JOURNAL OF MATERIALS SCIENCE 30 (1995) 601–606

Differential melting in compacted high-modulus melt-spun polyethylene fibres

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The compaction of high-modulus melt-spun polyethylene fibres has been investigated for compaction temperatures above the optimum. After such treatment the specimens are liable to be non-uniform because of differential melting. Individual compacted fibres are observed to melt not only from the outside inwards, but also in certain internal regions, depending upon the availability of local free volume. The regions of different stability have been identified and inferences drawn concerning the structure of the initial fibres. It is suggested in particular that the longitudinal regions of deficit density (which exhibit cratering in transverse sections and melt before their surroundings) are a result of initial crystallization occurring within a rigid framework inside the fibre, possibly nucleated on a strained molecular network. The presence of banded recrystallization around residual fibres demonstrates that this phenomenon develops via interaction of neighbouring lamellae as they grow.

1. Introduction

Previous papers [1–3] have described how high-modulus melt-spun polyethylene fibres can be compacted into large-section samples while preserving their exceptional mechanical properties. This is achieved by heat treatment under moderate pressure with the best properties being achieved when just sufficient polymer melts and recrystallizes to fill the interfibrillar voids. The preparation, properties and morphology of such optimal materials were investigated first [1, 2]. Subsequently, the morphologies resulting from other compaction temperatures, both below and above the optimum, have been examined leading to a greater understanding of the underlying physical processes [3]. In this paper we examine the consequences of compaction at temperatures as high as 142 °C and, in particular, the differential melting of the polyethylene fibres which then occurs. The results are of especial relevance to the substructure within fibres and its origin.

2. Experimental procedure

The materials and compaction procedures are the same as those described previously [1–3]. Fibres, nominally 10 μm diameter, of hot-drawn high-modulus melt-spun polyethylene ($\bar{M}_w = 150\,000$, $\bar{M}_w/\bar{M}_n = 8.8$) trade name TENFOR, manufactured by SNIA Fibre, Italy, have been compacted in the temperature range 134–142 °C. Multi-filament yarns, arranged unidirectionally in a matched mould, were heated to the compaction temperature under a holding pressure of 0.7 MPa (100 p.s.i.). Once at temperature, the higher pressure 21 MPa (3000 p.s.i.) was imposed and the heaters switched off after 10 s. The mould was cooled at $\sim 3\ K\ min^{-1}$, to below 110 °C under pressure, then removed from the press and cooled to room temperature.

Fibre composite specimens were cut open with a diamond knife on a microtome either normal or parallel to the mean fibre axis. The surfaces thus prepared were etched with permanganic reagents, as detailed previously [2]. In some cases, they were examined by scanning electron microscopy (SEM) after gold coating. But, for the most part, replicas of the etched surfaces were taken by a two-stage process using cellulose acetate softened with acetone. Once dried, the cellulose acetate films were coated obliquely with tantalum/tungsten and backed with carbon; the cellulose acetate was then dissolved away to leave the final replica. Unless stated otherwise, the photographs are of such replicas examined in the transmission electron microscope and refer to compaction at 142 °C.

3. Results

The observations in this paper extend those previously reported within the context of an increasing

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proportion of the initial fibres melting and subsequently recrystallizing as the compaction temperature rises. For these Tenfor fibres the melting range is about ten degrees, even under constrained conditions, implying that different regions have different thermal stabilities or, at least, melt at different times in the differential scanning calorimeter. The principal aim of the work reported in this paper is to identify the regions of different stability and hence to draw inferences concerning the structure of the initial fibres.

It was shown in the preceding paper [3] that (with some simplification) at first the increasing proportion of molten material with rising compaction temperature is mostly achieved by the solid/melt interface moving smoothly inwards into the fibres whose diameters thereby decrease. However, one also observes that, for compaction at 142 °C, a significant proportion of fibres has melted entirely and that many others have melted partly and non-uniformly leaving an irregular cross-section. For example, Fig. 1 shows an area in which most fibres have circular sections within a recrystallized matrix. However, one fibre has all but disappeared leaving just an outer crescent (A) while a second has been melted and recrystallized (B). As a second example, in Fig. 2 there is a fibre which has retained a circular cross-section down to an unusually small diameter. It has acted as a nucleus for subsequent recrystallization in which new growth has started on the fibre as substrate and shares its chain orientation initially but then deviates systematically to develop banding concentric with the fibre.

Within the fibre itself are circular regions of recrystallized lamellae. These are a development of a phenomenon identified previously for compaction at 138 °C [2]. It may be seen also in longitudinal sections as in Fig. 3 where there are both wide regions between fibres (A), and narrow regions within fibres (B) which have melted and recrystallized before their surroundings (the diffuse dark smears on the picture are from residual replicating material, which could not be removed completely, lest the replica fold up and detach from the grid). The identification of B as lying within a fibre is based partly on lateral dimensions, partly on consideration of how a cross-section, for example, Fig. 1, would appear, and partly from anticipation of the definitive assignment shown in Fig. 5b.

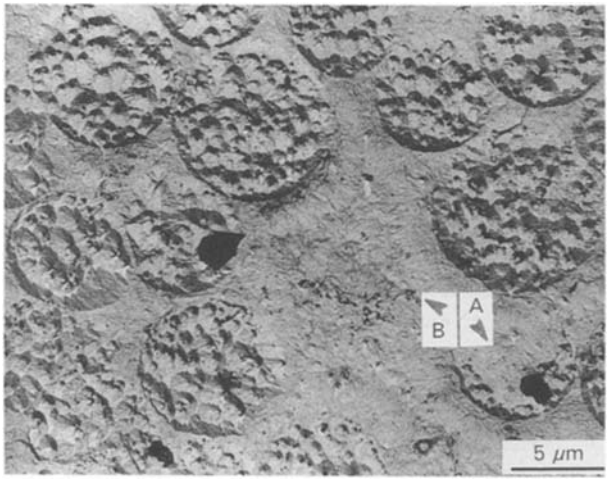

Figure 1 Etched transverse section of fibres compacted at 142 °C within a recrystallized matrix. That at A has almost melted, while one previously present at B has melted and recrystallized.

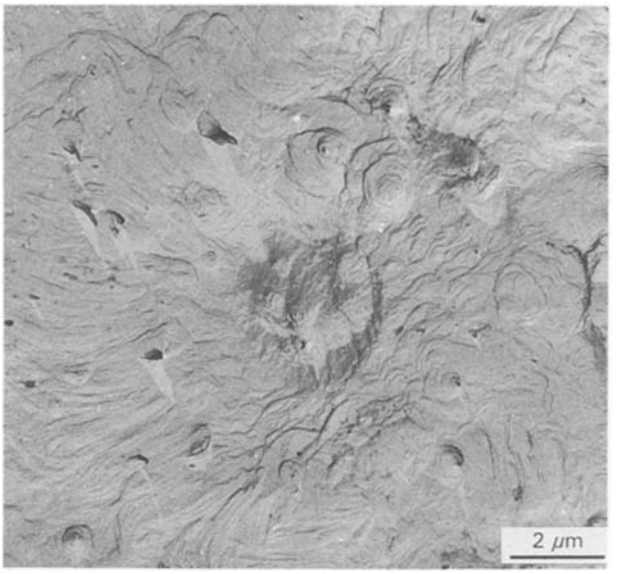

Figure 2 Reduced diameter core of a fibre which has mostly melted at 142 °C but has retained a circular cross-section. Note the regions within which there has been internal melting and also the external banded regrowth.

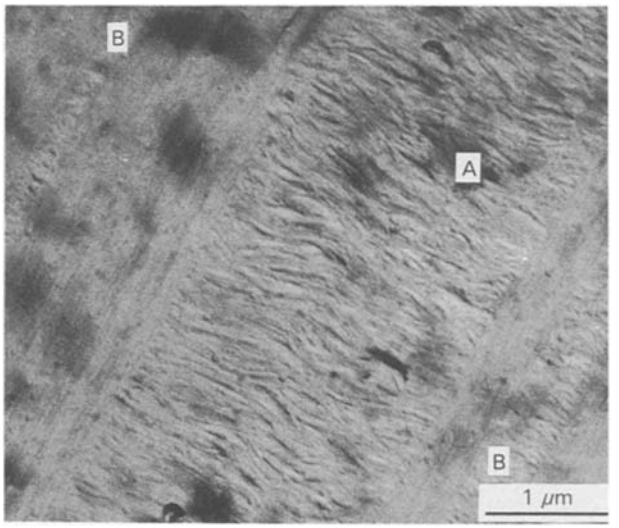

Figure 3 Etched longitudinal section, after compaction at 142 °C, of two fibres showing recrystallized lamellae between and within the fibres (See text for key to A and B).

With a higher temperature of compaction it would be expected that more of these internal regions would have melted. This is the case and is well illustrated in Fig. 4. The transverse section of Fig. 4a illustrates the cratered surface of a fibre; notice that many craters were filled with lamellar material of the kind etching has exposed. Fig. 4a and the detail of Fig. 4b not only show that the lamellae are flat-on, i.e. have the same *c*-axis orientation as the fibre, but also that, in certain cases, this lamellar material is itself cratered with a central deeply etched hole. This is an important observation showing that there are three levels of

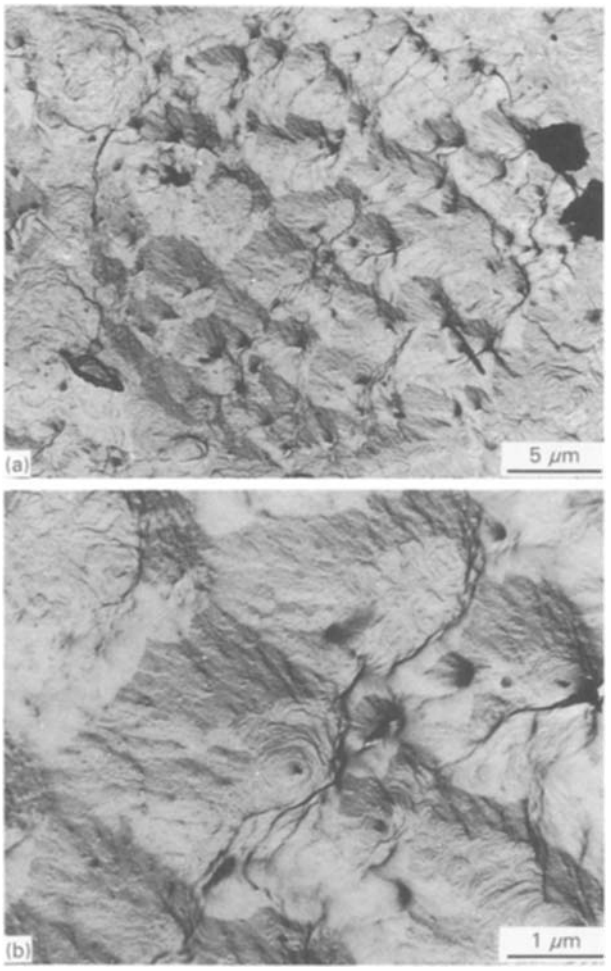

Figure 4 (a) Etched craters filled with lamellar material exposed in fibres compacted at 142 °C. (b) Detail showing the etched cavity within lamellae at the centre of a crater.

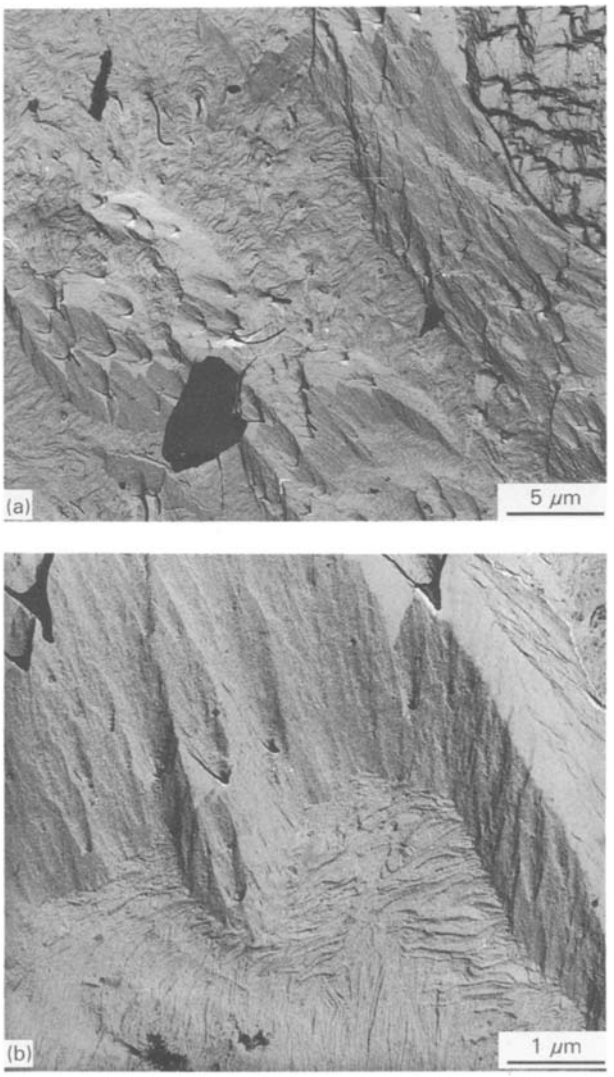

Figure 5 (a) Oblique view of etched fibres with irregular internal melting after compaction at 142 °C. (b) Detail revealing etched craters within an original fibre, lamellar recrystallization nucleating on residual fibrous material and, at the bottom, row nucleation of shish-kebab morphologies.

resistance to etching: the fibre, the lamellar material and its core as reflected in the final contours of what, before etching, was a flat surface.

Internal melting is shown in another perspective in Fig. 5. None of the fibres in Fig. 5a has retained its circular cross-section; all have melted non-uniformly. Moreover, the fibre in the upper right corner manifestly has a different orientation from the others being nearly normal to the page, but its boundary with its neighbours is not etched very deeply showing that a strong union has developed which may be of significance for the prospects of manufacturing compacts with crossed fibres. The more highly magnified detail of Fig. 5b has craters in the rear wall (of the lowest fibre in Fig. 5a) showing internal transverse lamellae and central holes identified by residual replicating material. On the right-hand side, the wall has nucleated lamellar growth which has fixed crystallography consistent with a common *c*-orientation with the fibre and a growth direction of *b*. At the bottom of the figure the recrystallized lamellae are differently orientated, with their plane more or less perpendicular to the page. These have formed on row nuclei and are evidence of recrystallization under strain in this location. It is plausible that the strain of the central (row) nucleus is a consequence of a continuous molecular network between its unmolten extremities. Crystallization at either end would place the network under tensile strain in a manner analogous to the intercrystalline links reported in other circumstances [4]. Such an oriented network could then nucleate transverse lamellae, sharing the same chain orientation, in the manner observed.

Etched craters indicate the presence of more penetrable, i.e. defective regions, both within fibres, as previously reported, but also here in lamellar recrystallized material, as we now illustrate. In Fig. 6a they occur in triangular interstices (A) and along the boundary between two fibres following compaction at 136 °C, conditions in which there is insufficient polymer melted to fill all interfibrillar cavities [3]. In Fig. 6b there are craters within the cushion-shaped interstice formed by the merging and enlarging of two triangular precursors when the temperature was taken to 142 °C. In Fig. 7, in a field covering an area in which only a crescent remains of one fibre (A) there are several craters, again highlighted by residual replicating material, a series of which (B) is located at what appears to be the meeting of two recrystallization

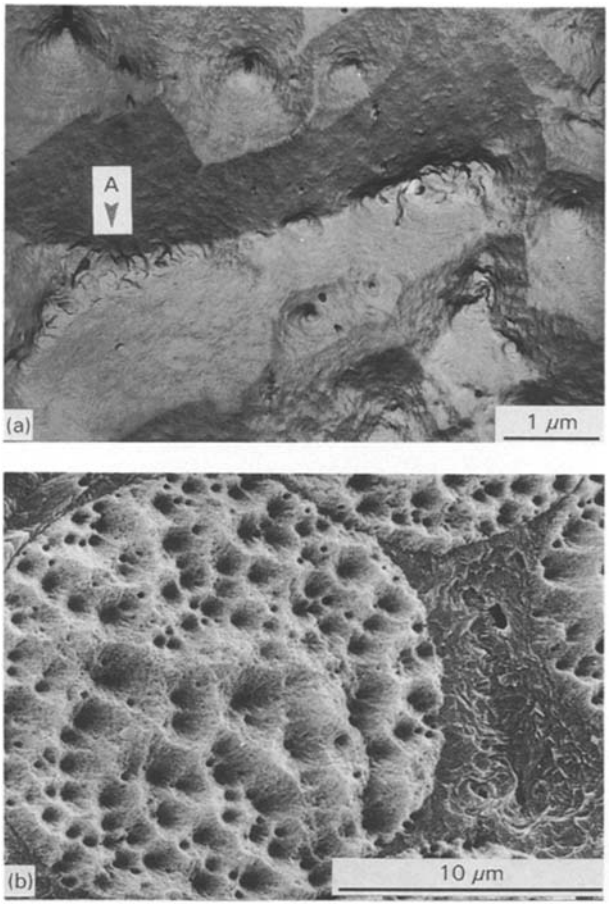

Figure 6 (a) Etched craters in interstices between fibres compacted at 136 °C. (b) Etched craters within fibres and in the large, filled interstice on the right, following compaction at 142 °C (scanning electron micrograph).

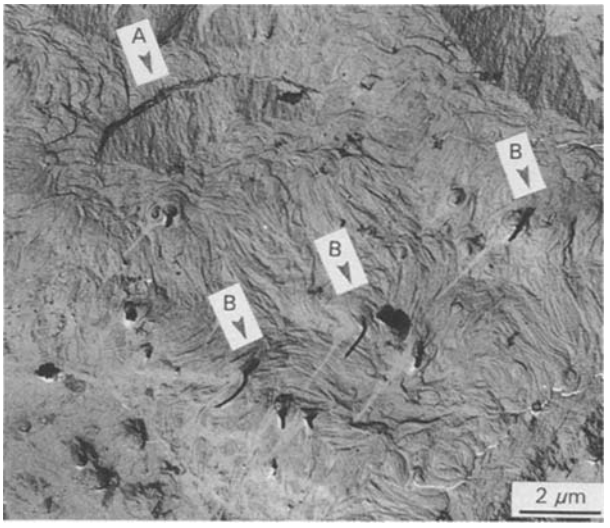

Figure 7 Etched craters identified by unremoved replicating material, surrounding a residual crescent of original fibre, at A, is concentrated where growth fronts have met, below B.

fronts although other prominent craters have no such obvious attribution. This point is emphasized by Fig. 8a in which there are no craters along the well-defined front where recrystallized growth from two fibres (at left and top right) has met.

The origin of recrystallized growth at the interface of a fibre is revealed in Fig. 8b which is notable for the

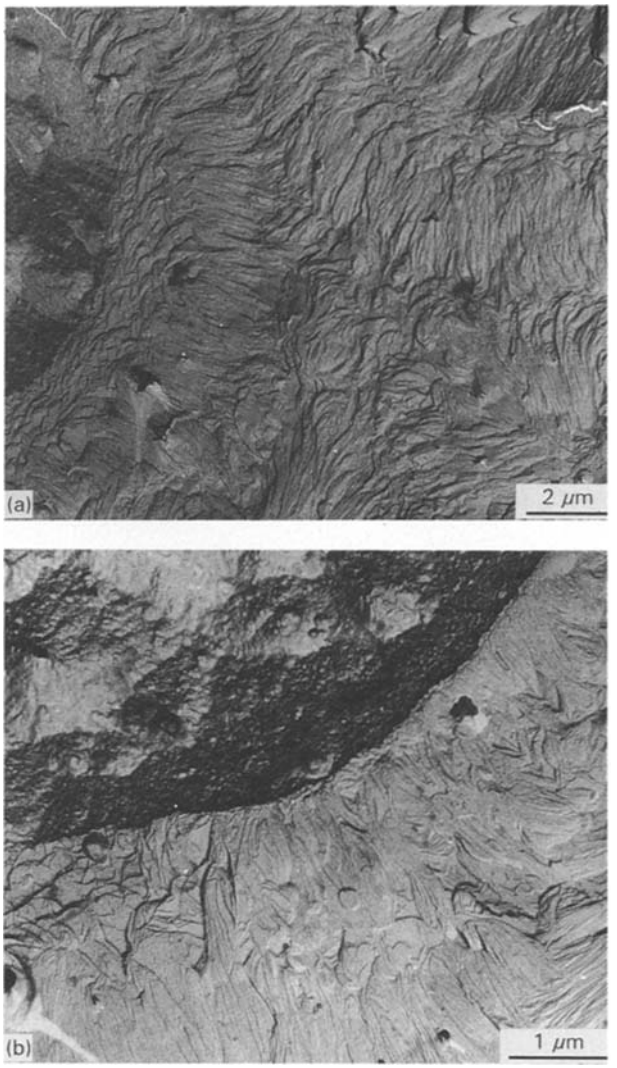

Figure 8 (a) Growth fronts of recrystallized lamellae, for compaction at 142 °C, which have fused without yielding craters on etching. (b) Detail of nucleation of oriented transcrystalline growth at a fibre surface leading to banded growth in compaction at 142 °C.

large number of small lamellae nucleated at the interface, many of which have not propagated significantly. This is presumably a consequence of kinetic competition whereby the fastest radial growth will be achieved by those lamellae oriented with *b* radial; others will fail to advance significantly.

4. Discussion

The principal point to be discussed is the significance of the textural inhomogeneities revealed by permanganic etching within compacted fibres. In further studies, the same features have been found within the original Tenfor fibres and various others before compaction. This morphology is, therefore, a matter of some generality in polymer fibres; the list includes some made from polypropylene and poly(ethylene terephthalate).

These regions which lie parallel to the fibre axis sometimes for tens of micrometres [3], and typically have diameters under 1 μm, are identified by two properties: first that they are more readily etched, leading to craters in transverse section and second that they have a propensity for earlier melting than

their surroundings. It was inferred previously that the regions must, therefore, have lower density which would both aid the penetration of the etchant and promote melting [2].

We base our discussion on the premise that in an oriented crystalline polymer system, the melting point will be raised, inasmuch as the melt has its entropy lowered and its Gibbs function raised, by being unable to relax to a random state. The actual melting point will depend on the extent to which relaxation is possible as is readily demonstrated by the melting point of a fibre being higher when it is held at constant length than when it is allowed to contract. The availability of free volume will, therefore, promote melting by facilitating relaxation. It follows that a constrained fibre would be expected to melt from the outside in, because initially free volume would only become available at the surface. When there are regions which have melted inside fibres before their surroundings one must also look to the availability of local free volume.

This argument has three relevant corollaries. One is that melting of the surface first is not of itself evidence for a lower melting skin: indeed such a skin is demonstrably absent in the fibres of these experiments [3]. The second is that there is no implication that the outside of the fibre is inherently lower melting in the sense of having a higher chemical potential than the interior, merely that it is able to relax earlier. The third is that if, during the compaction procedure individual fibres are able to relax and retract because of lower constraints, which could include being inclined to the majority of fibres, then they would lower their melting point. This factor is consistent with gross non-uniformity in melting, with much lower residual fibre density in some areas than others, as observed in the previous paper [3]. Local differences in the thermodynamic melting point are more likely to be involved when only portions of fibres remain, as at A in Fig. 1, where part of the outside of the fibre is the last to melt.

The cratering which etching has revealed and developed in these fibres is a new phenomenon and concerns the nature of oriented fibrous polymers. It is not found in samples crystallized from a quiescent melt and it is much more pronounced than preferential etching associated with crystal discontinuities, notably giant screw dislocations. This is evident in Fig. 2 where both craters and dislocations are present.

Cratering is associated principally with restricted internal regions of fibres, as is shown particularly clearly in Fig. 5b. That the phenomenon recurs, albeit with a different etched profile, in recrystallized lamellae (e.g. Fig. 4b) is a strong pointer to its origin. As Fig. 5b shows, internal lamellar growth nucleates on the residual walls then proceeds inwards. If there is insufficient polymer to fill the available space at crystalline density, a region of weakness and lower density (ultimately perhaps even a void) will be formed at the centre. Analogous behaviour is well known to be responsible for hollow pellets of polymer chip in which (chilled) crystallization starts at the outside, creating a deficit of material at the centre. A second analogue is that of the last regions to crystallize between spherulites where the exhaustion of the supply of molten polymer leads to weakness, sometimes voids, with significant consequences for subsequent mechanical behaviour, e.g. in tensile drawing [5–7].

In developing this argument for compacted fibres, one must have regard to the degree of isolation of the recrystallized regions. Those that are wholly confined within fibres will be unable to acquire more material so that the original mass deficit will remain, but may well be more concentrated at the centre, depending on relative densities and morphologies. On the other hand, if the region is not isolated then the initial volume defect may well simply be transmitted to the outside of the sample. The illustrations support this diagnosis.

In Figs 4b and 5b cratering is present in isolated internal regions within rigid confines for compaction at 142 °C. However, in Fig. 6, craters have been formed in etched interstitial material formed at 136 °C whereas previous experience showed no such effect for compaction at 138 °C. This is readily understood in terms of the smaller amount of material rendered molten at 136 °C, with some interstices remaining unfilled [3]. If, in a particular interstice, there is a shortage of material to fill it with recrystallized lamellae, the formation of craters on etching would be anticipated. This consideration appears to apply also in Fig. 6b. Notwithstanding the high treatment temperature, there is an indication in what appears to be an isolated, well-confined region, of greater depth of etching where growth fronts have met in addition to the craters. In general, one would expect that for recrystallization within an isolated rigidly bounded volume, any deficit of material would be concentrated where growth fronts have met, as in Fig. 7. When there is no such phenomenon (e.g. Fig. 8) and the morphology parallels that for crystallization of a quiescent melt, the initial deficit of material has presumably been transmitted to the outside and the sample contracted as a whole.

By extension of the above argument, the origin of the defective regions themselves would therefore lie in the initial crystallization being nucleated on surrounds providing a rigid framework which could neither relax to accommodate the density deficit created by crystallization nor provide material to fill it. The precise details involved, such as the surface zone of small craters in Tenfor fibres [3], will depend on the particular manufacturing process. Nevertheless, it is likely that the rigid framework would be sited approximately at the intersections of the etched craters because the linear rate of etching would tend to reverse the pattern of growth back towards its origins.

In Figs 2, 5b and 8a there are examples of growth nucleated on the outer surfaces of residual fibres. Fig. 8b shows details of these nuclei and, in particular, many small lamellae which have failed to grow far beyond the interface. This is entirely reasonable. At the surface of a fibre which has c as an axis of rotation, the orientation of the a- and b-axes will vary randomly in the transverse plane, so that nuclei grown from them will be similarly random. However, the fastest growing direction in polyethylene is the b-axis, which thereby becomes the radial direction of spherulites. It

follows that only those nuclei oriented with b radial to the fibre will extend significantly as growth proceeds outwards. In Fig. 5b, as explained above, this has given the growth outward from an oriented plane wall, a single crystallographic direction.

There is one further point of fundamental significance. It concerns the co-operative twisting present in banded textures (e.g. Figs 2 and 8a). Banding implies chirality and has, in other work, been related to the presence of isochiral dislocations related to chain tilt in developing spherulites [8, 9]. However, nucleation on fibres advances the argument because in spherulites (which can be idealized to start at zero radius) co-operative banding at finite radius can be extrapolated back to a common precursor. This is no longer the case with fibres of finite diameters: for these there will be multiple nuclei which, a priori, would be expected to produce both possible $\{2\,0\,1\}$ orientations of oblique lamellae, possessing the same b- and c-axes. Both chiral senses of screw dislocation should thus form in equal proportion. That this is not the case and that only one chirality propagates over a given growth front must imply either that there is correlation between nuclei in the original fibre or, more probably, that there is interaction between nucleated growth which suppresses one chirality at the expense of the other. The former possibility is excluded both from the rotational symmetry of individual fibres revealed by X-ray diffraction and by the generality of banding which does not reflect particular circumstances of nucleation. It follows, therefore, that the co-operative phenomenon of banding is developed by interaction of neighbouring lamellae during growth.

5. Conclusions

The investigation of differential melting phenomena in compacted melt-spun polyethylene fibres reported in this paper has emphasized the importance of the physical constraints, especially the availability of free volume, for the melting of an oriented system. Salient conclusions are given below.

1. There are longitudinal regions of lower density within oriented fibres which melt before and recrystallize within the surrounding rigid cage of material. Recrystallization as lamellae, which are nucleated on the surrounding walls, tends to concentrate the density into a narrow central region which may be identified by permanganic etching

2. It is inferred that these density-deficient regions formed in the initial fibres as a consequence of a fixed volume of material, crystallizing within and nucleating on, a rigid confining framework, possibly of entangled molecules. Other evidence for the existence of a stretched molecular network in drawn melt-crystallized polyethylenes comes from measurements of shrinkage, shrinkage force [10] and thermal expansion behaviour [11].

3. The development of concentric bands around individual compacted fibres from multiple nuclei demonstrates that banding results from interaction of neighbouring lamellae during growth.

Acknowledgement

MAK thanks the University of Al-Mansoura, Egypt for financial support.

References

1. P. J. HINE, I. M. WARD, R. H. OLLEY and D. C. BASSETT, *J. Mater. Sci.* **28** (1993) 316.
2. R. H. OLLEY, D. C. BASSETT, P. J. HINE and I. M. WARD, *ibid.* **28** (1993) 1107.
3. M. A. KABEEL, D. C. BASSETT, R. H. OLLEY, P. J. HINE, and I. M. WARD, *ibid.* **29** (1994) 4694.
4. H. D. KEITH, F. J. PADDEN and R. G. VADIMSKY, *J. Appl. Phys.* **37** (1966) 4027.
5. A. GAŁESKI and E. PIÓRKOWSKA, *J. Polym. Sci. Phys. Ed.* **B21** (1983) 1313.
6. Z. BARTCZAK and A. GAŁESKI, *Polymer* **27** (1986) 544.
7. R. H. OLLEY and D. C. BASSETT, *J. Macromol. Sci. Phys.* **B33** (1994) 211.
8. D. C. BASSETT, R. H. OLLEY and I. A. M. AL RAHEIL, *Polymer* **29** (1988) 1539.
9. D. C. BASSETT, *Phil. Trans. R. Soc. A* **348** (1994) 1.
10. G. CAPACCIO, I. M. WARD, *Coll. Polym. Sci.* **46** (1982) 260.
11. G. A. J. ORCHARD, G. R. DAVIES and I. M. WARD, *Polymer* **25** (1984) 1203.

Received 1 June
and accepted 27 July 1994