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Temperature and stem length dependence of the yield stress of polyethylene

N.W.J. Brooks*, M. Mukhtar

School of Polymer Technology, University of North London, Holloway Road, London N7 8DB, UK

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Abstract

Mechanical and structural analyses have been carried out on a range of bulk-cast polyethylenes, which differ widely with respect to their stem lengths (the length traversed by the polymer chains within the crystalline lamellae). The effects of temperature and stem length on the yield stress were evaluated at a strain-rate of 10^{-2} s^{-1}, over a temperature range from −60 to 60°C; a temperature range which includes the β-relaxation temperature for these materials. The results have shown that using a modified crystal plasticity approach, which takes into account the dislocation core energy, the temperature and stem length dependence of the yield stress can be modelled concurrently. This has not previously been attempted. The modified crystal plasticity approach is found to be valid both below the β-relaxation temperature, under conditions of elastic–plastic deformation; and above the β-relaxation temperature under conditions of viscoelastic deformation. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Previous studies on the structure–property relations in semicrystalline polymers have established links between the structure and the mechanical behaviour. However, due to the complex morphologies of these materials, the molecular mechanisms responsible for the yield behaviour are still the subject of much debate and quantitative modelling of the yield behaviour has been largely based on empirical models.

The yield behaviour of semicrystalline polymers has been modelled previously using two conflicting approaches. The first attributes yield behaviour to melting and recrystallisation of polymers under adiabatic conditions [1,2]. The second [3–8] is based on classical ideas of crystal plasticity, the deformation being considered in terms of dislocation motion within the crystalline lamellae, similar to slip processes observed in metals.

The Eyring equation for thermally activated processes has previously been used to model the temperature and strain-rate dependence of the yield stress for both semicrystalline [9,10] and amorphous polymers [11–14]. This approach assumes the yield process is propagation controlled and has been particularly successful in modelling the yield behaviour of polymers at comparatively high temperatures. However it does not make specific reference to the morphology of the materials under investigation and is essentially phenomenological in nature.

Young [3,4] has developed a theory to model the yield behaviour of semicrystalline polymers using ideas from classical crystal plasticity. This approach is consistent with the observed deformation of polyethylene lamellae by the process of *c*-shear [15,16]. In contrast to the more empirical Eyring activated rate approach it allows qualitative and quantitative predictions of the macroscopic yield behaviour to be made from a knowledge of materials morphology. Following Shadrake and Guiu [8], yield is assumed to be due to the thermal activation of screw dislocations within the crystalline lamellae, the Burgers vector of the dislocation being parallel to the chain axis. It has been shown [8] that the change in the Gibbs free energy, ΔG, (i.e. the energy which must be supplied by thermal fluctuations) associated with the creation of such a dislocation under an applied shear stress, τ, is given as:

$$\Delta G = \frac{Kb^2 l}{2\pi} \ln\left(\frac{r}{r_o}\right) - \tau b l r, \tag{1}$$

where l is the stem length; b the magnitude of the Burgers vector; K the crystalline shear modulus; r the radius of

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* Corresponding author. Tel: +44-0171-753-5128, fax: +44-0171-753-5081.

E-mail address: n.brooks@unl.ac.uk (N.W.J. Brooks)

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dislocation (distance from the dislocation line to the edge of lamellae); and r_o the core radius of dislocation. The first term on the right-hand side of Eq. (1) relates to the stored elastic strain energy and, the second, the work supplied by external shear forces. This equation assumes that the contributions of the core are negligible.

The critical radius, r_c, is the dislocation radius for which the Gibbs free energy is a maximum. It can be shown that:

$$r_c = \frac{Kb}{2\pi\tau.} \tag{2}$$

Substituting this into Eq. (1) gives the following equation for the critical value of the Gibbs free energy:

$$\begin{aligned}\Delta G_c = E - W &= \frac{Kb^2 l}{2\pi}\ln\left(\frac{r_c}{r_o}\right) - \tau b l r_c \\ &= \frac{Kb^2 l}{2\pi}\left[\ln\left(\frac{Kb}{2\pi\tau r_o}\right) - 1\right].\end{aligned} \tag{3}$$

Rearranging Eq. (3) leads to the following expression for the shear yield stress, τ_y:

$$\tau_y = \frac{Kb}{2r_o\pi}\exp - \left[\frac{2\pi\Delta G_c}{Klb^2} + 1\right]. \tag{4}$$

And finally, assuming that the Tresca yield criteria is valid, i.e. $\tau_y = \sigma_y/2$, then the tensile yield stress, σ_y, can be written as:

$$\sigma_y = \frac{Kb}{r_o\pi}\exp - \left[\frac{2\pi\Delta G_c}{Klb^2} + 1\right]. \tag{5}$$

Eq. (5) predicts that the yield stress is dependent on the stem length of the lamellae (and through geometry to the thickness of the lamellae), and is also dependent on the temperature and the strain-rate through the parameters K and ΔG_c.

It has previously been shown by a number of authors [3–8] that Eq. (5) independently models the temperature and stem length dependence of a wide range of polyolefins successfully, assuming that deformation is due to perfect dislocations. The actual slip plane is undefined, i.e. slip occurs on any {hk0} plane and constraints imposed on the slip planes due to the fold surfaces are not taken into account. Further, K is taken as a geometric mean of the shear moduli C_{44} and C_{55}, such that $K = (C_{44}C_{55})^{1/2}$, b is taken as the magnitude of the *c*-axis repeat unit distance and ΔG_c is directly proportional to the absolute temperature.

Although the crystal plasticity approach has proved successful in modelling the yield stress, the range of temperatures over which the theory is applicable is still the subject of debate. Recent research by Brooks et al. [17–19] on polyethylene suggests that the Young approach is applicable only below a transition temperature (associated with the β-relaxation) where the materials exhibit elastic-plastic behaviour and yield is considered as being a nucleation controlled process. In this temperature region yield is associated with *c*-shear within the crystalline lamellae. Crist et al. [7] have also suggested that the crystal plasticity approach is only valid for polyethylene over a similar temperature range, from −100 to −15°C.

Brooks et al. [19] have shown that above the transition temperature the materials exhibit non-linear viscoelastic behaviour and yield is believed to be propagation controlled and is associated with inter-lamellar shearing. In contrast, Young et al. [3–6] and Darras and Seguela [20] have used the crystal plasticity approach to successfully model the yield behaviour of bulk crystallised, solution crystallised and annealed semicrystalline polymers at temperatures well above the β-relaxation temperature. However, Galeski et al. [21] have shown that for HDPE at 80°C inter-lamellar shear is always accompanied by *c*-slip within the crystalline lamellae. It may therefore be that *c*-shear is the controlling mechanism for yield, and the crystal plasticity model applicable, under conditions of both elastic–plastic and viscoelastic deformation.

The previous results, although giving strong support to the crystal plasticity model, show a discrepancy between the results. Modelling the stem length dependence of the yield stress for a wide range of polyolefins [3,5,6,17,18], predicts that yield is associated with the most common lamellar species. Whereas, modelling the temperature dependence of the yield stress for similar polyethylenes [4,19] predicts that yield is associated with the deformation of thinner, in-fill lamellae, whose stem length is of the order of 25–50% of that of the most common species. In each case deformation by perfect dislocations was assumed. Therefore, Eq. (5), in its present form, cannot fit both the temperature and stem length dependence in a consistent manner without modification. It is believed that this discrepancy is possibly due to the fact that in deriving Eq. (5) it is wrongly assumed that the core energy term (the elastic strain energy of the screw dislocation within the core radius, r_o) can be ignored.

Assuming that the core energy, E_o, is not negligible then Eq. (2) becomes:

$$\Delta G = E - W = \frac{Kb^2 l}{2\pi}\ln\left(\frac{r}{r_o}\right) + E_o - \tau b l r. \tag{6}$$

Following the same steps, (2)–(5), as above, leads to an expression for the tensile yield stress, σ_y, such that:

$$\sigma_y = \frac{K}{\pi}\left\{\frac{b}{r_o}\exp\left[\frac{2\pi E_o}{Klb^2}\right]\right\}\exp - \left[\frac{2\pi\Delta G_c}{Klb^2} + 1\right] \tag{7}$$

Both the core radius, r_o, and the core energy, E_o, are contained in the pre-exponential multiplier. We will write the term within the first parentheses as an unknown temperature dependent function, $\alpha(T)$, where:

$$\alpha(T) = \frac{b}{r_o}\cdot\exp\left(\frac{2\pi E_o}{Klb^2}\right). \tag{8}$$

Eq. (7) can therefore be rewritten as:

$$\sigma_y = \frac{K}{\pi}\alpha(T)\exp - \left[\frac{2\pi\Delta G_c}{Klb^2} + 1\right]. \tag{9}$$

Table 1
Characteristics of polyethylene grades

Material	M_w	M_n	Crystallinity (%)	Density (kg m^{-3})	Branch content / 1000C and Branch Type	Stem length (Å)	Lamellar thickness (Å)
PE1	126,000	30,300	36.6	920	21, Butyl	110	91
PE2	206,000	12,900	53.8	938	6.2, Butyl	132	109
PE3	131,000	19,100	67.3	962	< 0.1, Butyl	343	283
PE4	395,000	32,800	61.3	955	< 0.1, Butyl	210	173
PE5	131,000	–	57.3	947	Butyl	160	132
PE6	75,000	–	59.6	950	Ethyl	186	153
PE7	57,000	–	60.3	952	Ethyl	153	126
PE8	210,000	–	61.6	954	Butyl	167	138

It is the aim of this present work to establish the validity of using Eq. (9) to concurrently model the stem length and temperature dependence of the yield stress for a wide range of polyethylenes grades which differ widely with respect to their stem lengths.

For the purposes of this investigation it is assumed that:

1. The chain axis (and therefore the Burgers vector) is tilted at an angle 34.5° to the surface normal, following the findings of previous structural studies on slow-cooled and pressure annealed polyethylenes [22,23].
2. Deformation is due to the action of perfect dislocation and is not split into partials. As a result, the magnitude of the Burgers vector, *b*, is taken to be the *c*-axis repeat unit distance, 2.54 Å.
3. Following previous works [3–7,17–20], the Gibbs free energy for nucleation of dislocation, $\Delta G_c = 60kT$ (k is the Boltzmann constant).
4. The value for the effective modulus, *K*, is taken from theoretical work carried out by Kawasawa et al. [24] which has been fitted to a third order polynomial over the temperature range 4–411 K, such that:

$$K(\mathrm{MPa})) = 3740.806 - 8.106T + 0.01897^2 - 0.000025T^3.$$

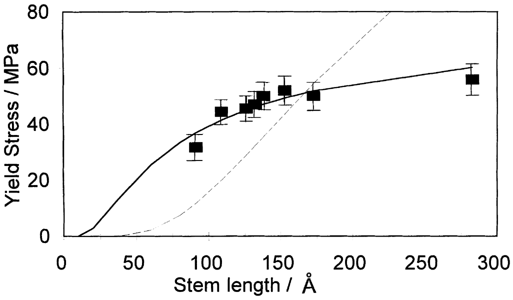

Fig. 1. Yield stress, σ_y, against stem length, l, at 60°C. Strain-rate = 10^{-2} s^{-1}.

2. Experimental

2.1. Sample preparation

Eight grades of polyethylene, which differ with respect to both short chain branch content and molecular weight, were selected for mechanical analysis. These materials were supplied by BP Chemicals Ltd., some of these are identical to those used in previous publications [17–19,25–28]. Details of these grades are given in Table 1.

Each of the eight materials was compression moulded to give sheets of approximately 0.5 mm thickness. These sheets were prepared by slow-cooling from 160°C to room temperature at approximately 2°C min^{-1}. Dumbell samples with an effective length of 28 mm and a width of 4 mm were cut from the compression moulded sheets and used in mechanical testing under tension.

2.2. Mechanical analysis

The tensile yield stress at 60, 20, −20 and −60°C was found for each of the eight samples at an initial applied strain-rate of 10^{-2} s^{-1}. In addition the tensile yield stress was found for materials PE1–PE3 at −40, 0 and 40°C, respectively.

The macroscopic yield point is identified either as the maximum on the force–elongation curve or by using the Brereton–Considère approach described in a previous publication [28]. The true yield stress and strain values were calculated assuming homogeneous deformation at constant volume.

2.3. Measurement of stem length and stem length

The stem length and lamellar thickness for each of the samples have been measured previously by Ghazali et al. [18]. For materials PE1–PE4 these were obtained using Gel Permeation Chromatography (GPC) analysis of nitric acid digested materials. For grades PE5–PE8 these were calculated using the Gibbs–Thompson relationship from the melting temperature determined using Differential Scanning Calorimetry (DSC). The DSC melting endotherms were

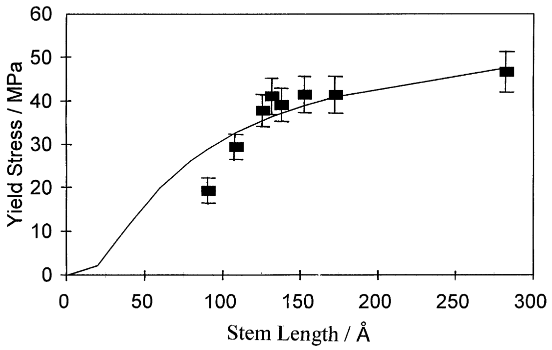

Fig. 2. Yield stress, σ_y, against stem length, l, at 20°C. Strain-rate = 10^{-2} s^{-1}.

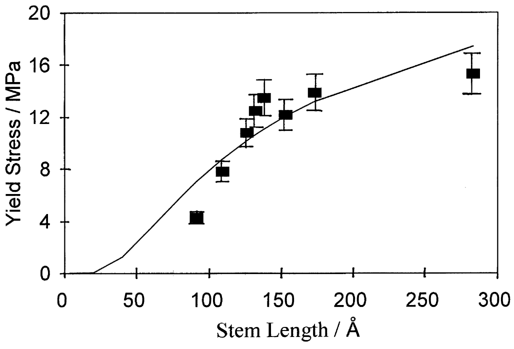

Fig. 4. Yield stress, σ_y, against stem length, l, at −60°C. Strain-rate = 10^{-2} s^{-1}.

obtained using a Perkin–Elmer Series 7 system at a heating rate of 10°C min^{-1} on samples weighing between 7 and 20 mg. The calorimeter was calibrated using a high-purity indium sample.

2.4. Results and discussion

The stem length and lamellar thickness for each of the materials PE1–PE8 are shown in Table 1. Plots of the tensile stress as a function of the stem length for each of the materials at −60, −20, 20 and 60°C are shown in Figs. 1–4. The yield stress data at each temperature is fitted to Eq. (9) using a least squares fitting procedure, such that:

$$\sum\left\{\frac{K}{\pi}\cdot\alpha(T)\cdot\exp-\left[\frac{2\pi\Delta G_c}{Klb^2}+1\right]-\sigma_y\right\}^2,$$

is minimised by finding an optimal value for the temperature dependent parameter, $\alpha(T)$. The values for the Gibb's free energy, ΔG_c, the crystalline shear modulus, K and the magnitude of the Burgers vector, b, are defined above, and the best-fit curve at each temperature is shown in Figs. 1–4 as the solid lines. The best fit values for $\alpha(T)$ obtained from the least squares fitting procedure are plotted as a function of temperature in Fig. 5.

It can be seen that the theoretical curves for the yield stress as a function of the stem length are in very good agreement with the experimental results over the entire range of stem lengths, at each of the four temperatures. Although the scatter increases as the temperature is increased, the results clearly indicate that even at 60°C (well above the transition temperature identified by Brooks et al. [19]) the experimental results are still accurately fitted by the theory. Indicating that, even in the region of propagation controlled yield, the data is accurately modelled in terms of the crystal plasticity approach.

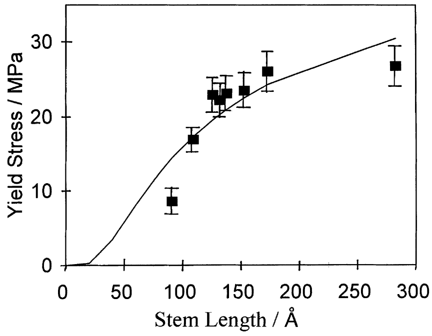

Fig. 3. Yield stress, σ_y, against stem length, l, at −20°C. Strain-rate = 10^{-2} s^{-1}.

Also shown in Fig. 1 (dotted line) is the best-fit curve obtained by fitting the data using Eq. (5), again using a least squares fitting procedure such that:

$$\sum\left\{\frac{K}{2\pi}\exp-\left[\frac{2\pi\Delta G_c}{Klb^2}+1\right]-\sigma_y\right\}^2,$$

is minimised by finding an optimal value for the Gibb's free energy, ΔG_c, assuming $r_o/b = 2$. It can be seen from Fig. 1 that this leads to a much poorer fit between the experimental and theoretical curves. Not only that, but, the best-fit value for ΔG_c was found to be 270kT, which is very much larger than would reasonably be expected.

The accurate modelling of the stem length dependence of the yield stress using Eq. (5) previously reported by Darras and Seguela [20] and Young [3] (assuming ΔG_c to be between 40 and 60kT) have used theoretical values for K which are approximately half of those of Kawasawa et al. [24]. Using similar values of K to those used here, Crist et al. [7] have found that, although the shape of the theoretical and

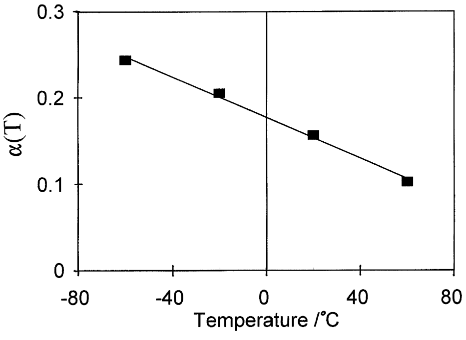

Fig. 5. $\alpha(T)$ against temperature, Strain-rate = 10^{-2} s^{-1}.

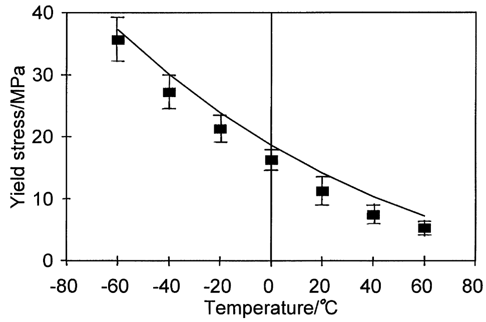

Fig. 6. Yield stress, σ_y, against temperature for material PE1, Strain-rate = 10^{-2} s^{-1}.

experimental curves are in good agreement for a range of bulk cast polyethylenes, the magnitude of the two are very different if the Gibbs free energy is taken to be 60kT. Therefore, if the Kawasawa et al values for K are accepted, then the results presented here, and those of Crist et al, show that the experimental data are best fitted to Eq. (5) by varying the pre- exponential multiplier, i.e. by introducing $\alpha(T)$ into the equation.

The results shown in Fig. 5 clearly show that $\alpha(T)$ is a decreasing function of temperature, which would seem intuitively reasonable. Assuming that the core radius, r_o, is a constant, then the material will become softer as the temperature is increased and as a result it would be expected that the core energy, E_o, and therefore $\alpha(T)$, should fall as the temperature is increased.

The values for $\alpha(T)$ in Fig. 5 are fitted to a linear equation (also shown), whose equation is:

$$\alpha = 0.4992 - 0.00119T. \tag{11}$$

It can be seen that the data is accurately fitted by this equation. It is not, however, suggested that $\alpha(T)$ is a linear function of the temperature, but this equation is used purely for simplicity in later analyses. It is very interesting to note that $\alpha(T)$ is a smooth, continuous function of the temperature over the temperature range of -60 to 60°C which includes the β-transition.

$\alpha(T)$ is a complex function of the core radius, r_o, and the core energy, E_o. Both of these terms evolve due to the discrepancy of modelling the crystalline lamellae in terms of continuum mechanics, and as such their meaning is somewhat obscure and reliable values difficult to calculate. It is perhaps unrealistic therefore to try to interpret the numeric values obtained for $\alpha(T)$. However, taking the crystalline shear modulus to be approximately 2.5 GPa, the dislocation energy for a screw dislocation of radius 32 Å [8], within a lamellae of thickness 200 Å is approximately 10^{-18}J. Assuming that the core energy, E_o, is 5–10% of this value, then $\alpha(T)$ should be of the order of 0.6 if $r_o = 2b$. This is in reasonable agreement with the experimentally determined values.

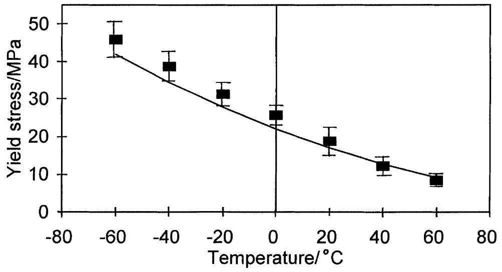

Fig. 7. Yield stress, σ_y, against temperature for material PE2, Strain-rate = 10^{-2} s^{-1}.

Although $\alpha(T)$ has been taken to be a function of the temperature only throughout this paper, it is reasonable to assume that it is also dependent on many other factors (testing rate, fold surfaces, anisotropic crystalline elasticity, chain tilting etc), although these have not been considered here.

The tensile yield stresses for materials PE1, PE2 and PE3 found at 20°C intervals over the temperature range of -60 to 60°C (strain-rate = 10^{-2} s^{-1}) are shown in Figs. 6–8. Also shown in Figs. 6–8 are the theoretical yield stress calculated from Eq. (9). The values for $\alpha(T)$ are taken from Eq. (11) and those for ΔG_c and K are as defined previously. For each of the three materials, the theoretical yield values are calculated using NO variable fitting parameters. It can be seen that the theoretical and experimental yield stress values are in excellent agreement over the entire range of temperatures for each of the materials.

At first sight it seems remarkable that the temperature dependence of the yield stress is fitted so well by the modified crystal plasticity equation, but it must be remembered that the individual yield stress values at -60, -20, 20 and 60°C are already fitted through the lamellar thickness dependence results by optimising $\alpha(T)$.

The results in Figs. 6–8 clearly show that the crystal plasticity approach accurately predicts the temperature dependence of the yield stress at temperatures both above and below the β-transition for these materials, even though there are expected to be significant changes in the amorphous phase of the materials in this temperature range.

3. Conclusions

The yield stress of a range of bulk cast polyethylenes has been modelled as a function of both stem length and testing temperature using a modified crystal plasticity model which includes a core energy term. The results have shown that the yield stress is accurately modelled over the range of temperatures from -60 to 60°C; a temperature range which includes the β-relaxation temperature for these materials. It is, therefore, concluded that the modified crystal plasticity approach is applicable both below the β-relaxation temperature (under conditions of elastic–plastic deformation and nucleation controlled yield) and above the β-relaxation temperature (under conditions of viscoelastic deformation and propagation controlled

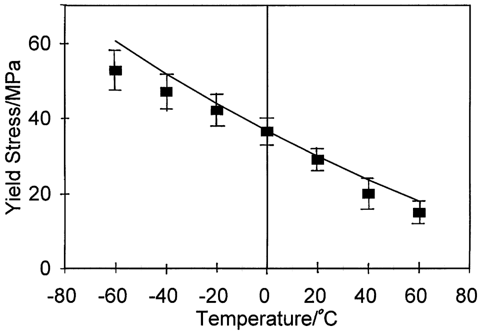

Fig. 8. Yield stress, σ_y, against temperature for material PE3, Strain-rate $= 10^{-2}$ s^{-1}.

yield). Based on the findings here, it is proposed that the nucleation and propagation of screw dislocations in the crystalline lamellae is the controlling mechanism at yield over the range of temperatures considered.

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