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Microstructure of bulk crystallized linear polyethylene: correlation of microhardness and yield stress

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The effect of molecular weight on the yield behaviour and microhardness of melt-crystallized polyethylene has been studied. The influence of the crystallization conditions on the mechanical properties has been examined. It is shown that Tabor's relationship between microhardness and yield stress applies if the strain rate of the tensile tests is comparable to that employed in the hardness indentation tests. Results are discussed in terms of surface free energy which depends on the number of molecular entanglements segregated on to the surface of the lamellar crystals controlling the yield behaviour of the polymer.

1. Introduction

In recent years, microindentation hardness, H, has been shown to be a powerful technique to determine accurately changes in morphology and microstructure of semicrystalline polymers [1, 2]. The indentation process involves a permanent deformation on a very small scale at the polymer surface. Consequently, the microhardness is directly correlated with the mechanisms of plastic deformation of the semicrystalline solid and depends on the average thickness, l_c, of the densely stacked lamellae within the polymer. The hardness of the crystals themselves, H_c, when indentation is done at $T_g < T$, can be derived from the hardness of the polymer by using the relation

$$H_c = H/\alpha \tag{1}$$

where α is the degree of crystallinity. This equation assumes that the semicrystalline polymer is a two-phase system and that yield is due to plastic deformation taking place only in the crystalline regions [3]. Young *et al.* [4] have demonstrated that the amorphous regions in PE undergo only elastic deformation at room temperature. Recent research by Brooks *et al.* [5] showed that the yield behaviour of polyethylene is complex and that two deformation processes can be identified. The high-stress process defines the onset of permanent deformation and has been associated with the c-slip process which is consistent with the conclusions of these previous studies. The crystal hardness, H_c, has been additionally correlated to the thickness of the lamellae by Baltá Calleja and Kilian [6] using a heterogeneous model of deformation. The hardness of the crystals can be accordingly described by

$$H_c = H_o^\infty/(1 + b/l_c) \tag{2}$$

where H_o^∞ is the hardness of an infinitely thick crystal and b is a parameter equal to $2\sigma_e/\delta h$, where σ_e is the surface free energy and δh is the enthalpy of the crystal destruction. This model has been successfully applied for different lamellar structures [7–10]. Equation 2 describes the depression of crystal hardness due to finite crystal thickness and is characterized by parameter b which is related to the equilibrium properties of the crystals.

The microhardness of a material can, furthermore, be derived macroscopically by a yield stress, Y, measurement using Tabor's relation [11]

$$H \approx 3Y \tag{3}$$

By combination of Equations 1, 2 and 3, Tabor's relation can be rewritten in a more general form as

$$Y \approx H/3 = \alpha H_o^\infty/(1 + b/l_c) \tag{4}$$

Hence, microhardness can be considered as a bridging parameter between microstructural quantities (l_c, α, b), on the one hand, and bulk mechanical properties (yield stress, elastic modulus, etc.) on the other. In a previous work, the microhardness of a series of melt-crystallized linear polyethylenes having a wide range of molecular weights, M_w, was investigated [12]. The X-ray long period was measured to study the variation of hardness-derived constant b as a function of M_W. The obtained data indicated an increase of b with M_w, showing a final leavelling-off of b for $M_w > 200\,000$, which was parallel to the concurrent increase in surface free energy derived from calorimetric experiments. Comparison of experimental and calculated data favoured the view that the number of chain defects (molecular entanglements) segregated on to the defective surface of the crystals, influenced the

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TABLE I Molecular weight characteristics of polymers

Sample	Polymer grade	Melt flow index[a]	M_n	M_w	M_w/M_n
1	140–160[b]	12.7	13 300	67 800	5.1
2	BXP 10[c]	4.6	16 800	93 800	5.6
3	R 25[b]	3.0	12 950	98 800	7.6
4	R 50[b]	6.0	6 530	101 400	15.5
5	R 9[b]	1.1	6 060	126 600	20.9
6	BP 206[c]	0.23	16 600	213 000	12.8
7	HO20-54P[b]	2.2	33 000	312 000	9.5
8	GUR[d]		383 000	2.3×10^6	6.0

[a] BS 2782 Method 105C

[b] BP Chemicals International Ltd.

[c] Experimental polymer.

[d] Farbwerke Hoechst A.G.

shearing mechanism under the point indentor controlling the yield behaviour of the material.

The aims of the present study were:

(i) to extend the above investigations to the case of polyethylene (PE) materials, crystallized under different cooling rates in order to examine the influence of molecular weight and, hence, of the number of molecular defects, on the mechanical parameter b;

(ii) to carry out parallel yield stress measurements on the same samples and investigate the influence of the strain rate on Tabor's relationship.

2. Experimental procedure

2.1. Materials

The polymers used were either commercial grades of linear polyethylene homopolymer manufactured by BP Chemicals International Ltd or Fabwerke Hoechst A.G., or experimental grades kindly provided by BP chemicals, Polymer Sciences Branch, Grangemouth, UK. The molecular weight characteristics of the polymers are given in Table I. Both M_w and M_n were obtained by gel permeation chromatography, for all samples.

Isotropic sheets of approximately 0.5 mm thickness were obtained by compression moulding polymer pellets (powder in the case of 7 and 8) between polished copper plates at 160 °C. The procedure has been described in more detail in previous publications [13, 14].

For the present investigation, two standard cooling procedures were adopted:

(i) the molten product was immediately quenched into water at ambient temperature (20 °C). These samples are designated "quenched",

(ii) the sheets containing the polymer were cooled slowly at about 10 °C min^{-1} to 110 °C, and then quenched into cold water. These samples are designated "slowly cooled".

2.2. Techniques

2.2.1. Measurements of microhardness

Microhardness was measured at room temperature using a Leitz Tester adapted with a square-based diamond indentor. The H-value was derived from the residual projected area of indentation according to the expression $H = kP/d^2$ (MPa), where d is the length of the impression diagonal in metres, P the contact load applied in N and k is a geometrical factor equal to 1.854. Four loads (0.1, 0.2, 0.5, and 1 N) and various loading cycles of 0.5, 0.1, 1 and 5 min, were used to correct for the instant elastic recovery.

2.2.2. Measurements of yield stress

Dumb-bell-shaped samples with gauge dimensions 2 cm × 0.5 cm were cut from the isotropic sheets. For the measurements of yield stress, these were extended in an Instron tensile testing machine at two crosshead speeds of 2 and 0.02 cm min^{-1} at a temperature of 21 ± 1 °C. The yield stress was measured arbitrarily as the peak force on the load–extension curve.

3. Results

The values of hardness, H (derived from the average of ten indentations on each polymer), crystal hardness, H_c, crystal thickness, l_c, and the mechanical parameter, b, together with M_w and crystallinity, α, derived from density are given in Table II. The l_c values were calculated from the long spacing, L, according to $l_c = L\alpha$ using the data from Capaccio and Ward [15, 16]. Fig. 1 clearly shows the gradual decrease of H with M_w for both cooling rates. However, the quenched samples show lower H values than the slowly cooled ones.

The yield-stress data and the H/Y ratios are shown in Table III where each value of the yield stress is the mean of three tests on each polymer. The yield stress is seen to be strain-rate dependent, as expected [17]. The strain rate for a crosshead speed of 0.02 cm min^{-1} is 1.6×10^{-4} s^{-1}, which is comparable to that employed in the hardness indentation tests. When the ratio H/Y is computed for this strain rate, it is seen that the ratio is very close to 3, as proposed by Tabor [11]. Fig. 2 shows the corresponding straight line with slope 3. For a higher strain rate, the H/Y ratio is much lower (~ 2) than predicted according to Tabor's relation. It is also observed that similar to the H value, the Y value tends to decrease slightly with increasing molecular weight and that the yield stress is higher for the slowly cooled samples than for the rapidly quenched ones.

4. Discussion

Previous studies [14, 15] have shown that there are remarkable differences in morphology between samples of different initial thermal treatment, and that these differences depend on the molecular weight characteristics. The rapidly quenched samples show the typical banded spherulitic texture. Crystallization has occurred under conditions of high supercooling, producing a complex spherulitic geometry with twisting and branching as the lamellae grow radially from the point of nucleation. On the other hand, in the slowly cooled samples, crystallization takes place initially at high temperatures, i.e. low supercooling and

TABLE II Values of H, α, H_c, l_c and b as a function of M_w for quenched and slowly cooled samples

Sample	M_w	H (MPa)	α	H_c (MPa)	l_c (nm)	b (nm)
Quenched						
1	67800	58	0.67	86	13.7	13.3
2	93800	56	0.66	85	–	–
3	98800	53	0.64	83	13.8	14.5
4	101450	54	0.67	81	12.7	14.1
5	126600	52	0.67	78	16.0	18.9
6	213000	47	0.64	73	–	–
7	312000	45	0.63	71	15.2	21.0
8	2.3×10^6	33	0.48	69	16.5	24.1
Slowly cooled						
1	67800	71	0.77	92	21.3	18.3
2	93800	65	0.74	88	–	–
3	98800	64	0.76	84	21.3	21.8
4	101450	64	0.78	82	19.5	20.8
5	126600	62	0.76	82	19.5	21.2
6	213000	58	0.72	81	–	–
7	312000	57	0.71	80	24.3	27.6
8	2.3×10^6	44	0.57	77	22.5	27.1

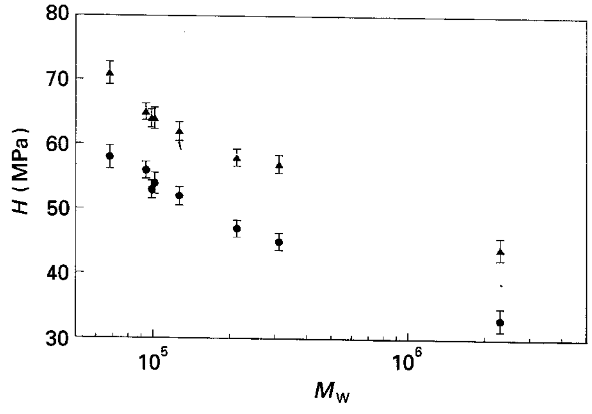

Figure 1 Variation of microhardness, H, as a function of molecular weight, M_w, for melt crystallized PE: (●) quenched, (▲) slowly cooled.

a more regular texture is produced, with the additional complexity that high molecular weight polymer crystallizes first, and low molecular weight on subsequent cooling, i.e. there is segregation by molecular weight. The implication of these observations on the drawing behaviour have been discussed in the previous publication [14]. Popli and Mandelkern [18] found, however, that spherulite size does not have a direct influence upon yield in PE. In preceeding studies, we recognized the direct influence of crystal thickness, l_c, upon microhardness, H, in the case of chain-folded and chain-extended PE samples [1, 6]. Popli *et al.* [18] and Crist *et al.* [19] have also given evidence for the dependence of yield stress on l_c.

However, in the present work, l_c, for the quenched and slowly cooled samples, is shown to be independent of M_w and thus, it does not affect the H_c values in Equation 2 (see Table II). Therefore, the decrease in hardness observed in Fig. 1 is obviously only due to the decrease in crystallinity with increasing M_w. On the other hand, because H_c does not depend on crystallinity, the initial decrease of H_c and final levelling off with M_w (Fig. 3) can be straightforwardly explained in terms of the variation of parameter b with M_w, shown in Fig. 4.

Holl *et al.* [20] have pointed out that the fraction of permanent defects in the semicrystalline state of polymers is related to the average density of the entanglements in the melt. However, after crystallization, defects are permanently located at the crystal surface and cannot be removed as occurs in the molten state. The surface free energy, σ_e, of the folded chain lamellae with chain defects corresponds to the lowest free energy and is proportional to b. Consequently, σ_e ought to increase with increasing concentration of defects. It is known that the concentration of entanglements in the melt is always constant for a given molecular weight. Because the slowly cooled materials show thicker crystals due to the slow cooling rate and lower supercooling, there is, therefore, a greater concentration of entanglements on the crystal surface, compared with the quenched materials where the entanglements are largely concentrated in the amorphous phase. From Fig. 4 one sees that the quenched samples have lower b values, as compared to those of the slowly cooled ones. On the other hand, if the length of the chains is increased, then the number of defects increases and, above a critical molecular weight value of M_c, the defective surface layer is saturated with defects. If the chain length is further increased beyond M_c, the density of the entanglements and the chain loops which are in the melt can no longer be located at the crystal surface. These equilibrium defects are then rejected into the amorphous phase. Hence, for slowly cooled samples, b remains constant beyond $M_w > 200000$. However, the quenched samples also show a clear influence of M_w on b, although for very high M_w, the saturation value of b is not achieved. This suggests that at the higher cooling rate, the number of chain defects and entanglements at the crystal surface is still lower than for the slowly crystallized samples.

TABLE III Yield-stress data for the quenched and slowly cooled samples

Sample	Yield stress, (MPa) 2 cm min^{-1}	H/Y_2	Yield stress, (MPa) 0.02 cm min^{-1}	$H/Y_{0.02}$
Quenched				
1	26.7	2.17	18.1	3.20
2	25.5	2.19	17.5	3.20
3	24.8	2.13	17.5	3.02
4	26.9	2.0	18.1	2.98
5	25.0	2.08	17.4	2.98
6	24.3	1.93	16.9	2.78
7	21.8	2.07	15.9	2.81
8	18.0[a]	1.83		
Slowly cooled				
1	31.12	2.28	22.09	3.21
2	28.76	2.26	21.46	3.03
3	30.14	2.13	21.77	2.93
4	30.79	2.08	21.62	2.96
5	28.86	2.15	22.03	2.81
6	27.75	2.11	20.23	2.86
7	28.22	2.02	19.70	2.89
8	22.84[a]	1.93	11.98[a]	3.67

[a] no definite yield point, change of slope only.

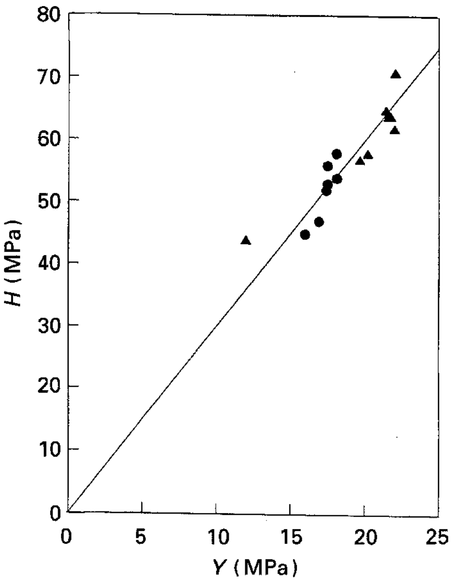

Figure 2 Correlation between microhardness, H, and yield stress, Y, for melt-crystallized PE: (●) quenched, (▲) slowly cooled.

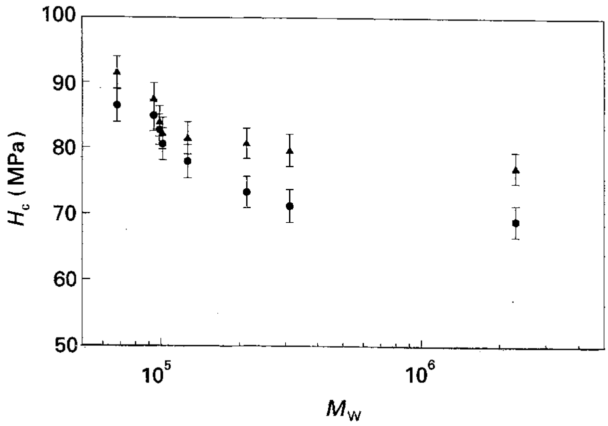

Figure 3 Variation of crystal hardness, H_c, as a function of molecular weight, M_w: (●) quenched, (▲) slowly cooled.

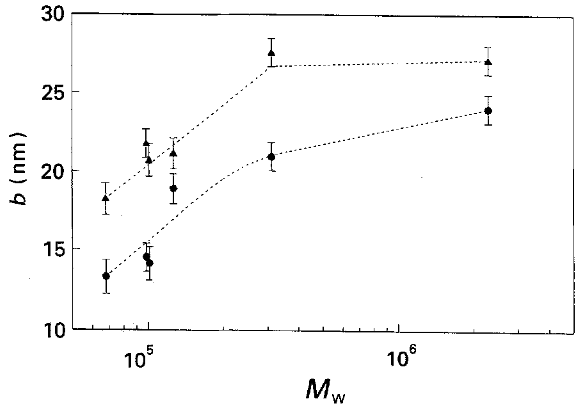

Figure 4 Dependence of the mechanical parameter, b, upon molecular weight, M_w: (●) quenched, (▲) slowly cooled.

We have seen that Tabor's relation [11] applies for the yield stress experiments in which the strain rate is similar to that under the indentor. These results show that Tabor's relation applies well for PE materials with widely varying morphologies, when recoverable viscoelastic deformation is minimized (loading time = a few seconds) (see Fig. 2). The data of Fig. 2 emphasize that crystallinity, on one hand, and surface free energy (molecular weight), on the other, are the two main parameters which monitor the yield stress values of these PE samples. The deviation from the $H \approx 3Y$ predictions for the slowly cooled high molecular weight sample could have the following reason: the yield point for this sample is not so well defined and, therefore, some uncertainty concerning the Y value is involved. On the other hand, the high H/Y ratio obtained for the slowly crystallized sample with the lowest molecular weight could be due to the influence of a strain-hardening effect, during the indentation of this highly crystalline sample.

5. Conclusions

From the above discussion, we can conclude that Tabor's relation applies when the strain rate of the tensile test is comparable to that employed in the hardness test. The rate of cooling affects the crystallinity and parameter b and consequently the hardness value, H. Results confirm for the slowly cooled samples the increase of b with increasing M_w, showing a final levelling off for $M_w > 200\,000$. However, for the quenched samples this levelling off is not so clear.

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