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Differential initial fold surface ordering: a new morphological indicator

M.I. Abo el Maaty[1], D.C. Bassett*

Department of Physics, J. J. Thomson Physical Laboratory, University of Reading Whiteknights, Reading RG6 6AF, UK

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Abstract

Linear polyethylene crystallized isothermally on linear nuclei from blends with low density, branched polyethylene, cellulates at low concentrations with individual lead lamellae, typically ~1 μm or so apart, advancing at a constant, faster rate than intervening lamellae whose growth is slowed by accumulated segregants. In these circumstances it is found that while initially all lamellae form with poor fold packing in {001} surfaces, only the faster-growing, lead lamellae continue to add molecules in this manner and eventually twist to relieve surface stress. For the majority, remaining lamellae growth slows and they soon adopt and retain {201} surfaces with their preferred fold packing. This not only illustrates how different lamellar components of texture can attain different habits with associated properties according to their respective growth rates, though with dominant lamellae determining the overall morphology, but in doing so, provides a new means to explore the intricacies of macromolecular self-organization.

Keywords: Polyethylene; Initial fold surfaces; Cellulation

1. Introduction

Previous studies using linear nucleation have shown that polyethylene, both linear [1] and linear-low-density [2,3], crystallizes from the melt as lamellae with one of two initial fold surface conditions according to the growth rate. For faster growth, at lower temperatures, lamellae initially have {001} surfaces and are perpendicular to the chain axis *c* and the nucleating fibre. Subsequent re-organization towards the preferred {201} fold surfaces leads to twisting and banded growth. For slower growth, at higher temperatures, lamellae form with and retain ~{201} fold surfaces and are inclined to *c* and the nucleating fibre. The change, which correlates closely with that from Regime I to Regime II kinetics [4], has been interpreted in terms of the time for fold surface packing to order being less or greater than that to add a single, 0.5 nm thick, molecular layer to the growing surface [1–3]. When preferred fold packing is not attained before the next layer is added, fold packing will initially be more poorly organized with fold surfaces rough and prone to subsequent readjustment to a more stable condition. Alternatively, when growth is slow, preferred fold surface packing is adopted from the outset.

The work of this paper is part of a wider investigation of the transition region, where faster growth gives way to slower which reveals that even in a homopolymer, the change from having all lamellae with one initial fold surface condition to the other occurs over a few degrees of crystallization temperature. This study of crystallization from blends with branched, low density, polyethylene was undertaken to establish whether, as the processes whereby fold surfaces order are molecular, the change of initial surface condition always occurs at more or less the same growth rate for the same polymer, i.e. at a lower temperature in a slower-crystallizing blend. This is found to be the case and, as will be reported elsewhere, the growth rate when all the sample has inclined lamellae from the outset decreases consistently with increasing molecular length and branch content.

The particular interest of the present paper is that it identifies conditions of cellulated growth in which the isothermal growth rate varies within the same sample with faster-growing lamellae forming with {001} surfaces then twisting to give an overall banded morphology, within which slower-growing lamellae have {201} surfaces. This is a striking illustration of how different lamellar components

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* Corresponding author. Tel.: 118-378-8540; fax: 118-975-0203.
E-mail address: d.c.bassett@rdg.ac.uk (D.C. Bassett).

[1] On leave from Physical Science Department, Faculty of Engineering, Mansoura University, Mansoura, Egypt.

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of texture may attain different habits—with correspondingly differentiated properties—corresponding to their different growth rates while the overall banded morphology is still determined by the faster-growing lead lamellae. At the same time the link between growth rate and initial fold surface condition is made more precise with the concept of a time for preferred packing of fold surfaces to be achieved thereby supported and strengthened; as mentioned above, work to be published separately shows that, as expected, this time increases for longer and more-branched polyethylene molecules.

2. Experimental

The linear polyethylene homopolymer used in these experiments was Rigidex 140-60 (BP Chemicals) for which $M_w = 91,700; M_n = 14,200$ while the low-density branched polyethylene was Escorene LD100BW (Exxon) with $M_w = 87,000$ and $M_n = 10,000$. Blends of 5 and 20% of the linear polymer in the branched one were prepared by melt-mixing at 160 °C for 30 min, under nitrogen, in a Winkworth twin z-blade mixer, model IZ.

The specimens studied were polyethylene sheets containing, parallel to the sheet, high-melting Tekmilon™ (Mitsui) polyethylene fibres as linear nuclei with approximately circular cross-sections. These allow inspection of the changing morphology with crystallization time both along and transverse to the growth direction, *b*, when the thickness is reduced, by etching, to a controlled depth to reveal appropriate sections through the row structure grown around a nucleating fibre.

In the first stage of preparation, flat discs of the polymer blend, $\sim 20 \times 30\ \text{mm}^2$ across and ~1 mm thick, were obtained by melt pressing, between a clean 13 μm thick Kapton sheet and a microscope slide, on a Kofler hot-bench at 150 °C for 5 min. At the end of this time each disc, with the Kapton sheet and the microscope slide, was quenched by placing on a large metal plate. After removal from the microscope slide it was cut into small squares of ~5 mm side which were stored in labelled jars ready to prepare a fibre/polymer composite as below.

For the examination of diametral sections, i.e. parallel to and passing through the diameter of the nucleating fibre, specimens with about seven Tekmilon™ fibres within the blended polyethylene matrix were prepared between microscope slide and cover slip. Initially the fibres were stacked parallel on a microscope slide to which their ends were lightly adhered with Araldite™ epoxy resin. This slide was inverted and placed carefully on one of the stored square discs already sitting on a cover slip at 130 °C on the Kofler hot bench, applying light pressure to the already-melted disc. The resulting fibre/polymer composite, with microscope slide and cover slip, was then transferred to the Mettler hot stage at 130 °C for 5 min before the temperature was lowered to the required crystallization temperature using a Mettler FP90 central processor. The composite specimen was quenched in ice–water mixture after the selected time of crystallization and carefully removed from the slide and cover slip. Nomarski differential interference optical microscopy showed that the fibres were usually embedded ~40 μm below the surface of the disc and more or less parallel to it.

For specimens used to examine textures looking down the growth axis, described as a radial view, a greater depth of ~60 μm was used to keep the fibres well away from the specimen surface. In this case the fibres were placed between two discs, one 1 mm thick, the other ~60 μm thick, both prepared as above, otherwise the same procedures were followed.

All specimens were etched in a 2 w/v% potassium permanganate solution in 10:4:1 parts by volume of concentrated sulphuric acid, 85% orthophosphoric acid and distilled water, respectively. The etching time was selected according to the particular view required. Four hours was used to expose a diametral section in longitudinal views, i.e. so that the final plane surface of each specimen passed close to the fibre axes. This was readily checked with Nomarski optics which showed the width of fibres to be close to their nominal diameter of 40 μm. A shorter period was used when it was desired to view the rows down the growth direction in planes outside the original fibre.

The micrographs in this paper are of etched specimens coated with gold prior to examination in the scanning electron microscope, SEM. The fibre axis is always more or less horizontal making perpendicular lamellae appear vertical on the page, whereas inclined lamellae have their traces usually at ~35° to the vertical.

3. Results

Because of the reduced growth rates which blending brings, the crystallization temperatures studied here for polyethylene blends extend to lower values, ≥113 °C, than those of the homopolymer itself for which 123 °C was the lowest convenient figure. The characteristic features of the morphology after crystallization of a 5% blend at 119 °C, when growth is banded, are illustrated in Fig. 1.

The diametral section of a row crystallized for 7 min (Fig. 1a) shows three zones of increasing radius. First, there is a region of densely packed lamellae, ~1 μm thick, adjacent to the nucleating fibre present at the bottom of the picture, followed by a more open but still reasonably uniform region into the next 1 μm and finally, to ~3 μm radius beyond the fibre, a few lamellae as much as 2 μm apart projecting individually into the melt. This is a cellulated morphology in which the separated lead lamellae are growing into melt of the original blend composition, whereas those nearer to the fibre will encounter an increased concentration of branched polyethylene, rejected when the linear polymer crystallizes, and grow more slowly.

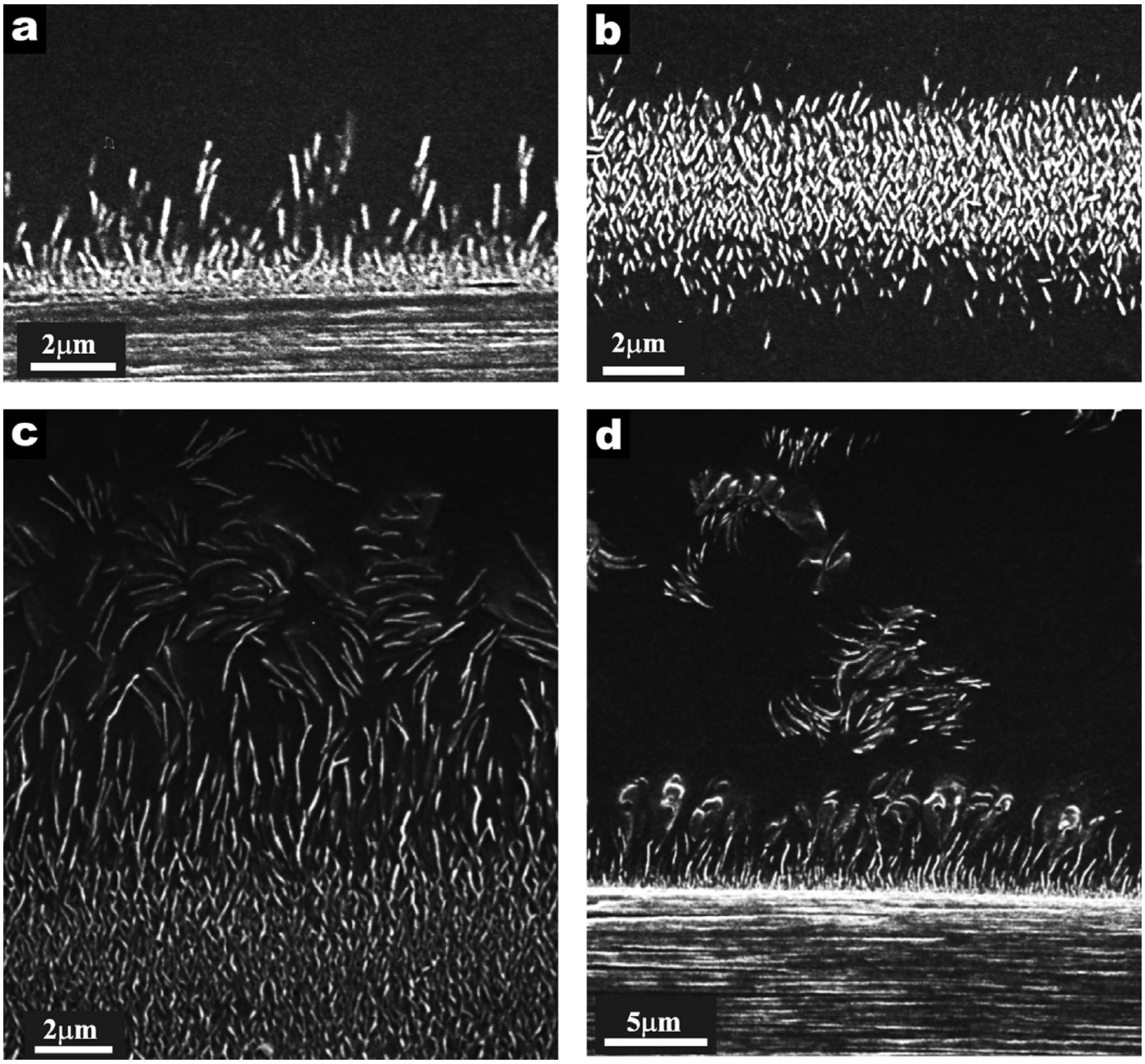

Fig. 1. Row structures of a 5% blend grown on a fibre nucleus at 119 °C: (a) diametral view after 7 min with a cellulated morphology; (b) radial view after 2 min with mostly inclined lamellae; (c) the upper half of a deep radial view after 10 min showing densely packed inclined lamellae at the bottom and twisted growth of lead lamellae at the top; (d) diametral view after 10 min showing different zones in the row together with twisted growth.

Fig. 1b, a radial view for just 2 min growth, also shows three radial zones with comparable densities of lamellae to Fig. 1a. In the densely packed centre and the less dense region beyond all lamellae are inclined. Only at the very outside are some perpendicular lamellae to be seen, with others still inclined. In Fig. 1c, which is one half of a deep radial section close to the nucleating fibre, after 10 min growth, there is again a dense central zone of inclined lamellae, then a more open one of linear traces perpendicular to the fibre with curved traces due to twisting growth of the lead lamellae at the outside. A diametral section (Fig. 1d) also after 10 min has the same three regions in the different perspective together with adjacent developing spherulites built with curved dominant lamellae.

The presence of inclined infilling lamellae in twisted growth has not previously been seen by us in linear polyethylene but is characteristic of crystallization of this blend and is still found for more rapid growth at 113 °C (Fig. 2). After 5 s, a diametral section (Fig. 2a) has both a dense region adjacent to the fibre and separated lead lamellae; adjoining spherulites contain highly curved lamellae. The corresponding radial view is in Fig. 2b which intersects the nucleating fibre on the right centre of the figure. Immediately to the left of this intersection, lamellae are perpendicular; these are the first to form. But moving further to the left one finds inclined lamellae, densely packed at first then more widely spaced as the section moves further away from the fibre to which it is not quite parallel.

The same sequence in a radial section is well seen in Fig. 3a after 30 s growth at 115 °C. Here perpendicular lamellae are adjacent to the nucleating fibre, then with increasing radial distance one moves to a similarly dense region of inclined lamellae which become thicker and more separated changing gradually until by the outer edge individual

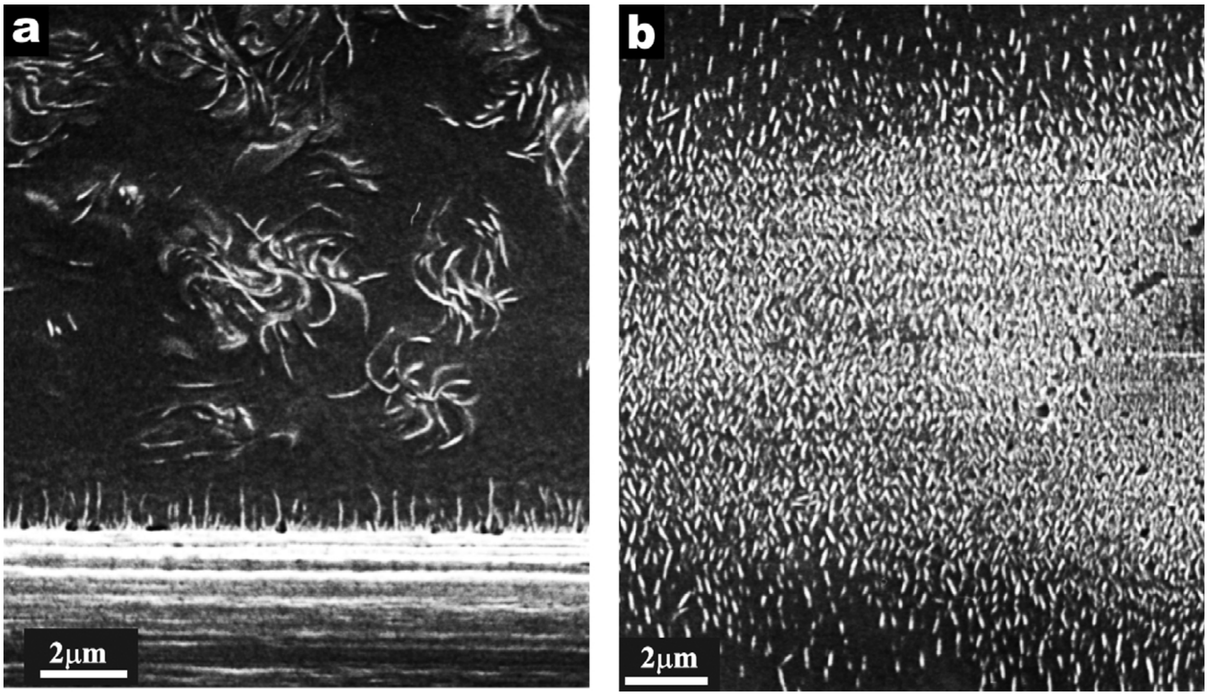

Fig. 2. Row structures of a 5% blend grown on a fibre nucleus for 15 s at 113 °C: (a) diametral view revealing incipient cellulation; (b) radial view with perpendicular lamellae formed on the fibre, right centre, inclined lamellae further left (i.e. at greater radial distance) and well-separated, thicker, perpendicular lamellae to the outside.

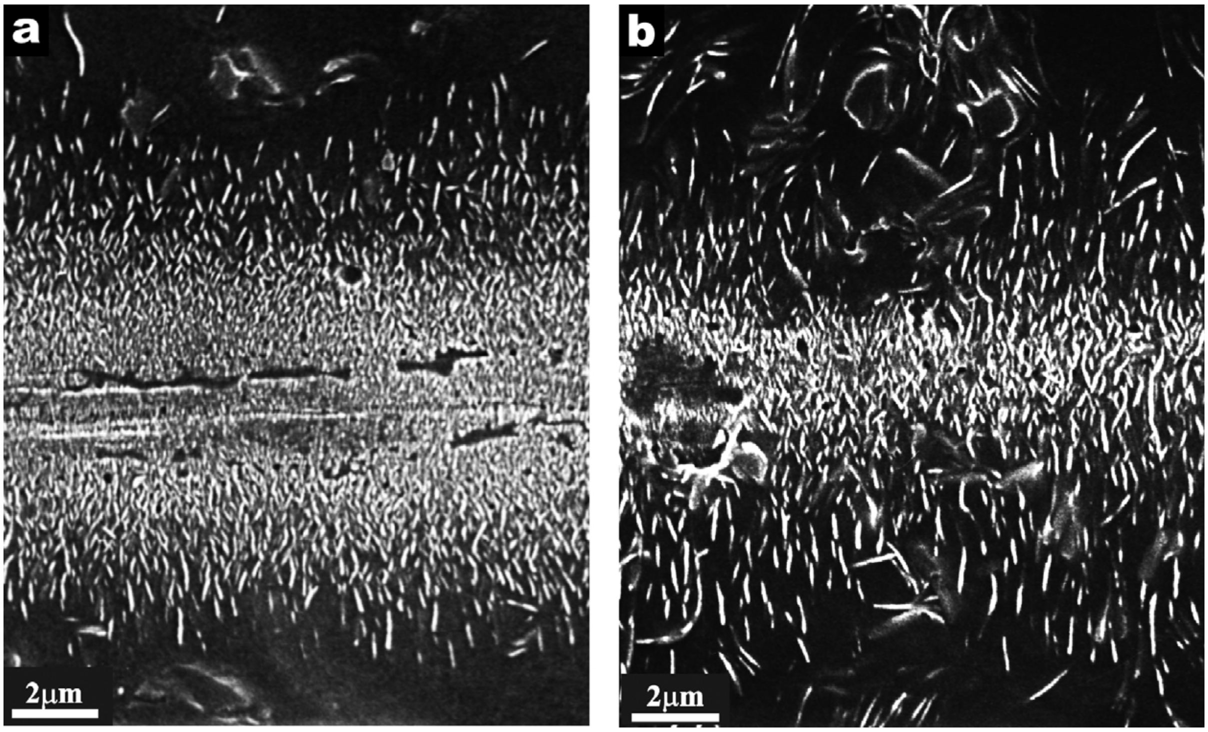

Fig. 3. Row structures of a 5% blend grown on a fibre nucleus: (a) a radial view, close to the fibre, after 30 s at 115 °C shows the progression from initial perpendicular through inclined lamellae in central regions with well-separated, thicker, perpendicular lamellae at the outer edges; (b) a similar progression is seen in a radial view after 5 min growth at 117 °C but with outer regions given greater prominence.

lamellae are perpendicular and as much as ~1 μm apart. The outer region is particularly prominent in Fig. 3b corresponding to 5 min growth at 117 °C but earlier regions can still be discerned, back to the initial perpendicular lamellae by the nucleating fibre at left centre. The observed pattern of successive regions is, therefore, characteristic of crystallization from this 5% blend throughout the temperature range investigated.

The growth lengths, i.e. the distance of the growth front from the nucleating fibre measured in diametral sections, may readily be recorded both for the dense central zone and the outermost lamellae. Their appearance as functions of crystallization time is shown for 119 and for 123 °C in Fig. 4 with the gradient being the local growth rate. The graphs have the same character at both temperatures namely a similar initial gradient (growth rate) for both morphological components, from which the central region slows, possibly towards an asymptotic steady state. Lead lamellae, on the contrary, more or less sustain the initial rate except for a consistent dip at ~5 and ~30 min for 119 and for 123 °C, respectively, a feature which may well be linked to establishing cellulation. Note that this sustained rate at 123 °C is only a few per cent of that for the unblended homopolymer at this temperature. This reduction affects the spherulitic morphology whose dominant lamellae will also grow into melt of the prescribed constitution, with minimal increased concentration of branched polymer [5]. At 121 °C, Fig. 5a shows a spherulite whose lamellae have twisted through ~90° between centre and edge at ~15 μm radius. By contrast, some dominant lamellae in the objects of Fig. 5b have grown at 124 °C with planar traces, i.e. untwisted, to over 20 μm radius (notably in the lower half of the uppermost spherulite) while other in the same object show ~90° twist over a ~20 μm radius; the end of twisted growth appears nigh and can be placed at ~125 °C.

At the higher blend concentration of 20% similar effects can be observed but they are less marked. For example, 30 s growth at 119 °C gives a diametral section (Fig. 6a) showing strong co-operative twisting with little evidence of cellulation as seen for the lower concentration. Fig. 6b, a radial view for the same conditions has perpendicular lamellae at the fibre surface, left centre, with just a few inclined lamellae as one moves to the right and further away from the fibre. Otherwise the morphological sequence is as reported previously for banded growth of linear polyethylene with dominant lamellae separating, thickening and twisting [1,6].

4. Discussion

The phenomena described above build on our earlier work [1–3] which revealed that the nature of as-grown fold surfaces of polyethylene depends upon the growth rate. There is a major division—within which there are, no doubt, nuances to be elaborated—between those associated with twisting and banded growth which form perpendicular to the

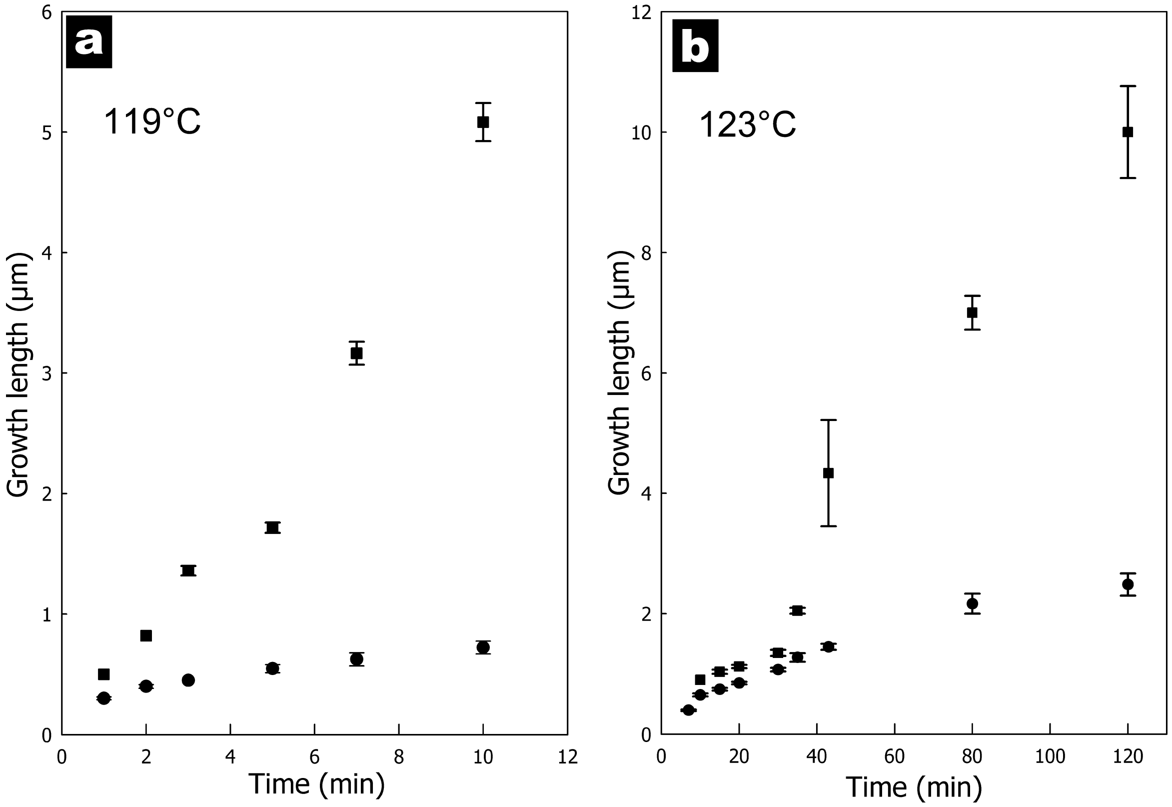

Fig. 4. Graphs of growth length against crystallization time for the inner and outer zones of row structures grown from a 5% blend; left 119 °C, right 123 °C.

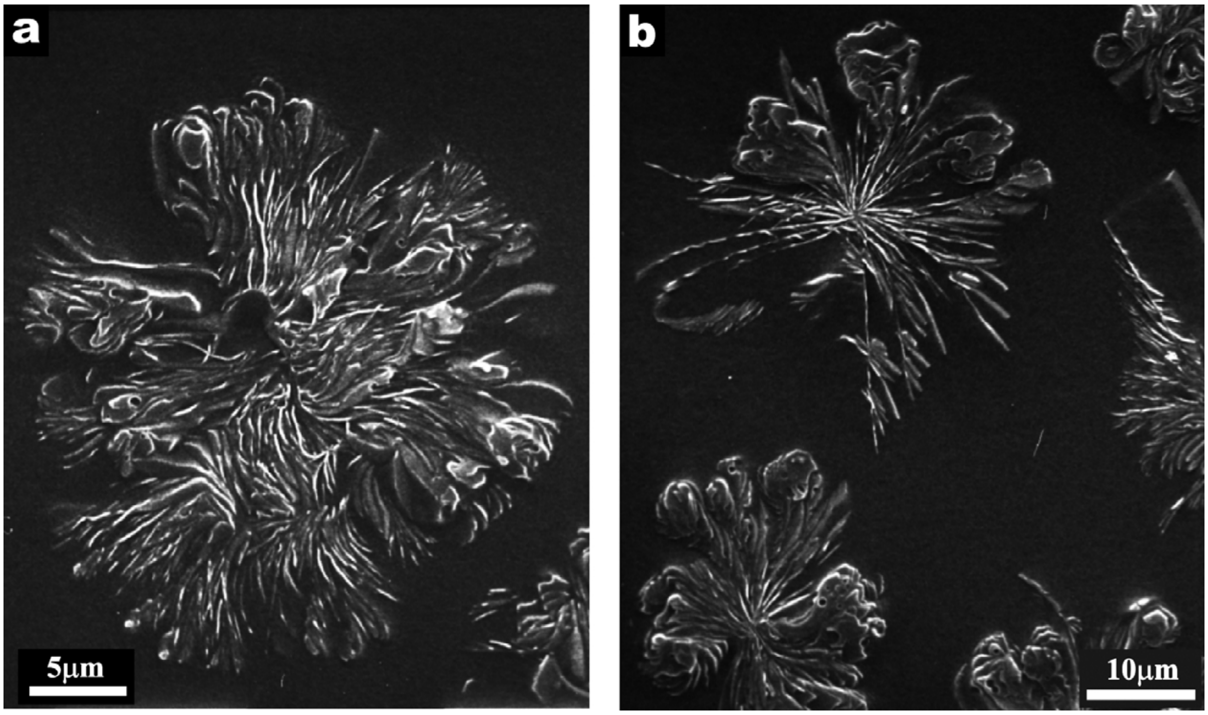

Fig. 5. Spherulites formed during crystallization of a 5% blend: (a) after 30 min at 121 °C the lamellar orientation has twisted through 90° from that at the centre; (b) 3 h at 124 °C produces objects containing both untwisted and twisted dominant lamellae; in the uppermost spherulite, the former occur in the lower half, the latter in the upper half.

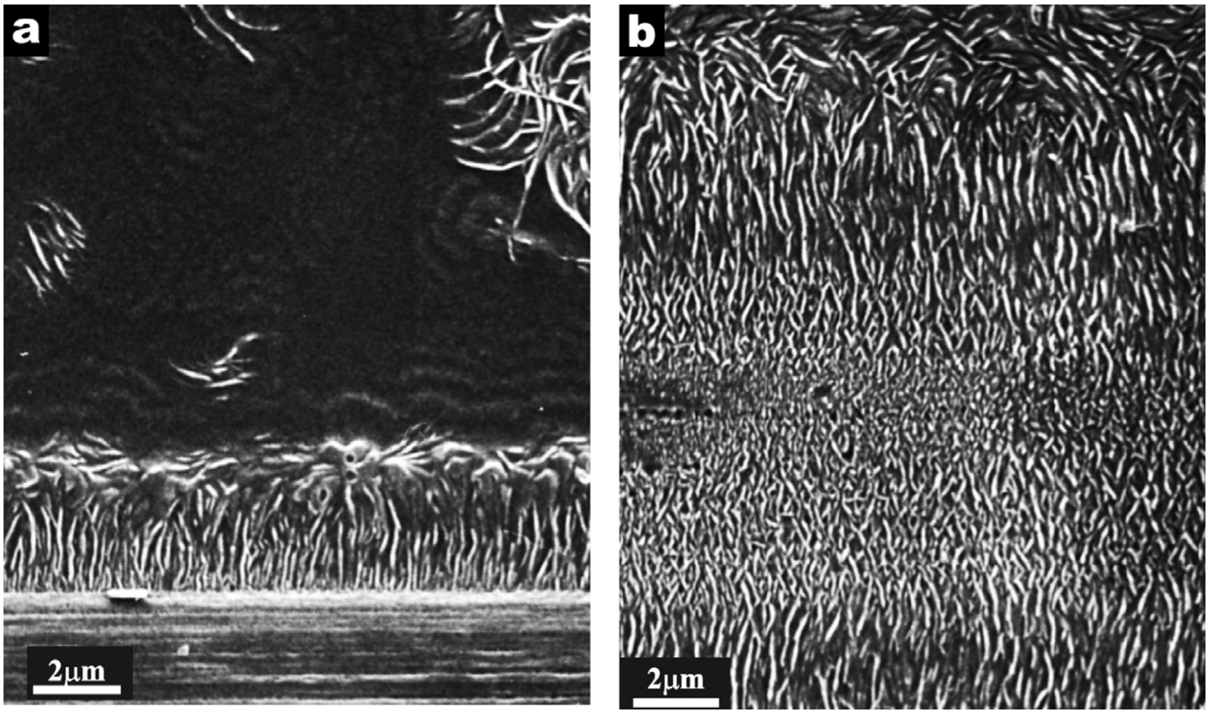

Fig. 6. Row structures of a 20% blend grown on a fibre nucleus for 30 s at 119 °C: (a) a diametral section reveals twisted growth with little or no cellulation; (b) a radial view shows perpendicular lamellae almost throughout, thickening and separating with increasing radial distance; only a narrow region of inclined lamellae is present.

chain axis, then re-organize and those which form directly as {201} whose lamellae do not twist spontaneously. Here this dichotomy is used to identify components within the morphology which have grown with different rates during isothermal crystallization and, in this instance, to relate these to the details of cellulation. This is a useful new means of exploring the subtleties of macromolecular self-organization.

The basic lamellar sequence for the 5% blend, observed from 113 to 123 °C, i.e. throughout the range for which twisting growth occurs, is that initial deposition is as perpendicular lamellae. Thereafter, growth slows as linear molecules are withdrawn from the melt and the concentration of branched molecules increases, thereby favouring constitutional supercooling and the onset of morphological instability. When cellulation occurs at lower temperatures, Figs. 2 and 3 show that lead lamellae continue to form perpendicular to the fibre and, therefore, with poor surface packing which is responsible for their eventual twisting to relieve the associated surface stress. At the same time, the majority of lamellae adopt an inclined habit (with ordered surface packing) a little, $\ll 1$ μm, into the row and so have no intrinsic reason to twist. They must, however, accommodate to the twisting framework previously established by the lead lamellae illustrating in a particularly clear manner that it is the latter which determines the overall morphology.

At 119 °C, Fig. 1 shows that the situation is more complex. Although eventually lead lamellae do form perpendicular and twist (Fig. 1c), after 2 min growth, Fig. 2b shows only a few perpendicular lamellae at the outer edge of the row. Here it is probable that the decrease in instantaneous growth rate revealed in Fig. 4a has caused most lamellae to grow inclined but once cellulation is established, lead lamellae grow faster and perpendicular into a melt with lower segregant concentration, ultimately that of the original composition.

The changes of fold surface, caused by a move from faster to slower growth with the latter allowing folds longer to attain their preferred packing, illustrate the differential growth occurring in cellulated blends because of different growth conditions at the interface with the melt.

Cellulation, prominent in the 5% blend but absent or nearly so at 20% concentration, arises because of constitutional supercooling, when the local equilibrium melting point is lowered as the constitution of the melt is altered by selective crystallization, so reducing the local supercooling below that of the distant melt of original composition [7]. In Fig. 1a, for example, the lead lamellae are able to grow faster because their growth interface is little, or no more, affected by the rejection of branched polyethylene than initially, unlike the intervening regions whose slower growth reflects the increased concentration of branched polymer as crystallization extracts linear molecules from the melt. The value of this excess concentration encountered by the slower-growing lamellae will depend upon the rate of diffusion away from the growth interface. The lack of evident cellulation for the 20% blend points to the quantity of branched molecules segregated as the determining factor for diffusion under the isothermal conditions. The concentration of branched molecules at the growth interface will be higher in the 5% blend, increasing the constitutional supercooling and favouring cellulation.

In terms of critical growth rate, i.e. that which divides the two surface conditions Fig. 4 allows an upper bound to be placed on the value for this homopolymer ignoring any fractional crystallization which may occur. Evidently the growth rate of lead lamellae at 123 °C, ~5 μm/h is too high a value but probably not very much so as the inclined habit sets in so soon in growth when the two populations are not strongly differentiated and so will advance at similar rates. This value is much less than that found for the unblended homopolymer previously [5] and corresponds to a time of 0.35 s to add a monomolecular layer 0.5 nm thick to the growth interface.

It is normally assumed in polymeric crystallization that the linear isothermal growth rate of a lamella is constant for a given molecular system and equal to the constant radial advance of corresponding spherulites. However, a number of circumstances, where this is not the case have recently been demonstrated experimentally. There is the declining growth rate with radial distance of certain linear-low-density polyethylenes in segregating conditions when the local composition of the melt changes [8]. There is the pulsating banded growth rate of similar copolymers linked to morphologically altered diffusion conditions for segregants and similar slight but consistent deviations from linearity in banded growth of linear polyethylene [9]. There is the temporary slowing in monodisperse *n*-alkanes when adjacent dominant lamellae begin to diverge [10]. There is the increase from one linear rate to another in slower growth of linear polyethylene attributed to the loss of internuclear interference when one molecule can no longer add simultaneously to two lamellae [5], as may well be the case for the previous *n*-alkane example. Now we have identified a slower-growing lamellar population in cellulated growth.

These several examples invite consideration of possible other departures from linearity with time. On the one hand there are examples, as here (Fig. 4), of systematic deviations during growth; on the other hand there is the fundamental issue of whether in the ubiquitous dominant/subsidiary construction of crystalline polymeric morphologies, the various subsidiary and infilling populations grow at the same rate as dominant lamellae, (which are the ones whose advance is almost invariably that measured) or have their rate affected by the increased constraints under which they grow. With suitable choice of growth conditions, when the fastest growth is close to but above the critical rate, it may well be possible to do as has been done here and distinguish slower-growing populations by their initial fold surface condition and so better inform the fundamental, intrinsic complexities of macromolecular self-organization.

5. Conclusions

1. Linear polyethylene crystallized on linear nuclei from blends with low density, branched polyethylene, cellulates at 5% but not significantly at 20% concentration reflecting the higher local concentration of segregated branched molecules.
2. When there is cellulation, individual lead lamellae, typically ~1 μm or so apart, grow at a constant faster rate than intervening lamellae whose growth is slowed by accumulated segregants.
3. All lamellae then form initially with poorly packed {001} surfaces but only the faster-growing lead lamellae continue in this manner, twisting to help relieve the consequent surface stress. Growth of the majority remaining lamellae slows and they soon adopt and retain {201} fold surfaces with their preferred packing.
4. The work not only demonstrates how different lamellar components of texture can attain different habits with associated properties, though with dominant lamellae determining the overall morphology but in so doing also provides a new indicator to help illuminate the intricacies of macromolecular self-organization.

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