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A counter-intuitive asymmetric habit of spherulites in polyethylene blends

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Abstract

An unusual but characteristic asymmetric development of immature spherulites of high-density polyethylene, forming isothermally in blends with the low-density polymer at temperatures when the latter is unable to crystallize, has been studied using scanning electron microscopy. Two interpenetrating sheaves of unequal length grow roughly at right angles within a single object. The longer sheaf with an open texture of individual lamellae forms later, and grows faster, than the other with its more compact texture, which directs kinetic measurements confirm. The phenomenon is explained as a consequence of differing initial concentrations of segregated low-density polyethylene at the growth front. Individual lamellae in a more open structure are expected to grow faster than those in a more-densely packed array because segregated molecules are then able to diffuse away more easily whereas their increasing greater concentration slows the growth rate of the latter monotonically. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

A constant isothermal growth rate is typical of polymer spherulites [1] and the dominant lamellae within them. However, that this is not a universal property has been demonstrated in the recent past by work on polyethylene copolymers [2] and other systems in which there is substantial segregation during growth. If such segregants are able to lower the growth rate significantly either by lowering the local supercooling because of a reduced melting temperature or slower transport, then it is possible, and indeed likely, that lamellae experiencing different segregant concentrations will grow at different rates. At the same time the presence of regions of lower segregant concentration there will tend to produce faster-growing lamellae as a consequence of fluctuations in growth.

The observations of this paper refer to an unusual but characteristic morphology found in developing spherulites of high-density polyethylene (HDPE) crystallized from blends with low-density polyethylene (LDPE) at temperatures, where LDPE is unable to crystallize. The novel habit reported consists of two interpenetrating sheaves growing transversely to each other. Contrary to intuition, the longer sheaf forms later than the shorter, having grown faster as kinetic data confirm. The associated geometries are more open for the faster-growing sheaf consistent with there being lower local concentrations of segregated LDPE.

2. Materials and experimental

Two types of polyethylene have been used in this work. One is HDPE and the other is LDPE. The HDPE is Rigidex 140-60 (BP Chemicals Ltd), a linear polymer for which $M_w = 54\,000$ and $M_n = 17\,000$ while the LDPE is Escorene LD100BW (Exxon), a conventional branched low-density polymer for which $M_w = 87\,000$ and $M_n = 10\,000$.

Blends with both 5 and 20 wt% HDPE in LDPE were melt-mixed at 160 °C for 30 min, under nitrogen, in a Winkworth twin z-blade mixer, model IZ. Melt-pressed sheets, 1.4 mm thick, of either blend were remelted between a clean Kapton sheet, 13 μm thick, and microscope slide, on a Kofler WME hot-bench at 160 °C for 5 min. At the end of this time, the disc with the Kapton sheet and the microscope slide were quenched using a large mass of metal plate. After this, the disc of around 20 × 30 mm in area and 1 mm thickness, was removed from the microscope slide and Kapton sheet and cut into small square discs of around 5 mm side and stored in suitable labelled jars to be ready for the next step.

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Around seven highly oriented Tekmilon™ polyethylene fibres, of melt-kneaded type from Mitsui, were parallel stacked on a microscope slide by adhering their ends using Araldite epoxy resin. The fibre/material was then prepared between the microscope slide and cover slip by placing one of the stored square discs on the cover slip on the Kofler hot bench at 133 °C. Onto this the microscope slide with the stacked fibres was carefully placed with light pressure on the already melted disc. The fibre/material composite with the microscope slide and cover slip was then moved into the Mettler hot stage at 133 °C for 5 min. The temperature of the hot stage was then dropped 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 then carefully removed from the slide and cover slip.

Each of the embedded fibres, linear growth therefrom (row structure) and spherulites in the same sample, were revealed by an etching process, where all specimens were etched for 4 h in a 2% (w/v) solution of potassium permanganate in 10:4:1 by volume of concentrated sulphuric acid, 85% *ortho*-phosphoric acid and distilled water. The etched specimens were coated with gold using an Emscap Sc500 Sputter Coater and then taken to examine in the scanning electron microscope. Growth lengths for kinetic data were measured on diametral sections, i.e. when the full fibre diameter of ~40 μm was present in the etched surface.

3. Results and discussion

The crystallization of HDPE when it is diluted in LDPE exhibits heterogeneous morphology, especially during development of axialitic structures to form eventual spherulites. This is seen well in a 20% blend crystallized at 125 °C. After 10 min crystallization, Fig. 1(a) shows an area of massive spherulitic nucleation. Most objects appear sheaf-like in projection although their three-dimensional geometry is expected to be axialitic, lacking full cylindrical symmetry about the axis of the sheaf. One such flat-on view is arrowed (left) with the slower-growing *a*-axis readily differentiated from the faster-growing *b*-axis.[2] Also, there are some open-textured spherulites of star-like appearance like that arrowed in the right top half of the figure. Dominant lamellae generally appear in brighter contrast with, often, intervening subsidiary lamellae in paler contrast. In this kind of structure, the lamellae are separated by large spaces which are expected to be rich in branched molecules of LDPE by comparison with the melt as a whole. This branched material, which represents the majority of the blend, which is still molten and unable to crystallize at 125 °C, will segregate at the growth surface, and then diffuse away from and between the crystallized lamellae of HDPE. Such segregation has been shown to be a general phenomenon during the crystallization of either co-polymers of some branch content [2] or polymer blends between linear and branched polymers [3] and of dilute binary blends of monodisperse *n*-alkanes [4].

After 20 min, according to Fig. 1(b), there are mainly two different situations. The object at bottom right, in which additional lamellae are added close to those in the main sheaf, trying to fill in the envelope to make it more circular in projection, represents one of these. The object in the top left of the same figure represents the other situation. In this, individual lamellae have grown out at an arbitrary angle, close to 90° to the sheaf axis. Although these individual lamellae started to grow later, according to what has been observed in this work, not before 10 min of crystallization, they grow faster than those do in the main sheaf. Later stages of development are shown in Fig. 1(c) and (d). The eventual outcome is a second, more open sheaf transverse to the first, which has developed later but has longer lamellae. This second sheaf is not symmetrical but has longer lamellae adjacent to the larger volumes of contiguous melt.

In some cases additional lamellae are added in both ways mentioned above to the same object. Fig. 1(c) shows an immature spherulite after 30 min crystallization. There is a kind of building up of spherulitic shape through continuous adding of new lamellae close-packed to those in the main sheaf. This is very clear in the half bottom right and less pronounced in the half top left. In addition to this, the individual lamellae, nearly perpendicular to the axis of the main sheaf, grow faster, and leave behind some gaps of uncrystallized material expected to be rich in LDPE.

Fig. 1(d) shows three types of competing isothermal growth, the first one, at the bottom of the figure, is the row structure. Although it began to grow earliest, where it nucleated on the fibre at the beginning of the measured crystallization time, its growth length is the shortest, i.e. it has the slowest growth rate. The second type is the majority of the principal axialitic structure comprising the main sheaf. This is longer and, therefore, faster growing than the row but shorter and slower growing than the third component, individual lamellae perpendicular to the main sheaf.

Fig. 2 shows the kinetics of the two kinds of lamellae in the immature spherulites, the lamellae in and around the main sheaf, denoted *axialites*, and those individuals growing roughly perpendicular to it, denoted *individual lamellae*. There is a high difference in growth rate, according to this figure, between the lamellae in the main sheaf, which are more close-packed, and the more open individual lamellae. The latter start later, with a faster growth rate (gradient) commensurate with that of the axialites at the origin. The final growth rate appears to be essentially the same for both components of the morphology.

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[2] This is an incidental confirmation that in the sheaf-like appearance *b* lies in the plane of the paper as has long been known to be characteristic of melt-grown polyethylene axialites.

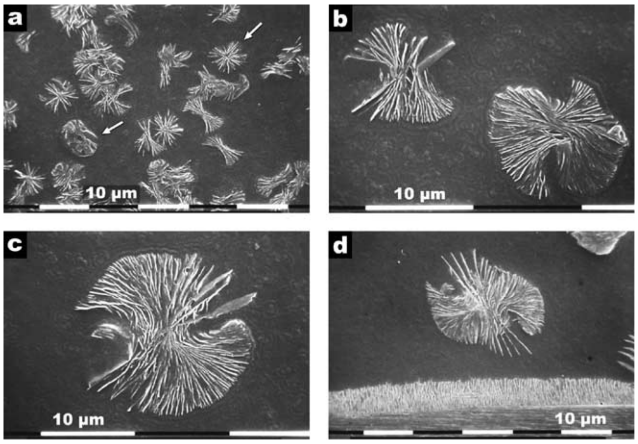

Fig. 1. (a) Scanning electron micrograph of etched surface for a blend of 20% HDPE, after 10 min crystallization at 125 °C. (b) 20% HDPE blend after 20 min crystallization at 125 °C; SEM of etched surface. (c) The same blend, 20% of HDPE, after 30 min at 125 °C; SEM of etched surface. (d) Both row and axialitic structure for the 20% blend of HDPE, after 45 min crystallization at 125 °C; SEM of etched surface.

Related differences, in morphological and kinetic behaviour, have been found in row structures for a blend with a lesser, 5%, proportion of HDPE. Fig. 3 shows this for two different crystallization times at 123 °C. At the shorter time (Fig. 3(a)), the lamellae in the row have grown uniformly with an approximately smooth growth front, while at the longer time (Fig. 3(b)), some lamellae have grown much longer and faster than the others.

All the above behaviours, morphological and kinetic, are readily explicable in terms of differing concentrations of segregated LDPE molecules in the melt adjacent to growing lamellae. This concentration is controlled by the amount rejected and the available diffusion volume. The former is simply proportional to the number of lamellae crystallizing per unit time while the latter depends upon the interlamellar separation. The effect of increased concentration is believed primarily to affect crystallization rate by lowering the local melting point and thus the isothermal supercooling.

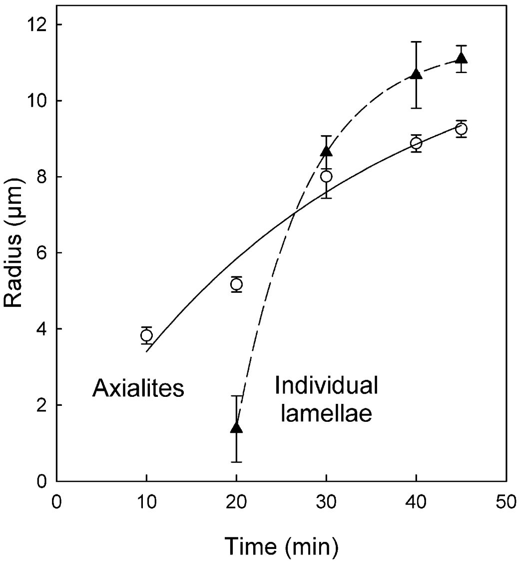

Fig. 2. The radii as functions of time of both the axialites and individual lamellae perpendicular to the main sheaves, for isothermal crystallization of the 20% HDPE blend at 125 °C.

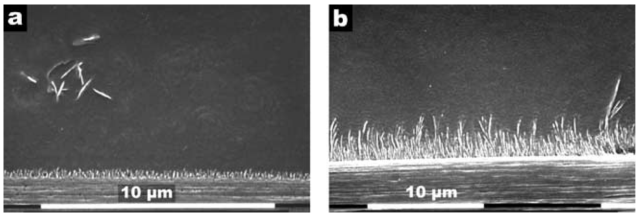

Fig. 3. Row structures of 5% HDPE blend crystallized at 123 °C; (a) after 2.7 min and (b) after 50 min.

The sequence of events leading to the double-textured objects of Fig. 1 is considered as follows. The initial object develops as an axialite with a low frequency of lamellar branching. In doing so rejected LDPE molecules concentrate ahead of and between the growing lamellae and reduce the growth rate monotonically. Their concentration will be least around the waist of the axialite because this is farthest from the growth front. Thus any lamellae which begin to grow out here from the axialite will grow at approximately the initial rate of the axialite and faster than when growth is reduced by segregation. The systematic lateral variation in the lengths of lamellae in the second sheaf, with the longer ones nearer to the greater volume of contiguous melt is in line with the general contention because local concentrations of LDPE would be expected to decline in the same order as the lamellar length increases. For the second sheaf as a whole so long as its lamellae keep their wider separation they will maintain their rate advantage over the remainder of the axialite unless and until transport of HDPE to the growing object may become a limiting factor. This may be the reason for the reduced growth rate of both types of lamellae in their later stages. The eventual growth of lamellae around the waist of an immature spherulite is in line with both previous experience of Popoff's leaves [5] and the principles of statistical thermodynamics according to which a system will explore all possible configurations.

The ranking of the three morphologies also follows straightforwardly on this basis. In general, lamellae in a row are both parallel and closer together than in spherulites while diffusion between them is more difficult which makes the growth of a row slower than adjacent spherulitic structures as was observed previously [6].

4. Conclusion

The isothermal crystallization of HDPE from a non-crystallizable LDPE matrix produces an asymmetric morphology within a single object due to lamellae growing at two different rates. This is a consequence of different local concentrations of segregated LDPE at the growth front related to the different volumes into which the segregants can diffuse. Individual lamellae in an open structure advance faster than those which grow closer together either in spherulites or rows. The greater the interlamellar space into which the non-crystallizing LDPE molecules can diffuse the lower is their concentration at the growth front and the greater is the growth rate of HDPE lamellae.

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