Morphology of zone-drawn polyethylene and dependence on thermomechanical conditions of drawing†

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By using scanning electron microscopy and applying the methods used in ref. 8, characteristic morphologies prepared by zone-drawing of polyethylene under various thermomechanical conditions are characterized in this paper. Depending on the regime of drawing (isothermal and nonisothermal), on the temperature of the zone and on the affecting stress applied, either the mechanism of drawing by plastic deformation of the solid phase (high stress, lower temperatures), or drawing of the melt (low stresses above the melting point of the undrawn polymer) is operative. In the former case a fibrillar structure with a minor amount of interfibrillar transverse lamellae is formed. In the latter case the shish-kebab structure is obtained, which gradually becomes a structure of smooth fibrils with extremely high draw ratios (up to 150). In both cases the original spherulites are transformed into fibrils, the thickness of which depends unambiguously only on the draw ratio. At high stresses, transverse cracks arise in the samples, and the size of the cracks increases while their frequency diminishes towards the place of fracture. Fracture relaxation of the structure arising from the oriented crystallization of the melt leads to the formation of interfibrillar cavities. In structures due to the deformation of the solid phase, surface waves and kink-bands are formed. The extent of the relaxation processes is influenced by the temperature and stress of drawing and fracture.

(Keywords: morphology; scanning slectron microscopy; zone-drawn polyethylene; solid-phase deformation; oriented melt crystallization; fracture relaxation)

INTRODUCTION

Recently, great attention has been devoted to the preparation of high modulus and high strength polymeric materials by orientational drawing and to an investigation of relations existing between the processing conditions, structure and properties of the drawn polymers[1-5]. In order to prevent thermal damage of the sample during drawing and relaxation of the drawn macromolecules, zone heating is advantageous. (Zone heating is a process in which the polymer passes through the zone of heating of a certain width at a defined rate.) A thermal exposure of the polymer in the zone makes orientation of the macromolecules possible, while the subsequent fast crystallization after cooling below the zone prevents relaxation. To date such a drawing technique has been used in the preparation of high modulus and high strength polymers by allowing the samples to pass gradually through the zone at increasing stress and temperature[6].

In an earlier study we have developed and described a simple modification of the zone technique of drawing at constant load[7], which makes it possible to optimize the thermomechanical conditions of drawing (temperature and stress) in order to obtain the required properties of the samples[8]. By employing this method, it is possible to prepare samples with continuously increasing draw ratios, starting from the onset of deformation, through necking and up to the highest λ_F value at the fracture point. In an earlier paper[8] we also demonstrated that under suitable conditions even melt-crystallized polyethylene can be drawn to high and orientationally effective draw ratios, and reported the effect of thermomechanical conditions on its drawability.

In this study we describe the morphology of high density polyethylene drawn by zone heating at constant load, using scanning electron microscopy. The investigation concerns the effect of thermomechanical conditions of drawing and draw ratio on the formation of morphology during the deformation process and during relaxation of the polymer after fracture of the samples drawn either below or above the melting point of the undrawn polymer T_m.

EXPERIMENTAL

Material

In this study we used linear high density polyethylene Liten VB 33 (manufactured in Litvínov Chemical Works, ČSSR, density 958 kg m^{-3}, molar mass 197 kg mol^{-1}) in the form of blown film (melt crystallized polymer). Pre-orientation from production gives a birefringence value of $0.0028 \pm 8.1 \times 10^{-5}$. The draw ratio determined by heat contraction is $\lambda_0 = 1.37 \pm 3.7 \times 10^{-2}$. The melting point from birefringence extinction between crossed nicols is 130–132°C.
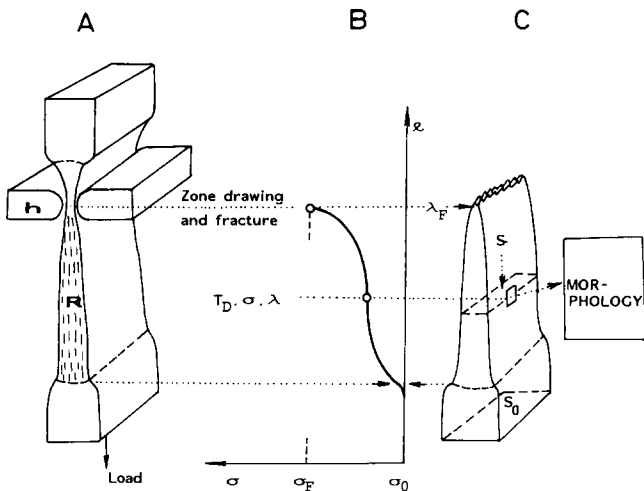
Figure 1 Scheme of drawing with zone heating and constant load. (A) Sample during drawing between heating plates (h); (B) the respective relation between elongation l of the drawn sample, the instantaneous stress σ and the draw ratio λ; σ_F and λ_F are values in the fracture site; (C) the drawn sample after fracture, R is the quickly cooled and recrystallized drawn polymer. Morphology in the designated place on the neck can be unambiguously attributed to T_D, λ and σ

Drawing process

Drawing took place on bands, $70 \times 5 \times (0.06 \pm 0.002)$ mm in size, fixed by clamps between plates of the heating zone. The length of the bands and the direction of pre-orientation of the film coincided with the direction of stress applied in the form of constant loading[8]. In the nonisothermal regime (NR) after application of the initial stress σ_0, the temperature T_D of the zone increases linearly at the rate $2°C\ min^{-1}$, while in the isothermal regime (IR) the zone has the required constant temperature T_D. Starting from the onset of deformation up to fracture in the zone the local draw ratio $\lambda = \lambda_0 S_0/S$ increases continuously (S_0 and S, respectively, are the cross-section of the original sample and the local cross-section of the drawn sample).

Transformation of the lamellar structure to the fibrillar structure takes place in the upper shoulder of the neck, after which the polymer flows into the heating zone, where it is homogeneously drawn. There it is subjected to the true stress $\sigma = \sigma_0 S_0/S$ during the process. On leaving the zone the polymer is quickly cooled and the oriented structure is fixed by recrystallization under stress. A scheme of the drawing process with varying quantities is shown in *Figure 1*. Morphology of a specific area of the neck can be unambiguously attributed to the thermomechanical conditions (T_D, σ) under which it was formed, and the respective draw ratio.

Scanning electron microscopy

A sample was cut out from the required place of the drawn polymer. Its surface was coated with a gold layer and investigated in the secondary electron mode in a Jeol JSM 35 scanning electron microscope.

RESULTS AND DISCUSSION

The starting polymer has a fine structure of imperfect spherulites with individual discernible lamellae, as can be seen in *Figure 2*. The average sizes of slightly anisotropic spherulites were estimated by SEM at high sample tilt as being 9.7 and 6.2 μm.

Characteristic morphologies of the drawn samples were observed depending on the starting thermomechanical conditions (T_D, σ_0) and are outlined in the diagram in *Figure 3*. Region I has a morphology typical of drawing of the solid phase. In region II the morphology is typical of oriented crystallization from the melt.
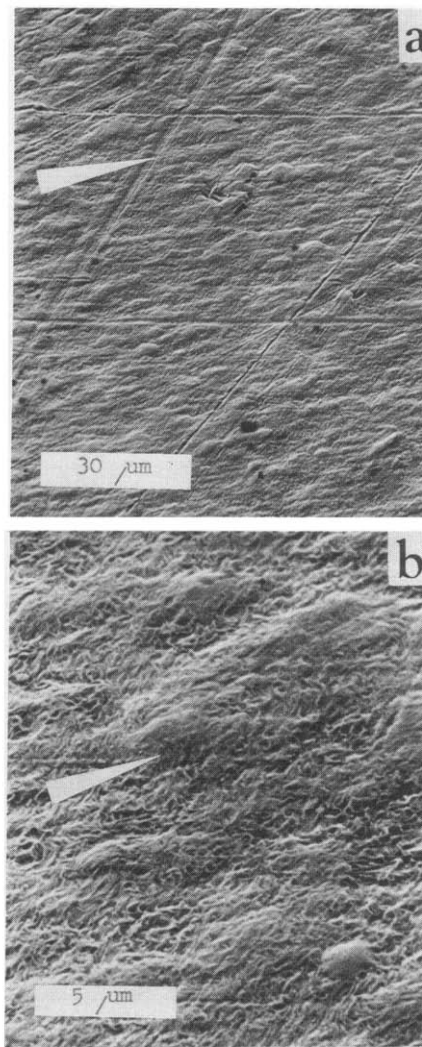

Figure 2 Scanning electron micrographs of the starting morphology of the polyethylene film at lower (a) and higher (b) magnification. Arrow shows the direction of pre-orientation
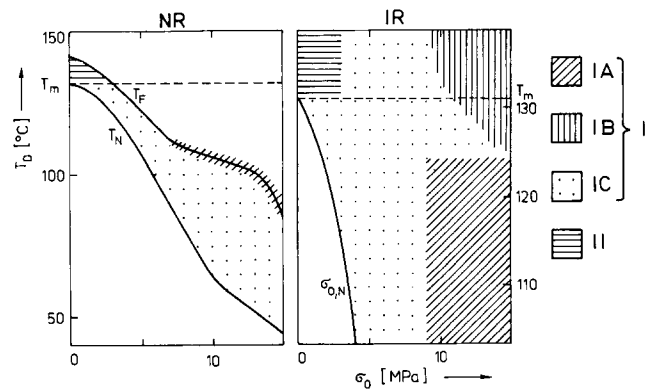

Figure 3 Diagram showing the effect of temperature T_D and of applied stress σ_0 on the morphology of zone drawn polyethylene. NR, IR, nonisothermal and isothermal regime of drawing; T_N, T_F, heating zone temperature of neck formation and fracture in NR; $\sigma_{0,N}$, threshold value of applied stress below which there is no necking (cf. ref. 8); T_m, melting point of undrawn polymer. The meaning of the individual regions is discussed in the text

Moreover, the samples show different features of mechanical relaxation after fracture: In region IA, relaxation is reflected in the formation of transverse surface waves (below, only surface waves); in region IB, relaxation takes the form of kink-bands; in region IC, relaxation is not reflected. In region II fracture relaxation results in the formation of longitudinal cavities in the fibrillar structure. The individual morphological regions are variously distributed in diagrams of thermomechanical conditions for NR and IR. However, it is not the regimes that are important here: the only important conditions are the drawing temperature, stress, and the draw ratio reached.

Formation of morphology during drawing

Region I of the starting thermomechanical conditions under which drawing proceeds via deformation of the solid phase is restricted in NR by the drawing temperature $T_D < T_m$ within the whole range of applied stress σ_0. In IR this mechanism is operative even at $T_D > T_m$ when $\sigma_0 > c$. 3 MPa. In the case of zone drawing at constant load this is connected with the rate of plastic flow of the polymer through the zone of heating. An increase in the applied stress leads to an increase in the flow rate, and at $\sigma_0 > 3$ MPa the rate is already so high that the time the drawn sample volume remains in the zone is insufficient for its perfect melting. No such situation arises in NR[8]. The temperature interval of drawing $T_F - T_N$ is unambiguously defined by the choice of the applied stress, and at $\sigma_0 > 3$ MPa $T_D < T_m$. Rheology of the drawing process will be dealt with in a forthcoming paper.

Morphological changes occurring during the transformation of the original spherulitic structure (*Figure 2*) into the fibrillar structure in region I are represented by a sample drawn nonisothermally at $\sigma_0 = 7$ MPa (*Figure 4*). Before necking, axial deformation of the structure, in which we assume the spherulites are still not perturbed as a whole, takes place (*Figure 4a*). Lamellae oriented statistically in the starting structure (cf. *Figure 2*) tend to become oriented between the spherulites, perpendicular to the direction of stress. This is evident after necking (*Figure 4b*) when the spherulites are already perturbed and extended to fibrils. The fibrillar texture is still not compact enough, the space between the fibrils is filled in with material the surface of which is distinctly transversely wrinkled. This indicates that the material consists of lamellar crystals oriented perpendicularly to the fibril axes. In further stages of drawing the fibrillar texture becomes increasingly compact, the fibrils are thinner and longer (*Figure 4c, d*).

Lamellar material between the fibrils gradually becomes fibrillar. At λ values above 10–12 it is already completely transformed, and the fibrils are laterally closely packed (*Figure 4d*). At higher draw ratios, in further stages of drawing the fibrils only become finer (*Figure 4e*). If at the same time the polymer is subjected to an instantaneous stress which is too high it may be damaged by cross cracks, or in other words, the polymer may be overdrawn (*Figure 4f*). At high draw ratios transverse lamellae can be seen, bridging over the adjacent fibrils. Transverse interfibrillar lamellae have been observed throughout region I in both regimes, both at low and at high draw ratios (*Figure 5*).

To explain their formation, it is necessary to analyse the transformation of lamellar spherulite crystals into fibrils, described either as its mechanical destruction

under load[9] or as its melting and recrystallization accompanied by the formation of a structure similar to the shish-kebab structure[10]. None of these models has yet been proved to be unambiguously correct. We believe that both mechanisms may be operative in drawing, depending on the thermomechanical conditions. At low temperatures the mechanical destruction of the lamellae predominates. With increasing temperature the fraction of partial melting and recrystallization increases (preferentially, for less perfect crystals).

On the basis of this assumption, the origin of lamellae in region I may be as follows. At low $\lambda < 10$–12 lamellae may be lamellar components of shish-kebab crystals due to the partial melting and to the recrystallization of the starting structure in the neck. At very low values of λ a certain fraction of these lamellae may be the residue from equatorial regions of the spherulites. Axially oriented lamellae are preferentially transformed and included in the fibrils during the deformation[11]. The possibility of survival of the lamellae during necking obviously decreases with increasing temperature of drawing, i.e. with increasing participation of partial melting and recrystallization.

At $\lambda > 10$–12 the fibrils are already closely packed laterally. Transverse lamellae can only be components of shish-kebabs of partially molten and recrystallized material. Quantification of the lamellar fraction cannot be performed by the method used. However, a comparison between *Figure 5a* and *c* shows that the lamellar fraction is indeed higher at a higher temperature of drawing, where a higher fraction of melting and recrystallization may also be expected at the expense of mechanical destruction of the lamellae.

The lamellar nature of interfibrillar links is indicated by the fact that deformation of drawn samples perpendicularly to the axis led to splitting of the polymer, accompanied by the formation of cavities between the fibrils bridged over by thin microfibrils drawn from the original interfibrillar lamellae (*Figure 6*). These are probably molecularly fixed in the structure of the fibrils. Interfibrillar lamellae may be a source of difficulties in the fibrillation of oriented polyethylene films in the textile industry.

The development of cross cracks in the sample during drawing in region I can be seen in *Figure 7*. The cracks are situated at a right angle to the axis of orientation. Distortion in the micrographs is due to the tilt of the sample in the microscope. In *Figure 7* the cracks arise only in close proximity to the fracture and their average length, $\bar{L}_c$, increases and the surface concentration κ decreases towards the sample fracture. Within the scatter of data one may state that the sizes of the cracks and the tendency towards their formation increase in proportion to the increase in fracture stress σ_F acting upon the fractured polymer in the heating zone. Hence, the higher the stress affecting the sample near the fracture, the greater the damage of the polymer, and the more pronounced the cracks. At the same time, for samples with high σ_F values, extreme birefringence values were recorded. These greatly exceed the value of 0.0585 of the orthorhombic polyethylene crystal[12] (as much as 0.081; ref. 13).

Crack dimensions for chosen thermomechanical conditions of drawing along with the respective draw ratios are given in *Table 1*. No effect of the draw ratio on the formation and size of cracks has been observed. The
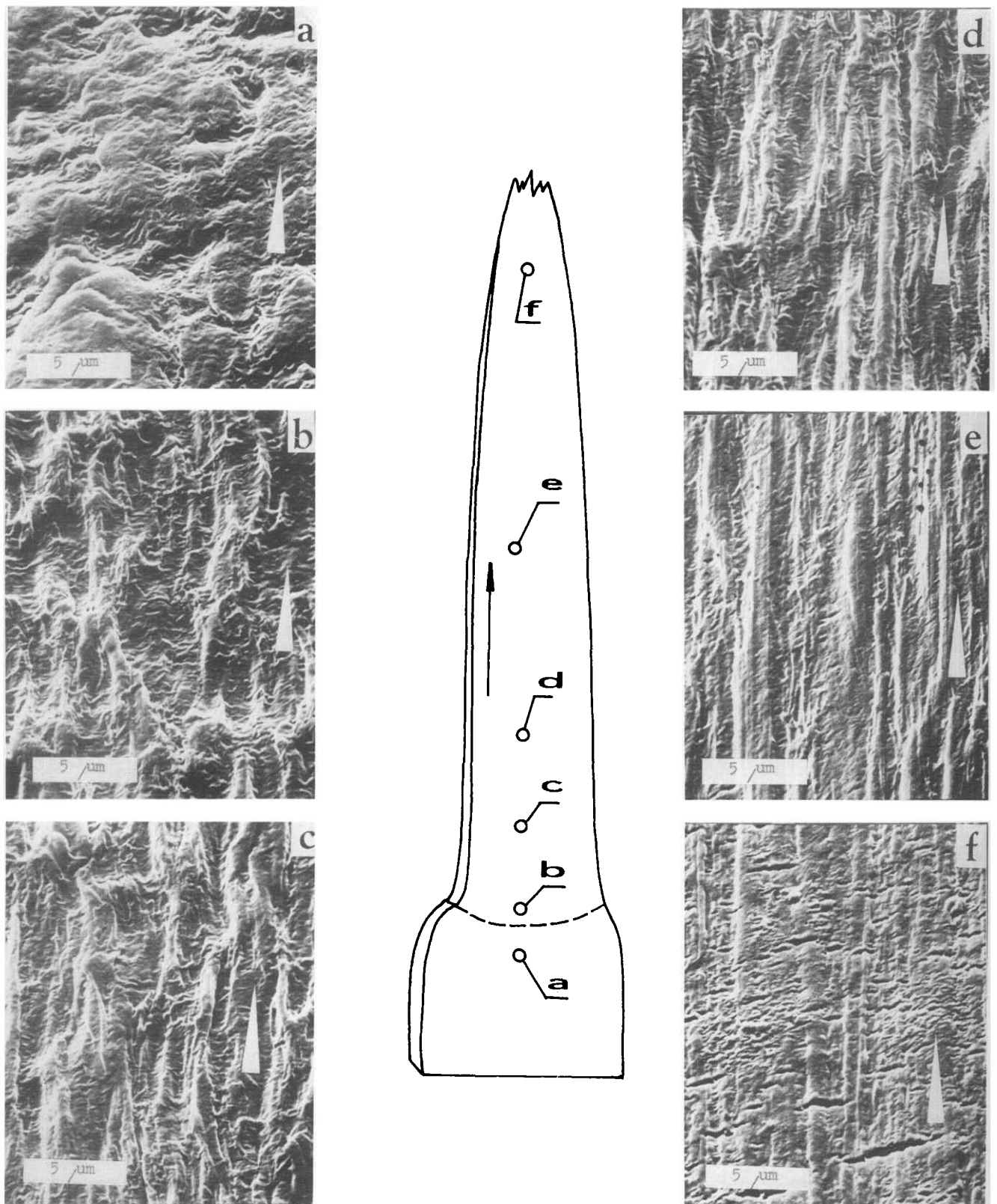
Figure 4 Morphological changes in the solid-phase drawing of polyethylene (region I of the starting thermomechanical conditions). NR: $\sigma_0 = 7$ MPa, $T_N = 89°C$, $T_F = 112.2°C$. T_D (°C), σ (MPa) and λ values in the scanned places: (a) 88.1; 10.2; 2.0; (b) 92.2; 20.4; 4.0; (c) 93.9; 28.1; 5.5; (d) 95.8; 33.7; 6.6; (e) 99; 61.8; 12.1; (f) 111.7; 204.4; 40. The arrow denotes the direction of drawing

drawing process is dependent only on the starting thermomechanical conditions (T_D, σ_0). At certain values of the starting conditions, the instantaneous true stress increases to maximal fracture values following the decrease in the cross-section of the sample in the zone (e.g. in NR σ_F reaches a maximum of more than 0.6 GPa at $\sigma_0 = 9$ MPa and $T_D > 100°C$)[8]. These values favour

damage of the polymer. Hence, the formation and the size of the cracks depend only on the magnitude of the affecting true stress and are influenced by stretching of the chains.

Using the facts reported above, we propose the following mechanism of polymer damage during drawing. High instantaneous stress near sample fracture
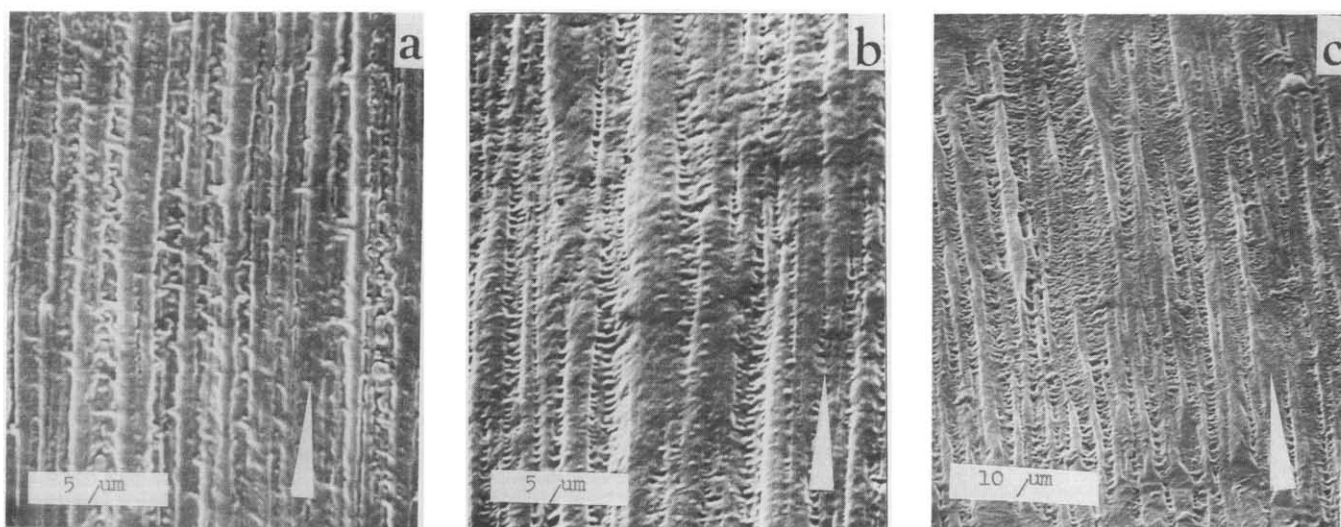
Figure 5 Transverse interfibrillar lamellae in the structure of solid-phase drawn polyethylene under various conditions. (a) NR, $\sigma_0 = 14$ MPa, $T_N = 50.5°C$, $T_F = 95.3°C$ ($T_D = 93.5°C$, $\sigma = 388$ MPa, $\lambda = 38$); (b) NR, $\sigma_0 = 10$ MPa, $T_N = 63°C$, $T_F = 103.9°C$ ($T_D = 98.2°C$, $\sigma = 423$ MPa, $\lambda = 58$); (c) IR, $T_D = 129.5°C$, $\sigma_0 = 2$ MPa ($\sigma = 24$ MPa, $\lambda = 16.5$)

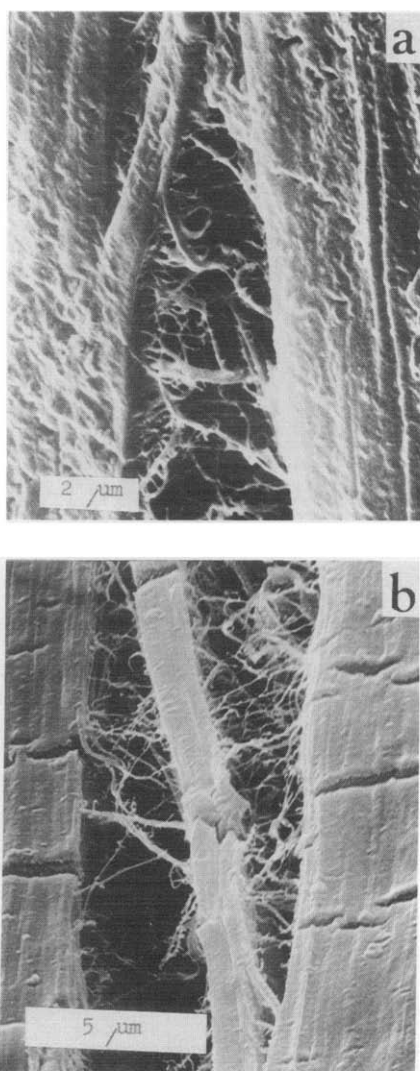**Figure 6** Microfibrils in interfibrillar cavities of drawn polyethylene. (a) NR, $\sigma_0 = 4$ MPa, $T_N = 115°C$, $T_F = 125.9°C$ ($T_D = 124.7°C$, $\sigma = 231$ MPa, $\lambda = 38$), (b) IR, $T_D = 138°C$, $\sigma_0 = 5$ MPa ($\sigma = 113$ MPa, $\lambda = 31$). In addition, samples were perpendicularly deformed by drawing in the deformational device of the microscope

Table 1 Effect of thermomechanical conditions near sample fracture on the average length of cross cracks $\bar{L}_c$. T_D, temperature of drawing; σ_0, applied stress; λ, draw ratio; σ_F, fracture stress

Regime	T_D (°C)	σ_0 (MPa)	λ	σ_F (MPa)	$\bar{L}_c$ (μm)
NR	122.0	5	83	303	1.51
	117.2	8	101	590	3.45
	99.9	14	37	378	0.57
IR	104	6.5	38	180	0.46
	104	9	54	355	0.56
	104	15	40	438	0.59
	129.5	2	17	25	0.44
	129.5	4.5	66	217	0.53
	129.5	15	11	120	0.45

causes cracking of extremely stretched amorphous chains (high birefringence) and leads to the formation of a large number of microcracks. Cracks propagate across the fibrils and join each other (increase in size accompanied by a decrease in surface concentration). Propagation and joining of cracks results in a total fracture of the sample.

Under the given conditions, formation of cracks is obviously a limiting factor for the preparation of a structure possessing favourable properties, and should be borne in mind in the optimization of the drawing process.

Morphological changes in the starting structure during drawing in region II are illustrated in *Figure 8* by a sample isothermally drawn at $T_D = 138°C$ and $\sigma_0 = 0.6$ MPa. Region II is restricted by the starting conditions $T_D > T_m$ and $\sigma_0 < 3$ MPa. In this case, drawing proceeds via oriented crystallization of the melt. Prior to necking, the statistically oriented lamellae of the starting polymer (cf. *Figure 2*) are oriented in a direction perpendicular to the deformation axis (*Figure 8a*). At a low applied stress the cause may be the tendency of the polymer to entropic shrinkage at high temperature[13] as a result of pre-orientation of the starting film (cf. Material section). At the beginning, contraction predominates over deformation. After melting, the neck and the first fibril embryos are formed. At first, these embryos look as if they were embedded into the matrix of transversely
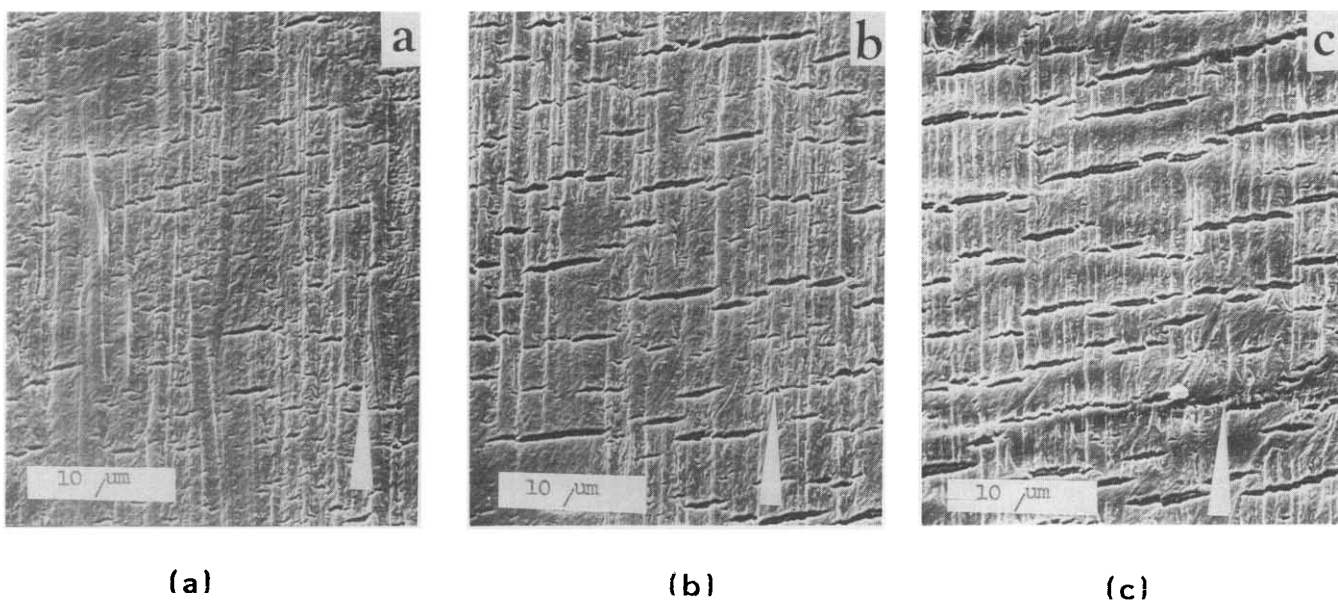
(a) (b) (c)

Figure 7 Cross cracks near the fracture site of drawn polyethylene. IR, $T_D = 129.5°C$, $\sigma_0 = 9$ MPa. Local σ (MPa) and λ values (a) 315, 48; (b) 342, 52; (c) 368, 56. Mean crack length $\bar{L}_c$ (μm) and their surface concentration κ (mm^{-1}) (a) 0.72; 2.25×10^5; (b) 1.40; 1.02×10^5; (c) 1.79; 0.68×10^5. Arrow shows the direction of drawing

oriented lamellae (*Figure 8b*). In the following stages of the process the typical shish-kebab structure is already formed, which at a parallel position of the fibrils with respect to the scintillator of the microscope has a ladder-like appearance (*Figure 8c*). By rotating the sample by 90° the characteristic shish-kebab appearance is stressed (*Figure 9*). Lamellar growths are very densely arranged on the fibrillar cores, and they also may join several adjacent fibrils. Their thickness is smaller than 80 nm and decreases in the direction of the sample fracture.

If the instantaneous stress on the sample exceeds approximately 40–55 MPa, shish-kebabs assume the structure of smooth fibrils (*Figure 8d*). This phenomenon can be explained so that the increase in σ above 40–55 MPa during drawing brings about perfect extension of chains in the melt. At the same time, their crystallization takes place soon after they have left the heating zone (quick cooling), which prevents relaxation and folded crystallization. One may expect, therefore, that smooth fibrils will predominantly consist of extended chain fibrillar crystals with high crystalline continuity. This is also indicated by the heat stability of such structure[13] (shrinkage after 30 min of thermostating at 134°C was only 7% in a sample extended in IR at $T_D = 138°C$, $\sigma_0 = 0.8$ MPa to $\lambda = 107$). The transition region between the shish-kebabs and smooth fibrils is characterized by a small fraction of transverse lamellae, which is distinctly seen in the cavities between the fibrils (*Figure 10*).

During transformation of the starting structure to an

oriented structure mechanical destruction of the original lamellae in region II can be ruled out. Also, the polymer is not damaged by cross cracks, as is the case in region I. The affecting stresses are too low, and in the melt fracture one may rather expect sliding and disentanglement of chains from the physical molecular network than their cracking.

Fibril thickness

SEM micrographs were used to evaluate the fibril thickness L_f as the length of an intercept cut out by the fibril on the straight line normal to the deformation axis. It was found that the average fibril thickness $\bar{L}_f$ is markedly dependent on the draw ratio and is independent of thermomechanical conditions of drawing within the limits of scattering. This is shown in *Figure 11*. In region II the measurements were performed only in the case of smooth fibrils arising in later stages of deformation (cf. *Figure 8*) because in the shish-kebab structure fibrils cannot be considered as structural units.

One can see that at λ values below 10–15, when the lamellar structure is transformed into the fibrillar structure[9], $\bar{L}_f$ rapidly decreases. If the draw ratio exceeds approximately 12–15, the plastic deformation of the fibrillar structure is operative and the experimental dependence also reflects values recorded for smooth fibrils in region II, where orientation took place after the preceding total melting of the polymer. This finding could be interpreted as suggested below.

One of the properties of crystallizable polymers is the ability of their crystal nuclei to remain after the polymer
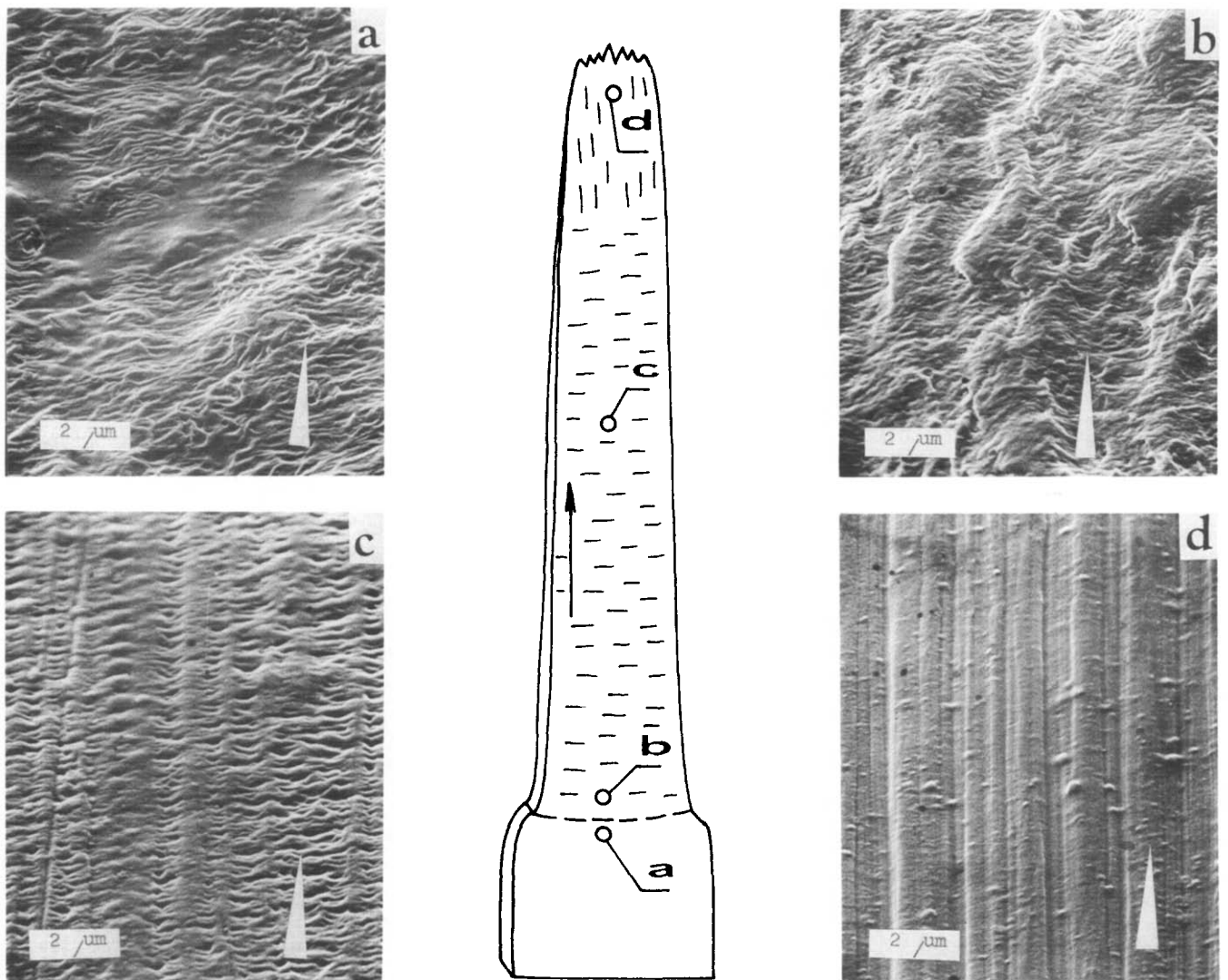
Figure 8 Morphological changes in the drawing of polyethylene from melt (region II of the starting thermomechanical conditions). IR, $T_D = 138°C$, $\sigma_0 = 0.6$ MPa; σ (MPa) and λ values in scanned places (a) 0.88; 2; (b) 1.9; 4.3; (c) 9.2; 21; (d) 61; 139. Arrow shows the direction of drawing, horizontal hatching denotes the shish-kebab region, vertical hatching denotes the region of smooth fibrils
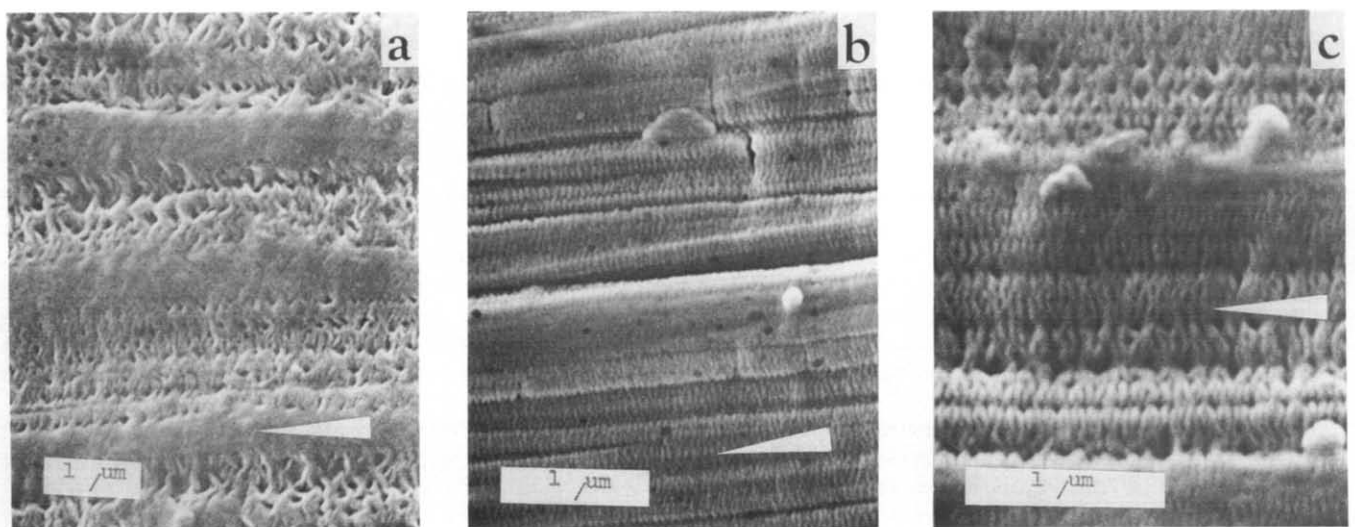

Figure 9 Shish-kebab structure of polyethylene drawn in region II. The same sample as in *Figure 8*, but rotated by 90°C with respect to the microscope scintillator. $\lambda = 21$ (a), 59 (b, c). Arrow shows the direction of drawing
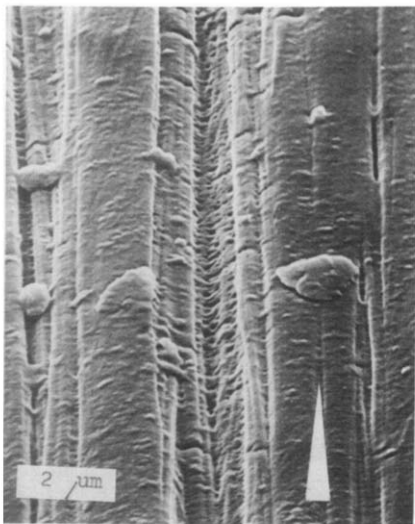
Figure 10 Transverse lamellae between fibrils in the transition of shish-kebab–smooth fibrils in region II. IR, $T_D = 138°C$, $\sigma_0 = 1$ MPa ($\sigma = 49$ MPa, $\lambda = 67$). Arrow shows the direction of drawing
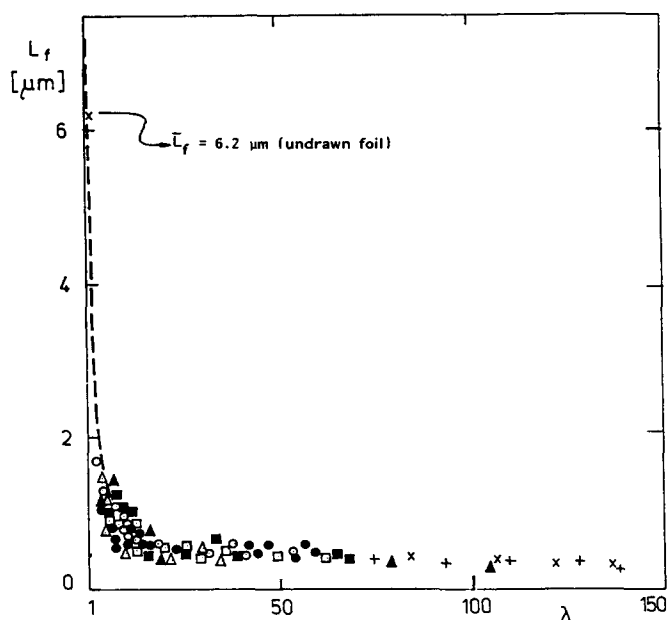

Figure 11 Dependence of the mean fibril thickness $\bar{L}_f$ on the local draw ratio irrespective of stress conditions of drawing. Polymer drawn in IR at $T_D(°C) = 104$ (○), 112.5 (●), 121 (□), 129.5 (■), 138 (△, region I; +, region II) and in NR (▲, region I; ×, region II)

has been heated above T_m and to act as crystallization sites in recrystallization. The new crystals can then be essentially identical with the original ones. The polymer also maintains a certain order in the melt and preserves its crystallization memory. This ability has been observed in both the isotropic and oriented state, and disappears with increasing temperature of heating and with the duration of heat exposure[14].

The fact that in our case the thickness of fibrils of the remolten polymer fits in with the deformation process of the spherulite in the solid state suggests that the polymer melt also preserves a certain order during the orientation. We may call this the orientation crystallization memory. The structure of a physical molecular network arising during the crystallization of the original film is preserved.

This is also corroborated by the fact that when the polymer is thermally exposed in the zone for a short time only, at a temperature not greatly exceeding T_m (by 8°C at most), the destruction of the network is not too pronounced.

Morphological aspects of fracture relaxation

Fracture of the neck subjected to drawing is accompanied by a sudden drop in stress to zero and by relaxation of the polymer, which may be reflected in some morphological inhomogeneities. The latter have various forms, depending on thermomechanical conditions of drawing as presented in *Figure 3*.

At lower temperatures and high fracture stresses σ_F (region IA) surface waves are formed near the fracture site, which are normal to the direction of deformation (*Figure 12*). Formation of the waves requires fracture stress higher than approximately 200–250 MPa. At the same time, the occurrence of surface waves was not observed to depend on the temperature of drawing or on the draw ratio. At high T_D values no waves arise, because no higher σ_F values are reached[8]. The waves are most pronounced in the place of neck fracture and become less pronounced with increasing distance. They finally disappear (*Figure 13*) at a maximum distance of 8 mm from the fracture site (drawn samples are 50–250 mm long). At the same time, the width of waves L_w and their mutual distance l_w in the deformation axis increase (these values are defined in *Figure 12c*). The L_w values lie in the range 1–6 μm, the wave density varies between 50 and 170 per millimetre of the sample length. The wavelength cannot be determined because the waves intertwine and branch.

Similar surface waves have been observed earlier by Marikhin *et al.*[15,16] in samples subjected to zone drawing at constant stress close to their strength, and have been regarded as kink-bands which also appear in those samples. According to Marikhin *et al.*, their formation is connected with the occurrence of microcracks and cracks. Chain breaking is accompanied by release of the accumulated elastic energy, due to which local axial compression and formation of kink-bands take place. Peterlin[17] maintains a view that the cause of surface waves formation should be seen in the relaxation of the polymer following the decrease in stress.

In our case the cause of wave formation is doubtless mechanical relaxation after sample fracture. No waves arise during drawing, as is demonstrated by polymer drawing under suitable conditions in region IA interrupted at high stress immediately before fracture by cooling with vapours of liquid N_2. After careful removal of stress no surface waves could be detected on the sample. This also suggests that there is no mutual connection between cracks and surface wave formation during drawing. In some cases both waves and cracks were present simultaneously (*Figure 12c*), while in others there were either only waves (*Figure 12b*), or only cracks (*Figure 7*).

The mechanism of formation of surface waves still cannot be fully elucidated using the existing results, but we believe that they may be a consequence of a local elastic irreversible contraction of extremely stretched amorphous chains (high birefringence[13]) after the accumulated energy has been released after fracture.

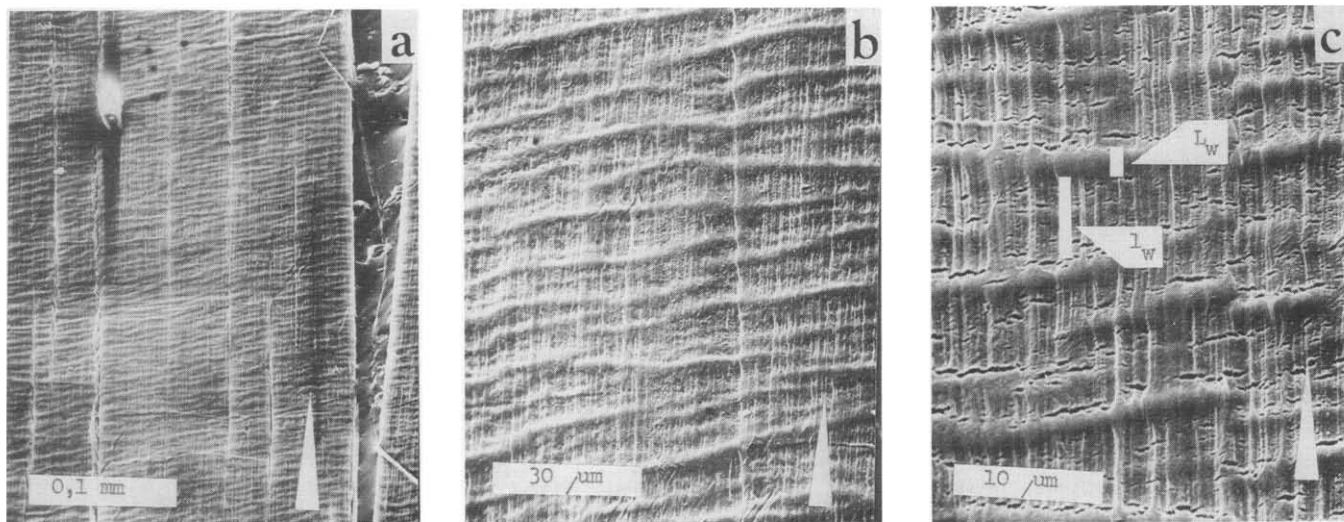The finding that no waves arise at fracture stress values

Figure 12 Surface waves of chosen samples of drawn polyethylene near fracture site. (a) IR, $T_D = 104°C$, $\sigma_0 = 11$ MPa, $\sigma_F = 353$ MPa, $\lambda_F = 44$; (b) NR, $\sigma_0 = 10$ MPa, $T_F = 102.9°C$, $\sigma_F = 628$ MPa, $\lambda_F = 86$; (c) IR, $T_D = 104°C$, $\sigma_0 = 17$ MPa, $\sigma_F = 347$ MPa, $\lambda_F = 28$. L_w and l_w respectively are the wavelength and the wave distance in the direction of deformation. Arrow shows the direction of drawing
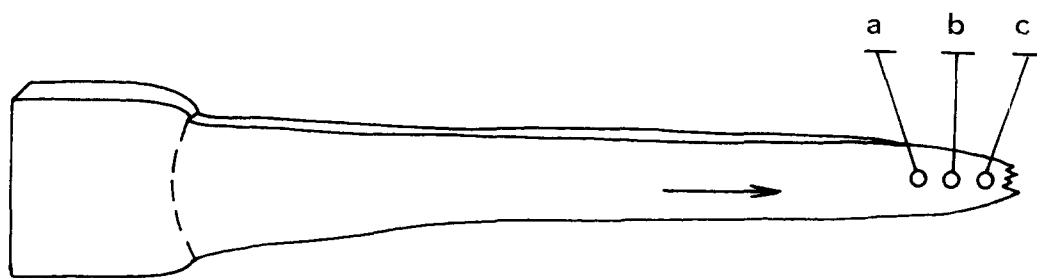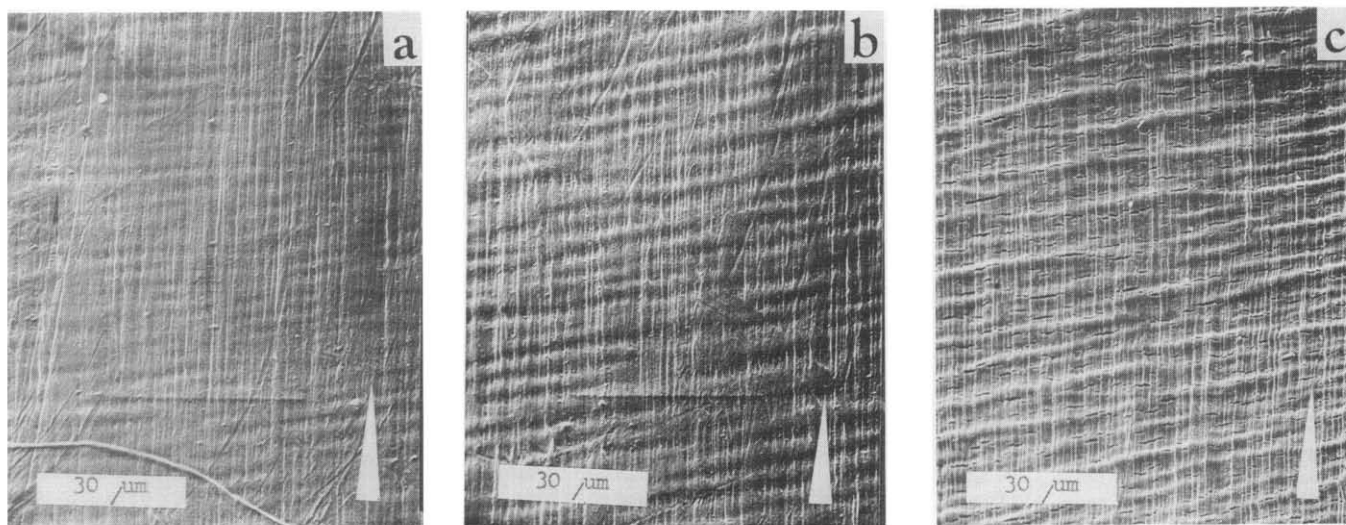

Figure 13 Development of surface waves near fracture site. IR, $T_D = 112.5°C$, $\sigma_0 = 15$ MPa, $\sigma_F = 262$ MPa, $\lambda_F = 24$. Distance from fracture (a) 6 mm; (b) 2.5 mm; (c) 0.5 mm. Arrow shows the direction of drawing

below approximately 200 MPa can be explained by the different character of the fracture process. At high stress values in zone drawing at constant load the rate of passage of the polymer volume subjected to drawing through the zone is also high, and it may also be anticipated that the fracture will be fast and will be accompanied by chain breaking (brittle fracture). Hence, the energy release will occur suddenly. A change in the period of the waves suggests that the release of energy is

quenched during the propagation from the fracture. On the other hand, at low stress values the rate of the fracture process will be lower. The chains have time to relax and may be disentangled from crosslinks of the physical network rather than undergo breaking (ductile fracture). Energy will be released gradually, without any elastic contraction, and hence formation of surface waves does not take place. This explanation is corroborated by the fact that at low σ_F values, fracture

is not preceded by formation of cracks which are due to chain breaking. At high fracture stresses it is the other way round.

In region IB (*Figure 3*) high draw ratios are not reached[8] ($\lambda < 15$). In this case the fracture relaxation is reflected in macroscopic bending of the samples. This is followed by formation of characteristic populations of kink-bands in the bends as described earlier, due to the compression acting in the opposite direction[18] (*Figure 14*).

At drawing temperature $T_D > T_m$ and low stresses applied (region II) the fracture stress values are low ($\sigma_F < 100$ MPa). In spite of this, however, consequences of fracture relaxation were observed here as lateral loosening of the fibrillar structure in domains of smooth fibrils, not further than 1–1.5 mm from the fracture site (*Figure 15*). After lowering of the stress, local back elastic contraction takes place, and longitudinal cavities arise between the fibrils. These are bridged by microfibrils drawn from the so far imperfectly crystallized (high temperature in the fracture site) transverse lamellae, the content of which is low in the case of smooth fibrils. Here we can see a difference from relaxation phenomena at lower temperature and high fracture stresses. Local elastic contraction is reflected in the surface waviness and not in the lateral loosening, because a major amount of transverse lamellae is better crystallized and better ensures mutual fixation of adjacent fibrils.

No fracture relaxation appears in the region IC of intermediate fracture stresses (100 MPa $< \sigma_F <$ 200 MPa). The σ_F values are low for the formation of surface waves. At the same time the structure is sufficiently strongly fixed laterally against formation of longitudinal cavities.

CONCLUSIONS

Formation of morphology in the zone drawing proceeds either via plastic deformation of the solid phase or via oriented crystallization of the melt, depending on thermomechanical conditions. The existence of transverse interfibrillar lamellae also indicates that during plastic deformation of the solid phase partial melting and epitaxial recrystallization of lamellae with folded chains

on central fibrils takes place. At lower draw ratios this fact can also be regarded as one of the likely causes of periodicity detected by the small-angle X-ray scattering on samples of drawn polyethylene[19].
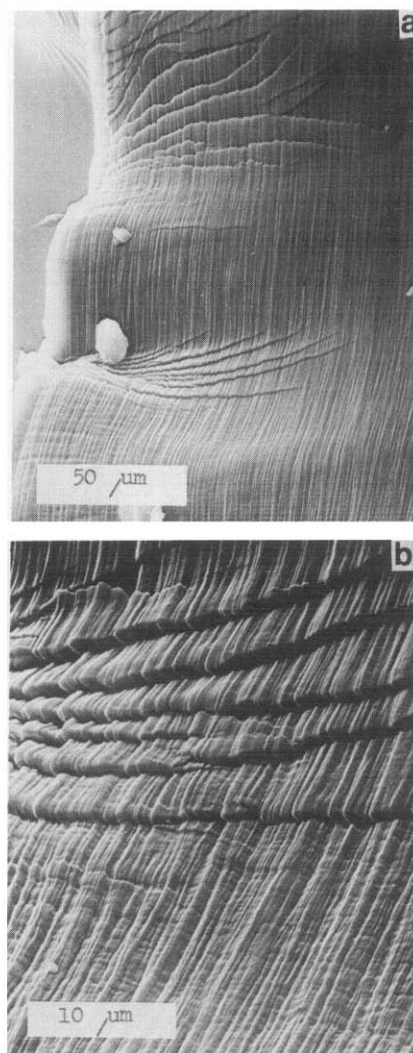
Figure 14 Kink-bands in the bend of the polyethylene sample drawn in the IC region at lower (a) and higher (b) magnification. IR, $T_D = 129.5°C$; $\sigma_0 = 17$ MPa; $\sigma_F = 159$ MPa; $\lambda_F = 12.8$
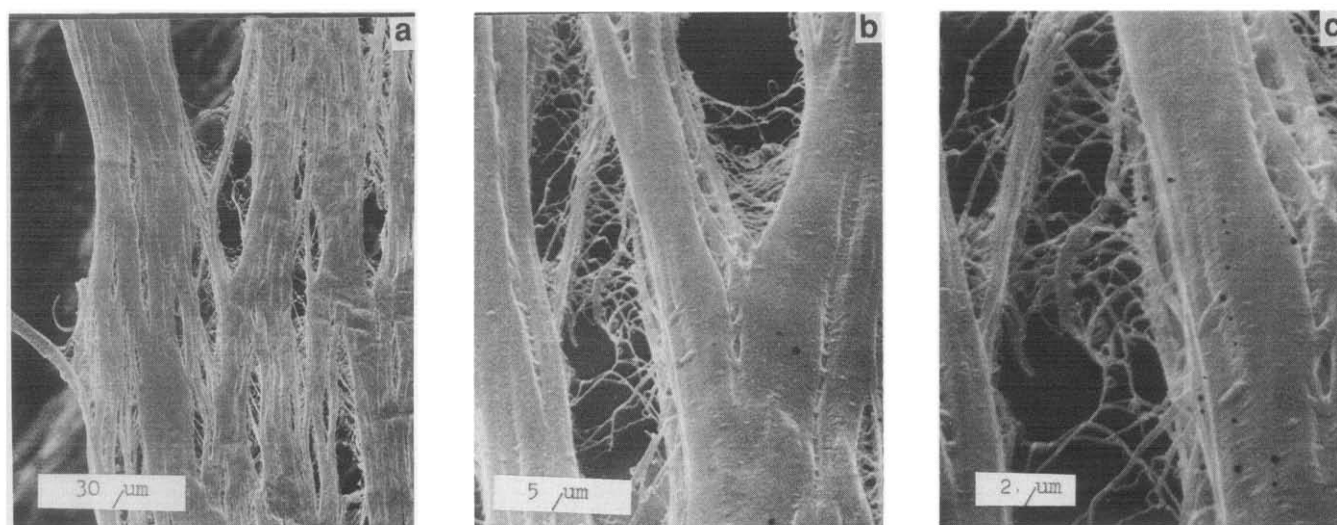
Figure 15 Formation of interfibrillar cavities as a result of fracture relaxation of polyethylene in region II at different magnifications. NR, $\sigma_0 = 1$ MPa, $T_F = 139.2°C$, $\sigma_F = 80$ MPa, $\lambda_F = 109$

At high stress values the polymer is overdrawn in the region of the solid phase deformation. Cracks are formed in the polymer, which propagate with increasing stress. The occurrence and size of the cracks depend on the instantaneous stress and not on the temperature of the zone and on the draw ratio.

In the oriented crystallization from the melt zone heating under adequate conditions gives a polymer with a negligible content of lamellar growths on the fibrils, i.e. a structure usually characterized by high modulus and strength values. This is also supported by results obtained by, for example, Bashir and Keller[20].

The thickness of fibrils depends only on the draw ratio. The observed dependence suggests that after its transformation into a fibril the spherulite preserves its orientational crystallization memory.

Mechanical relaxation of the polymer after fracture at lower temperatures and high fracture stresses in the case of solid phase drawing is reflected in the formation of surface waves. If drawing proceeds from the melt, and high temperatures $(T_D > T_m)$ and low stresses are used, interfibrillar longitudinal cavities are formed. At high temperatures and medium stress values the relaxation is reflected in a macroscopic bending of the broken sample and in the formation of kink-bands. In the region between these two extreme cases no fracture relaxation can be seen. The occurrence of relaxation morphologies is not affected by the draw ratio, only by the fracture stress and temperature.

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