JOURNAL OF MATERIALS SCIENCE **29** (1994) 4694–4699

Compaction of high-modulus melt-spun polyethylene fibres at temperatures above and below the optimum

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In the process of hot compaction developed at the University of Leeds, high-modulus fibres are compacted to form coherent thick-section products with stiffnesses unobtainable by current processing techniques. Using high-modulus polyethylene fibres (trade name TENFOR) produced by the melt-spinning/hot-drawing route as the starting material, it was discovered that under optimum conditions of pressure and temperature it is possible controllably to melt a small proportion of each fibre. On cooling, this molten material recrystallizes to bind the structure together and fill all the interstitial voids in the sample, leading to a substantial retention of the original fibre properties. For a hexagonal close-packed array of cylinders, only 10% of melted material is needed for this purpose. If the compaction temperature is too low, there is insufficient melt to fill the interstices, the fibres deform into polygonal shapes, and insufficient transverse strength is developed. Above the optimum temperature, the proportion of melt increases, causing the stiffness of the composite to be reduced. The recrystallization of the melt is nucleated on the oriented fibres, giving similarly oriented cylindrulitic growth. Where the regions of melt are large enough, and cooling sufficiently rapid, development away from the nucleus is accompanied by a cooperative rotation in chain orientation, analogous to banding in spherulites.

1. Introduction

For the past two years, a joint programme of research between Leeds and Reading Universities has been concerned with studying the structural changes that occur during the process of hot compaction of polymeric fibres. The initial studies have concentrated on the compaction of high-modulus polyethylene fibres produced by the melt-spinning/hot-drawing route. This fibre is easily compacted allowing a detailed study of the nature of the compaction process to be carried out, while also allowing detailed analysis of the structure of the fibres to be pursued.

In the case of polyethylene fibres, the compaction process offers a route to high-stiffness, large-section, composite materials which cannot easily be made any other way. Conventional epoxy-based polyethylene fibre-reinforced composites require expensive surface treatments [1], and are also composed of two different materials. Polyethylene/polyethylene composites, with low-melting, low-density polyethylene as the matrix, are comparatively easily made, e.g. [2], but have the disadvantages of the lower density component. To make composites with high-density polyethylene (HDPE) with its superior mechanical properties, much more precise temperature control is required, close to 138 °C, above the melting point of bulk HDPE but below the onset of melting of gel-spun fibres [3, 4].

A novel and singular approach has been to compact only the fibres themselves at a temperature where they are beginning to melt. Two recent papers [5, 6] have described how certain melt-spun high-modulus polyethylene fibres can be compacted into large-section products with exceptional mechanical properties (see also [7]). Under optimal conditions, some 90% of the tensile modulus of the original fibres can be retained, while the transverse strength developed is such that failure occurs within, rather than between, fibres. Morphological examination of such optimally compacted materials showed not only that just sufficient material had melted and recrystallized to fill the gaps between the fibres, but also identified defective regions

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within them. Further investigations have concerned products compacted at temperatures above and below the optimum. In this paper we report the general phenomena which occur under these conditions and their implications, while a further paper will consider the significance of differential melting phenomena observed at the highest compaction temperatures studied.

2. Experimental procedure

Melt-spun and hot-drawn high-modulus polyethylene ($\bar{M}_w = 150\,000$, $\bar{M}_w/\bar{M}_n = 8.8$) fibres produced by SNIA (trade name TENFOR) were used. The salient features of the compaction procedure, which has been described in detail previously [5], are that multifilament yarns of fibres, nominally 10 µm diameter, are arranged unidirectionally in a matched metal mould. This is heated to the compaction temperature (in the range 134–142 °C) under the moderate pressure of 0.7 MPa (100 p.s.i.), then a higher pressure of 21 MPa (3000 p.s.i.) is imposed. Heaters are switched off after 10 s, and the mould cooled to below 110 °C at $\sim 3\ \mathrm{K\,min^{-1}}$ while maintaining high pressure. The compact is then removed from the press and cooled to room temperature.

In this work, compacted samples were examined by scanning electron microscopy after being cut open with the diamond knife of a microtome; in most cases sections transverse to fibres were examined but a smaller number of longitudinal sections was also studied. These were then etched as in previous work [6]: transverse sections required a reagent without water while longitudinal sections need one with added water to reveal the salient detail. The etched surfaces were coated with gold and examined under a Philips 515 scanning electron microscope.

3. Results

It was shown in previous work [5] that increasing the compaction temperature within the melting range of the fibres caused an increasing proportion of the sample to melt and recrystallize. At 138 °C, the proportion of 9% is close to that of the space between close-packed identical cylinders. This is the temperature giving best mechanical properties; in this paper, by examining the products of a range of compaction temperatures we add to the understanding of the structure/property relationships.

Fig. 1 shows a cross-section of fibres after compaction at 134 °C. A striking feature is the tendency to polygonalization, i.e. for contacting fibres to have developed extensive mutual interfaces as opposed to the linear (point in plan) contacts of hard cylinders; this is the behaviour of soft fibres. If contacting fibres are equally soft, their interface should be planar and contribute to a hexagonal network, in-plan view. But if fibres are mechanically unequal, then the harder ones will tend to penetrate the softer ones, so that their interface will be convex outwards to the harder fibre. Both features are visible in Fig. 1: fibre A remains nearly circular in cross-section having penetrated into softer neighbours, while fibre B has achieved a nearly hexagonal outline.

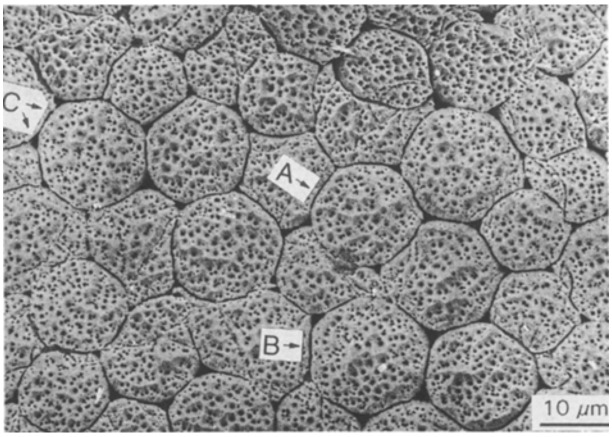

Figure 1 Transverse section of fibres compacted at 134 °C.

The small amount of melting which has occurred has left practically all the "triangular" interstices between fibres empty. Where there is evidence for melting and recrystallization, it is in the contact zones between fibres (C). This is an indication of melting point being lowered by deformation rather than the existence of a lower melting surface skin, in agreement with previous inferences [6]. Had there been a low-melting skin, its presence would have been evident in the interstices. Empty interstices point rather to the role of physical factors in melting.

Within the cross-section of each fibre, dark spots identify the defective regions; these have been deeply etched and have become the centres of craters in the etched surface. Fig. 1 shows clearly that there is a non-uniform distribution in these fibres with smaller spots concentrated towards their periphery. Lines associated with deformation to achieve dense packing also appear dark and often link a series of dark spots.

The principal change observable in going to the slightly higher compaction temperature of 136 °C, Fig. 2, is that unfilled interstices are now in the minority. In addition, some are partly filled (e.g. A) with a central dark area within grey contrast. The contact zones between the fibres also do not appear to be so heavily etched. This has the consequence, in parallel work for transmission electron microscopy, that whereas the contact zones are effectively continuous at 136 °C, and are readily replicated, those formed at 134 °C are so deeply etched, that their replication has not been possible.

When compaction is at 138 °C, all interstices are filled (Fig. 3a) and, on average, they are larger than at 134 °C (Fig. 1); there is corresponding reduction in the width of interfibrillar interfaces, reflecting less deformation of the fibres. The concentration of small spots (defective regions) in peripheral regions is much reduced and, on occasion, as in the centre of Fig. 3b, softer regions are evident which have been near to melting (because of a lower melting temperature than their neighbours). Surrounding fibres have mostly retained near-circular profiles while, significantly, the number of defective regions and their craters has clearly fallen during the compaction procedure.

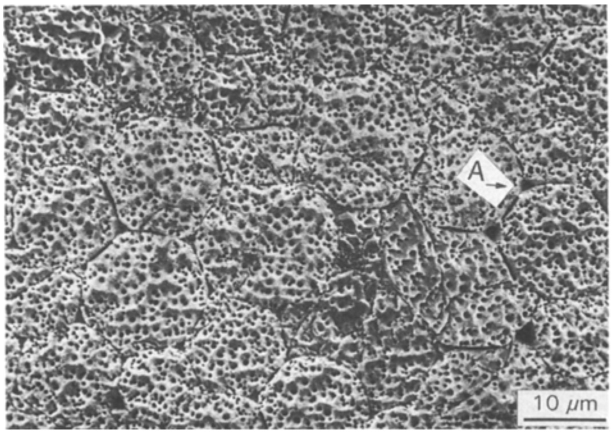

Figure 2 Transverse section of fibres compacted at 136 °C.

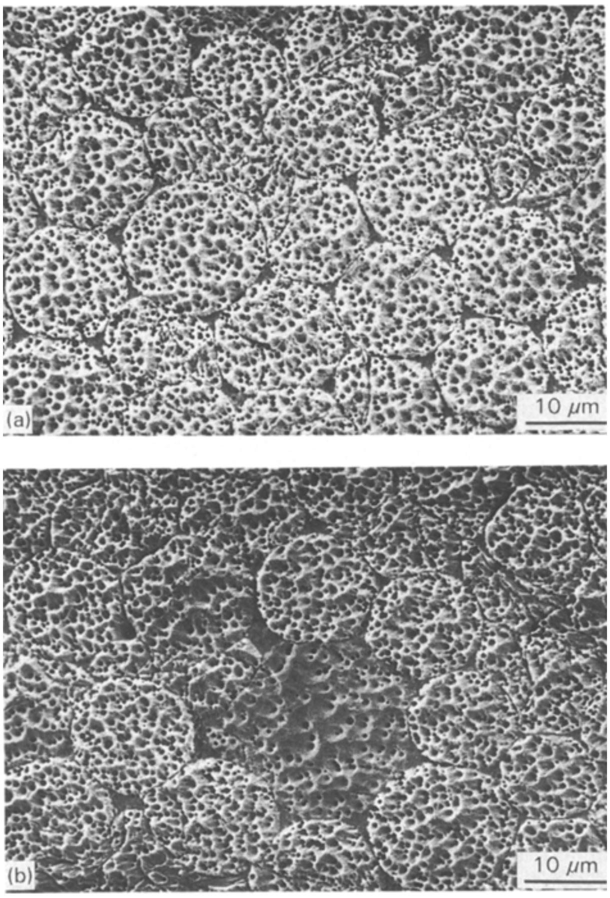

Figure 3 Fibres compacted at 138 °C: (a) typical region, (b) a softer region.

For compaction at 140 °C, the extent of melting is such that most fibres have a more-or-less circular outline (Fig. 4a); interfibrillar contacts are further reduced, being zero in some instances, with many neighbouring fibres now being separated by recrystallized regions. This is behaviour expected of hard cylinders in a soft matrix, but linear traces of deformation can also be seen, often linking sites where fibres are in contact (Fig. 4b). In a slightly oblique view (Fig. 4c) such features are emphasized, as is the extent to which defective regions and recrystallized material have been preferentially etched.

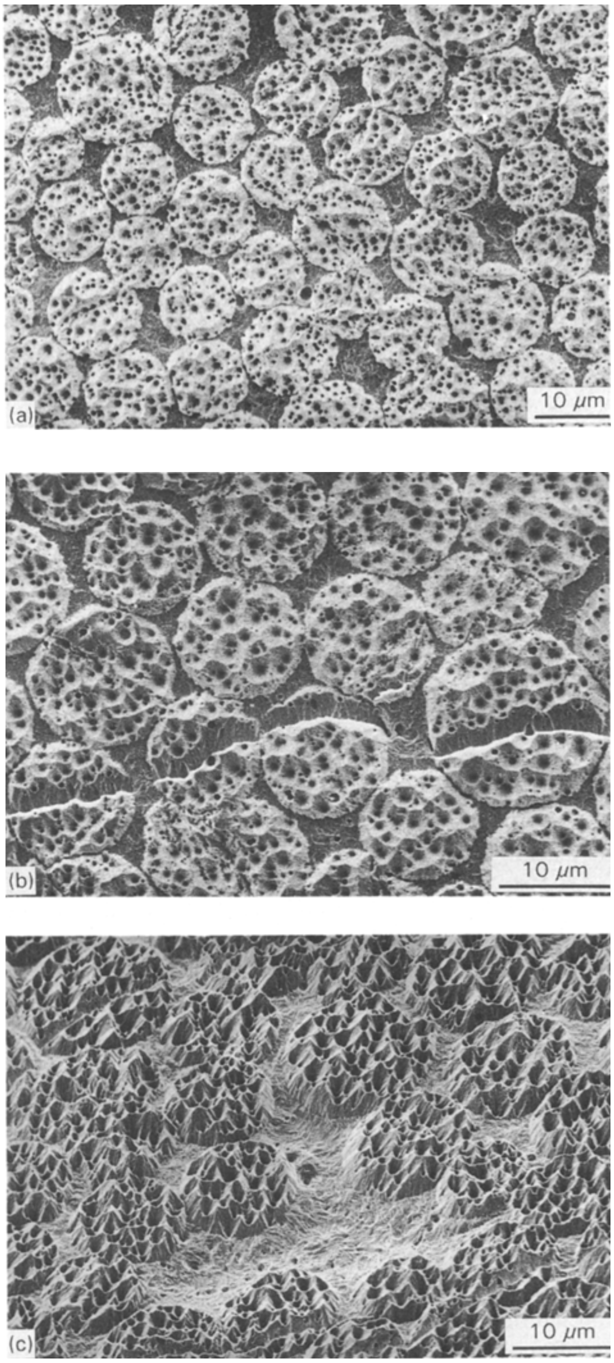

Figure 4 Fibres compacted at 140 °C: (a) typical region, (b) a "fault-line" of deformation, (c) oblique view showing different depths of etching.

At the higher temperatures investigated, the specimens are liable to be non-uniform because of differential melting. Fig. 5a shows an example in which the number of residual fibres is much less near the surface of a compacted sheet compared to its interior. Fig. 5b illustrates a region of this sample with high fibre density after compaction at 142 °C. Nearly all fibres are now circular in profile indicating that their interface with the melt has advanced uniformly inwards, leading to a reduction in the average fibre diameter by about 25%, compared to the original material.

Differential melting phenomena are often encountered within compacted materials; one such is featured in Fig. 6. At low magnification, Fig. 6a, two patches of recrystallized material stand out in a longitudinal

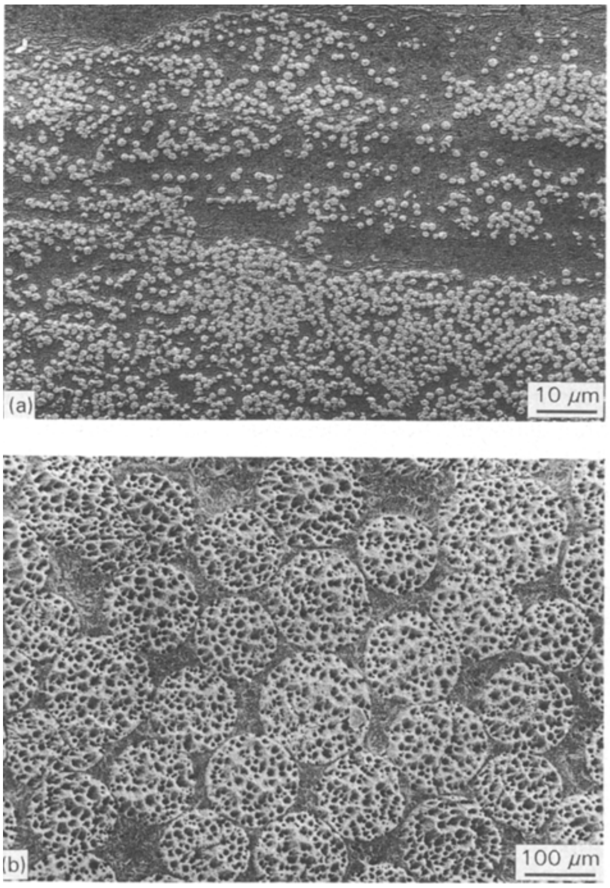

Figure 5 Fibres compacted at 142 °C showing: (a) the decrease in residual fibres near the specimen surface (top), and (b) a typical interior region of higher fibre density.

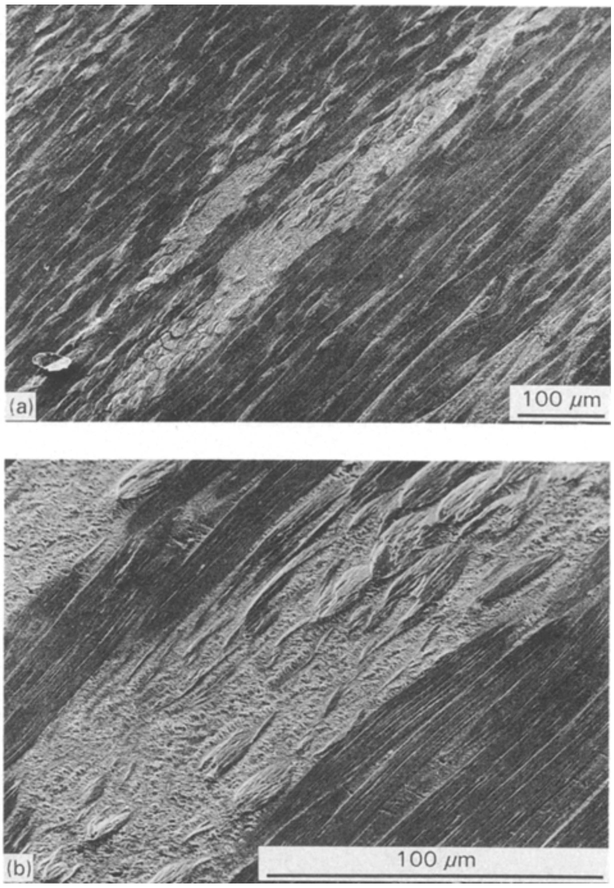

Figure 6 Longitudinal section of fibres compacted at 142 °C, revealing earlier melting (and recrystallization) of fibres inclined to the plane of the section: (a) low magnification, (b) medium magnification.

section. Higher magnification, Fig. 6b, shows that these are associated with a number of elliptical sections, indicative of fibres inclined to the plane of the paper [6]. The inclination of chain axes to the page in these regions is confirmed by the recrystallized lamellae which protrude from the etched surface of the sample. Also present are residual linear morphologies within a recrystallized matrix, a phenomenon discussed in detail in the following paper.

On the adjacent regions in Fig. 6a and b showing long lengths of fibre, note the etched grooves parallel to the axis; these are defective regions giving rise to the craters in transverse sections. Between the fibres the lamellar, recrystallized, component of the sample is present, displaying an occasional inter-lamellar groove where the etchant has penetrated more deeply. The space adjacent to the ends of fibres is also filled with lamellae. That there is such space is consistent with differential retraction which would be expected to accompany differential melting.

Finally, in Fig. 7, we show how recrystallization occurs in regions where the volume fraction of melt is high. There is nucleation on the surface of the fibres, of lamellae sharing the chain-axis orientation of the fibre, thereby creating a giant row nucleus. The recrystallization temperature, in this instance, is low enough for banding to develop, which then reproduces the contours of the nucleating surface (Fig. 7a). The higher magnification of Fig. 7b not only confirms that lamellae start growing in the plane normal to the fibre axis and sharing its chain direction, but also shows the origin of banded relief. This occurs because lamellae are etched less when their resistant fold surfaces are exposed, than when their edges are presented to the etchant. In addition, craters are visible, etched within the wholly recrystallized material, indicating the presence of more-penetrable regions there also.

4. Discussion

4.1. General features

This exploration of compaction at non-optimal temperatures has confirmed and amplified the conclusions drawn previously [5, 6] concerning the compaction process and the microstructure (defective regions) of the constituent fibres. In broad terms, the increasing proportion of molten polymer which higher temperatures produce acts to distribute the pressure more uniformly between the individual fibres. At the highest temperature, those fibres which have survived will have become smaller but will also be surrounded by melt so that they will remain as cylinders, with circular profiles, when subject to compressive stress. Conversely, the lower limit of compaction is when there is little or no molten polymer but the raised temperature has induced softness so that the application of pressure compresses the fibres into a near-solid mass.

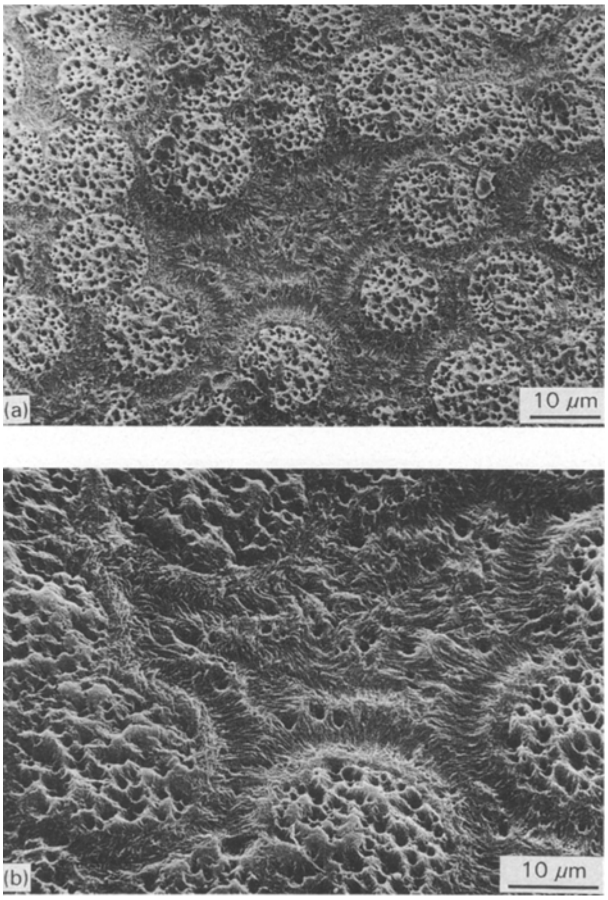

Figure 7 Fibres compacted at 142 °C, showing large regions of recrystallized melt: (a) medium magnification showing banding, (b) higher magnification, tilted to show details of etching.

This circumstance produces hexagonal arrays for sixfold co-ordination with appropriate distortion for different co-ordination numbers. The situation observed at 134 °C (Fig. 1) is approximately this, with just small interstitial voids remaining between the compacted fibres. When there is melting at this temperature it is virtually confined to the contact zones of fibres confirming previous deductions [6] that there is no low-melting skin to the fibres and that causes of differential melting are physical in origin – in this case deformation.

The morphology which produces optimal mechanical properties is that which just fills all the voids between the fibres with molten recrystallized polymer. It was previously shown that this corresponds to some 9% of the original polymer having melted [1], a figure which is close to the 10% volume fraction enclosed between congruent hard close-packed cylinders, and a similar figure for hard cylinders, even if they are not all of equal diameter. The change of shape to which fibres have been subjected has thus not markedly changed the interstitial volume at 138 °C. However, the evidence of Figs 1 and 2, respectively, is that it has been reduced at 136 °C and markedly so at 134 °C, when the fibres have become quasi-hexagonal; even so, these regions have been incompletely filled. This indicates minimal melting, a factor which will be responsible also for the poor continuity in the contact zones between fibres, already referred to, and the grossly inferior mechanical connectivity of the 134 °C specimens.

One of the features of Figs 1 and 2 is the division between hard and soft fibres based on the convexity of their interface. There is no obvious correlation of this division with other parameters, especially the fibre diameter. For example, that the greater extent of melting present at the higher compaction temperatures leaves fibres still cylindrical shows that melting has advanced at a uniform rate into the fibrous material. The fact that, for example in Fig. 4a, there is still a substantial disparity of fibre diameters, indicates that there is no clear correlation of melting point and fibre diameter. Nevertheless, one must ask why fibres do have different diameters when they have all been extruded through orifices of the same diameter. If this is due to different degrees of retraction, and to occur at constant volume then, on thermodynamic grounds, one might expect the larger diameter fibres to be more retracted (and therefore less extended) with a lower melting point and hence to be softer at a given temperature. There does not seem to be a simple correlation and it may be that fibre length is affecting the behaviour. A second consideration is that if two fibres which are in initial contact deform by the same displacement this will give a higher strain to the smaller diameter fibre which should lower its melting point more, although the effects of strain energy are expected to be small compared to those due to constrained molecular conformation. Nevertheless, the observations of earlier melting of fibres inclined to the general direction (Fig. 6) does provide some support for the concept of differential retraction because of the weaker constraints such inclined bundles of fibres must experience.

Clearly, optimal compaction is occurring at a temperature just below that at which differential melting becomes prominent leading, as in the case of Fig. 5a, to gross variations in the local volume fraction of melt (and recrystallized material). At the optimum temperature, the interstices are still small enough for the recrystallized material to be effectively continuous crystallographically with the fibres. At the higher temperatures, the morphological development of the recrystallized polymer, such as the cylindrulitic banding displayed in Fig. 7, may lead to interstitial material with its *c*-axis perpendicular to the fibre axis, a factor which must contribute to the reduced stiffness at high compaction temperatures.

4.2. Fibrillar defects

The conspicuous craters present in etched cross-sections of compacted fibres were previously inferred [6] to mark the emergence (at the central black spot) of linear defective regions within the fibre with the craters themselves being an artefact of the etching process and due to the different rates of attack along and perpendicular to the axis. As can be seen by inspection of Fig. 4c, the fibres etch more slowly than the lamellar material in directions parallel to the fibre axis. The slope of the crater then represents the vector sum of the two rates of attack parallel and perpendicular to this axis. The defects themselves can be seen in longitudinal sections (Fig. 6b) while the predominance of small ones in the periphery of fibres compacted at 134 °C (Fig. 1) is noteworthy. It appears from Figs 2 and 3, for which there is little more melting than in Fig. 1, that such small defects tend to have healed at the higher temperatures. (At still higher temperatures it might be argued that their absence is simply because the outer regions of the fibre have melted away.) The concept of healing is a plausible one, not least because of the considerable molecular motions present as the melting point is approached and the applied pressure, both of which will tend to remove regions of lower density. Finally, in Fig. 7 the observation of cylindrical nucleation around the residual core of fibres reveals a profitable route to studying crystallization which bears significantly on fundamental aspects of behaviour. The growth from such nuclei possesses initially a common orientation, unlike that of spherulites, and so provides a much better system for studying and quantifying the way in which this orientation is lost in developing its space-filling character. This is an aspect which will be reported elsewhere.

5. Conclusions

1. Optimal compaction occurs at the temperature at which all interstitial voids are just filled by recrystallized polymer.
2. At sub-optimal temperatures, compaction causes fibres to become quasi-polygonal in cross-section. Higher temperatures, giving increasing proportions of molten polymer which distributes the pressure more evenly between the fibres, tend increasingly to leave cross-sections circular.
3. The absence of a low-melting skin region is confirmed; differential melting effects have physical origins.
4. The presence of longitudinal defects within the fibres has been confirmed, and significant differences in their distribution observed.

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Received 17 January
and accepted 21 March 1994