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An infra-red spectroscopic and X-ray diffraction study of cold-drawn high density polyethylene samples

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Three samples of high-density polyethylene, one linear, the second with one ethyl branch per thousand carbon atoms and the third with a comparable concentration of butyl branches, cold drawn at 60° C to elongations of 300, 800 and 1600%, have been examined by infra-red spectroscopy and wide- and small-angle X-ray diffraction. The results are consistent with, and give additional information about, the Peterlin model of plastic deformation. The change in crystallinity with draw ratio has been measured by infra-red spectroscopy and a wide-angle transmission X-ray diffraction method that minimizes the effect of the uniaxial orientation of the drawn specimens. Wide-angle measurements by reflection proved to be unreliable. Changes in the relative concentrations of methylene groups in crystalline regions, in gauche conformations and in tie chains in amorphous regions, and the alignment of tie molecules, have been followed by unpolarized and polarized infra-red spectroscopy. Small-angle X-ray diffraction measurements show that microvoids, with average dimensions of 250 and 80 Å parallel to and perpendicular to the draw direction respectively, are formed during the transition from the lamellar to the fibrillar structure.

1. Introduction

The morphological changes that occur during the cold-drawing of polyethylene have been the subject of much study and a great deal of information has emerged from the application of a variety of techniques. As long ago as 1949, Brown [1] made X-ray diffraction measurements on samples stretched at 96° C and at room temperature and was able to follow the resulting preferred orientation as a function of the extension. Stein [2–5] used the techniques of X-ray diffraction, birefringence and infra-red dichroism to examine specimens which had been subjected to various mechanical and thermal treatments. One of his conclusions was that appreciable orientation of the amorphous phase occurs. The results were expressed primarily as mathematical orientation functions and no detailed information in terms of chain morphology was forthcoming. Aggarwal *et al.* [6] made a series of interesting measurements in the necked regions of stretched specimens, using a microbeam X-ray diffraction camera, and were able to obtain information about *a*-, *b*- and *c*-axis orientation.

However, the more detailed picture which has emerged of recent years is largely the result of the extensive studies of Peterlin and co-workers, a very useful review of which has been provided by Peterlin [7]. By combining the results of measurements using wide- and small-angle X-ray diffraction, electron microscopy and infra-red dichroism with mechanical studies a fairly detailed molecular model for plastic deformation was developed. The existence of three stages in the cold-drawing process became apparent, although they are to some extent intermixed in the necked region. These stages are the plastic deformation of the original spherulitic structure, the discontinuous transformation of the spherulite into fibre structure by micronecking and the plastic deformation of the fibre structure.

The second stage of this process is of particular interest. It begins once the draw ratio has reached the point where stack rotation of the parallel lamellae has occurred, together with other changes such as chain slip and tilt; there is then a position of maximum compliance for fracture by micronecking. The micronecks transform each lamella into microfibrils consisting of folded chain blocks broken off the lamella. The chains bridging the crack are partially unfolded during this process and act as interfibrillar tie molecules. The microcracks in every stack of lamellae in a thin destruction zone are concentrated to produce bundles of microfibrils of a rather uniform draw ratio. These fibrils, a few thousand angstroms in width, include the interlamellar ties of the original sample as interfibrillar tie molecules connecting adjacent microfibrils. There is a more or less random distribution of destruction zones in the neck and this makes the transformation from a spherulitic to a fibre structure appear to be a gradual process in spite of the discontinuous transformation in the micronecks.

In interpreting a large amount of experimental work in terms of this plastic deformation model Peterlin [7] was careful to emphasize that it must not be considered as a complete and final version. He suggested that new experimental data were needed to clarify many details and when such results were forthcoming the model might require modification and would certainly have to be made more quantitative. Some of these new results have subsequently become available. For example, Bessell and Young [8] have recently made small-angle X-ray diffraction measurements on a linear polyethylene oriented in compression at different temperatures. The results were identical with those obtained from orientation by tension and they concluded that the aspect of Peterlin's model which postulates the formation of a pseudo-melt, as the result of hydrostatic tensile stress, in which there is sufficient chain mobility for recrystallization to occur requires modification. Furthermore, by the use of more sophisticated X-ray diffraction techniques, Suehiro *et al.* [9] have studied lattice distortion and mosaic block crystal size as a function of draw ratio and have interpreted the results in terms of the formation of a fibre structure.

The purpose of the present work has been to provide additional experimental evidence to aid a fuller interpretation of the Peterlin model. Previous studies [10] on a series of heavily cold-drawn polyethylene samples of varying stress crack resistance, using unpolarized and polarized infra-red spectra, showed the value of studying the absorbance ratios of pairs of bands characteristic for methylene groups in the lamellae and in gauche and trans conformations in the amorphous phase. The gauche methylene groups are present in random chains and the trans methylene groups in tie molecules. This approach offers interesting possibilities when applied to specimens drawn to various extents. Although wide-angle X-ray diffraction studies have been reported [11, 12] they were concerned with the orientation and the change in crystallite size and in paracrystallinity which occur during drawing. No attempt appears to have been made to measure changes in crystallinity, to supplement the infra-red measurements of Glenz and Peterlin [13]. Such measurements pose problems because of orientation and paracrystallinity effects but they merit study. Finally, rather more detailed information may emerge from additional small-angle X-ray diffraction studies.

2. Experimental

Three types of linear polyethylene have been studied: Rigidex 140-60, a substantially linear material having less than one branch per thousand carbon atoms, Rigidex 2000 with about one ethyl branch per 10^3 C and an experimental polymer having about one butyl branch per 10^3 C. The three were compression-moulded into sheets, at 170° C and 20 tons pressure on a 4 in. ram ($25\,\mathrm{MN\,m^{-2}}$). They were allowed to cool to ambient temperature over a 5 min period. Dumbbell shaped strips were cut from the sheets and were cold-drawn in an Instron tensile testing machine at a rate of $2\,\mathrm{cm\,min^{-1}}$ in air at 60° C. Extensions of approximately 300, 800 and 1600%, measured from marks drawn on the specimen surfaces before stretching, were used. In the case of the 1600% extension the sample was drawn initially to about half of this extent and then reclamped at the two ends of the necked portion for the additional drawing. This stretching of the already necked regions introduced more orientation than would have resulted by continuing the original stretching, which was leading primarily to an increase in length of the necked region. The samples broke at extensions greater than 1600%.

Infra-red spectra were measured on a Grubb Parsons "Spectromaster" spectrometer. In order to minimize any effects resulting from partial polarization of the radiation by the optical system of the spectrometer [14, 15] the measurements with both polarized and unpolarized radiation were made with the long axis of the drawn strips (the draw direction) at an angle of 45° to the spectrometer entrance slit. In order to intercept the whole of the radiation beam it was necessary to mount four of the 4 mm wide drawn strips side by side; this posed no problems. A wire grid polarizer was used to make the infra-red dichroic measurements.

The degree of uniaxial orientation of the drawn specimens was established by X-ray diffraction pole figure measurements. These were made with a Philips PW 1010 generator, a Schulz texture goniometer and computer assessment of the results [16]. The (0 2 0), (2 0 0) and (0 0 2) pole figures were obtained.

The X-ray diffraction measurements of crystallinity were made with a Philips powder diffractometer using Ni filtered Cu*Kα* radiation. The conventional methods for crystallinity determinations are based on the assumption that the crystallites are oriented randomly, a condition clearly not met in the case of drawn specimens. In order to minimize possible errors from this factor the specimens were examined by two methods. In the first the strips were mounted in the reflection position, first parallel to and then perpendicular to the plane containing the incident and reflected beams. In the second method the drawn strips were mounted for transmission measurements and were rotated at 80 rpm. The requisite range of 2θ values was step-scanned, using a counting time of 100 sec for each step, thus eliminating the effect of sample orientation.

The interpretation of the diffractometer traces constructed from the step-scanning measurements was based on the method of Matthews *et al.* [17] and has been described by Preedy [18]. The small-angle X-ray diffraction patterns were recorded photographically with a Rigaku Denki camera.

3. Results and discussion

3.1. Infra-red spectroscopic measurements

Values for the reduced structural factor A' at $1894\,\text{cm}^{-1}$, defined [19] as $A1894/A$ (ITB), where A (ITB) is the absorbance of a convenient internal thickness band which eliminates the effect of sample thickness and density, were calculated using the $910\,\text{cm}^{-1}$ vinyl out of plane deformation mode as the internal thickness band. The reduced structural factor for a fully crystallized sample, $A'_{\alpha=1}$, where α is the fractional crystallinity, was obtained from A' measurements on a series of undrawn samples whose crystallinities were measured by the conventional X-ray diffraction method, by extrapolation to $\alpha = 1$. Then, because the $1894\,\text{cm}^{-1}$ band is known to be associated with methylene groups in crystalline regions only [20] the ratio of the A' and $A'_{\alpha=1}$ values gives the fractional crystallinity. The results for the three samples at the three draw ratios are given in Table I; the values in parentheses for the undrawn materials are those from the X-ray diffraction measurements. The results are in line with those of Glenz and Peterlin [13]. They show a reduction in crystallinity at intermediate draw ratios followed by a recovery towards the initial value. In the case of Rigidex 2000 this recovery is complete at 1600% draw but it falls short with the other two polymers. This indicates differences in drawing behaviour between three substantially crystalline near-linear polyethylenes where the only structural difference is in the type of the low level of chain branches present.

TABLE I Results of infra-red spectroscopic crystallinity measurements on three cold drawn polyethylenes

Sample	Degree of draw (%)	Crystallinity (%)
Rigidex 2000	Undrawn	(78)
	300	72
	800	74
	1600	79
Rigidex 140-60	Undrawn	(84)
	300	78
	800	79.5
	1600	81.5
Experimental polymer	Undrawn	(79)
	300	71
	800	72
	1600	76

These differences are also evident from absorbance measurements on the three bands at 1894, 1303 and $1080\,\text{cm}^{-1}$. The method of calculating the absorbance ratios $A1894/A1303$ and $A1894/A1080$, which proved useful in a recent study on specimens drawn from linear polyethylenes having different stress crack resistances [10], has been applied and the results are given in

TABLE II Changes in the concentrations of methylene groups in crystalline regions and in gauche conformations and tie chains in amorphous regions as a function of draw ratio for three cold drawn polyethylenes

Sample	Degree of draw (%)	Infra-red band absorbance ratio	
		1894/1303	1894/1080
Rigidex 2000	Undrawn	0.370	2.14
	300	0.271	1.50
	800	0.308	1.72
	1600	0.347	3.22
Rigidex 140-60	Undrawn	0.450	3.66
	300	0.524	4.50
	800	0.594	6.18
	1600	0.612	7.28
Experimental polymer	Undrawn	0.418	2.16
	300	0.252	1.41
	800	0.267	1.50
	1600	0.326	2.40

Table II. The 1894 $\mathrm{cm^{-1}}$ band is associated wholly with methylene groups in crystalline regions whereas the one at 1303 $\mathrm{cm^{-1}}$ relates to such groups in gauche conformations in amorphous regions and the one at 1080 $\mathrm{cm^{-1}}$ to methylene groups in both gauche and trans conformations in the amorphous phase. The trans conformations are present in extended tie chains passing between the lamellae.

Both absorbance ratios pass through a minimum, as a function of draw ratio, in the case of Rigidex 2000 and the experimental polymer, but increase steadily from the undrawn value in the case of Rigidex 140-60. However, in each case the increase in $A1894/A1080$ from undrawn to 1600% drawn material is significantly greater than in $A1894/A1303$. These results fit into the general pattern required by the Peterlin model. At the lower draw ratios, as the spherulitic structure breaks down, an increased number of extended tie molecules in the amorphous phase are formed at the expense of regularly folded chains in the crystalline lamellae. However, at higher draw ratios regions of very highly aligned tie molecules are formed. These are no longer amorphous regions in the conventional sense and the methylene groups present in them do not contribute to the absorption at 1080 $\mathrm{cm^{-1}}$ which therefore decreases. The smaller changes in the $A1894/A1303$ ratios show that the methylene groups in gauche conformations, presumably in random chain loops, play a less significant part in the transition from the spherulitic to the fibrillar structure. The differing behaviour of Rigidex 140-60 may be a consequence of the substantial absence of branching, or the fact that its $\bar{M}_w$ value is approximately half that of the other two samples studied.

The alignment of tie molecules into what constitute essentially fibrillar crystalline regions, accounting for some 30% of the sample at high draw ratios [21], is also evident from the results of the dichroic measurements. These were made on the 1080 $\mathrm{cm^{-1}}$ band and also on the one at 2010 $\mathrm{cm^{-1}}$, which is characteristic of extended trans sequences in both crystalline and amorphous regions. The results given in Table III show that the dichroic ratio of the 2010 $\mathrm{cm^{-1}}$ band changes much more markedly as a function of draw ratio than that of the band at 1080 $\mathrm{cm^{-1}}$. This is to be expected once regions of highly aligned tie molecules begin to form. The precise values of the two dichroic ratios, for a given draw ratio, differ among the three samples. However, as it has already been shown [10] that these values are influenced by the stress crack resistance of the polymer, and this parameter varies considerably among the three polymers examined, it is the change of dichroic ratio with draw ratio that is of significance in the present context.

TABLE III Results of infra-red dichroic ratio measurements on three cold-drawn polyethylenes

Sample	Degree of draw (%)	Dichroic ratio	
		2010 $\mathrm{cm^{-1}}$	1080 $\mathrm{cm^{-1}}$
Rigidex 2000	300	8.0	0.734
	800	9.3	0.680
	1600	22.3	0.405
Rigidex 140-60	300	14.0	0.705
	800	15.0	0.610
	1600	25.4	0.400
Experimental polymer	300	7.45	0.734
	800	9.6	0.652
	1600	19.2	0.520

The overall conclusion to be drawn from the three types of infra-red measurements is that they are in line with and provide additional confirmation for the Peterlin model of plastic deformation. However, secondary factors, such as those manifesting themselves in terms of varying stress crack resistance also come into the reckoning, in a way as yet not fully understood. This may also be true of molecular weight differences. It is probably not unreasonable to surmise that it is these secondary factors which lead to the differences in drawing behaviour among the three linear polymers studied.

3.2. Wide-angle X-ray diffraction measurements

Because the interpretation of the X-ray diffraction crystallinity measurements may depend upon the type and degree of orientation present in the drawn specimens these parameters were measured by pole figure analysis. Specimens drawn to 300 and 1600% were examined; the (0 2 0) amd (2 0 0) pole figures are essentially similar. They show that there is random orientation of the *a*- and *b*-axes about the sheet normal/transverse direction plane with only a small spread towards the draw direction. The degree of alignment of the molecular chain axis, the *c*-axis, along the draw direction was determined from the (0 0 2) pole results and has been expressed in terms of the usual orientation function, $f = (3\langle\cos^2\theta\rangle - 1)/2$, where $\langle\cos^2\theta\rangle$ is the mean square cosine of the angle between the (0 0 2) plane and the fibre axis. Typical results are $f = 0.948$ for a sample drawn by 300% and $f = 0.968$ for a 1600% drawn specimen. In all cases there is substantial uniaxial orientation along the fibre axis, as anticipated, and this symmetrical type of orientation should present fewer problems for quantitative crystallinity measurements than would a partial non-symmetrical type of orientation.

The methods commonly used for such measurements tacitly assume that there is random orientation of the chains and crystallites in the samples being examined. This is clearly not the case in the present instance and two experimental methods have been used to examine the errors which may result. With the first, the sample is examined in the normal reflection mode whereas, with the second, transmission measurements are made. The reflection method involves diffracting planes normal to the sheet direction. The pole figure measurements show that the (*hk*0) planes are distributed randomly when this particular geometry is used. Hence, because the crystallinity determination only involves measurements on the (1 1 0) and (2 0 0) peaks, the requirement of random orientation is satisfied.

The results of the infra-red dichroic measurements show that there is some orientation of tie molecules in amorphous regions, so that essentially crystalline fibrillar regions are formed on drawing. Hence, it may be anticipated that this will lead to some differences in the measured crystallinities when the samples are mounted first with the machine direction parallel to the X-ray beam direction and then with the transverse direction parallel to the beam direction. That this is so is evident from the results given in Table IV. As expected, the difference appears to increase with increasing draw ratio, although the size of the effect is clearly not very much greater than the random errors inherent in the crystallinity measurements. Taking the six sets of measurements as a whole there is no clear indication for a significant decrease in crystallinity at intermediate draw ratios.

TABLE IV Results of X-ray diffraction crystallinity measurements by the reflection method, on three cold-drawn polyethylenes

Sample	Degree of draw (%)	Crystallinity (%)	
		Draw direction parallel to X-rays	Draw direction perpendicular to X-rays
Rigidex 2000	300	78	78
	800	83	81
	1600	88	83
Rigidex 140-60	300	83	81
	800	89	85
	1600	91	90
Experimental polymer	300	79	77
	800	83	83
	1600	89	84

The transmission method was used in an attempt to obtain randomized diffraction data from both crystalline and amorphous phases. The use of transmission geometry with sample rotation during the measurement is equivalent to tracking around the edge of a pole figure. With the experimental conditions used, the sample rotating at 80 rpm and a counting time of 100 s for each 2θ value, the accumulated counts for a particular value are a good measure of the intensities from all the appropriate diffracting planes having normals parallel to the sheet surface. This is then equivalent to random orientation in three dimensions and meaningful values should be obtained for the intensities of the (1 1 0) and (2 0 0) peaks, particularly as the mean values from five replicate measurements for each 2θ were used. It is more difficult to predict the degree of randomization that will be achieved for amorphous regions but it will probably be a good approximation to three dimensional.

The results of the measurements made by the transmission method are given in Table V. Although some differences in behaviour between the three samples are apparent there are very clear

TABLE V Results of X-ray diffraction crystallinity measurements, by the transmission method, on three cold-drawn polyethylenes

Sample	Degree of draw (%)	Crystallinity (%)
Rigidex 2000	Undrawn	78
	300	60
	800	70
	1600	79
Rigidex 140-60	Undrawn	83
	300	78
	800	78
	1600	82
Experimental polymer	Undrawn	78
	300	65
	800	75
	1600	80

indications for a significant decrease in the crystallinities at intermediate draw ratios, followed by a recovery to about the initial values. The results of these measurements, therefore, parallel those obtained by infra-red spectroscopy and the crystallinity values are also very similar. Doubt must attach to those from the X-ray reflection method and reasons are not difficult to find. In addition to the problem arising from partial orientation the method had the disadvantage that it does not sample the whole of the specimen with respect to thickness as it is concerned with the surface layer only.

As long ago as 1949, Matthews *et al.*, in their classic paper on the X-ray measurement of the amorphous content of polyethylene, noted a type of orientation which they called planar orientation, very different from that occurring during cold-drawing. It is due to the orientation of crystallites in the surface layer with the (1 1 0) planes approximately perpendicular to the plane of the specimen. This behaviour has subsequently been studied in more detail by a variety of techniques [22–25] and in some circumstances [26] it is possible to prepare thin films which consist substantially of this oriented material. The term transcrystalline layer is now generally used to describe such oriented surface layers. In circumstances where they are present to a significant degree, the reflection method will clearly yield erroneous crystallinity values, and it is obviously very difficult to quantify the errors which will occur. Hence, the reflection method is not to be recommended.

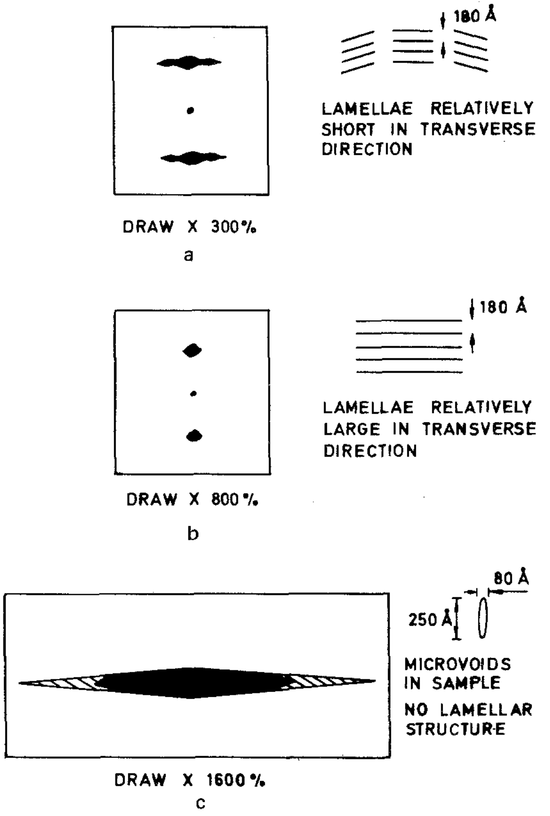

Figure 1 Small-angle X-ray diffraction patterns of cold-drawn Rigidex 2000 high-density polyethylene, and the structures derived from them. (a) 300% drawn, (b) 800% drawn, (c) 1600% drawn.

3.3. Small-angle X-ray diffraction measurements

Good quality small-angle X-ray diffraction patterns were obtained by the photographic method. Those for Rigidex 2000 are typical as are the interpretations placed on them. To ensure clarity the patterns, shown in Fig. 1, have been reproduced as drawings from the original photographs. The pattern for 300% elongation (Fig. 1a) is a combination of a four point diagram and two additional larger spots, elongated in the equatorial direction, situated along the meridional line. The overall interpretation is that the lamellar spacing is 180 Å; this result had been anticipated in view of the findings of Corneliussen and Peterlin [27] that, irrespective of the lamellar thickness of the undrawn material, the final value always lies in the narrow range 170 to 180 Å. Secondly, the lamellae are inclined over an angular range some 20° on either side of the normal to the draw direction.

Hence the tilting process is more marked than that observed by Corneliussen and Peterlin. However, the extent to which tilting occurs depends both on the draw ratio and the draw temperature and the present results fit into the previously reported pattern [27]. The change is most marked at low draw ratios [28] and at 300% elongation it is nearing completion. Finally, and this does not appear to have been reported previously, the elongation of the spots in the equatorial direction may be interpreted in terms of relatively small lateral lamellar dimensions, i.e. perpendicular to the thickness. This deduction is not wholly unambiguous because wide tilted lamellae would also give the same type of small angle pattern. However, it appears to be a sensible interpretation of the measurements.

The pattern for 800% elongation (Fig. 1b) is simpler. It consists of two spots along the meridional direction. Their shape contrasts markedly with the corresponding points of Fig. 1a, which are considerably more elongated in the equatorial direction. This pattern indicates a lamellar thickness of 180 Å with the lamellae all aligned perpendicular to the draw direction. Furthermore, the lateral dimensions of the lamellae are appreciably greater than at 300% elongation.

At 1600% draw, the small-angle pattern (Fig. 1c) has changed dramatically and consists of a central zero-order spot elongated in the equatorial direction. The lamellar structure has been destroyed and the pattern indicates the presence of microvoids, as would be expected from the fact that the sample had become partially opaque and whitish in appearance. This type of pattern was first interpreted, in part, for cellulose by Statton [29]; he obtained values for the dimension of the microvoids along the draw direction. The lengths of the spot of Fig. 1c along the two principal directions indicate that the average dimensions of the microvoids are 250 Å along the draw direction and 80 Å in perpendicular directions. Such values do not seem to have been reported previously and their magnitudes appear very reasonable in the light of the lamellar thickness prior to destruction.

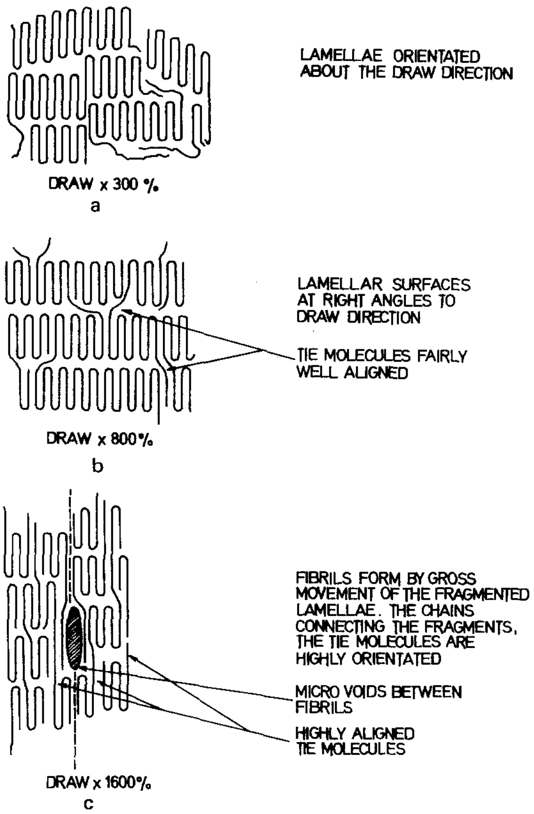

Figure 2 Schematic representations of the morphological changes which occur when high-density polyethylene is cold drawn. (a) 300% drawn, (b) 800% drawn, (c) 1600% drawn.

These small-angle X-ray diffraction results are complementary to the findings by infra-red spectroscopy and wide-angle X-ray diffraction in filling in further details of the plastic deformation of polyethylene on the basis of the Peterlin model. For purposes of summarizing the various stages of cold-drawing, which do not occur in well separated sequential steps but are overlapping processes, the schematic diagrams shown in Fig. 2a, b and c are useful. The initial samples had 300% elongation and at this point in the drawing process the polymers have passed the yield point and necking is occurring. The lamellae are already aligned approximately perpendicular to the draw direction and the small-angle measurements show that the spread on either side of this direction is limited to 20° (Fig. 2a).

When the elongation reaches 800% the alignment of the lamellae into the direction perpendicular to the draw direction is complete and significant changes are taking place in the amorphous regions between the lamellae (Fig. 2b). There is increasing alignment of the tie molecules but this has not yet reached the stage where an ordered fibrillar structure is present to a significant degree. Tie molecules are being formed at the expense of regularly folded chains in the crystalline lamellae and as this process is rather more extensive than the ordering of the tie chains the crystallinity decreases somewhat. This conclusion emerges very clearly from the infra-red spectroscopic and wide-angle transmission X-ray diffraction measurements.

At 1600% draw the lamellar structure no longer exists. At this high draw ratio the lamellae segment and the small units physically move to reform as part of a fibrillar structure. Ellipsoidal microvoids, whose average dimensions are 250 Å parallel to the draw direction and 80 Å normal to it are formed during the movement of the segments (Fig. 2c). The presence of these microvoids therefore marks the change from a lamellar to a fibrillar structure. There is a considerable degree of order in the fibrils, with the tie molecules lining up in such a way as to give this order. The results of the infra-red spectroscopic measurements, both with polarized and unpolarized radiation, are also important in helping to clarify this final stage of the conversion from a lamellar to a fibrillar structure.

4. Conclusions

(1) When high-density polyethylene is cold-drawn at 60° C there is a change of crystallinity with draw ratio. There is an initial decrease at low and intermediate degrees of draw as the original spherulitic structure is broken down to an oriented lamellar structure. This is followed by an increase, at high draw ratios, to a value as great as or greater than that of the undrawn material, as the new fibre structure is formed. There are detectable differences in behaviour between an essentially unbranched polyethylene, one with a low level of ethyl branches and a third with a comparable concentration of butyl branches.

(2) These crystallinity changes are readily followed by infra-red spectroscopy. It has also proved possible to make meaningful quantitative X-ray diffraction measurements on the highly oriented drawn specimens by the transmission method. The results from reflection measurements are suspect because of orientational effects and possible surface inhomogeneity of the samples.

(3) The infra-red spectroscopic evidence suggests that the tie molecules, which are originally part of the amorphous phase, become increasingly closely packed and aligned with increasing draw ratio and probably contribute to the crystallinity at high draw ratios. Therefore, it returns to or even exceeds the value in the undrawn state. The orientation of the extended trans methylene sequences present in the tie molecules increases with increasing draw ratio.

(4) New information is forthcoming from the small-angle X-ray diffraction measurements. An increase in the lamellar lateral dimensions with increasing draw ratio is found. At the highest draw ratio, when the lamellar structure has broken down, microvoids are formed and values for their dimensions have been obtained.

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