Formation and properties of single texture polyethylene produced by rolling

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The formation of single textured low density polyethylene by unidirectional rolling has been investigated. It was found to be associated with the shear of the sample during annealing, which is a reversal of the shear imparted by the rolling process. Single texture could be produced from double texture by compressing it obliquely in such a way as to simulate this shear. It is concluded that the material probably contains another component besides the single orientation of lamellae which would need to be taken into account when using it as a model for the study of lamellar properties.

1. Introduction

The formation of single texture polyethylene exhibiting only one orientation of both chains and lamellae has been reported previously [1]. It is formed by strong rolling followed by annealing of melt-pressed sheets of low-density polyethylene. The textures obtained are in many ways similar to those of double texture polyethylene, prepared by drawing followed by rolling [2, 3] except that only one set of orientations is present. The same axes and orientation symbols are used, and these are summarized in Fig. 1, which also shows typical double texture wide and low angle X-ray diffraction patterns. The lamellae are pictured as being composed of a crystalline core surrounded by disordered material which includes the fold surface. Thus the long spacing d is given by $d = l \cos(\phi + \theta) + d_a$ where l is the length of chain in the cores, $(\phi + \theta)$ is the chain obliquity, and d_a is the thickness of the interlamellar layer.

The single texture forms in the surface layers of the sheet, as shown in Fig. 2, the two surfaces giving diffraction patterns which are mirror images of each other. The central zone, which is turbid and milky, in contrast to the clear edge zones, possesses a double texture. The single texture layer can be detached by microtoming. To enable this the specimen is glued down to a flat metal surface with Araldite after careful cleaning and "casing" (crosslinking by activated species of inert gases) in low pressure helium subjected to an r.f. field [4]. The single texture can be obtained with varying degrees of per-

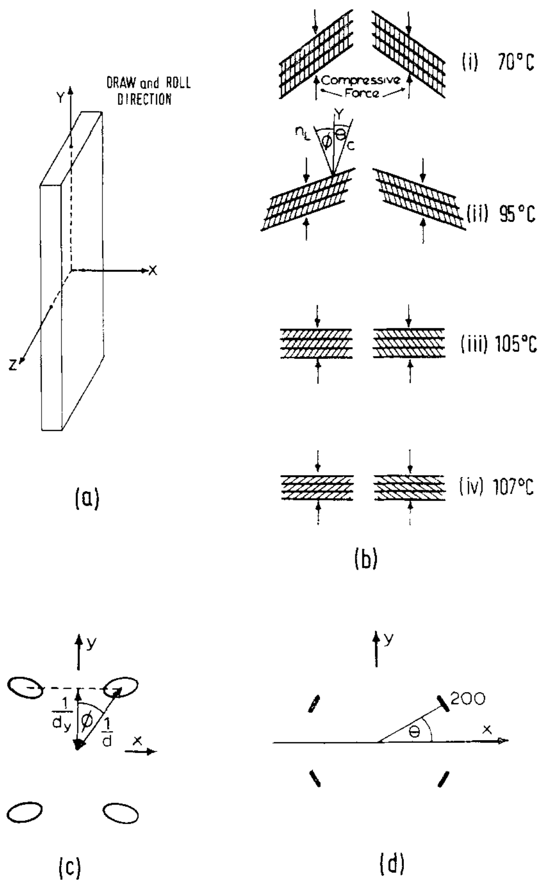

Figure 1 (a) Definition of axes relative to rolled sheet. (b) Lamellar textures deduced for double texture polyethylene annealed at different temperatures. (c) Typical low-angle X-ray diffraction pattern. (d) Typical wide-angle X-ray diffraction pattern.

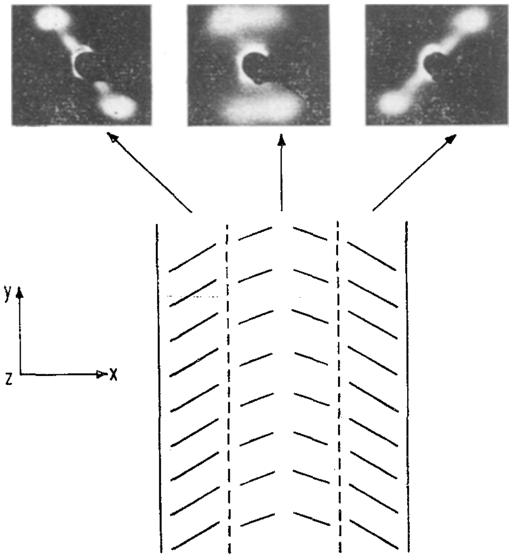

Figure 2 Schematic diagram of zone structure of rolled and annealed sheet, and corresponding low-angle diffraction patterns (after Point *et al* [1]).

fection, faint X-ray reflections corresponding to a second texture sometimes being present. As it was found difficult to obtain reproducible results an investigation was carried out into the conditions of its formation.

2. The rolling process

Strips of melt-pressed sheet about 5 cm wide and nearly 5 mm thick were rolled down to different thicknesses, both in one pass and gradually in a number of passes, though always

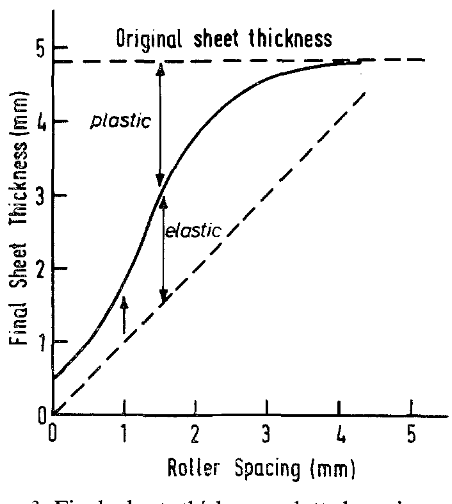

Figure 3 Final sheet thickness plotted against roller spacing. The graph does not pass through the origin because of separation of the rollers under pressure.

passed through the rollers in the same direction. The results are shown in Fig. 3. Whether the rolling was sudden or gradual did not affect the final thickness of the sheet, but single texture was only found to form after annealing if the rolling had taken place in one, or at most two, passes, and if the strip thickness had been reduced beyond the point, marked on Fig. 3 with a heavy arrow, at which the strip became very transparent and corrugated. For wide roller openings the deformation is mostly elastic (see Fig. 3) whereas for larger amounts of deformation it is almost entirely plastic. This explains the corrugated effect, as the material at the edges can expand laterally to relieve the pressure. It thus suffers less plastic strain and contracts on release of the pressure, forcing the rest of the strip to bend into corrugations. Apart from such edge effects the width of the strip remained constant during rolling.

The cross-section of a strip after rolling down in one pass is shown in Fig. 4. The top and

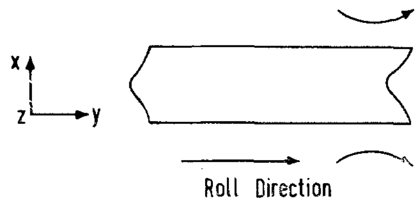

Figure 4 Cross-section of sheet after heavy rolling.

bottom surfaces have been sheared. As this shear was only present in samples rolled down in one or two passes it is probably associated with the production of the single texture. The amount of shear produced is likely to depend on the radius of curvature of the rollers and the friction at the roll surface, which could explain why differing degrees of success in producing good single texture were obtained on using different rollers. The speed of rolling is another variable which may affect the friction, hence the amount of shear, and also the amount by which the material warms up during rolling. The effect of roller speed was not investigated, however, as the large amount of slip which occurred at the roller surfaces rendered the results meaningless.

An attempt was made to produce thicker single texture by rolling a sheet 10 mm thick. The roll force necessary to produce the desired reduction, however, severely damaged the surface of the strip, cancelling any advantage in increased thickness of the single texture layer.

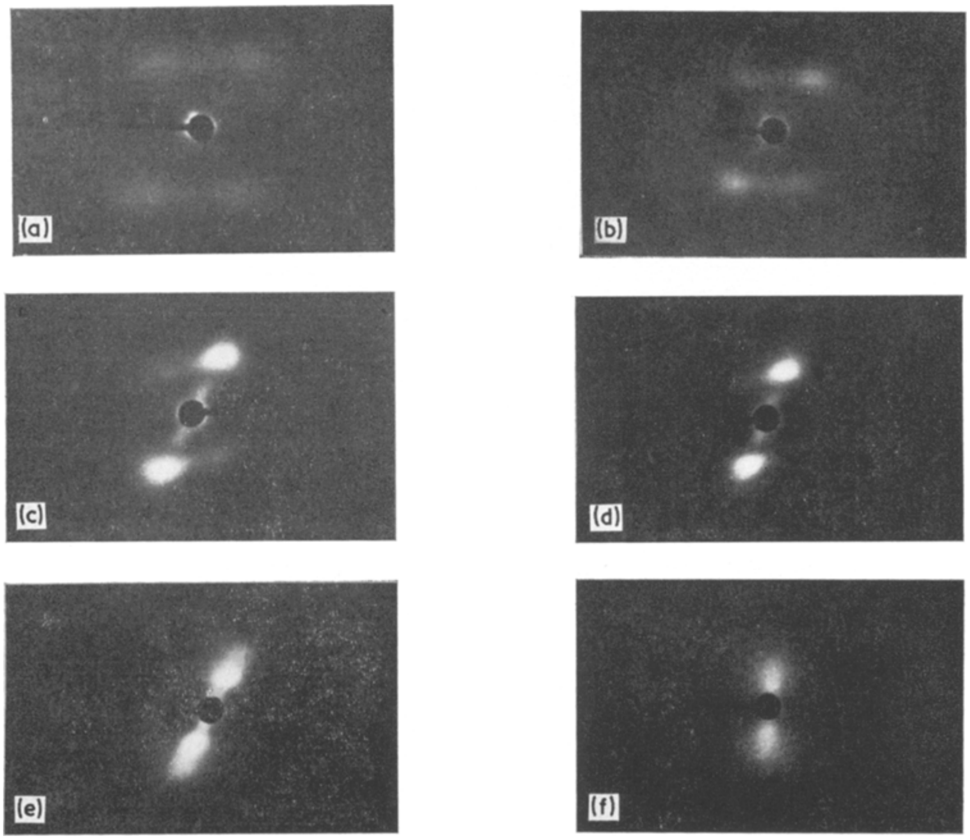

Figure 5 Low-angle diffraction patterns obtained from single texture for different annealing temperatures. The X-ray beam is along z, y is vertical. (a) unannealed; (b) 75°C; (c) 85°C; (d) 95°C; (e) 102°C; (f) 105°C.

3. The formation of single texture

The low-angle diffraction pattern obtained from the edge of an unannealed strongly rolled sheet is shown in Fig. 5. Two sets of lamellae are seen to be present though the pattern shows a slight amount of asymmetry as if it had been sheared along y, this shear being in the opposite sense in the other side of the sheet. Thus a single lamellar orientation is not present in the unannealed samples, and as can be seen from Fig. 5, only forms during annealing. A wide-angle photograph of an unannealed sample shows that the chains are aligned along the draw direction, y, and pole figure analysis has shown [1, 4] that there is a twinned texture similar to that seen in double texture obtained by drawing followed by gradual rolling [2]. After annealing, the crystal b-axis lies in the plane of the sheet and the wide-angle texture is similar to that of double texture except that only one orientation of the chains is present.

The changes in the low-angle diffraction pattern on annealing at successively higher temperatures are shown in Fig. 5. The asymmetry of the pattern increases and one reflection intensifies, as usually occurs on annealing, while the other grows fainter and eventually disappears. Thus the single texture develops during annealing and is not present before annealing. Fig. 6 shows the deformation of a rolled strip on annealing. Apart from thickening it has also sheared, by a reversal of the shear produced by rolling (compare Fig. 4), as shown by the tilt of the

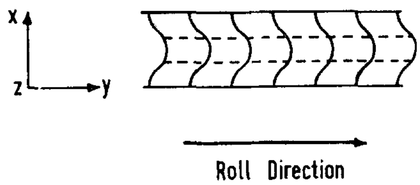

Figure 6 Cross-section of sheet after annealing at 100°C. The section was rectangular before annealing. The dotted lines represent the boundaries between the clear outer and turbid central zones.

initially straight lines marked on the edge of the rolled sheet. This shear became apparent on annealing at about 90° C, which is the minimum annealing temperature required to produce good single texture, and so appears to be associated with the single texture. The absence of shear at the very surface of the sheet explains why double texture diffraction patterns were sometimes obtained from the extreme edge [1]. This pattern of deformation on rolling has been predicted theoretically for metals [5].

The view that the single texture is produced by shear during annealing was confirmed by an experiment in which single texture was produced from double texture. A double texture specimen annealed at 75° C was cut at approximately 45° to y in the x-y plane and compressed, as shown in Fig. 7, at 75° C. As there is little deformation

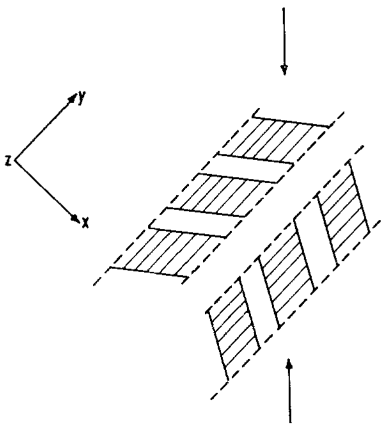

Figure 7 Diagram to show the relationship between the compression direction, marked by arrows, and the two orientations of lamellae.

along z the strain produced by compression in this direction is mechanically equivalent, for small strains, to a shear parallel to y in the x-y plane, plus a rotation. It thus approximately reproduces, by externally applied forces, the conditions under which single texture is annealed. The internal forces which cause the contraction and shear of the sample on annealing are attributed to the contraction of stretched chains, which, aided by partial melting of the sample, should act to restore the sample to its original state.

The results of this experiment are shown in Fig. 8. The diffraction patterns are remarkably similar to those obtained from single texture. One reflection has intensified and the other has

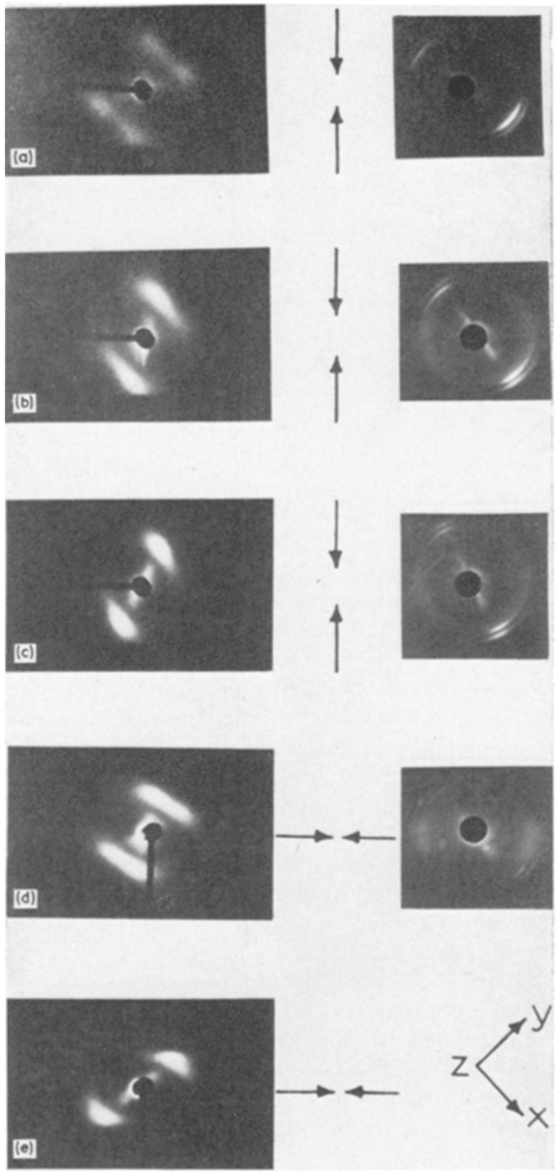

Figure 8 Results of compressing double texture in the directions indicated by arrows: (a) zero strain; (b) compressed 16%; (c) stress released after compression of 34%. Irreversible strain = 25%; (d) compressed at 90° to original compression direction; (e) compressed further.

disappeared, though it is not clear whether it has actually disappeared or has merged with the intense reflection.

The deformation is largely irreversible on release of the stress, but on rotating the sample and compressing it at 90° to the original compression direction, the symmetry of the

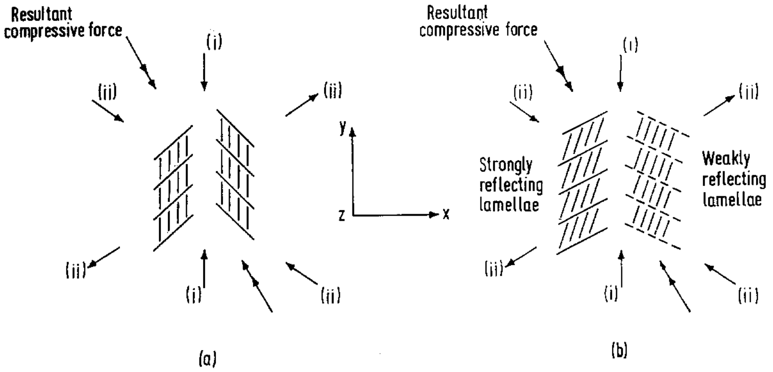

Figure 9 Diagram to show the forces acting on the lamellae during annealing: (a) in relation to the un-annealed structure; (b) in relation to the annealed structure.

pattern is restored. Further compression in this direction again produced a single texture pattern.

A similar experiment carried out at room temperature did not have the effect of producing single texture, but one at 85°C did. It appears, therefore, that the high temperature is a necessary requirement for the single texture to form. It can be seen from Fig. 8 that there is an irreversible increase in long spacing and low-angle diffraction intensity, indicating that recrystallization is involved. If this were associated with the formation of the single texture it would account for the need for elevated temperatures. However, the apparent reversibility of the process suggests that the two sets of lamellae retain separate identities.

It has been brought to our notice (Point, private communication) that by specially strong rolling single texture can be obtained without the intervening double texture. Irrespective of the exact route along which the single texture has established itself in such a case the following generalization of our present experiment should still hold, i.e. that a portion of the lamellae initially present will be unfavourably oriented to begin with and will suffer the fate of the vanishing lamellae of the double texture. Further, with the increasing severity of rolling there could be substantial retraction on removal of the roller pressure which, combined with increased heating effects, could provide some of the reverse shear which in our case was introduced by the annealing treatment.

4. The annealing sequence

The annealing sequence of single texture can now be understood in more detail if the development

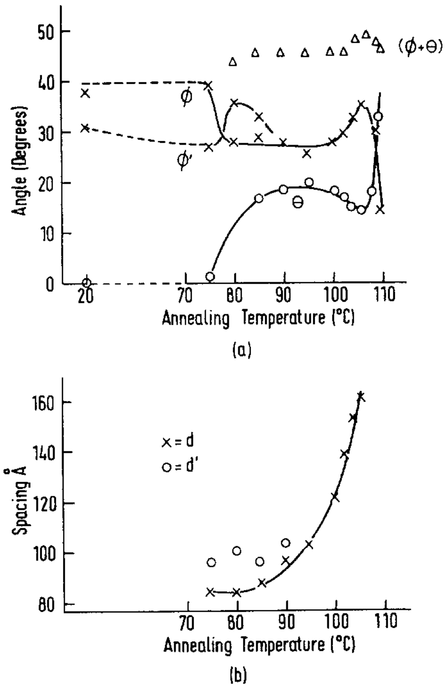

Figure 10 Orientations of chains, θ, and lamellae, ϕ, ϕ', and long spacings d, d', plotted against annealing temperature for single texture samples.

of the texture is interpreted in terms of a combination of two internal stresses. One of these, denoted (i) in Fig. 9, is a compressive stress acting along the roll direction. It is responsible for the shrinkage of the sample along y and is similar to that which has been used to explain the formation of double texture. The second set of forces is responsible for the shear of the sample indicated in Fig. 6, and can be approximated by a combination of a compressive force and a tensile

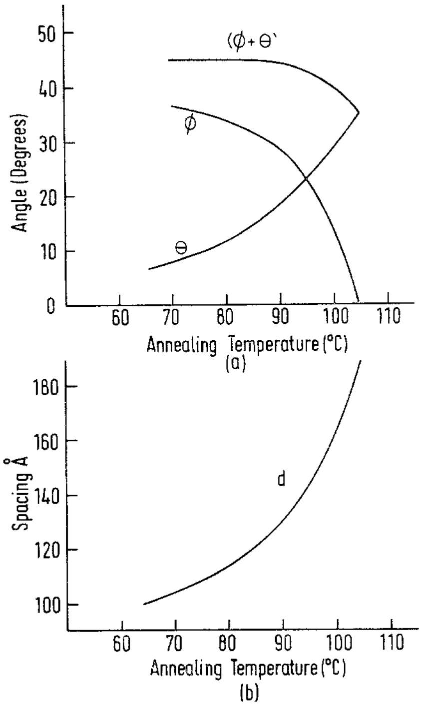

Figure 11 Orientations of chains, θ, and lamellae, ϕ, and long spacings, d, plotted against annealing temperature for double texture.

force acting at about 45° to y, denoted (ii) in Fig. 9. The resultant of these forces will be a compressive stress acting at some angle between 0° and 45° to y, as shown in Fig. 9. A quantitative analysis of the relationship between sample dimensions and changes in lamellar texture has not been attempted, as this has not been found possible in the simpler double texture case. However, the development of the low-angle diffraction pattern can be interpreted qualitatively, as follows.

Orientations and spacings for both the strong and weak reflections are plotted against annealing temperature in Fig. 10, while Fig. 11 shows, for the sake of comparison, the corresponding plots for double texture. No significant orientation changes take place on annealing below 75°C, although the long spacings increase and the low angle diffraction intensifies. Between 75 and 85°C ϕ decreases and θ increases, while $(\phi + \theta)$ increases slightly. Equal and opposite changes in ϕ and θ can be explained by rotation of lamellar normals towards the compression axis caused by lamellar slip, while the increase in $(\phi + \theta)$ can be explained by chain slip within the lamellae caused by the same compressive force. Meanwhile ϕ' shows a more complicated behaviour, first decreasing, then increasing, and finally decreasing. As only one chain orientation is observed the obliquity of the chains in the weakly diffracting lamellae must be $(\phi' - \theta)$. As can be seen from Fig. 10, this decreases continuously to a value of 10° at 90°C. Lamellar slip will tend to decrease ϕ, while chain slip causes a change in ϕ proportional to $[\cos^2\theta - \cos^2(\phi' - \theta)]$ [9]. Hence, when $(\phi' - \theta) > \theta$ chain slip will cause ϕ' to increase, and when $(\phi' - \theta) < \theta$ it will cause ϕ' to decrease. Thus the initial decrease in ϕ' can be attributed to a combination of chain and lamellar slip, and the subsequent rise and fall to the predominance of chain slip. Beyond 90°C the weak reflection becomes indiscernible.

Returning to the strong reflection it can be seen from Fig. 10 that the orientation remains constant over a wide range of annealing temperatures. This is probably due to the fact that the lamellae are normal to the resultant compressive force (Fig. 9). A changing balance between the two components of this resultant, thus altering its direction, can be held responsible for the increase in ϕ and $(\phi + \theta)$ between 100 and 105°C. To cause an increase in ϕ the shearing forces must increase, causing the resultant to move away from y. In the final stages of annealing the resultant must move towards y to account for the observed rapid decrease in ϕ. Above 110°C the texture randomizes.

The long spacing values for the strongly reflecting lamellae are smaller than are observed in double texture samples annealed at the same temperatures. This can be attributed to the compressive force acting in a direction normal to these lamellae, which also explains the higher values of $(\phi + \theta)$ often observed. $(\phi + \theta)$ was found to be a particularly variable quantity, ranging from 40° to 54° in samples prepared in slightly different ways. Presumably the higher values correspond to a greater compressive force normal to the lamellar faces. The long spacings of the weakly reflecting lamellae are longer, corresponding to the smaller obliquity of the chains within these lamellae ($d = l \cos(\phi' - \theta) + d_a$).

There remains the problem of just what has happened to the material making up the weakly reflecting lamellae. It seems that they are disrupted by the large amount of chain slip which takes place in them and are prevented from developing in a coherent manner by the opposing orientational effects of lamellar slip and chain slip. It is uncertain, however, whether these lamellae comprise approximately half of the total sample, and do not reflect because they are irregularly formed, or whether most of the material has instead been incorporated in the strongly reflecting lamellae. There is some similarity with the case of kink bands formed by compression of doubly oriented high-density polyethylene, whose low-angle diffraction patterns are very similar to those of single texture [6]. The kink band boundary coincides with the faces of one set of lamellae, which continue to reflect, while the other set of lamellae are so grossly deformed that they cease to produce a low-angle diffraction pattern.

5. Properties of single texture

At first sight, single texture polyethylene would appear to be useful for studying the properties in terms of lamellae, as it apparently consists of a single orientation of both lamellae and chains. The anisotropy of thermal expansion and of swelling have been studied from this point of view by Point *et al* [7]. The thermal expansion between -15 and $+20°$C, was found to be a minimum along the chain direction whereas at higher temperatures it was a minimum along y. At the lower temperatures the expansion will be dominated by the anisotropy of the crystal expansion coefficients, hence the minimum along c. At higher temperatures melting and rubber elastic forces will be involved, and in this situation there is symmetry about y. In other words, the anisotropy of the thermal expansion seems to be determined not by the crystal axis orientation or the lamellar orientation, but by a larger scale element of the structure which is symmetrical about y. The swelling anisotropy is also inconsistent with a simple model of oriented lamellae, and it is concluded that the material contains another phase which is relatively disordered, and which is arranged in layers parallel to the rolling plane. This claim is also made on the basis of thermal and annealing studies [8]. From the above discussion of the formation of single texture it seems likely that this disordered phase could be the remnants of the weakly reflecting lamellae. It is probable, however, that double texture itself contains a certain amount of disordered extra-lamellar material, its nature depending on the annealing temperature. For high annealing temperatures, around 100°C, differential scanning calorimetry shows the presence of a large amount of low melting material which presumably crystallizes in the form of small, imperfect crystals on cooling from the high annealing temperature. As the change in low-angle X-ray periodicity is found to be equal to the change in sample length on stretching or swelling at room temperature [9], indicating a series coupling of lamellae and inter-lamellar material, the additional material crystallised on cooling cannot be part of this series. Consequently, it is visualized as being arranged essentially in parallel with the lamellae which contribute to the main low-angle diffraction peaks. The sort of structure which is envisaged is shown in Fig. 12 for a single texture sample. The existence of the extra-lamellar material explains the lateral contraction observed on stretching and the fact that the samples swell by about 5% along x, which in parallel lamellar samples is parallel to the lamellar surfaces [9]). (The samples also swell about 10% along y with a corresponding increase in long spacing d). Single texture, however, shows a larger amount of swelling in this direction: a sample annealed at 100°C expanded 10% along x on swelling in xylene at room temperature. According to Point *et al* [7] the maximum degree of swelling occurs in a direction parallel to the lamellar surfaces. This difference between double and single texture suggests that in the latter case there is a higher proportion of disordered material lying in parallel with the lamellar stacks, which has its origin in the remnants of the stacks of lamellae which disappeared except for the weakly reflecting residue.

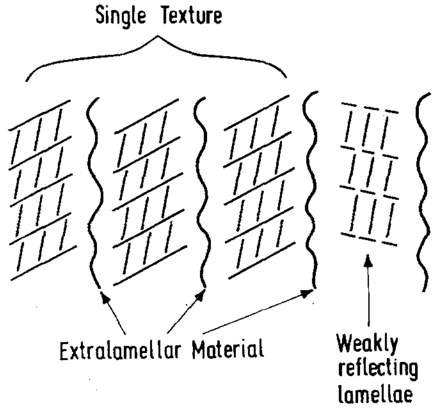

Figure 12 Schematic diagram of envisaged structure of single texture.

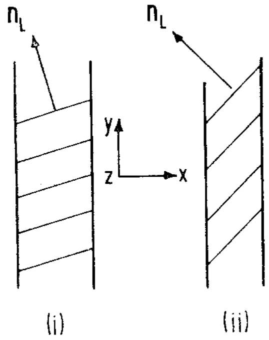

Figure 13 Shear of sample expected if deformation proceeded by lamellar slip alone: (i) before, (ii) after, stretching along y.

The proposition that the lamellae are arranged in stacks parallel to y rather than being indefinitely extended is supported by the fact that the sample does not shear when extended along y. Fig. 13 shows the rotation of the lamellar slip planes expected on extension, and if this were the only deformation mechanism present it should be reflected in a shear of the whole sample, as in a metal single crystal. It has been shown by X-ray diffraction [9] that in single texture samples the change in sample length along y can be explained almost entirely by the lamellar slip, but when a grid was printed on the xy face of a specimen before stretching, the grid lines were observed to remain parallel to x and y. This suggests that there are planes of discontinuity perpendicular to x along which adjacent stacks of lamellae can be displaced relative to each other. They must lie along y, rather than, for example, along the chain direction, in order to preserve the observed equality between change in sample length and change in lamellar periodicity [9].

The above considerations mean that the apparently single textured nature of the samples is probably indicative of a more complex structure than that of double texture, rather than a simpler one. In this connection the transparency of single texture should be mentioned. This transparency is striking when a rolled and annealed sheet is viewed edgewise along z[1] and has been cited as evidence for the material possessing a simple uniform texture. In fact transparency was not found to be necessarily indicative of good single texture and double texture as normally prepared appears just as transparent. Transparency to light is indicative of uniformity on a scale somewhat larger than that of lamellae, i.e. of the absence of voids of the order of thousands of Angstroms in size, and it seems that this is achieved when shear forces are involved. These have been shown to be involved in the formation of single texture, and will also be involved in any rolling process, as when double texture is formed. In addition, it has been reported recently that highly transparent material is obtained when high density polyethylene crystallizes under shear conditions [10].

6. Conclusions

It has been shown that single texture polyethylene can be produced from double texture both by the action of internal forces released during the annealing process, and by external forces which simulate their effect. The details of the annealing process can also be explained by these internal forces, in a manner analogous to the explanation of the formation of double texture. Although in the present case single texture was observed to develop from double texture, Point has demonstrated that it is not a necessary intermediate stage. This does not affect the general argument however, that lamellae in certain orientations tend to develop at the expense of those less favourably oriented.

The discussion of the properties of single texture polyethylene revealed that their anisotropy is not determined simply by the orientation of the lamellae, which appear to be arranged in stacks separated by layers of disordered material possibly comprising the remnants of the weakly diffracting lamellae. Thus, while of interest for their own sake, they do not represent such a decisive simplification for the correlation between lamellar structures and properties as the X-ray diffraction patterns suggest, i.e. the uniquely oriented parallel lamellar arrangement revealed by the X-rays cannot be scaled up to the macroscopic sample dimension without the introduction of further structural features.

Acknowledgements

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