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Maximum strength and drawing mechanism of hot drawn high molecular weight polyethylene

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An investigation of the hot drawing of high molecular weight polyethylene fibres containing a substantial amount of solvent, and of fibres with a porous structure that were dried after solution spinning, was conducted. It was found that the tensile strength as well as the Young's modulus of the polyethylene fibres were linearly related to the applied stress up to values of 0.3 GPa. Drawing stresses exceeding 0.3 GPa could produce polyethylene fibres with a tensile strength of 3.7 GPa and a Young's modulus of 120 GPa. The ultimate mechanical properties appeared to be affected by the nature of the solvent, the polymer concentration and the spinning temperature. Chain extension in the hot drawing and the ultimate draw ratio depended substantially on the number of intermolecular entanglements initially present in the fibre.

1. Introduction

In recent papers [1–3] it has been shown that extremely high molecular weight linear polyethylene can be drawn at high temperatures from solution or from a porous fibre (prepared from solution) to form ultra-high strength and modulus fibres. The occurrence of few molecular entanglements in the undrawn fibre, as a result of its preparation by crystallization from solution, appears to be of utmost significance for this fibre formation process. The presence of fewer entanglements in solutions than in polymer melts [4] results in considerably higher molecular mobilities during drawing and therefore a higher drawability of the fibre. The tensile strength of the fibres was found to be influenced by the drawing stress or draw ratio and the drawing temperature conditions.

The present paper is mainly concerned with investigations of the maximum fibre strength and the influence of molecular entanglements on the drawing behaviour of the fibre. It will be shown that the preparation of the solution influences the strength of the drawn fibres, and that the spinning conditions influence the drawing behaviour of the fibre. In the second section of this paper, consideration will be given to the molecular mechanism of drawing and to the role of entanglements in the present process. Further, the maximum draw ratio reflecting full molecular extension as a function of the molecular weight will be estimated and the effect of entanglements on the draw ratio will be discussed.

2. Experimental procedure

The dissolution of the high molecular weight linear polyethylene (Hifax 1900) with a weight average molecular weight of about $4 \times 10^6\,\mathrm{g\,mol^{-1}}$, as well as the spinning of the fibres, was carried out as described earlier [2, 3]. The solutions were prepared at 0.5% and 5% by weight in decalin, dodecane and paraffin oil of high purity. Before spinning, the 0.5 wt% solution was precipitated and concentrated by filtration to between 5 and 10 wt%. To prevent large effects of polymer diffusion, the time of solution spinning was kept to less than 30 min. The drawing was performed in a temperature gradient supplied by a drawing tube, as previously described [2, 3]. Throughout the experiments, the temperatures at the entrance

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and the exit of the tube were maintained at 100° C and 148° C respectively. Nitrogen was allowed to flow through the tube in order to avoid degradation of the polymer. The speed of the undrawn fibre at the entrance of the tube for continuous runs was 2.65 cm min^{-1}. At a certain time after start, when constant conditions for continuous drawing were achieved, the fibre feed at the entrance of the tube was stopped, whereupon the cross-sectional area of the drawn fibre decreased steadily until fracture occurred at a maximum drawing stress.

3. Results and discussion

Throughout the experiments, the homogeneity of the spun fibre to a large extent determined the continuity of the drawing process. Inhomogeneities were caused by variations in diameter, polymer concentration, and orientation, as well as by the inclusion of impurities in the spun fibre. Accordingly, the probability of fracture at high stresses was decreased by carrying out drawing experiments on a relatively short section of each spun fibre. As described in the experimental section, this was accomplished by stopping the fibre feed into the drawing tube, thus obtaining a steadily increasing stress in the fibre and producing fracture at the maximum drawing stress. The drawing stress is defined as the drawing force divided by the cross-sectional area of the final fibre, where the cross-sectional area was calculated from the weight of the fibres and the density (which was assumed to be 1000 kg m^{-3}).

In order to investigate the influence of entanglements on the fibre strength and the drawing behaviour, solutions of polyethylene were prepared at 0.5% and 5% by weight polymer concentration. It should be noted that the inferior drawability and strength of high molecular weight polyethylene at high concentrations, where the bulk is highly entangled, were shown by other authors [5–7]. Fig. 1 shows results of drawing experiments on fibres spun and drawn under different conditions from polyethylene which was precipitated from a 0.5 wt% solution in decalin and concentrated thereafter for spinning and drawing to about 10 wt%. Here, the tensile strength, σ_T, is plotted as a function of the drawing stress, σ_D, for fibres spun at different temperatures (full curves). It can be seen in Fig. 1 that σ_T increases, at first linearly with σ_D, and then begins to level off at tensile strengths between about 2.5 and 3.0 GPa to approach a maximum tensile strength with increasingly higher drawing stresses. The highest limiting σ_T, of 3.7 GPa, was obtained for fibres spun at a temperature of 130° C, which appears to be the optimum temperature.

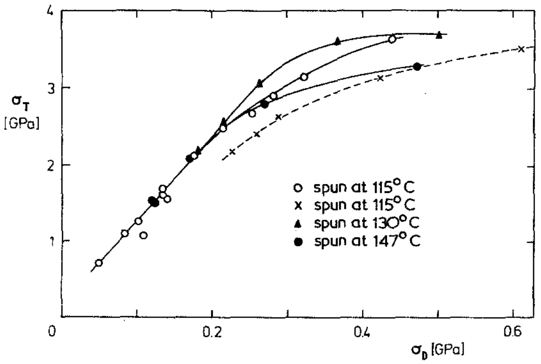

Figure 1 The tensile strength, σ_T, plotted as a function of the drawing stress, σ_D, for fibres drawn from polyethylene crystallized from a solution containing 0.5 wt% polyethylene in decalin. The unbroken lines show the influence of the spinning temperature on the tensile strength, while the broken line represents experimental results obtained at an exceptionally high drawing force.

Points produced when σ_T values were plotted against σ_D values for the fibres spun at 130° C were found to lie above those produced for fibres spun at other temperatures. This indicates that the molecular mobility, and therefore the rate of removal of defects in the fibre, is probably highest at this temperature, since the rate of molecular creep is dependent on the stress applied [3]. At 115° C, a fraction of the molecules may assume a higher extension because of crystallization phenomena in the capillary and therefore produce a higher resistance to deformation which results in a lower overall mobility. Accordingly, σ_D must be higher in order to achieve the same σ_T as for homogeneous fibres. Similarly, at 147° C, the additional entanglements, which were formed due to molecular diffusion (e.g. reptation [8]) at the higher concentration of the spinning dope and the relatively high temperature, reduce the molecular mobility. However, since the removal of a higher number of entanglements may be difficult, the maximum obtainable strength is lower.

The broken line in Fig. 1 shows the results of experiments performed at an exceptionally high drawing force, which caused the fibre, during drawing, to change its cross-section within a much smaller region than in the other experiments. Apparently, since the value of σ_T for a given σ_D value is considerably lower, the formation of a neck promotes, in the fibrous crystals, the inclusion of defects which, in order to obtain strong fibres, have to be removed in a highly extended state of the molecules at very high stresses. The lower points are data from continuous drawing experiments which generally showed a higher scattering of the data due to inhomogeneities in the fibres. Values of σ_T plotted against the draw ratio, λ, (calculated from the ratio of the velocities or from the ratio of the cross-sectional areas obtained at a density of $1000\,\mathrm{kg\,m^{-3}}$ for the fibre), showed a behaviour similar to that displayed by σ_T against σ_D plots (see Fig. 1), i.e. they exhibited a levelling off of σ_T at high draw ratios. There was no linear region in the curves. The maximum achievable draw ratios were in the range between 60 and 90. Since the drawing stress appears to be a better measure of the drawing behaviour and is more closely related to molecular mobilities than the draw ratio, more attention has been paid to the drawing stress in the present paper. An example of the dependence of the elastic modulus, E, on the drawing stress is presented in Fig. 2 for the same fibres used in Fig. 1. A striking feature is the linear increase of E with σ_D, and, in agreement with the results for σ_T, the highest modulus of 121 GPa is obtained for fibres spun at 130° C. Further experimental data are shown in Fig. 3 for fibres which were spun from polyethylene solutions in paraffin oil (the paraffin oil was subsequently extracted from the fibres in hexane, thus yielding porous fibres after drawing [3]) and dodecane at a polymer concentration of 5% by weight. The maximum strength for solution spun samples at $\sigma_D = 0.4$ GPa, is about 0.5 GPa lower than for the fibres drawn from polyethylene which was prepared at 0.5% by weight. However, results from recent experiments [9] have shown that σ_T increases very slowly with σ_D, and actually reaches a value of $\sigma_T = 3.7$ GPa at $\sigma_D = 0.7$ GPa. The apparent maximum of 3.1 GPa might therefore have occurred due to undefined experimental influences. Nevertheless, it appears that the higher number of entanglements in the more concentrated solution (similar to the fibre spun sample at a high temperature) makes it necessary to apply a much higher stress in order to remove the entanglements and to achieve the maximum strength of 3.7 GPa. It may be concluded from these results that the number of entanglements has a negligible influence on the maximum tensile strength, since at this point they are almost completely removed.

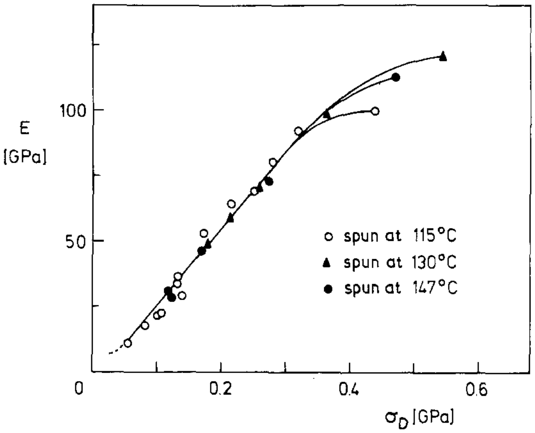

Figure 2 The elastic modulus, E, plotted against the drawing stress, σ_D for fibres drawn from polyethylene crystallized from a solution containing 0.5 wt% polyethylene in decalin and spun at various temperatures.

The maximum tensile strength appears therefore to be dependent mainly on stable crystalline defects, such as chain ends, and may only be increased by using higher molecular weight polyethylene. The influence of the different solvents has to be further investigated.

Also shown in Fig. 3 is the development of a σ_T against a σ_D curve for a porous fibre drawn without a temperature gradient at a temperature of 148° C (dotted curve in Fig. 3). In this case, the formation of a neck apparently leads to a low value of σ_T; the explanation is similar to that for the fibre drawn at an exceptionally high drawing force. Particularly from this experiment and from that where the high drawing force was applied (Fig. 1), it may be concluded that, in order

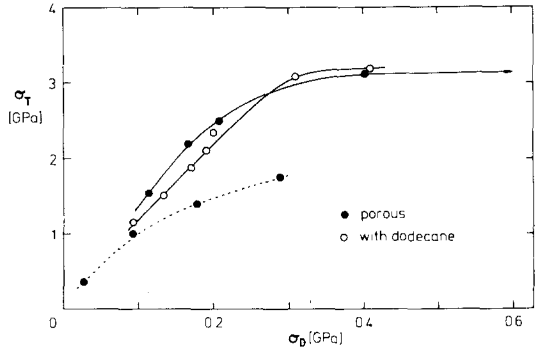

Figure 3 The tensile strength, σ_T, plotted against the drawing stress, σ_D, for fibres produced from solutions containing 5 wt% polyethylene in paraffin oil (porous fibre, since solvent was extracted) and in dodecane. An example of the strength development of fibres drawn without a temperature gradient is shown by the broken line.

to achieve strong fibres, the conditions for drawing have to be adjusted so that the formation of a neck can be prevented.

Figs. 1 and 3 demonstrate a dramatic change in the slope of σ_T versus σ_D at drawing stresses between 0.2 and 0.4 GPa. Below this transition region, the large increase in σ_T is attributed to the high molecular mobility during the deformation of chain folded crystals, according to a drawing mechanism proposed by Peterlin [10]. Above this transition, a process similar to the super-drawing studied by Capaccio *et al.* [5, 6] and by Clark and Scott [11] may produce the increase in strength through the removal of molecular entanglements and the migration of crystal defects into amorphous regions. Such a process requires high drawing stresses in order to obtain sufficiently high rates of creep [3].

It should be noted that the maximum tensile strengths of the fibres obtained in the present work are the same as the maximum theoretical tensile strength for polyethylene estimated at 3.7 GPa by Schaefgen [12] on the basis of a creep failure process. Other experiments conducted in this laboratory resulted in fibres with a similar maximum strength of 4 GPa [13]. At present, however, the validity of the theoretical maximum strength, which has been given by other authors [14] as 19 GPa, is subject to further investigations, since it is believed that the fibres investigated in this study still contain a remarkable number of defects producing stress concentrations which lead to fracture through the breaking of covalent bonds. This follows from theoretical calculations predicting that the number of defects has a marked influence on the tensile strength, as has been shown by the example of brittle fracturing materials containing small cracks [15]. Moreover, it was found that a considerable number of radicals is formed in a mechanical deformation process at low temperatures [16, 17], indicating that the breaking of covalent bonds also occurs during drawing and suggesting that the mechanism of fracture may be based on the breaking of covalent bonds.

4. Discussion of the present drawing mechanism

Since the conditions of solution preparation apparently control, to the greatest extent, the formation of molecular entanglements and the strength of the fibres, it is of interest to discuss in more detail the influence of these entanglements on the drawing mechanism.

A solution of ultra-high molecular weight polyethylene at higher concentrations consists of interpenetrating random coils which form a large number of coupling entanglements [4]. The number of entanglements is expected to increase with the concentration and becomes a maximum for the polymer melt [4]. The entanglements can be of intra- and inter-molecular nature, where the number of the former is expected to be determined by the quality of the solvent (a good solvent gives larger coil dimensions) and that of the latter by the concentration of the polymer in solution. Upon cooling the molecules in solution (Fig. 4a), a large number of the entanglements becomes trapped between crystallites, as illustrated in Fig. 4b. Fig. 4b shows the possible structure of a single long-chain molecule which is surrounded by the solvent and fixed in position by other molecules at the entanglement sites. If the concentration is greater than that necessary for gel formation, it may be assumed that the radius of gyration of the molecules, R_g, remains constant during crystallization, as has been observed for the crystallization of polymer melts [18]. For lower concentrations, the radius of gyration might decrease during crystallization. During drawing, the chain folds may be deformed and pulled apart according to a mechanism proposed and described by Peterlin [10]. However, due to the presence of entanglements, this process becomes very complex and slow, since the entanglements show a high frictional resistance to deformation [4]. The interference of an extremely high number of entanglements, as is the case in bulk polymers, might even lead to considerable local stress concentrations and, therefore, to fracture of the material at low draw ratios [5–7]. Furthermore, it might also be suggested that lamellar crystals which consist of switchboard model structures are highly undesirable because they increase the complexity of the drawing process and introduce further entanglements, mainly of the intramolecular character. Lamellar crystals having few interlamellar links and consisting essentially of an adjacent re-entry structure might therefore be the optimum morphology for which the drawing proceeds at a high rate for a small drawing stress. Experimental evidence for the ease of drawing of lamellar crystal mats has already been given for branched ethylene–propylene co-polymer

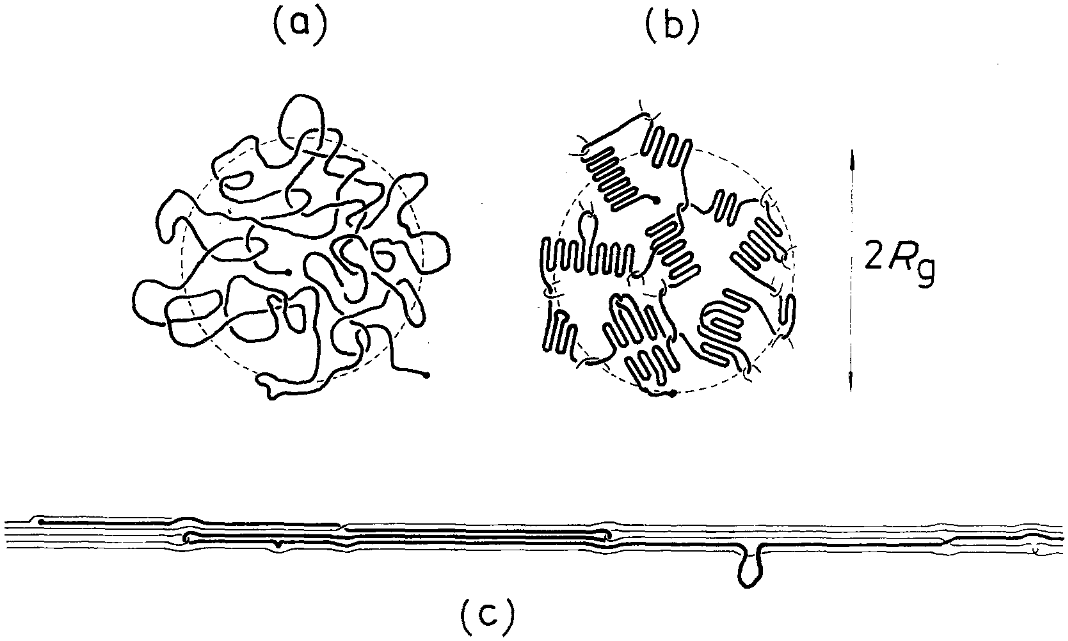

Figure 4 Illustration of occurrences on the molecular level during solution preparation and drawing: (a) A molecule in a concentrated polymer solution; (b) Crystallization from a concentrated solution, which may start at entanglement sites, and trapping of entanglements. The radius of gyration, R_g, remains approximately constant when crystallization takes place; (c) Part of a molecule which has generated numerous crystal defects in a drawn fibre.

[19] and annealed linear polyethylene mats [20]. The annealing appears to introduce a degree of cohesion into the mats in the form of interlamellar links. The question whether these links are entanglements cannot be answered at present.

As has been pointed out [3], the rate of drawing is given by the rate of unrecoverable creep, which is a function of morphological parameters (activation energy and volume), temperature and stress. Further, the rate of drawing may be expressed by

$$\dot{\epsilon} = \frac{\sigma_D}{D(t)}, \tag{1}$$

where $\dot{\epsilon}$ is the rate of drawing and $D(t)$ is the tensile creep function (which may be interpreted in certain cases as an extensional viscosity). The steady value [4] of $D(t)$ is influenced by the molecular weight (an average that is slightly higher than the weight average), the polymer concentration and the temperature. Since $D(t)$ is a function of time, it is also dependent on the molecular extension and therefore on the draw ratio. Most of the parameters above influence the tightness of the polymer network and the number of coupling entanglements between the molecules. Accordingly, the rate of drawing is expected to increase with diminishing numbers of entanglements. In any case, the polymer molecules are extended in the drawing process and assume, for negligible slippage, a degree of extension which is related to the draw ratio. However, it should be noted that the draw ratio cannot be an accurate measure of molecular extension, due to the occurrence of slippage phenomena which are amplified by high temperatures. Ideally, for complete extension, assuming negligible molecular slippage and a constant R_g during crystallization, the maximum draw ratio may be given approximately by

$$\lambda_{\max} = \frac{L}{2R_g}, \tag{2}$$

where L represents the length of the extended molecule, which is equal to the degree of polymerization, n, multiplied by the length of the repeat unit l ($L = nl$). The radius of gyration may be expressed by

$$R_g = cl(n/6)^{\frac{1}{2}}, \tag{3}$$

where c is the characteristic ratio for coil expansion. Combining Equations 2 and 3 gives

$$\lambda_{\max} = (6n)^{\frac{1}{2}}/2c. \tag{4}$$

Assuming an average value [21] of c to be 6.8 and introducing a molecular weight for the repeat

TABLE I Influence of the molecular weight for a monodisperse system (M) and the number of entanglements in which a molecule is involved (e) on the draw ratio, λ_{max} and λ, assuming that for small values of e, every entanglement reduces the molecular contour length by an average of 20%

M	λ_{max}	λ			
	$e = 0$	$e = 1$	$e = 2$	$e = 3$	$e = 5$
1×10^4	4.8	3.9	3.1	2.5	1.6
5×10^4	10.8	8.6	6.9	5.5	3.5
1×10^5	15.2	12.2	9.7	7.8	5.0
5×10^5	34.0	27.2	21.8	17.4	11.1
1×10^6	48.0	38.4	30.7	24.6	15.7
5×10^6	107.5	86.0	68.8	55.0	35.2

unit of 14, λ_{max} may be written in terms of the molecular weight, M, of a narrow fraction as

$$\lambda_{max} = \frac{M^{\frac{1}{2}}}{20.8}. \qquad (5)$$

It can be seen that λ_{max} increases with the square root of the molecular weight, and the quantitative dependence of λ_{max} on different molecular weights is shown in Table I. At low molecular weights of between 10 000 and 50 000 the value of λ_{max} is remarkably close to the natural draw ratio ($\lambda = 5$–10), usually achieved as these molecular weights for linear polymers by cold drawing [22]. This agreement does not seem to be a coincidence, since short molecules are involved in few entanglements [4], and full molecular extension might actually be accomplished in simple cold drawing procedures. For high molecular weights, however, a certain number of entanglements may be stable during cold drawing, and also to a smaller extent during hot drawing, which are incorporated into the fibrous crystals, thus giving rise to a draw ratio which is lower than λ_{max}. An example of a molecule which is involved in at least two entanglements is shown in Fig. 4c. The figure shows, besides entanglements, other defects in the fibrous crystal originating from chain ends, intertwinings, point defects and loops. The defects may be partly removed by further hot drawing at high drawing stresses [11]. The reduction in draw ratio due to entanglements may be estimated for a small number of entanglements by

$$\lambda = \lambda_{max}(0.8)^e, \qquad (6)$$

where e is the number of entanglements and when it is roughly assumed that, on an average, every entanglement reduces the contour length of the molecule by about 20%. The results are shown in Table I, where it can be seen for example that the draw ratio reduces to 1/3 when a molecule is involved in 5 stable entanglements. This simple model explains the inferior drawability and the achievement of only small draw ratios in high molecular weight materials drawn in the bulk [6]. On the other hand, since the draw ratio should increase with the molecular weight, the above relationship (Equation 4) may be an indication of how far drawing should proceed in order to achieve full molecular extension.

It should be noted that the molecular weight distribution, which has not been considered above, might also have a pronounced effect on the drawing behaviour and on the draw ratio achieved experimentally. Since the maximum draw ratio increases with the molecular weight, shorter molecules which are extended before the longer ones might cause serious stress concentrations, and accordingly a high probability of fracture, as well as a large resistance to deformation resulting in a low rate of drawing. In the case of Hifax 1900, which is known to have a broad molecular weight distribution, λ_{max} is 96 and 21 for the weight average (4×10^6 g mol^{-1}) and the number average (2×10^5 g mol^{-1}) molecular weights respectively. This indicates, firstly, that the molecular extension achieved in the experiments ($\lambda = 60$–90) is extremely high, because λ is very close to λ_{max} calculated from the weight average molecular weight. Nearly all loops and entanglements may therefore have been removed and only a small fraction of molecules with higher molecular weights than the weight average may be the origin of such defects. Secondly, starting from $\lambda = 21$, nearly all molecules that are smaller than the number average are fully extended and strongly resist further deformation, which results in a high increase in the drawing stress.

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