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Lamellar deformation and its variation in drawn isolated polyethylene spherulites

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Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

Abstract

Observations of individual lamellae within spherulites of linear polyethylene, drawn under affine conditions between room temperature and ~100 °C, show lamellae surviving to sample failure, thereby providing a strong memory of the initial morphology in the final product. Lamellae rotate and deform according to the angle their plane makes with the draw direction. Those parallel to the draw direction extend, to the full draw ratio, by shear in the basal plane, probably in {110} planes and at constant lamellar thickness. The same mechanism appears to occur for lamellae at higher angles with chain slip expected increasingly to operate. This latter mechanism is responsible for lamellar thinning, which becomes universal in elongated lamellae at higher draw ratios. Lamellae whose planes are transverse to the draw direction contract, with kinking—also by chain slip—to produce bands of sheared lamellae in spherulite centres. The temperature of drawing has little pronounced effect on the drawn morphology unlike draw rate whose influence is evident. Faster draw produces more severe local damage and less-well-organized co-operative kinking. The amelioration of these effects at a slower rate is attributed to molecular mobility and the influence of the surrounding molecular network.

Keywords: Lamellar deformation; Polyethylene; Spherulites

1. Introduction

Among Ian Ward's many contributions to polymer physics, those on mechanical properties are particularly prominent, not least in modelling the complicated overall deformation of solid polymers by straightforward means [1]. By contrast, the complex details of deformation in a semi-crystalline polymer have usually had to be inferred indirectly from crystallographic textures, post draw [2], and by analogy with mechanisms revealed by electron imaging and diffraction studies of individual solution-grown lamellae drawn on an extensible substrate [3,4]. Such processes are not only complicated but it has also been doubted whether, in any case, they do affect the final product because the long period of polymers drawn at higher temperatures is a function of that temperature rather than of the starting material suggesting that the material reforms during draw [5]. One recurring suggestion is that drawing, at least at higher temperatures, proceeds via melting and recrystallization [6] although there is also unambiguous evidence, from the examination of thick polyethylene lamellae produced at high pressure [7], that this is not universal. Moreover, recent examination of transverse morphologies has shown that a memory of the initial material does, after all, persist to draw ratios ~50 showing that the nature of the final product does depend upon the precise starting material [8,9]. Knowledge of how deformation proceeds in a semi-crystalline polymer is thereby given renewed importance and is essential if the product is to be related to the original material.

The present paper addresses this topic by reporting further on direct observations of how individual lamellae, in isolated spherulites of linear polyethylene within a matrix of the branched polymer, respond to tensile deformation. A previous overview [10] showed that behaviour falls into two temperature ranges, above and below ~100 °C, depending on whether the matrix is or is not molten at the drawing temperature, with deformation in the former being affine. Here, we report more fully on the details of lamellar deformation in the lower temperature range, at ambient and 100 °C. Particular deformation modes are identified in

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relation to the lamellar inclination to the draw direction and their variation with draw ratio, rate and temperature is investigated.

A central feature is the persistence of lamellae, which carries a memory of the original texture through to the final product. If not transversely oriented, lamellae rotate towards the draw direction and become greatly extended while retaining, at least initially, the dominant/subsidiary distinction. Geometry requires that shear in the basal plane is responsible for extension at zero and low angles of inclination. Internal disruption, indicative of modified texture, is revealed by modulated or interrupted contrast which appears first towards the ends of lamellae near parallel to the draw direction. Modulation becomes more extensive and spreads through the drawn spherulite with lower draw temperature and faster draw rate. These changes are consistent with greater molecular adjustment occurring at longer times.

The novel kinking in transverse lamellae when they contract does not appear to change in scale significantly with these variables. This forms by shear along c, in {010} planes, which reduces the lamellar thickness. Co-operative kinking is more pronounced in spherulite centres, where lamellae are more closely packed and more inter-connected, than in outer regions but the organization is poorer for faster draw. Lamellar thinning, implying c shear, becomes general in extended lamellae as the draw ratio increases to 4.5 and beyond. The changes in lamellae and how they survive in substantially drawn polyethylene helps provide a basis of understanding why the nature of the final drawn product depends on the morphology of the initial material.

2. Experimental

The polyethylenes used in this study were Rigidex 140-60 (BP), a linear polymer for which $M_w = 54,000$; $M_n = 17,000$ and Escorene LD100BW (Exxon), a conventional branched low-density polymer for which $M_w = 87,000$; $M_n = 10,000$. Henceforth, these are referred to as HDPE and LDPE, respectively.

Blends of 5% by weight of HDPE in LDPE were melt-mixed for 30 min, under nitrogen, in a Winkworth twin z-blade mixer, model IZ, at 160 °C. Melt-pressed sheets, 1.4 mm thick, of this blend were remelted at 160 °C, crystallized for 1 h. at 123 °C then quenched in cold water to provide the material for drawing. Dumb-bell specimens cut from the above, 5 mm wide over the 20 mm gauge length, were drawn either at 5 or 1,000 mm min^{-1} in the high temperature oven of a Monsanto Tensometer 2000. All samples not drawn at room temperature were heated over some 10 min to the chosen nominal temperature, then maintained there for 5 min. This temperature was measured by a thermocouple located to the side of the specimen giving values systematically high by ~5 K, according to the changes in melting endotherm of samples taken from the undrawn shoulders of specimens. The precise value of drawing temperature does not, however, materially affect the significance of the results of this paper.

Samples drawn above ambient were cooled, initially at 30 K min^{-1}, to room temperature and only then removed from their clamps. Unclamping produced a retraction of some 20% for those drawn at 70 and 100 °C; specimens drawn at room temperature did not retract. Local draw ratios were measured, after removal from the clamps, from the distance apart of carbon bars, applied by coating through a grid before drawing.

Drawn specimens were cut open at −70 °C, with a glass knife and microtome, either *parallel* or *transverse* to the draw direction, then etched prior to examination by scanning electron microscopy (SEM). Etching was for 1 h at room temperature with a 1% w/v solution of potassium permanganate in a 10:4:1 mixture (by volume) of sulphuric acid, 85% orthophosphoric acid and water, respectively, a procedure which removes a few μm from the cut surface. Etched specimens were coated with gold prior to SEM examination which was found to be very suitable for these specimens, with strong contrast. The examination of shadowed replicas in transmission, TEM, was used only to reveal fine lamellar detail. The micrographs are all SEM images of etched surfaces; in parallel sections of deformed samples the draw direction is horizontal.

3. Results

An undeformed HDPE spherulite of the type used in this work is shown in Fig. 1. It contains lamellae with uniform linear traces ~2 μm across, i.e. essentially untwisted, in an immature development which retains the early sheaflike appearance together with a few longer individual lamellae approximately at right angles to the main sheaf which have been shown to develop late in growth [11]. (It was not possible, in this system, to grow separated mature spherulites with radial lamellae uniformly present at the

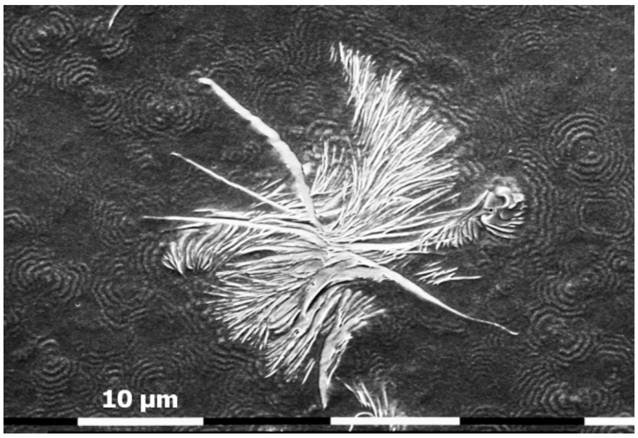

Fig. 1. An immature spherulite of linear polyethylene in the undeformed material.

perimeter.) From room temperature to a nominal 100 °C, deformation is affine in the sense that the aspect ratio of the drawn objects scales as the 1.5 power of the extension, with objects contracting laterally within cylindrical boundaries extending along the draw direction [10]. In so doing lamellae change: depending on the inclination to the draw direction, they rotate (maintaining reasonably linear traces but developing shallow curves), lengthen, become thinner, contract and kink. Such changes modify the contrast of the initially uniform linear traces which may become regularly modulated or interrupted, according to the angle the lamellar plane makes to the draw direction, more so for fast draw.

From the wider range of specimens which has been examined, here we confine ourselves to reporting the morphologies produced with increasing draw ratio in specimens drawn at the lowest and highest temperatures (i.e. room temperature, ~25 °C, and 100 °C) and the two extreme rates available to us, 5 and 1,000 mm min^{-1}, called slow and fast, respectively. To determine how lamellae respond as a function of angle to the tensile axis, it is convenient to examine symmetrical objects of the two kinds shown in Figs. 2 and 3. Both approximate to axialites whose axes are perpendicular to the draw direction, but they differ in their lamellar distribution.

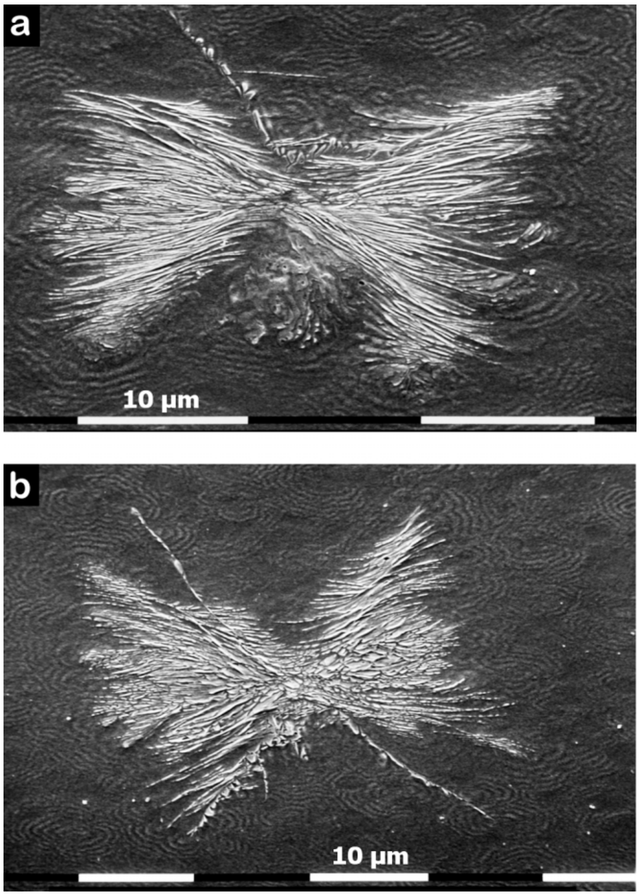

Fig. 2. Parallel sheaves of linear polyethylene drawn to 1.5 × extension at 100 °C at (a) 5 mm min^{-1} and (b) 1000 mm min^{-1}.

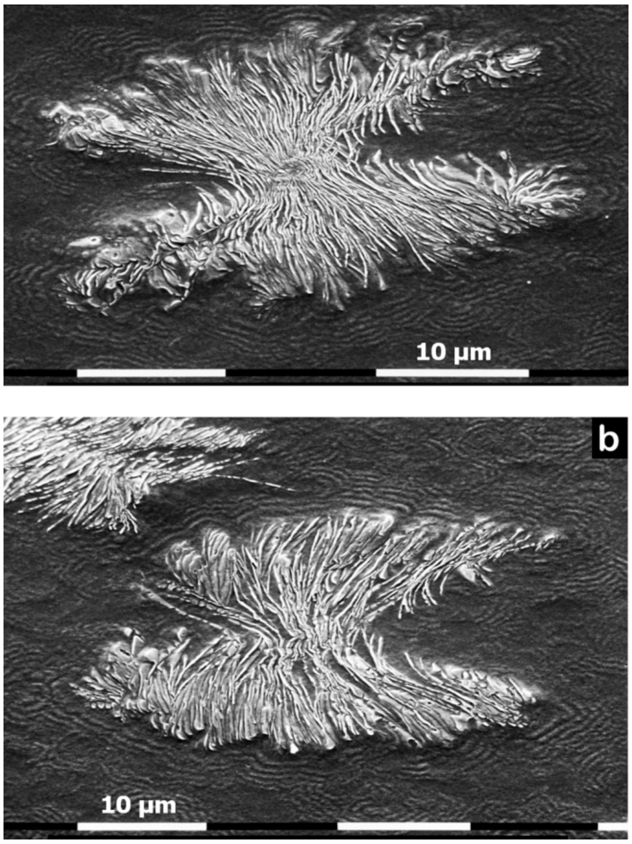

Fig. 3. Perpendicular sheaves of linear polyethylene drawn to 1.5 × extension at 100 °C at (a) 5 mm min^{-1} and (b) 1000 mm min^{-1}.

Those in Fig. 2 are *parallel* sheaves with the length of the extended sheaf along the draw direction and the lamellar distribution centred around it. Conversely, the sheaves in Fig. 3 are *perpendicular* with lamellae distributed about the vertical. For specimens cut parallel to the draw direction, selection of the widest entities ensures that the section passes close to the centre of the drawn spherulite. When specimens are cut transverse to the draw direction, the width is more or less constant with all sections of the drawn object contained within roughly circular boundaries; those which are hollow are of sections towards the extremities, as in Fig. 8(b) below.

In a parallel sheaf stretched slowly, Fig. 2(a), the sheaf shape is elongated and accentuated compared with an undeformed specimen. Lamellae have not only rotated towards the draw direction, still with linear traces, but have also extended by the draw ratio, more or less. Contrast remains reasonably uniform for most lamellae but is modulated or interrupted regularly when the lamellar plane is about parallel to the draw direction, most prominently at the centre of the right hand edge but also just above centre in the very middle. The distinction between dominant and subsidiary lamellae persists with the former present in brighter contrast and associated lamellar groups at the periphery. (The holes in the flat-on lamellae below centre are not a deformation feature, being present in undeformed material; they are probably etched-out cores of giant screw dislocations.) Bright contrast in such SEM images relates to variations in surface topography so the change from uniform brightness to a greyer and/or interrupted tone represents a change in local texture. This will have been developed by etching, so one must be cautious before ascribing the contrast to fragmentation before etching although there is no doubt that fragmentation can be present after etching as later specimens show clearly.

A change to the fast draw rate in another parallel sheaf (Fig. 2(b)) reveals contrast to be disrupted much more widely through the spherulite with, at lower left, some affected lamellae at ~45° to the draw direction. The great majority of disrupted contrast remains, however, in lamellae nearly parallel to the draw direction. Increased disruption is characteristic of the change to faster stretching as subsequent results confirm.

Lamellar rotation away from the vertical is also evident for a sheaf in perpendicular orientation (Fig. 3(a)) while contrast remains rather uniform and is disrupted only near the centre line at either side of the sheaf in lamellae which have rotated to approach parallelism with the draw direction. Fig. 3(b), at the fast rate, shows more disrupted contrast with fragmentation of the etched lamellae apparent to the upper left. In both Fig. 3(a) and (b) co-operative kinking of transverse lamellae has occurred in the very centre of the deformed spherulites.

The extent of internal lamellar deformation increases for the slightly higher draw ratio of 2.0 as shown first for parallel sheaves in Fig. 4. The slow-drawn object of Fig. 4(a) shows paler contrast in its centre and at its extremities where the influence of the dominant lamellae survives in the grouping at the perimeter; the contrast is finely modulated throughout. At the higher draw rate of Fig. 4(b) the same features are present but the contrast differential appears larger than for slow draw.

Fig. 5 shows perpendicular sheaves also drawn to twice the original length; Fig. 5(a) is for the slow draw rate and Fig. 5(b) for the fast. Both show rather strong contrast except for the faint flat-on portions to the right of the respective waists. Kinking is very regular in the centre of Fig. 5(a) and extends, albeit less-well-organized, to the top and bottom of the deformed sheaf. After fast draw, there is kinking in Fig. 5(b) but present in a more rudimentary and less-organized fashion.

In Fig. 6 are the central regions of two perpendicular sheaves drawn at the two rates to 4.5 draw ratio, Fig. 6(a) at the slower rate, Fig. 6(b) at the faster. While kinking is present in both, for example in individual lamellae at the upper and lower edges, the co-operative organization is much more obviously present in Fig. 6(a). Note here that, in some instances, alternate bands within the kinked region have lamellae of very different thicknesses. Adjacent regions, to the left of Fig. 6(a) and (b) which show regions where lamellae have extended greatly are displayed in Figs. 7(a) and (b), respectively. Of particular note is the manner in

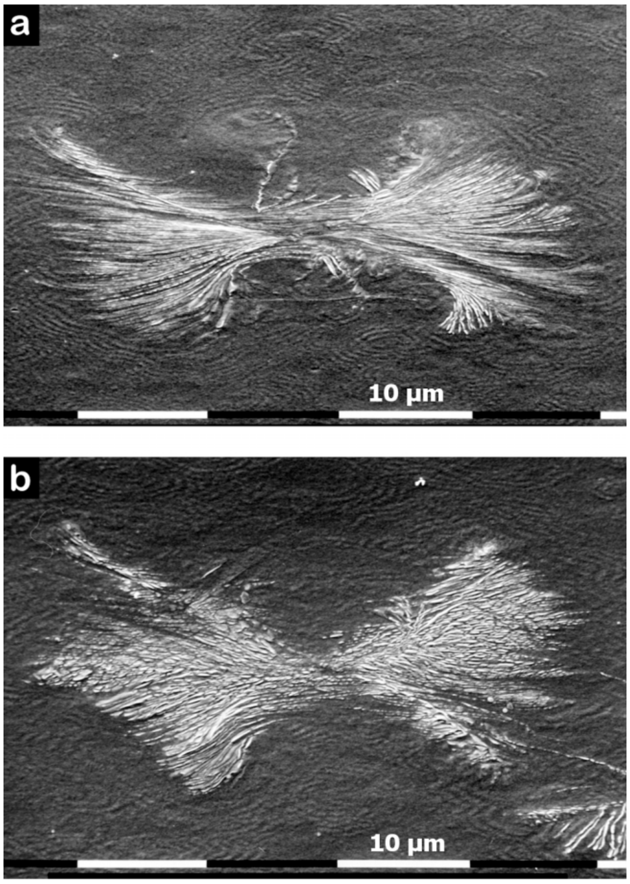

Fig. 4. Parallel sheaves of linear polyethylene drawn to 2× extension at 100 °C at (a) 5 mm min^{-1} and (b) 1000 mm min^{-1}.

which lamellae are much more obviously fragmented after etching in Fig. 7(b), i.e. for faster draw.

Twofold drawing at room temperature produces rather similar morphologies to those formed at 100 °C including disrupted lamellar contrast. This shows in Fig. 8(a), for a parallel sheaf drawn slowly to draw ratio 2, along the length of lamellae approximately along the draw direction. Note that the uppermost lamellae at top left, seen approximately flat-on, are continuous though with somewhat eroded edges suggesting that the latter is more likely to be the cause here of the variable contrast than fragmentation into discrete units. This object illustrates well the change in dimensions for its constituent lamellae parallel and perpendicular to the draw direction but does not show the paler contrast at centre and edge noted for Fig. 4(a) and (b).

A transverse section for draw ratio 2.5, Fig. 8(b), shows kinking in individual or small groups of lamellae even when, as here, the section is towards the outer edge of the drawn sheaf where the lamellae sectioned will have been somewhat elongated. In a more-highly drawn perpendicular sheaf, Fig. 8(c), co-operative central kinking remains a striking feature. The only suggestion of a difference when ambient drawing is done at the fast rate is that kinking appears to be less regular in the centre of a transverse sheaf.

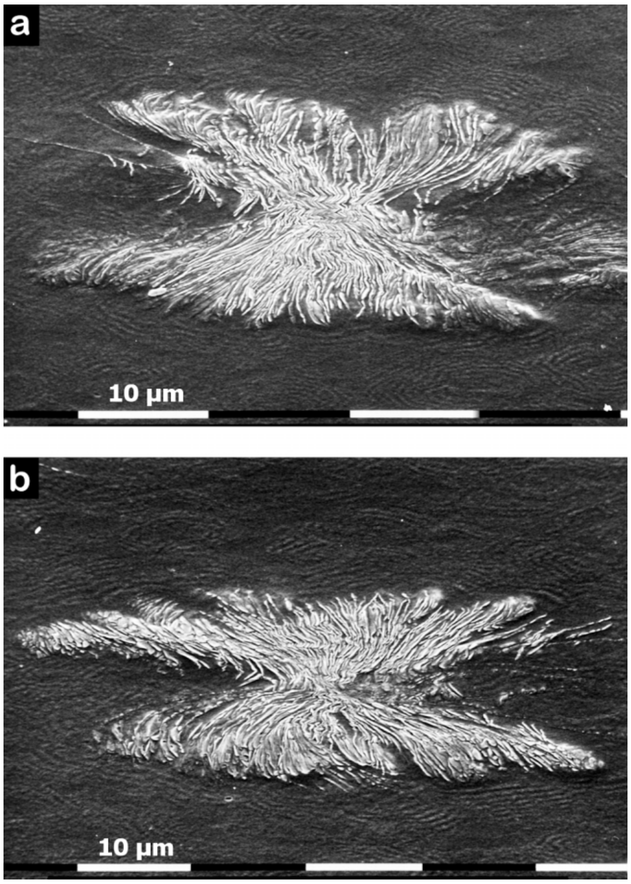

Fig. 5. Perpendicular sheaves of linear polyethylene drawn to 2 × extension at 100 °C at (a) 5 mm min^{-1} and (b) 1000 mm min^{-1}.

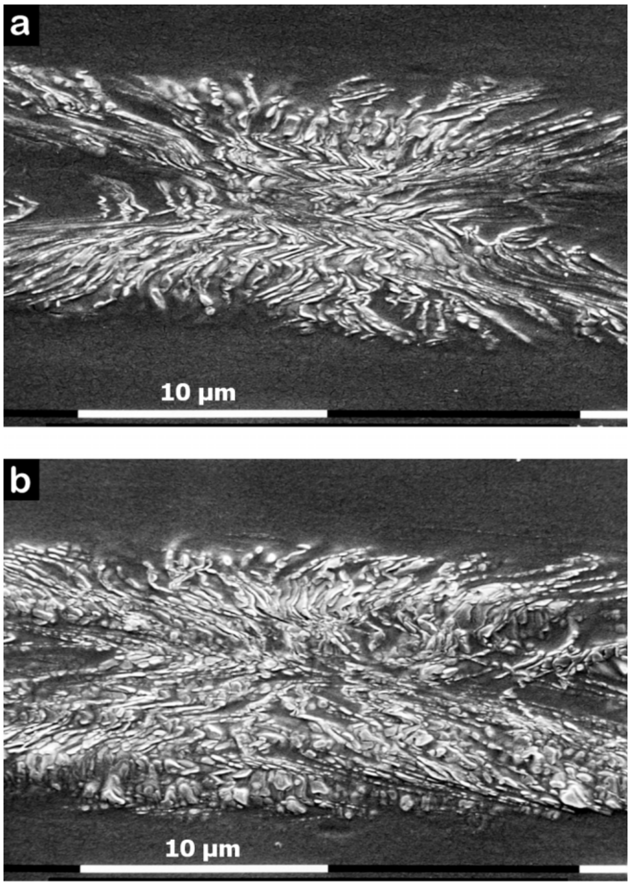

Fig. 6. The central portions of perpendicular sheaves of linear polyethylene drawn to 4.5 × extension at 100 °C at (a) 5 mm min^{-1} and (b) 1000 mm min^{-1}.

4. Discussion

Throughout the temperature range, from ambient to 100 °C, lamellae retain their identity to the maximum draw ratio, 7, beyond which these samples break [10]. This leaves a memory of the original texture in the final product which, if failure had not occurred, could have continued to still higher draw ratios. In other systems drawn to ~50 × extension, a legacy of the original banded spherulitic texture survives [8,9] indicating that the initial lamellar orientation is still remembered, and not lost, at much higher draw ratios than considered here.

The first departure from uniform lamellar contrast occurs, as in Fig. 2, selectively in lamellae approximately parallel to the draw direction, especially near their ends. When, as in the objects viewed here, the exposed surface passes through the drawn spherulite near its centre, the growth axis, *b*, will lie along lamellae close to the plane of the paper. The *c* axis, in projection, will then lie perpendicular to the lamellar traces albeit inclined by ~35°, out of the plane, to the normal to the expected {201} fold surfaces [12]. In these circumstances, the considerable extension suffered by lamellae with planes parallel to the draw direction can only feasibly occur by shear in the basal plane, normal to *c*, there being no shear stress parallel to the *c* axis. The probable slip plane will be {110} as this is the low index plane closest to the 45° direction of maximum shear stress. New facets will result at the intersections of the slip planes with the lamellar growth surfaces and the changed topography could be the origin of the modulated contrast. This would be more likely to be revealed near lamellar ends, where they are thinnest, as there is then a greater probability for a section, once exposed, to be near the faceted surface; modulated contrast could also occur elsewhere but would be less probable. It is also possible that lamellae are more compliant, extending more easily, near their ends where they grow in isolation than when tie molecules connect adjacent lamellae and increase their modulus.

When modulated or disrupted contrast has spread through all lamellae parallel to the draw direction, its presence indicates that etching has revealed structural discontinuities in lamellar interiors and not just proximate to the growth surfaces. This is consistently a consequence of faster draw whose greater damage suggests that, in contrast to slow draw, internal disruption has been unable to. Moreover, as lamellar traces remain linear, albeit modulated, it is reasonable to take this as an indication of shear has occurred in the basal plane as opposed to chain slip

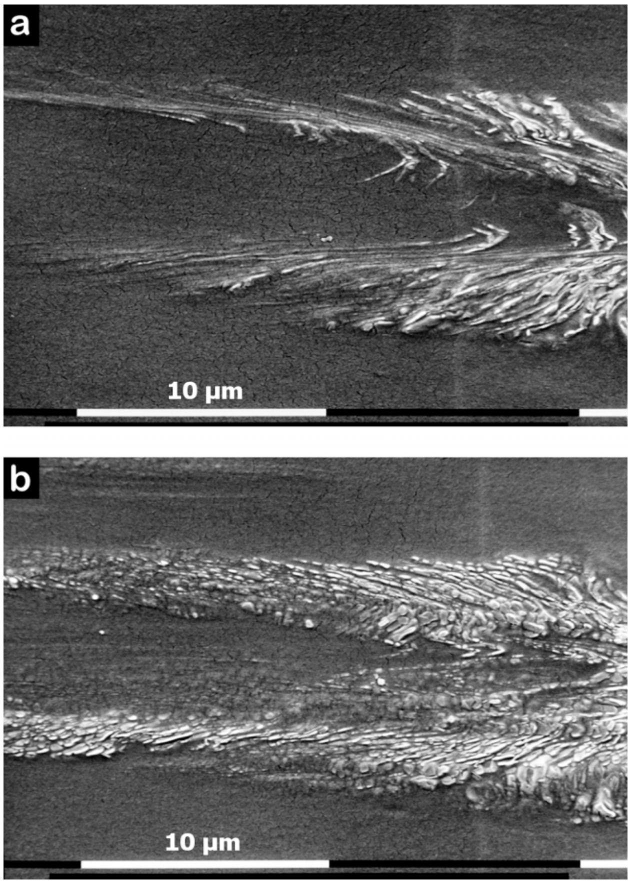

Fig. 7. Adjacent portions, to the left of the perpendicular sheaves of (a) Figs. 6(a) and (b) Fig. 6(b) to show the detail of lamellae at higher extension.

which would displace adjacent portions of lamellae along the *c* axis. Furthermore, slip normal to *c* will not reduce the lamellar thickness although the {201} fold surface will be displaced at each active {110} slip plane. Only when there has been chain slip, i.e. slip parallel to *c*, will thinner lamellae result. An observed reduction in thickness indicates that this process has occurred. It is activated by shear stresses, whose maximum is at 45° to the draw direction with systems becoming active once their critical resolved shear stress has been reached.

Shear yielding has also been responsible for kinking in lamellae with planes perpendicular to the draw direction. It is present, albeit somewhat haphazardly, in all regions: in individual lamellae out to the edges of the object (e.g. Fig. 5(a)) and away from the waist of the sheaf (Fig. 8(b)). The displacement is normal to the growth direction, *b*, i.e. in {010} planes and presumably along *c*. For {201} fold surfaces seen edge-on, the *c* axis of a lamella will be inclined at 55° to the draw direction and so subject to relatively high shear stress.

Co-operative kinking, to form sheared bands parallel to the draw direction, is confined to the centre of objects where geometrical factors are likely to be relevant: not only are lamellae close together but they are probably then linked by tie molecules requiring groups of lamellae to respond as a whole. This will apply to further shearing when to maintain uniform extension across a transverse cross-section, lamellar thickness and the magnitude of the angle of sheared lamellae to the draw direction must be the same throughout. This is not always the case, as in, e.g. Figs. 6(a) and 8(c), when lamellae within one kinked band are clearly thinner than in their neighbours. This is evidence of local non-uniform deformation.

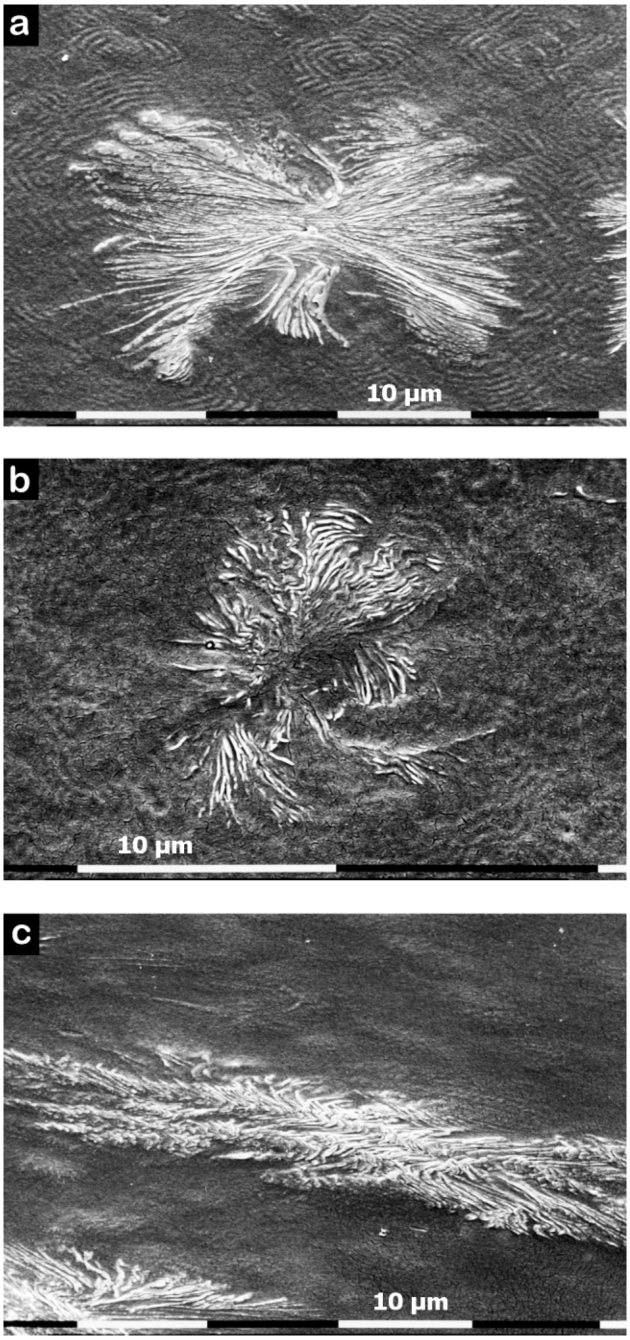

Fig. 8. Sheaves of linear polyethylene drawn at room temperature and 5 mm min^{-1}: (a) a parallel sheaf drawn 2×; (b) a transverse section of a spherulite drawn 2.5× and (c) a perpendicular sheaf of draw ratio 4.5.

The effect of a reducing the draw temperature from 100 °C to ambient is modest with the main observation that, comparing Figs. 4(a) and 8(a), deformation appears somewhat more uniform at the lower temperature. The effects of changing the draw rate are much more pronounced: disrupted lamellar contrast is more widespread with co-operative kinking much reduced for faster draw. Evidently, the same draw ratio achieved more slowly gives a more orderly product with less internal disruption. This behaviour is likely to involve molecular mobility and the viscoelastic nature of the materials. Accordingly, the morphology after fast draw would reflect more the instantaneous behaviour of lamellae while the slower draw rate would allow molecules more time to adjust with a greater opportunity for changes to be subject to the restoring forces of the enveloping molecular network.

5. Conclusions

Observations of individual lamellae within spherulites of linear polyethylene, drawn under affine conditions between room temperature and ~100 °C, show lamellae surviving to sample failure, thereby providing a strong memory of the initial morphology in the final product.

Lamellae rotate and deform according to the angle their plane makes with the draw direction. Those parallel to the draw direction extend, to the full draw ratio, by shear in the basal plane, probably in {110} planes and at constant lamellar thickness. The same mechanism appears to occur for lamellae at higher angles with chain slip expected increasingly to operate.

Chain slip is responsible for lamellar thinning, which becomes universal in elongated lamellae at higher draw ratios.

Lamellae whose planes are transverse to the draw direction contract, with kinking—also by chain slip—to produce bands of sheared lamellae in spherulite centres.

The temperature of drawing has little pronounced effect on the drawn morphology unlike draw rate whose influence is evident. Faster draw produces more severe local damage and less-well-organized co-operative kinking. The amelioration of these effects at a slower rate is attributed to molecular mobility and the influence of the surrounding molecular network.

Acknowledgements

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References

[1] Hadley DW, Ward IM. An introduction to the mechanical properties of solid polymers. New York: Wiley; 1993.
[2] Bowden PB, Young RJ, Ritchie JM, Rider JG. J Mater Sci 1973;8:23–36.
[3] Haas K, Geil PH. J Polym Sci A 1966;2:289–98.
[4] Allan P, Bevis M. Proc Roy Soc A 1974;341:75–90.
[5] Peterlin A. J Mater Sci 1971;6:490–508.
[6] Phillips PJ, Philpot RJ. Polym Commun 1986;27:307–9.
[7] Attenburrow GE, Bassett DC. J Mater Sci 1977;12:192–200.
[8] Amornsakchai T, Olley RH, Bassett DC, Al-Hussein MOM, Unwin AP, Ward IM. Polymer 2000;41:8291–8.
[9] Amornsakchai T, Bassett DC, Olley RH, Unwin AP, Ward IM. Polymer 2001;42:4117–26.
[10] Lee SY, Bassett DC, Olley RH. J Mater Sci 2000;35:5101–10.
[11] Abo el Maaty MI. Polymer 2002;43:5639–42.
[12] Bassett DC, Hodge AM. Proc Roy Soc A 1981;377:25–37.