

Strain-rate sensitivity index of thermoplastics

D. L. GOBLE, E. G. WOLFF

Department of Mechanical Engineering, Oregon State University, Corvallis, OR 97331, USA

Strain-rate sensitivity index, m , values of several thermoplastics (HDPE, PP, PMMA, PS, PVC, PC, and PA) were determined at ambient temperature by both variable strain-rate and stress-relaxation methods. Specimens were loaded in tension in the elastic portion of the stress-strain curve at various strain rates and the load was recorded as a function of elongation. Index values were determined from the relation $m = [\partial \ln(\sigma)] / [\partial \ln(\dot{\epsilon})]_{\epsilon, \tau}$. Specimens were also loaded in tension at constant strain rate to the proportional limit, loading was halted, and the load was recorded as a function of time at constant strain. A numerical algorithm was implemented to minimize the root-mean-square difference between an empirical equation and the experimental data, i.e.

$$\Phi(n, \tau) = \left(\frac{1}{N} \sum_i \{ P_0 \exp[-(t_i/\tau)^n] - P(t_i) \}^2 \right)^{1/2}$$

The characteristic time parameter, (τ) , and the rate-of-decay parameter, n , were found when $\Phi(n, \tau)$ was minimized. Index values were determined from the relation $m = [\partial \ln(P)] / [\partial \ln(-\dot{P})]_{\epsilon, \tau}$. A marked difference in index values derived from both experimental methods indicates that different processes are operative in each case. Index values are qualitatively evaluated in terms of cohesive energy density, side-chain group molar volume, and main-chain group flexibility.

1. Introduction

Viscoelastic phenomena in thermoplastics are of considerable importance to the design process in applications where the material is subject to loading at a constant level of deformation for a prolonged period of time, such as filaments in tension and seals in compression. The strain-rate sensitivity index, m , is then indicative of the degree to which the load will have diminished over the time period and is dependent upon the molecular structure of the particular thermoplastic and the environmental temperature. In this instance, the magnitude of a material's index value would be indicative of the performance characteristics of an *in situ* structure.

Time-dependent properties are also of interest in the forming of thermoplastics where the material is subject to incremental deformation for a short period of time. The strain-rate sensitivity index is then a measure of the change in dynamic stiffness with variations in strain rate. In this instance, the index value is indicative of the deformation characteristics of the bulk material.

This paper compares strain-rate sensitivity behaviour in variable strain-rate testing with stress-relaxation testing for several thermoplastics. The results are qualitatively evaluated in terms of cohesive energy density, side-chain group molar volume, and main-chain group flexibility. The thermoplastics tested were high-density polyethylene (HDPE), polypropylene (PP), polymethylmethacrylate (PMMA), polystyrene

(PS), polyvinylchloride (PVC), polycarbonate (PC), and polyhexamethylene apidamide (PA).

Although each sample was repeatedly tested, all deformation was conducted in the elastic region, with the exception of the final relaxation measurement which strained the material at or beyond the proportional limit. This paper makes no attempt to incorporate the strain history into the analysis.

2. Theory

In thermoplastics, the strain-rate sensitivity effect is manifested as the strain-rate dependence of the elastic modulus of the material loaded in tension. When thermoplastics are loaded at a low strain rate, the molecular chains have sufficient time to adjust to the imposed stress and the modulus value is lower than would be the case for the same material loaded at a higher strain rate.

Chandra and Roy [1] reported that virtually all thermoplastics exhibit some degree of room temperature strain-rate sensitivity. Thus, the material is characterized as viscoelastic, where a part of the response to deformation is that of an elastic solid with a unique stress-strain relationship and no dissipation of deformational energy. The remainder of the response is that of a viscous fluid where the stress state is independent of the strain and there is dissipation of deformational energy through flow processes.

2.1. Strain-rate sensitivity index development

The stress–strain-rate behaviour of metals at low temperatures and strain rates was reported by Backofen *et al.* [2] to obey the power law relation

$$\sigma = [C(\dot{\epsilon})^m]_{\epsilon, T} \quad (1)$$

where m is the strain-rate sensitivity index ($0 < m < 1$) and C is a dynamic modulus (e.g. MPas) that is a function of temperature, strain and structure. In this form, linear viscous flow is the upper limiting case (C is equivalent to the viscosity) where an index value of unity allows high levels of material deformation with complete suppression of the necking phenomenon. The strain-rate sensitivity index varied directly with both temperature and strain rate below a certain critical temperature for a superplastic alloy.

Equation 1 may also be related to common models for linear viscoelastic materials. For example, in the Maxwell model (series spring and dashpot) it may be shown that $\sigma = n\dot{\epsilon} - (n/E)\dot{\sigma}$, where n is the viscosity. If $\sigma = 0$ at $t = 0$, then $\sigma = n\dot{\epsilon}[1 - \exp(-(E/n)t)]$. Thus for all t , or $0 < t < \infty$, we have $0 < [1 - \exp(-(E/n)t)] < 1$, similar to $0 < m < 1$. In the Voigt–Kelvin element (parallel spring/dashpot), the equivalent shear stress relation is $\tau = n\dot{\gamma} + G\gamma$ which gives a good description of creep behaviour but is difficult to use for stress–strain behaviour as an instantaneous strain would, in turn, require an infinite stress in the dashpot.

Leterrier and G'Sell [3] reported a similar relationship between the strain-rate sensitivity index and temperature in thermosetting polyurethane resin (PUR). They found that the index m increased with increasing temperature below the glass transition temperature, T_g , at which point further temperature increase resulted in a decrease in the value of the index. For the relationship between the strain-rate sensitivity index and strain rate, they found that, at constant temperature, the index decreased at an exponential rate with increasing strain rate. In addition, they found that, at constant temperature, an increase in the initially imposed strain caused a corresponding increase in the index (especially for strains on the order of 0.001) and that the effect was intensified by an increase in temperature for temperatures below the glass transition temperature.

2.2. Strain-rate sensitivity index determination

The strain-rate sensitivity index for viscoelastic materials loaded in tension was demonstrated by Hart [4] to be given as

$$m = [\partial \ln(\sigma) / \partial \ln(\dot{\epsilon})]_{\epsilon, T} \quad (2)$$

where it is assumed that the conditions approximate a steady-state process. Determination of the strain-rate sensitivity index may, in principle, also be achieved by stress-relaxation testing. Hart demonstrated that if stress is proportional to strain, then stress rate is proportional to strain rate and the index could be determined by plotting $\ln(\sigma)$ as a function of $\ln(-\dot{\sigma})$

$$m = [\partial \ln(\sigma) / \partial \ln(-\dot{\sigma})]_{\epsilon, T} \quad (3)$$

where $\sigma = \sigma(t)$ is relaxed stress as a function of time and $\dot{\sigma} = \sigma'(t)$ is the stress-relaxation rate. Although studies of superplastic alloys have demonstrated that there is not much deviation between strain-rate sensitivity index values obtained from variable strain-rate and stress-relaxation testing, a search of the literature has revealed no confirmation of the equivalence of Equations 2 and 3 for thermoplastics.

2.3. Stress-relaxation modelling

The question as to what model should be employed to approximate the relaxation response is seen as the key issue in the resolution of the problem of the correlation of structural response to mechanical stimuli. In this regard, Halsey *et al.* [5] suggested that though the fit of relaxation data to a general distribution function may provide parameters for an approximation function, they are not likely to have any physical significance and cannot be viewed as an effective model of internal processes. The objective then, is not only to approximate successfully the relaxation response, but also to employ a function that models the kinetic mechanisms within the material that effect the observed behaviour.

Models for stress relaxation $\sigma(\epsilon, \dot{\epsilon}, t, T, \dots)$ have traditionally employed combinations of Hookean (elastic) and Newtonian (viscous) elements. A promising model for the approximation of the relaxation response of polymers is that proposed by Kohlrausch [6] and since used by numerous workers [3, 7]. The relaxation response function of the Kohlrausch model is given by

$$\sigma(t) = \sigma_0 \exp[-(t/\tau)^n] \quad (4)$$

where σ_0 is the stress (Pa) initially imposed on the material, t is the decay response time of interest (s), τ is the characteristic time parameter (s), and n is the rate-of-decay parameter. This extended exponential function was employed by Kohlrausch because it is a tractable approximation of the continuous series expansion

$$\sigma(t) = \int_0^{\infty} \Psi(\tau) \exp(-t/\tau) d\tau \quad (5)$$

where $\Psi(\tau)$ is a function representing the entire spectrum of the relaxation response. In general, the characteristic time parameter is a function of strain and temperature and its magnitude describes the position of the relaxation curve on the logarithmic time scale. The rate-of-decay parameter is, in general, a function of strain, temperature, and molecular weight and its magnitude characterizes the distribution of active relaxation times. Thus, a decrease in the value of the rate-of-decay parameter will cause a corresponding increase in the width of the range of active relaxation times.

2.4. Stress-relaxation considerations

Although Aran [8] described numerous methods that have been utilized for the determination of the strain-rate sensitivity index, Hedworth and Stowell [9]

cautioned against some methods as exhibiting little correlation to actual physical processes. Stress relaxation was generally regarded [3, 8, 9] as the preferred method for strain-rate sensitivity index determination when the objective of the investigation was the correlation of mechanical properties and structural kinetic mechanisms. Leterrier and G'Sell [3] suggested that stress-relaxation testing would assess the viscoelastic behaviour more appropriately than variable strain-rate testing. They reasoned that, as the stress decays, the ratio of the viscous strain component to the elastic strain component increases and the viscoelastic response is enhanced. They also pointed out that, because loading is halted immediately after the proportional limit is reached, the total strain in the specimen is such that there is no significant plastic deformation to mask the viscoelastic response.

Hedworth and Stowell [9] have identified problems that exist with the stress-relaxation technique which include the finite amount of time required to halt the crosshead, the time delay between the actual loading and the measurement of the loading, and that the halting of the crosshead at higher velocities causes a momentary reverse motion of the crosshead which results in the imposition of an initial compressive strain on the specimen.

In regard to testing machine stiffness, Dieter [10] reported that the stress-relaxation method requires that the stiffness of the testing device be much greater than the stiffness of the specimen for accurate results. Nielsen [11] has reported that it is important to compare stress-relaxation and strain-rate tests at the same strain level, because the stress-relaxation modulus is highly dependent on the strain level (especially so in the case of polyhexamethylene apidamide and polyethylene). ASTM testing standards [12] indicate that a state of constant strain is difficult to achieve in stress-relaxation testing.

2.5. Macromolecular viscoelastic mechanisms

In regard to factors that influence the viscoelastic properties of thermoplastics, Billmeyer [13] suggested that it is the magnitude of the cohesive energy density $U = \Delta E/V$ associated with a particular molecular structure that acts as the primary restraint on long-chain flexibility. Because cohesive energy density (energy per unit molar volume required to disassociate a molecule) is a function of intermolecular bonding forces, it is the strength of the dipole, dispersion, and induction forces that most profoundly influence molecular mobility within a polymer. In addition, the size and complexity of the pendant groups are factors which influence the ease of rotational movement about carbon-carbon single bonds in the polymer chain. In this case, it is considered probable that the sum of pendant group molar volumes $V = \sum_i (V_p)_i$ [14] is a very strong contributory factor in the steric hindrance mechanisms involved in the rate at which molecular reorganization processes evolve. In condensation polymers, steric hindrance can also be influenced by different types of main-chain groups. In this case, the macromolecules of the thermoplastic

consist of main-chain groups that exhibit a greater or lesser degree of flexibility.

Thus, in addition to the impediment to motion of pendant groups, the existence of more rigid main-chain groups as constituent elements of a macromolecule support an argument for a relatively slower relaxation response in some condensation polymers compared with the response of a typical addition polymer. From this analysis of the factors which influence chain flexibility, it can be expected that a thermoplastic with smaller, less complex, and less polar side-chain constituents and more flexible main-chain constituents will relax at a faster rate than one with larger, more complex, and more polar side-chain constituents and less flexible main-chain constituents.

3. Experimental procedure

3.1. Specimen characterization

The thermoplastics tested were high-density polyethylene (HDPE, $-\text{CH}_2\text{CH}_2-$), polyvinylchloride (PVC, $-\text{CH}_2\text{CHCl}-$), polystyrene (PS, $-\text{CH}_2\text{CH}[\text{C}_6\text{H}_5]-$), polymethylmethacrylate (PMMA, $-\text{CH}_2\text{C}[\text{CH}_3][\text{COOCH}_3]-$), polypropylene (PP, $-\text{CH}_2\text{CH}[\text{CH}_3]-$), polyhexamethylene apidamide (PA, $-\text{NH}[\text{CH}_2]_6\text{NHCO}[\text{CH}_2]_4\text{CO}-$), and polycarbonate (PC, $-\text{C}_6\text{H}_4\text{C}[\text{CH}_3]_2\text{C}_6\text{H}_4\text{OCO}_2-$). Tensile specimens (eight of each for HDPE, PVC, PMMA, PA and six of each for PS, PP, PC) were machined from extruded rod stock in accordance with the ASTM standard [7]. The specimens were provided with threaded ends for gripping in the test instrument fixtures and were tested in an unmodified condition. An Instron Model TTC was used for both variable strain-rate and stress-relaxation testing.

The HDPE, PVC, PS, PP, PA, and PC specimens were produced with a nominal gauge length of 61 mm and a nominal gauge diameter of 13 mm. The PMMA specimens were produced with a nominal gauge length of 57 mm and a nominal gauge diameter of 10 mm. Typical ranges of values for physical, mechanical, and thermal properties of the thermoplastics tested are shown in Table I.

3.2. Variable strain-rate testing procedure

The variable strain-rate testing approach was to repeatedly load the specimen in the elastic stress-strain region at consecutively higher crosshead rates (0.0085, 0.0212, 0.0423, 0.0847, 0.2117 mm s^{-1}). This procedure generated load versus elongation data plots with successively steeper slopes. The strain-rate sensitivity index was then determined from the relation $m = \Delta \ln(\sigma) / \Delta \ln(\dot{\epsilon})$ from the load versus elongation data at strain levels identical to those achieved in stress-relaxation testing.

3.3. Stress-relaxation testing procedure

In stress relaxation testing, the specimen was loaded [12] at a constant rate (0.0423 mm s^{-1}) to a load level immediately above the proportional limit at which point elongation was halted. This procedure resulted

TABLE I Physical, mechanical, and thermal properties of PP, HDPE, PS, PA, PMMA, PC, and PVC thermoplastics

Type	ρ (g cm ⁻³)	V (cm ³ mol ⁻¹)	U (J mol ⁻¹)	E (10 ⁹ Pa)	ν	T_g (K)	T_m (K)
PP	0.90–0.91	32.4	251–254	0.6–1.6	0.43	238–299	385–481
HDPE	0.95–0.97	12.8	187–281	1.0–1.1	0.47	143–250	368–414
PS	1.04–1.05	74.3	302–470	2.3–3.4	0.38	353–373	498–523
PA	1.13–1.15	81.2	654–774	1.9–2.8	0.44	318–330	523–545
PMMA	1.17–1.20	72.7	332–417	2.2–3.2	0.40	266–399	433–473
PC	1.19–1.21	53.2	378–470	2.3–2.5	0.42	393–420	513–573
PVC	1.30–1.58	29.5	302–507	2.4–4.1	0.42	247–354	485–583

Notes: ρ = density, V = pendant group molar volume, U = cohesive energy density, E = elastic modulus, ν = Poisson's ratio, T_g = glass transition temperature, T_m = melting temperature.

Property values were extracted from the literature [14–18].

in a constant strain being maintained in the material. From then on until the strain was released, the specimen exhibited a decay response in which the load decreased as a function of time from the initially imposed load level to a lower load level according to some function $P = P(\text{time, temperature, structure, } \dots)$. The strain-rate sensitivity index was then determined from the relation $m = \Delta \ln(P) / \Delta \ln(-\dot{P})$ from the load versus time data.

4. Analysis

4.1. Variable strain-rate data analysis

The data for load ($P = P_f y/k$) as a function of specimen elongation ($\delta = vx/u$) for each crosshead velocity, v , and chart velocity, u , combination were used to calculate stress and strain from the relations

$$\sigma = P/A_0(1 + \delta/l_0) \quad (6)$$

$$\varepsilon = \ln(1 + \delta/l_0) \quad (7)$$

where x is the elongation chart displacement (m), y is the load chart displacement (m), k is the displacement-to-load conversion factor (m), P_f is the full scale load (N), l_0 is the gauge length (m), and A_0 is the cross-sectional area (m²). These data pairs were then used to form an array and the elastic modulus was derived by linear regression from the relation $E = \Delta\sigma/\Delta\varepsilon$. The derived modulus value and a constant strain value were then used to calculate $\ln(\sigma)$ and $\ln(\dot{\varepsilon})$ for each crosshead velocity from the relations

$$\ln(\sigma) = \ln\{E\varepsilon\} \quad (8)$$

$$\ln(\dot{\varepsilon}) = \ln\{v/[l_0 \exp(\varepsilon)]\} \quad (9)$$

where the strain value used in the calculation was identical to the strain value obtained in stress-relaxation testing. These data pairs were then used to form an array and the strain-rate sensitivity index was derived by linear regression from the relation

$$m_\varepsilon = \Delta \ln(\sigma) / \Delta \ln(\dot{\varepsilon}) \quad (10)$$

where m_ε is the slope of $\ln(\sigma)$ data plotted as a function of $\ln(\dot{\varepsilon})$ data and is given by

$$m_\varepsilon = a/b \quad (11)$$

where

$$a = n \sum [\ln(\dot{\varepsilon}) \ln(\sigma)] - \sum [\ln(\dot{\varepsilon})] \sum \ln(\sigma)$$

$$b = n \sum [\ln(\dot{\varepsilon})]^2 - [\sum \ln(\dot{\varepsilon})]^2$$

In this analysis, the correlation coefficient, $r = (r^2)^{1/2}$, represents a measure of the goodness-of-fit of the $\ln(\sigma)$ versus $\ln(\dot{\varepsilon})$ data points to a straight line ($r = 1$ when linear) and is given by

$$r = c/d \quad (12)$$

where

$$c = n \sum [\ln(\dot{\varepsilon}) \ln(\sigma)] - \sum [\ln(\dot{\varepsilon})] \sum \ln(\sigma)$$

$$d = \{n \sum [\ln(\dot{\varepsilon})]^2 - [\sum \ln(\dot{\varepsilon})]^2\}^{1/2} \{n \sum [\ln(\sigma)]^2 - [\sum \ln(\sigma)]^2\}^{1/2}$$

4.2. Stress-relaxation data analysis

In view of its advantage as a good indicator of the physical mechanisms operative during the relaxation process [3, 19], the Kohlrausch function was implemented to model the relaxation response of the thermoplastics tested. The data for load, P , as a function of time, t , was thus used to derive the parameters for the load relaxation equation

$$P(t) = P_0 \exp[-(t/\tau)^n] \quad (13)$$

where P_0 is the initially imposed load. This initial load was typically at an elongation level a few per cent above the elongation level at the proportional limit.

In order to determine the parameters n and τ , an error function $\Phi(n, \tau)$ was defined

$$\Phi(n, \tau) = (1/N \sum_i \{P_0 \exp[-(t_i/\tau)^n] - P(t_i)\}^2)^{1/2} \quad (14)$$

which is the root-mean-square difference between the empirical load relaxation equation and the experimental data. An exhaustive grid search algorithm was implemented to minimize the error function with the result that suitable parameters were found for each data set.

A number of equal-spaced time increments (whose last term was equal to the time duration of the relaxation test) were input into the response equation and the load relaxation rate equation

$$P'(t) = -(nP_0/\tau)(t/\tau)^{n-1} \exp[-(t/\tau)^n] \quad (15)$$

and the strain-rate sensitivity index was derived by linear regression from the relation

$$m_\sigma = \Delta \ln(P) / \Delta \ln(-\dot{P}) \quad (16)$$

where m_{σ} is the slope of $\ln(P)$ data plotted as a function of $\ln(-\dot{P})$ data and is given by

$$m_{\sigma} = a/b \quad (17)$$

where

$$a = n \sum [\ln(-\dot{P}) \ln(P)] - \sum [\ln(-\dot{P})] \sum \ln(P)$$

$$b = n \sum [\ln(-\dot{P})]^2 - [\sum \ln(-\dot{P})]^2$$

In this analysis, the correlation coefficient represents a measure of the goodness-of-fit of the $\ln(P)$ versus $\ln(-\dot{P})$ data points to a straight line and is given by

$$r = c/d \quad (18)$$

where

$$c = n \sum \ln(-\dot{P}) \ln(P) - \sum \ln(-\dot{P}) \sum \ln(P)$$

$$d = \{n \sum [\ln(-\dot{P})]^2 - [\sum \ln(-\dot{P})]^2\}^{1/2} \{n \sum [\ln(P)]^2 - [\sum \ln(P)]^2\}^{1/2}$$

5. Results

5.1. Variable strain-rate testing results

Mean and standard deviation strain-rate sensitivity index values, $m_{\dot{\epsilon}}$, variance values, q , and mean correlation coefficient values, r , derived from variable strain-rate testing are presented in Table II. Linear regression analysis yielded an average correlation coefficient value on the order of 0.96 for all specimens that were strain-rate tested. To demonstrate the variation in magnitude of the strain-rate sensitivity index values, $m_{\dot{\epsilon}}$, generated by the variable strain rate method, Fig. 1 has $\ln(\sigma)$ plotted as a function of $\ln(\dot{\epsilon})$ for representative specimens of each type of thermoplastic.

5.2. Stress-relaxation testing results

Minimization of the error function $\Phi(n, \tau)$ by means of the numerical algorithm for each type of thermoplastic that was stress-relaxation tested yielded mean parameter values, mean and standard deviation strain-rate sensitivity index values, $m_{\dot{\epsilon}}$, variance values, q , and mean strain values, ϵ_0 , as shown in Table III.

Fig. 2 presents the normalized load response plotted as a function of time using the Kohlrausch function and average parameter data for each type of thermoplastic that was relaxation tested. To demonstrate the variation in magnitude of the strain-rate sensitivity

TABLE II Mean and standard deviation strain-rate sensitivity index values, variance values, and mean correlation coefficient values derived from variable strain-rate testing

Type	$m_{\dot{\epsilon}}$	s	q	r
HDPE	0.1291	0.0148	0.1146	0.9749
PP	0.0629	0.0102	0.1622	0.9785
PMMA	0.0418	0.0057	0.1364	0.9830
PS	0.0293	0.0182	0.6212	0.9485
PVC	0.0260	0.0086	0.3308	0.9283
PC	0.0191	0.0089	0.4660	0.9548
PA	0.0184	0.0054	0.2935	0.9408

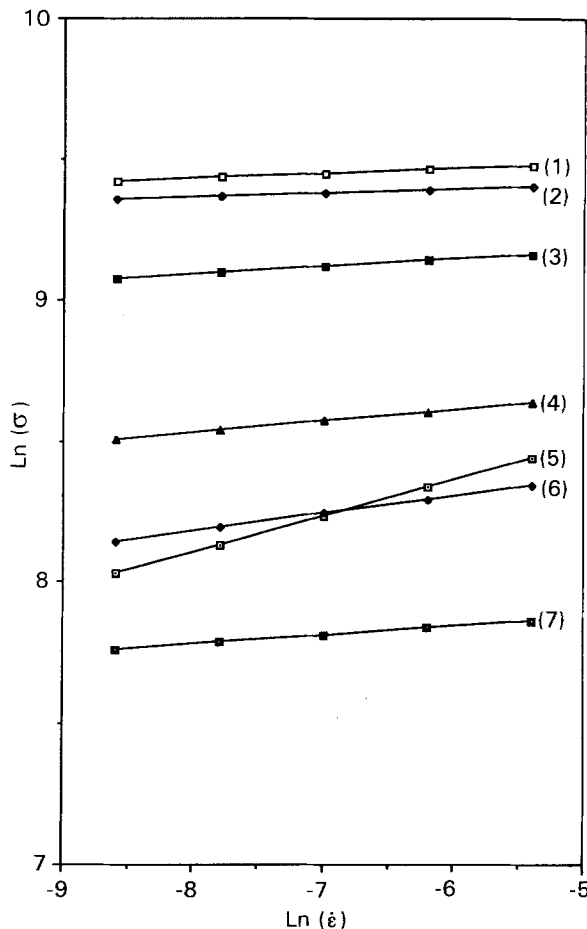


Figure 1 Strain-rate sensitivity index for representative thermoplastic specimens derived from variable strain-rate testing. (1) PC, $m = 0.0182$; (2) PA, $m = 0.0142$; (3) PVC, $m = 0.0271$; (4) HDPE, $m = 0.1287$; (5) PMMA, $m = 0.0411$; (6) PP, $m = 0.0622$; (7) PS, $m = 0.0319$.

index values, $m_{\dot{\epsilon}}$, generated by the stress relaxation method, Fig. 3 has $\ln(P)$ plotted as a function of $\ln(-\dot{P})$ for representative specimens of each type of thermoplastic.

5.3. Testing results comparison

Mean strain-rate sensitivity index values, $m_{\dot{\epsilon}}$, derived from variable strain-rate data are compared with mean strain-rate sensitivity values, $m_{\dot{\sigma}}$, derived from stress-relaxation data (using the same strain in each case) in Table IV for the different thermoplastics. The corresponding strain levels for $m_{\dot{\epsilon}}$ are 0.005–0.01 and the strain levels for $m_{\dot{\sigma}}$ are 0.02–0.06 (Table III). The per cent difference between these values is calculated according to $\Delta = 100 [(m_{\dot{\sigma}} - m_{\dot{\epsilon}})/m_{\dot{\epsilon}}]$.

6. Discussion

6.1. Variable strain-rate results

From the plots of $\ln(\sigma)$ as a function of $\ln(\dot{\epsilon})$ (Fig. 1) it can be seen that HDPE is at the upper extreme of the spectrum with a steep slope and a high strain-rate sensitivity index and that PA is at the lower extreme of the spectrum with a shallow slope and low strain-rate sensitivity index. These results are as expected from theory in terms of the steric hindrance offered to chain

TABLE III Mean parameter values, mean and standard deviation strain-rate sensitivity index values, variance values, and mean strain values derived from stress-relaxation testing

Type	P_0 (Ibf)	τ (s)	n	m_σ	s	q	ϵ_0 (in in ⁻¹)
HDPE	432	13,290	0.279	0.1318	0.0052	0.0395	0.0468
PS	485	64,350	0.204	0.0915	0.0146	0.1596	0.0222
PP	482	67,320	0.271	0.0893	0.0063	0.0705	0.0445
PA	2001	109,000	0.297	0.0785	0.0076	0.0968	0.0344
PVC	1541	203,100	0.242	0.0687	0.0034	0.0501	0.0398
PC	1974	805,700	0.292	0.0460	0.0062	0.1348	0.0647
PMMA	501	1,523,500	0.253	0.0429	0.0031	0.0723	0.0217

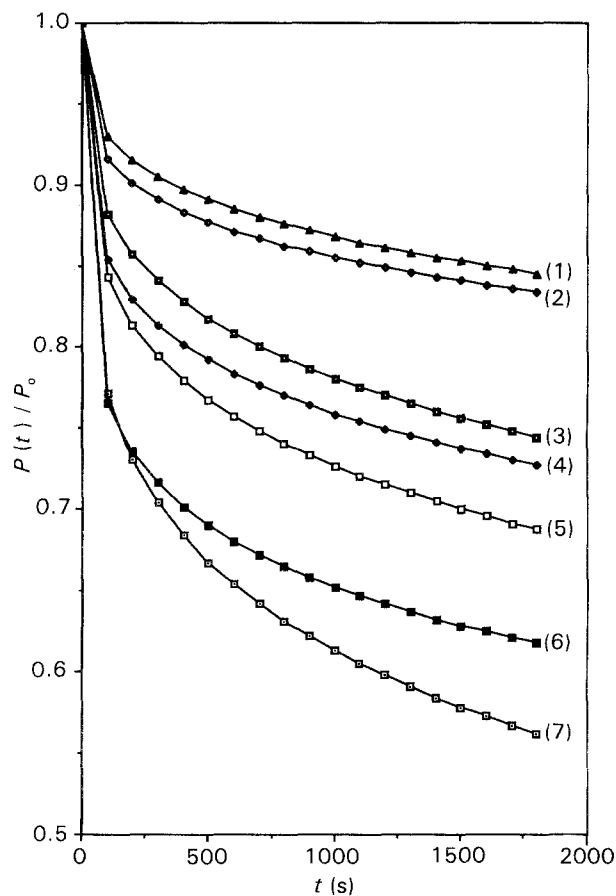


Figure 2 Normalized relaxation response for PC, PMMA, PA, PVC, PP, PS, and HDPE derived from average parameter data.

TABLE IV Comparison of strain-rate sensitivity index values derived from variable strain-rate and stress-relaxation testing

Type	m_ϵ	m_σ	Δ (%) ^a
HDPE	0.1291	0.1318	2
PMMA	0.0418	0.0429	2
PP	0.0629	0.0893	41
PC	0.0191	0.0460	142
PVC	0.0260	0.0687	165
PS	0.0293	0.0915	217
PA	0.0184	0.0786	339

$$^a \Delta = 100 [(m_\sigma - m_\epsilon) / m_\epsilon]$$

mobility due to intermolecular bond energy density. It can also be seen from Fig. 1 that for an equivalent change in $\ln(\dot{\epsilon})$, HDPE exhibits almost an order of magnitude larger change in $\ln(\sigma)$ that does PA. The

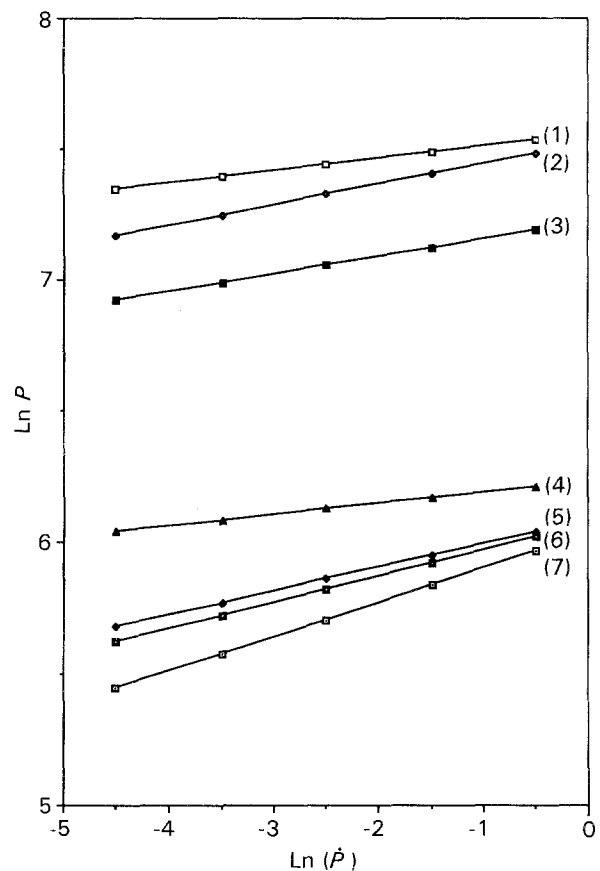


Figure 3 Strain-rate sensitivity index for representative thermoplastic specimens derived from stress-relaxation testing. (1) PC, $m = 0.460$; (2) PA, $m = 0.0766$; (3) PVC, $m = 0.0682$; (4) PMMA, $m = 0.0419$; (5) PS, $m = 0.1010$; (6) PP, $m = 0.0896$; (7) HDPE, $m = 0.1317$.

result is that the strain-rate sensitivity index value for HDPE is almost an order of magnitude larger than the strain-rate sensitivity index value for PA.

6.2. Stress-relaxation results

From the plots of the normalized load response as a function of time (Fig. 2) for the representative thermoplastic specimens, it can be seen that the relaxation response is in accordance with macroscopic-scale viscoelastic theory. Specifically, it is apparent from each plot that the stress decays rapidly in the early part of the response while the viscous component exhibits a more gradual decay that is still active in the latter part of the response. The plots of Fig. 2 are also in accordance with accepted theory concerning inter-

nal mechanisms operating at the molecular level within the materials. Specifically, the plots of the thermoplastic responses illustrate the role of steric hindrance from both side-chain and main-chain groups in their relaxation behaviour.

In the case of high-density polyethylene, each pendant group consists of a small hydrogen atom ($V \approx 3 \text{ cm}^3 \text{ mol}^{-1}$). Thus, the high relaxation rate exhibited by HDPE is consistent with that expected for a small and non-complex side-chain constituent. On considering the bonding between the long-chain macromolecules, the instantaneous dipole-induced dipole bonds present are very weak ($\Delta E \approx 2 \text{ kcal mol}^{-1}$) and thus contribute little hindrance to main-chain mobility.

In the case of polystyrene, every fourth side group consists of a large and complex benzene ($-\text{C}_6\text{H}_5$) molecule ($V \sim 65 \text{ cm}^3 \text{ mol}^{-1}$) in place of a hydrogen atom. It is also known that adjacent benzene rings prefer to be oriented with their major surfaces stacked parallel to one another. Although the initial high relaxation rate exhibited by PS is inconsistent with that expected for one large and complex side-chain constituent, evaluation of the relaxation response (Fig. 2) suggests that the long-term relaxation rate would be consistent with those exhibited by PMMA and PC and the index value would be correspondingly lower.

In the case of polypropylene, every fourth pendant group consists of a moderately complex methyl ($-\text{CH}_3$) molecule ($V \approx 23 \text{ cm}^3 \text{ mol}^{-1}$). Thus, the moderately high relaxation rate exhibited by PP is consistent with that expected for a relatively large and moderately complex side-chain constituent.

In the case of polyvinylchloride, every fourth side group consists of a relatively large chlorine atom ($V \approx 20 \text{ cm}^3 \text{ mol}^{-1}$) in place of a hydrogen atom. Thus, the intermediate relaxation rate exhibited by PVC is consistent with that expected for one large and non-complex side-chain constituent. Also, because chlorine is relatively electronegative (E.N. ≈ 3.0), it has a high affinity for hydrogen (E.N. ≈ 2.1). Thus, the resultant dipole-dipole secondary bonds ($\Delta E \approx 6 \text{ kcal mol}^{-1}$) contribute to chain hindrance.

In the case of polymethylmethacrylate, every third pendant group consists of a relatively complex methyl molecule in place of a hydrogen atom and every fourth pendant group consists of a highly complex methacrylate group ($-\text{COOCH}_3$) molecule ($V \approx 41 \text{ cm}^3 \text{ mol}^{-1}$) in place of a hydrogen atom. Thus, the slow relaxation rate exhibited by PMMA is consistent with that expected for the existence of two large and complex side-chain constituents. In addition, the existence of dipole-dipole secondary bonds between the chains offers considerable impediment to chain mobility.

In the case of the condensation polymer polyhexamethylene apidamide, the most significant factor appears to be the contribution of the large number of methylene (CH_2) groups to chain flexibility. Although the amide (NHCO) groups do provide some chain stiffening and though the sum of pendant group molar volume is high ($V \approx 81 \text{ cm}^3 \text{ mol}^{-1}$), the presence of ten flexible methylene groups along the macromolecu-

lar backbone allows an intermediate relaxation response. To compensate for methylene flexibility, the pendant groups of PA are highly polar and thus retard main-chain motion by the formation of strong hydrogen bonds ($\Delta E \approx 10 \text{ kcal mol}^{-1}$) between the oxygen and hydrogen atoms in adjacent chains.

In the case of the condensation polymer polycarbonate, the most significant factor appears to be the presence of two bulky methyl ($-\text{CH}_3$) molecules adjacent to each other across the chain and the presence of a carbonyl (CO) group and a pair of benzene (C_6H_4) groups in the chain to provide stiffening. Although there are ether (O) groups along the backbone to provide some flexibility, the aforementioned side-chain and main-chain groups have the predominant affect on the relaxation response of PC.

From the plots of $\ln(P)$ as a function of $\ln(-\dot{P})$ (Fig. 3) it can be seen that HDPE at one extreme of the relaxation response spectrum with a fast relaxation rate, has a high strain-rate sensitivity index value compared with PMMA at the other extreme of the spectrum. This is in accordance with theory in terms of the steric hindrance offered to chain mobility due to side-chain molar volume and main-chain flexibility considerations. It can also be seen from Fig. 3 that, for an equivalent change in $\ln(-\dot{P})$, HDPE exhibits almost an order of magnitude larger change in $\ln(P)$ than does PMMA. The result is that the strain-rate sensitivity index value for HDPE is almost an order of magnitude larger than the index value for PMMA.

6.3. Strain-rate sensitivity index comparison

Strain-rate sensitivity index values derived from variable strain-rate testing, m_ϵ , and stress-relaxation testing, m_σ , are plotted as a function of the cohesive energy density, U , in Figs 4 and 5 and as a function of

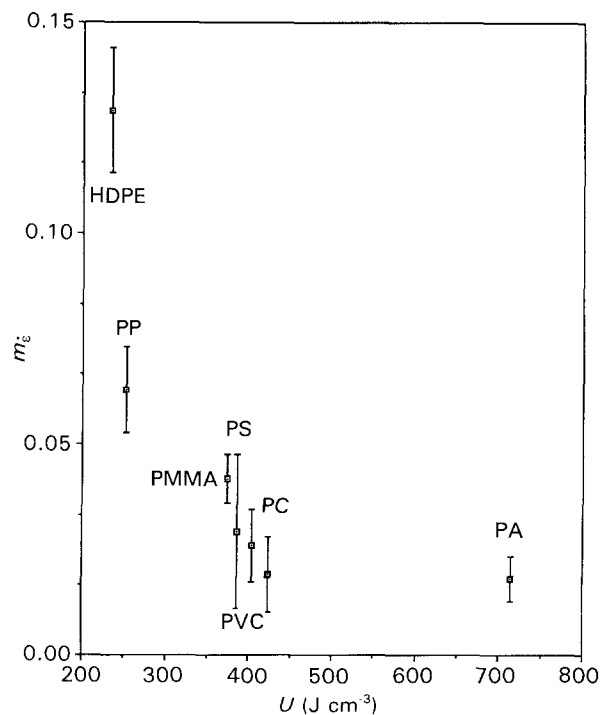


Figure 4 Strain-rate sensitivity index derived from variable strain-rate testing as a function of cohesive energy density.

the sum of the pendant group molar volumes, V , in Figs 6 and 7, respectively. A comparison of these figures demonstrates that different hindrance mechanisms are operating preferentially in each case. As Fig. 4 demonstrates that $m_{\dot{\epsilon}}$ has a relatively high dependence on U , it is concluded that, in the case of the variable strain-rate testing technique, the chain reorientation process is primarily dependent on the strength of the intermolecular bonding forces in-

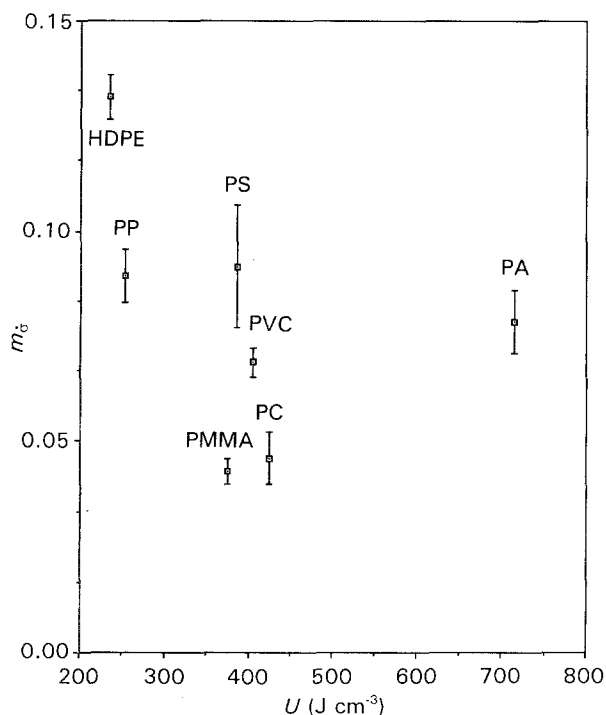


Figure 5 Strain-rate sensitivity index derived from stress-relaxation testing as a function of cohesive energy density.

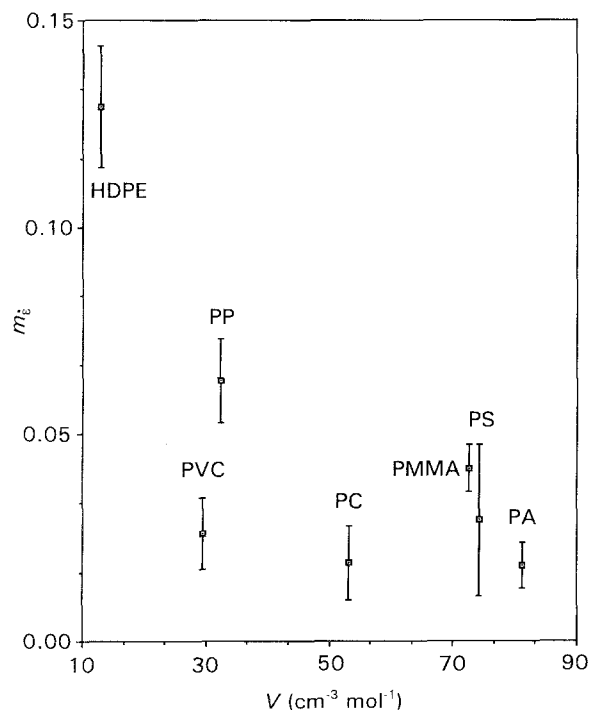


Figure 6 Strain-rate sensitivity index derived from variable strain-rate testing as a function of molar volume.

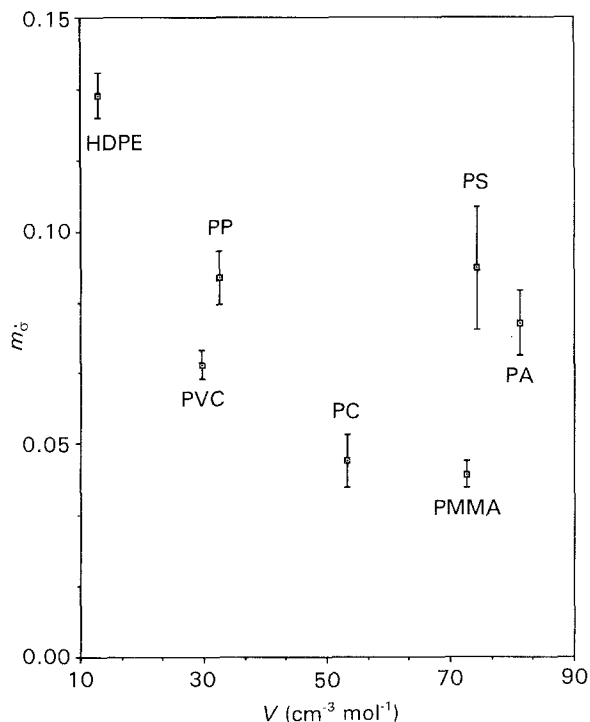


Figure 7 Strain-rate sensitivity index derived from stress-relaxation testing as a function of molar volume.

involved; i.e. a thermoplastic with a high value of cohesive energy density has low chain mobility which is expressed as a higher modulus value for a given strain rate. Because $m_{\dot{\epsilon}}$ has a low correlation with U (Fig. 5), the conclusion is that some other factor is operating preferentially to impede chain mobility during the relaxation process.

The importance of pendant group molar volume as a chain mobility hindrance factor is not as clear. In the case of $m_{\dot{\epsilon}}$ plotted as a function of V (Fig. 6), it appears that the correlative relation between them is relatively significant. Fig. 6 thus suggests that pendant group molar volume is a factor of some importance to chain mobility under the variable strain-rate testing regime. Because Fig. 7 demonstrates that $m_{\dot{\epsilon}}$ is (for some of the thermoplastics tested) a relatively strong function of V , it is concluded that the chain reorientation process is (especially in the case of addition polymers) highly dependent on constituent pendant group considerations during the stress-relaxation process. As previously indicated, the case of PA seems to be an exception to the relationship in that the large number of methylene groups in the main-chain backbone seem to enhance chain flexibility; i.e. in this case, not only the magnitude of the pendant group molar volume, but the character of the constituents as well, should be considered as a hindrance factor. Although the strain-rate sensitivity index derived from relaxation testing also appears to be a function of main-chain group flexibility in the case of condensation polymers, the lack of a quantitative measure of this phenomenon prevents a graphical presentation of the relationship of strain-rate sensitivity index as a function of group flexibility.

It is concluded that hindrance mechanisms affecting strain-rate sensitivity, in the case of thermoplastics,

depend on the measurement technique. From this conclusion, it seems appropriate to define different parameters to characterize related but inherently different phenomena that are made manifest (in thermoplastics) as a result of the particular testing technique employed. It is proposed that $m_{\dot{\epsilon}}$ retains its original meaning with respect to strain-rate testing and that m_{σ} now refers to the parameter derived from stress-rate testing. Furthermore, it is proposed that m_{σ} be referred to as the stress-rate sensitivity index.

In qualitative terms, in the case of the variable strain-rate testing technique, it appears that the process is less random in nature in that the chains reorganize with emphasis on the precedence of energy density. Conversely, in the case of the stress-rate testing technique it seems clear that the process is more random in nature in that the chains reorganize according to a precedence established by steric hindrance considerations based on side-chain and main-chain characteristics.

7. Conclusion

The viscoelastic material parameters of strain-rate sensitivity index and characteristic time can be predicted in thermoplastics from a knowledge of their molecular chemistry. A knowledge of pendant constituents alone is sufficient to yield a better than order of magnitude parameter values for the addition polymers, while parameter value prediction for condensation polymers requires a more extensive characterization of main-chain components and configurations. Although prediction of material parameters is more complex in the case of condensation polymers where large and/or complex molecules are an integral part of the long-chain molecular structure, flexibility considerations for main-chain groups are probably indicative of the relaxation response that can be expected. An understanding of the factors that determine the degree of steric hindrance and main-chain flexibility is important to the successful selection and implementation of thermoplastics for specific design purposes.

From an examination of the experimental results, it is clear that the strain-rate sensitivity index is a testing technique-dependent parameter. In this regard, the study demonstrated that the experimental data validated macromolecular theory in that there was a correlation of the index parameters of the materials in agreement with cohesive energy density values in

the case of variable strain-rate testing and the character of the side-chain and main-chain groups in the case of stress-rate testing. Specifically, in the case of variable strain-rate testing, the experimental work demonstrated an inverse relationship between the strain-rate sensitivity index, $m_{\dot{\epsilon}}$, and cohesive energy density, U , dependent on intermolecular bond strength. In the case of stress-rate testing, the experimental work demonstrated an inverse relationship between the stress-rate sensitivity index, m_{σ} , and molar volume, V , dependent on side-chain group size and complexity and dependent on main-chain flexibility.

References

1. M. CHANDA and S. K. ROY, "Plastics Technology Handbook" (Dekker, New York, NY, 1987).
2. W. A. BACKOFEN, I. R. TURNER and D. H. AVERY, *Trans. Am. Soc. Metals* **57** (1964) 980.
3. Y. LETERRIER and C. G'SELL, *J. Mater. Sci.* **23** (1988) 4209.
4. E. W. HART, *Acta Metall.* **15** (1967) 351.
5. G. HALSEY, H. J. WHITE, and H. EYRING, *Textile Res. J.* **15** (1945) 295.
6. R. KOHLRAUSCH, *Ann. Phys. Leipzig* **12** (1847) 393.
7. ASTM Standard D638-89, "Standard Test Method for Tensile Properties of Plastics", Annual Book of ASTM Standards 08.01 (American Society for Testing and Materials, Philadelphia, PA, 1989).
8. A. ARAN, *Scripta Metall.* **13** (1979) 843.
9. J. HEDWORTH and M. J. STOWELL, *J. Mater. Sci.* **6** (1971) 1061.
10. G. E. DIETER, "Mechanical Metallurgy", 3rd Edn (McGraw-Hill, New York, NY, 1986).
11. L. E. NIELSEN, "Mechanical Properties of Polymers and Composites" (Dekker, New York, NY, 1974).
12. ASTM Standard E328-86, "Standard Methods for Stress Relaxation Tests for Materials and Structures", Annual Book of ASTM Standards 08.01 (American Society for Testing and Materials, Philadelphia, PA, 1989).
13. F. W. BILLMEYER, "Textbook of Polymer Science" (Wiley, New York, NY, 1984).
14. D. W. VAN KREVELEN, "Properties of Polymers" (Elsevier, New York, NY, 1976).
15. P. C. HIEMENZ, "Polymer Chemistry" (Dekker, New York, NY, 1984).
16. R. B. SEYMOUR and C. E. CARRAHER, "Polymer Chemistry", 2nd Edn (Dekker, New York, NY, 1988).
17. H. R. ALLCOCK and F. W. LAMPE, "Contemporary Polymer Chemistry" (Prentice-Hall, Englewood Cliffs, N.J., 1980).
18. D. H. KAELBLE, "Computer-Aided Design of Polymers and Composites" (Dekker, New York, NY, 1985).
19. L. C. E. STRUIK, in "Failure in Plastics", edited by W. Brostow and R. D. Corneliusen (Hanser, Munich, 1986) pp. 218-20.

Received 19 June 1991

and accepted 28 April 1993