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The influence of the extraction process and spinning conditions on morphology and ultimate properties of gel-spun polyethylene fibres

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The morphology of gel-spun polyethylene fibres prior to hot-drawing, depends on the spinning conditions and the extraction process. Paraffin oil containing fibres spun at relatively low spin temperatures and high take-up speeds show a *c*-axis orientation parallel to the fibre axis due to shish-kebab formation in the spinline. The extraction of the paraffin oil is accompanied by stresses leading to morphological changes. For fibres spun at low take-up speeds and/or high spin temperatures this leads to a craze-like disturbance and a preferential *c*-axis orientation perpendicular to the fibre axis. Fibres with this type of orientation exhibit an equatorial SAXS maximum corresponding to a periodicity of 12 nm ascribed to regular packing of 12 nm thick lamella oriented with the *c*-axis perpendicular to the fibre axis. The formation of extended chain crystals in the case of low spin temperatures and high take-up speeds is accompanied by the introduction of flaws, which have a deteriorating effect on the ultimate properties of the fibres.

(Keywords: polyethylene; gel-spinning; extraction process; morphology; X-ray scattering; crazing)

INTRODUCTION

A recently introduced process of preparing ultra-high strength polyethylene fibres consists of gel-spinning from semi-dilute solutions followed by hot-drawing. Compared with the use of more concentrated solutions this amounts to a considerable reduction in the number of entanglements and fibres with a tensile strength level of 5 GPa and Young's moduli up to 200 GPa can easily be produced¹⁻³. More recently, fibres with a still higher tensile strength of about 7 GPa were obtained⁴⁻⁶. In general, the procedure followed in our laboratory consists of extruding a solution of polyethylene in paraffin oil followed by quenching in air and extracting the paraffin oil using *n*-hexane. During the extraction process longitudinal shrinkage is prevented by keeping the fibre taut on a bobbin. After the evaporation of hexane hot-drawing is performed which transforms the porous fibrillar structure into smooth fibrils.

In a previous paper⁷ we discussed high-speed gel-spinning at temperatures around 200°C. It was shown that 5 wt% solutions of ultra-high molecular weight polyethylene (UHMWPE) in paraffin oil could be extruded through a conical die at a rate of 100 m/min without the appearance of filament irregularities due to elastic solution fracture. Spinning at 170°C the maximum take-up speed, i.e. the take-up speed just before the spinline breaks, was about 1000 m/min. After spinning, the gel fibres were extracted with hexane; dried and subsequently hot drawn at 148°C to the maximum draw ratio. The tensile strength-at-break of these fibres was found to be a function of the take-up speed, decreasing from 3.5 GPa for a take-up speed of 100 m/min (free extrusion) to 1.0 GPa for a take-up speed of 1000 m/min.

However, fibres spun at 250°C had a tensile strength of 3.5 GPa for take-up speeds ranging from 100 m/min to 1000 m/min.

It is the main objective of this paper to show that the tensile strength-at-break of fibres obtained by hot-drawing to the maximum draw ratio, is closely related to the morphology of the extracted gel fibres. This morphology depends on the spinning conditions and the extraction process in a way which will be discussed in some detail. We will start with the observed stress/time behaviour in fibres during the evaporation of the extraction agent, in most cases hexane but, for reasons which will become clear, decalin also. In the case of hexane these stresses lead to a craze-like disturbance of the lamellar structure. Frequently, a preferential *c*-axis orientation perpendicular to the fibre axis is found, especially for fibres spun at low take-up speeds (100 m/min) and/or high spin temperatures (250°C). This type of orientation is characterized by an equatorial SAXS maximum corresponding to a periodicity of 12 nm. Paraffin oil containing gel fibres spun at relatively low temperatures (170°C) and high take-up speeds show a clear *c*-axis orientation parallel to the fibre axis due to shish-kebab formation in the spinline. The presence of this type of orientation in the gel fibre is also an indication that certain flaws are present which will have a deteriorating effect on the ultimate tensile strength of the fibres.

EXPERIMENTAL

The starting polymer for the preparation of the filaments was Hifax 1900 ($M_w = 4 \times 10^6$ kg mol⁻¹). 5 wt% of this

polyethylene was dissolved in paraffin oil, containing 0.5 wt% DBPC antioxidant, at 150°C and 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°C to 250°C with a spinning speed of 100 m/min. A conical die with an exit diameter of 1 mm was used. Filaments containing decalin were obtained by prolonged immersion at room temperature of the paraffin oil containing gel fibres in decalin.

For the X-ray diffraction experiments CuK α radiation ($\lambda = 0.154$ nm) was used, produced by a Philips X-ray generator connected to a closed cooling circuit and operated at 45 kV and 45 mA. The equatorial SAXS experiments (fibre aligned parallel to the entrance slit) were carried out with the aid of a Kratky camera equipped with a proportional counter and an electronic step scanner. An entrance slit of 80 μ m was used. Monochromatization was achieved by using a Ni-filter and pulse-height discrimination. WAXS measurements were carried out with the aid of a Statton camera. Azimuthal scattering intensities were obtained with a densitometer.

The stress/time behaviour during drying of fibres extracted at room temperature with hexane and decalin were carried out at room temperature with an Instron 4301 Tensile Tester.

SEM micrographs were obtained with an ISI DS-130 scanning electron microscope operated at 25 kV.

RESULTS AND DISCUSSION

Free extrusion

To demonstrate the stress development in fibres during the evaporation process, hexane-containing fibres obtained by free extrusion and subsequent extraction were quickly put into a tensile tester. A characteristic result of a stress/time curve is given in *Figure 1*. A rapid stress build-up occurs leading to local high stress concentrations. The values of the force F given are only approximate because inevitably some hexane evaporates

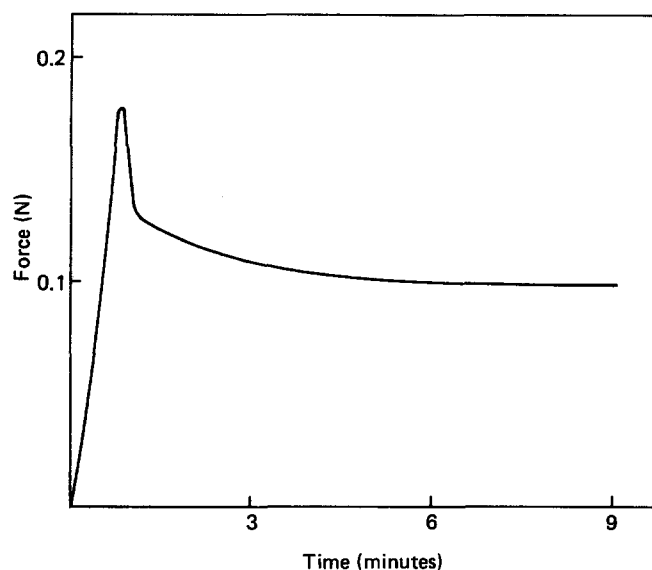


Figure 1 Stress/time curve of a hexane-extracted polyethylene fibre during drying. The fibre was spun at $T_{\text{spin}} = 170^\circ\text{C}$ and a speed of 100 m/min. The take-up speed was 100 m/min. The fibre diameter before drying was approximately 1 mm

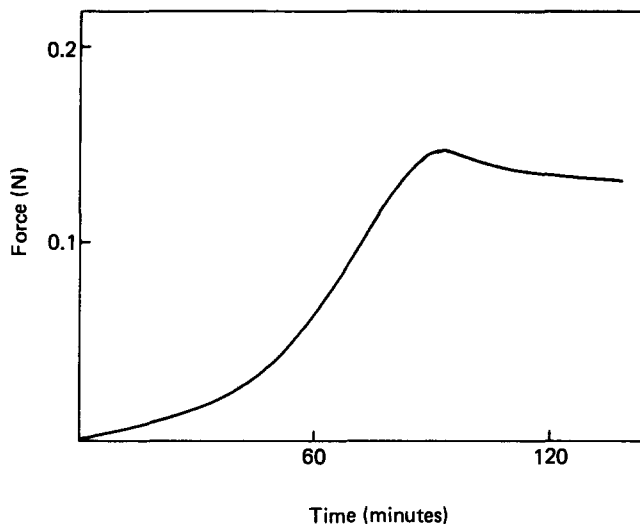


Figure 2 Stress/time curve of a decalin-extracted polyethylene fibre during drying. The fibre was spun at $T_{\text{spin}} = 170^\circ\text{C}$ and a speed of 100 m/min. The take-up speed was 100 m/min. The fibre diameter before drying was approximately 1 mm

before the measurement starts. A similar procedure was performed using decalin as the extraction agent. *Figure 2* shows an example of the stress/time development with this less volatile solvent and, as expected, it takes much longer to reach the maximum stress and the stress relaxation is also much slower.

The stresses developing in the extraction process are due to elastic forces of the amorphous regions and to surface tensions accompanying the creation of new air/polyethylene interfaces instead of solvent/polyethylene interfaces⁸. Especially in the case of hexane these stresses lead to morphological changes. SEM micrographs, presented in *Figures 3a* and *3b*, show a porous fibrillar craze-like structure in the case of extraction with hexane and a more dense lamellar structure in the case of decalin. The evaporation of hexane leads to local stress concentrations, high enough to produce fibril formation probably involving principles underlying crazing⁹⁻¹⁵, and subsequent rapid stress relaxation. In the case of decalin the stress build-up is much slower and the local stress concentrations are too low to introduce substantial fibril formation.

Besides the distortion of the lamellar structure due to crazing the evaporation process also gives rise to a change in crystal orientation. *Figure 4a* shows a WAXS picture of a paraffin oil-containing fibre showing the nearly random orientation of the polyethylene crystallites. After constraint extraction with hexane and drying, the intensities of the 110, 200 and 020 reflections are somewhat higher around the meridian (*Figure 4b*). The evaporation process introduces a preferential c -axis orientation perpendicular to the fibre axis. The same phenomenon is observed if decalin is used instead of hexane. This type of orientation is not found if longitudinal shrinkage is allowed during the evaporation.

The absence of a clear preferential c -axis orientation parallel to the fibre axis after the evaporation of hexane suggests that the extent of crazing is rather small. To investigate this, the integral observable intensity or invariant K of the small-angle X-ray scattering was determined:

$$K = \int I(\vec{b}) dv_b = I_c V_c \bar{\eta}^2 \quad (1)$$



Figure 3 Scanning electron micrographs of a polyethylene fibre extracted with different solvents. The fibre was spun at $T_{\text{spin}} = 170^\circ\text{C}$ and a speed of 100 m/min. The take-up speed was 100 m/min. (a) fibre extracted with hexane; (b) fibre extracted with decalin

where $I(\vec{b})$ is the scattered intensity for a scattering vector \vec{b} , V_x the irradiated volume, I_e the intensity scattered by one electron and $\bar{\eta}^2$ the scattering power or mean square electron density fluctuation. Assuming a two-phase system of polyethylene and voids, the invariant is related to the volume fraction of voids ϕ by

$$\bar{\eta}^2 = \phi(1 - \phi)\rho^2 \quad (2)$$

where ρ is the electron density of the polyethylene phase. In the case of hexane ϕ is indeed found to be rather small, of the order of 5%. In the case of decalin ϕ is too small to be determined.

Equatorial SAXS curves of decalin containing fibres which were kept at a constant strain show the development of an equatorial maximum in the course of time, due to the evaporation of decalin (Figure 5). It starts with a shoulder at low angles and finally ends at a position corresponding to a long period of approximately 12 nm. The long period is caused by a packing of neighbouring lamella oriented with the c -axis perpendicular to the fibre axis. During the evaporation of decalin a closer packing of the lamella is obtained resulting in a decrease of the long period. This phenomenon resembles the observations of Keller and O'Conner¹⁶. They crystallized polyethylene from a dilute xylene solution and showed that plate-like crystals were packed together and formed a compact film by slow filtration. WAXS measurements

showed that the c -axis was oriented perpendicular to the film surface due to a horizontal crystal sedimentation. SAXS patterns of these films revealed a periodicity of 12 nm (4 orders) which was ascribed to this regular stacking of 12 nm thick platelets along the c -axis. Similar WAXS and SAXS patterns were found by Smith *et al.*¹⁷ and Matsuo *et al.*^{18,19} for samples obtained by drying decalin containing gel films. In our case only a first order maximum and a weak second order maximum (Figures 6b and c) are found. This is in agreement with observation of Matsuo *et al.*¹⁹ that the maxima become more diffuse for increasing polyethylene concentration.

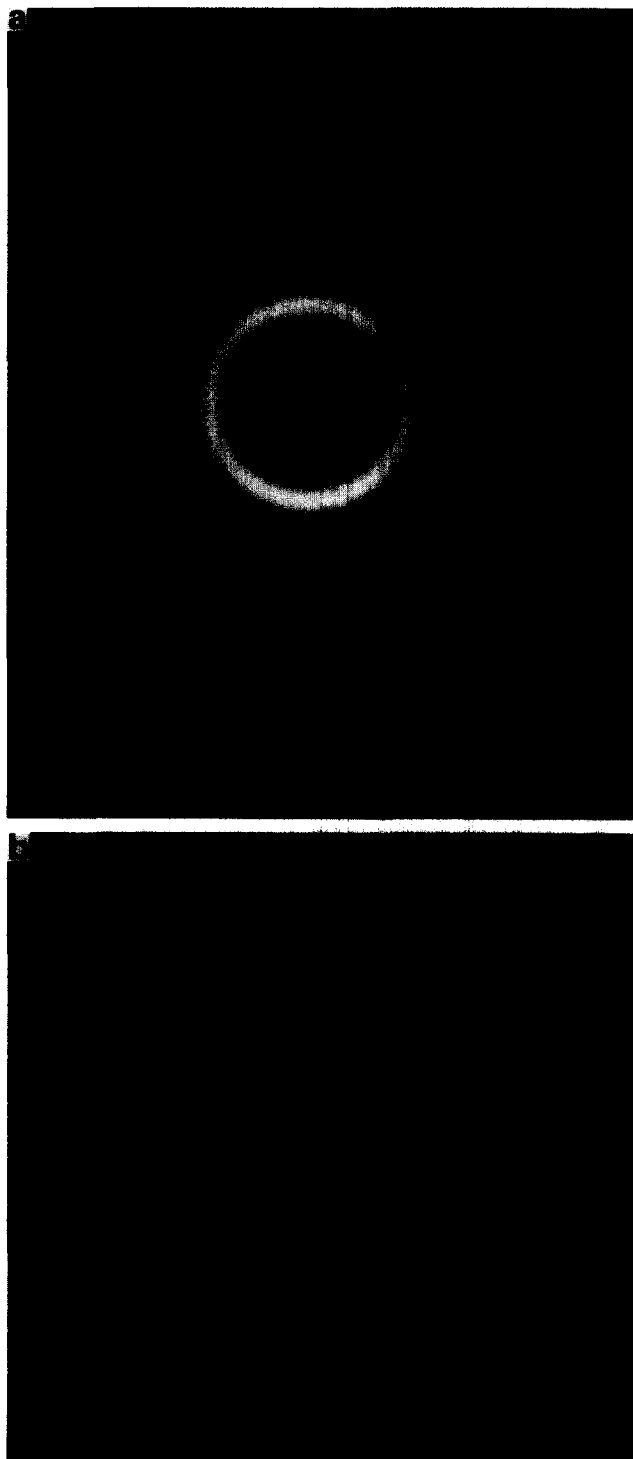


Figure 4 Wide-angle X-ray diffraction patterns of a polyethylene fibre spun at $T_{\text{spin}} = 170^\circ\text{C}$ and a speed of 100 m/min. The take-up speed was 100 m/min. (a) paraffin oil-containing fibre; (b) same fibre after constraint extraction with hexane

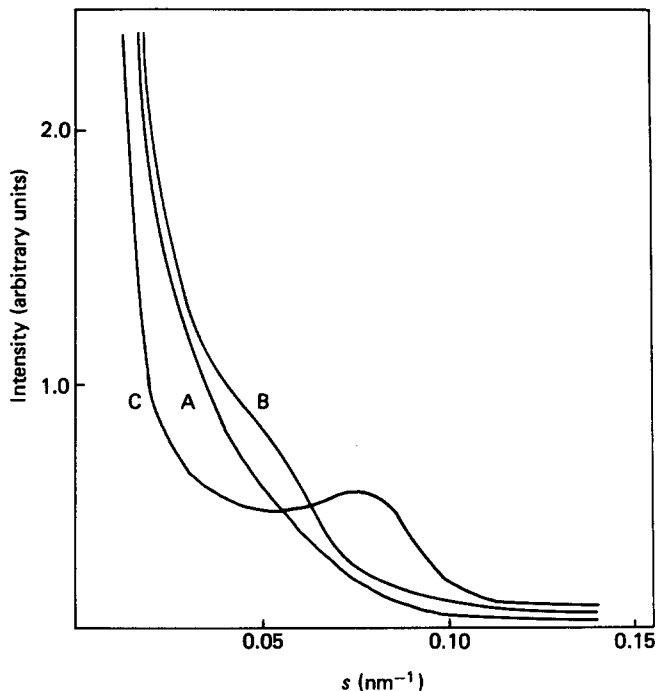


Figure 5 Development of an equatorial SAXS maximum for a decalin-containing polyethylene fibre kept at constant strain during the evaporation of the solvent. The fibre was spun at 170°C with a speed of 100 m/min and a take-up speed of 100 m/min. (A) $t = 40$ min; (B) $t = 80$ min; (C) $t = 120$ min. Blank subtracted

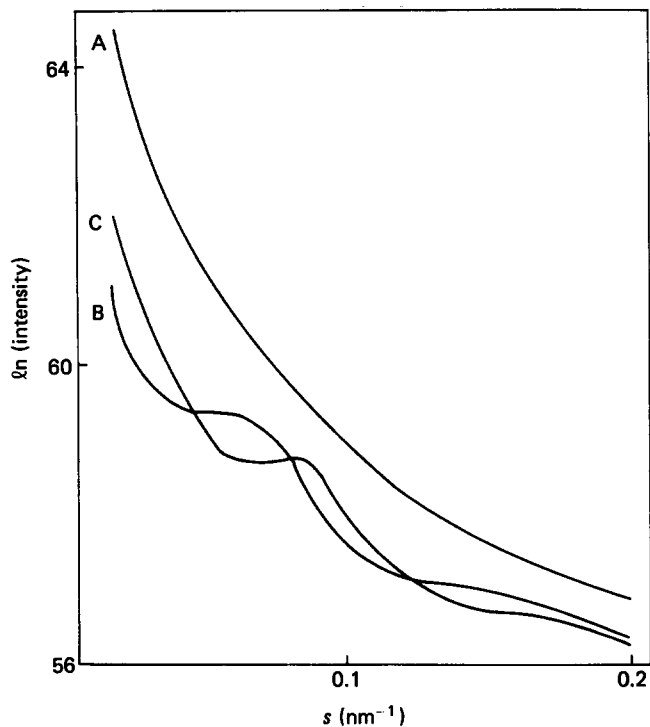


Figure 6 Equatorial SAXS curves of a polyethylene fibre spun at $T_{\text{spin}} = 170^\circ\text{C}$ with a speed of 100 m/min and a take-up speed of 100 m/min. (A) fibre extracted with hexane; (B) same fibre after filling the voids with paraffin oil; (C) fibre extracted with decalin. Blank subtracted

In contrast to decalin-extracted fibres, hexane-extracted fibres showed no equatorial SAXS maximum, in spite of identical WAXS patterns. This is due to the porous structure which, as shown in *Figure 6*, leads to a much higher SAXS intensity. The scattering due to the void/fibril structure dominates the scattering curve making the detection of a possible equatorial SAXS

maximum impossible. The void/fibril scattering can be reduced by filling the voids with the non-volatile paraffin oil. This again leads to a shoulder/maximum in the equatorial SAXS curve (*Figure 6b*). Because the fibre is somewhat swollen, the maximum occurs at a smaller angle. Hence, as far as the orientation of the crystallites is concerned, there is no essential difference between extracting the paraffin oil with hexane or decalin.

Influence of spinning conditions

To investigate the influence of the spinning conditions on the morphology of the fibres, the temperature and take-up speed were varied systematically. WAXS was used to study the crystal orientation of paraffin oil-containing gel fibres. In general higher take-up speeds result in preferential c -axis orientation parallel to the fibre axis due to stretching in the spinline (see *Figure 7* for example). For higher spin temperatures this kind of orientation levels off again because of the higher mobility of the polymer chains. This is clearly demonstrated by the diffractometer analysis of the 110 reflection as a function of the azimuthal scattering angle Ω (*Figure 8*). Preferential c -axis orientation parallel to the fibre axis results in a concentration of the 110 reflection around the equator ($\Omega = 90^\circ$). The same holds for the 200 and 020 reflections, but given the lower intensities of these reflections, the analysis is restricted to the 110 reflection.

As described before, constraint extraction with hexane of 'free extruded' fibres at 170°C gives rise to a preferential c -axis orientation perpendicular to the fibre axis. A diffractometer analysis (*Figure 9*) demonstrates that constraint extraction of fibres containing a considerable c -axis orientation parallel to the fibre axis, also yields



Figure 7 Wide-angle X-ray diffraction pattern of a paraffin oil-containing polyethylene fibre stretched in the spinline. The fibre was spun at $T_{\text{spin}} = 170^\circ\text{C}$ and a speed of 100 m/min. The take-up speed was 400 m/min

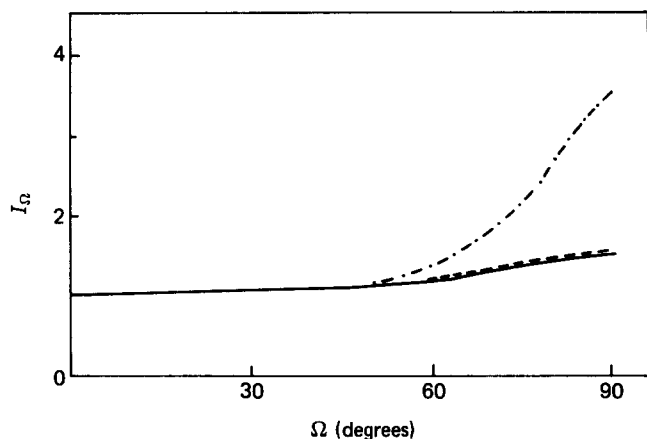


Figure 8 Relative intensity of the 110 reflection as a function of the azimuthal scattering angle Ω for as-spun polyethylene fibres containing paraffin oil and spun at different spin conditions. The spin speed was 100 m/min. (—) $T_{\text{spin}} = 170^\circ\text{C}$, $V_{\text{take-up}} = 100$ m/min; (- - -) $T_{\text{spin}} = 170^\circ\text{C}$, $V_{\text{take-up}} = 400$ m/min; (- · - ·) $T_{\text{spin}} = 250^\circ\text{C}$, $V_{\text{take-up}} = 500$ m/min

some preferential *c*-axis orientation perpendicular to the fibre axis. Figure 9 shows that after the extraction process preferential *c*-axis orientation parallel to the fibre axis dominates for relatively low take-up speeds and/or high spin temperatures.

SAXS measurements show a similar behaviour. Using decalin as the extraction agent, a maximum in the scattering curve develops during the evaporation of decalin if the fibres are obtained at low take-up speeds (100 m/min) and/or high spin temperatures ($> 200^\circ\text{C}$). In all cases the final position corresponds to a periodicity of approximately 12 nm. For high take-up speeds and low spin temperatures an enormous increase in scattering intensity is found. Furthermore, the scattering curve is a smoothly decreasing function of the scattering angle. The increased intensity is due to void/fibril scattering. The decalin extracted fibres spun under these conditions are porous and show a shish-kebab morphology. This structure is already introduced in the spinline as is clear from the preferential *c*-axis orientation parallel to the fibre axis of the paraffin oil-containing gel fibres. The voids between the shish-kebabs survive the extraction process and are responsible for the high equatorial SAXS intensity. Furthermore, filling the voids with paraffin oil yields no shoulder or maximum in the SAXS curve.

A similar morphology can be obtained by cold-drawing decalin-extracted fibres spun at low take-up speeds and/or high spin temperatures. In this way voids are also easily introduced, accompanied by a strong increase in the SAXS intensity. WAXS experiments show that the preferential *c*-axis orientation perpendicular to the fibre axis changes into a preferential *c*-axis orientation parallel to the fibre axis. The deformation mechanism of gel-spun fibres subjected to cold-drawing at temperatures up to 120°C was thoroughly investigated by van Hutten *et al.*²⁰ They concluded that the deformation mechanism is very similar to crazing especially in the case of unoriented gel-spun fibres.

A fibrillar structure can be introduced in the spinline as well as during the extraction process. If the amount of fibrillar material is sufficiently large a clear preferential *c*-axis orientation parallel to the fibre axis is found. This is primarily the case for gel fibres spun at relatively low spin temperatures and high take-up speeds. The extraction

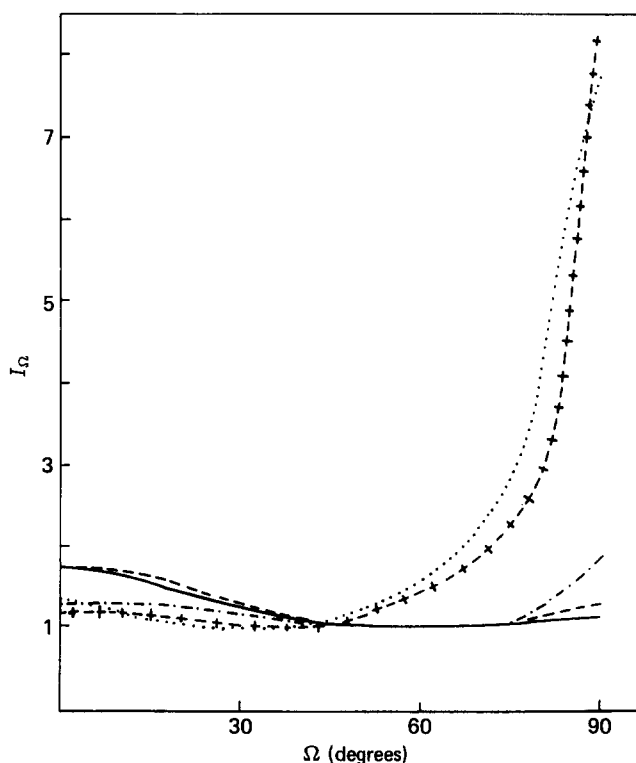


Figure 9 Relative intensity of the 110 reflection as a function of the azimuthal scattering angle Ω for polyethylene fibres constraint extracted with hexane. Influence of the spinning conditions. The spin speed was 100 m/min. (—) $T_{\text{spin}} = 170^\circ\text{C}$, $V_{\text{take-up}} = 100$ m/min; (- - -) $T_{\text{spin}} = 170^\circ\text{C}$, $V_{\text{take-up}} = 300$ m/min; (- + - + - +) $T_{\text{spin}} = 170^\circ\text{C}$, $V_{\text{take-up}} = 500$ m/min; (· · · ·) $T_{\text{spin}} = 215^\circ\text{C}$, $V_{\text{take-up}} = 500$ m/min; (- - -) $T_{\text{spin}} = 250^\circ\text{C}$, $V_{\text{take-up}} = 500$ m/min

process is less important. The tensile strength of fibres obtained by hot-drawing to the maximum draw ratio of gel fibres obtained under these conditions is reduced. In fact a distinct relation between the ultimate tensile strength and the extent of preferential *c*-axis orientation parallel to the fibre axis of the gel fibre is observed. It indicates that the formation of extended chain crystals is accompanied by the introduction of flaws which have a deteriorating effect on the ultimate properties of the fibres. In our experimental set-up, the distance between the spinneret orifice and the take-up device is about 50 cm. It is well known that within the first 30 cm the temperature may easily drop by 100°C or more^{21,22}. Furthermore, we observed that for spin temperatures of 170°C , the gel fibres became opaque due to crystallization at a distance of 10 cm behind the exit. In this region the parallel velocity gradient will, in the case of high take-up speeds, be considerable and the deformation that takes place is partly the result of cold-drawing. During this process entanglements may accumulate and chain scissions will occur²⁴. Tight knots may also be introduced²⁵. All these flaws will be difficult to remove afterwards. In particular since the hot-drawing takes place at 148°C , which necessarily is below the transition temperature of the orthorhombic to hexagonal phase of the extended chain crystals^{26,27}.

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