

Effects of morphology on the yield stress of polyethylene

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Abstract

The effects of crystallinity, lamellar thickness and stem length on the yield behaviour of a range of bulk crystallized and pressure annealed polyethylenes have been analysed. The materials studied differ greatly with respect to lamellar thickness, stem length and the degree of crystallinity. Measurements of the yield stress were carried out at -60°C and at a strain rate of $3.5 \times 10^{-3} \text{ s}^{-1}$, where the materials are known to exhibit elastic–plastic deformation. The results show that, under these conditions, the yield behaviour is a nucleation-controlled process which is accurately modelled in terms of crystal plasticity, with the yield stress being determined by the stem length of the chains in the crystalline lamellae. Detailed measurements of the stem length and crystallinity have shown that, for these materials, there is an interrelationship between the crystallinity and the stem length. This interrelationship, combined with the crystal plasticity model, leads to the prediction that the yield stress increases as a power-law relationship with crystallinity. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Two principal approaches have been used previously to model the yield behaviour of polymers. The first models the temperature and strain-rate dependence of the yield stress in terms of the Eyring equation for thermally activated processes [1]. This approach has been applied successfully to many amorphous and crystalline polymers [2,3], and, although it is essentially phenomenological, attempts have been made to establish links with relaxation processes [4] and nonlinear viscoelastic behaviour [5]. The ‘Eyring’ approach assumes that the yield process is velocity controlled, i.e. the yield stress relates to existing thermally activated processes, and it is particularly successful in modelling the yield behaviour of polymers at comparatively high temperatures.

An alternative approach, based on classical ideas of crystal plasticity, considers that yield is a nucleation-controlled process, with the yield behaviour being determined by either dislocations or disclinations, as originally proposed by Bowden and Raha [6] and Argon [7] respectively. More recently, Young [8,9] has pursued the crystal plasticity approach, assuming that the yield stress can be determined from the energy required to nucleate screw dislocations

within the crystalline lamellae, the direction of the Burgers vector for this dislocation being parallel to the chain axis. This theory predicts that the yield stress relates to the stem length of the molecular chain in the crystal. Recent research by Brooks et al. [10] on polyethylene suggests that this approach is applicable at low temperatures where yielding can be related to *c*-shear chain slip parallel to the crystallographic *c*-axis. Although Crist et al. [11] have also shown that the Young model is valid only for polyethylene over the temperature range -100°C to -15° , similar to that established by Brooks et al., Young and co-workers [8,9,12,13] and Darras and Seguela [14] have used the same approach to model successfully the yield behaviour of bulk crystallized and annealed semicrystalline polymers at much higher temperatures.

The research in the present paper analyses the yield behaviour of several different grades of polyethylene which differ with respect to both the short-chain branch content and the molecular weight. The yield data were obtained at -60°C and an applied strain rate of $3.5 \times 10^{-3} \text{ s}^{-1}$, to ensure that the behaviour was likely to be nucleation controlled. Measurements of crystallinity and lamellar thickness have been undertaken to explore the influence of these variables (and the derived stem length) on the yield stress. In these respects this research relates to the previous research by Young and co-workers and to that

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of Popli and Mandelkern [15], who have related yield stress to the lamellar thickness and the degree of crystallinity, respectively.

2. Theory

Young [8,9] has used classical ideas of crystal plasticity to develop a theory to explain yield behaviour in semicrystalline polymers. This theory assumes that yield is due to the thermal activation of screw dislocations within the crystalline lamellae, the Burgers vector of the dislocation being parallel to the chain axis. The change in the Gibbs free energy associated with the nucleation of a screw dislocation within a lamella of thickness d , having a Burgers vector of magnitude b in the chain direction, has been calculated by Shadrake and Guiu [16]. Following their approach, Young derived an expression for the shear yield stress, τ_y , such that

$$\tau_y = \frac{K}{4\pi} \exp \left[- \left(\frac{2\pi\Delta G_a}{dKb^2} + 1 \right) \right] \quad (1)$$

where ΔG_a = Gibbs free energy for nucleation of dislocation, b = magnitude of the Burgers vector, and $K = (C_{44}C_{55})^{1/2}$ (C_{44} and C_{55} are shear moduli).

K is taken as the geometric mean of the two shear moduli, C_{44} and C_{55} , as the actual slip plane is undefined. Slip is assumed to occur on any $\{hk0\}$ plane; constraints imposed on the slip planes due to the fold surfaces are not taken into account.

Eq. (1) assumes that the chain axis is normal to the lamellar surface. In the general case where the chain axis, and therefore the Burgers vector, is not perpendicular to the lamellar surface the term d should be interpreted as the stem length (i.e., the length traversed by the polymer chains within the crystalline lamellae) and not the lamellar thickness. To avoid ambiguity, throughout this work d will continue to denote the lamellar thickness but it is replaced directly in Eq. (1) by the stem length, denoted by ℓ . Previous structural studies carried out on slow-cooled and pressure annealed polyethylenes [17,18] have shown that for these materials the chain axis, and therefore the Burgers vector, lies at an angle of 34.5° to the surface normal. This is assumed to be the case in all the materials examined here.

Assuming that $\tau_y = \sigma_y/2$ (the Tresca yield criterion), the tensile yield stress, σ_y , is given by the expression

$$\sigma_y = \frac{K(T, \dot{\epsilon})}{2\pi} \exp \left[- \left(\frac{2\pi\Delta G_a(T)}{\ell K(T, \dot{\epsilon})b^2} + 1 \right) \right] \quad (2)$$

Eq. (2) predicts that the tensile yield stress is dependent on the temperature T , strain rate $\dot{\epsilon}$ and stem length ℓ . If the temperature and strain rate are kept constant, the tensile yield stress σ_y is a function of the stem length ℓ only and Eq. (2) can be written in the form

$$\ln(\sigma_y) = \left[\ln \left(\frac{K}{2\pi} \right) - 1 \right] - \left(\frac{2\pi\Delta G_a}{\ell K b^2} \right) \quad (3)$$

The crystal plasticity theory, therefore, predicts that $\ln(\sigma_y)$ is a linear function of $1/\ell$ at constant temperature and strain rate and that the intercept and gradient can be used to test the validity of this model. For the purposes of this investigation we assume:

1. The magnitude of the Burgers vector b is equal to the c axis repeat unit distance, 2.54 \AA .
2. The value of the effective elastic modulus K at -60°C is taken from theoretical work carried out by Karasawa et al. [19], such that $K = 2630 \text{ MPa}$.
3. Following previous work [8,10,12,13], the value of the Gibbs free energy for nucleation of a dislocation, $\Delta G_a = 60kT$ (k is the Boltzmann constant). Therefore, $\Delta G_a = 1.76 \times 10^{-19} \text{ J}$ at -60°C .

3. Experimental

3.1. Sample preparation

Four grades of polyethylene, differing markedly with respect to both short chain branch content and molecular weight, were selected for mechanical analysis. These materials were supplied by BP Chemicals Ltd and are identical to those used in previous publications [20–23]. Details of these grades are given in Table 1.

Each of the four materials was compression moulded using a semipositive technique to give sheets of approximately 12 mm thickness. These sheets were prepared by slow cooling from 160°C to room temperature at approximately 2°C min^{-1} . Cylindrical samples (12 mm in length and 6 mm in diameter) with the unique axis parallel to the sheet surface were machined from the sheet and used in mechanical testing under compression.

One of the four grades, namely material C, was also subjected to pressure annealing. This process is known to produce a much higher crystallinity and lamellar thickness than can be achieved using conventional processing. Details of the procedure are given elsewhere [24]; the particular annealing conditions were varied slightly to produce three other samples, C1, C2 and C3, with differing stem lengths, much greater than those of the initial bulk crystallized material.

Table 1
Chemical characteristics of polyethylene grades A–D

Material ^a	\bar{M}_w	\bar{M}_n	Branch content/ 1000 carbon atoms	Crystallinity (%)	Density (kg m ⁻³)
A	126 000	30 300	21 ethyl	39.8 (SC)	920
B	206 000	12 900	6.2 butyl	56.1 (SC)	938
C	131 000	19 100	< 0.1	76.3 (SC)	962
D	395 000	32 800	< 0.1	62.1 (SC)	955

^aGrades C and D are homopolymers.

Table 2
Chemical characteristics of polyethylene grades PE1–PE8

Material	\bar{M}_w	Density (kg m^{-3})	Branch type
PE1	301 000	945	butyl
PE2	210 000	954	butyl
PE3	138 000	955	butyl
PE4	131 000	947	butyl
PE5	75 000	957	ethyl
PE6	75 000	950	ethyl
PE7	75 000	938	ethyl
PE8	57 000	952	ethyl

A further eight grades of polyethylene (again supplied by BPCL) were selected for limited investigation. These differed with respect to both the degree of short chain branching and molecular weight. Details are given in Table 2. These materials were subjected to thermal analysis only, to determine their lamellar thickness and degree of crystallinity. Sheets (~0.5 mm thick) were prepared by compression moulding the pellets at 170°C and then slow-cooling to room temperature at approximately 2°C min⁻¹.

3.2. Mechanical measurements

The compressive yield stress at -60°C was measured for an initial applied strain rate of $3.5 \times 10^{-3} \text{ s}^{-1}$. The yield stress and strain values were calculated using the Brereton–Considère approach described in a previous publication [22].

3.3. Measurement of crystallinity and melting point

Values for crystallinity and melting point were determined by differential scanning calorimetry (DSC). Melting endotherms were 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. The crystallinity of the samples is determined from the ratio of the melting enthalpy for the samples to the melting enthalpy for 100% crystalline polyethylene, assumed to be 293.13 J g⁻¹ [25]. The average crystallinity was found for five different samples of each material.

3.4. Measurement of stem length and lamellar thickness

The stem length for materials A to D, including the pressure annealed samples, was obtained using GPC analysis of nitric acid digested materials. The lamellar size in these materials could then be found, knowing the inclination of the chain axis to the lamellar surface. In grades PE1–PE8 the melting temperature directly provided values of the lamellar thickness through the Gibbs–Thompson relation [26].

3.4.1. Nitric acid etching and gel permeation chromatography (GPC)

100 mg of material was degraded in 15 ml of fuming nitric acid at 60°C over different set periods of time ranging from 6 h to 14 days. After separation from the acid, the samples were washed with water and then acetone and finally dried under vacuum. GPC analysis was carried out on a Waters 150CV gel permeation chromatograph using 1,2,4 trichlorobenzene as solvent. Following the method established by Ward and co-workers [27–29], the peak molecular weight was plotted as a function of the digestion time and the linear region extrapolated to zero time. The stem length was then calculated from this value, taking the atomic mass of a CH₂ repeat unit to be 14 and the linear repeat distance between CH₂ units as 1.27 Å. The lamellar thickness is calculated from the stem length, assuming a tilt angle of 34.5°.

3.4.2. Gibbs–Thompson relation

In semicrystalline polymers the melting temperature T_m is related to the lamellar thickness d through the Gibbs–Thompson equation [26],

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta h_f^0 d} \right) \quad (4)$$

where T_m^0 is the thermodynamic melting temperature for an infinitely thick crystal, Δh_f^0 is the enthalpy of fusion and σ_e is the surface free energy. If the enthalpy of fusion and the surface free energy are constant, Eq. (4) predicts that the melting temperature T_m is a linear function of the reciprocal lamellar thickness $1/d$. This relationship has been shown to be valid over a wide range of lamellar thicknesses in polyethylene [30].

The melting temperature T_m is plotted against the inverse lamellar thickness values found from GPC analysis of nitric acid digested materials for grades A to D in Fig. 1. There is clearly a linear relation with the intercept at infinite lamellar thickness, T_m^0 , having a value of $145 \pm 2^\circ\text{C}$, in reasonable agreement with previous results [24,30]. The value for the surface free energy σ_e calculated from the above is approximately 72 mJ m⁻², which is in good agreement with the value found by Shahin et al. [24]. These parameters were

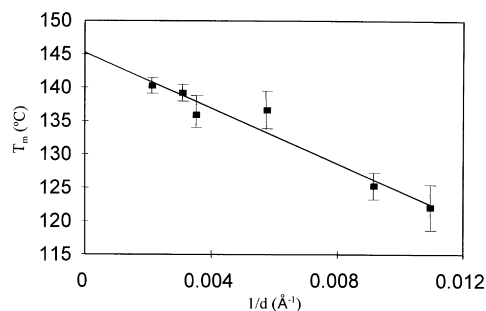


Fig. 1. Dependence of melting temperature T_m on reciprocal lamellar thickness $1/d$ for polyethylene grades A–D.

Table 3
Crystallinity, lamellar thickness and compressive yield stress for materials A–D

Material	Crystallinity (%)	Stem length (Å) (GPC)	Lamellar thickness (Å) (GPC)	Yield stress (MPa)
A	36.6	111	91	41.7 ± 0.5
B	53.8	132	109	51.5 ± 0.8
D	61.3	210	173	58.3 ± 1
C	67.1	343	283	64 ± 3
C1	86.9	567	467	78.0 ± 0.2
C2	84.2	391	322	70.7 ± 3
C3	79.3	366	302	65 ± 1

used in Eq. (4) to calculate the lamellar thicknesses for grades PE1 to PE8 from the melting temperature.

4. Results and discussion

The crystallinity, lamellar thickness, stem length and compressive yield stress of samples A–D and C1, C2 and C3 are shown in Table 3. The errors quoted for the crystallinity and the yield stress are the standard deviations for five measurements. The error in the lamellar thickness is assumed to be ± 10%. Fig. 2 plots the natural logarithm of the yield stress, $\ln(\sigma_y)$, against the reciprocal stem length, $1/\ell$, following Eq. (3). The linear fit to these data has a regression coefficient of 0.969. The gradient is $-(72.6 \pm 8.2) \times 10^{-10} \text{ m}^{-1}$. Using the values of K , G_a and b given above, Eq. (3) predicts a gradient of $-65.3 \times 10^{-10} \text{ m}^{-1}$. This good degree of agreement gives strong support for the crystal plasticity theory.

The results shown here, and those found by previous authors [8,9,12–14], indicate that, for polyethylene, the yield stress for infinitely large crystals, where the other parameters in Eq. (2) remain constant, is determined solely by the stem length. Other work [15,20], however, has shown that the yield stress depends on the degree of crystallinity. These different findings suggest that, for polyethylene, there is a relationship between the crystallinity and the stem

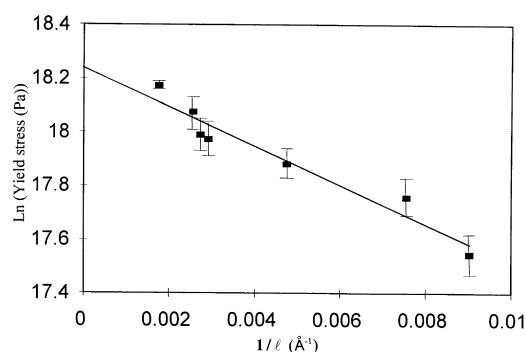


Fig. 2. Relationship between yield stress at -60°C and reciprocal stem length $1/\ell$ for polyethylene grades A–D.

Table 4
Crystallinity and lamellar thickness for materials PE1–PE8

Material	Crystallinity (%)	Lamellar thickness (Å) (DSC)	Stem length (DSC)
PE1	54.9	131	159
PE2	61.6	153	186
PE3	62.0	154	187
PE4	57.2	126	153
PE5	64.0	149	181
PE6	59.6	139	168
PE7	45.9	110	134
PE8	60.3	132	160

length. Although it is generally accepted that similar factors (such as crystallization temperature) affect both the crystallinity and the stem length, little work has been carried out previously to establish a link between the two. Msuya and Yue [31] have shown a relationship between the crystallinity and the peak melting temperature for bulk crystallized and annealed polyethylene, which implies a relationship between the crystallinity and the stem length.

The possibility of a relation between crystallinity and stem length can be tested using the wide range of samples analysed here. The crystallinity and stem length values for materials A to D and C1, C2 and C3 have already been established and are shown in Table 3. Values of the crystallinity, lamellar thickness and stem length found for materials PE1 to PE8 are shown in Table 4.

Fig. 3 plots the natural logarithm of the crystallinity against the reciprocal of the stem length for this wide range of polyethylenes. The linear fit to the data is surprisingly good, with a regression coefficient of 0.935. This interrelationship between the stem length and the crystallinity applies well to the wide range of polyethylenes examined here. It is not, however, the intention of this paper to attempt to explain this interrelationship nor to suggest it applies universally.

The linear relations shown in Figs 2 and 3 can be used to predict the relationship between the yield stress and the crystallinity. Using the gradients and intercepts in these

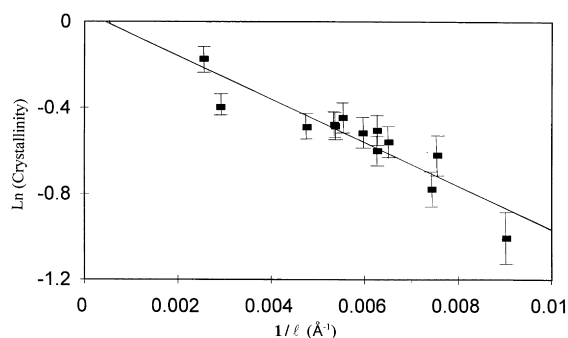


Fig. 3. Relationship between crystallinity and reciprocal stem length $1/\ell$ over a wide range of polyethylene samples.

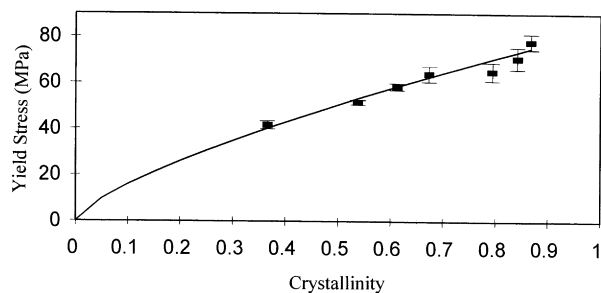


Fig. 4. Variation in yield stress with crystallinity for materials A–D.

figures it is found that, for data collected at -60°C ,

$$\sigma_y = 83.3\chi^{0.723} \quad (5)$$

i.e., the yield stress is related to the degree of crystallinity through a power law relationship, not a linear relationship as proposed by previous authors [15]. Fig. 4 plots the values of yield stress against crystallinity obtained in this work. The data appear to suggest a linear relation, yet the power law relationship proposed in Eq. (5) fits the data very well, suggesting that more extensive measurements are necessary to distinguish between the two.

5. Conclusions

The current work has shown that, under conditions of elastic–plastic deformation and constant temperature and strain rate, the yield stress in bulk crystallized and pressure annealed polyethylenes is influenced mainly by the stem length. The precise dependence can be predicted using Young's model based on crystal plasticity which assumes that yield behaviour is a nucleation-controlled process.

Detailed measurements of the stem length and crystallinity for a wide range of polyethylenes have shown that there is an interrelationship between the crystallinity and the stem length. By combining this interdependence with the crystal plasticity approach, it has been shown that the yield stress is related to the degree of crystallinity by a power law relationship. Although this differs in form from the linear dependence reported previously [15,20], the restricted range of experimental results means that, in practice, there is little to distinguish between the two relationships.

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