Abstract

The use of high-melting fibres as linear nuclei for quiescent polymeric melts is instrumental in providing the superior mechanical properties of polymeric self-composites. It also has inherent advantages in the elucidation of fundamental aspects of polymeric crystallization and self-organization, not least in allowing systematic microscopic studies of polymeric crystallization from nucleation through to the growth interface. This has demonstrated explicitly that lamellae develop in two distinct ways, for slower and faster growth, depending on whether fold packing has or has not time to order before the next molecular layer is added with only the former leading to banded growth in linear polyethylene. Other gains in understanding concern cellulation and morphological instability, internuclear interference, isothermal lamellar thickening and banded growth being a consequence of the partial relief of initial surface stress.

Keywords: Polyethylene; Linear nucleation; Oriented crystallization

1. Introduction

The properties of crystalline polymers are probably more affected by nucleation, both primary and secondary, than those of any other major class of material making the potential for nucleation control of microstructure and consequent behaviour exceptionally large. Recently, the use of linear, rather than point, primary nucleation in quiescent melts has been particularly effective both in the enhancement of properties via the manufacture of polymeric self-composites and in advancing the fundamental understanding of crystallization processes at molecular and lamellar levels. These latter relate, inter alia, to cellulation and morphological instability, fold surface ordering and re-ordering, internuclear interference, isothermal lamellar thickening and banded growth.

2. Oriented crystallization and row structures

Polymeric crystallization from quiescent melts normally leads to spherulitic growth of chainfolded lamellae [1] with a consequent spread of local environments and properties in a macroscopically isotropic solid. In this case, primary nucleation effectively occurs at a point. The nature of the nucleus changes when molecules are elongated, e.g. because of extensional strain in the melt, giving oriented products. In the simplest cases, the nucleus is an extended thread, which acts as a linear nucleus for epitaxial lamellar overgrowths and so produces the so-called shish–kebab morphologies of row structures, a term which signifies the cylindrical products of linear nucleation. More complicated nucleation geometries, based on an extended molecular network, may be inferred to be present in macroscopic fibres from their transverse microstructure [2]. Nevertheless, in all instances, chainfolded lamellae emanate from the primary nuclei and secondary nucleation, at their growing edges, is also a major determinant of properties through the dependence of lamellar thickness on inverse supercooling [3].

Row structures with shish–kebab morphologies have been observed since the earliest reports of chainfolded lamellae, formed both from solution and melt in conditions of (local) extensional strain or flow. Their backbone contains extended molecules, having an elevated melting point, with longer molecules selected preferentially [4]. Although the development of molecular extension in flow is well understood [5], the conditions under, which crystallization, as opposed to nucleation, actually occurs are not well defined because it disrupts the flow fields making them turbulent [6], with consequent uncertainties in specifying the equilibrium melting point (which is a function of strain).

What can be said is that once there is primary nucleation, chainfolded growth will follow as the fastest available mode.
Although it has been presumed [7] that this would proceed independently of the applied stress (which would be sustained by the extended molecular network giving the nucleus) this is not the case and the lamellar habit changes with shear rate [8]. Early work [9] had reported that polyethylene lamellae in row structures grown at higher stress were less twisted but, at that time, there was no means of characterizing melt-crystallized lamellar habits, nor were the crystallization conditions well defined and no particular conclusions were drawn. It has now been shown that, for polyethylene crystallized isothermally from the melt under applied shear, the lamellar habits known for quiescent melt-crystallization persist at low shear rates but give way to lamellae normal to molecules (and the local extensional strain) at higher rates [8]. Later work [10] has shown that comparable habit changes occur during crystallization from quiescent melts depending on the relative rates of fold surface ordering and lateral growth; similar considerations may well apply here.

There are several advantages in examining row structures, however formed, to elucidate morphological matters in comparison to individual melt-crystallized lamellae. One is that the crystallographic orientation of lamellae is apparent by inspection when the row lies in the specimen plane, normal to the viewing direction and does not require taking a diffraction pattern of electron-beam-sensitive material. The chain axis, $c$, is along the row and the radial growth direction ($b$ for polyethylene, $a^*$ for the $\alpha$ form of isotactic polypropylene) normal to it. In this situation, lamellae are correctly oriented for their thicknesses (along $c$) to be measured and the interlamellar separation (Fig. 1(a)) Accordingly, and producing linear nuclei by extensional strain, the thickness of $\alpha$-i-polypropylene lamellae has been determined for a series of fractions, by length and tacticity, as a function of crystallization temperature [11]. In general, the cross-hatching component of the morphology is thinner, and melts at a lower temperature, than the radial lamellae. At 140 °C, the difference falls from $\sim 2$ nm at $5 \times 10^5$ mass to zero at $6 \times 10^4$ mass; the difference also reduces with falling crystallization temperature and is no longer present at 115 °C.

Transverse views of row structures have rarely been presented but, for isotactic polypropylene, have demonstrated that crystallographic continuity is rapidly over-ridden in order for crystallization to fill space, which would otherwise be inaccessible [12]. In Fig. 1(b), for example, with strict continuity, the characteristic narrow radial laths can only grow out as spokes in a wheel, in the plane of the figure, with intervening regions inaccessible. That they are filled, and rapidly, to give a circular cross-section—by distortion and/or incoherent nucleation—makes the point.

3. Linear nucleation of quiescent melts

The interpretation of shish–kebab morphologies formed in strained conditions, e.g. as a function of supercooling, is complicated by two factors. First, the effects observed are due to extensional strain but the applied stress is often a shear making their relationship ill-defined. Second, chainfolded growth depends upon supercooling, which will vary with the local strain, again in an undetermined way. These disadvantages may be avoided by crystallizing in quiescent conditions using highly-extended (and, therefore, higher melting) polyethylene fibres as linear nuclei.

Among other advantages are that, for an array of parallel lamellae advancing together in the melt, any lamella deviating from the norm is conspicuous as is any perturbation of the growth front (Fig. 2). Both factors aid the study of morphological instability and cellulation, which benefits further from the enhanced concentration of segregants, compared to spherulites, with their diverging, more open growth [13,14]. If the segregants are such that they lower the local equilibrium melting point as, e.g. branched polyethylene or poorly tactic $i$-polypropylene molecules then spherulites also grow faster than rows because of their less-reduced supercooling [15]. This does not happen within experimental

![Fig. 1. Row structures in isotactic polypropylene crystallized at 140 °C viewed along (a), showing the axial linear nucleus, and (b) down the axis of the row. From Ref. [12].](image)
error for different nucleation geometries when the segregated molecules differ only in being shorter [16] indicating that the reduction in supercooling is then too small.

Linear nucleation also has significant practical benefits. Among the more interesting new polymeric materials are the high modulus polyethylenes developed to move properties towards the theoretical Young’s modulus of the unit cell along its extended covalent bonds, approximately twice that for steel [17,18]. Various means have been found to extend the long molecules during crystallization, creating elongated nuclei, and manufacture high-modulus fibres [19–21]. Their small diameter, typically \( \sim 10 \mu m \), limits potential applications unless more macroscopic products can be made. A successful means of achieving this is hot compaction whereby parallel arrays of certain such fibres, heated to precise temperatures under holding pressure, can be fused into a continuous product retaining as much as 90% of the fibres’ longitudinal modulus and with greatly enhanced transverse strength [22]. Such self-composites are attained by partly melting, then recrystallizing, just sufficient of the surface regions to form a continuous matrix around the reduced fibres, which act as linear nuclei for the regrowth (Fig. 3(a)). The fibre/matrix bond thus formed is strong, with transverse failure now occurring within rather than between fibres, which is attributed [22] to its epitaxial character (Fig. 3(b)).

A succession of recent studies has used linear nucleation on high-melting polyethylene fibres to reveal a series of fundamental features underlying polymeric crystallization in general. First was the demonstration of morphological instability during the crystallization of linear-low-density polyethylenes while the concentration of segregated highly-branched molecules increased radially during growth [13]. The effect was absent from neighbouring spherulites whose more open texture gave lesser segregant concentrations and faster growth rates. For banded growth, the radial growth rate pulsates in phase with the bands as the segregant concentration oscillates due to a repetitively changing texture [24]. Greater segregant concentrations are required to observe cellulation in spherulites. When it does occur, it does so late in growth (Fig. 4), with monotonically declining rate, towards an asymptotic, steady state limit, thereby confirming unambiguously that cellulation is an effect, not the cause, of spherulitic growth [25]. The origin of spherulitic growth [26] is the repetitive branching and divergence of dominant lamellae caused, in polymers, by repulsion of adjacent lamellae at branch points by uncrystallized cilia and/or non-parallel packing of lamellae with rough fold surfaces.

4. Fold surface reorganization

The above observations were made on diametral sections, parallel to and through the centre of the nucleating

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Fig. 2. Morphological instability in linear-low-density polyethylene. Just visible at the top is the edge of a high-modulus polyethylene fibre from which a row structure is growing. The growth front has broken up into individual units (one arrowed) as a result of accumulated segregants. From Ref. [14].

Fig. 3. Unidirectional Certran™ polyethylene fibre compactions viewed (a) parallel and (b) transverse to the (vertical) fibre axis. From Ref. [23].
polyethylene fibre, exposed by etching down from the free surface of the crystallized specimen (Fig. 5). Additional new information comes from observing sections etched to lesser depths and passing through the row but outside the nucleating fibre. These provide what are termed radial views, down the growth axis, \( b \), along a central line and others, increasingly inclined, out to the edge of the row at either side. The precise information varies according to the particular chord exposed of the near-circular cross-section of the row (Fig. 6). This ranges from the narrowest chord, which shows essentially just the view down the growth axis at the edge of the row, through to the start of growth, which is visible at the interface with the fibre in sections tangential to it.

This experimental arrangement is the only one which has allowed growth to be observed all the way from primary nucleation on the fibre through to the growth front. It has revealed that, under typical conditions of faster growth (Régime II), the fold surfaces of polyethylene lamellae reorganize behind the growth front, attempting to reduce surface strain by increasing the surface area per fold and so causing banded growth. Only at high temperatures and slower growth (Régime I), sufficiently so for fold packing to organize before the next molecular layer is added, are fold surface normals inclined to the chain axis, \( c \), from the outset with no twisting [10].

The pertinent observation is that of the inclination of lamellar fold surfaces to the nucleating fibre and the chain axis. There are two outcomes depending on the temperature of crystallization and corresponding to the known change of profile for lamellae crystallized quiescently. Below 127 °C, for linear polyethylene of \( \sim 10^5 \) mass, lamellae are deposited normal to the fibre, i.e. with \{001\} fold surfaces, (Fig. 7(a)) then subsequently separate and reorganize, with dominant lamellae adopting S profiles, viewed down \( b \), (Fig. 7(b)) and twist around \( b \), the growth axis. The S-profile, also found in isolated lamellae, results from increasing the surface area per fold in the central, oldest part of the lamella. Its axis is not constrained to lie along \( b \), because fold packing is irregular, but is inclined to it at \( \sim 20° \), thereby introducing the asymmetry into the system which banding propagates [27]. The twisting is a means of reducing the surface stress built in during faster growth.

At 127 °C and above, again for linear polyethylene of \( \sim 10^5 \) mass, fold surfaces are deposited as \( \sim \{201\} \) on the fibre and maintain this index thereafter. However, while initially lamellae are inclined at \( \pm 35° \) to the fibre axis (Fig. 7(c)) they change beyond a certain radial distance to being normal to the fibre (Fig. 7(d)). Each of these two conditions has a constant isothermal growth rate but the outer one is necessarily the faster, by a factor \( \sim 3 \). The change correlates with the
separation between adjacent lamellae becoming greater than molecular lengths and has been attributed [28] to the presence, then loss, of internuclear interference when one molecule is able to add to two lamellae simultaneously.

The interpretation offered for the change in initial fold surface index from {001} to {201}, in terms of the relative rates of radial advance and fold surface organization, has been significantly strengthened by the demonstration [29] that, for a given polyethylene, the change always occurs at approximately the same radial growth rate whether it is crystallized alone or in a blend with highly-branched polymer (when the crystallization temperature is lower). A corresponding characteristic time may be expressed as that for the growth front to advance by a single monomolecular layer of ~0.5 nm at the temperature when lamellae first nucleate with {201} surfaces. This is ~30 ms for a typical linear polyethylene of ~10^5 mass with a measured changeover radial growth rate of 1 μm min^{-1}. The time falls to a few milliseconds for linear polymer of 2 × 10^4 mass but increases to seconds for 4 × 10^5 mass. For linear-low-density polyethylenes of ~10^5 mass, an increase from 60 to 150 ms results for an increase in branch content from 1.2 to 4.8 per 1000 C atoms [29]. Accordingly, the {001} surfaces produced under typical Régime II conditions occur because there has been insufficient time to organize fold packing before the next molecular layer has been added. Ordering of fold packing and surfaces as molecules are added to a lamella only occurs when there is sufficient time allowed by a growth rate less than the changeover one, i.e. in Régime I.

Although this is the first explicit demonstration of fold surface reordering, the concept has long been considered as likely to occur. Transformation to inclined fold surfaces, after nucleation as {001} was suggested to explain the formation of

Fig. 6. Scanning electron micrograph of an etched transverse section of a row in linear polyethylene grown around a high modulus polyethylene fibre. From Ref. [28]. The banding in the matrix forms during quenching.

Fig. 7. Row structures, within a quenched matrix, of linear polyethylene presented horizontally on the page. That in (a), grown at 123 °C for 25 s, shows dense central growth near and perpendicular to the underlying nucleating fibre giving way to more open textures, with thicker and wider lamellae, at top and bottom. After 40 s at 123 °C, half of a deeper section (b) shows the progress, with increasing radial distance, from closely-packed perpendicular lamellae at the bottom to S-profiled lamellae, aligned along the fibre axis, at the top. The same polymer grown as a row at 129 °C for 3 h (c) has inclined lamellae in a chevron pattern throughout with denser packing of thinner, smaller lamellae at the centre. After 11 h growth at 129 °C, lamellae in an equivalent row (d) grow with their planes normal to it. From Ref. [10].
either hollow pyramidal or chair polyethylene crystals from solution [30]. Smoothing of the initial rougher fold surfaces has also been invoked in crystallization theory [31]. Nevertheless, the magnitude of the decrease in fold surface free energy may well have been underestimated. Chainfolded growth occurs when the free energy gain from crystallization of the fold stems exceeds the increase from the new surfaces sufficiently to allow a finite growth flux. As the former quantity is a function of supercooling whereas the latter is mainly topographical, varying less strongly with temperature, fold surfaces can be expected to be strongly disordered and rough at fast crystallization rates. Their subsequent reorganization at times far too short for most examination techniques means, however, that measured fold surface energies will fall below, probably substantially so, the values appropriate to rapid crystallization. The use of surface free energies measured on melting has been suggested to be why, in the high pressure crystallization of polyethylene, the claim [32] that formation of the hexagonal phase will always precede that of the orthorhombic conflicts with the facts [33].

5. Isothermal lamellar thickening

Isothermal thickening of polymer lamellae towards a thermodynamically more stable state when heated above their crystallization temperature was observed in early studies of solution-grown lamellae [34,35]. It was also detected in small-angle X-ray measurements during the crystallization of linear polyethylene from the melt [36] and required to explain the raised melting point of polyethylene lamellae above their crystallization temperature [37]. While the phenomenon is not easy to observe and quantify microscopically for spherulitic growth [38], the study of row structures offers an exceptionally favourable means to do both. The increasing thickness with radial distance and thus time is clearly evident in, e.g. Fig. 7(a) and (b).

Radial views of linear polyethylene row structures have allowed the isothermal thickening of melt-crystallized lamellae to be measured in real space for the first time, showing that there are two effects, which normally occur in parallel. One is that the thickness of the growth edge increases linearly with the logarithm of elapsed time, the other that there is thickening that the thickness of the growth edge increases linearly with the logarithm of elapsed time, i.e. indicating lesser twist.

Such behaviour is to be expected when excluded branches affect isothermal lamellar thickening. Only those inter-branch molecular sequences at least equal to the lamellar thickness can be incorporated in a lamella and excluded branches must inhibit thickening once the local lamellar thickness becomes equal to their separation. Any further thickening can only accentuate fractional crystallization and tend to force an excluded branch deeper into the surface region with concomitant surface stress. It is this surface stress, which being in initially ordered, i.e. unstressed fold surfaces, will be less than for faster growth whose partial relief generates the banded growth with reduced twist.

6. Conclusions

Linear nucleation has several important advantages to offer polymeric materials, both scientific and technological. With them the portfolio of properties, which can be designed for a given starting material by choice of nucleation and crystallization conditions is considerably widened. Linear nucleation of quiescent melts by high-melting fibres is responsible for improved mechanical properties of polymeric self-composites and has led to several advances in the understanding of crystallization processes. These include cellulation and morphological instability, fold surface ordering and re-ordering, internuclear interference, isothermal lamellar thickening and banded growth.

References

[3] Hoffman JD, Lauritzen JJ. Theory of formation of polymer crystals with {201} orientations, the kinetics then slow, becoming non-linear, while growth starts to twist around the radius with an associated discontinuous increase in the gradient of band period plotted against crystallization temperature, i.e. indicating lesser twist.