Effects of chain structure and orientation on the morphology and fracture properties of polyethylene

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The fracture behaviour of isotropic and oriented polyethylene has been combined with studies of the internal microstructure using optical and electron microscopic observations of permanganic etched samples. Very considerable differences in fracture toughness were obtained for oriented polymers of different molecular weight or degree of branching, and it has been found that there are corresponding differences in morphology.

(Keywords: morphology; fracture; polyethylene)

INTRODUCTION

In previous publications[1,2], the fracture behaviour of both isotropic and oriented polyethylene has been described, using a unique tensile testing facility where fracture occurs under high superimposed hydrostatic pressure. Polymers were carefully chosen with a range of molecular weights and short chain branch content to give a wide range of mechanical properties.

The fracture properties were characterized by fracture toughness values K_c, which for the oriented materials depended on whether the applied stress was parallel K_c^{long} or perpendicular K_c^{trans} to the orientation direction. The results revealed that there were only small differences in fracture toughness between all the grades of polyethylene tested in the isotropic state. For all the oriented materials, K_c^{long} increased with draw ratio, K_c^{trans} was relatively independent of draw for materials with weight average molecular weight $\langle M_w \rangle < \sim 180\,000$, but increased significantly with orientation for polymers with $\langle M_w \rangle > 180\,000$. These effects were particularly noteworthy for two polymers: a medium density copolymer; and a homopolymer of particularly broad molecular weight distribution confirming the importance of both short chain branching and molecular weight in determining the fracture toughness.

This paper describes a study of the crystal morphologies of these two polymers compared to those of a relatively low molecular weight homopolymer in an attempt to establish a structure–property relationship.

MATERIALS

Three commercially available polymers were selected for study. They were the homopolymers Hizex 7000F (Mitsui Petrochemicals Ltd) and Rigidex 066-60 (BP Chemicals Ltd), and the copolymer Rigidex 002-40 (BP Chemicals Ltd). *Table 1* shows their molecular weight characteristics measured by g.p.c. together with their melting temperatures in both the isotropic and oriented state. *Figures 1–3* show the melting endotherms obtained by d.s.c. at a heating rate of 10K min^{-1} (all curves were normalized to the same sample mass). They reveal relatively high melting points for polyethylene, indicative of crystallization at low supercoolings. This resulted from the slow cooling from the melt which was required to produce the thick section isotropic polymer needed for die-drawing. The d.s.c. melting peaks were narrower for the oriented polymers, with a rise in melting temperature over the isotropic value for 006-60 and a fall in the other two cases.

The total area under the curves is a measure of the crystallinity. This falls from sample 006-60, through Hizex, to sample 002-40, but it should be noted that especially in the unoriented Hizex and 002-40, the peak includes a long initial tail of reduced stability, and the peak heights are correspondingly reduced.

Preparation of oriented sheets

All of the oriented polyethylene specimens were prepared by a die-drawing technique developed at Leeds University[3]. The isotropic polyethylene billet for die-drawing was first prepared by melt extrusion. It was then annealed under pressure in an oven at 180°C for 10 h. After cooling, the rectangular billet was machined to a suitable size and shape for drawing at 100°C to a ratio 9.5:1.

High-pressure tensile testing

Specimens were cut from both the undrawn isotropic billet and the oriented sheet for the fracture testing at high pressure. Two types of specimens were prepared

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Table 1 Molecular weights and melting temperatures for the polyethylenes tested

Grade	$\bar{M}_n$	$\bar{M}_w$	Branch conc.	Melting temperature (°C) Isotropic	Oriented
006-60	16900	109100	0	137.4	138.2
002-40	20500	182600	~4 butyl/10^3C	130.6	125.5
Hizex	9600	282400	0	133.4	132.7

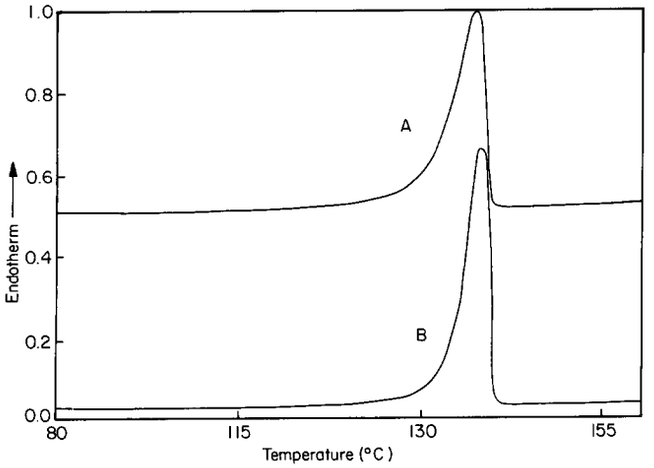

Figure 1 D.s.c. traces for Rigidex 006-60: (A) isotropic; (B) oriented

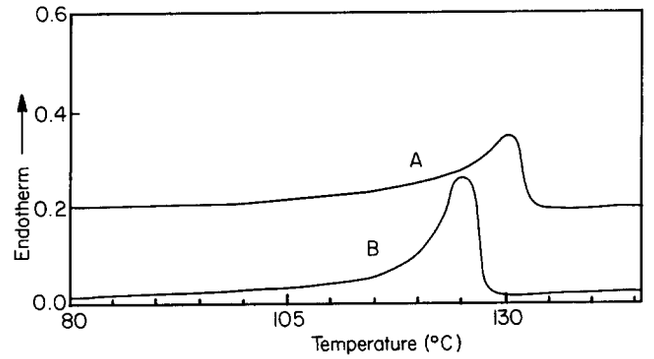

Figure 2 D.s.c. traces for Rigidex 002-40: (A) isotropic; (B) oriented

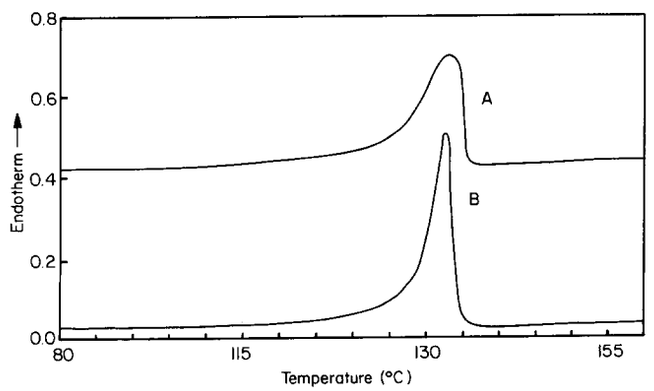

Figure 3 D.s.c. traces for Hizex 7000F: (A) isotropic; (B) oriented

from the oriented sheet, namely, the longitudinal and transverse specimens which were cut along and perpendicular to the draw direction. All specimens had a gauge length of 30.0 mm and a width of 15.0 mm. The thicknesses for the drawn specimens were ~2.5–3.0 mm. The thicknesses, for the isotropic specimens, were ~10.0 mm in order to ensure a brittle failure in the test. Symmetrical double-edge notched specimens were prepared with notch depth/half specimen width ratios (a/w) in the range of 0.33–0.60 (*Figure 4*). The notching process involved sharpening a saw cut using a hand operated shaping machine in which the tool was a carefully notched razor-blade which was advanced by a micrometer thread between cuts.

The high-pressure tensile testing machine used to study the fracture behaviour of polyethylenes has been described previously[2], and is shown in *Figure 5*. During the test, the specimen was gripped firmly by the jaws which were attached to the lantern and the hollow pull rod as shown in *Figure 6*. The specimen and the lantern were then placed inside the specimen chamber of the cylindrical steel pressure vessel (*Figure 5*). High-pressure fluid was pumped into the testing machine to establish the required pressure at 700 MPa. In order to avoid environmental stress corrosion cracking, the specimen was separated from the pressure fluid by a thin rubber sheath, which contained a neutral medium of deionized water to transmit the pressure to the surface of the specimen. After the system had achieved an equilibrium pressure and temperature, a tensile load was applied to the specimen by the downward movement of the crosshead at a constant speed of 2 mm min^{-1}. The testing machine was stopped immediately after a crack had been detected via a (small) increase in compliance noted on the load–displacement curve. The fracture toughness value (K_{IC}) was then calculated using equation (1):

$$K_1 = Y\sigma(\pi a)^{1/2} \quad (1)$$

where Y, σ and a are the geometry correction factor, applied stress at initiation of crack growth and notch depth of the specimen, respectively. The geometry correction factor, Y, was calculated using equation (2):

$$Y\pi^{1/2} = 1.98 + 0.36(a/w) - 2.12(a/w)^2 + 3.42(a/w)^3 \quad (2)$$

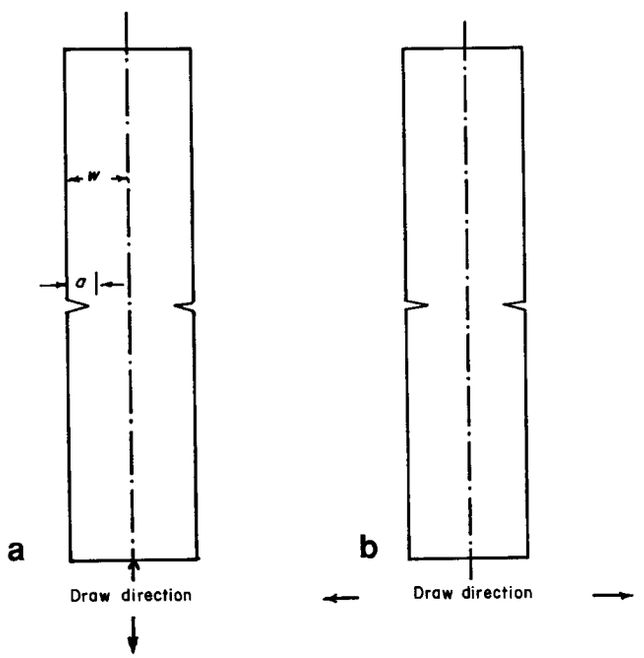

Figure 4 Double-edge notched specimen geometry for high pressure tensile tests: (a) longitudinal specimen; (b) transverse specimen

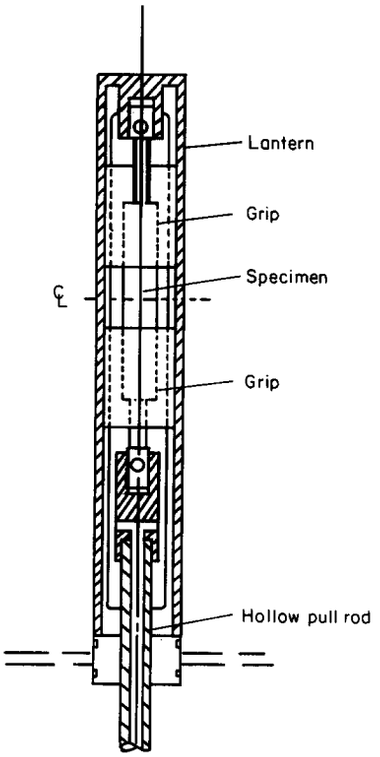

Figure 5 High pressure tensile test apparatus

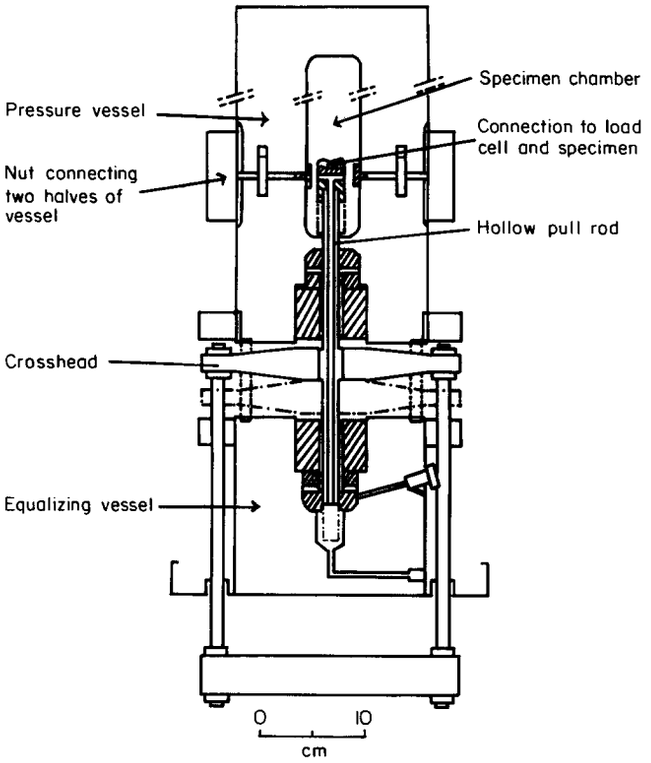

Figure 6 Detail of specimen holder

Note that although this calibration factor is strictly appropriate only for isotropic materials, extensive finite element calculations have shown that the errors involved in applying it to oriented polymers leads to maximum errors of $<2\%$[2].

FRACTURE RESULTS AND DISCUSSION

Full details of the high-pressure tensile test results for the three polyethylenes are given in reference 1 and are summarized in *Table 2*.

Note, that although the K_{IC} values quoted are measured at 700 MPa, previous work[2] on hydrostatic pressure has revealed that the fracture toughness values have negligible pressure dependence in sharply notched samples at sufficiently high pressures.

The effects of molecular weight and the short side groups on the fracture behaviour can be seen in *Table 2*. The comparatively low molecular weight die-drawn homopolymer Rigidex 006-60 has the lowest K_{IC} values in comparison with the other two drawn polymers. Although the average K_{IC} value along the longitudinal direction can be increased by ~ 4.5 times, the average K_{IC} value for the transverse loading is only 1.2 MN m$^{-3/2}$, which is lower than the value for its isotropic material (1.8 MN m$^{-3/2}$). This accounts for the ease with which this polymer can be split at high draw ratios.

The copolymer Rigidex 002-40 is known to be a tough polyethylene in its isotropic state. It is also less prone to splitting during die-drawing than many polyethylenes. It is shown in *Table 2* that the K_{IC} values for its drawn specimens are much higher than the corresponding ones for Rigidex 006-60, showing the effect of a low concentration of short side groups on the fracture behaviour of polyethylene.

The K_{IC} values for the die-drawn high molecular weight homopolymer Hizex 7000F are comparable to those for the copolymer Rigidex 002-40. This polymer is much tougher than its lower molecular weight counterpart Rigidex 006-60. This reveals that molecular weight and/or molecular weight distribution can also affect the performance of polyethylene after orientation.

It is clearly shown in *Table 2* that despite the similar K_{IC} values for these three polyethylenes in their isotropic state, the K_{IC} values for the oriented copolymer Rigidex 002-40 and the high molecular weight homopolymer Hizex 7000F are much higher than the corresponding ones for homopolymer Rigidex 006-60. It is believed that this is associated with differences in morphology among these polymers. It will be shown below that these differences are accentuated and become more prominent after die-drawing to high ratios.

In studies of the plastic deformation of polyethylene and polypropylene in cold drawing, Peterlin described the changes in morphology from the plastic deformation of the original spherulitic structure to the final fibrous structure[4]. The initial unoriented material has low strength and high ductility, consisting of stacks of parallel lamellae with few interlamellar links by tie molecules. The number of tie molecules increases with molecular weight and rate of crystallization[5]. In this model, the microfibrils

Table 2 Summary of the high-pressure tensile test results

Grade	Average K_{IC} (MN m$^{-3/2}$)		
	Isotropic	*Trans* ~9.5:1	Long ~9.5:1
006-60	1.8±0.24	1.2±0.16	8.0±1.7
002-40	2.1±0.17	5.0±0.4	12.0±1.3
Hizex[a]	1.5±0.1	4.6±0.15	14.0±1.0

[a] From reference 2

in the fibrous material contain highly oriented folded chain crystalline blocks alternating with amorphous layers in the axial direction. A great many tie molecules connect the blocks in the axial direction to give the microfibrils a high tensile strength.

Capaccio and Ward have shown that the drawing behaviour of polyethylene is markedly affected by molecular weight and the nature and concentration of branches[6]. They have proposed that this is due to the increased physical entanglements of the polymer chains, probably because of the increased number of tie molecules. Clements and Ward have shown that these factors also influence the tearing behaviour of oriented sheets of polyethylene[7]. All of these previous findings suggest that it is valuable to study the morphology of the three polymers under investigation in order to understand the effect of molecular weight and low concentration of small side groups on the fracture behaviour of polyethylene.

MORPHOLOGICAL STUDIES

Experimental

The internal microstructure of all specimens has been exposed by permanganic etching as an aid to optical and electron microscopic observation. For etching, blocks roughly $4 \times 2 \times 2.5$ mm were cut from each of the undrawn and drawn specimens, and 0.5 mm pared from one of the 4×2 faces with a microtome to remove the layer damaged by the coarse cutting to leave a relatively smooth surface for examination after etching. The whole block was then shaken in an etchant for 2 h at room temperature. Undrawn specimens were treated with the standard published reagent[8]. Drawn specimens required etching with a more aqueous mixture and a particular formulation optimized for revealing fine detail in polyethylene[9] was used.

After etching, the surfaces were first examined optically in reflection using Nomarski differential interference contrast to assess any overall differences in rugosity (and to achieve optimal etching). Suitable etched surfaces were then replicated using a two-stage technique involving a cellulose acetate intermediary. These were shadowed with Ta/W at 45° to the draw direction and coated with carbon. After dissolution of the acetate the shadowed carbon films supported on grids were examined by transmission electron microscopy.

Isotropic materials

The different molecular characteristics of the three starting polymers can be distinguished in their lamellar morphologies. Comparison with a previous comprehensive study of lamellar textures as functions of molecular weight and crystallization temperature[10] shows that their textures are consistent with the specified grades of polymer. In *Figure 7a* the 006-60 sample displays morphology typical of slowly crystallized medium molecular weight polyethylene. The broad and extensive (dominant) lamellae are substantially flat rather than curved as in higher molecular weight or branched polyethylene; when viewed edge on their traces are linear. Inset intervening smaller subsidiary lamellae are crisply resolved and are well-packed so that they substantially fill the space available. This appearance is similar to that of Figure 11 in the previous survey[10]. Note that in this and the other samples nucleation is sufficiently heavy

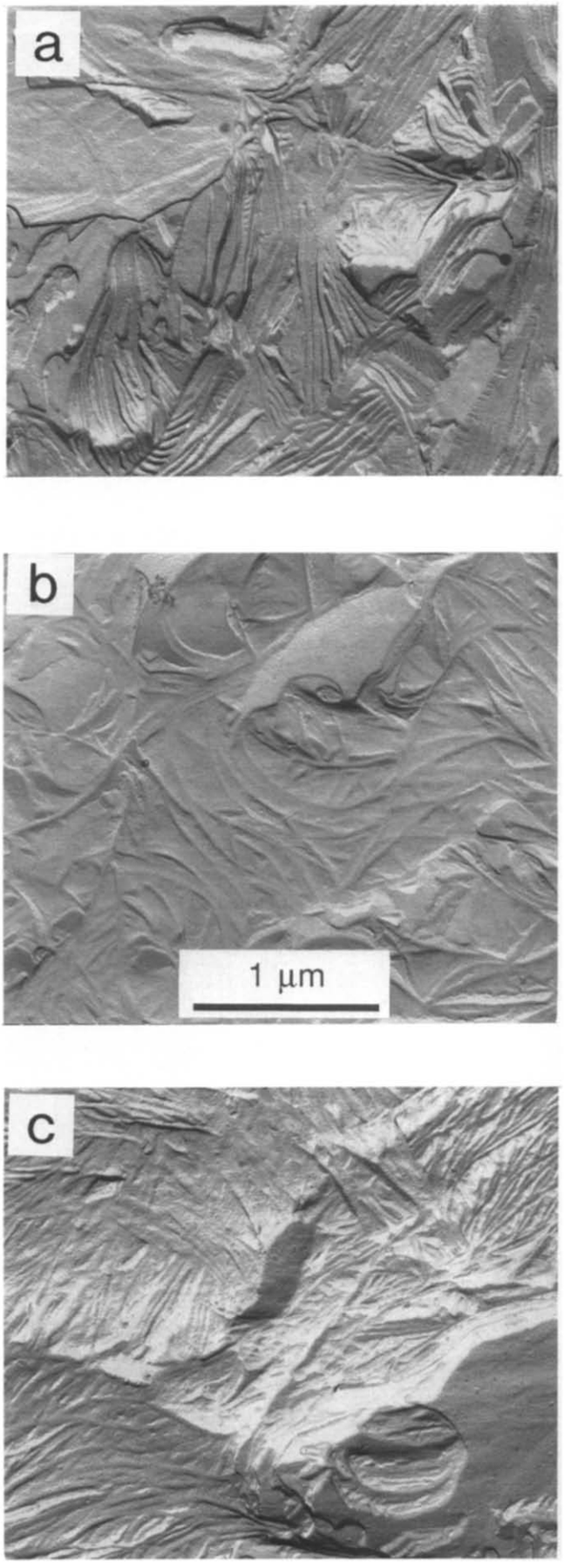

Figure 7 Transmission electron micrographs of replicas of etched surfaces of isotropic polymers: (a) 006-60; (b) 002-40; (c) Hizex. All to same scale. Micrometre bar is on (b)

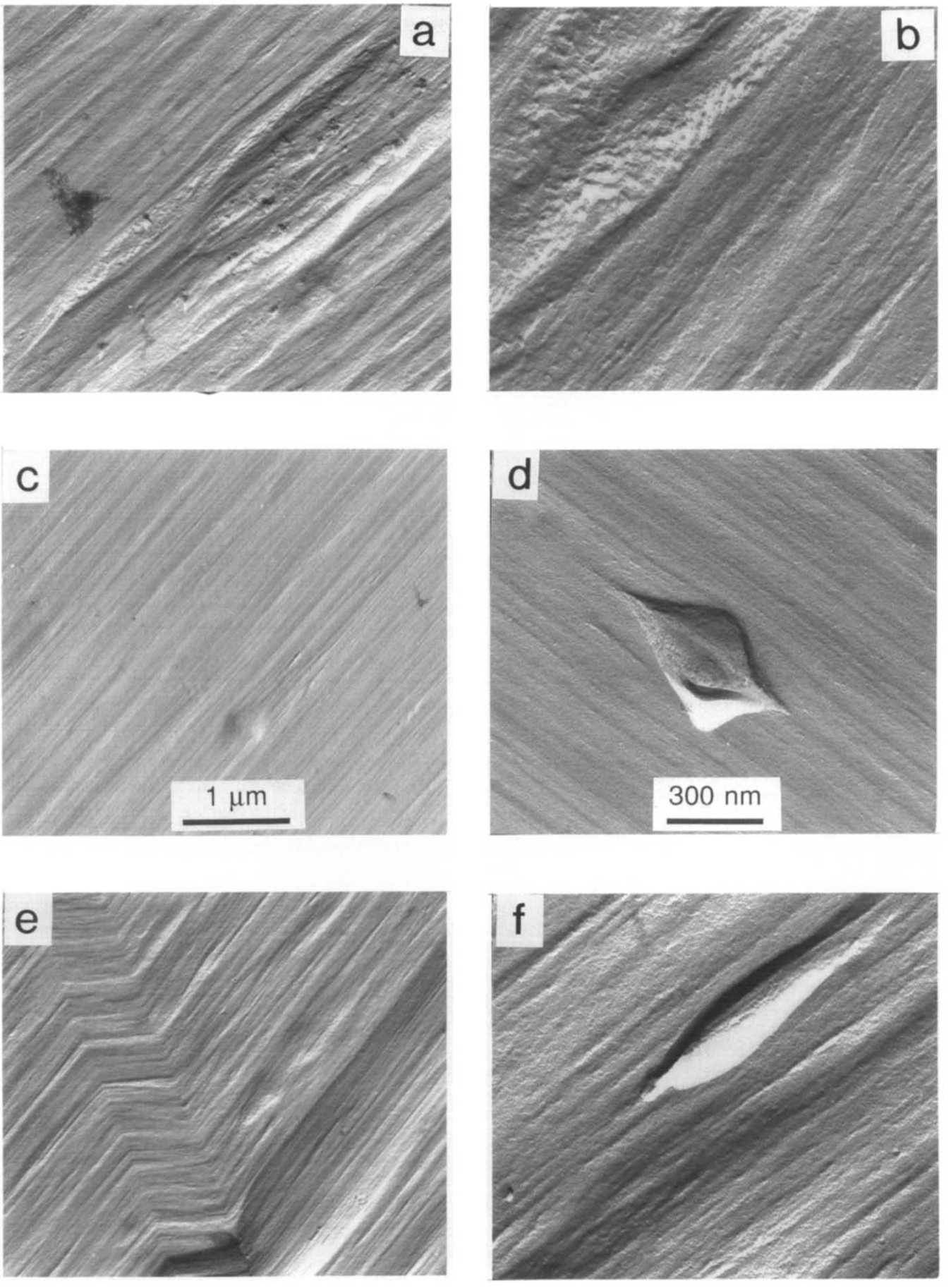

Figure 8 Transmission electron micrographs of replicas of etched surfaces of oriented polymers: (a, b) 006-60; (c, d) 002-40; (e, f) Hizex. For (a), (c) and (e) take scale from (c); for (b), (d) and (f) take scale from (d)

that there is no obvious large-scale ordering into spherulites or related entities.

In *Figure 7c*, illustrating the initial morphology of the Hizex 7000F, one can discern slight but consistent differences between the upper half and the (darker grey) lower half. The latter contains dominant lamellae whose traces (left-hand side) are consistently curved. They are thicker at 40–60 nm than those in the upper half (30–40 nm). Moreover, a branching substructure is prominent in the upper right corner. From previous experience one would infer that the upper structure is that of a wider molecular weight distribution with a significant lower tail, crystallizing at a higher supercooling (lower temperature) compared to the higher molecular weight polymer below. However, these characters are not sufficiently differentiated in the sample as a whole to be resolved in its melting endotherm. The thicknesses of both regions would melt within the single peak in *Figure 2A*. Finally, the lamellae are not generally so crisply resolved as in 006-60 in agreement with the previous observations of high molecular weight polyethylene.

These trends are accentuated for the third sample 002-40 whose appearance in *Figure 7b* is altogether more bland than the two others. Dominant lamellae are now thinner, almost invariably curved but occasionally ridged. When seen edge on they are very well separated, with poorly defined regions separating them. Such regions are known to contain lower melting material, i.e. they do possess some crystallinity and it is possible that a different etchant would reveal further lamellae in them[11], but at this first stage we have preferred to compare samples under the same etching conditions. Nevertheless the character of 002-40 closely resembles features seen previously in various linear low-density polyethylenes[11].

Oriented materials

The morphologies of the three drawn specimens can be seen to differ markedly even under the reflection optical microscope. The oriented 006-60 has the most rugose surface and in addition contains numerous 'flaws' similar to those seen in oriented polyethylenes annealed at high pressures[12], i.e. lens-shaped regions aligned along the draw direction and possibly in specific planes related to sample preparation. In such specimens 'flaws' were shown to be formed from segregated low molecular weight species[12].

Under the electron microscope the overall texture appears as lines more or less along the draw direction, with very fine lines in the transverse direction (*Figure 8*). Their periodicity appears least in Hizex and is most marked in 006-60. Also most evident in this polymer is a large-scale longitudinal pattern, which may lie along or at a small angle to the draw direction. A similar feature has previously been observed in drawn polyethylene and shown there to be a much-deformed legacy of the original lamellae[13]. The kink band illustrated in *Figure 8e* is the only one found in any of the materials; roughly 4 mm^2 surface of each was examined under TEM.

Turning attention to the flaws in the oriented structure, their size and frequency vary between the different materials. The linear medium molecular weight polymer (006-60) contains the most, with some larger objects as in the centre of *Figure 8a*, and a profuse scattering of smaller ones such as that seen traversing the top left-hand corner of the same figure. In Hizex, the flaws are much fewer, and typically (*Figure 8f*) are smaller than the large ones in 006-60. In the copolymer 002-40, the flaws are few, and not elongated along the draw direction (*Figure 8d*). In the 006-60, the structure within the flaws (*Figure 8b*) is markedly coarser than the surroundings, and resembles that found in an earlier study[12], where it was found that material in the flaws consists of shorter molecules which have recrystallized on stretched nuclei. In Hizex, although its molecular weight distribution extends lower than 006-60 implying an even larger proportion of short molecules capable of segregation, the flaws are fewer and smaller and the overall rugosity is less. However the molecular weight distribution of Hizex also extends much higher than that of 006-60, and this suggests interestingly that it is the respective high molecular weight end of each distribution that determines the propensity to form flaws. In the copolymer 002-40 the overall impression is even blander: flaws such as that in *Figure 8d* are very sparsely scattered. Fractionation during crystallization of branched polyethylenes is generally by branch content[14] and so does not necessarily involve particularly short molecules.

One further comment should be made regarding the oriented polymers. X-ray diffractometry has confirmed that the process of die drawing strip material at approximately constant width has the effect of producing a '*b*-*c* texture' in all polyethylenes so far examined[1,2].

CONCLUSIONS

It appears that the optimum morphology for high toughness polyethylene can be achieved by tailoring the chemical composition of the polymer either in terms of molecular weight distribution, or branch content, or perhaps by a suitable combination of both. Clear morphological differences have been revealed between a low toughness homopolymer and tough polymers produced by either route. These preliminary results suggest that there is a very valuable area for future research, with extremely important implications.

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