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Gel-spun polyethylene fibres

Part 2 *Influence of polymer concentration and molecular weight distribution on morphology and properties*

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In addition to spinning temperature, spinline stretching and spinning speed, the properties of gel-spun polyethylene fibres hot-drawn to the maximum draw ratio also depend on the polymer concentration, molecular weight and molecular weight distribution. Reducing the polymer concentration reduces the number of entanglements, and fibres with better properties are obtained. However, a minimum number of entanglements is necessary to ensure sufficient coherence of the entanglement network and avoid premature breakage of the spinline. Therefore, an optimal concentration exists which is shown to shift to a lower value for polyethylene with a smaller molecular weight distribution. Fibres with a tensile strength exceeding 6 GPa and a modulus of about 160 GPa can be prepared as long as spinline stretching is avoided. A smaller molecular weight distribution enhances the deteriorating effect of spinline stretching. The difference in morphologies for as-spun fibres prepared from different gel compositions and under different spinning conditions also strongly affects the cold-drawing behaviour of the extracted as-spun fibres.

1. Introduction

Gel-spinning of semi-dilute ultra-high molecular weight polyethylene (UHMWPE) solutions is one of the many techniques [1–3] developed to prepare high-strength polyethylene fibres. Spinning from semi-dilute solutions [4–8] results in fibres with improved properties compared to more concentrated systems [9–11] due to a reduction in the number of entanglements. On the other hand, some entanglements are necessary to warrant sufficient coherence of the starting structure to allow drawing without premature breakage [12, 13]. For this reason there is an optimal concentration [14].

Gel-spinning of UHMWPE is performed in the usual way: a solution of 1 to 5 wt % polyethylene in paraffin oil is extruded through a conical die and quenched in air. The paraffin oil is removed from the gel-spun fibres by extraction with *n*-hexane and the fibre is subsequently dried. Then the extracted fibre is hot-drawn to the maximum draw ratio and the lamellar/fibrillar structure is transformed into smooth fibrils. The properties obtained depend strongly on the spinning conditions such as spinning speed, spinning temperature and stretching in the spinline. In Part 1 of this paper [15] the influence of these variables on the ultimate properties was described for a solution of 5 wt % polyethylene. It turned out that poor properties are obtained if preferential *c*-axis orientation parallel to the fibre axis is already present in the extracted fibres, i.e. before the hot-drawing step. This type of orientation increases with increasing draw ratio in the spinline and decreases with increasing spinning temperature. The introduction of defects such as chain scission and tight knots rather than the orientation itself is responsible for this behaviour. Both occur at the same time because they are the result of high spinline stresses [16–21]. Introducing preferential *c*-axis orientation parallel to the fibre axis also has its impact on the mechanical properties of the extracted fibres. A composite-like behaviour due to a combination of lamellae and shish-kebab structures is observed [15]. It is the aim of this paper to take a closer look at the effects of polymer concentration and molecular weight/molecular weight distribution on all these phenomena.

2. Experimental details

Two samples of linear polyethylene Hifax 1900 were used, one with a broad molecular weight distribution ($\bar{M}_w = 4 \times 10^6\,kg\,mol^{-1}$, $\bar{M}_w/\bar{M}_n = 20$; referred to as HifaxA) and one with a smaller molecular weight distribution ($\bar{M}_w = 5.5 \times 10^6\,kg\,mol^{-1}$, $\bar{M}_w/\bar{M}_n \approx 3$; referred to as HifaxB). 1 to 5 wt % polyethylene solutions in paraffin oil were prepared (containing 0.5 wt % DBPC anti-oxidant) at 150° C. These solutions were homogenized for 48 h at this temperature. Upon cooling this solution forms 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 an extrusion rate of 1 or $100\,m\,min^{-1}$ using a conical die with an exit of 1 mm [22]. 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

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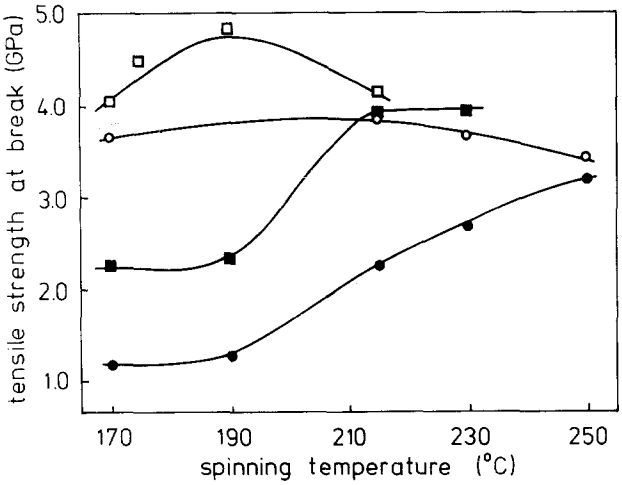


Figure 1 Tensile strength at break obtained after hot-drawing to the maximum draw ratio, as a function of the spinning temperature for gel-spun polyethylene fibres (HifaxA) spun at a spinning speed of 100 m min^{-1} and different polymer concentrations and winding speeds. (○) 5 wt %, V_{wind} = 100 m min^{-1}; (●) 5 wt %, V_{wind} = 500 m min^{-1}; (□) 2 wt %, V_{wind} = 100 m min^{-1}; (■) 2 wt %, V_{wind} = 500 m min^{-1}.

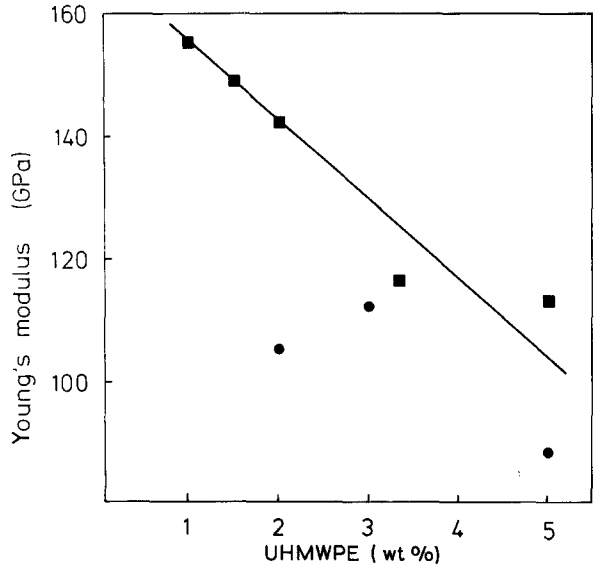


Figure 3 Young's modulus obtained after hot-drawing to the maximum draw ratio, as a function of the polymer concentration for gel-spun polyethylene fibres spun at a temperature of 190° C, a spinning speed of 1 m min^{-1} and a winding speed of 1 m min^{-1}. (●) HifaxA, (■) HifaxB.

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 (λ = 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 micrographs (SEMs) were obtained with an ISI DS-130 scanning electron microscope operated at 25 kV.

3. Results and discussion

Sawatari *et al.* [14] showed that for ultra-high molecular weight polyethylene gel films the optimal concentration, i.e. the concentration at which just enough entanglements connecting the lamellae are present to allow good drawing at 135° C, was about 0.4 wt %. Although they used a polyethylene with a somewhat higher molecular weight (and probably a smaller $\bar{M}_w/\bar{M}_n$ value) than HifaxA (a polyethylene sample with $\bar{M}_w/\bar{M}_n$ = 20, $\bar{M}_w$ = 4 × 10^6 kg mol^{-1}) it suggests that the concentration of 5 wt % used so far can be lowered considerably leading to even better properties. To a certain extent, this is indeed the case, as can be seen from Fig. 1 where the tensile strength at break for fibres obtained from a 2 and a 5 wt % gel and spun under various spinning conditions are compared. However, 2 wt % is already close to the minimum concentration at which gel-spinning is still possible. Spinning at a temperature of 250° C could not even be

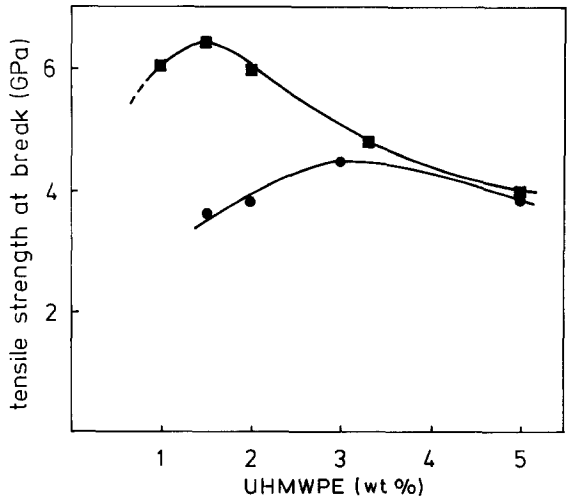


Figure 2 Tensile strength at break obtained after hot-drawing to the maximum draw ratio, as a function of the polymer concentration for gel-spun polyethylene fibres spun at a spinning temperature of 190° C, a spinning speed of 1 m min^{-1} and a winding speed of 1 m min^{-1}. (●) HifaxA, (■) HifaxB.

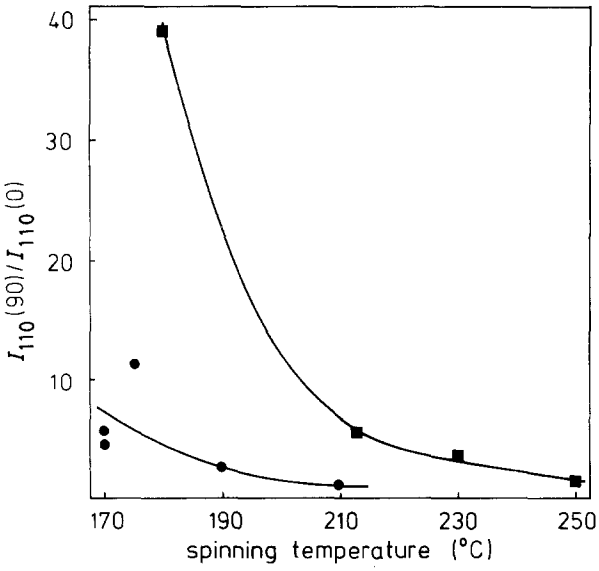


Figure 4 Degree of preferential c-axis orientation parallel to the fibre axis in the extracted gel-spun polyethylene fibres as a function of the spinning temperature for fibres spun with a spinning speed of 100 m min^{-1}, a winding speed of 500 m min^{-1} and a polymer concentration of 2 wt %. (●) HifaxA, (■) HifaxB.

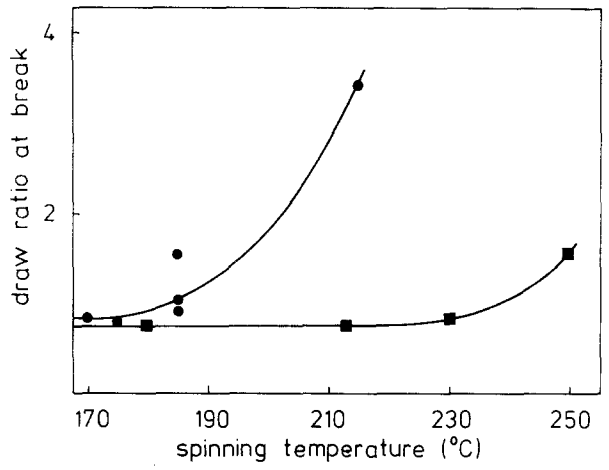


Figure 5 Draw ratio at break of extracted gel-spun polyethylene fibres as a function of the spinning temperature for fibres spun with a spinning speed of 100 m min^{-1}, a winding speed of 500 m min^{-1} and a polymer concentration of 2 wt %. (●) HifaxA, (■) HifaxB.

realized at this concentration. It should be borne in mind that 2 wt % is much higher than the critical concentration for film drawing mentioned before which is probably due to the difference between fibre and film preparation. During gel-spinning of solutions with less than 2 wt % HifaxA the intermolecular entanglement network cannot, in the time scale of the experiment, sustain the spinline stresses, and premature breakage of the spinline occurs. In the case of gel films, stresses are applied during drawing of the solid crystalline structure obtained after evaporation of the solvent.

The curves for the tensile strength at break as a function of the spinning temperature without and with spinline stretching to a draw ratio of 5, merge at a spinning temperature of about 215° C for the 2 wt % concentration compared to 250° C for the 5 wt % concentration. The low tensile strengths obtained at low spinning temperatures for fibres drawn in the spinline to a draw ratio of 5 can, as before, be ascribed to the introduction of defects as a result of high spinline stresses associated with spinline drawing [15]. For 5 wt % solutions the spinline stresses created by spinline drawing will be higher than for the 2 wt % solutions due to a higher entanglement concentration. To keep the spinline stress below the threshold value for defect introduction, faster relaxation times are necessary. This accounts for the higher temperature at which the tensile strength at break becomes independent of spinline drawing, at least for draw ratios up to 5, for the 5 wt % solution.

The coherence of the entanglement network can be improved by using HifaxB, a polyethylene with a much smaller molecular weight distribution ($\bar{M}_w/\bar{M}_n \approx 3$) and a somewhat higher $\bar{M}_w$ (5.5×10^6 kg mol^{-1}). Lower concentrations can be tolerated because of the reduction of the number of chain ends reducing the number of entanglements lost by chain slippage. In Fig. 2 the tensile strength at break as a function of the polymer concentration for HifaxA and HifaxB are compared for fibres spun at a spinning temperature of 190° C with a spinning speed of 1 m min^{-1} and without spinline stretching. Under these conditions the optimal concentration for HifaxA is seen to be about 3 wt % whereas for HifaxB it is reduced to about 1.5 wt %. Moreover the tensile strength at break at these optimal concentrations is considerably higher for HifaxB than for HifaxA. Fig. 3 shows similar results for the moduli.

The degree of preferential c-axis orientation parallel to the fibre axis introduced during spinline stretching depends also on the molecular weight distribution. The ratio of the intensity of the 1 1 0 reflection at the equator (azimuthal scattering angle $\Omega = 90°$) and at the meridian ($\Omega = 0°$), $I_{110}(90)/I_{110}(0)$, is, for reasons discussed before [15], used as a semi-quantitative measure for this type of orientation. Fig. 4 presents this ratio for 2 wt % solutions of HifaxA and HifaxB as a function of the spinning temperature for an extrusion rate of 100 m min^{-1} and a winding speed of 500 m min^{-1}. As expected, the degree of preferential c-axis orientation parallel to the fibre axis decreases, with increasing spinning temperature. However, the degree of preferential c-axis orientation parallel to the fibre axis is at the same temperature considerably higher for HifaxB than for HifaxA. This indicates that the stress in the spinline during gel-spinning is under similar conditions higher for HifaxB than for HifaxA. The difference between HifaxA and HifaxB is also reflected in the stress–strain behaviour at room temperature of the extracted fibres. Fig. 5 shows the draw ratio at break as a function of the spinning temperature. In all cases the spinning speed is 100 m min^{-1}, the winding speed is 500 m min^{-1} and the polymer concentration is 2 wt %. The preferential c-axis orientation parallel to the fibre axis corresponds to a shish-kebab structure and shows a much lower strain at break (10 to 30%) than the lamellar structures. In general both structures are present and a composite-like behaviour is observed [15]. Fig. 5 shows that the strain at break for HifaxA increases with spinning temperature whereas the strain at break for HifaxB hardly increases as long as the spinning temperature remains below 230° C. Above this temperature the strain at break is also an increasing function of temperature. This implies that for HifaxB the spinline stresses are high enough to produce sufficient shish-kebab structure to determine the strain at break for spinning temperatures below 230° C. Above this temperature the contribution of the lamellar structure becomes visible. For HifaxA, the degree of shish-kebab structure is, under the same conditions, much lower.

The optimal concentration for HifaxB for a spinning temperature of 190° C was determined to be 1.5 wt % (Fig. 2). From now on we will focus our attention on the properties of HifaxB fibres spun at this concentration. In Fig. 6 the tensile strength at break of HifaxB fibres hot-drawn to the maximum draw ratio is given as a function of the spinning temperature for different spinning speeds and winding speeds. The fibres extruded with an extrusion rate of 1 m min^{-1} are about 0.5 to 1.0 GPa stronger than fibres extruded with an extrusion rate of 100 m min^{-1}, as long as no stretching in the spinline takes place. The tensile strength of these fibres is nearly independent of

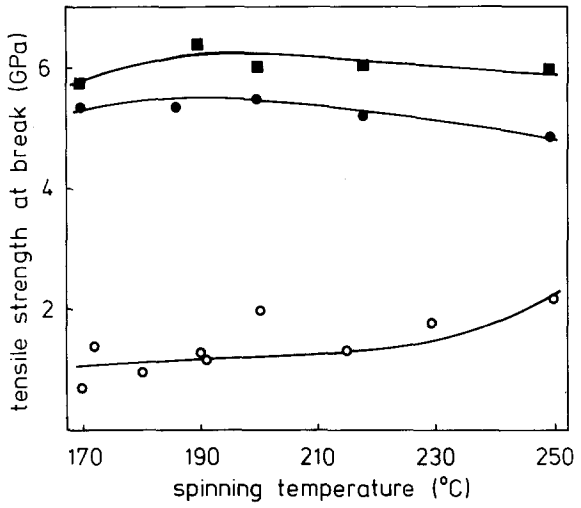


Figure 6 Tensile strength at break obtained after hot-drawing as a function of the spinning temperature for gel-spun polyethylene fibres (HifaxB) spun at a polymer concentration of 1.5 wt % and different spinning speeds and winding speeds. (■) V_{spin} = 1 m min^{-1}, V_{wind} = 1 m min^{-1}; (●) V_{spin} = 100 m min^{-1}, V_{wind} = 100 m min^{-1}; (○) V_{spin} = 100 m min^{-1}, V_{wind} = 500 m min^{-1}.

spinning temperature in the temperature range 170 to 250° C. They contain, in agreement with this observation, no preferential *c*-axis orientation parallel to the fibre axis ($I_{110}(90)/I_{110}(0)$ = 1). The tensile strengths at break of fibres spun with an extrusion rate of 100 m min^{-1} and a winding speed of 500 m min^{-1} are very low. As in the case of HifaxA this is due to high spinline stresses leading to the introduction of defects. At spinning temperatures above 230° C the tensile strength starts to increase with increasing spinning temperature. On the basis of the results for HifaxA we expect the curves of the tensile strength at break for fibres extruded with an extrusion rate of 100 m min^{-1} and winding speeds of 100 and 500 m min^{-1} to merge at some temperature above 250° C. The degree of preferential *c*-axis orientation parallel to the fibre axis for fibres extruded with an

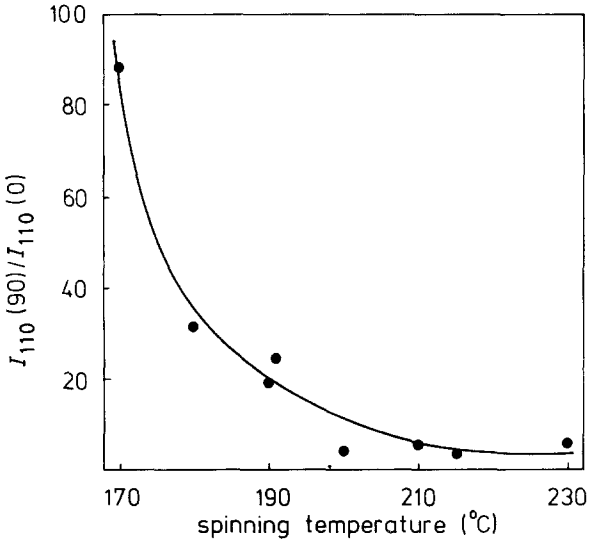


Figure 7 Degree of preferential *c*-axis orientation parallel to the fibre axis in the extracted gel-spun polyethylene fibres (HifaxB) as a function of the spinning temperature for fibres spun at a spinning speed of 100 m min^{-1}, a winding speed of 500 m min^{-1} and a polymer concentration of 1.5 wt %.

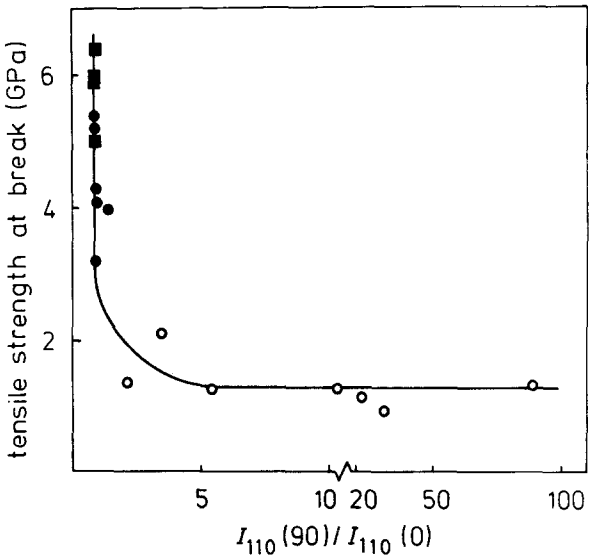
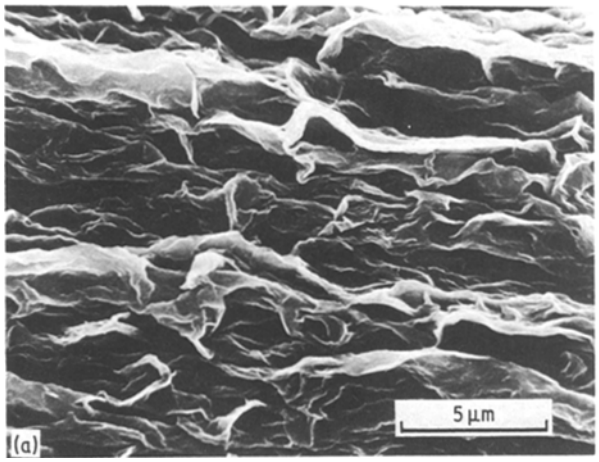
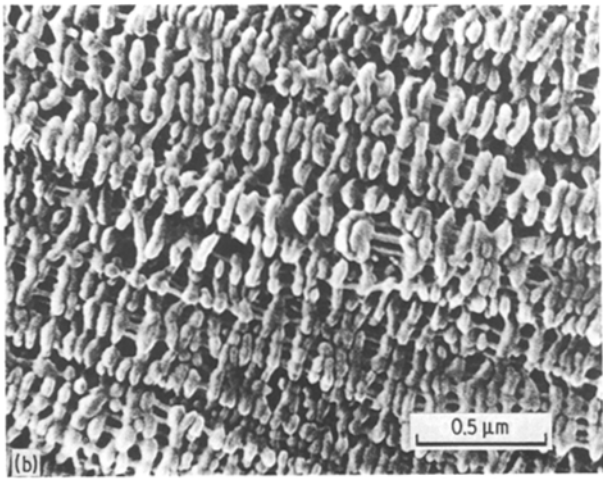


Figure 8 Tensile strength at break obtained after hot-drawing to the maximum draw ratio as a function of the degree of preferential *c*-axis orientation parallel to the fibre axis for gel-spun polyethylene fibres (HifaxB) spun at a polymer concentration of 1.5 wt % and different spinning speeds, winding speeds and spinning temperatures. (■) V_{spin} = 1 m min^{-1}, V_{wind} = 1 m min^{-1}; (●) V_{spin} = 100 m min^{-1}, V_{wind} = 100 m min^{-1}; (○) V_{spin} = 100 m min^{-1}, V_{wind} = 500 m min^{-1}.

extrusion rate of 100 m min^{-1} and a winding speed of 500 m min^{-1} is presented in Fig. 7. It decreases with increasing spinning temperature, as in the case of HifaxA. Combining the results of Figs 6 and 7 leads to Fig. 8 where the tensile strength at break is presented as a function of the degree of preferential *c*-axis orientation parallel to the fibre axis.

As observed before for HifaxA [15], the properties obtained after hot-drawing strongly depend on the morphology of the extracted fibres. There are, however, a number of observations which are typical for the lower polymer concentrations considered here. Scanning electron microscopy gives valuable information about the structure of the fibre but it should be realized that in the case of skin/core structures [23, 24], the structure observed with this surface-sensitive technique is not representative for the whole fibre. Moreover, fibres often contain many different surface structures. For example, in our case the fibres are kept constrained on a bobbin during extraction. The structure of that part of the surface which during extraction is in contact with the bobbin differs from the structure of the other parts. In Fig. 9 characteristic SEMs for HifaxB spun under different spinning conditions are presented. Fibres extruded with an extrusion rate of 1 m min^{-1} without stretching in the spinline show a lamellar structure (Fig. 9a), whereas fibres extruded with an extrusion rate of 100 m min^{-1} drawn in the spinline to a draw ratio 5 show a shish-kebab structure (Fig. 9b) very similar to the results for HifaxA [15, 25]. On the other hand, fibres extruded with a spinning speed of 100 m min^{-1} without spinline drawing show a skin/core type structure consisting of a shish-kebab-like skin and a dense lamellar core (Fig. 9c). The thickness of the skin tends to decrease with increasing spinning temperature.





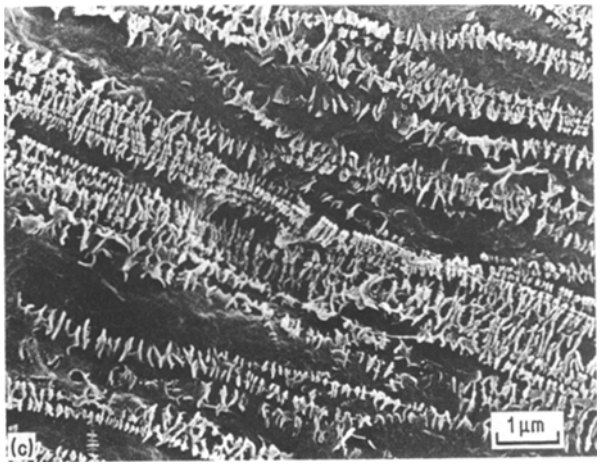
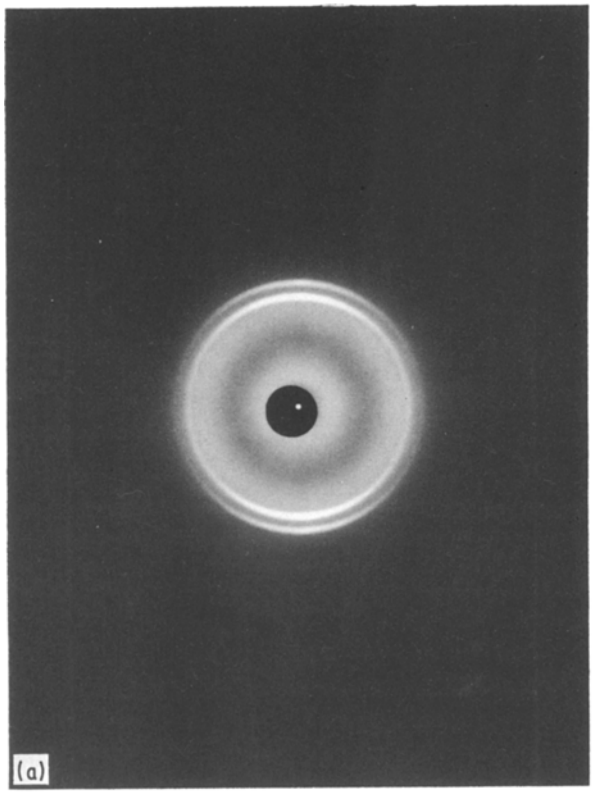


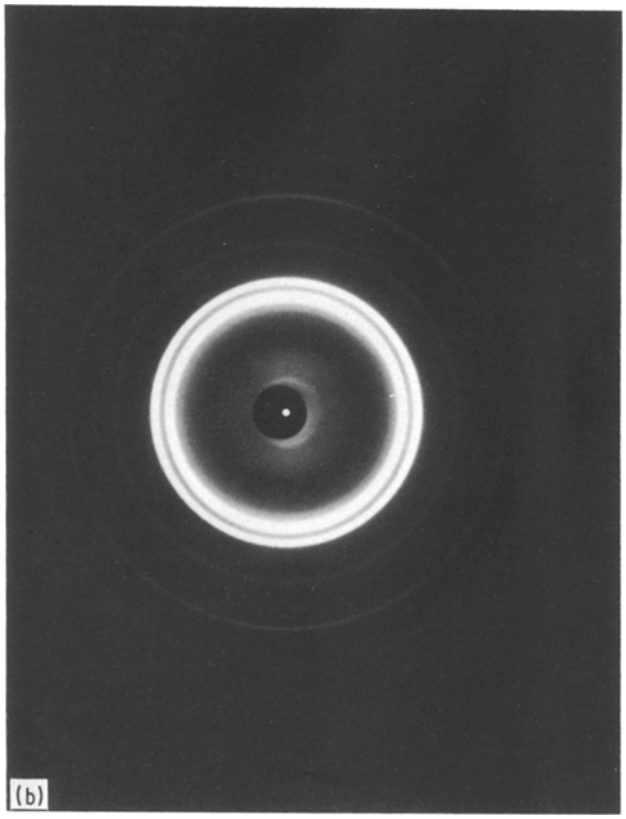
Figure 9 Characteristic scanning electron micrographs of extracted gel-spun polyethylene fibres (HifaxB) spun at a polymer concentration of 1.5 wt % and different spinning speeds and winding speeds. (a) $V_{spin} = 1\,m\,min^{-1}$, $V_{wind} = 1\,m\,min^{-1}$, $T_{spin} = 200°C$; (b) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 500\,m\,min^{-1}$, $T_{spin} = 233°C$; (c) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 100\,m\,min^{-1}$, $T_{spin} = 250°C$.

Another peculiar feature of the fibres obtained by a spinning speed and winding speed of $100\,m\,min^{-1}$ is their ribbon-like shape, probably created during the taking up of the still hot, partially liquid fibre on the bobbin. This phenomenon is only observed if the polymer concentration is low enough. It does not occur for the 5 wt % solutions of HifaxA discussed in Part 1. Fig. 10 shows the WAXS patterns of these ribbons obtained for three different directions of the incident X-ray beam. Fig. 10a, showing the X-ray pattern obtained with the incident X-ray beam along the fibre axis, demonstrates that the structure is not uniaxially symmetric around the fibre axis. The *c*-axis turns out to have a preferential orientation perpendicular to the large flat surface of the ribbon. The occurrence of this type of orientation, observed before for mats of single crystals [26] and thin gel films [27–29], is confirmed by two equatorial small-angle X-ray scattering (SAXS) measurements taken edge-on and flat-on. In the first case a maximum is observed due to a regular packing of lamellae, whereas for the flat-on measurement the intensity decreases continuously with increasing scattering angle. The dense packing of lamellae in these ribbons leads to a less porous structure than the lamellar structure with a more or less random *c*-axis distribution around the fibre axis of fibres extruded with an extrusion rate of $1\,m\,min^{-1}$. Moreover, the flat-on WAXS picture (Fig. 10b), showing a highest intensity for the 200 reflection at the equator and a highest intensity for the 020 reflection at the meridian, and the edge-on WAXS picture (Fig. 10c) indicate that there is a slight tendency for the *b*-axis to align along the fibre axis.

The cold-drawing behaviour of polyethylene fibres strongly depends on the type of preparation process (e.g. melt-spinning or fibres prepared from semi-dilute polymer solutions) and the process variables, as extensively described in the literature [27, 29, 30–35]. During cold-drawing the lamellar structures are transformed into fibrillar structures by rotation/translation of (parts of) lamellae and/or by local melting of the lamellae due to local high stress concentrations. For the ribbon-like fibres, two different types of stress-strain curves are observed (Fig. 11). Some curves show sharp yield points followed by strain hardening, which is the result of the deformation of the newly created fibrillar structure. This behaviour is mainly observed for fibres spun at relatively high spinning temperatures (Fig. 11c), containing only a very thin skin with a shish-kebab-like structure. In other cases this sharp yield point is absent but rapid strain hardening takes place (Fig. 11b). This type of behaviour is observed often for fibres spun at relatively low spinning temperatures. Fibres giving rise to sharp yield points show many bands of stress whitening perpendicular to the fibre axis across the whole cross-section of the fibre. In these crazes lamellar material is transformed into fibrils. This type of deformation was observed before for ribbons of HifaxA prepared from a 2 wt % solution [36]. The sharp neck-type of deformation running across the whole fibre cross-section is responsible for the sharp yield point observed during cold-drawing. Fibres containing a thicker skin of shish-kebab-like structure show no clear yield point. Obviously this type of skin structure opposes sharp neck formation.

The stress–strain curves of these ribbons differ considerably from those for fibres extruded and wound-up at a rate of $1\,m\,min^{-1}$ (Fig. 11d). No sharp yield point is observed and the yield stress is lower. This can be ascribed to the more porous character of the





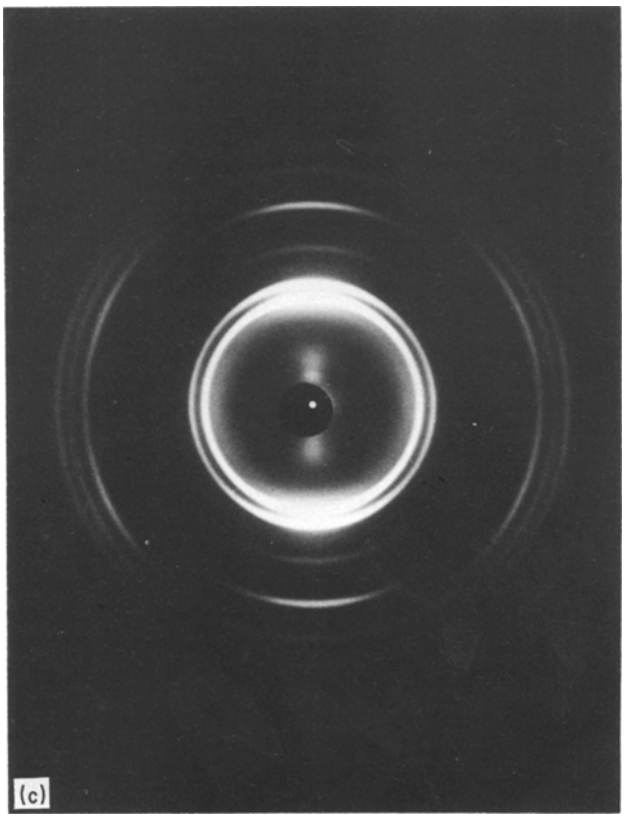


Figure 10 Wide-angle X-ray diffraction patterns of a ribbon-shaped polyethylene fibre (HifaxB) spun at a polymer concentration of 1.5 wt % at a spinning temperature of 215° C with a spinning speed and winding speed of 100 m min^{-1}. (a) Incident X-ray beam along the fibre axis, flat fibre surface vertical; (b) incident X-ray beam flat-on, fibre axis vertical; (c) incident X-ray beam edge-on, fibre axis vertical.

lamellar structure of these more or less round fibres. Lamellae are to some degree free to move with respect to each other. In the case of ribbons the dense packing of lamellae prevents them moving separately. Moreover, for the fibres prepared at the low extrusion rate, a much higher strain at break (up to about 2500%) is observed. The more homogeneous deformation for this fibre results in a more homogeneous stress distribution compared to the ribbons where locally high stress concentrations lead to breakage at relatively low strain. On the other hand, during hot-drawing similar maximum draw ratios can be obtained for fibres extruded with an extrusion rate of 1 and 100 m min^{-1} and not subjected to stretching in the spinline. The favourable effect of the original porosity is lost for high drawing temperatures. During hot-drawing the ribbon shape of the fibres extruded at a rate of 100 m min^{-1} is preserved. They are very sensitive to fibrillation (Fig. 12), which may be the result of poor coherence between adjacent fibrils due to less connectivity between the lamellae in the original structure of fibres prepared from dilute solutions. The fibrillation is more pronounced for the ribbon-shaped fibres than for the round fibres.

The cold-drawing behaviour of extracted fibres drawn in the spinline to a ratio of 5 is totally different. These fibres contain a considerable degree of shish-kebab structures resulting in a small strain at break of about 30% (Fig. 11a).

Figs 13 and 14 show the strain at break and tensile strength at break of extracted HifaxB fibres spun under different spinning conditions as a function of the preferential *c*-axis orientation parallel to the fibre axis. Qualitatively the results are very similar to those obtained for 5 wt % HifaxA. The observations can, as before, be described by a composite-like model. The shish-kebab structures in the fibres are responsible for the observed degree of preferential *c*-axis orientation parallel to the fibre axis. For fibres containing lamellae

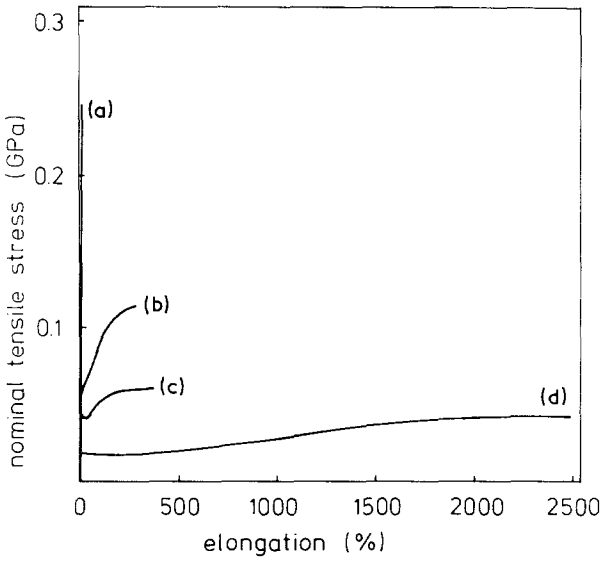


Figure 11 Stress–strain curves of extracted gel-spun polyethylene fibres (HifaxB, 1.5 wt %) spun under different spinning conditions. (a) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 500\,m\,min^{-1}$, $T_{spin} = 205°C$; (b) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 100\,m\,min^{-1}$, $T_{spin} = 180°C$; (c) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 100\,m\,min^{-1}$, $T_{spin} = 219°C$; (d) $V_{spin} = 1\,m\,min^{-1}$, $V_{wind} = 1\,m\,min^{-1}$, $T_{spin} = 186°C$.

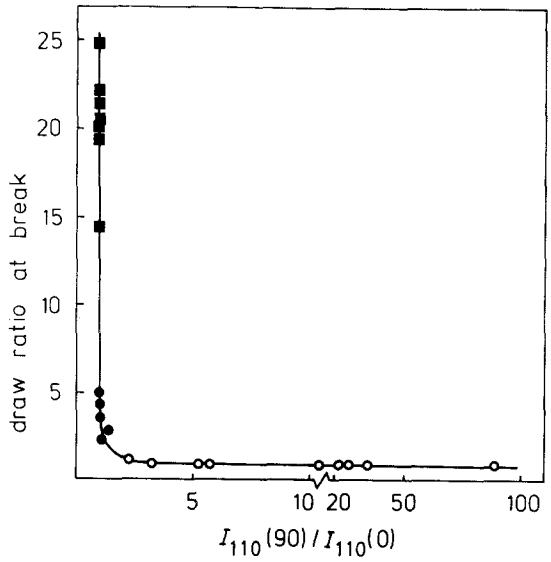


Figure 13 Draw ratio at break of the extracted polyethylene fibres (HifaxB, 1.5 wt %) as a function of the preferential *c*-axis orientation parallel to the fibre axis for fibres spun with different spinning speeds, winding speeds and spinning temperatures. (■) $V_{spin} = 1\,m\,min^{-1}$, $V_{wind} = 1\,m\,min^{-1}$; (●) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 100\,m\,min^{-1}$; (○) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 500\,m\,min^{-1}$.

as well as shish-kebab structures, the stiff shish-kebab structures determine the stress and strain at break. Once the shish-kebab structure breaks the lamellae cannot sustain the high stresses. Only fibres containing no or very little shish-kebab structures ($I_{110}(90)/I_{110}(0) \approx 1$) can be cold-drawn to high draw ratios during which the lamellar structure is transformed into fibrils. This fibrillar structure obtained by cold-drawing to high draw ratios is responsible for the relatively high tensile strengths at break observed (Fig. 14). Obviously, the tensile strength at break will start to increase again with an increasing amount of shish-kebab structure and/or increasing orientation within a shish-kebab (increasing degree of preferential *c*-axis orientation parallel to the fibre axis in the original fibre). The minimum in the tensile strength at break against $I_{110}(90)/I_{110}(0)$ curve (Fig. 14) is a consequence of this composite like-behaviour.

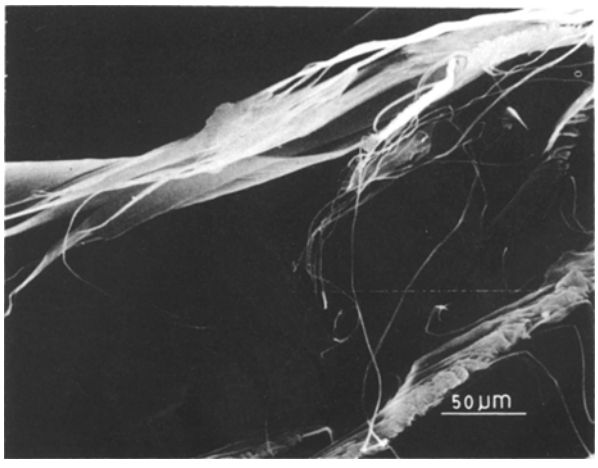


Figure 12 Scanning electron micrograph of a ribbon-shaped polyethylene fibre (HifaxB, 1.5 wt %) hot-drawn to the maximum draw ratio and afterwards used in a tensile test experiment showing the fibrillar character of these hot-drawn fibres. $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 100\,m\,min^{-1}$, $T_{spin} = 229°C$.

4. Conclusion

We have shown that various properties of gel-spun polyethylene fibres depend strongly on the molecular weight distribution. At a spinning temperature of 190° C the optimal concentration of HifaxB ($\bar{M}_w/\bar{M}_n \approx 3$, $\bar{M}_w = 5.5 \times 10^6\,kg\,mol^{-1}$) turned out to be 1.5 wt % compared to 3.0 wt % for HifaxA ($\bar{M}_w/\bar{M}_n = 20$, $\bar{M}_w = 4 \times 10^6\,kg\,mol^{-1}$). Although HifaxB also has a somewhat higher molecular weight, the main difference is its much smaller molecular weight distribution. Under favourable conditions, which as before implies avoiding spinline stretching, the tensile strength at break is 6.4 GPa and the modulus 155 GPa.

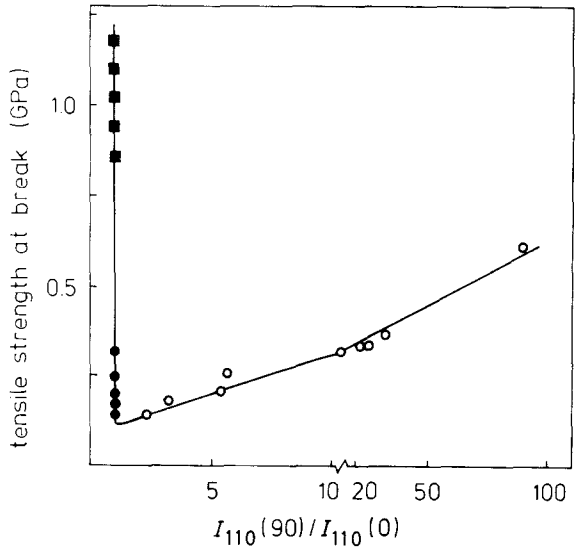


Figure 14 Tensile strength at break of the extracted gel-spun polyethylene fibres (HifaxB, 1.5 wt %) as a function of the preferential *c*-axis orientation parallel to the fibre axis for fibres spun with different spinning speeds, winding speeds and spinning temperatures. (■) $V_{spin} = 1\,m\,min^{-1}$, $V_{wind} = 1\,m\,min^{-1}$; (●) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 100\,m\,min^{-1}$; (○) $V_{spin} = 100\,m\,min^{-1}$, $V_{wind} = 500\,m\,min^{-1}$.

Another interesting observation concerns the ribbon-like shape of fibres spun from 1.5 wt % solution at a spinning rate and a winding speed of 100 m min^{-1}. In these as-spun fibres a preferential *c*-axis orientation perpendicular to the flat surface is found. They consist of a skin/core structure with a lamellar core and a shish-kebab containing skin. Because of this structure the cold-drawing behaviour is characterized by yielding rapidly followed by strain hardening.

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