ELSEVIER

Polymer 42 (2001) 3791–3797

polymer

www.elsevier.nl/locate/polymer

The effects of morphology on the yield behaviour of polyethylene copolymers

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Received 15 August 2000; received in revised form 12 October 2000; accepted 17 October 2000

Abstract

Three poly(ethylene-1-hexene) copolymers (which are characterised by different degrees of branching) were cast as flat film discs from a decalin solution at various initial dilutions. Structural analyses of these materials have shown that the stem length (the length traversed by a polymer chain within the crystal lamellae) for each grade is varied widely by altering the solutions initial dilution. Tensile yield stress measurements have been performed on these cast films in the temperature range −80 to +80°C, a temperature range which includes the β-relaxation temperature for these materials. The results have shown that, above T_β, the stem length dependence of the yield stress is generally in agreement with the modified crystal plasticity approach previously used successfully to model the yield behaviour of a range of bulk cast polyethylenes. However, the results have also shown quite clearly, that in terms of morphology, it is not just the stem length which determines the yield stress but there is also a contribution due to the morphology of the lamellar fold surface. It is thought that the contribution of the fold surface to the macroscopic yield stress is attributable either to the energy to nucleate a screw dislocation within the crystalline lamellae or to the inter-lamellar shearing process. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Yield; Polyethylene; Deformation

1. Introduction

The developing interest in polymer materials with enhanced properties has led to attempts to relate their macroscopical mechanical behaviour to that of the microscopic constituents. The difficulties encountered when studying the deformation behaviour of polymers are mainly due to the complex structure of these materials and the wide range of structural variables that are encountered. In this respect polyethylene has been one of the most studied semi-crystalline polymers due to its relatively simple chemical and crystalline structure, and well-characterised physical properties. In addition, polyethylene has a relatively low glass transition temperature (approximately −130°C). Thus, the amorphous phase contributes very little to the plastic process(es) over a wide range of temperatures, but does participate in orientation effects on deformation. At the same time tie molecules, which link parts of crystalline phase dispersed in a rubbery amorphous phase, work well in stress transfer.

There is currently a debate as to the underlying molecular processes of the yield in semi-crystalline polymers, especially polyethylene. Several approaches have been used in an attempt to relate the morphology of polymers to their deformation and mechanical characteristics.

Previous work carried out by Brooks et al. [1–3] have shown that a range of bulk cast polyethylenes exhibit two yield points. The first marks the onset of temporary plastic deformation (recoverable over a few days), and the second the onset of permanent plastic deformation. This double yield phenomenon has been observed by other authors [4–7], although there is disagreement to some extent over the underlying deformation process(es) at the first yield point. Brooks and co-workers have concluded that the first yield point is associated with a recoverable reorientation of the crystalline lamellae due to inter-lamellar shear. Whereas Seguela and co-workers have concluded that the first yield point is associated with fine chain slip (c-slip) within the actual lamellae. Galeski et al. [7] have shown that for HDPE (at elevated temperatures) inter-lamellar shear and fine c-slip occur concurrently. It is therefore believed that the findings of Brooks and Seguela and their respective co-workers are not inconsistent. The second yield point is associated by both sets of workers with the destruction of the crystalline lamellae by the process of coarse c-slip.

A number of different approaches have been used to model the yield behaviour of polymers in terms of their

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PII: S0032-3861(00)00762-X

morphology and deformation behaviour. The Eyring approach considers yield as a thermally activated process and is successful in modelling the yield behaviour of amorphous polymers [8,9–11] at relatively high temperatures. However, this approach does not specifically refer to polymer morphology. Another approach suggests that yielding and deformation of polymers in general proceeds through a partial melting and recrystallisation mechanism (even at temperatures below the melting point) [12].

Other workers have attempted to model the yielding behaviour of semi-crystalline polymers in terms of classical ideas based on crystal plasticity. Plastic deformation in metallic single crystals, and many other low-molecular mass crystalline materials takes place predominantly through slip processes, which involve the nucleation and propagation of dislocations. Bowden and Raha [13] and Argon [14] have proposed that dislocations or disclinations determine the yield behaviour in crystalline and amorphous polymers, respectively.

The presence of dislocations in polymer crystals was demonstrated from moiré fringes between lamellae observed under electron microscopy [15–17]; and it is now thought [18] that much of the irreversible plastic deformation observed in polyethylenes under load are mainly crystallographic in nature. Among these mechanisms, the crystallographic slip modes in the chain direction have the lowest critical resolved shear stress (CRSS) and are therefore most likely to occur.

Based on these assumptions, a theory has been developed [15–17,19] in an attempt to model the yield behaviour of semi-crystalline polymers. This approach is consistent with the observed deformation of polyethylene lamellae by the process of c-shear. The model developed by Young assumes that the yield stress of a semi-crystalline polymer is governed by the energy required to *nucleate* a screw dislocation within the crystalline lamellae, the Burgers vector of the dislocation being parallel to the chain axis. Using this approach Young has shown that the yield stress, σ_y, can be given by the equation

$$\sigma_y = \frac{K^*}{2\pi} \exp - \left[\frac{2\pi \Delta G_C}{K^* \ell b^2} + 1 \right] \tag{1}$$

where ΔG_C is Gibb's free energy for dislocation nucleation; ℓ the stem length; K^* the crystalline shear modulus; and b is the magnitude of the Burgers vector.

Eq. (1) has been used successfully by previous authors [5,20–22] to model the temperature and stem length dependence independently for a wide range of polyolefins, using the following assumptions:

1. The actual slip plane is undefined and that K^* can be taken as a geometric mean of the shear moduli C_{44} and C_{55} such that $K^* = (C_{44}C_{55})^{1/2}$. (The values for C_{44} and C_{55} are taken from theoretical works.)
2. Deformation is due to the nucleation of perfect dislocations, and the magnitude of the Burger's vector, b, is thus the c-axis repeat unit distance. For polyethylene this is taken to be 2.54 Å.
3. $\Delta G = 60\mathrm{k}T$ (where k is the Boltzmann constant and T the absolute temperature).
4. The contribution of the dislocation core energy and the fold surfaces can be ignored.

Recently Brooks and Mukhtar [23] have modified the Young theory to include an additional term due to the core energy of the screw dislocation. Using this modified crystal plasticity approach Brooks and Mukhtar have been successful in modelling the stem length and temperature dependence of the yield stress of a range of bulk cast polyethylenes concurrently. The modified crystal plasticity approach predicts that the yield stress is given by the following equation:

$$\sigma_y = \frac{K^*}{\pi} \alpha(T) \exp - \left[\frac{2\pi \Delta G_C}{K^* \ell b^2} + 1 \right], \tag{2}$$

where $\alpha(T)$ is an unknown function which is dependent on the temperature (as well as other factors).

Eq. (2) can be rewritten in the form

$$\ln(\sigma_y) = \ln\left(\frac{K^* \alpha(T)}{\pi} - 1 \right) - \left(\frac{2\pi \Delta G_C}{K^* \ell b^2} \right) \tag{3}$$

The modified crystal plasticity theory, therefore, predicts that $\ln(\sigma_y)$ is a linear function of $1/\ell$ at constant temperature and strain-rate.

Darras and co-workers [5,24] have previously cast a range of polyethylene copolymers from a decalin solution and carried out structural and mechanical analyses under tensile deformation. Using this casting technique these authors have been able to vary the stem lengths of each grade of polyethylene widely. Their results have shown that at 60°C the crystal plasticity model accurately models the yield stress in terms of the stem length. However, no experiments at other temperatures and no structural measurements to identify the deformation behaviour of the materials were reported. These authors have identified the yield point in a similar way to that used in the present paper. It is therefore assumed that the yield stress measured by these authors is associated with the first yield point.

The success of the crystal plasticity approach in modelling the yield stress behaviour for a wide range of polyolefins [5,20–24] provides further strong evidence to show that the deformation at the first yield point is associated with fine c-slip within the lamellae.

The present work extends the investigation of Darras and co-workers [5,24] to a much wider temperature range. In addition, further structural measurements of solution crystallised polyethylenes have been carried out.

2. Experimental details

2.1. Materials and sample preparation

Three grades of ethylene/1-hexene copolymer, characterised by different molecular mass and butyl branch

Table 1
Chemical characteristics of polyethylene copolymers

Material	M_w	M_n	Branch content (mol%)	Density (g cm^{-3})
Material A (LLDPE)	126,000	30,300	2.1	0.920
Material B (MDPE)	206,000	12,900	0.6	0.938
Material C (HDPE)	138,000	–	–	0.955

content, were selected for this investigation. The grades are the same as those used by Brooks and co-workers [2,3] in their earlier investigations. The materials were produced by British Petroleum Ltd and supplied in a pelletised form. Details of the materials' characteristics are given in Table 1. Decalin, used as a solvent, was purchased from Aldrich Chemical Co., Inc.

The sample preparation technique was based on the procedure developed by Darras et al. [24] to produce polyethylene films cast from decalin. In the present work, various concentrations of polyethylene were dissolved in decalin (varying from 40 to 100 wt% of polymer) at 160°C. These solutions were then cast into flat discs by means of a steel injection-moulding device under a pressure of 15 MPa. To avoid bubble formation, or, when it was impossible, to locate bubbles near the centre of the cast disc, a "breathing" moulding technique was used [25,26].

The mould was cooled to room temperature at a rate of approximately 10°C/min. The cast polyethylene discs produced were left to dry in a fume-cupboard for a period of 7–10 days. Drying was carried out between two metal grids to prevent curling and waving due to contraction. The polyethylenes were considered dry when their weight stabilised. No noticeable orientation or bubbles present were evident from analysis of a dried polyethylene disc under polarised light optical microscopy.

2.2. Sample characterisation

2.2.1. Crystallinity

2.2.1.1. Differential scanning calorimetry (DSC). DSC was used to determine values for crystallinity and melting temperature. Melting endotherms were obtained using Perkin–Elmer Series 7 system at a heating rate of 10°C/min on samples weighing between 7 and 20 mg. The calorimeter was calibrated using a high-purity indium sample.

Crystallinity values were determined using the ratio of the melting enthalpy of the samples to that of a perfect and infinite polyethylene crystal, $\Delta H_m^0 = 293.13\ \mathrm{Jg}^{-1}$ [27].

The melting temperature values were also obtained and later used in conjunction with Small Angle X-ray Scattering (SAXS) technique to establish the fold surface free energy values.

2.2.2. Stem length

The long period, D, was measured using the method of SAXS Analysis. Three cast film samples were tested for each grade corresponding to initial solution concentrations of 40, 70 and 100 wt%.

The experiments were carried out at Station 2.1 of the Daresbury Synchrotron Radiation Source. The beamline was configured with an X-ray wavelength, λ, of 1.52 Å and a bandwidth $\Delta\lambda/\lambda \leq 4 \times 10^{-3}$. Small angle scattered X-ray photons were detected on an area detector located 3.5 m from the sample. The calibration of the q scale of the detector ($q = 4\pi \sin\theta/\lambda$, where the scattering angle is defined as 2θ) was performed using the first 25 orders of diffraction from wet rat tail collagen. A sixth order polynomial was fitted to the inverse collagen spacings over the detector range. This corrects for the positional nonlinearity of the detector. All diffraction intensities were normalised by the beam flux, which was monitored by an ionisation chamber located behind the sample. The two-dimensional scattering patterns were found to be symmetric. In order to carry out further analysis, one-dimensional data was obtained through integrating arcs of 20° from the vertical part of the pattern. The experimental data were corrected for background scatter using the scatter from an empty sample holder, and for nonuniform detector sensitivity using the response to a ^{55}Fe X-ray source. Each of the one-dimensional SAXS scattering patterns was Lorentz corrected [28].

The lamellar thickness, L_c, is calculated using the crystalline volume fraction, Φ, and the long period, D, such that

$$L_c = \Phi D \tag{4}$$

The stem length was then calculated assuming that the chain axis is tilted at an angle 34.5° [29,30] to the fold surface normal.

For Material A, SAXS, DSC and previous SEM [31] results have shown that there appears to be two populations of lamellar species, with smaller (infill) lamellae separating the dominant (thicker) lamellae. For Material A, the lamellar thickness and stem lengths for the dominant lamellae have been found as described above. The lamellar thickness and stem length of the infill lamellae have been found from the Thompson–Gibbs equation taking the melting point from DSC and assuming that the surface free energy of the dominant and infill lamellae are the same.

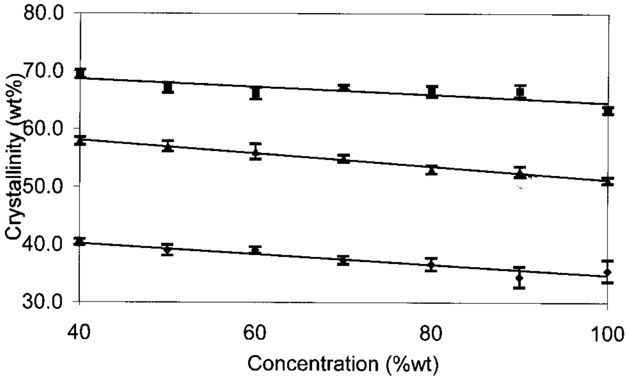

Fig. 1. Crystallinity vs initial solution concentration for Material A (◆), Material B (▲) and Material C (■).

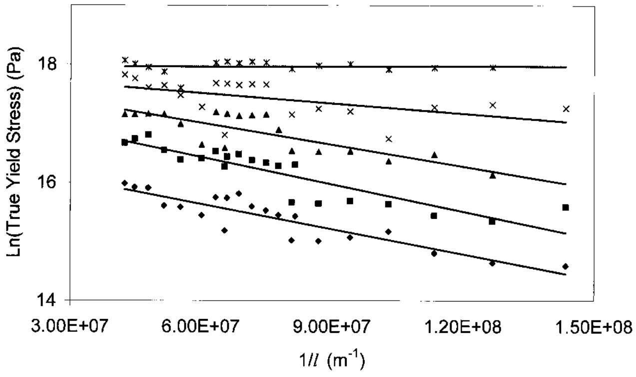

Fig. 3. ln(σ) vs 1/ℓ for all three materials at 80°C (◆), 40°C (■), 0°C(▲), −40°C (×) and −80°C (∗).

2.2.3. *Surface free energy*

The surface free energy per unit area of the fold surface, σ_e, was found by using the simplified form of the Thompson–Gibbs equation [32], such that

$$T_m = T_m^0\left[\frac{1-2\sigma_e}{\Delta H_m^0 \rho_c L_c}\right] \tag{5}$$

where L_c and T_m are the lamellar thickness and melting temperature, respectively; T_m^0 the temperature of melting of an infinite crystal, 145.21°C [33,34]; ΔH_m^0 the enthalpy of melting per unit mass of an infinite crystal, 293.13 J g^{-1} [27]; and ρ_C is the crystalline density, 0.990 g cm^{-3} [27].

2.3. *Mechanical analyses*

The solution cast polyethylene sheets were cut into dumbbells with an effective gauge length of 30.22 mm. This is calculated following the method used by Harris [35].

Tensile tests were performed on the two tensile machines: an Instron 3111, which was used for the low temperature experiments (room temperature and below); and a computerised Instron 4466 which was used for the high temperature experiments (room temperature and higher). Five measurements were made under each condition to establish the average and standard deviation values. Liquid nitrogen was used as a cooling agent to carry out experiments at subzero temperatures. All tests were conducted at a strain rate of 1.103×10^{-2} s^{-1}.

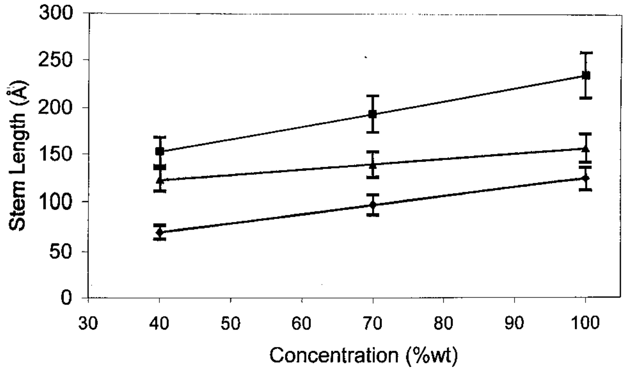

Fig. 2. Stem length vs initial solution concentration for Material A (◆), Material B (▲) and Material C (■).

The macroscopic yield point is identified either as the maximum on the force-elongation curve or by using the Brereton–Considére approach described in a previous publication [1]. The true yield stress and strain values were calculated assuming homogenous deformation at constant volume. In each instance the yield point measured corresponds to the first yield point.

A series of tests were carried out on both Instron testing machines at room temperature. The results obtained from these tests showed that the force and elongation values at yield agreed within the standard error of the experiments.

3. Results and discussion

3.1. *Structural analyses*

The degree of crystallinity and stem length as a function of the initial polymer concentration in decalin, for each of the three copolymers, is shown in Figs. 1 and 2, respectively. For all three grades, the results clearly show that as the dilution of the initial solution is decreased the crystallinity is reduced but the stem length is increased, in agreement with the findings of Darras et al. [24].

The stem length for each of the three grades has been found at three concentrations only: 40, 70 and 100 wt%. The stem lengths for the other concentrations were found by linear interpolation of these points. For Material A (LLDPE) the stem length of the thinner lamellae are considered as it is assumed that it is these which yield first, at the lowest stress and strain values.

Using these results, plots of the natural logarithm of the yield stress, ln(σ_y), against the reciprocal of the stem length, 1/ℓ were obtained, and are shown in Fig. 3. It can be seen that, over the range of temperatures considered, ln(σ_y) is an approximate linear function of 1/ℓ, in agreement with the

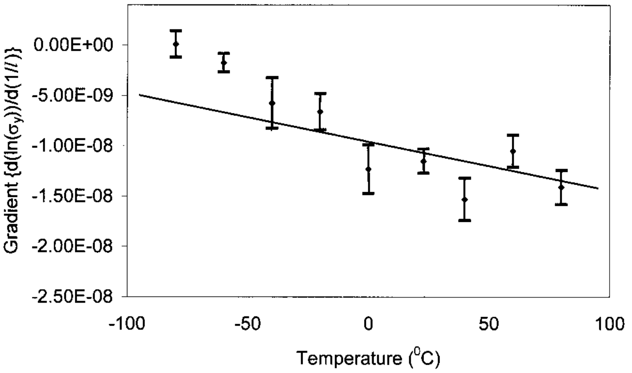

Fig. 4. Gradient, $d(\ln(\sigma_y))/d(1/\ell)$, vs temperature (◆), theoretical curve shown by solid line taken from Ref. [36].

crystal plasticity model (Eq. (3)). The gradients of the straight lines shown in Fig. 3 were found and plotted as a function of temperature, these results are shown in Fig. 4.

From Eq. (3), the gradient of the linear function, $\ln(\sigma_y)$ against $1/\ell$, is given by

$$\frac{d(\ln(\sigma_y))}{d\left(\frac{1}{\ell}\right)} = \frac{2\pi\Delta G_C}{K^* b^2} = \frac{120\pi k T}{K^* b^2} \qquad (6)$$

Taking the value of b to be 2.54 Å and using the values of the crystalline shear moduli from Kawasawa et al. [36], the theoretical gradients have been calculated as a function of temperature. The theoretical curve is also shown in Fig. 4.

The results shown in Fig. 4 clearly show that there is good agreement between the theoretical and experimental values for the gradient at temperatures at and above −40°C. The β-relaxation temperature, T_β, for these materials lies between −10 and −60°C depending on the grade and initial solution concentration. The results in Fig. 4 therefore give strong support for the crystal plasticity theory in the temperature range above T_β. Below T_β, however, the experimental and theoretical values appear to diverge. This is in contrast to the results obtained by Brooks et al. [37] who found good agreement between experimental and theoretical values at −60°C for a range of bulk cast and high pressure annealed polyethylenes in compression, using the same analysis as above. This discrepancy could be due to the fact that Brooks et al. obtained their results over a wider range of stem lengths and that their work was carried out in compression, rather than tension. In addition (and perhaps most importantly) the polyethylenes in the present investigation are cast from solution, this will be discussed in more detail below.

Plots of the true yield stress as a function of the stem length at +80, +40, 0, −40 and −80°C are shown in Figs. 5–9, respectively. Following the approach of Brooks and Mukhtar [23], the results at each temperature are fitted to Eq. (2) using a sum of squares method, with α the only fitting parameter. At each temperature only the three films cast from bulk with no decalin, i.e. 100% polymer by weight solutions, were fitted to Eq. (2). Using these values, a master curve is fitted to the data at each temperature and is shown in each of the figures.

The best-fit values of α have been plotted against temperature in Fig. 10. Also shown in Fig. 10 is the best-fit line taken from Brooks and Mukhtar for their data. It can clearly be seen that there is good agreement between the α value found in the present work and those found by Brooks and Mukhtar at temperatures approximately above T_β (above −20°C). Below this temperature the values for α found here diverge from those established by Brooks and Mukhtar. Thus, as for Fig. 4, a 'step-like' change is seen to occur near to T_β.

It can be seen from Figs. 5–9 that the master curve found using the modified crystal plasticity approach is generally a reasonable fit to the data at each temperature. However, for each of the three grades it can clearly be seen that the yield stress deviates from the theoretical curve as the stem length is decreased. This deviation is seen to be dependent on the grade of material and also on the testing temperature.

It is important to remember that the reduction in stem length for each grade is brought about by an increase in the dilution of the initial solution. Therefore, the deviation from the master curve shown in Figs. 5–9 increases as the dilution of the initial solution is increased.

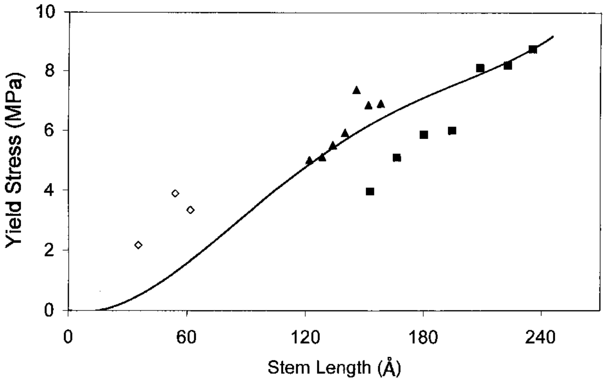

Fig. 5. True yield stress vs stem length at +80°C for Material A (◇), Material B (▲) and Material C (■).

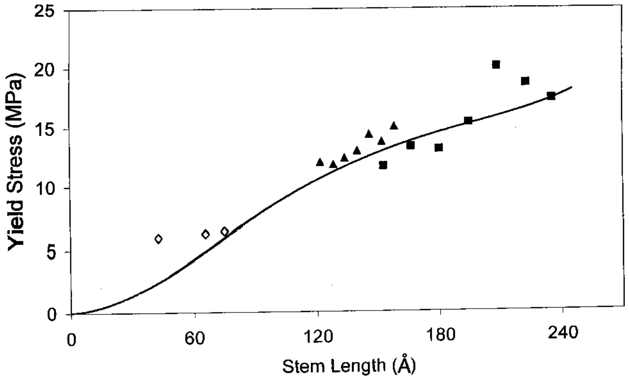

Fig. 6. True yield stress vs stem length at +40°C for Material A (◇), Material B (▲) and Material C (■).

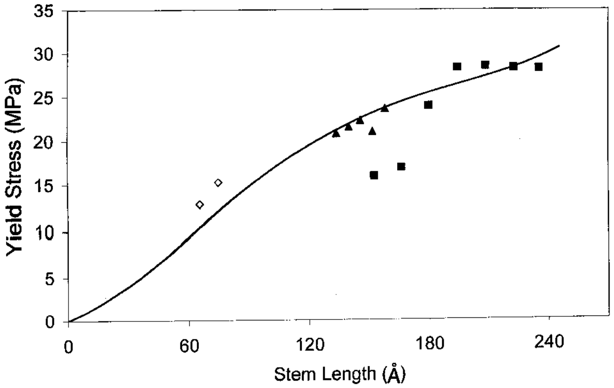

Fig. 7. True yield stress vs stem length at +0°C for Material A (◇), Material B (▲) and Material C (■).

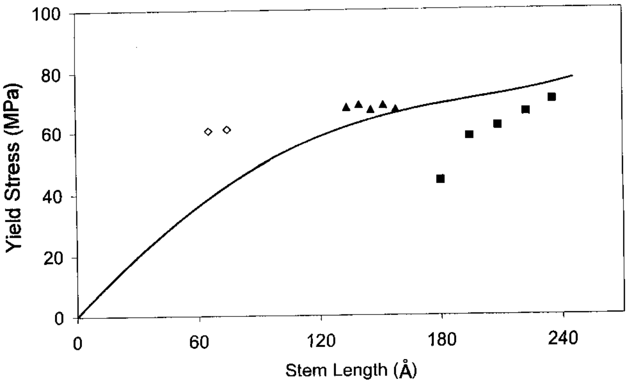

Fig. 9. True yield stress vs stem length at −80°C for Material A (◇), Material B (▲) and Material C (■).

For Material C (HDPE) the yield stress of the solution cast materials falls below the master curve as the stem length is decreased (that is the initial solution dilution is increased). This is in agreement with the results shown by Darras and Seguela [5]. In addition, the results at each temperature show that in the range of stem lengths from approximately 160–180 Å the yield stress of Material C falls below that of Material B, even though the stem lengths are the same in this range.

For Material B (MDPE) deviation from the master curve is less, except at low temperatures where the deviation becomes more pronounced.

For Material A (LLDPE) the deviation from the master curve is very different to that of Material C, and contrary to that shown by Darras and Seguela. It can clearly be seen that as the stem length decreases (initial solution dilution increased) the yield stress falls above the master curve, and at −40 and −80°C (below T_β) the yield stress appears to increase as the stem length is decreased.

These results clearly show that the yield stress at the first yield point is not solely determined by the stem length. This finding is in contrast to the findings of previous work carried out on similar materials cast from bulk [1–3,6,18,19,31,38–42] which have concluded that the stem length alone determines the yield stress in polyethylene, in agreement with the predictions of the crystal plasticity model.

Darras and Seguela [32], in addition to the mechanical analyses already discussed, also carried out structural analyses on the polyethylene copolymers which they cast from solution. These authors have shown that by casting from a decalin solution the surface free energy of the crystalline lamellae fold surfaces decreases as the dilution of the initial solution is increased. They attributed this reduction in the surface free energy as being due to two factors: firstly the fold surfaces become less disordered and secondly chain folding becomes more regular.

The surface free energy for each of the three materials under investigation here is shown in Fig. 11 as a function of the initial solution concentration. The results show that the surface free energy falls with increased dilution for all three materials, in agreement with the findings of Darras and Seguela. We therefore conclude that the morphology of the fold surfaces for the materials under investigation here changes with dilution in a similar manner to that described by Daras and Seguela, and that the macroscopic yield behaviour is affected by the fold surface morphology. This has not been previously considered.

The actual process by which the fold surface morphology

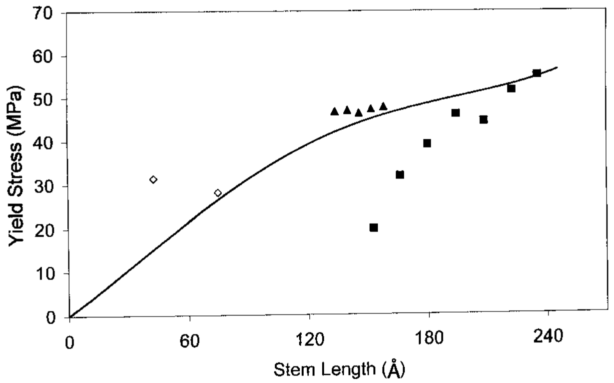

Fig. 8. True yield stress vs stem length at −40°C for Material A (◇), Material B (▲) and Material C (■).

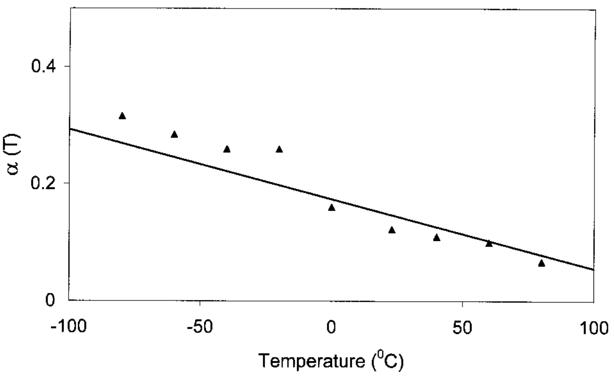

Fig. 10. Coefficient $\alpha(T)$ vs temperature (▲), theoretical curve shown by solid line taken from Ref. [23].

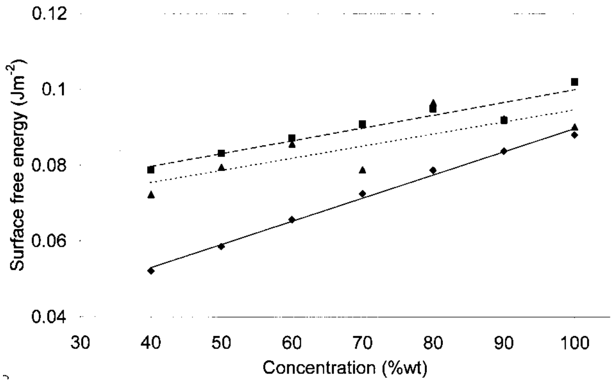

Fig. 11. Surface free energy vs initial solution concentration for Material A (◆), Material B (■) and Material C (▲).

affects the macroscopic yield behaviour at the first yield point cannot be identified at the present time. As stated previously the first yield point is associated with a simultaneous inter-lamellar shear and fine c-slip. Therefore, it is proposed that one of two processes maybe responsible:

1. The fold surface morphology may affect the energy required to nucleate a screw dislocation within the crystalline lamellae and thus this may have to be taken into account in the crystal plasticity model.
2. The fold surface morphology may directly affect the inter-lamellar shearing process where the surfaces of the shearing lamellae are in intimate contact, i.e. the coefficient of friction of the fold surfaces may change significantly with the surface morphology.

4. Conclusions

The yield behaviour of three poly(ethylene-1-hexene) copolymers cast from a decalin solution have been analysed over a wide range of temperatures including, the β-relaxation temperature for these materials. The results have shown that above T_β, the yield behaviour is generally well modelled using a modified crystal plasticity approach. However, the results also clearly show that the fold surface morphology also affects the macroscopic yield stress. This is in contrast to earlier works, which have suggested that the only morphological feature affecting the yield stress is the stem length. It is tentatively suggested that the fold surface morphology affects the macroscopic yield stress either due to its influence on the nucleation energy to form a screw dislocation within the crystalline lamellae or due to changes in the coefficient of friction of the fold surfaces affecting interlamellar shear.

Acknowledgements

We would like to thank Dr Christine Adams and Dr Paul Unwin (IRC in Polymer Science and Technology, Leeds University) for their work on the SAXS experiments. Mr Peter Cracknell who assisted in the manufacture of the transfer mould and consulted on moulding technique. We would also like to thank the Committee of Vice-Chancellors and Principals of the Universities of the UK for their Overseas Research Student award to Rostislav Sirotkin.

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