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On the influence of initial morphology on the internal structure of highly drawn polyethylene

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Abstract

Morphological investigations on a range of polyethylenes, which differ with respect to their molecular weight characteristics and which possess quite distinctly different superstructures, non-spherulitic and banded spherulitic, have been performed to follow structural developments during drawing. Of particular significance is the detailed examination of transverse sections, in addition to the more commonly undertaken longitudinal studies. The key point that emerges is the retention of a memory of the original superstructure by the highly drawn products. This is strikingly evident in the lateral morphology, which clearly transforms in a continuous fashion, in contrast to the axial morphology, which is transformed out of all recognition by drawing. © 2000 Published by Elsevier Science Ltd.

Keywords: Polyethylene; Highly drawn products; Memory of initial structure

1. Introduction

Previous structural understanding of the drawing process in semicrystalline polymers has stemmed from two principal directions. At the morphological level, detailed studies show a major discontinuity as the material transforms to a fibrillar structure showing no evidence of the initial spherulitic structure. At the same time, however, the concept of a molecular network invokes a recollection of the initial molecular conformation to high deformation ratios. The current work presents evidence that a memory of the initial structure also persists at the morphological level.

Detailed morphological studies, combining wide and small angle X-ray scattering (WAXS, SAXS), differential scanning calorimetry (DSC) and electron microscopy (EM), have shown conclusively that, during drawing, the initial spherulitic structure is transformed into a new fibrillar structure. Peterlin [1,2] and Keller [3–5] contributed significantly to our understanding in this area. Deformation initially proceeds in an inhomogeneous fashion via the processes of interlamellar shear, intralamellar shear and interlamellar separation, depending on the local orientation of lamellae. At larger strains microfibrils are said to be formed from the destruction of individual lamellae by incorporating blocks of folded chains. This transformation is essentially complete by a deformation ratio of about 9, after which, deformation proceeds in a more continuous manner. Very detailed WAXS, SAXS and EM studies of this transformed morphology in highly drawn polyethylenes show the development of long crystals with retention of a gradually less intense SAXS long period. Continuity in the transformed morphology is further supported by the establishment of excellent correlations between structural parameters and Young's modulus [6]. It is important, however, to emphasise that this transformation and the correlations are essentially one-dimensional, and it is on this basis that there appears to be no continuity between the morphology of the initial spherulitic structure and that of the drawn polymer.

In contrast, there is considerable evidence, through the concept of a molecular network, that molecular continuity persists through the deformation process, irrespective of the morphology in the initial solid. The deformation behaviour of a molecular network, underpinning the semi-crystalline morphology, was identified as a key factor in the drawing process by Capaccio and Ward [7,8], and this understanding has been successfully exploited by Smith and Lemstra [9] to produce ultra-high deformation. The persistence of a molecular network into the deformed material is strongly supported by shrinkage and shrinkage force measurements

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Table 1
Characteristics of polyethylenes used in the present study

Material	Manufacturer	Catalyst	M_w	M_w/M_n
HD6007	BP Chemicals	Ziegler–Natta	149,400	8.7
GX555-2	Hoechst	Metallocene	171,700	7.2
PF3	BP Chemicals	Metallocene	154,200	2.7
Sclair 2907	DuPont (Canada)	Ziegler–Natta	93,600	5.6

[10]. Convincing evidence for the concept is also provided by neutron diffraction measurements, although these can be subject to problems of interpretation [11]. Early work appears to confirm that the overall network topology is that expected for a random molecular chain, and that this is not affected by the chain-folded structure formed in crystallising from the melt [12,13]. Later measurements of the molecular radius of gyration in oriented samples suggest that the network deforms affinely [14]. Indirect evidence in support comes from a number of areas. The concept of an oriented network was successfully used by Orchard et al. [15] to explain the thermal expansion behaviour of drawn material. It was also the impetus for the concept of a unique true-stress/true-strain/strain rate surface, central to the development of new methods for quantitative modelling of polymer processing, tensile drawing, die drawing and hydrostatic extrusion [16,17].

There are clearly two contrasting views on structural continuity in the drawing process and both of these have considerable weight of evidence in support. A major limitation with the morphological perspective is its one-dimensionality. In the present work morphological examination of transverse sections shows that, in contrast to the picture seen in longitudinal studies, a degree of continuity persists through and beyond the spherulitic-to-fibrillar transformation. In addition, these more extensive morphological investigations are proving invaluable in attempts to develop a new model for fibre structure prompted by recent studies of the internal morphologies of highly drawn advanced polyethylene fibres prepared using a range of processes [18].

2. Experimental

Attention has concentrated on four high-density polyethylenes which differ with respect to their molecular weight characteristics and which possess quite distinctly different superstructures, non-spherulitic and banded spherulitic. Two commercial linear polyethylenes (LPE), produced using Ziegler–Natta (ZN) catalysts, and two

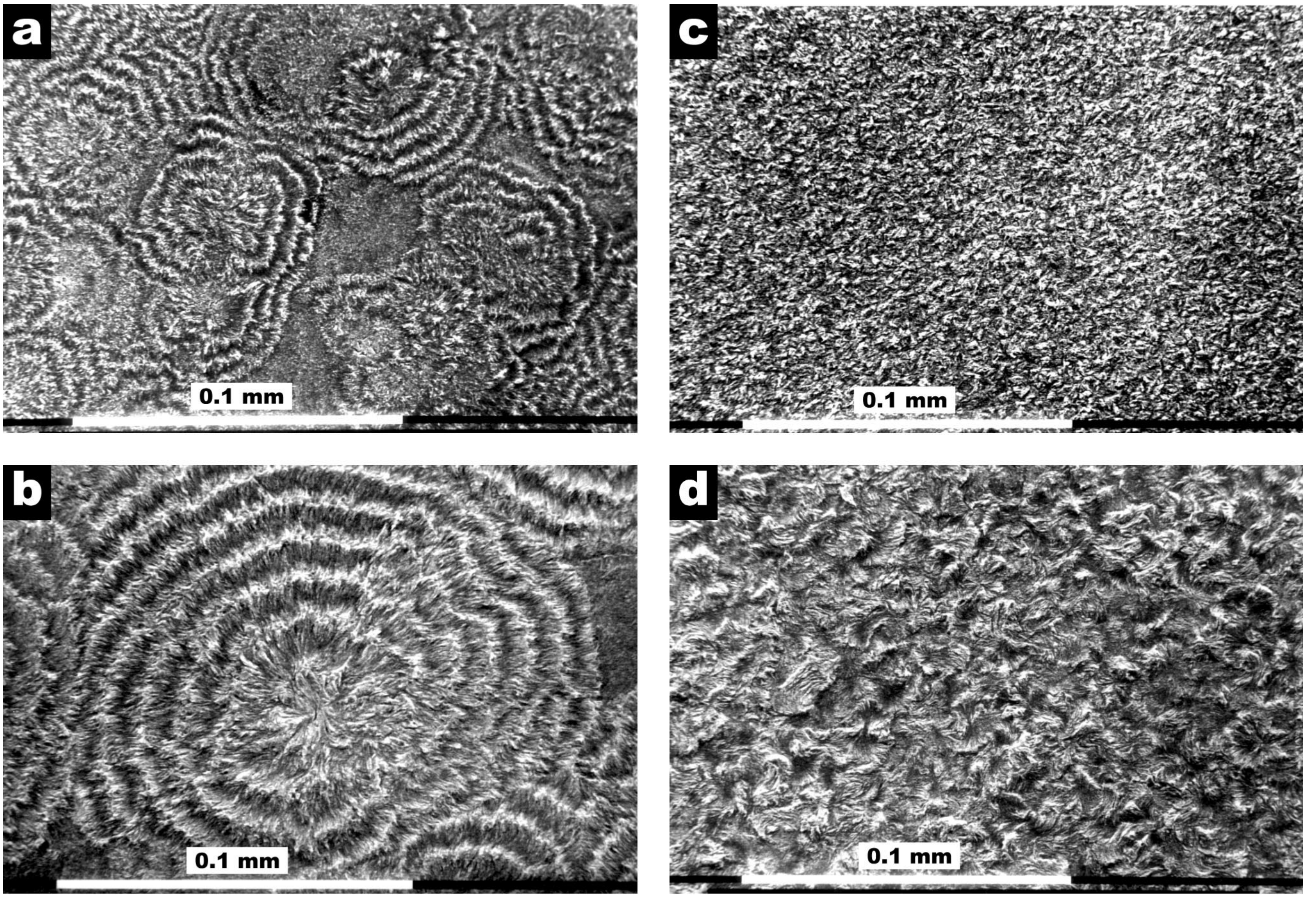

Fig. 1. SEM of isotropic starting materials showing scaling of different starting morphologies: (a) PF3; (b) Sclair 2907; (c) HD6007; and (d) GX555-2.

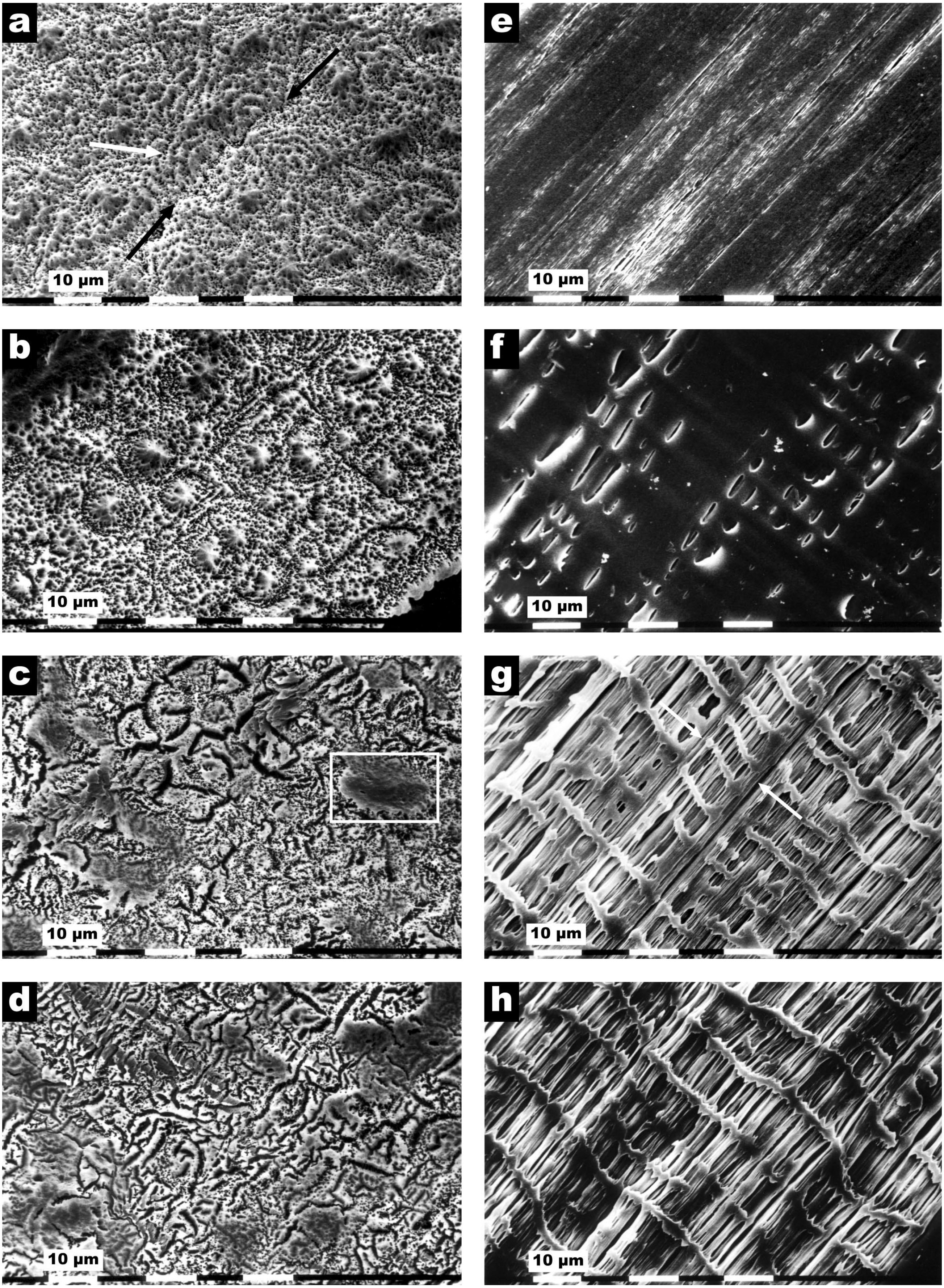

Fig. 2. SEM of transverse (a–d) and longitudinal (e–h) morphologies of PF3 at different draw ratios: (a,e) 10 ×; (b,f) 20 ×; (c,g) 35 ×; and (d,h) 40 ×.

experimental grades, produced using metallocene catalysts, have been investigated here; their characteristics are shown in Table 1. Sheets of approximately 1 mm thickness were produced by compression moulding polymer pellets, as supplied, at a temperature of 160°C. After hot-pressing, samples were crystallised by slow cooling at a rate of approximately $1\ \mathrm{K\ min^{-1}}$. Dumbbell specimens (gauge length = 20 mm and width = 5 mm) were cut from these sheets and drawn at 75°C and $100\ \mathrm{mm\ min^{-1}}$ using an Instron tensile testing machine. The draw ratio was calculated from changes in the separation of ink marks on the sample surface.

2.1. X-ray characterisation

Measurements of the long period in the isotropic samples and some of the oriented samples have been performed using small angle X-ray scattering. In addition, the lamellar thickness in oriented samples has been measured from the breadth of the (002) reflection in wide angle X-ray scattering. The SAXS measurements confirm there are no significant differences between the isotropic samples. There is also no evidence of differences between the oriented samples, in regard to long period or crystallite size, when comparison is made on the basis of equivalent draw ratio or modulus.

2.2. Electron microscopy

In preparation for microscopy, both isotropic and drawn materials were embedded in a Kraton® block copolymer (Shell) for ease of handling and microtoming. Their internal surfaces were exposed by cutting, at about −70°C, longitudinal and preliminary transverse sections with a glass knife in a Bright microtome, final transverse sections with a diamond knife. These exposed surfaces were etched with a permanganic reagent [19] for 1 h at room temperature before being examined microscopically. The etchant was a 1% solution of potassium permanganate in a 10:4:1 (by volume) mixture, respectively, of concentrated sulphuric acid, 85% orthophosphoric acid and water [20]. Etched specimens were coated with gold and examined under a Philips 515 Scanning Electron Microscope (SEM) with no specimen tilt.

3. Results

Fig. 1 displays the distinct morphologies of the starting materials which were all slowly cooled from the melt under the same conditions. PF3 and Sclair 2907 contain banded spherulites with those in Sclair 2907 having a band period about twice that of PF3. HD and GX, on the other hand, are much more densely nucleated, especially HD, and are filled with ‘axialites’, i.e. the early stages of spherulitic growth with relatively infrequent lamellar branching.

Historically, morphological investigations of oriented samples have concentrated on longitudinal sections but there is growing recognition of the value of studying transverse sections, not least because of the ability to highlight density deficient regions, whose high free volume leads to cratering when transverse cross-sections are exposed to permanganic etchants. Such craters were first seen in compacted materials where the fibres had been taken close to their melting points [21–23] but have also been observed in the fibres as manufactured [18] and, consequently, transverse sections can help reveal information on the microstructure produced by deformation.

The transverse and longitudinal morphologies of PF3 drawn to different draw ratios are displayed in Fig. 2. Considering transverse sections first, clearly craters also occur in these materials but, significantly, they form distinct patterns linked to the banded spherulitic texture. At 10× draw ratio remnants of the banding are evident, in many cases linked to differences in relief with the craters confined to the valleys between annular ridges (Fig. 2a). Note in the middle of the figure that a diagonal fault has sliced through the centre of one spherulite leaving the upper half more or less intact. At 20× draw ratio (Fig. 2b) the banding has become less apparent but can still be seen along with small cones at the centres of residual spherulites. With further drawing, to 35× and 40×, a very distinct morphology develops, especially for the latter. Two features in particular are evident: large voids, which will have been opened up by the etchant, and occasional rather featureless raised patches, such as that indicated in Fig. 2c. These features appear dark as the result of poor scattering of electrons and examination of tilted samples confirms that they are not cracks but raised sections of material. For convenience this type of morphology will henceforth be called ‘mesa structure’, since it resembles the geological features in the N. American desert, where isolated regions of a resistant layer remain while their surroundings have been eroded.

The corresponding longitudinal morphologies of PF3, drawn to the same ratios, are shown in Fig. 2e–h. Grooves of varying length parallel to the draw direction, the longest exceeding 50 μm, are the principal features at 10× draw. But at 20× draw, an alternating banded texture of etched voids between entire zones starts to occur similar to that reported previously in overdrawn polypropylene [24]. In that case, with a draw ratio of 8.3, the ‘voids’ were inferred to be of low density but not necessarily holes prior to etching, a conclusion reinforced by cavities not being seen in as-microtomed internal surfaces. Their origin was ascribed to yielding to the transverse internal stresses associated with alternating draw ratios at constant cross-section as discussed in the next section. In this paper the description ‘voids’ refers to the etched morphology leaving open the precise nature of that present initially.

Further drawing to 35× and 40×, transforms the structure to one of more or less regular alternating bands throughout the longitudinal cross-section. Within this description one can recognise lateral discontinuities which outline an area not dissimilar in appearance to the leaning tower of

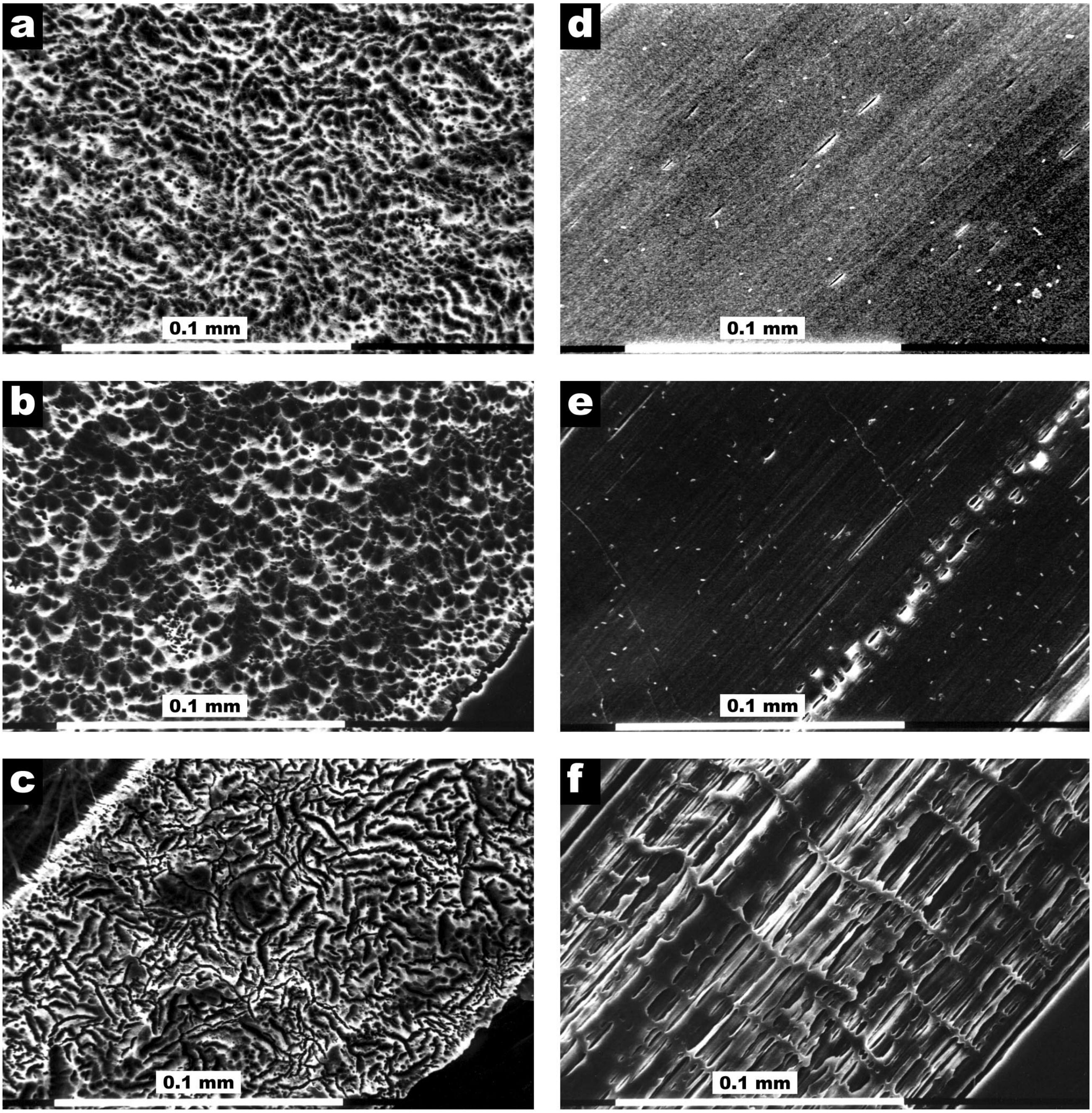

Fig. 3. SEM of transverse (a–c) and longitudinal (d–f) morphologies of Sclair 2907 at different draw ratios: (a,d) 10 ×; (b,e) 20 ×; and (c,f) 33 ×.

Pisa (as indicated in Fig. 2g). Both here and in the aforementioned polypropylene fibres [24] the apparent simultaneous emergence of the mesa and Pisa structures at high draw ratio and the dimensional similarities suggest that these are different aspects of the same phenomenon.

Fig. 3 displays the morphologies of drawn Sclair 2907, which also showed banded spherulitic morphology in the isotropic state. A banded structure is still present in transverse sections after 10 × draw (Fig. 3a) with a band period about twice that of equally drawn PF3; the same factor relates the band periodicity in the isotropic materials. For 20 × draw, the banded structure is hardly seen (Fig. 3b) while the mesa structure dominates the appearance for 33 × draw (Fig. 3c). In longitudinal morphology, Sclair 2907 parallels PF3 but is less developed at a given draw ratio. A few grooves are present after 10 × draw in an otherwise rather featureless morphology (Fig. 3d). At 20 × the beginning of the alternating banded structure is apparent (Fig. 3e) and this has become well developed by 33 × draw (Fig. 3f).

The morphologies of the two other materials in which there are no banded spherulites are shown in Fig. 4. Fig.

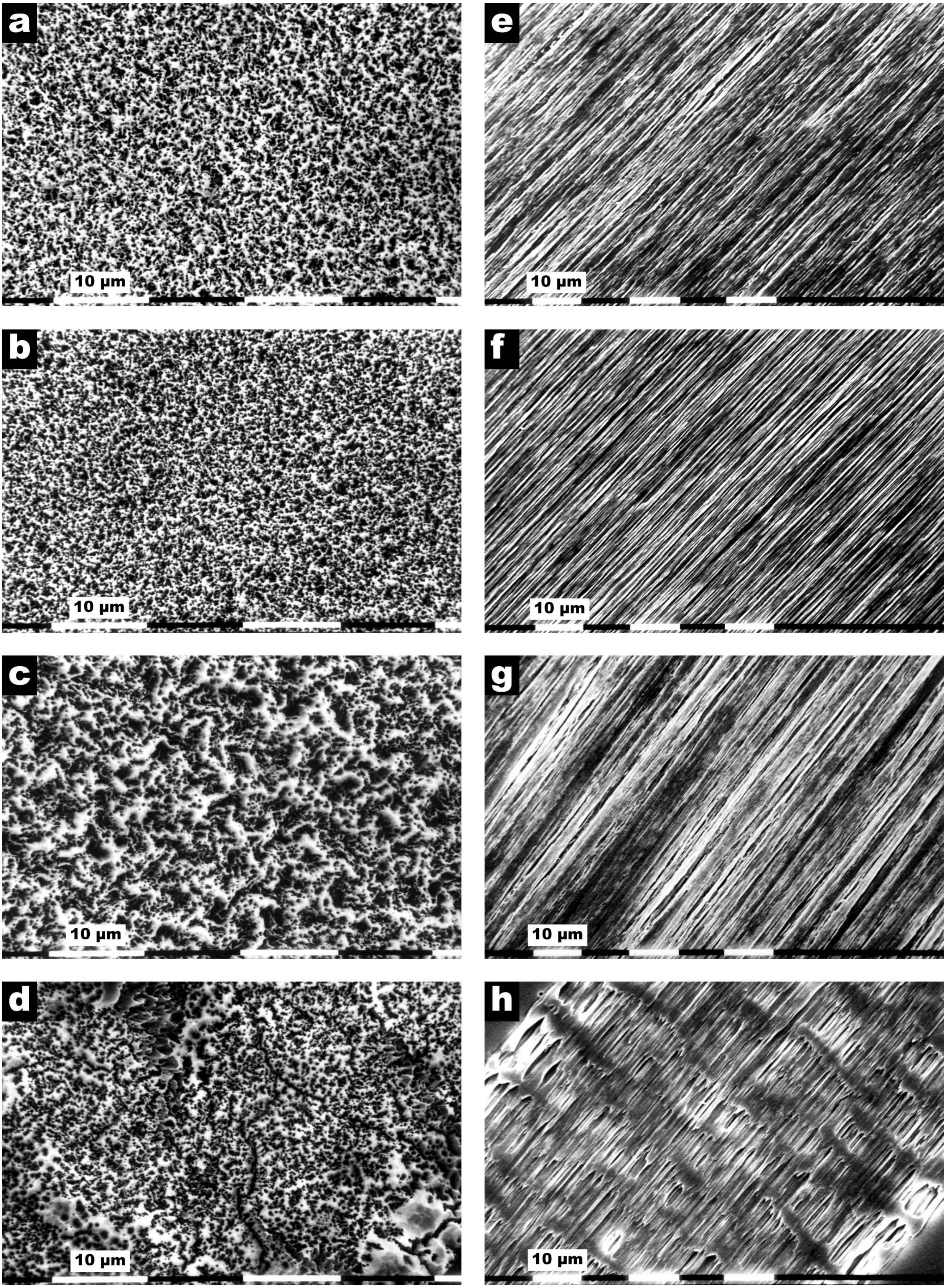

Fig. 4. Transverse (a–d) and longitudinal (e–h) morphologies of materials with no initial banded structure at low and high draw ratios: HD6007 at (a,e) 13× and (b,f) 37×; GX at (c,g) 12× and (d,h) 50×.

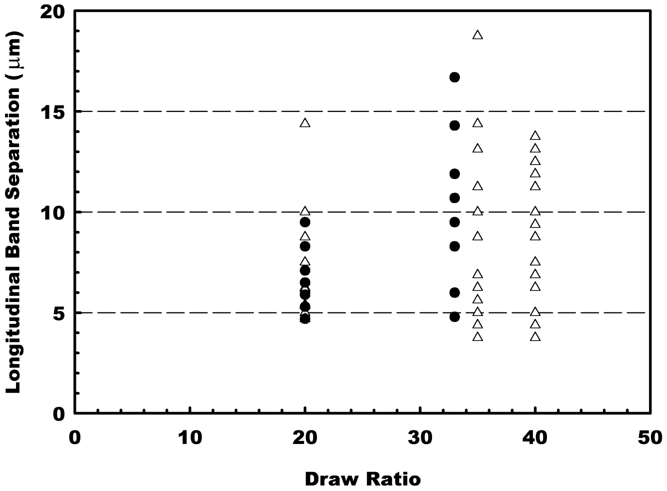

Fig. 5. ‘Entire’ band separation in the longitudinal direction for PF3 (△) and Sclair 2907 (●) drawn to various draw ratios.

4a–d show the transverse morphologies of, respectively, HD drawn 13× and 37×; GX drawn 12× and 50×. Note that the morphology of 12× drawn GX (Fig. 4c) is significantly coarser than that of its HD equivalent in accord with their undrawn textures. In both polyethylenes the structure becomes finer with higher draw ratio: compare Fig. 4a with Fig. 4b and Fig. 4c with Fig. 4d. The longitudinal morphologies of drawn HD and GX are shown in Fig. 4e–h; in all cases the scale of the strongly grooved texture accords with that seen in transverse section in Fig. 4a–d. Only for GX drawn 50× is the alternating banded texture present; this is the only one of the two non-banded specimens to show this texture and that at very high draw ratio.

4. Discussion

Conventional wisdom is that the initial morphology of polyethylene hardly affects the mechanical properties of the drawn product provided that comparison is made on the basis of equivalent draw ratio. The initial morphology has been thought only to limit the extent to which the polymer could be drawn with this quantity diminishing as the molecular weight of the polymer increases. Detailed characterisation of the samples examined here has confirmed that the modulus correlates with the draw ratio irrespective of the starting morphology [25]. Furthermore, the observation in the present work that all four isotropic polyethylenes showed the same long period (the long period of drawn polymer is known to depend principally on draw temperature [26] so that the similarity between the materials in this respect is not unexpected) and crystallite size from X-ray measurements might suggest that the materials would show no significant differences in textural ordering. However, microscopy not only reveals significant morphology within all these drawn polyethylenes but also shows that it varies markedly between samples.

There are two notable results, namely the memory in lateral textures, to high draw ratios, of the initial spherulitic banding and the development in some samples of alternating longitudinal bands akin to those described previously in ‘overdrawn’ polypropylene. To take these in turn, the finding of retained spherulitic banding, with cratering confined to the valleys, is an indication that modes of deformation have differed locally according to the orientation of the lamellae in the original banded spherulite. It is understood that the mechanism of crater formation by the etchant is similar to that in fibres [18], however the generation of the density deficient regions does not necessarily take place by the same mechanism. Nevertheless, local differences in their distribution would be expected of cold drawing when pronounced pre-existing morphology is deformed and, as a second paper will demonstrate, the remnant banding is strongly accentuated by suitable annealing of drawn samples. The scale of the initial morphology is also remembered in the remaining two polymers (cf. Figs. 1d and 4c) although it is less conspicuous in the absence of banding. The reduction in band period accompanying tenfold drawing is from 6 to 2.4 μm for PF3 and from 11 to 4.7 μm for Sclair 2907. These ratios are, respectively, 0.4 and 0.43 somewhat above the 0.32 for deformation at constant volume. This is consistent with earlier work on Sclair 2907 [27] confined to lower draw ratios, when the measured band periods were found to depart longitudinally from affine behaviour beyond 60% strain but still to be consistent with it laterally up to, but not beyond, 2.2 draw ratio. In effect the material has not contracted laterally as much as required so that, to maintain mass, regions of lower density must be introduced into the cross-section.

This has occurred when longitudinal banding is present. As was pointed out in earlier discussion of such features [24], both components of this banding—which we shall term voided and entire—must sustain the same longitudinal applied stress implying a bistable response. The etched voided regions have yielded transversely in response to greater extension and insufficient lateral contraction. The delayed onset of longitudinal banding in polymers GX and HD is very probably a reflection of their greater ability to sustain transverse tensile stress. While lateral yielding, potentially leading to fibrillation, is not unexpected, it is remarkable that alternate bands are entire with no visible signs of deformation. The band periodicity is not well defined (Fig. 5) with, for 20 × drawn PF3, separations scattered between 5–10 μm with one band as long as 15 μm. Similar dimensions and scatter were found in PF3 polymer drawn 35 × and 40 × but less so for Sclair 2907. As the entire bands remain so with increasing draw ratio and decreasing cross-section, they must undergo strain hardening. The underlying cause of this ability could well be that they are the residual locations of molecular entanglements which have become concentrated as extension proceeds.

The findings of this study should help in the development of an emerging common model for fibre structure. Recent work [18] has revealed a common substructure of density deficient regions in highly drawn advanced polyethylene fibres, whether prepared by melt spinning, gel drawing or melt kneading. In consequence, a new model of fibre structure has been proposed which ascribes the density deficiency to these regions crystallising within a rather rigid framework of the entangled molecular network and so being increasingly under tension because of the contraction from the volume of the melt. The retention of a memory of the original superstructure, and the regularity of cratering in samples showing a banded spherulitic texture, should help link features of the drawn material to regions of particular lamellar orientation within the spherulites of the initial material. Although the evidence of a morphological memory is most obvious for samples possessing a banded spherulitic morphology, it is still evident for axialite starting morphologies, so that any findings may be generally applicable. The presence of other common features provides additional incentive to seek a more universal model. In this respect, it is significant that, regardless of the starting morphology, there is a tendency for samples to develop, at very high draw ratio, a ‘mesa’ structure, attributed to etching resistance of harder regions, with an apparent parallel development in longitudinal sections of the ‘Pisa’ structure, again incorporating harder regions, this time with an approach to periodic regularity. It is interesting to speculate that these harder regions are equivalent and, as mentioned above, perhaps the residual locations of molecular entanglements which have become concentrated as extension proceeds.

5. Conclusions

The primary significance of the present research is that it establishes key continuity of the morphology from the spherulitic to the drawn structures. The new insight is to emphasise the importance of studying the lateral morphology which clearly transforms in a continuous fashion, in contrast to the axial morphology which is transformed out of all recognition by drawing. To summarise:

1. The transverse cross-sections of linear polyethylene, from both Ziegler–Natta and metallocene catalysts, drawn to high extensions at 75°C, retain a memory of the initial morphology which is most pronounced for those containing banded spherulites. This is a consequence of spatial variation in deformation according to the initial orientation of lamellae.
2. At higher draw ratios a longitudinal alternation of entire and etched voided bands develops in certain cases, being most pronounced for the materials containing banded spherulites. Otherwise, it does not occur until higher draw ratios and has still to be observed for the sample with the finest-grained texture. The etched voided regions result from yielding to transverse tensile stresses as materials fail to contract sufficiently to accommodate the increase in draw ratio; the internal cohesion appears to be texturally related. The entire bands, it is suggested, may be the location of residual molecular entanglements.

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