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Gel-spun polyethylene fibres

Part 1 *Influence of spinning temperature and spinline stretching on morphology and properties*

W. HOOGSTEEN, R. J. van der HOOFT, A. R. POSTEMA, G. ten BRINKE, A. J. PENNINGS
Department of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

The tensile strength of gel-spun polyethylene fibres hot-drawn to the maximum draw ratio depends on the spinning conditions such as spinning speed, spinline draw ratio and spinning temperature. High deformation rates during spinning introduce defects and fibres with poor ultimate properties are produced. These defects are already present before the hot-drawing step and can be detected indirectly by wide-angle X-ray scattering, since they are accompanied by preferential *c*-axis orientation parallel to the fibre axis and a shish-kebab structure. The introduction of flaws such as chain scission and tight knots can be prevented by avoiding spinline stretching and/or increasing the spinning temperature. This is due to the fact that higher spinning temperatures reduce the span of time in which the chains remain entangled and behave like a real network. Due to their lamellar/shish-kebab structure, the extracted fibres show a mechanical behaviour which to some extent is characteristic of composites.

1. Introduction

Gel-spinning of semi-dilute ultra-high molecular weight polyethylene solutions is a by now familiar technique to obtain ultra-high strength polyethylene fibres. Due to the reduction of the number of entanglements compared to more concentrated systems (eg. melt-spinning [1–3] or hydrostatic extrusion [4, 5]) better properties can be obtained [6, 7]. Currently, fibres with a tensile strength of more than 6 GPa and a Young's modulus of 160 GPa can be prepared [8–11]. For an overview of the many different techniques developed for preparing ultra-high strength polyethylene fibres we refer to recently published review papers [12–14].

The method used in our laboratory consists of extruding a solution of 1 to 5 wt % polyethylene in paraffin oil followed by quenching in air. To remove the paraffin oil the gel-spun fibre is extracted with n-hexane and subsequently dried. Then, the extracted fibre is hot-drawn which transforms the lamellar/fibrillar structure into smooth fibrils. During this stage a large improvement of the properties is achieved. The ultimate properties obtained depend strongly on the spinning conditions such as spinning speed, spinning temperature, stretching in spinline, geometry of the die and polymer concentration. It is the aim of this paper to describe the influence of some of these spinning variables on the morphology of the as-spun fibres and to show how they affect the ultimate properties of the polyethylene fibres.

One of the problems encountered during gel-spinning polyethylene solutions is the adsorption of the polyethylene on the wall of the die [15]. This results in fibres with poor properties, because stretching the entanglement network at one end while the other end is anchored by the adsorbed layer on the wall of the die leads to rupturing of the entanglement structure. This problem can be solved in a number of ways. Adding 1 wt % aluminium stearate to the polyethylene solution spun at a rate of 1 m min^{-1} and a spinning temperature of 170° C suppresses the adsorption [15, 16], as is reflected by higher tensile strengths compared to fibres spun under the same conditions without aluminium stearate. A second way to suppress adsorption is to reduce the residence time of the polymer solution in the spinneret below the time required for adsorption. Indeed, for solutions extruded at a rate of 100 m min^{-1} instead of 1 m min^{-1} the effect of the addition of 1 wt % aluminium stearate on the ultimate tensile strength is insignificant [16]. Finally, the adsorption can also be suppressed by raising the spinning temperature [17].

Besides adsorption, stretching of the spinline can also have a deteriorating effect on the ultimate properties of gel-spun polyethylene fibres hot-drawn to the maximum draw ratio. This is in particular true at spinning temperatures of about 170° C and spinning speeds of approximately 100 m min^{-1} [16]. The tensile strength decreases with increasing take-up speed. The high deformation rate in the orifice and in the spinline creates defects in the transient entanglement network, which on the time-scale of the experiment behaves as a more or less permanent network. At higher spinning temperatures the polymer chains are more flexible and the permanent-network behaviour is lost to some degree. Disturbances introduced by high deformation rates are restored by fast relaxations. The degree of *c*-axis orientation parallel to the fibre axis introduced

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during stretching of the spinline is a measure of the permanence of the entanglement network on the time-scale of the experiment. This type of c-axis orientation is at the same time a measure of the number of defects such as tight knots and chain scissions introduced during this rather crude method of spinning. These flaws determine the ultimate tensile strength obtained after hot-drawing. In this paper the influence of the spinning conditions on the degree of c-axis orientation parallel to the fibre axis will be discussed, and its effects on the mechanical behaviour of the as-spun as well as the hot-drawn fibres will be described. This paper is restricted to polyethylene fibres obtained from a solution of 5 wt % Hifax 1900 dissolved in paraffin oil. In a subsequent paper the influence of the polymer concentration and molecular weight distribution will be considered.

2. Experimental procedure

The linear polyethylene sample used throughout this study was Hifax 1900 with $\bar{M}_n = 2 \times 10^5 \text{ kg mol}^{-1}$ and $\bar{M}_w = 4 \times 10^6 \text{ kg mol}^{-1}$. 5 wt % of this polyethylene was dissolved in paraffin oil (containing 0.5 wt % DBPC anti-oxidant) at 150° C and homogenized for 48 h at this temperature. Upon cooling, this solution formed a gel which was fed to the spinning apparatus. The gel was extruded into a filament at temperatures varying from 170 to 250° C with a spinning speed of 1 or 100 m min^{-1} using a conical die [16] with an exit of 1 mm. The paraffin oil was extracted from these filaments with n-hexane. Afterwards hot-drawing was carried out at 148° C in a nitrogen atmosphere, always to the maximum draw ratio. The mechanical properties of the fibres were investigated with an Instron 4301 tensile tester. For the hot-drawn fibres the original sample length was 25 mm and a tensile speed of 12 mm min^{-1} was used. For the extracted fibres these values were 22 mm and 30 mm min^{-1}, respectively. Wide-angle X-ray scattering (WAXS) experiments were carried out with a Statton camera using Cu$K\alpha$ radiation ($\lambda = 0.154$ nm) produced by a Philips X-ray generator connected to a closed cooling circuit and operated at 45 kV and 45 mA. Azimuthal scattering intensities were obtained with a densitometer. Scanning electron microscopy (SEM) micrographs were obtained with an ISI DS-130 scanning electron microscope operated at 25 kV.

3. Results and discussion

The organization of this section is as follows. First the influence of the spinning conditions on the ultimate tensile strength of the hot-drawn polyethylene fibres will be discussed. Next, the connection between the ultimate tensile strength and the degree of preferential c-axis orientation parallel to the fibre axis in the extracted fibres not yet hot-drawn will be established. Finally the morphology and mechanical behaviour of these extracted fibres will be considered in relation to the degree of preferential c-axis orientation parallel to the fibre axis.

Fig. 1 shows the tensile strength obtained after hot-drawing as a function of the spinning temperature for freely extruded fibres and fibres drawn in the spinline to a draw ratio of 50. In all cases the extrusion rate was 1 m min^{-1}. At a spinning temperature of 170° C the difference in tensile strength observed can be ascribed to the deteriorating effect of adsorption combined with spinline stretching as described before [15–17]. In contrast to freely extruded fibres, the tensile strength of the fibres drawn in the spinline to a ratio of 50 increases considerably with increasing spinning temperature. The tensile strengths are observed to merge at a spinning temperature of about 250° C. This implies that at this temperature the ultimate tensile strength becomes independent of spinline stretching, at least for draw ratios smaller than 50. Higher spinning temperatures imply improved chain flexibility and therefore a loss of permanence of the transient entanglement network on the time-scale of the experiment. The viscosity of the polymer solution becomes too low to build up stresses high enough to create defects. Moreover, even if some defects are introduced, fast relaxations may prevent them from existing long enough to become trapped by solidification. The adsorption of the polyethylene chains on the wall of the die is also suppressed. For freely extruded fibres adsorption has, even at a spinning temperature of 170° C, no effect on the ultimate tensile strength. Stretching of the spinline is necessary for the

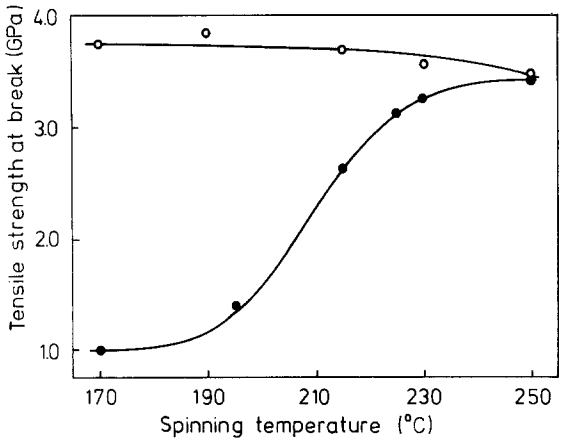

Figure 1 Tensile strength at break obtained after hot-drawing to the maximum draw ratio, as a function of the spinning temperature for gel spun polyethylene fibres spun with a spinning speed of 1 m min^{-1} and different winding speeds: (○) 1, (●) 50 m min^{-1}.

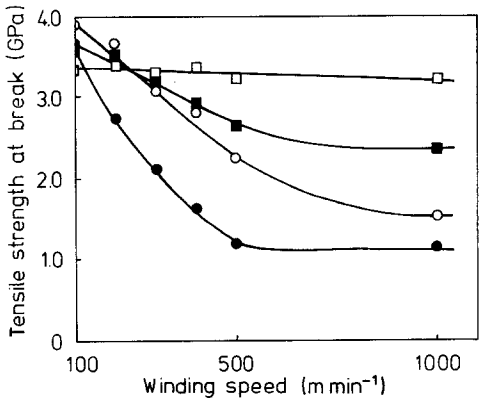

Figure 2 Tensile strength at break obtained after hot-drawing to the maximum draw ratio, as a function of the winding speed for gel-spun polyethylene fibres spun with a spinning speed of 100 m min^{-1} and different spinning temperatures: (●) 170, (○) 215, (■) 230, (□) 250° C.

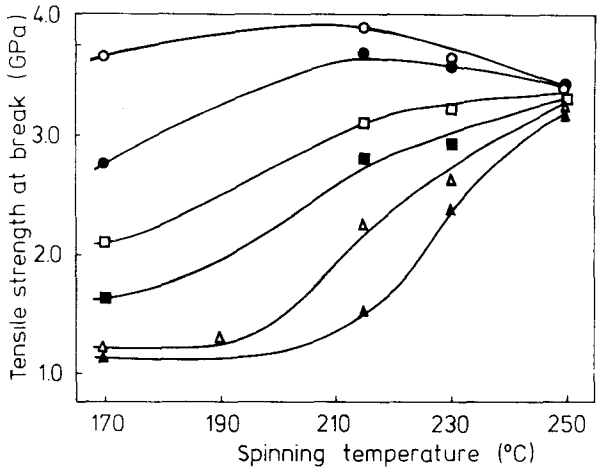

Figure 3 Tensile strength at break obtained after hot-drawing to the maximum draw ratio, as a function of the spinning temperature for gel-spun polyethylene fibres spun with a spinning speed of 100 m min^{-1} and different winding speeds: (○) 100, (●) 200, (□) 300, (■) 400, (△) 500, (▲) 1000 m min^{-1}.

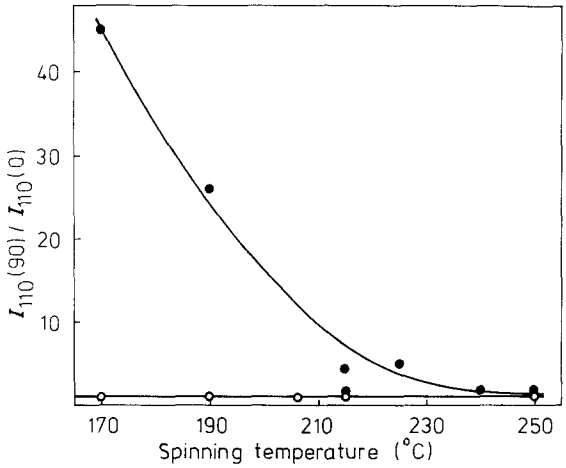

Figure 4 Degree of preferential *c*-axis orientation parallel to the fibre axis in the extracted gel-spun polyethylene fibres as a function of the spinning temperature for fibres spun with a spinning speed of 1 m min^{-1} and different winding speeds: (○) 1, (●) 50 m min^{-1}.

effect of adsorption to become observable. In fact adsorption only amplifies the deteriorating effect of spinline stretching.

Increasing the spinning speed from 1 to 100 m min^{-1} suppresses adsorption, as demonstrated by the fact (among others) that the effect of adding aluminium stearate vanishes. In this case the deteriorating effect of the spinline stretching itself determines the tensile strength. Fig. 2 shows clearly that at a given spinning temperature the unfavourable effect of spinline stretching is enhanced at higher draw ratios (higher winding speeds). As in the case of a spinning speed of 1 m min^{-1}, the effect of spinline stretching diminishes at higher spinning temperatures. Again the ultimate tensile strengths for different winding speeds merge at a spinning temperature of about 250° C. (Fig. 3) although the maximum draw ratios compared are different (50 and 10 for spinning speeds of 1 and 100 m min^{-1}, respectively).

In a previous paper [18] a relation between the spinning conditions (spinning temperature and draw ratio of the spinline), preferential *c*-axis orientation parallel to the fibre axis introduced during spinline stretching, and ultimate tensile strength after hot-drawing, was already noticed. A high degree of preferential *c*-axis orientation parallel to the fibre axis introduced during spinline stretching resulted in fibres with poor ultimate mechanical properties. To obtain a more quantitative relation between the degree of preferential *c*-axis orientation parallel to the fibre axis and the ultimate tensile strength a determination of orientation functions as used by Stein and co-workers would be helpful [19, 20]. However, our as-spun fibres show in many cases a second type of orientation. Tilting of the lamellae during constraint extraction (longitudinal shrinkage of the fibre is prevented) results in preferential *c*-axis orientation perpendicular to the fibre axis [18]. This type of orientation predominates in fibres which contain little or no preferential *c*-axis orientation parallel to the fibre axis. Due to this complication we preferred to express the degree of preferential *c*-axis orientation parallel to the fibre axis by the ratio of the intensity of the 1 1 0 reflection at the equator (azimuthal scattering angle $\Omega = 90°$) and the intensity of this reflection at the meridian ($\Omega = 0°$) corrected where necessary for the preferential *c*-axis orientation perpendicular to the fibre axis.

In Fig. 4 this measure of the degree of preferential *c*-axis orientation parallel to the fibre axis is presented as a function of the spinning temperature for freely extruded fibres and fibres drawn in the spinline to a ratio of 50. In all cases the extrusion rate was 1 m min^{-1}. For freely extruded fibres there is no preferential *c*-axis orientation parallel to the fibre axis ($I_{110}(90)/I_{110}(0) = 1$). For fibres stretched in the spinline the degree of *c*-axis orientation decreases with increasing spinning temperature.

Orientation of polymer molecules in the melt as well as in solution by a flow-field is a subject of many investigations [21–33]. Orientation by a flow-field can be obtained if the orientational action of the flow-field prevails over the relaxation of the deformed molecule. According to Mackley and Sapsford [23] this is the case if $\dot{\varepsilon}_{ii}\tau > 1$ where $\dot{\varepsilon}_{ii}$ is the elongational deformation rate and τ is the largest relaxation time, i.e. the relaxation time associated with the mechanical response of a random coil to a small deformation. Moreover the exposure time t of the polymer molecules to the orientational action of the flow-field should be long enough to achieve orientation. This is the case if $\dot{\varepsilon}t \gg 1$ [23]. In the gel-spinning process, elongational flow is obtained during stretching of the spinline and during the flow of the polymer solution through the conical die. In the last case elongational flow will compete with shear flow, for which the orientational action is considerably less. To obtain orientation by a shear flow-field, $\dot{\varepsilon}_{ij}\tau$ should be much larger than unity, where $\dot{\varepsilon}_{ij}$ is the shear deformation rate.

Peiffer *et al.* [24] discussed the influence of entanglements on the orientation introduced by a flow-field. They state that entanglements do not allow the individual chains to reach their maximum elongation because there is not enough time to disentangle. On the other hand, compared to dilute solutions it is easier to orient short segments within an individual

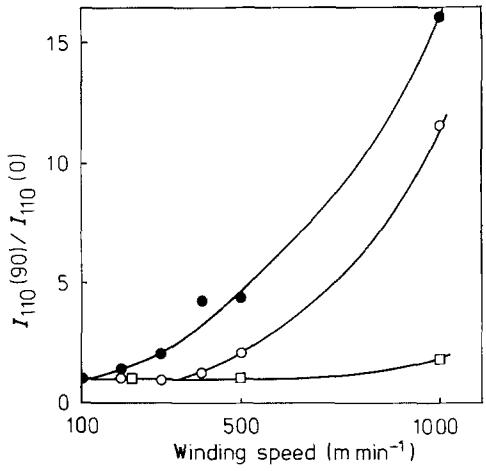

Figure 5 Degree of preferential *c*-axis orientation parallel to the fibre axis in the extracted gel-spun polyethylene fibres as a function of the winding speed for fibres spun with a spinning speed of 100 m min^{-1} and different spinning temperatures: (●) 170, (○) 215, (□) 250° C.

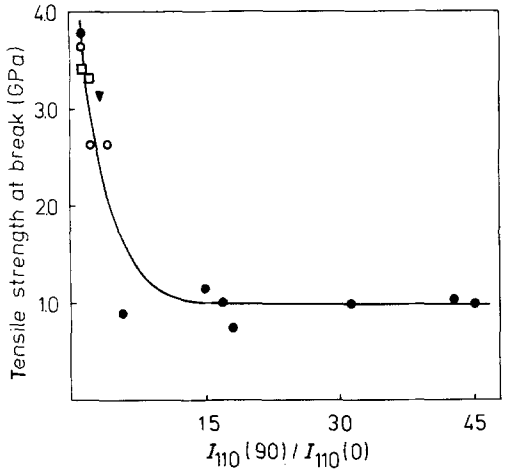

Figure 6 Tensile strength at break obtained after hot-drawing to the maximum draw ratio, as a function of the degree of preferential *c*-axis orientation parallel to the fibre axis in the extracted fibres for fibres spun with a spinning speed of 1 m min^{-1} and different winding speeds and spinning temperatures: T_{spin} = (●) 170, (○) 215, (▼) 225, (□) 250° C.

chain [24, 25]. The creation of orientation becomes exceedingly difficult at higher temperatures because τ decreases. For a single chain, this is demonstrated clearly by the Kirkwood expression [26]

$$\tau \cong \frac{\eta_s R^3}{T} \quad (1)$$

where η_s is the solvent viscosity and R the hydrodynamic radius of the unperturbed polymer coil. The effect of the temperature on τ accounts for the observed vanishing of the preferential *c*-axis orientation parallel to the fibre axis at spinning temperatures of approximately 250° C (Figs 4 and 5). In Fig. 5 the degree of preferential *c*-axis orientation parallel to the fibre axis is presented as a function of the winding speed for different spinning temperatures.

The efficiency of creating *c*-axis orientation parallel to the fibre axis created by a flow-field and trapped by crystallization is determined by the deformation rate (elongation or shear), the exposure time to the orientational action of the flow-field, and the relaxation time. These variables depend in a complex way on spinning variables such as spinning temperature, extrusion rate, take-up speed, geometry of the die, cooling rate of the spun fibre and the distance from the spinneret to the take-up device [31, 33]. Changing one of the spinning variables leads therefore to a different degree of preferential *c*-axis orientation parallel to the fibre axis. For example a higher extrusion rate will result in higher elongational deformation rates in the die, but this may be compensated by a shorter exposure time to the orientational action of the flow-field. Moreover the contribution of different types of flow (elongational or shear) may change with the extrusion rate as a result of different degrees of adsorption of the polymer chains on the wall of the die. A change in extrusion rate will in general result in a change of the temperature along the fibre as a function of the distance to the die and therefore to an onset of crystallization at a different distance from the spinneret. Assuming that no cold-drawing occurs, this distance determines the path-length in which spinline stretching can take place and hence the deformation rate. From all this it is clear that the relation between spinning conditions and degree of orientation is rather complex.

Figs 6 and 7 are obtained by combining all of the results mentioned so far. The tensile strengths obtained after hot-drawing to the maximum draw ratio decreases with increasing degree of preferential *c*-axis orientation parallel to the fibre axis introduced during spinline stretching. Although we have already hinted at a possible explanation, it is a somewhat curious observation since in order to obtain polyethylene fibres with good ultimate properties the chains have to be aligned parallel to the fibre axis as well as possible. In the case of gel-spinning this is accomplished by the hot-drawing process. However, the introduction of some orientation during the gel-spinning turns out to have the opposite effect. The introduction of orientation is apparently accompanied by the introduction of flaws

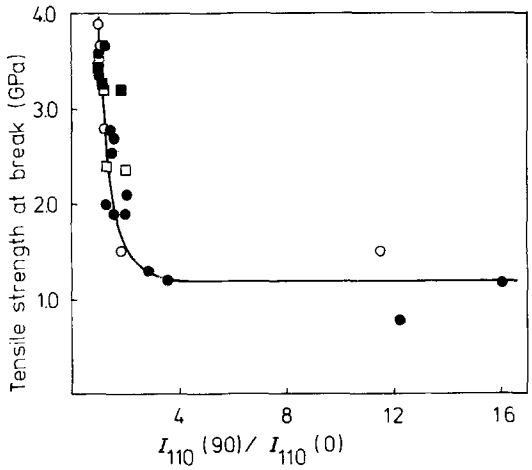

Figure 7 Tensile strength at break obtained after hot-drawing to the maximum draw ratio, as a function of the degree of preferential *c*-axis orientation parallel to the fibre axis in the extracted fibres for fibres spun with a spinning speed of 100 m min^{-1} and different winding speeds and spinning temperatures: T_{spin} = (●) 170, (○) 215, (■) 230, (□) 250° C.

which are responsible for the poor ultimate mechanical properties. The stresses necessary for the creation of orientation also introduce defects, and both will only be found if the entanglement network behaves as a more or less permanent structure on the time-scale of the experiment. Thus the degree of preferential c-axis orientation introduced during spinning seems directly related to the number of defects in our gel-spun fibres.

An indication of the occurrence of the probably most important defect, local chain scission, can be obtained by viscosity measurements. The intrinsic viscosity determined in Decalin at 130° C for the starting polymer was $20\,dl\,g^{-1}$. After the preparation of the gel the intrinsic viscosity decreased to $19.4\,dl\,g^{-1}$. Spinning the gel at 170° C with a spinning speed of $100\,m\,min^{-1}$ and a take-up speed of $100\,m\,min^{-1}$ reduced the intrinsic viscosity further to $17.1\,dl\,g^{-1}$. If in addition a fivefold stretching in the spinline took place the intrinsic viscosity reduced even further to $15.5\,dl\,g^{-1}$ [16]. Although the absolute values are somewhat unreliable for these high molecular-weight polymers, they clearly show the reduction in molecular weight due to chain scission.

That the presence of localized flaws rather than the reduction in molecular weight itself is responsible for the lower values of tensile strength and modulus was shown by the following experiment. The as-spun fibres, spun under conditions leading to poor ultimate properties, were re-used. A gel was made and this time the fibre was spun under the most favourable conditions. The values for the tensile strength and modulus turned out to be comparable with those obtained by using the polyethylene as supplied and also spun under the most favourable conditions.

The correlation observed between the preferential c-axis orientation parallel to the fibre axis and the tensile strength is process-dependent. This is clear from a comparison with the surface-growth technique [34]. During surface-growth an equilibrium between the crystal growth rate and the take-up speed exists. The resulting fibres contain a high degree of preferential c-axis orientation parallel to the fibre axis but have a tensile strength of up to 4 GPa [35], which after hot-drawing may even increase to 4.7 GPa [36]. The number of defects trapped during this more controlled method of fibre preparation will be far less than in the case of gel-spinning where high deformation rates are encountered. Some evidence for the conclusion that the relation between the preferential c-axis orientation parallel to the fibre axis and the ultimate tensile strength depends on the way the orientation is introduced can also be found in Figs 6 and 7. The ultimate tensile strength decreases somewhat faster with increasing preferential c-axis orientation parallel to the fibre axis for a spinning speed of $100\,m\,min^{-1}$ than for a spinning speed of $1\,m\,min^{-1}$.

Preferential c-axis orientation parallel to the fibre axis introduced during gel-spinning not only has its impact on the mechanical properties of the hot-drawn fibres but also on the mechanical properties of the as-spun fibres. To show this we will restrict ourselves to fibres spun with a spinning speed of $100\,m\,min^{-1}$.

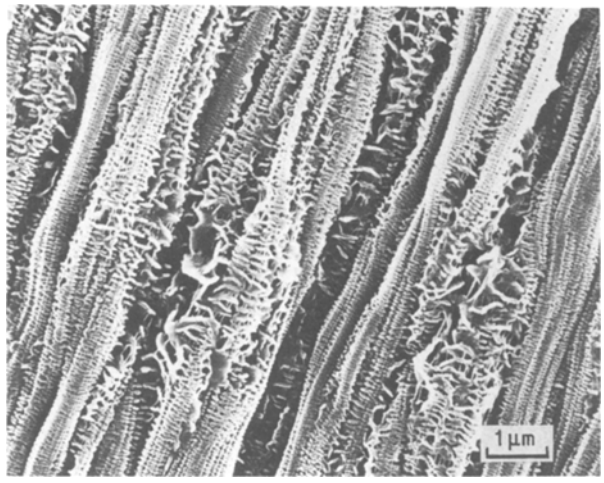

Figure 8 Scanning electron micrograph of an extracted gel-spun polyethylene fibre containing shish-kebab structure, spun at a spinning speed of $100\,m\,min^{-1}$, a winding speed of $500\,m\,min^{-1}$ and a spinning temperature of 170° C.

The results for fibres spun with a spinning speed of $1\,m\,min^{-1}$ are similar. The morphology of the as-spun fibres depends on the spinning conditions in a way described in a previous paper [18]. Fibres without preferential c-axis orientation parallel to the fibre axis show a lamellar/crazelike structure, whereas fibres with preferential c-axis orientation parallel to the fibre axis introduced during spinning contain shish-kebab structures due to oriented crystallization.

A SEM photo of the latter structure is shown in Fig. 8. SEM is a surface-sensitive technique, and the morphology of the surface of a fibre is not necessarily representative of the morphology of the whole fibre (for example fibres with a skin/core structure due to fast cooling/crystallization of the fibe surface [31, 32]). Using only SEM pictures to determine the morphology may easily lead to an incorrect description. Moreover, even the surface structure of fibres is often locally different. Cutting the fibre to look at the inside structure may be one way to circumvent the first problem, but artefacts can be introduced in this process especially if the material is plastically deformable. X-ray scattering gives a better but more abstract picture of the overall morphology of the fibre. A combination of both techniques will give the most reliable information. In our case this combination shows that the amount of shish-kebab structure increases with increasing preferential c-axis orientation parallel to the fibre axis. The high $I_{110}(90)/I_{110}(0)$ values, the increased porosity of fibres with a high degree of preferential c-axis orientation parallel to the fibre axis, determined from the small-angle X-ray scattering, as well as SEM pictures of the inside of the fibre, clearly prove that the whole fibre consists of a shish-kebab structure.

Fig. 9 shows the stress–strain curves of the extracted fibres spun under different spinning conditions. Fibres containing preferential c-axis orientation parallel to the fibre axis (Curve (a)) have an elongation at break of about 10 to 30% and no yielding is observed. On the other hand fibres with no preferential c-axis orientation parallel to the fibre break at much larger strains (up to about 900%, Curves (b) and (c)). These

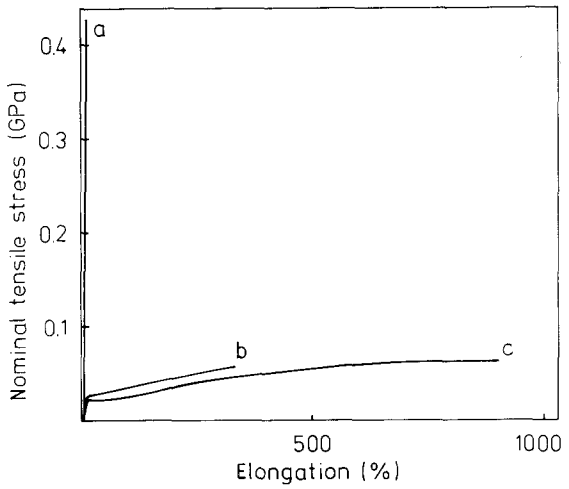

Figure 9 Stress–strain curves of extracted gel-spun polyethylene fibres spun under different spinning conditions with a spinning speed of 100 m min^{-1}: (a) T_{spin} = 170° C, V_{wind} = 1000 m min^{-1}; (b) T_{spin} = 170° C, V_{wind} = 100 m min^{-1}; (c) T_{spin} = 250° C, V_{wind} = 100 m min^{-1}.

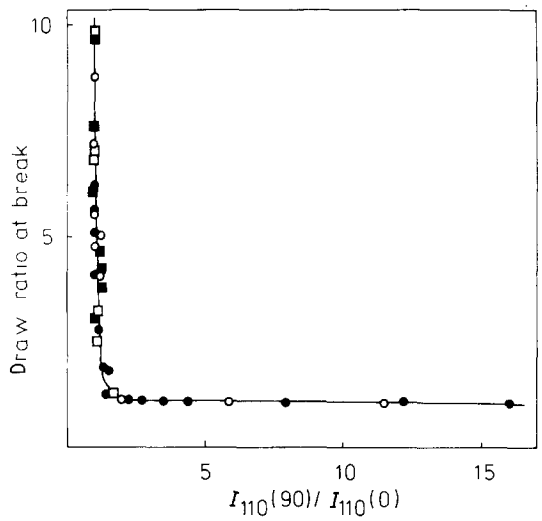

Figure 10 Draw ratio at break of the extracted gel-spun polyethylene fibres as a function of the preferential *c*-axis orientation parallel to the fibre axis for fibres spun with a spinning speed of 100 m min^{-1} and different winding speeds and spinning temperatures: T_{spin} = (●) 170, (○) 215, (■) 230, (□) 250° C.

fibres show extensive yielding. Cold-drawing of high molecular-weight polyethylene (HMWPE) is a subject extensively described in the literature [37–44]. The cold-drawing behaviour strongly depends on the preparation process of the fibre. Melt-spun HMWPE fibres show no clear yield-point and a high degree of strain-hardening [39, 40]. This strain-hardening is ascribed to the deformation of the fibrillar structure [37] introduced at an earlier stage of the cold-drawing process.

The transformation of a lamellar into a fibrillar structure can be described by the microfibrillar model of Peterlin [37, 38, 44] based on lamellae connected by tie-molecules and entanglements. Fibres or films prepared from dilute solutions yield and very little strain-hardening is observed [41, 42]. This difference may be due to a difference in connectivity between the original lamellae, which will be far less for fibres prepared from dilute solutions. By cold-drawing these fibres, lamellae are also transformed into fibrils but these fibrils will contain fewer interfibrillar tie-molecules and therefore less strain-hardening. Our gel-spun fibres (5 wt %) with an original lamellar structure show a cold-drawing behaviour in between: Curves (b) and (c) show some degree of strain hardening. The crazelike transformation of lamellae to fibrils observed for these fibres (at a temperature of 120° C) show a strong resemblance to the results obtained for cold-drawing at room temperature of gel films prepared from dilute solutions [41, 42]. This is in contrast to melt-spun HMWPE, which shows no void formation due to the high connectivity (entanglements and tie molecules) between the lamellae. The difference in entanglement concentrations also accounts for the high strain at break for our fibres compared to melt-spun fibres. During the cold-drawing of fibres with a lamellar structure the original preferential *c*-axis orientation perpendicular to the fibre axis is transformed into a preferential *c*-axis orientation parallel to the fibre axis. The elongation at break for fibres originally containing a lamellar structure depends on the spinning temperature. Fig. 9 shows (Curves (b) and (c)) that at higher spinning temperatures higher elongations at break are found. This suggests that some disentangling occurs at elevated temperatures.

The tremendous influence of the presence of preferential *c*-axis orientation parallel to the fibre axis on the stress–strain behaviour is demonstrated more clearly in Fig. 10. It shows a very steep drop of the draw ratio at break of the extracted fibres with increasing preferential *c*-axis orientation parallel to the fibre axis. This implies that in a fibre containing lamellar as well as shish-kebab structure the stiff shish-kebabs which are responsible for the observed preferential *c*-axis orientation parallel to the fibre axis determine the elongation at break. When the shish-kebab structure breaks, the lamellar structure which normally can be deformed plastically to a high elongation is in most cases not able to sustain the high stresses, and the whole fibre breaks without yielding. Only when a small amount of shish-kebab structure is present can yielding of the lamellar material take place.

Another property indicative of the shish-kebab structure is the tensile strength at break of the extracted fibres. This is demonstrated in Fig. 11, which shows the tensile strength at break as a function of the preferential *c*-axis orientation parallel to the fibre axis. For a ratio $I_{110}(90)/I_{110}(0) \geqq 2$, the tensile strength at break increases with increasing *c*-axis orientation parallel to the fibre axis, which is as expected. The draw ratio at break is high for extracted fibres containing no or very little preferential *c*-axis orientation parallel to the fibre axis. Around the minimum in the tensile strength at break curve, the small amount of shish-kebab structure prevents the lamellar material from becoming oriented parallel to the fibre axis due to premature breakage of the fibre as discussed before. The stress–strain behaviour of the shish-kebab-containing fibres shows a great resemblance to the stress–strain behaviour of surface-grown fibres before hot-drawing, although the tensile strength at break is considerably lower [34]. This is the result of the lower

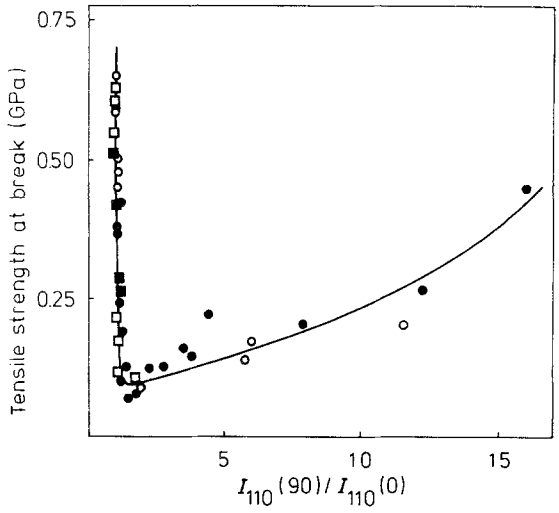

Figure 11 Tensile strength at break of the extracted gel-spun polyethylene fibres as a function of the preferential *c*-axis orientation parallel to the fibre axis for fibres spun with a spinning speed of 100 m min^{-1} and different winding speeds and spinning temperatures: T_{spin} = (●) 170, (○) 215, (■) 230, (□) 250° C.

degree of orientation and/or the higher number of defects formed during gel-spinning. A lower degree of orientation may be due to a higher amount of lamellar material in these fibres, and a lower degree of orientation within the shish-kebabs compared to surface-grown shish-kebabs. It is the higher number of defects in the gel-spun shish-kebabs which largely determines the tensile strength.

4. Summary

The results described in this paper show that gel-spinning of polyethylene only leads to fibres with good ultimate properties if the introduction of defects is prevented. The stresses should be kept below the threshold value for the introduction of defects by avoiding spinline stretching and/or increasing the spinning temperature. If these conditions are not satisfied, shish-kebab structures containing many flaws are obtained. The resulting lamellar/shish-kebab morphology exhibits a mechanical behaviour which is to some degree characteristic of composites. After the final hot-drawing step, fibres are obtained with rather poor properties.

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