

Mechanical properties of ultra-high molecular weight polyethylene fibres in relation to structural changes and chain scissioning upon spinning and hot-drawing

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Gel- and suspension-spun fibres of ultra-high molecular weight polyethylene have been subjected to hot-drawing at 148°C. It has been found that for these fibres and drawing conditions, strength and modulus are uniquely determined by the draw ratio, analogous to observations by Capaccio *et al.* [1] for melt-spun fibres. Draw ratios of 100 could be achieved, leading to a tensile strength at break of 3.8 GPa and a Young's modulus of 120 GPa. Chain scissioning occurs both in spinning and hot-drawing. There seems to be a limiting molecular weight of approximately 1.5×10^6 . Extraction of the low molecular weight polyethylene from the as-spun fibres by controlled swelling, whereby an entanglement network of only the very long chains remains, substantially reduced the drawability of the fibres and only a draw ratio of 40 and a tensile strength of 1.7 GPa could be attained for such filaments.

1. Introduction

It has been recognized for quite some time that very strong polymeric materials can only be produced if one succeeds in crystallizing high molecular weight polymers in fully extended conformation [2]. The requirement of high molecular weight polymer stems from the demand for optimizing the number of covalent bonds per unit volume and for reducing the number of defects in the crystal lattice arising from the chain ends [3-5]. The difficulty in achieving this goal is primarily due to the ease with which these long elastic chains disturb the flow field in the course of spinning [6, 7], but also due to mechanical degradation of very long molecules [8-12] and to the virtual impossibility of removing all complex topological defects, such as trapped entanglements and disclinations [5, 13].

This paper deals with a study of the influence of draw ratio on the mechanical properties of gel-spun fibres of ultra-high molecular weight poly-

ethylene (UHMWPE) [14, 15]. In the hot-drawing of these gel-spun fibres at 148°C, the lamellar texture will be destroyed by partial melting, and fibrillar crystals are formed in the stretched entanglement network. This process also encompasses the removal of a number of entanglements and chain scissioning, leading to a limiting molecular weight of approximately 1.5×10^6 . Careful extraction of the low molecular weight polyethylene from the as-spun fibres by limited swelling followed by hot-drawing diminished the drawability and the tensile strength. Apparently the low molecular weight components play an important role in removing the topological constraints in the fibres. The Young's modulus and tensile strength were found to increase sharply with draw ratio, resembling the relationship established for melt-spun polyethylene fibres by Capaccio *et al.* [1]. In the present investigation draw ratios of 100 and a tensile strength up to 3.8 GPa were achieved.

2. Experimental details

The filaments used in the present work were prepared from two different grades of UHMWPE, i.e. Hi-fax 1900 and Hostalen Gur. Hi-fax 1900 is a linear polyethylene with a weight average molecular weight \bar{M}_w of 4×10^6 . Hostalen Gur is a linear polyethylene with $\bar{M}_w = 1.5 \times 10^6$. The number average molecular weight (\bar{M}_n) of both polyethylenes is about 2×10^5 . All the filaments were spun under comparable conditions. The Hi-fax 1900 samples were gel-spun from a 5 wt% solution of the UHMWPE in paraffin-oil at a spinning temperature of 170°C and an extrusion rate of 1 m min^{-1} . The Hostalen Gur samples were produced by suspension-spinning at a spinning temperature of 190°C and an extrusion rate of 1 m min^{-1} . Further details of this technique have been described elsewhere [16].

After the spinning treatment, the fibres were extracted with *n*-hexane, to remove the solvent, and dried in vacuum. Hot-drawing of the porous as-spun fibres was carried out under standard conditions at a drawing temperature of 148°C [17].

The mechanical properties of the fibres were investigated with a Zwick Z1.3B tensile tester at a tensile speed of 12 mm min^{-1} and an original sample length of 25 mm. For each filament the tensile strength at break, the Young's modulus and the elongation at break were determined as the average of at least six measurements.

Viscometric data were obtained from solutions of the UHMWPE powder (or fibre material) in an Ubbelohde viscometer at 135°C . The polyethylene was dissolved in decalin, a mixture of *cis*- and *trans*-decahydronaphthalene, together with 0.5 wt% anti-oxidant, i.e. 2,6-di-*t*-butyl, 4-methylcresol. Dissolution of the UHMWPE occurred at 135°C with occasional gentle stirring and required 4 h for the original powder material and 17 h for the as-spun and hot-drawn fibre material. The measuring of the flow times occurred according to the procedure described by Wagner and Dillon [18].

In view of the rather broad molecular weight distribution of the UHMWPE a considerable reduction in the number of chain ends in the fibres would be accomplished by removal of the low molecular weight fraction. For this purpose, some porous as-spun fibres were subjected to an extraction procedure in 1,2,4-trichlorobenzene, at a few degrees below their dissolution tem-

perature. This occurred by placing a metallic frame around which the fibre was wound, in the solvent. Special care was taken that the several windings of the fibre on the frame did not touch each other. The extraction time was between 6 and 42 h. In this period of time the frame was occasionally rotated gently. After the extraction, the frame was carefully removed from the solvent and placed in acetone to deswell the fibre. Thereafter the fibre was dried in vacuum. Subsequent hot-drawing of the filaments was again carried out under standard conditions [17] at 148°C .

Scanning electron microscopy (SEM) was performed in an ISI-DS 130 microscope, operated at 40 kV. Transmission electron micrographs of fragmented fibre samples were obtained in a Jeol 200 CX microscope operated at 100 kV. Fragmentation of the fibres was accomplished by etching with 95% fuming nitric acid, followed by ultrasonic agitation.

3. Results and discussion

3.1. Morphology

The gel-spun polyethylene fibres used in hot-drawing were spun at a spinning rate of about 1 m min^{-1} . This slow flow rate guarantees more or less the preservation of the entanglement network in the spinning solution [7]. Quench crystallization of this network results in the formation of large lamellar crystals which have been strung together by a few thin fibrils, as is shown by the SEM-micrograph of Fig. 1. Drawing of these porous structures at room temperature to a draw ratio (λ) of 6 leads to fracturing and tilting of the lamellae and the formation of a large number of fibrillar entities from the edges of the

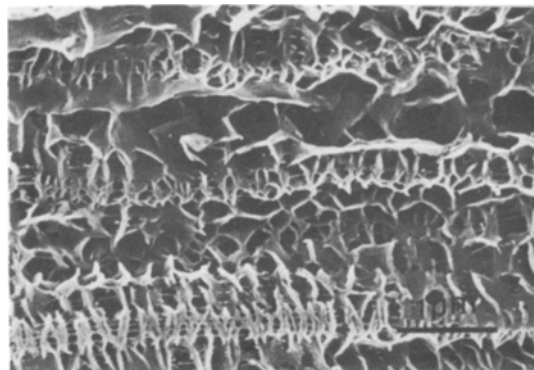


Figure 1 SEM of a porous as-spun fibre, prepared by gel-spinning of a 5 wt% solution of Hi-fax 1900 in paraffin-oil at a spinning rate of 1 m min^{-1} .

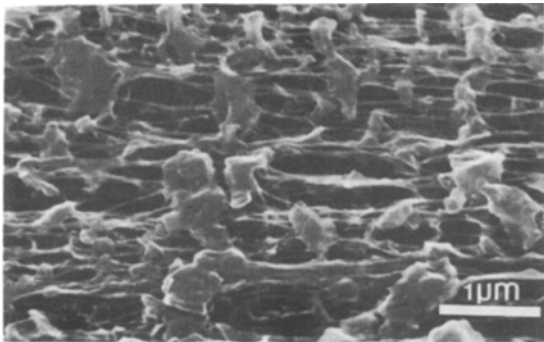


Figure 2 SEM of a porous as-spun fibre, prepared by gel-spinning, which was drawn at room temperature to a draw ratio $\lambda = 6$.

lamellae, as is demonstrated by the scanning electron micrograph of Fig. 2. Cold drawn fibres have tensile strengths of the order of 0.1 GPa. If these fibres were further drawn at 148°C the strength increased to about 2 GPa, which is far less than the values between 3.5 and 4 GPa, which are attained after drawing the as-spun fibres directly at 148°C. The changes in structure and morphology that take place upon hot-drawing at 148°C could not be studied by scanning electron microscopy, because of the agglomeration of the

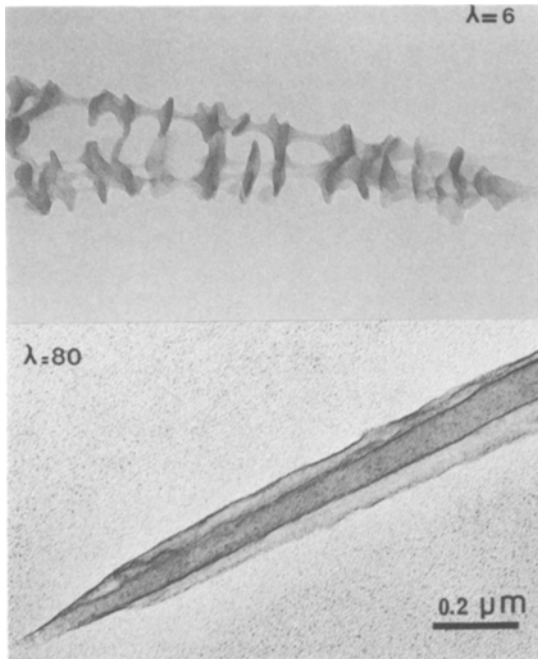


Figure 3 TEM of fragments of UHMWPE fibres which were hot-drawn at 148°C to draw ratios $\lambda = 6$, respectively, $\lambda = 80$. The fibres were fragmented by etching with 95% fuming nitric acid at 72°C, followed by ultrasonic agitation.

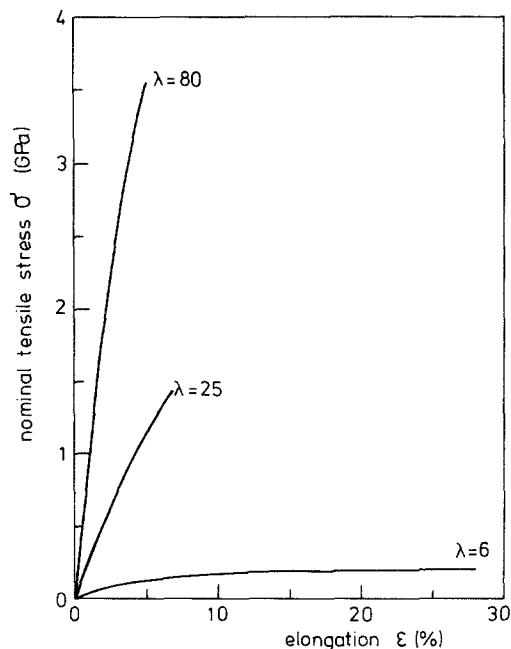


Figure 4 Stress–elongation curves for gel-spun fibres which were hot-drawn at 148°C to various draw ratios. The curves were measured at room temperature.

structural units, caused by partial melting of the lamellae [19]. Hot-drawn fibres were therefore etched with nitric acid and the remaining fragments were examined by transmission electron microscopy.

Some results, for draw ratios of 6 and 80, are presented in Fig. 3. At this intermediate draw ratio of 6 the polyethylene fibre is found to be composed of shish-kebabs. Fully drawn fibres at $\lambda = 80$ consist of smooth layered fibrils with tapered tails. Apparently, also at a drawing temperature of 148°C, shish-kebab morphologies are generated as precursors of the smooth fibrils in the fully drawn fibres. The transformation of the platelets into fibrils at this elevated temperature (where the lamellae are molten) proceeds by breaking up of the droplets, rather than by extension of the fibrils as occurs at 110°C (where the lamellae are still crystalline) [20].

3.2. Mechanical properties

The marked influence of the draw ratio on the mechanical properties of the polyethylene fibres is demonstrated by the curves in Fig. 4, where the stress has been plotted against elongation. All graphs are slightly curved, but the most pronounced features are the reduction in elongation

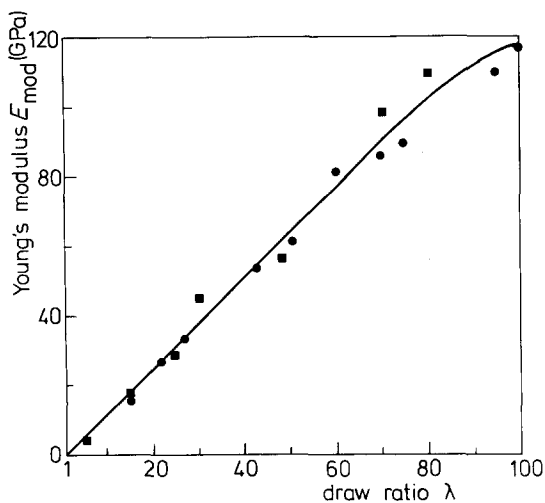


Figure 5 Young's modulus (E_{mod}) as a function of draw ratio (λ) for hot-drawn UHMWPE fibres prepared by gel-spinning (\blacksquare) and suspension-spinning (\bullet) at a spinning rate of 1 m min^{-1} .

at break, and the strong increase in Young's modulus (E_{mod}) and tensile strength at break (σ_b) with increasing draw ratio (λ). The modulus did not depend so much on the molecular weight and spinning conditions, because the data for gel-spun fibres with $\bar{M}_w = 4 \times 10^6$ and suspension-spun fibres with $\bar{M}_w = 1.5 \times 10^6$ indeed followed the same $E_{\text{mod}}-\lambda$ relationship (Fig. 5). The experimental results in Fig. 5 are similar to the Capaccio-Ward relationship [1] for melt-spun polyethylene, except that they extend to a draw ratio of 100 and moduli of 120 GPa.

Values for the Young's modulus as a function of λ for melt-spun fibres have been described by Fischer *et al.* [21] by the empirical relationship

$$\frac{1}{E_{\text{mod}}} = \frac{1}{E_{\text{lim}}} + \frac{a}{\lambda^2}, \quad (1)$$

where E_{lim} is the maximal attainable modulus and a is a constant (which has been related to the alteration of the entanglement network upon hot-drawing by Grubb [22]). This equation also seemed to fit the data of Smith and Lemstra [22, 23]. Our measurements from Fig. 5 do not comply with Equation 1, as is manifested by the curved line connecting the data points for the reciprocal modulus plotted against $1/\lambda^2$ in Fig. 6. The deviation from a straight line in Fig. 6 may very well be due to the fact that drawing at this high a temperature could possibly release many more entanglements, as can be judged from the extreme draw ratios of 100 that could be reached.

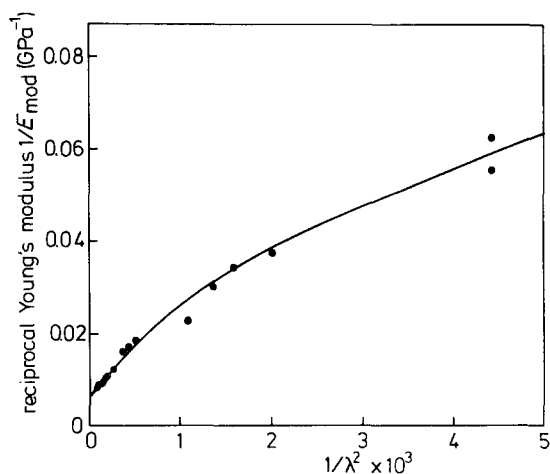


Figure 6 Reciprocal Young's modulus ($1/E_{\text{mod}}$) as a function of $1/\lambda^2$, where λ is the draw ratio.

The development of strength in the fibres with draw ratio is quite impressive as is manifested by Fig. 7, in which the tensile strength (σ_b) is plotted against λ . But at a draw ratio of 6 the tensile strength is only 0.25 GPa, which is approximately 1% of the theoretical strength of a perfect polyethylene fibre. Filaments drawn to $\lambda = 6$ consist of shish-kebabs (as demonstrated in Fig. 3). These entities consist of about 90% of lamellar material and 10% fibrils. If these backbone fibrils were perfect and continuous, one would expect a tensile strength of 1/10 of the theoretical value of the strength, which would amount to $\sim 2.5 \text{ GPa}$. The experimental value of 0.25 GPa thus points to a significant portion of defects in the backbones, which interrupt the crystallites.

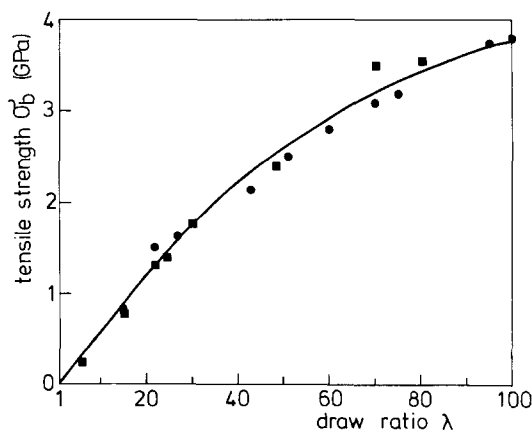


Figure 7 Tensile strength at break (σ_b) plotted against draw ratio (λ) for hot-drawn gel-spun (\blacksquare) and suspension-spun (\bullet) fibres.

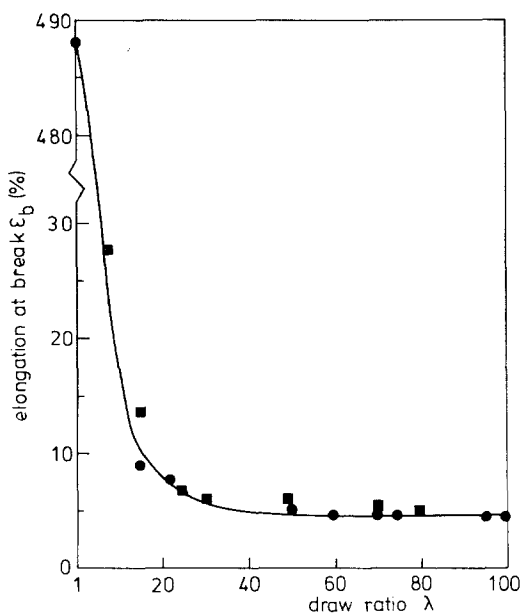


Figure 8 Elongation at break (ϵ_b) as a function of draw ratio (λ) for hot-drawn gel-spun (■) and suspension-spun (●) fibres.

It is interesting to note that the Young's modulus reaches about one-half to one-third of the theoretical value while the tensile strength does not exceed one-sixth to one-seventh of the theoretical strength. The experimentally observed strength is far below one-tenth of the modulus [5] and this again may point to the presence of flaws in the fibre in addition to the defect regions between the crystallites.

In terms of Peterlin's model for hot-drawn fibres [24] a Young's modulus of 120 GPa means that to a first approximation 50% of the chains in one crystalline block run through the defect zones as taut tie molecules to the neighbouring crystallite.

Rather surprising and unexplained is the rapid fall of the elongation at break (ϵ_b) with draw ratio (Fig. 8). It quickly diminishes from almost 500% in the as-spun fibre to 5% at $\lambda = 25$ and remains from there on nearly constant up to $\lambda = 100$. If the entanglement network would have been pulled taut at about $\lambda = 25$ one could speculate that the 5% elongation at break may be attributed to the ultimate extension of a trapped entanglement up to fracture. Evidently this sort of consideration calls for further investigations.

3.3. Chain scissioning

The observation that both the polyethylene sam-

ple with $\bar{M}_w = 4 \times 10^6$ and that with $\bar{M}_w = 1.5 \times 10^6$ gave the same strength and modulus against λ curve, was to some extent surprising because both the disturbance of the flow field during spinning and drawing and the defects in the solid fibres depend on chain length [4, 8, 16, 25]. A simple explanation might be that the largest chains degrade mechanically in the course of spinning and hot-drawing, so that one ends up with approximately the same molecular weight [8]. This point was further investigated by measuring the intrinsic viscosities of the starting polyethylene, of the fibre after gel-spinning, and after hot-drawing. Some of the most conspicuous data have been collected in Table I. These data only give an impression of the relative changes that take place in molecular weight, because we did not correct the intrinsic viscosity values for the shear-rate dependence, which seems to be an important factor for flexible polymers of very high molecular weight [18].

Nevertheless, the drastic reduction in intrinsic viscosity from 22.8 dl g^{-1} for the parent polyethylene powder to 18.5 dl g^{-1} for the as-spun fibres speaks for itself. Hot-drawing causes a further decrease in intrinsic viscosity to 17.1 dl g^{-1} . Our attempt to increase the molecular weight by applying the stirred solution crystallization fractionation method [26] also failed in preparing longer chains, because during this flow-induced fibrillar crystal precipitation, also chain rupture, took place. In fact, application of this method to the parent UHMWPE resulted in the same ultimate value of the intrinsic viscosity of 17.3 dl g^{-1} , as found after gel-spinning and hot-drawing. After hot-drawing at a drawing temperature of 110°C it was possible to detect the formation of free radicals in the UHMWPE

TABLE I Intrinsic viscosities of UHMWPE (Hi-fax 1900 with originally a molecular weight $\bar{M}_w = 4 \times 10^6$) after various stages of gel-spinning/hot-drawing and after stirred solution crystallization in decaline. The viscosity measurements were performed in decaline at 135°C in an Ubbelohde viscometer [18]

Sample	Intrinsic viscosity [η] (dl g^{-1})
Hi-fax 1900 polyethylene	
Original powder	22.8
As-spun fibre	18.5
Hot-drawn fibre	17.1
Fibres, obtained by stirred solution crystallization	17.3

TABLE II Effect of extraction with 1,2,4-trichlorobenzene on the drawing properties of porous as-spun UHMWPE fibres prepared by gel-spinning

Sample	Hot-drawing prior to extraction		Extraction conditions			Hot-drawing after extraction	
	Draw ratio λ	Tensile strength σ_b (GPa)	Time (h)	Temperature ($^{\circ}$ C)	Weight reduction (%)	Draw ratio λ	Tensile strength σ_b (GPa)
I	80	3.55	42	105	51	40	1.7
II	107	3.2	6	107	60	46	0.95
II	107	3.2	18	107.5	90	Undrawable	

fibres by the electron paramagnetic resonance (EPR) technique [27]. How the chains fracture is not known, but it is likely that they break somewhere in the middle, as follows from Frenkel's theory for individual coil molecules [28] and from Bueche's theory for entangled chains [29]. Odell *et al.* [12] have presented strong evidence for fracturing of polymer chains in the middle in elongational flow fields. Shear degradation studies reviewed by Casale and Porter [30] indicate that in addition to pure chain rupture, branching of molecules may occur in the case of linear polyethylene as a result of hydrogen abstraction by chain end radicals somewhere along the polymer molecule [31]. The intrinsic viscosity is, therefore, only a very crude measure of the chains that have been ruptured or branched in the flow field. The weakest spots in the molecules are likely to be the chain segments involved in complex entanglements, but whether breakage would occur or not depends on the length of the chain portion through the entanglement and the local stress [32].

Considerations of this kind suggest a strong molecular weight dependence of the probability that fracture might occur and would explain the fact that usually a limited molecular weight is found below which no further degradation is to occur under certain conditions [8]. In our case of spinning and hot-drawing of ultra-high molecular weight polyethylene, this limited molecular weight seems to be approximately 1.5×10^6 [33, 34].

3.4. Fibre extraction

Whether this finding of a limiting molecular weight implies that it is virtually futile to attempt at spinning higher molecular weight polyethylene is difficult to assess. One way to circumvent the reduction of molecular weight in the course of spinning was tried out in the following way. After spinning, the gel was dried and subsequently swollen in 1,2,4-trichlorobenzene at 107° C. The

entanglement network swells to a degree of swelling of about 50. The low molecular weight polyethylene diffuses out of the network which is held together by some crystallites in addition to the long-lifetime entanglements. This is a very effective way of molecular fractionation and what remains is only the very large chains as judged by their gel point upon crosslinking with dicuymylperoxide [35]. This swelling caused an extension of the fibre length of only about 10%, whereas the diameter increased as much as seven times the diameter of the dry fibre. The molecular weight between network junction points amounts to roughly 1×10^5 and the extraction procedure has, therefore, also reduced the number of entanglements. Nevertheless the hot-drawing of these extracted fibres yielded poor mechanical properties of 1.7 GPa in tensile strength in one case and when 90% of the polyethylene was extracted, the remaining network was found to be completely undrawable (Table II).

The extracted transient networks were composed of very large lamellar crystals after quench crystallization, as is revealed by the scanning electron micrograph in Fig. 9. These extracted fibres appeared to be substantially weaker than the unswollen as-spun fibres, as demonstrated by the stress-strain curves taken at room temperature in Fig. 10. Apparently the drawability is not exclusively determined by the number of remaining entanglements. Otherwise one would expect draw ratios in excess of 100 rather than 40 for the swollen fibres (Table II).

These results clearly show that the low molecular weight components, which are present in the non-extracted as-spun fibres, play a very essential role in the transport process [36, 37] that leads to the release of an excess of entanglements and allows the entanglement network to be pulled fully taut upon hot-drawing at 148° C. The number of 2.3 entanglements per molecule, which remain in the fully drawn fibres with a

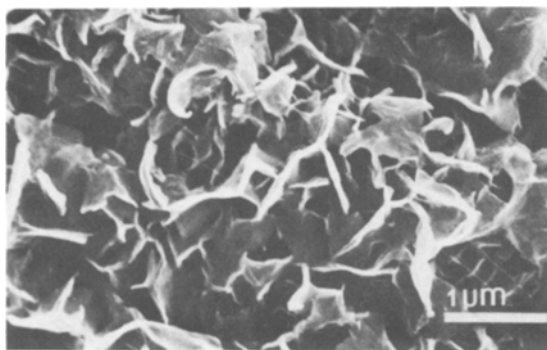


Figure 9 SEM of a porous as-spun fibre which was subjected to a swelling treatment with 1,2,4,-trichlorobenzene at 105° C for 42 h.

draw ratio of 100 (as we have found by analysing swelling measurements of ⁶⁰Co-γ radiation cross-linked strong polyethylene fibres and by shrinkage measurements on fully drawn fibres [13, 38]) may be the very long-lifetime chain intertwinings. It would require an extremely long time if they had to be released by a Reneker type diffusion process [39] of defects through the crystallites, which have considerably grown in length at the final draw ratios [38]. Another process by which the number of trapped entanglements can be further reduced was developed by Kanamoto *et al.* [40]. They deformed mats of single crystals of UHMWPE first by solid-state coextrusion and

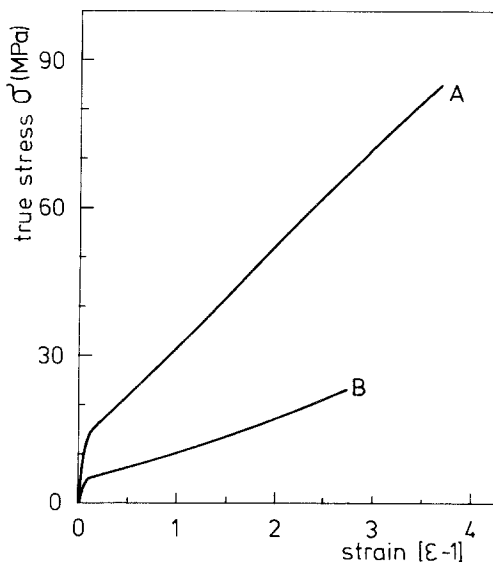


Figure 10 Stress-strain curves at room temperature of (a) a porous as-spun fibre, prepared by gel-spinning at a spinning rate of 1 m min⁻¹, and (b) a porous as-spun fibre which was subsequently swollen in 1,2,4-trichlorobenzene at 107° C for 6 h.

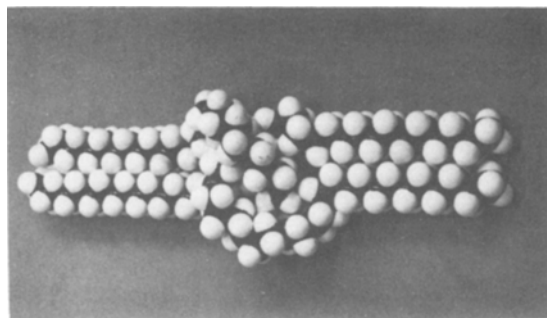


Figure 11 Model of a trapped entanglement represented by Stuart models of two polyethylene chains.

subsequently subjected it to post-drawing at 115° C. They were able to achieve draw ratios of 250 and Young's moduli up to 222 GPa. This combined technique, especially the single crystal growth step, may be very effective in diminishing the number of intra molecular entanglements which turn out to be unable to be removed under superdrawing [41] conditions. In the light of the chain scissioning found in this study it is also conceivable that the final entanglements have been removed in the solid-state coextrusion process by chain fracturing. The crystalline structure would thus not be disturbed by the bulky trapped entanglements [5] (which lower the modulus, but form chain connections which are essential for achieving strength). The bulky character of entanglements may be visualized by a Stuart model of two polyethylene chains involved in an entanglement, as shown in Fig. 11.

4. Conclusion

The Young's modulus and the tensile strength at break of gel-spun fibres of UHMWPE increase markedly with draw ratio upon hot-drawing at 148° C. At a draw ratio of 100, a value for the Young's modulus of 120 GPa and for the tensile strength at break of 3.8 GPa have been achieved. The fraction of the polyethylene material with a molecular weight above 1.5×10^6 did not have an effect on this modulus and strength—draw ratio relationship, due to molecular degradation during spinning and hot-drawing.

Extraction of the low molecular weight components from the as-spun fibres by pseudo-equilibrium swelling at elevated temperatures did not only affect the molecular weight distribution, but also lowered the number of entanglements in the as-spun fibre. As a result of this extraction procedure, the drawability of the fibres

was strongly reduced and thereby also the mechanical properties of the drawn fibres. This reduced drawability was attributed to the absence of a low molecular weight fraction as a result of which the removal of entanglements in the drawing process is hampered. Accordingly the remaining number of entanglements in fully drawn non-extracted fibres must have been less than in the fully drawn extracted fibres, notwithstanding the fact that the extracted as-spun fibres contained a smaller amount of entanglements than the non-extracted as-spun fibres. The remaining long-lifetime entanglements in the fully drawn gel-spun fibres with a draw ratio of ~ 100 possibly lower the modulus, as compared to solid-state coextruded and hot-drawn single crystal mats, in which probably no entanglements are left. On the other hand, the few entanglements in the fully drawn gel-spun fibres provide a chain connectedness which is necessary for achieving a high strength.

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