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Structural deformation in polyethylene during cold-drawing

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A permanganic etching technique is used to study the morphology of blow-moulded polyethylene before and after cold-drawing. The morphological changes that occur in the necked region during drawing are also examined. The etching technique reveals an initial unoriented spherulitic structure, only 35% of which is changed on drawing to a fibrillar texture in the form of 30 μm diameter columnar entities. Transformation in the necked region is shown to involve (a) trans-spherulitic slip or cleavage, (b) alignment of spherulites into extending rows in the draw direction, (c) destruction of the aligned spherulites to form the columnar entities, which contain plates whose planes are normal to the column axis and hence the draw direction.

1. Introduction

The deformation at yield in polymers may be considered both macroscopically and microscopically. Polyethylene exhibits a distinct load drop on the tensile load–extension curve at yield which is associated with the formation of a necked region. At slow speeds of extension, the neck formation stabilizes and the drawn region then propagates along the entire length of the specimen. The morphological changes associated with both cold-drawing and other forms of deformation in polyethylene have been reviewed by Perkins and Porter [1]. Such changes have been studied using X-ray, polarized light microscopy and electron microscopy [2] on solution or melt-cast films.

The as-cast undeformed structure of polyethylene is normally a semicrystalline spherulitic structure, with the degree of crystallinity varying from 50 to 90% [1], depending on the type of polymer, crystallization conditions and the molecular weight. The highest value is rarely encountered except under laboratory conditions and would not be expected in commercially processed material. Many studies of the spherulitic structure have been reported in the literature and subsequently reviewed [1–4]. These studies have shown that spherulites are composed of radiating lamellar crystalline fibrils which twist [5–7]. Such morphology has been established largely from experiments on thin films and therefore two-dimensional spherulites. Examination of the spherulitic structure in thick case sections has received less attention due to the lack of experimental techniques. Recently, etchant techniques have been developed for polyolefines [8] which allow structure to be revealed in a manner similar in many ways to that extensively used in metallography. The etchant technique has also revealed lamellar structure in polyethylene with a banded spherulitic form in a commercial polyethylene chip [8].

Two different categories of spherulitic deformation were identified in thin cast films of high-density polyethylene by Hay and Keller [2]. In the first category spherulites deform inhomogeneously with yield in one part of the spherulite while the remaining microstructure is unaltered. In the second category all parts of the spherulite deformed homogeneously. Increasing the thickness of the sample was found to favour inhomogeneous deformation, which was noted to include deformation either within the spherulites or between spherulites.

Further deformation in the cold-drawing process results in the formation of a fibrillar structure in the necked portion. Wide-angle and low-angle

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X-ray studies reveal that the crystalline lamellae take on a preferential direction with the c-axis parallel to the drawing direction and the microfibrils comprising blocks of crystalline material separated by amorphous regions. Models have been proposed to account for the transformation from the spherulitic to the microfibrillar structure [9–13]. Peterlin proposes that the spherulitic morphology is virtually completely transformed at a draw ratio of about 10 with tie-molecules linking the crystalline sections together within the microfibrils. The Prevorsek model is similar to that of Peterlin's with extended non-crystalline molecules passing between the microfibrils.

Development of etchant techniques permit studies of deformation and morphological changes within bulk material in contrast to the extensive earlier studies on thin films. The etchant techniques have been applied to a range of polymers [8, 14–16] including polyethylene, polypropylene, poly(4-methyl-pentene-1), polytetramethylene terephthalate and polybutylene terephthalate. Olley *et al.* [8] have used a permanganic etch followed by a two-stage replication process to reveal the fine detail in undeformed and drawn polyethylene, concentrating on the arrangement of the lamellae. Other studies [14, 15, 17] have revealed interpenetrating spherulites and variation in morphology between skin and core in injection-moulded samples. These studies, particularly that of Olley *et al.*, have served to confirm predicted morphologies previously determined by indirect techniques and by analogy with solution-crystallized materials.

The purpose of the present paper is to report on the use of the permanganic etchant technique to study the spherulitic deformation and fibrillar formation in commercially produced high-density polyethylene (HDPE) during cold-drawing at slow rates of deformation.

2. Experimental details

Dumb-bell (or dog-bone) shaped specimens were machine cut from the walls of blow-moulded 210 litre drums. The drum material was a high molecular weight, high-density polyethylene containing 1% phthalinecyanine blue as pigment. The material used had a measured density of 951 kg m^{-3} and quoted molecular weights of $\bar{M}_n = 33\,000$ and M_w of 31 2000. Studies on this particular material rather than laboratory-produced sheets were undertaken to complement other studies on the impact performance of such containers. The drums had a diameter of 0.6 m and a height of 1 m, with a wall thickness of approximately 3 mm. Specimens with a parallel section of length 33 mm and width 6 mm and thickness 3 mm were prepared which were essentially flat due to the large curvature of the barrel wall. The specimen dimensions conformed to BS 2782 method 301 F.

The specimens were subjected to conventional tensile tests at an extension rate of 5 mm min^{-1} on an Instron Universal testing machine. At this speed, the specimen exhibited localized yielding in which the neck stabilized and subsequently propagated along the entire specimen length. A draw ratio of about 9 was achieved before rupture occurred. Fig. 1 shows a cold-drawn sample taken to rupture together with an original undeformed specimen. The drawn material showed considerable stress whitening which contrasted with the blue of the pigmented material.

Sections were cut from the undeformed and drawn regions of the tested specimens as well as in the neck itself of partially drawn specimens. In preliminary work, such specimens were prepared for etching by only polishing on successively finer grades of carborundum paper. However, whenever such polished specimens were etched, they were found to reveal parallel line artefact textures corresponding with the last applied polishing direction. Presumably residual grooves or stresses in the prepared surface led to preferential etching. The preparation problem was overcome either by applying further polishing using diamond paste impregnated wheels or using a sledge microtome with a very carefully prepared knife. The latter method was adopted for all work reported in this paper. The zone to be examined

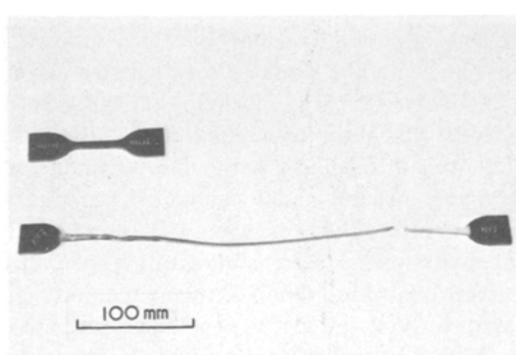

Figure 1 Cold-drawn and undeformed polyethylene tensile specimens.

was first cut from the deformed specimen with a razor blade and then the required surface revealed by successive cutting with the sledge microtome knife terminating with a very light cut. In the present work all sections were taken parallel to the draw direction.

The etchant technique applied, generally followed that proposed by Olley *et al.* [8] but with some variation. The etchant used was a 7% solution of potassium permanganate in concentrated sulphuric acid, taking the precautions recommended by Olley. The sample to be etched was totally immersed in the etchant for 24 h at room temperature and to obtain a uniform deep etch over the whole surface it was necessary to stir the etchant with the sample on a magnetic stirrer for the whole period. Failure to stir resulted in an irregular etching of the surface and reducing the time merely produced a lighter etch. After 24 h, the etchant with sample were cooled to 0° C and after removal from the permanganic etch, the sample was first washed in a mixture of 2 parts suphuric acid to 7 parts water precooled to almost its freezing point with dry ice, until the surface to be examined was observed to be clean. The blue pigmentation was an asset in this instance, since the etched surface appeared to be coated with a thin brown powdery film which was removed by the first washing. Subsequently the specimens were rinsed in hydrogen peroxide, then in distilled water and finally in acetone before being allowed to dry.

In contrast to the two-stage replication technique used by Olley *et al.* [8] to study the etched surfaces, all the etched surfaces were examined directly using scanning electron microscopy (SEM) after they had been sputter-coated with gold/palladium. Such coating and the use of SEM rather than TEM suppresses the resolution of the fine detail which was the subject of previous work [8]. The interest here, however, is the larger scale resolution of the transformation of the spherulitic form to the cold-drawn structure.

3. Morphological changes on deformation

3.1. Undeformed structure

Fig. 2 shows the undeformed structure in the centre of the specimen. The structure appears to be spherulitic, with little or no evidence of orientation remaining from the extrusion and blow-moulding operations used to produce the material. The average size of the spherulites is 10 μm, with the largest about 20 μm. The spherulites appear as shaggy spheres set in a deeply etched background. Fig. 3 shows an enlarged view of a small collection of the spherulites. Each etched spherulite appears as a fluffy ball, the nature of which can only be speculative at this stage. It may be the crystalline lamellae separated by deeply etched regions, which are still in their original positions. Alternatively, it is possible that inter-spherulitic material has been preferentially etched away leaving straggling crystalline filaments that have collapsed on to

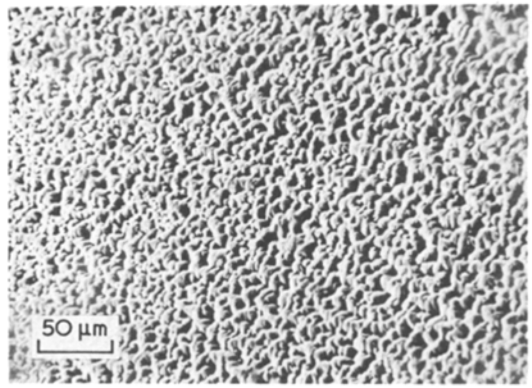

Figure 2 Undeformed spherulitic structure in etched polyethylene.

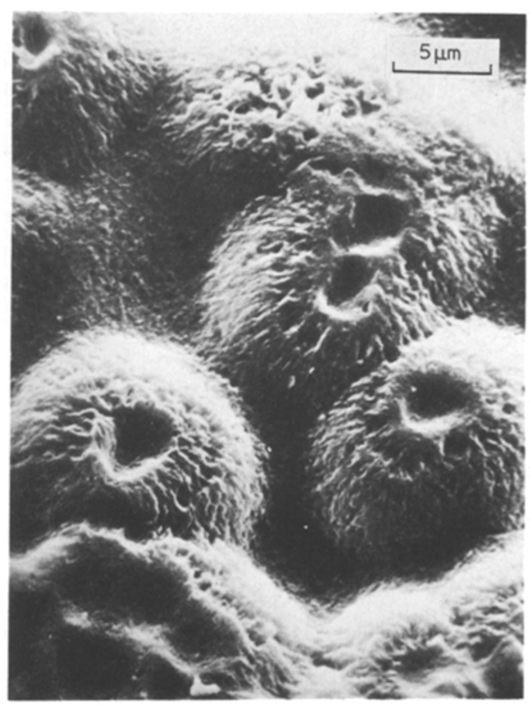

Figure 3 A selection of spherulites in the undeformed, etched polyethylene.

each other once the etchant has been removed. The dimple in the centre of each spherulite in Fig. 3 is most intriguing. They have not been observed in every section studied. This may indicate some preferential growth direction for the spherulite, as was observed in crystallization studies in stretched films [18] giving rise to preferential etching along the core of the spherulite. However, the possibility of an artefact due to the etching technique cannot be excluded.

Fig. 3 also shows large spaces between the spherulites and interpenetrating spherulites. A previous study by Winram *et al.* [21] on the structure of HDPE, revealed the existence of two forms of crystalline material which were associated with molecular-weight segregation during crystallization. It was shown that large, coarse-textured spherulites crystallized from the higher molecular weight material, which melted at relatively high temperatures (~ 136° C), while lower molecular weight material segregated to crystallize in a fine texture between the large spherulites. It was found that the inter-spherulitic material melted at a lower temperature (~ 129° C) and was preferentially etched by the xylene solvent used. The material used in the present work is also HDPE and the large spaces between the spherulites may also be due to the preferential etching of low molecular weight segregated material which crystallized between the larger spherulites. The process time in the production of the large containers is relatively short (~ 3 min) and does not match the crystallization time of 31 h adopted by Winram *et al.* Hence if the inter-spherulitic space shown in Fig. 3 is due to preferential etching of low molecular weight segregated material, such segregation must have occurred within the relatively short time of the production process.

3.2. Cold-drawn structure

Fig. 4 shows the cold-drawn morphology of polyethylene as revealed by etching. It comprises a mixture of fibrillar material, oriented in the drawing direction, residual spherulitic material and space between these two types of feature which has been preferentially etched. The proportion of fibrillar material in Fig. 4 is estimated as 35%: this quantity has been determined by measuring the total length of fibrils in the photograph, multiplying by an average fibril width and expressing that as a percentage of the viewed area. Estimates of the relative proportions of spherulitic to preferentially etched regions are less readily determined. If it is assumed that the areas covered by spherulites and etched materials are the same (see also Fig. 5), this would indicate that the drawn material contained approximately 30 to 35% spherulites. The condition of the preferentially etched material after drawing cannot, of course, be determined by the etching technique. The high proportion of spherulitic material is surprising, since the specimen received a draw ratio of about 9, which from earlier studies [11] should have ensured complete transformation of the spherulitic structure.

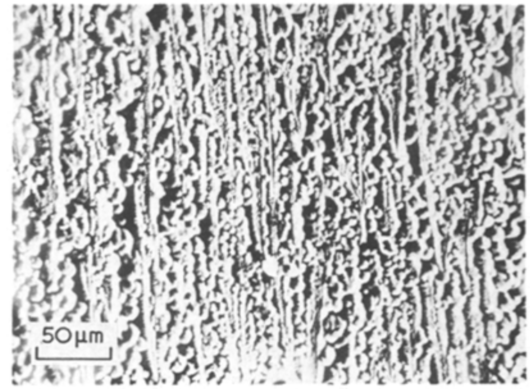

Figure 4 **Structure of the cold-drawn and etched polyethylene. The draw direction is parallel to the fibrillar entities.**

Some of the fibrillar entities in Fig. 4 extend for at least 200 μm, although others are considerably shorter. Fig. 5 shows an enlarged detail of the same drawn specimen. The fibrillar material is now seen as roughly cylindrical columns consisting

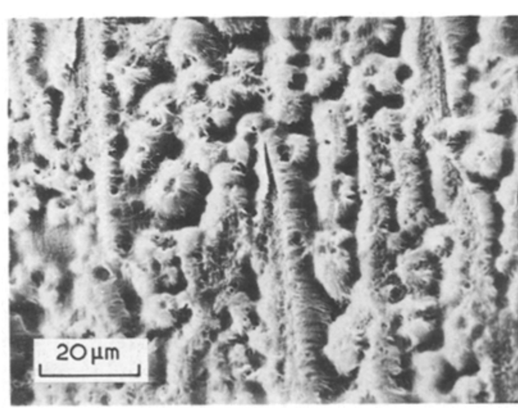

Figure 5 **Structure of the cold-drawn and etched polyethylene, showing the construction of fibrillar entities in Fig. 4.**

of stacks of circular plates or lamellae. The columns have a diameter of approximately 30 μm, which is similar to the diameter of the original spherulites. Many of the columns, particularly the less well-developed shorter columns, appear to have spherical bulges along their outline which have been retained from the original spherulites from which they have formed. Another feature is the longitudinal splitting, which is particularly noticeable at the end of the largest column in the centre of Fig. 5. The split leads to a differently etched region along the central ridge of the column. It is also noticeable that several of the surrounding undeformed spherulites also contain dimples at the centre. If this is due to preferential etching at the uppermost cap, the same process could also account for preferential etching along the ridge of the columns accentuating the longitudinal splitting effect. However, some splitting of the spherulitic material does occur as will be discussed in the next section.

Fig. 6 shows a detail at increased magnification of one of the columns in the drawn material. The stack of plates constituting the column is more readily identifiable. Measurement of the thickness of an individual plate taken as a striation at the edge of the column gives a value of 80 nm. Lamellar thicknesses are usually quoted as 10 to 20 nm. Hence the observed plates are likely to contain 3 or 4 lamellae in a sandwich structure. Fig. 6 also reveals cracking in the column between the plates and further cracking between spherulites adjacent to the column. The faces of the cracks appear to be joined by some fibrillar material. This voiding, which is normal to the draw direction, may be the source of the stress-whitening observed. However, the cracking may also be due to preferential etching of either less organized material or regions of high residual stress.

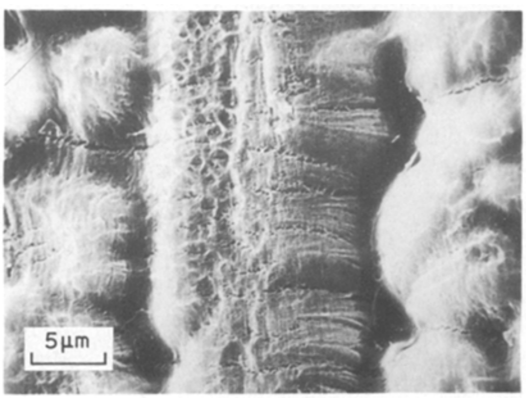

Figure 6 **Detail of a column in drawn polyethylene, showing plate texture and inter-plate cracking.**

Fitchman and Mencik [22] studied the morphology of injection-moulded polypropylene using a strong oxidizing etchant, similar in some ways to that used in the present work. In that instance it was found that the etching technique gave rise to stress cracking, particularly in freshly moulded material in which the internal stresses had not had time to relax. Significantly, the stress cracking decreased with lapse of time after moulding. Hence the cracking present in Fig. 6 may be attributable to stress cracking caused by the etchant on residually stressed, deformed material. The cracks are observed to be transverse to the draw direction and hence normal to the most probable direction of residual stress. Fortunately the stress cracking is not so severe as in Fitchum and Mencik's original work using strong etchants and does not severely distort the structure. Indeed it could be argued that such cracking could be beneficial, since it indicated the residual stress pattern in the deformed structure and accentuates the plate-like texture of the columnar entities.

3.3. Transformation from spherulitic to columnar structure

Fig. 7a to d shows a sequence of sections taken longitudinally through the neck of the cold-drawn polyethylene and indicate the development of the columnar structure. At entry to the necked region (Fig. 7a), the randomly arranged spherulitic structure shows little sign of deformation at low magnification. Further into the neck, some of the spherulites have arranged themselves into short rows of 3 to 8 spherulites length and oriented in the drawing direction as shown in Fig. 7b. A suggestion of this organization may now be observed in Fig. 7a, although it would be anticipated statistically that such short-range order would occur in any random arrangement of spheres. Fig. 7c shows the result of further elongation as the material necks down. Many of the previous obvious rows of spherulites have changed into the columnar features in which the spherulitic form is now almost absent. At this stage the columns are relatively short (less than 100 μm) and account for only 10 to 20% of the drawn material. However, further alignment of spherulites can be seen in Fig. 7c initiating further columnar structures. Fig. 7d shows the fully developed drawn structure at the minimum

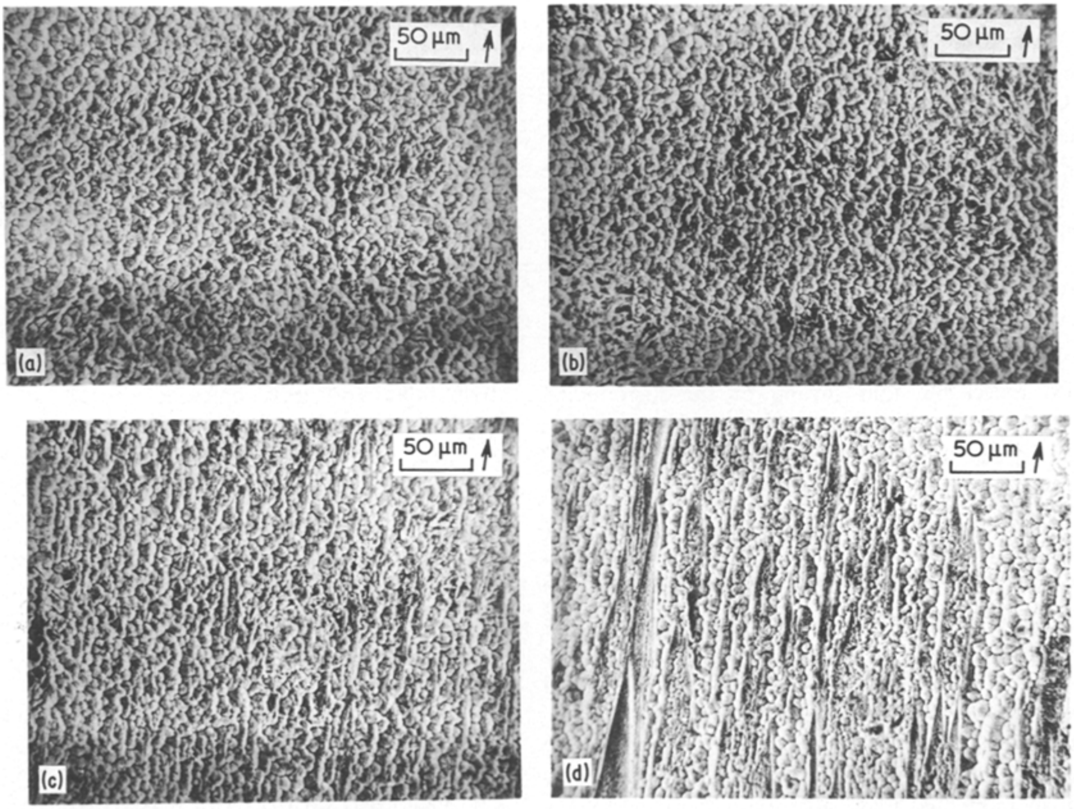

Figure 7 (a) Spherulitic structure at entry to the neck of the drawn polyethylene sample. (b) Development of the drawn texture at approximately one-third of the way into the neck. (c) Development of the drawn texture of approximately two-thirds of the way into the neck. (d) Fully developed drawn texture at the base of the neck. All SEMs recorded applying a tilt angle of 20° to the specimen.

section of the neck, which contains a high proportion of long columns oriented in the draw direction plus further spherulitic material sandwiched between the columns.

Fig. 8a to d shows details of deformed structures corresponding to Fig. 7a to d, respectively. Fig. 7a showed a randomly arranged spherulitic texture at entry to the neck. On closer examination (Fig. 8a), it is seen that many of the spherulites are cleaved, most likely due to stress cracking following etching. A high proportion of the cleaving occurs in the draw direction and therefore parallel to the uniaxially applied stress, although a triaxial stress state exists in the neck region. If the spherulitic cracking observed in Fig. 8a is attributed to stress cracking, it could indicate that certain regions of the spherulites are preferentially deformed and hence residually stressed, leading to trans-spherulitic stress cracking in those regions during etching. Further deformation (Fig. 8b) results in widening of the splits in the spherulites plus continuation of the localized deformation through several adjacent spherulites, particularly, in the draw direction. This concerted deformation of adjacent spherulites aligned in the draw direction is thought to initiate the transformation to the columnar form. In Fig. 8c it can be seen that further deformation has resulted in extension of the number of aligned spherulites and the accompanying trans-spherulitic deformation band. Instances of aligned spherulites with several cleavage or shear bands running in the draw direction can be observed. In the latter case, the spherulitic form becomes very diffuse and the transformation to columnar form is very clear. Fig. 8d shows the texture at the base of the neck. Fully developed columnar forms are present and spherulites still present show various degrees of cleavage. The major fibrillar column in Fig. 8 is bifurcated and it is thought that this originates in the substantial axial division of spherulites of the kind shown in Fig. 8c. Bifurcation of the columnar forms is common in samples deformed at low rates of deformation.

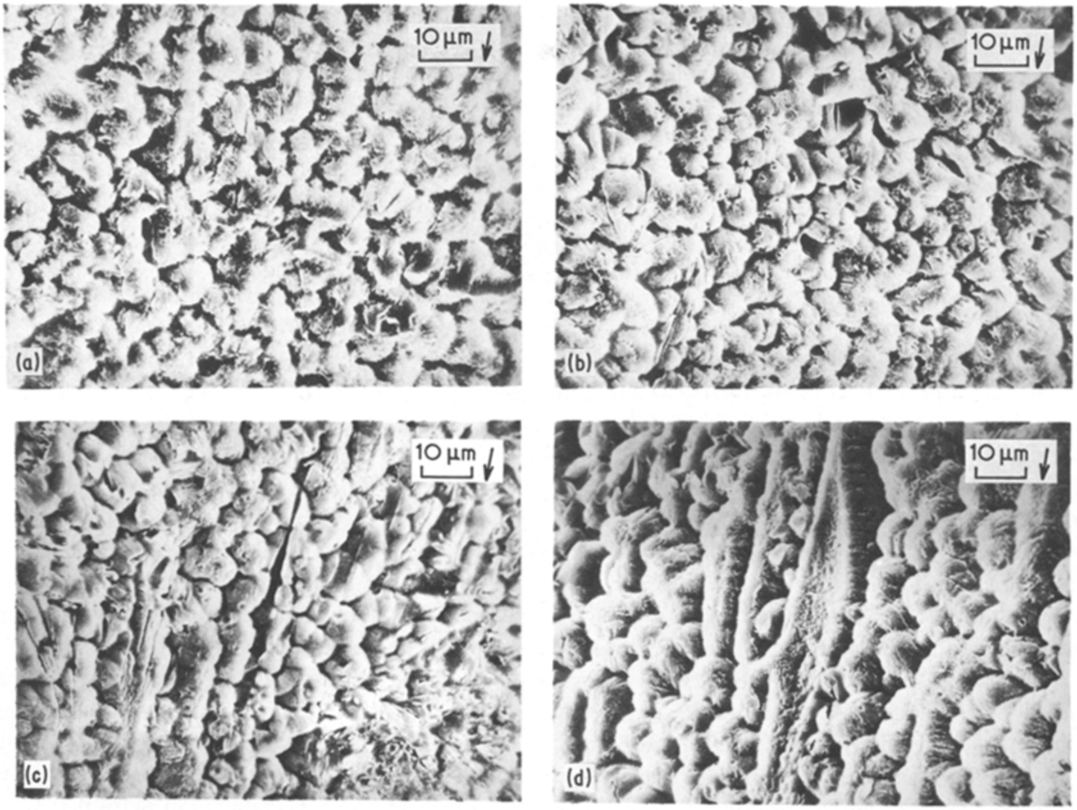

Figure 8 (a) Detail of spherulitic structure at entry to the neck in cold-drawn polyethylene, showing possible intra-spherulitic stress cracking along highly stressed zones after etching. (b) Detail from Fig. 7b, showing progression of intra-spherulitic deformation at one-third of the way into the neck. (c) Detail from Fig. 7c, showing concerted splitting after etching of several aligned spherulites in the draw direction. (d) Detail from Fig. 7d, showing fully developed columnar structures at the base of the neck, aligned in the draw direction. Draw direction as indicated by arrows.

4. Discussion

The permanganic etching technique has revealed the internal structure of the as-moulded and cold-drawn polyethylene drum material and has also outlined information on the mechanisms of cold-drawing.

The as-moulded polyethylene was found to consist of spherulitic material, with little sign of orientation effects throughout its thickness except at the outer surfaces. Absence of orientation in the bulk of the material occurs due to the relatively long time and slow cooling rates associated with the production of large blow-moulded items. Hence any orientation of the molecular structure has time to relax during the parison extrusion, blowing and cooling components of the production cycle. Spherulites observed were found to have diameters in the range 10 to 20 μm. Such diameters are large for polyethylene spherulites formed in quenched thin films, but compare with those in compression-moulded and injection-moulded bars of nylon 66. [19]. Hence the large diameter spherulites produced may relate to the long cooling time of the production cycle.

The deep etching technique adopted showed the spherulites as shaggy spheres, with little detail of the lamellar structure within any individual spherulite. However, the detail has been the concern of other workers [8, 21]. The matter of interest in the present paper is the gross deformation of the spherulitic structure during cold-drawing. The information gained on the as-cast spherulitic structure does not contradict earlier statements from other workers.

The fully drawn structure comprising approximately equal parts of fibrillar, (columnar forms) virtually undeformed spherulitic material and preferentially etched inter-spherulitic material is surprising in the quantity of spherulites remaining at a draw ratio of 9. Previously it has been considered that a draw ratio of this magnitude was sufficient to destroy all spherulitic material [11]. It now appears that spherulites are more persistent, at least in the particular grade of material used for the drum manufacture. The remaining spherulites become arranged in rows between the columnar entities and are thus in the required configuration for further column formation should extra drawing occur. Such extra drawing would be achieved in fibre formation as opposed to cold-drawing bulk material. Hence it seems most likely that a much higher spherulitic conversion would occur in fully drawn fibres.

The columnar entities in the cold-drawn material were found to have diameters of approximately 30 μm similar to those of the original spherulites and also to be derived from preferentially aligned groups of spherulites in the drawing direction. Such dimensions are much larger than the widths of the microfibrils envisaged in the Prevorsek and Peterlin models for drawn materials. They are also much wider than the shish-kebab forms in melt crystallized, oriented thin films [20], which generally have widths of 100 to 500 nm. Apart from their overall dimensions, the columnar entities in the drawn material show considerable similarity with the model structures of Prevorsek and Peterlin. They appear to comprise plate-like entities, with their planes normal to the draw direction, arranged in stacks. The alignment of the plates, coupled with the known crystal orientation in drawn polyethylene [9–13, 20], initially suggests that the observed plates are lamellae formed from the crystalline filaments in the spherulites. However, their thickness of about 100 nm probably indicates that each etched plate comprises of 3 to 4 lamellae. The columnar diameter of 30 μm may indicate that lamellae can grow laterally much more than had been suggested previously. However, it seems more likely that each columnar entity is a complex arrangement of microfibrils, the details of which have not been revealed in the etching technique applied. The observed large diameter plates are then attributed to preferential etching on certain planes in the stack of microfibrils. It is then possible that the fibres seen connecting the plates in Fig. 6 are individual microfibrils.

The deformation in the neck has previously been considered only in terms of the slip and rotation of crystalline lamellae and chain extension [20], although studies on thin cast films have indicated that inhomogeneous deformation of spherulites contributes to the drawing operation [2]. The sequence of structural deformation in the neck presented in this paper suggests that the drawing operation involves:

(a) trans-spherulitic slip or cleavage at an early stage of drawing;

(b) alignment of spherulites into rows of increasing length as drawing continues;

(c) inter-spherulitic slip or cleavage in the draw direction along the aligned spherulites;

(d) transformation of the aligned, deformed spherulites into a high proportion of columnar structures. These columnar structures appear to contain plates or groups of lamellae whose planes are normal to the draw direction.

While the deep permanganetic etching combined with SEM studies provide useful information of the gross morphological changes during cold-drawing, it is not possible to comment either on the detail of the intra-spherulitic slip mechanisms or the detailed transformation from spherulite to columnar form at this stage. Indeed it has been argued that the etching technique removes some of the detail, particularly in respect of inter-spherulitic material which is preferentially etched and can lead to stress cracking in deformed structures. Further studies will aim to clarify the detail of the mechanisms involved and the columnar structures now observed.

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References

1. W. G. PERKINS and R. S. PORTER, *J. Mater. Sci.* **12** (1977) 2355.
2. I. L. HAY and A. KELLER, *Kolloid-S-Polym.* **204** (1965) 43.
3. A. LOW, D. VESELY, P. ALLAN and M. BEVIS, *J. Mater. Sci.* **13** (1978) 711.
4. D. C. BASSETT and A. M. HODGE, *Polymer* **19** (1978) 469.
5. H. D. KEITH and F. J. PADDEN Jr, *J. Polymer Sci.* **39** (1959) 101.
6. A. KELLER, *ibid.* **39** (1959) 151.
7. F. P. PRICE, *ibid.* **39** (1959) 139.
8. R. H. OLLEY, A. M. HODGE and D. C. BASSETT, *J. Polymer Sci. Phys.* **17** (1979) 627.
9. A. PETERLIN, *J. Polymer Sci.* **C15** (1966) 427.
10. *Idem, Ann. Rev. Mater. Sci.* **2** (1972) 349.
11. G. MEINEL and A. PETERLIN, *J. Polymer Sci. A-2* **9** (1971) 67.

12. D. C. PREVORSEK and R. K. SHARMA, *Polymer Eng. Sci.* **14** (1974) 778.
13. D. C. PREVORSEK, P. J. HARGET, R. K. SHARMA and A. C. REIMSCHUESSEL, *J. Macromol. Sci. Phys.* **B-8** (1–2) (1973) 127.
14. S. R. BARNES, *Polymer* **21** (1980) 723.
15. J. E. CALLEAR and J. B. SHORTALL, *J. Mater. Sci.* **12** (1977) 141.
16. D. FORTHERINGHAM and B. PARKER, *ibid.* **11** (1976) 979.
17. S. Y. HOBBS and C. F. PRATT, *J. Appl. Polymer Sci.* **19** (1975) 1701.
18. E. H. ANDREWS, *Proc. Roy. Soc.* (*London*) **A277** (1964) 562.
19. H. W. STARKWEATHER and R. E. BROOKS, *J. Appl. Polymer Sci.* **1** (1959) 236.
20. I. L. HAY, "Methods of Experimental Physics", Vol. 16, Part C, edited by R. A. Fava (Academic Press, New York, 1980) Ch. 13.
21. M. M. WINRAM, D. T. GRUBB and A. KELLER, *J. Mater. Sci.* **13** (1978) 791.
22. D. R. FITCHMUN and Z. MENCIK, *J. Polymer Sci. Phys.* **11** (1973) 951.

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