is the frequency in Hertz. Thus, the oscillatory moduli can be precisely determined under the condition that the frequency of the oscillatory deformation is much higher than the elongational strain rate. The experimental conditions determining whether or not Equation 35 is satisfied can be obtained by measuring the Lissajous figure.

When a strain given by Equation 32 is applied to a specimen under the conditions of Equation 35, the stress wave can be expressed by the Fourier expansion:

$$\sigma(t) = a_0(t)/2 + \sum_{\mathrm{n}} a_{\mathrm{n}}(t)\sin n\omega t + \sum_{\mathrm{n}} b_{\mathrm{n}}(t)\cos n\omega t \quad (36)$$

The coefficient a_0 is calculated by:

$$a_0(t) = \frac{\omega}{\pi}\int_{\mathrm{t}}^{2\pi/\omega + \mathrm{t}} \sigma(t')\,\mathrm{d}t' \quad (37)$$

The fundamental components ($n = 1$) can be calculated from:

$$a_1(t) = \frac{\omega}{\pi}\int_{\mathrm{t}}^{2\pi/\omega + \mathrm{t}} \sigma(t')\sin\omega t'\,\mathrm{d}t' \quad (38)$$

$$b_1(t) = \frac{\omega}{\pi}\int_{\mathrm{t}}^{2\pi/\omega + \mathrm{t}} \sigma(t')\cos\omega t'\,\mathrm{d}t' \quad (39)$$

The absolute value of the complex modulus $|E^*|$, storage modulus E', loss modulus E'', and the phase difference δ with respect to the oscillatory strain are calculated using the following equations [9].

$$|E^*(\mathrm{i}\omega)| = \left.\frac{[a_1(t)^2 + b_1(t)^2]^{1/2}}{\gamma_{\mathrm{os}}(t)}\right|_{\mathrm{t} = \gamma/\mathrm{R}} \quad (40)$$

$$E' = |E^*(\mathrm{i}\omega)|\cos\delta \quad (41)$$

$$E'' = |E^*(\mathrm{i}\omega)|\sin\delta \quad (42)$$

$$\delta = \cos^{-1}\{a_1(t)/[a_1(t)^2 + b_1(t)^2]^{1/2}\} \quad (43)$$

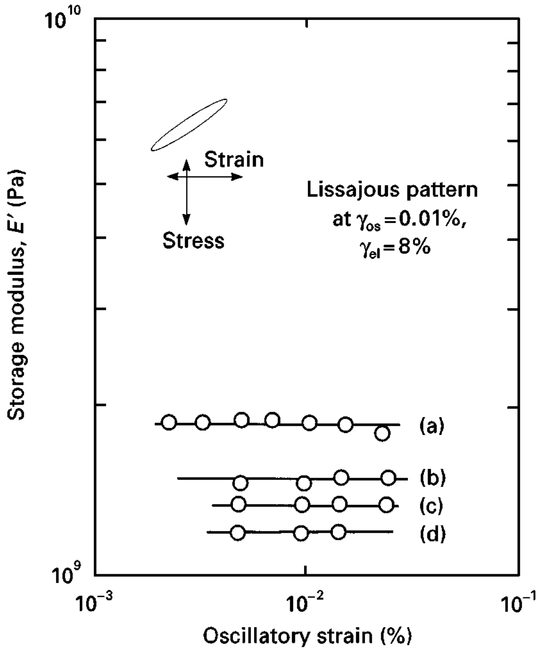

Figure 2 Dependence of the oscillatory amplitude at 100 Hz and 298 K on the storage modulus during the elongation for a constant rate of strain for i-PP. Data taken at γ_{el} values of (a) 0%, (b) 2%, (c) 4% and (d) 8%.

The elongational stress was determined by Equation 37 and the complex moduli were determined from Equations 40–43 using Equations 38 and 39.

The measurements were performed using the following conditions: the elongational rate was 1.0 mm min^{-1}, the initial length between the clamps was 20 mm, the amplitude of oscillatory deformation was 10 μm, the oscillatory frequency was 100 Hz, and the temperature was 298 K.

Fig. 2 shows the dependence of the oscillatory deformation amplitude γ_{os} on the storage modulus E' measured during elongation for i-PP. It was found that the E' value is independent of γ_{os} and the Lissajous pattern is assumed to be closed under elongation, indicating that the linear transient moduli can be precisely measured during elongation using the reported experimental conditions.

The linear relaxation function $E(t)$ was estimated from the master curves of the oscillatory moduli in the undeformed states [27] using:

$$E(t) = E'(\omega) - 0.560E''(\omega/2) + 0.200E''(\omega)|_{\omega = 1/\mathrm{t}} \quad (44)$$

The master curve for i-PP is shown in Fig. 3. The oscillatory moduli were measured over the frequency range of 0.02–200 Hz in the temperature range of 290–353 K. The master curves of the oscillatory moduli were obtained in terms of both vertical and horizontal shifts.

5. Results and discussion

Fig. 4 shows the stress–strain curves obtained in the strain range below 10% in which both films showed no stress-whitening or necking. It was confirmed (but

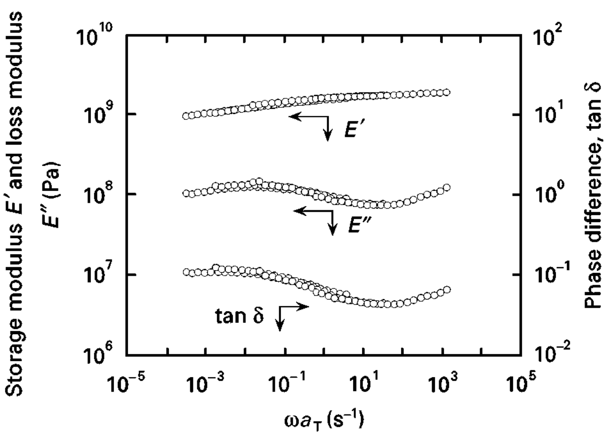

Figure 3 The master curves of the oscillatory moduli of i-PP.

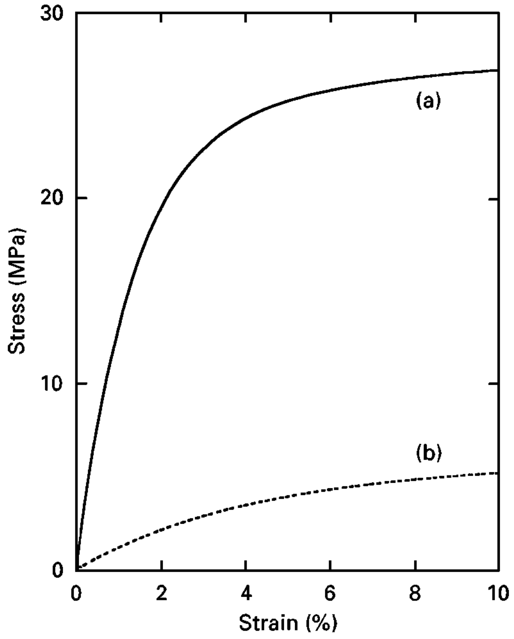

Figure 4 Stress–strain curves of (a) i-PP and (b) LDPE.

not shown here) that the stress–strain curves measured using oscillatory deformation were identical with the curves measured simultaneously without any oscillatory deformation.

In Fig. 5, the complex moduli $|E^*|$ are plotted against the elongational strain. The magnitude of $|E^*|$ decreases monotonically with increasing γ. The decreases in $|E^*|$ for i-PP is greater than that for LDPE. The decreases in $|E^*|$ with γ indicates a deviation from Hooke's law which is due to the anharmonicity of the intermolecular potential, the plastic deformation, and the viscoelasticity. Values for $h(\varepsilon)$ can be estimated from $|E^*|$ as a function of elongational time using Equation 29.

Substituting the numerical values of $\sigma(t)$ estimated from Fig. 4 and the values of $E(t;\varepsilon) = E(t)h(\varepsilon)$ into Equation 26, the transient effective strain fraction $\Psi(t)$ can be calculated as a function of elongational time. Moreover, the fraction of plastic deformation $\phi_{\mathrm{pl}}(t)$ can be estimated using Equation 31. Figs 6 and 7 show the dependence of the elongational time on $\Psi(t)$ and $\phi_{\mathrm{pl}}(t)$, respectively. As seen in these figures, the magnitude of plastic deformation for both films shows a monotonic increase with the elongation. It is observed that the plastic deformation for i-PP with a higher crystallinity is much greater than that of LDPE.

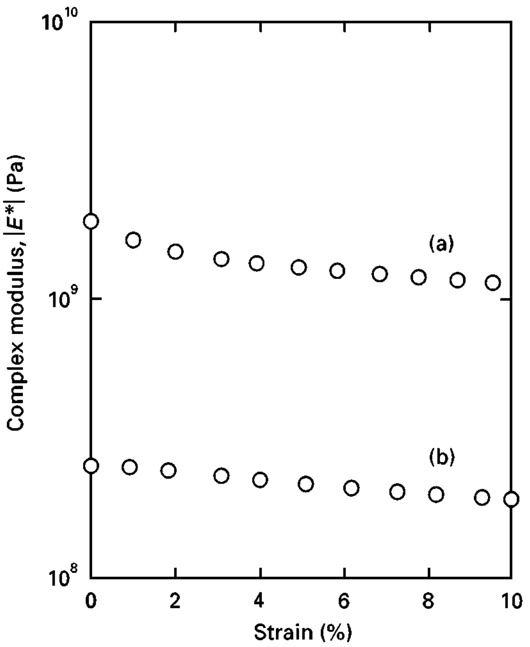

Figure 5 Oscillatory complex moduli $|E^*|$ during elongation plotted against the applied elongational strain for (a) i-PP and (b) LDPE.

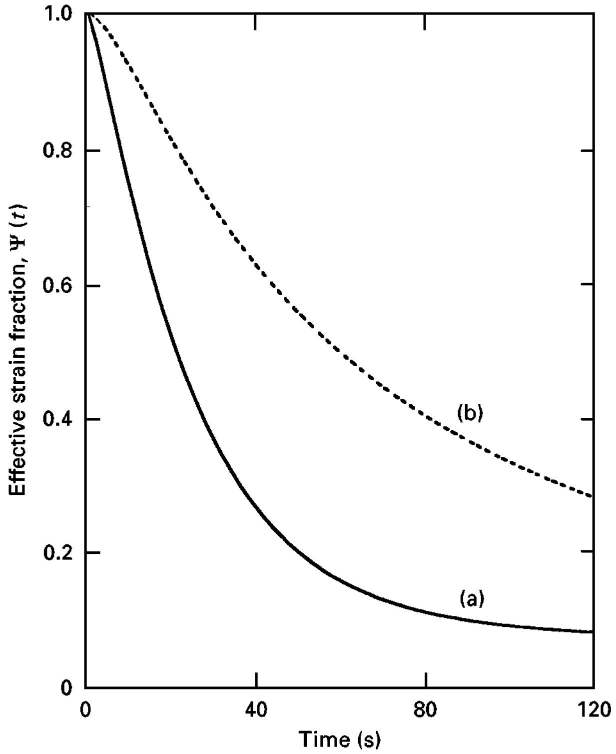

Figure 6 Effective strain fraction $\Psi(t)$ plotted against the elongational time for (a) i-PP and (b) LDPE.

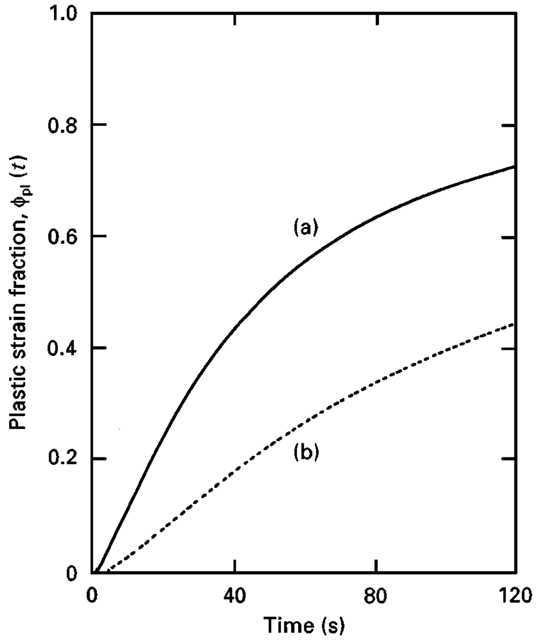

Figure 7 Plastic strain fraction $\phi_{\rm pl}(t)$ plotted against the elongational time for (a) i-PP and (b) LDPE.

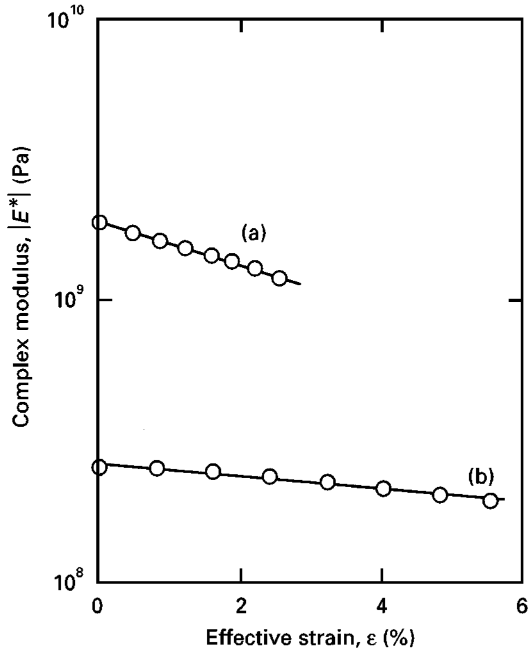

Figure 8 Oscillatory moduli during elongation plotted against the effective strain ε for (a) i-PP and (b) LDPE.

In Fig. 8, the transient moduli under elongation are plotted against the effective strain ε calculated using Equation 30. The semilogarithmic plot gives a line with a negative slope as expected from Equation 20. This indicates the validity of the present constitutive equation to describe the tensile behaviour of crystalline polymers. The Grüneisen constant $\gamma_{\rm G}$, which represents the nonlinearity of elasticity, can be estimated from the slope of the line using Equation 5, giving $\gamma_{\rm G} = 8.9$ for i-PP and $\gamma_{\rm G} = 2.5$ for LDPE. It was found that the nonlinearity of i-PP is much greater than that of LDPE. These values are comparable with the values published elsewhere [28, 29].

6. Conclusions

We have proposed a new integral nonlinear constitutive equation for crystalline polymers, in which the plastic deformation and the anharmonicity of the spring constant are taken into account. Data on the transient moduli during elongation are needed for the determination of the nonlinear viscoelastic behaviour of i-PP and LDPE. As a result, the simultaneous measurements of small oscillatory and elongational deformation were performed and the values of the factors were used to calculate values for physical quantities such as the plastic deformation fraction and the Grüneisen constant.

The following points about the present analytical method should be noted. If the frequency of oscillation is too low, the oscillatory moduli can not be precisely evaluated because the Lissajous pattern is unclosed. On the other hand, if the frequency is much higher, the oscillatory moduli become the adiabatic (dynamic) moduli rather than the isothermal (static) ones. Thus, the higher frequency oscillation is no longer identical with the transient moduli during elongation at a lower strain rate. In general, the relationship between the adiabatic bulk modulus, $K_{\rm S}$, and the isothermal bulk modulus, $K_{\rm T}$, can be given by:

$$K_{\rm S} = K_{\rm T}\frac{C_{\rm p}}{C_{\rm v}} \qquad (45)$$

where $C_{\rm p}$ and $C_{\rm v}$ are the specific heats at constant pressure and at constant volume, respectively. Thus, we must be careful to distinguish between the adiabatic (dynamic) modulus and the isothermal (static) modulus.

Moreover, if we obtain data on the transient Poisson's ratios, assumption 3 can be omitted. Then, the nonlinear parameters such as the plastic deformation fraction and the Grüneisen constant can be more precisely determined by the extension of the one-dimensional constitutive equation to a three dimensional representation.

Appendix

For simplicity, we introduce a reduced stress defined by:

$$\tau_{\rm i} = \sigma_{\rm i}/a_{\rm i} \qquad ({\rm A1})$$

Then, Equation 11 can be rewritten as:

$$\left(1 + \frac{\lambda_{\rm i}}{1-\tau_{\rm i}}\frac{{\rm d}}{{\rm d}t}\right)\tau_{\rm i} = 2\lambda_{\rm i}\gamma_{\rm G}\dot{\varepsilon} \qquad ({\rm A2})$$

We let $J_{\rm i} = 1/(1-\tau_{\rm i})$. Then Equation A2 can be rewritten as:

$$\dot{J}_{\rm i} + P_{\rm i}(t)J_{\rm i} = \lambda_{\rm i}^{-1} \qquad ({\rm A3})$$

and

$$P_{\rm i}(t) = \lambda_{\rm i}^{-1}(1 - 2\lambda_{\rm i}\gamma_{\rm G}\dot{\varepsilon}) \qquad ({\rm A4})$$

Equation A3 becomes the Bernoulli equation. The solution for J_i is given by:

$$J_i = e^{-\int_0^t P_i(t')\,dt'}\left[\lambda_i^{-1}\int_0^t e^{\int_0^{t'} P_i(t'')\,dt''}\,dt' + C_i\right] \tag{A5}$$

where C_i is a constant. In the case of the stress relaxation test, putting $\dot{\varepsilon} = 0$ into Equation A5, we obtain:

$$J_i = 1 + (C_i - 1)\,e^{-t/\lambda_i} \tag{A6}$$

Equation A6 can be rewritten as Equation 12 in the text.

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References

1. I. M. WARD and P. W. HADLEY, "An introduction to the mechanical properties of solid polymers" (Wiley, New York, 1993).
2. H. LEADERMAN, "Elastic and creep properties of filamentous material" (Textile Foundation, Washington D.C., 1943).
3. R. G. LARSON, "Constitutive equations for polymer melts and solutions" (Butterworths, Boston, 1988).
4. B. BERNSTEIN, E. A. KEARSLEY and L. J. ZAPPAS, *Trans. Soc. Rheol.* **7** (1963) 391.
5. R. A. SCHAPERY, *Polym. Engng Sci.* **9** (1969) 295.
6. A. GREEN and R. S. RIVLIN, *Arch. Rat. Mech. Anal.* **1** (1957) 1.
7. O. NAKADA, *J. Phys. Soc. Jpn.* **15** (1960) 2280.
8. K. OKANO and O. NAKADA, *ibid.* **16** (1961) 2071.
9. A. TANAKA and S. ONOGI, *Polym. Engng Rev.* **3** (1983) 235.
10. J. LAI and A. BAKKER, *Polym. Engng Sci.* **35** (1995) 1339.
11. L. LIN and A. S. ARGON, *J. Mater. Sci.* **29** (1994) 294.
12. R. J. SAMUELS, in "Plastic deformation of polymers", edited by A. Peterlin (Marcel Dekker, New York, 1971) p. 241.
13. J. M. SCHULTZ, *Polym. Engng Sci.* **24** (1984) 771.
14. R. S. BRETZLAFF and R. P. WOOL, *J. Appl. Phys.* **52** (1981) 5964.
15. Y. WADA, A. TANAI, T. NISHI and S. NAGAI, *J. Polym. Sci. A* **27** (1969) 201.
16. H. G. OLF and A. PETERLIN, *ibid.* **28** (1969) 753.
17. K. IOHARA, K. IMADA and M. TAKAYANAGI, *Polym. J.* **4** (1973) 239.
18. T. KIJIMA, K. KOGA, K. IMADA and M. TAKAYANAGI, *ibid.* **7** (1973) 14.
19. J. C. RODRIGUEZ-CABELLO, J. C. MERINO, T. JAWAHARI and J. M. PASTOR, *Polym.* **36** (1995) 4233.
20. M. TODA, *J. Phys. Soc. Jpn.* **22** (1967) 431.
21. *Idem., ibid.* **23** (1967) 501.
22. C. KITTEL, "Introduction to solid state physics" (Wiley, New York, 1966).
23. S. ONOGI, A. TANAKA and M. ISHIKAWA, *Polym. J.* **7** (1975) 467.
24. A. TANAKA, K. TANAI and S. ONOGI, *Bull. Inst. Chem. Res. Kyoto Univ.* **55** (1977) 177.
25. T. YAMAGUCHI, T. YANAGAWA and S. KIMURA, *Sen-i Gakkaishi* **32** (1976) 403.
26. G. W. BECKER and H. J. RADEMACHER, *J. Polym. Sci.* **58** (1962) 621.
27. F. R. SCHWARZL, *Rheol. Acta* **14** (1975) 581.
28. B. K. SHARMA, *Polym.* **24** (1983) 314.
29. E. L. RODRIGUEZ and F. E. FILISKO, *J. Mater. Sci.* **22** (1987) 1934.

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