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The Cold-Drawing of High Density Polyethylene

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The cold-drawing of high density polyethylene has been studied over a wide range of temperatures and strain rates for a series of samples of very different molecular weight distribution. A natural draw-ratio was observed which was almost independent of temperature and strain rate, but was sensitive to the weight average molecular weight. A good correlation was observed between the Young's modulus of the drawn monofilaments and the natural draw-ratio, and it is proposed that the Young's modulus is primarily related to molecular orientation rather than to interlamellar ties.

1. Introduction

The remarkable phenomenon of cold-drawing is common to both amorphous and semi-crystalline polymers. In this paper two facets of the cold-drawing behaviour of high density polyethylene will be examined in some detail. First, the effect of molecular weight and molecular weight distribution on the natural draw-ratio will be reported. Secondly, the Young's modulus of the drawn polyethylene has been found to correlate with the natural draw-ratio. The significance of these results will be discussed.

In a previous publication [1] the constancy of the natural draw-ratio with respect to strain rate and temperature was established for polyethylene terephthalate. It was shown that the natural draw-ratio depended on the degree of pre-orientation and could be regarded as the ultimate extensibility of a network formed during quenching from the molten state. In this paper, care has been taken to assure that the initial samples are isotropic and not pre-orientated to any significant extent. After establishing constancy with respect to strain rate and temperature the effects of molecular weight were then examined.

In the drawing process the isotropic starting material is transformed into a highly anisotropic fibre structure. It is found that the molecular chains are oriented along the draw-direction and that the crystal lamellae are stacked roughly perpendicular to the draw-direction.

Corneliussen and Peterlin [2] have studied the influence of temperature on the drawing of polyethylene, using a variety of structural techniques including low-angle X-ray diffraction. They concluded that drawing occurs by melting followed by recrystallisation. In the necking zone there is a high concentration of deformational energy and this suffices for local melting. Corneliussen and Peterlin propose that recrystallisation from a highly ordered melt occurs. To support this view they observe that the long period relates directly to and depends only on the temperature of drawing.

Peterlin [3] also presents a folded chain model of highly drawn polyethylene. In order to explain the morphological and mechanical properties of highly drawn polyethylene neither the fringed micelle, fringed fibril nor extreme folded chain models are adequate. The insufficiencies of these models are avoided by a modified folded chain model in which there are a substantial number of tie molecules interconnecting the folded chain lamellae which are oriented more or less perpendicular to the draw-direction. The Peterlin model seems inadequate to describe the results presented in this paper. We have found that the greater the molecular weight, the lower the natural draw-ratio. We have also found that an increase in natural draw-ratio leads to an increase in the modulus of the drawn material. If Peterlin's model is correct, one would expect that an increase in molecular weight would result in a greater number of interlamellar ties, and hence an increase in the modulus of the drawn polymer, since the ties will render the

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structure less extensible. The opposite has in fact been observed.

The modulus properties and viscoelastic behaviour of several polymers have been shown to fit an aggregate model of mechanically anisotropic units which are aligned by the drawing process [1, 4-6].

On this view the Young's modulus of the oriented polymer in the draw-direction relates directly to the degree of molecular orientation, and hence the draw-ratio. Thus it would be expected that high modulus would be associated with high draw-ratio. It will be shown that this expectation is fulfilled for the high density polyethylene specimens examined in this investigation.

2. Experimental

2.1. Characteristics of Samples for Molecular Weight

The molecular weight distributions of the high density polyethylene samples were measured by gel permeation chromatography [7, 8] (GPC) using a Water Associates Model 200 gel permeation chromatograph. The chromatograph was operated at 130° C and the samples injected in *o*-dichlorobenzene at a concentration of 0.5%. The calibration of the chromatograph was carried out using samples of known weight average and number average molecular weight *n*-paraffins and polystyrene fractions, as described in previous publications [9, 10].

The following polyethylene samples were used in this investigation:

(i) Rigidex 2, 9, 25, 35, 50.

(ii) Two samples of high density polyethylene supplied in connection with an international survey: (a) broad molecular weight distribution (BMWD); (b) narrow molecular weight distribution (NMWD).

(iii) Marlex 6009.

(iv) A Marlex sample with the low molecular weight material removed (kindly supplied by Dr D. Sadler).

(v) Four samples kindly supplied by Birmingham University (Dr F. Peaker).

2.2. Preparation of Specimens

(i) Only small amounts (~ 3 g) of some of the polymer fractions were available. A small scale melt-spinning machine (designed by ICI Fibres Ltd, Harrogate) was therefore used to produce monofilaments for tensile tests. The polymer is heated to 180° C in a small pack and pushed successively through a 200 mesh* grid, a 50 mesh grid, a bridge plate with a 1.6 mm diameter hole and finally through a spinneret with a hole diameter of 0.38 mm. Continuous extrusion is maintained by drawing a ram down the pack by means of a screw.

(ii) For the extensive tests of the effect of strain rate and temperature, dumb-bell shaped specimens of Rigidex 2 were cut from compression-moulded sheets. These sheets were produced as follows: pellets of polymer were placed between clean copper plates separated by copper strips, which also serve to keep the polymer within bounds. These plates were placed in a hydraulic press which was maintained at 170° C. A pressure of 0.4 ton in.$^{-2}$† was quickly applied and held for 3 min before increasing the pressure to 1.2 ton in.$^{-2}$ for a further 3 min. The pressure was then released and the sheets quenched into cold water.

2.3. Tensile Tests

For the studies of the effects of molecular weight and strain rate, load-elongation curves were obtained at room temperature, using an Instron tensile testing machine. The molecular weight effects were examined at a fixed elongation rate of 1 cm min^{-1}.

The effect of temperature on the drawing process was studied using a Hounsfield E-type tensometer fitted with an environmental chamber. Temperature was measured with a mercury thermometer suspended near the specimen, the system being allowed to equilibrate for 30 min prior to a tensile test.

The monofilaments were gripped by pin-chucks, the ends in the chucks being wrapped in masking tape. The dumb-bell shaped specimens were gripped between ordinary flat grips.

The yield and drawing stresses were calculated as the load at yield and the drawing load, respectively, divided by the original cross-sectional area of the specimen. Thus they are conventional rather than true stresses.

The *natural draw-ratio* is defined as the ratio of the cross-sectional areas before and after drawing. All measurements were taken under zero stress. This definition assumes constant volume.

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* 200 meshes per in. ~ 80 meshes per cm.

† 1 ton in.$^{-2}$ = 15.4 × 10^{5} N m^{-2}.

2.3.1. Measurement of Modulus

The Young's modulus of the drawn and undrawn monofilaments were measured with a vibrating reed apparatus [11]. For a polymer reed of circular cross-section the Young's modulus E is given by $E = (50.99\ d\, L^4/A^2) W_r^2$ dyn cm^{-2}, where W_r is the resonant frequency, d is the density of the polymer in g cm^{-2}, L is the free length of the reed in cm, and A is the diameter of the reed in cm.

2.3.2. X-ray Diffraction Measurements

Wide-angle X-ray diffraction photographs were taken using a Unicam camera and filtered CuK radiation. A collimated X-ray beam was used. Low angle X-ray photographs were taken with a Franks camera.

3. Results and Discussion

3.1. Effect of Strain Rate on Yield and Drawing

The effect of strain rate on the yield stress and drawing stress is shown in fig. 1. The yield stress appears to be a linearly increasing function of the logarithm of the strain rate. However, the drawing stress, after increasing initially at about the same rate as the yield stress, later decreases.

The strain rate-dependence of the natural draw-ratio is shown in fig. 2. As the strain rate increases from 2 × 10^{-4} sec^{-1} to about 5 × 10^{-2} sec^{-1} there is no change in the natural draw-ratio. A further increase in strain rate produces a rapid increase in the natural draw-ratio.

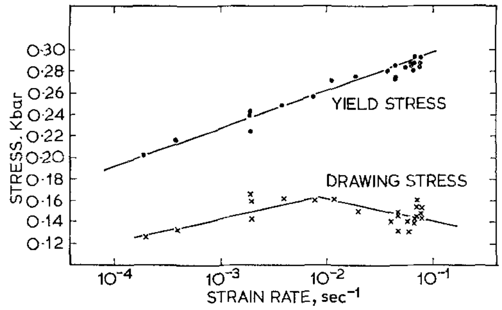

Figure 1 The effect of strain rate on the yield stress and drawing stress.

When plastic deformation occurs there is an inherent energy loss which leads to generation of heat [12]. At low strain rates the heat generated is conducted away from the neck sufficiently fast for no temperature rise to occur. As the strain rate increases the process becomes more nearly adiabatic. Thus the effective drawing temperature is increased. Heat is conducted into the unyielded portion of the specimen so reducing the force necessary to propagate the neck. Hence the drawing stress decreases.

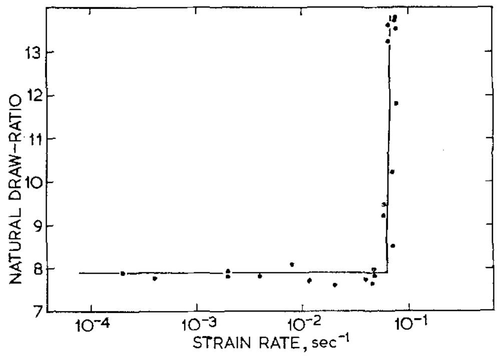

Figure 2 The effect of strain rate on the natural draw-ratio at room temperature.

It is interesting to note that the sudden increase in natural draw-ratio with strain rate occurs at a higher value of the strain rate in polyethylene than in poly(ethylene terephthalate) [1]. The values of thermal conductivities are as follows (taken from Kaye and Laby's Tables):

Polyethylene
6 to 8 × 10^{-4} cal sec^{-1} cm^{-2} °C^{-1} cm^{-1}
Poly(ethylene terephthalate)
5 × 10^{-4} cal sec^{-1} cm^{-2} °C^{-1} cm^{-1} .

Polyethylene has a higher thermal conductivity, so heat can be conducted away from the neck more efficiently than in poly(ethylene terephthalate). Thus there seems to be a correlation between thermal conductivity and the transition point. It would be interesting to test this for other polymers.

The increase in natural draw-ratio at high strain rates could be due to the formation of voids caused by an increase in hydrostatic stress associated with an increase in the applied axial stress required to cause yielding at higher strain rates. This implies a breakdown of homogeneous deformation.

Another possible explanation is as follows. At the high strain rates, localised melting occurs. This is the situation envisaged by Corneliussen and Peterlin where the polymer melts under stress so that one can envisage all the chains lining up in the draw-direction and solidifying in a fringe-micelle type structure [3]. In this structure, microfibrils are parallel to the fibre

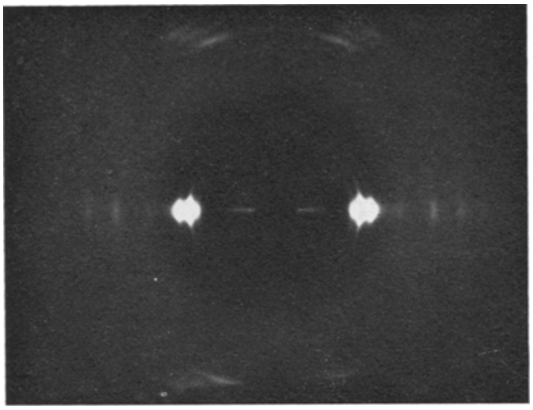

Figure 3 Wide angle X-ray diffraction photograph of a specimen drawn at a strain rate of 4×10^{-3} sec^{-1}.

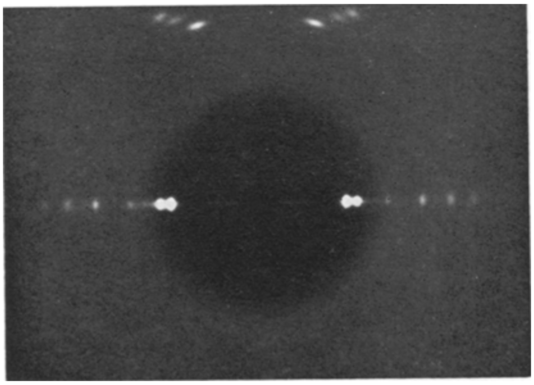

Figure 4 Wide angle X-ray diffraction photograph of a specimen drawn at a strain rate of 10^{-1} sec^{-1}.

axis and contain a bundle of linear chains alternately passing through crystalline and amorphous regions. The chain folds are no longer present in the drawn structure and high natural draw-ratios relate to the drawing out of folded chains.

Wide-angle X-ray diffraction photographs were taken of a specimen drawn at 4×10^{-3} sec^{-1} and a specimen drawn at 10^{-1} sec^{-1} (figs. 3 and 4 respectively). The (110) and (200) arcs are larger for the lower strain rate, indicating a lower degree of orientation than that obtained at high strain rates. This result is consistent with the above explanation.

3.2. Effect of Temperature on Yield and Drawing

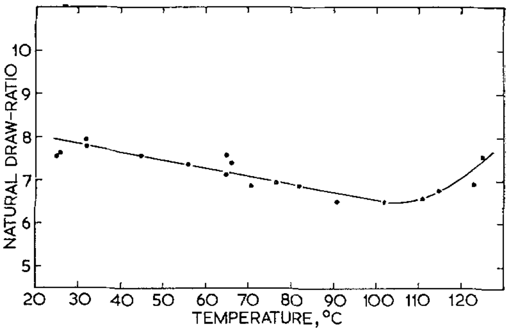

Figure 5 Natural draw-ratio as a function of temperature at a strain rate of 0.01 sec^{-1}.

A graph of natural draw-ratio against temperature is shown in fig. 5. The natural draw-ratio appears to decrease linearly with temperature up to about 100° C, after which it increases. A possible explanation of why there is a decrease lies in annealing, since the specimens were left in the oven for half an hour before being drawn. Also the specimens may have been under a slight stress due to the weight of the grips. However, it will shortly be shown that the effect of temperature is only a secondary effect compared to the large primary effect of molecular weight on the natural draw-ratio.

The increase in natural draw-ratio at temperatures above 100° C could be due to melting of low molecular weight material, leading to non-homogeneous deformation on drawing.

The yield stress and drawing stress both decrease as the temperature increases (fig. 6). They approach each other as the softening point of 128° C is reached.

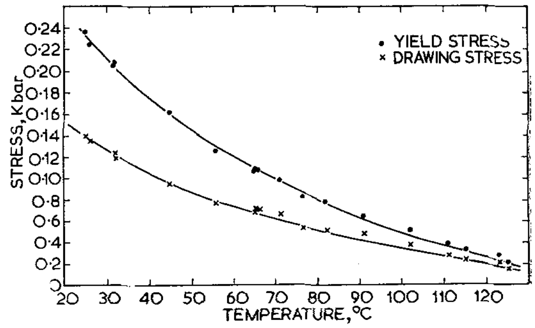

Figure 6 Yield stress and drawing stress as a function of temperature.

These results are similar to those of other investigations, notably Andrews and his coworkers (see, for example, [13]).

3.3. Effect of Molecular Weight on Yield and Drawing

Table I gives the natural draw-ratio, yield stress

TABLE I

Sample	$\bar{M}_n$	$\bar{M}_w$	Natural draw-ratio	Yield stress (kbar)	Drawing stress (kbar)
B'ham A	19 800	148 000	8.65	0.235	0.179
B	25 200	41 200	13.03	0.267	0.180
C	34 000	99 000	8.2	0.230	0.196
D	72 000	168 000	4.0	0.220	0.197
HDPE(NMWD)	21 400	53 000	11.5	0.245	0.168
(BMWD)	16 000	121 500	8.8	0.242	0.178
PENNINGS* 12	12 000	153 000	9.0	0.227	0.175
35	35 000	550 000	6.65	—	—
98	98 000	142 000	8.0	0.204	0.190
RIGIDEX 2	27 500	202 000	7.9	0.234	—
9	18 900	155 000	8.1	—	—
25	17 200	100 000	8.8	0.239	—
35	14 300	85 000	9.8	0.247	—
50	17 000	88 000	9.8	0.246	—
MARLEX 6009	14 850	88 000	8.3	0.241	0.181
DS 43T†	50 000	110 000	7.1	0.21	0.178

* Samples used to characterise the GPC supplied by Dr A. J. Pennings (Holland).
† The sample of Marlex with the low molecular weight material removed which was supplied by D. Sadler.

and drawing stress of the various linear polyethylenes used together with their number and weight average molecular weights. The natural draw-ratio is plotted as a function of weight average and number average molecular weights in figs. 7 and 8 respectively.

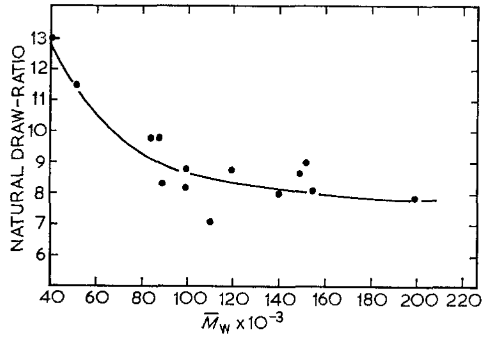

Figure 7 Natural draw-ratio at room temperature as a function of weight average molecular weight.

It appears that the yield and drawing processes are independent of molecular weight. The sliding of molecules past each other presumably depends on short-range intermolecular forces and is independent of entanglements which occur along the length of a crystallite.

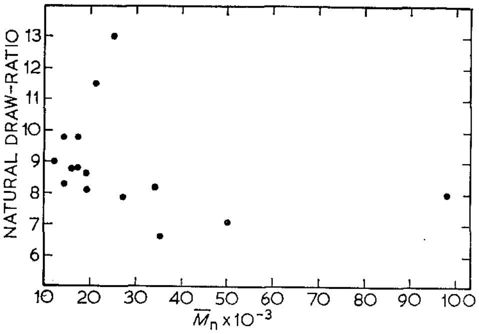

Figure 8 Natural draw-ratio at room temperature as a function of number average molecular weight.

The investigation of the effect of strain rate and temperature show that, provided the drawing takes place at low strain rates, the natural draw-ratio is sensibly constant over a wide range of temperature. In particular, it does not change rapidly with temperature near to room temperature, where the effect of molecular weight was studied.

The results in table I show a general trend in which the natural draw-ratio decreases with increase in molecular weight. There is a rapid decrease at first but above a weight average molecular weight of about 100 000 there is a levelling off. When the natural draw-ratio is plotted against $\bar{M}_w$ there appears to be a rather better curve than if it is plotted against $\bar{M}_n$. Thus it seems that $\bar{M}_w$ is more important in determining the natural draw-ratio. Several examples serve to illustrate the point:

(i) Birmingham B has a higher natural draw-ratio than Birmingham A but $\bar{M}_n$ is greater for B than A, whereas $\bar{M}_w$ is greater for A than B.
(ii) A similar situation exists for HDPE(NMWD) and HDPE(NMWD).
(iii) When the low molecular weight material was removed from Marlex 6002, $\bar{M}_n$ increased by a factor of 3.5 whereas $\bar{M}_w$ only increased a small amount. This slight increase in $\bar{M}_w$ did decrease the natural draw-ratio. However if $\bar{M}_w$ is increased by a factor of 3.5, as in Birmingham A and B, there is a far more drastic effect on the natural draw-ratio.

The weight average molecular weight is particularly sensitive to the presence of larger species. The results therefore suggest that the larger molecules bind the structure together, making it less extensible. They can do this by forming interlamellar ties between crystallites. In the drawing process the crystallites stack up perpendicular to the draw-direction. The interlamellar ties prevent the crystallites from lining up perfectly. The more perfectly they are lined up, the greater the natural draw-ratio. As the molecular weight increases, the number of interlamellar ties preventing the structure from drawing to the maximum possible extent will also increase. This leads to a decrease in natural draw-ratio with increase in molecular weight.

Wide-angle X-ray photographs taken of several drawn specimens showed that the (110) and (200) arcs are longer in the case of the high molecular weight material. This confirms that the crystallites in high molecular weight material are less highly oriented than those in low molecular weight material. We can therefore conclude that the high molecular weight polymer cannot achieve so great a degree of crystalline orientation as the low molecular weight polymer, presumably because a greater concentration of interlamellar ties increases the rate of strain-hardening. In this connection it is relevant to note that Vincent [14] has shown that there is a minimum molecular weight for cold-drawing to occur, below which there is insufficient strain-hardening to stabilise the neck.

3.4. The Young's Modulus of the Drawn Monofilaments

The molecular weight has little, if any, effect on the modulus of the isotropic material. This suggests that the effect of molecular weight on natural draw-ratio is direct rather than an effect on some property of the undrawn material which ultimately affects the natural draw-ratio.

The Young's modulus of the drawn monofilaments as a function of the natural draw-ratio is shown in fig. 9. It can be seen that there is a very good correlation and that the Young's modulus increases monotonically with increasing natural draw-ratio, as was found for polyethylene terephthalate. This has also been shown to hold for hot-drawing processes (see for example [1]). In polyethylene terephthalate it was concluded that the modulus (and the birefringence which was also measured) related directly to the degree of molecular orientation and hence to the natural draw-ratio. It seems likely that a similar explanation can be given to these results for high density polyethylene, and that the modulus is determined by orientation, not by the number of interlamellar ties.

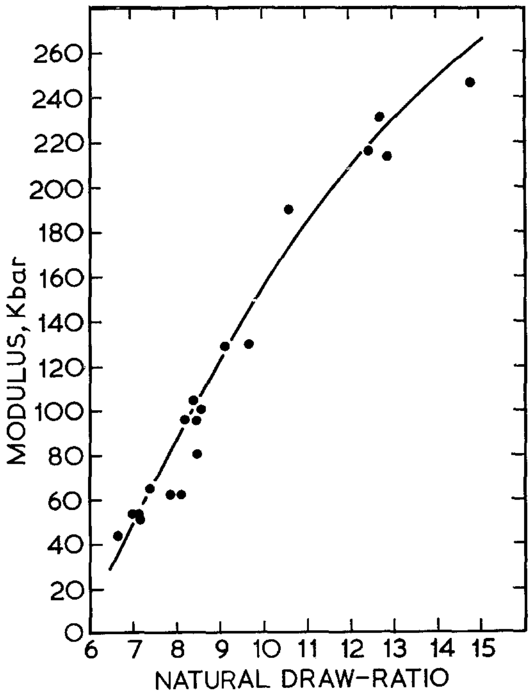

Figure 9 Young's modulus of the drawn monofilaments as a function of the natural draw-ratio.

If the structure drew to its full extent on drawing it might be expected that the modulus of the drawn material would be determined by the number of interlamellar ties. The greater the molecular weight, the more ties are present, leading to a higher modulus because the ties would render the structure less extensible. In these experiments the opposite is observed since, in order to get a high modulus, a large natural draw-ratio is required which is obtained by drawing a sample of low molecular weight.

Finally, these results do not support the idea that the drawing process entails melting followed by recrystallisation. If this were the case one would expect the process to be independent of molecular weight because melting and recrystallisation would lead to a structure not determined by molecular weight [15].

4. Conclusions

(i) The yield and drawing stress of high density polyethylene was found to be independent of molecular weight whereas the natural draw-ratio was very appreciably affected. It can therefore be concluded that yield and drawing are probably determined by the short range interlamellar forces involved in local chain slippage.
(ii) The natural draw-ratio was unaffected by strain rate over a wide range of strain rates and only affected to a small degree by temperature of drawing compared to the considerable effect of molecular weight. These results indicate that the natural draw-ratio is a property of the material.
(iii) The natural draw-ratio decreased with increasing molecular weight, and was more sensitive to the weight average molecular weight than to the number average. This behaviour fits a model in which the isotropic polymer is considered to be an aggregate of randomly oriented mechanically anisotropic units; on drawing these anisotropic units somehow rotate to stack up roughly perpendicular to the draw-direction. Since $\bar{M}_W$ is sensitive to additions of small amounts of long chain molecules it is postulated that these long molecules prevent the crystallites from lining up to the full extent because interlamellar ties hold the structure of units together.
(iv) There was a good correlation between the Young's modulus of the drawn monofilaments and the natural draw-ratio. This suggests that the modulus is determined more by molecular orientation than by the number of interlamellar ties since the latter decrease with decreasing molecular weight, whereas the modulus increases due to the greater natural draw-ratio.

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