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DSC experiments on gel-spun polyethylene fibers

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Abstract: The tensile strength of gel-spun polyethylene fibers obtained after hot-drawing depends on spinning conditions such as spinning speed, spinning temperature, spinline stretching, polymer concentration, and molecular weight/molecular weight distribution. High deformation rates in the spinline result in shish-kebab structures which after hot-drawing lead to fibers with poor properties. This is in contrast to hot-drawn fibers obtained from gel-spun fibers with a lamellar structure. Lamellar or shish-kebab structures in the gel-spun fibers can be distinguished by means of DSC experiments on strained fibers. On the basis of these experiments a qualitative prediction of the final tensile properties can be made. DSC experiments on (un)strained hot-drawn fibers show that in the case of shish-kebab structures an incomplete transformation into a fibrillar structure takes place which partly explains the low tensile strength. Chain slippage which becomes possible after the orthorhombic-hexagonal phase transition is involved in the fracture mechanism. The shift of the orthorhombic-hexagonal phase transition to higher temperatures with increasing tensile strength indicates that the increase in strength corresponds to an increase in length of the crystal blocks. Consequently, creep failure also occurs at higher stresses. The melting behavior of cold-drawn and hot-drawn fibers is qualitatively similar, but the transformation into a fibrillar structure is more complete in the latter case.

Key words: Fibres, polyethylene, gel-spinning, spinning conditions, differential scanning calorimetry, shish-kebab structure, lamellar structure.

1. Introduction

During the last decades various routes leading to high strength polyethylene fibers have been explored [1–3]. The preparation of polyethylene fibers using semi-dilute solutions as an intermediate stage [4–9] results in improved properties compared to more concentrated systems [10–12] due to a reduction in the number of entanglements. The surface-growth and gel-spin methods are two examples used routinely in our laboratory. The precise details of the preparation process are very important for the morphology and corresponding stress-strain behavior [8, 9, 13–19].

Usually the gel-spinning process is carried out in the following way: first a 1–5 wt% polyethylene solution in paraffin oil is extruded through a conical die followed by quenching in air. To remove the paraffin oil, the gel-spun fiber obtained in this way is extracted with *n*-hexane and subsequently dried. Finally, the extract-

ed fiber is hot-drawn, which can be accompanied by a large improvement of the fiber properties. However, the ultimate properties depend strongly on spinning conditions such as spinning speed, spinning temperature, stretching in the spinline [18], molecular weight/weight distribution, polymer concentration [19], solvent quality, and die geometry [20]. In our previous papers the correlation between the final tensile strength and the precise nature of the spinning process was described. The conclusions can be briefly stated as follows. High deformation rates in the spinline lead to shish-kebab structures, first at the periphery of the spinline, which after hot-drawing lead to fibers with poor ultimate tensile strengths. Therefore, spinline stretching should be avoided especially at relatively low spinning temperatures [18]. Using polyethylene with a very narrow molecular weight distribution allows spinning at a relatively low optimal concentration which results in fibers with even better properties

[19]. So far all the correlations established were based on stress-strain measurements in combination with small- and wide-angle x-ray scattering (SAXS, WAXS) experiments and scanning electron microscopy (SEM). To confirm these ideas differential scanning calorimetry (DSC) is a useful complementary technique, especially if measurements are extended to fibers which cannot shrink during the scanning process. In this paper the results of a systematic DSC study of gel-spun polyethylene fibers prepared under different spinning conditions and in different stages of the preparation process (extracted fibers, hot-drawn and also cold-drawn fibers) are presented. Special attention will be paid to the DSC information about the morphology of the hot-drawn fibers which improves our understanding of how spinning conditions influence the tensile strength after hot-drawing [18, 19]. It will be shown that the DSC information of different fibers at different stages of the gel-spinning process suffices to predict semi-quantitatively the ultimate tensile properties. The results will be compared with similar observations for surface-grown fibers. Barham has shown that the gel-spinning and the surface-growth process, where fibers are produced from a gel-layer on the rotor surface, are strongly related [21].

2. Experimental

Two samples of linear polyethylene Hifax 1900 were used, one with a broad molecular weight distribution $\bar{M}_w = 4 \times 10^6$ kg/kmol, $\bar{M}_w/\bar{M}_n = 20$; referred to as HifaxA) and one with a narrow molecular weight distribution ($\bar{M}_w = 5.5 \times 10^6$ kg/kmol, $\bar{M}_w/\bar{M}_n \approx 3$; referred to as HifaxB). 1–5 wt% polyethylene solutions in paraffin oil were prepared (containing 0.5 wt% 2,6-di-*t*-butyl,4-methyl cresol 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 using a conical die with an exit of 1 mm [16]. The paraffin oil was extracted from these filaments with *n*-hexane. Afterwards hot-drawing to different draw ratios was carried out at a temperature in the range of 144–148 °C in a nitrogen atmosphere. The mechanical properties of the fibers were investigated with an Instron 4301 Tensile Tester. For the hot-drawn fibers the original sample length was 25 mm and a tensile speed of 12 mm/min was used. The Instron Tensile Tester was also used for cold-drawing in which case the tensile speed was 30 mm/min.

The melting behavior of the fibers was investigated with a Perkin Elmer DSC 7 differential scanning calorimeter. The heating rate was 10 °C/min in all cases. Sample sizes were between 0.2 and 2.0 mg and scans were conducted from 353 ° to 473 °K. Two methods of sample preparation were adopted. For melting experiments on unstrained fibers, the fibers were cut into small pieces of ca. 3 mm in length. In the case of melting experiments on strained fibers, the fibers were tightly wound around a small aluminum frame

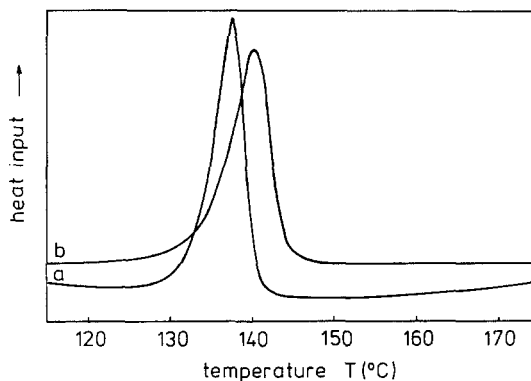


Fig. 1. Thermograms showing the melting behavior of a lamellar-containing gel-spun polyethylene fiber prepared from a 1.5 wt% HifaxB solution at a spinning temperature of 180 °C. The spinning speed and winding speed were 100 m/min; (a) unstrained; (b) strained

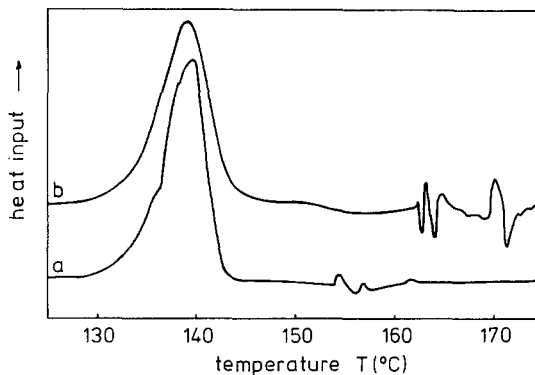


Fig. 2. Thermograms showing the melting behavior of a shish-kebab containing gel-spun polyethylene fiber prepared from a 1.5 wt% HifaxB solution at a spinning temperature of 170 °C. The spinning speed was 100 m/min and the winding speed 500 m/min; (a) unstrained; (b) strained

with dimensions of 4×4 mm². The fibers were knotted onto the frame and the loose fiber ends were cut off. To provide good thermal contact between sample and pan a droplet of silicone oil was added. The reference sample pan was equipped with a droplet of silicone oil (and in the case of strained melting also with an aluminum frame).

3. Results and discussion

3.1. Melting behavior of extracted gel-spun polyethylene fibers

In Figs. 1 and 2 the strained and unstrained melting behavior of two different types of extracted gel-spun fibers is presented. Figure 1 is characteristic for fibers

Table 1. DSC characteristics of melting experiments on unstrained, extracted gel-spun polyethylene fibers

poly-ethylene	spinline stretching	$c\parallel^a$	T_m (°C)	ΔT (°C)	φ_c (%)
HifaxA	no	no	135.9	4.0	66.1
HifaxA	yes	no	135.9	4.4	59.0
HifaxA	yes	yes	136.0	5.0	60.4
HifaxB	no	no	137.9	3.3	68.6
HifaxB	yes	no	137.7	4.0	62.2
HifaxB	yes	yes	138.8	5.2	63.9

^a) $c\parallel$ is the preferential c -axis orientation parallel to the fiber axis introduced during spinline stretching [18, 19]

containing mainly lamellar structure, a structure which is obtained if spinline stretching is avoided or if it is carried out at relatively high spinning temperatures [17–19]. Figure 2 is characteristic for extracted gel-spun fibers containing a shish-kebab structure which is obtained as a result of spinline stretching at relatively low spinning temperatures. These fibers contain a considerable amount of preferential c -axis orientation parallel to the fiber axis [17–19].

Qualitatively the unstrained melting of both type of fibers is rather similar. However, from Table 1 containing average values of the peak melting temperature T_m , peak width (full width at half maximum height) ΔT and degree of crystallinity φ_c for fibers prepared under different spinning conditions and using two types of polyethylene (HifaxA and HifaxB, resp.), we conclude that small differences do exist. The melting peaks for shish-kebab containing fibers are broader than for lamellae containing fibers. The crystallinity decreases with increasing draw ratio in the spinline independent of whether this results in the introduction of preferential c -axis orientation parallel to the fiber axis (relatively low spinning temperatures) or not. In the first case spinline stretching results in a shift of the peak melting temperature to higher temperatures. There is a tendency for this shift to increase with an increasing degree of preferential c -axis orientation parallel to the fiber axis, i.e., an increasing effectivity of spinline stretching [18, 19]. Superimposed on the effects of differences in morphology, created by the flowfield during gel-spinning, small effects due to the cooling history of different fibers may exist. Different spinning conditions such as spinning temperature and spinning speed/winding speed, leading for instance to different fiber diameters, can influence the crystallization during the quenching in air. At present there are not enough data available to investigate this systematically.

Comparing the melting behavior of strained fibers (Figs. 1 and 2) two striking observations can be made. In the first place, a small shoulder is observed at the high temperature side of the melting peak in the case of fibers containing a considerable amount of shish-kebab structure. Due to the presence of highly oriented regions (backbones of extended chain crystals) the stress during partial melting of less stable (folded chain) crystals increases and an orthorhombic to hexagonal solid state phase transition occurs [22–25]. A second characteristic feature of the DSC curve in Fig. 2 is the presence of endotherm/exotherm peaks in the temperature range of 160–175 °C. Most probably these peaks correspond to fiber breakage: fibers showing this effect turned out to be broken at several places during the melting experiment whereas fibers with a lamellae structure or very little shish-kebab structure survive the heating experiment. The endothermic part is due to melting of the hexagonal phase and the trans to gauche conformational change that occurs after stress relaxation [22]. Flory has calculated the energy difference between trans and gauche conformations [26, 27] and these results can be combined with a calculation of the fraction of bonds that assume a gauche conformation when fully extended chain structures melt [28]. Experimental data were obtained by measuring the heat content between a completely relaxed melt and the strained amorphous component in a drawn fiber [29, 30]. A reasonable agreement between the theoretical calculations and the experimental results was found [22]. The observed exotherm peak(s) may be caused by kinetic effects occurring during breakage of the highly stressed fibers.

The study of the melting behavior of strained as-spun fibers is important since the melting behavior of the as-spun fiber and the tensile strength obtained after hot-drawing are strongly related. Strained fibers showing a melting behavior as presented in Fig. 2 invariably result in weak fibers. These curves therefore contain all the necessary information to predict, at least semi-quantitatively, the final outcome of the gel-spinning hot-drawing process.

3.2. Melting behavior of hot-drawn gel-spun polyethylene fibers

Figures 3–5 represent the melting behavior as a function of the hot-draw ratio λ obtained by DSC experiments on three different types of extracted unstrained gel-spun fibers. The results in Fig. 3 corre-

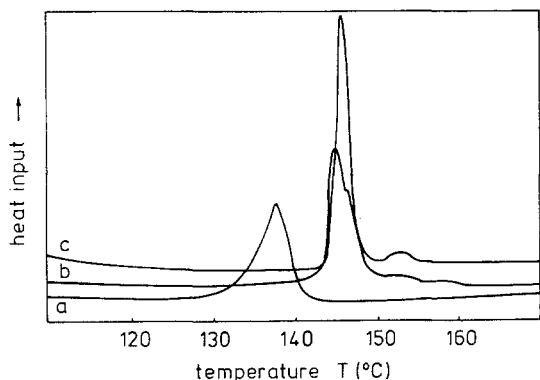


Fig. 3. Thermograms showing the melting behavior of an unstrained, originally lamellae containing fiber prepared from a 1.5 wt% HifaxB solution at a spinning temperature of 180 °C and a spinning speed/winding speed of 100 m/min and afterwards hot-drawn to various draw ratios λ ; (a) undrawn; (b) $\lambda = 40$; (c) $\lambda = 80$

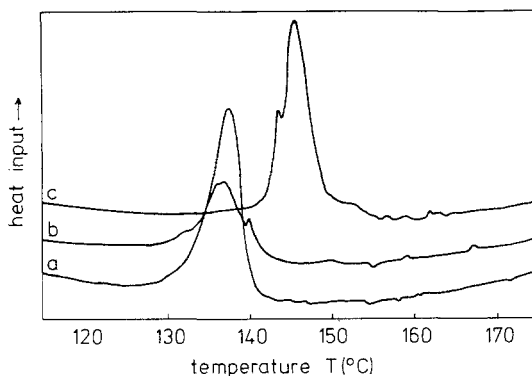


Fig. 5. Thermograms showing the melting behavior of an unstrained, originally lamellae containing fiber prepared from a 2.0 wt% HifaxB solution at a spinning temperature of 250 °C, a spinning speed of 100 m/min, a winding speed of 500 m/min, and afterwards hot-drawn to various draw ratios λ ; (a) undrawn; (b) $\lambda = 5$; (c) $\lambda = 16$

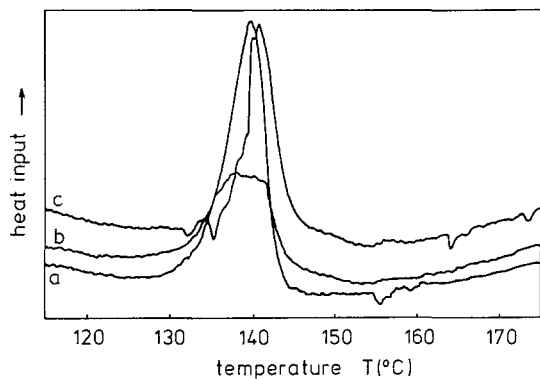


Fig. 4. Thermograms showing the melting behavior of an unstrained, originally shish-kebab containing fiber prepared from a 1.5 wt% HifaxB solution at a spinning temperature of 180 °C, a spinning speed of 100 m/min, a winding speed of 500 m/min, and afterwards hot-drawn to various draw ratios λ ; (a) undrawn; (b) $\lambda = 2.7$; (c) $\lambda = 4.5$

spond to a starting fiber not stretched in the spinline and therefore containing a lamellar structure. The starting material for the results presented in Fig. 4 has a shish-kebab containing structure introduced during spinline stretching at relatively low spinning temperatures. Finally, the fiber used in the melting experiments of Fig. 5 is also drawn in the spinline but because this took place at a relatively high spinning temperature a lamellar structure instead of a shish-kebab structure is present. Table 2 summarizes the data of the samples used together with the main results of these melting experiments.

The changes in melting behavior obtained after hot-drawing extracted gel-spun polyethylene fibers were also investigated by Smook and Pennings [31]. The extracted gel-spun fibers used in their experiments

Table 2. Characteristic values of melting experiments on unstrained, hot-drawn gel-spun polyethylene fibers^a)

T_{spin} (°C)	V_{spin} (m/min)	V_{wind} (m/min)	λ	T_m (°C)	ΔT (°C)	φ_c (%)	σ_b (GPa)
180	100	100	—	137.8	4.0	64.9	0.32
180	100	100	40	145.0	3.1	68.3	3.12
180	100	100	80	145.7	1.8	75.3	3.68
180	100	500	—	139.7	5.2	62.7	0.37
180	100	500	2.7	138.1	8.5	36.0	0.96
180	100	500	4.5	140.8	4.0	43.1	—
250	100	500	—	137.7	4.0	62.2	0.21
250	100	500	5	137.1	6.0	31.6	0.77
250	100	500	16	145.7	3.2	62.3	2.52

^a) The polyethylene used in these experiments was HifaxB; for the fibers spun at 180 °C the starting polymer concentration was 1.5 wt%, in the case of the fiber spun at 250 °C the concentration was 2 wt%. T_{spin} , V_{spin} , and V_{wind} are resp. the spinning temperature, spinning speed, and winding speed

were not stretched in the spinline and contained therefore mainly lamellar structure. Hot-drawing was possible up to a maximum hot-draw ratio of 80 and this resulted in a fiber with a tensile strength of 3.55 GPa. SEM and SAXS studies of the hot-drawing process of these gel-spun fibers revealed that for high hot-draw ratios the lamellar structure was transformed into a fibrillar structure [32, 33]. Hot-drawing to low draw ratios resulted in a decrease of the crystallinity and a shift of the peak melting temperature T_m to somewhat lower temperatures due to a recrystallization of the lamellar material into less perfect crystals, due to fast cooling of the thin hot-drawn fibers. At higher hot-draw ratios the fraction of extended chain crystals increased, leading to a shift of T_m to higher temperatures and to an increase of the crystallinity up to 93.5% [31]. The influence of hot-drawing on our extracted gel-spun fibers not stretched in the spinline (presented in Fig. 3) is similar although the maximum amount of crystallinity obtained is considerably less (about 85%). The observed increase of peak width at low hot-draw ratios (Table 2) is caused by the presence of lamellar as well as fibrillar material.

The melting behavior of hot-drawn gel-spun fibers originally containing shish-kebab structures differs to a certain degree from the melting behavior described above as can be seen from Fig. 4 and Table 2. At low hot-draw ratios the melting behavior is similar, i.e., a decrease of crystallinity and a shift of T_m to a somewhat lower temperature. However, because high hot-draw ratios cannot be obtained, the maximum crystallinity and peak melting temperature are very low compared to fibers which can be hot-drawn to high draw ratios.

Morphological changes during hot-drawing of shish-kebabs have been studied with SEM and SAXS [32, 34–36]. In the case of hot-drawing shish-kebab structures obtained by surface-growth at a temperature of 120 °C the transformation of shish-kebab structure into smooth fibrils was incomplete and relatively low maximum hot-draw ratios were found (up to about 5) [34]. It was also observed that shish-kebab structures prepared by gel-spinning could be hot-drawn at a temperature of 108 °C to a hot-draw ratio of 27 which resulted in smooth fibrils [32, 35]. However, Van Hutten et al. [34] suggested that this difference in hot-drawing behavior was caused by a difference in the molecular weight of the two samples. Because surface-growth leads to fractionation [9, 37, 38] only the high molecular fraction is incorporated in the growing fiber (original polymer used was HifaxA; $\bar{M}_w = 4 \times 10^6$

kg/kmol, $D = 20$). In the case of the gel-spun fibers a 95 : 5 mixture of Hostalen Gur ($\bar{M}_w = 1.5 \times 10^6$ kg/kmol, $D = 7.5$) and a lower molecular weight polyethylene (Marlex 6002; $\bar{M}_w = 2 \times 10^5$ kg/kmol, $D \approx 10$) was used. Our observations that hot-drawing of shish-kebab structures prepared by gel-spinning of HifaxA and HifaxB ($\bar{M}_w = 5.5 \times 10^6$ kg/kmol, $D \approx 3$) lead to low maximum hot-draw ratios but that HifaxB is more difficult to draw than Hifax A supports the suggestion of van Hutten et al. [34] that the molecular weight distribution is an important factor concerning drawability of shish-kebab structures.

The hot-draw behavior of fibers stretched in the spinline at high spinning temperatures and therefore containing lamellar structures (Fig. 5) is approximately the same as for fibers not stretched in the spinline although the maximum hot-draw ratio is smaller. The shift of the peak melting temperature to higher temperatures and the melting peak width are approximately the same (Table 2). Moreover, after a decrease at low hot-draw ratios the crystallinity as a function of the hot-draw ratio increases again to more than 60%.

In three previous papers [17–19] correlations were established between the spinning conditions such as spinning temperature, spinning speed, spinline stretching, polymer concentration, and molecular weight/molecular weight distribution, and the tensile strength of fibers obtained by hot-drawing to the maximum draw ratio. The dependence of the morphology of the extracted gel-spun fibers on the spinning conditions was described. The morphological changes introduced during the hot-drawing step were not addressed. The melting experiments on unstrained fibers described above give information about this aspect of the gel-spinning hot-drawing process. There is a strong correlation between the peak melting temperature, crystallinity, and tensile strength of the hot-drawn fibers. In Fig. 6 the tensile strength of fibers hot-drawn to various draw ratios is presented as a function of the peak melting temperature T_m . Although there is a considerable scatter in data points, the tensile strength increases with T_m . Fibers originally containing a lamellar structure not hot-drawn to the maximum draw ratio give rise to datapoints at low T_m and low tensile strength. This is in agreement with the fact that the tensile strength of gel-spun fibers increases with increasing hot-draw ratio [39]. Fibers which contain shish-kebab structure before hot-drawing give after hot-drawing to the maximum draw ratio also rise to points at low tensile strength and low melting temperature. If a lamellar structure is the starting point,

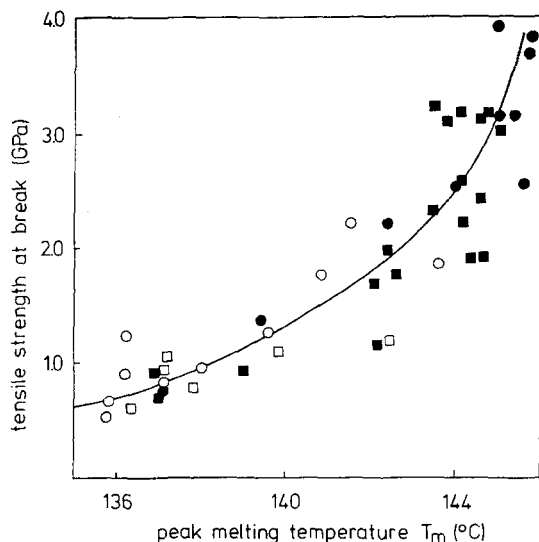


Fig. 6. Tensile strength at break of hot-drawn gel-spun polyethylene fibers prepared at various spinning conditions and hot-drawn to different hot-draw ratios, as a function of the peak melting temperature of unstrained melting endotherms. ● HifaxB, no $c\parallel$; ○ HifaxB, $c\parallel$; ■ HifaxA, no $c\parallel$; □ HifaxA, $c\parallel$. $c\parallel$ is the preferential c -axis orientation parallel to the fiber axis introduced during spinline stretching

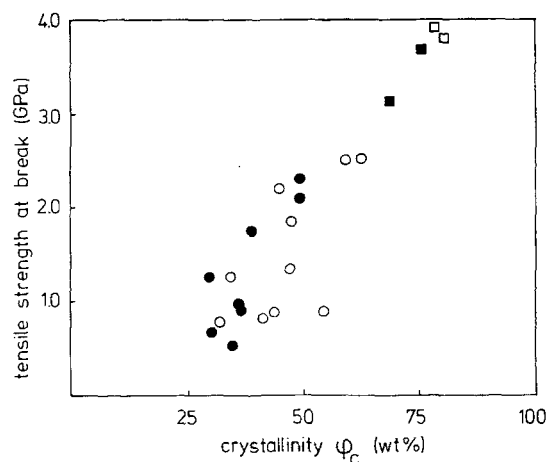


Fig. 7. Tensile strength at break of hot-drawn gel-spun polyethylene fibers (HifaxB), prepared at various spinning conditions and hot-drawn to different hot-draw ratios, as a function of the crystallinity. ○ 2.0 wt%, $V_{\text{spin}} = 100$ m/min, $V_{\text{wind}} = 500$ m/min; ● 1.5 wt%, $V_{\text{spin}} = 100$ m/min, $V_{\text{wind}} = 500$ m/min; ■ 1.5 wt%, $V_{\text{spin}} = 100$ m/min, $V_{\text{wind}} = 100$ m/min; □ 1.5 wt%, $V_{\text{spin}} = 1$ m/min, $V_{\text{wind}} = 1$ m/min

drawing to a maximum hot-draw ratio produces fibers with high tensile strengths and high melting points. A similar behavior is observed for the tensile strength as a function of the crystallinity (Fig. 7). The strongest fibers have a high degree of crystallinity because hot-drawing is accompanied by a nearly complete transformation of the lamellar structure into fibrillar structure. On the other hand, if the starting material contains a shish-kebab structure, an incomplete transformation into fibrillar structure takes place. The presence of lamellar overgrowth results in relatively weak fibers, most probably because this lamellar overgrowth bears no load during stress/strain experiments. The poor drawability of the shish-kebab structures may be caused by an accumulation of entanglements in certain regions during the formation of extended chain crystals. It is unlikely that sufficient time is available to disentangle in the short period between orientation of the molecules by the flowfield and solidification of the fiber structure by quenching in air. The presence of regions with a high density of entanglements (tight knots [40]) may prevent a complete transformation of the lamellar overgrowth into a fibrillar structure.

These results may lead to the impression that shish-kebab structures always lead to fibers with poor properties. This is not necessarily true — fibers obtained by

the surface-growth method contain shish-kebab structures and can have excellent mechanical properties if prepared under suitable conditions [8, 9]. The properties of surface-grown shish-kebab containing fibers improve as the degree of lamellar overgrowth decreases [8] although this degree of overgrowth is hard to measure since it may appear in different shapes depending on the cooling/washing history [41]. Moreover, the lengths of the crystal blocks in the backbones have an effect on the tensile strength of these fibers. It has been shown that the length of the crystal regions in the backbone as well as the tensile strength increases with the growth temperature independent of the cooling/washing history [41]. The tensile strength of surface-grown shish-kebab containing fibers can be improved by hot-drawing [36, 42] but the tensile strength obtained after hot-drawing depends on the strength of the undrawn surface grown fiber, i.e., the stronger the undrawn surface-grown fiber, the stronger the fiber after hot-drawing to the maximum draw ratio [42]. Comparing the tensile strength of our undrawn gel-spun shish-kebab containing fibers ($\sigma_b < 0.6$; [18, 19]) with undrawn surface-grown fibers leads to the conclusion that the structure of our fibers closely resemble surface-grown fibers prepared under unfavorable conditions (low growth temperature) [8]. The great similarity between a DSC melting curve of a more or less unstrained undrawn free growth fiber

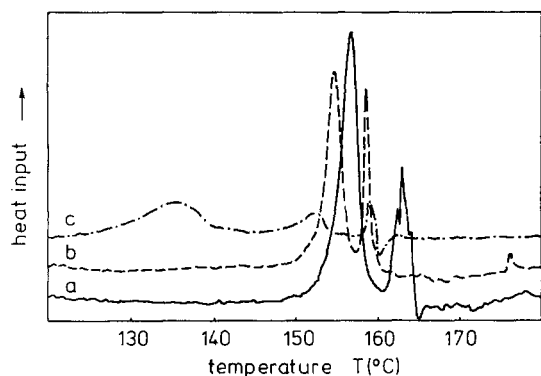


Fig. 8. Thermograms showing the melting behavior of strained, hot-drawn gel-spun polyethylene fibers (HifaxB) prepared under different spinning conditions (Table 3) and hot-drawn to the maximum hot-draw ratio

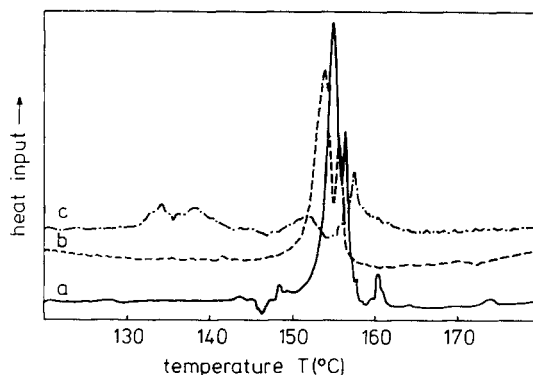


Fig. 9. Thermograms showing the melting behavior of strained, hot-drawn gel-spun polyethylene fibers (HifaxA) prepared under different spinning conditions (Table 3) and hot-drawn to the maximum hot-draw ratio

crystallized at 103 °C [22; Fig. 14 a] and the melting behavior of our unstrained undrawn shish-kebab containing fibers confirms this point of view. Apparently, the conditions for shish-kebab formation during our gel-spinning experiments are unfavorable: the obtained shish-kebabs contain too much lamellar overgrowth and/or the crystal blocks in the backbone are too short, leading to fibers with poor properties.

So far we considered melting behavior of unstrained fibers. Figures 8 and 9 show the melting behavior obtained by DSC experiments on three strained fibers prepared from HifaxB (Fig. 8) and HifaxA (Fig. 9), respectively, all hot-drawn to their maximum draw ratio. Tables 3 and 4 summarize the essential preparation conditions for these fibers and the characteristics of their melting curves, respectively. Previously the melting behavior of strained undrawn surface-grown fibers was investigated by several authors [22, 38, 43]. Moreover, Smook et al. studied melting behavior of strained, not spinline stretched, hot-drawn gel-spun

polyethylene fibers [31]. Curves (a) of Figs. 8 and 9 represent melting of our not-spinline-stretched gel-spun fibers hot-drawn to the maximum ratio. They are qualitatively similar to the results of Smook et al. The DSC curves contain two endotherm peaks, the first (T_{m2}) corresponds to the orthorhombic-hexagonal solid state phase transition and the second (T_{m3}) represents the melting of the hexagonal phase. In the melting curves (labeled c) of originally shish-kebab containing fibers a third melting peak around 136 °C is observed (T_{m1}). This corresponds to melting of unstrained lamellar material. The fact that during melting of strained fibers no complete transformation of the orthorhombic structure into the hexagonal crystal structure occurs is a strong indication that not all the material is load bearing. It confirms that during hot-drawing of high molecular weight material the transformation of lamellar structure into the backbone is incomplete. Eventually, this lamellar overgrowth may be aligned along the backbone by shear [42] due to

Table 3. Preparation conditions of the hot-drawn gel-spun polyethylene fibers used in the melting experiments on strained fibers

Figure nr.	Hifax	pol. conc. (wt%)	T_{spin} (°C)	V_{spin} (m/min)	V_{wind} (m/min)	λ
8a	B	1.5	190	1	1	100
8b	B	2.0	250	100	500	16
8c	B	1.5	180	100	500	2.7
9a	A	2.0	190	100	100	81
9b	A	2.0	215	100	500	37.5
9c	A	2.0	170	100	500	4.2

Table 4. Characteristics of the melting curves of strained hot-drawn gel-spun polyethylene fibers

Figure nr.	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	φ_c (%)	σ_b (GPa)
8a	—	156.8	163.0	75.8	> 4.0
8b	—	154.6	158.8	62.7	2.5
8c	136	152.0	159.0	38.3	1.0
9a	—	154.9	156.4	74.1	3.1
9b	—	153.9	155.8	58.6	2.5
9c	136	151.5	157.5	44.4	0.6

slippage of the separate shish-kebabs past each other. This leads to an increase of the *c*-axis orientation parallel to the fiber axis, but its contribution to the tensile strength remains small. The melting behavior of strained lamellar containing fibers stretched in the spinline (curves labeled b) is similar to the behavior of the hot-drawn fibers which were not stretched in the spinline. The most important feature of these curves is the absence of a lamellar melting peak. The transformation of the orthorhombic structure into the hexagonal phase is complete and nearly all crystallites are load-bearing in a stress/strain experiment, thus leading to a high tensile strength at break.

Another striking observation is the fact that for relatively strong fibers the temperature difference between T_{m2} and T_{m3} is considerably greater for HifaxB than for HifaxA (see Table 4; Figs. 8 a,b; 9 a,b). Retractive force measurements of the HifaxA fibers showed that fiber breakage at several places occurred as soon as the transformation of the orthorhombic to hexagonal phase had taken place. This is due to the slippage of chains out of the entanglements under the entropic driving force for recoiling [31]. Because HifaxB has a higher \bar{M}_w and a narrower molecular weight distribution, fibers prepared from this polyethylene sample contain less chain ends, leading to a more slippage resistant entanglement network. This results in a shift of T_{m3} to higher temperatures. The retractive force increases with an increasing degree of orientation of the chains in the fiber axis direction. It explains why for relative moderately oriented fibers such as undrawn shish-kebab containing gel-spun fibers (Fig. 2 b) the difference between T_{m2} and T_{m3} increases, and why strained undrawn, unoriented gel-spun fibers do not break during melting upon heating to temperatures in the range of 180–200 °C.

In Fig. 10 the tensile strength obtained after hot-drawing to various draw ratios is presented as a function of the orthorhombic-hexagonal transition temperature. The tensile strength is seen to increase with increasing T_{m2} . The tensile strength at break of hot-drawn gel-spun fibers decreases above room-temperature linearly with the temperature of the stress/strain experiments [44, 45]. The temperature obtained by extrapolation to zero tensile strength coincides with the orthorhombic-hexagonal phase transition temperature. This behavior shows that creep failure is involved in the fracture mechanism of the fiber. From literature it is known that the orthorhombic to hexagonal phase transition temperature can be changed in a number of ways. For low *n*-paraffins the transition

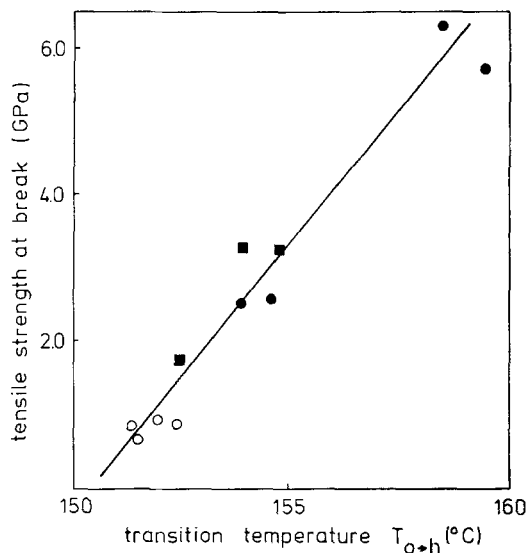


Fig. 10. Tensile strength at break of hot-drawn fibers, prepared at various spinning conditions and hot-drawn to various hot-draw ratios, as a function of the orthorhombic to hexagonal phase transition temperature $T_{o \rightarrow h}$ obtained from strained melting experiments. ○ HifaxB, $c \parallel$; ■ HifaxA, no $c \parallel$; ● HifaxB, no $c \parallel$. $c \parallel$ is the preferential *c*-axis orientation parallel to the fiber axis introduced during spinline stretching

temperature increases with the chain length [23, 24, 46]. In the case of chain folded polyethylene fibers the orthorhombic to hexagonal transition temperature increases with the crystal thickness [47]. For irradiated samples this transition decreases with increasing radiation dose due to a combination of the introduction of chemical defects and a reduction of the conformational entropy of the melt caused by the introduction of crosslinks [47]. Torfs [44] showed that an increase of the applied stress during melting experiments on strained fibers leads to a reduced T_{m2} . Shrinkage measurements of fibers prepared by stirring induced crystallization and surface-growth have led to the conclusion that the backbones of these fibers do not exist of “infinitely long” extended chain crystals but rather crystal regions of extended chain crystals and defect regions [21, 41, 43, 48]. The same holds for drawn gel fibers [21]. Taking these results into account, the increase of the tensile strength with an increasing orthorhombic to hexagonal transition temperature observed during melting of strained fibers can be explained by the dependence of the strength on the length of the crystallites. The longer the crystallites, the higher the temperature at which the orthorhombic-hexagonal solid-solid phase transition occurs. The stresses needed for fiber fracture increase with an

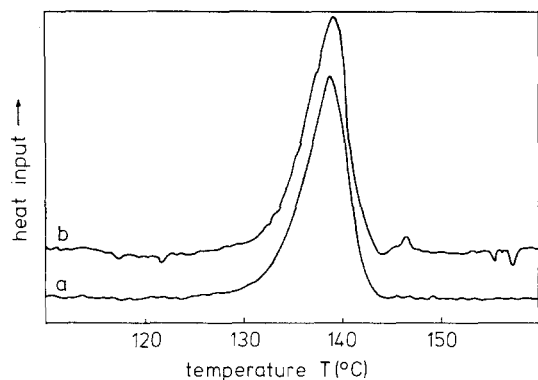


Fig. 11. Thermograms showing the melting behavior of an unstrained, originally shish-kebab containing gel-spun fiber, prepared from a 1.5 wt% HifaxB solution at a spinning temperature of 190 °C, a spinning speed of 100 m/min, a winding speed of 500 m/min, and afterwards cold-drawn to various draw ratios λ ; (a) undrawn; (b) $\lambda = 1.2$

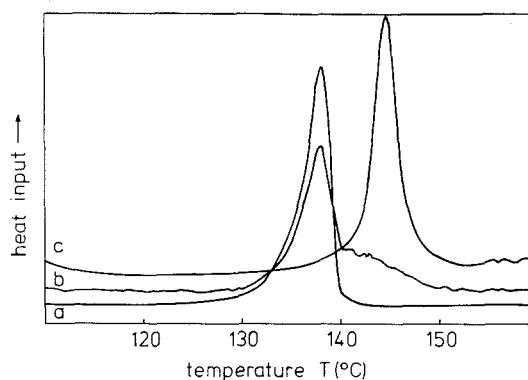


Fig. 12. Thermograms showing the melting behavior of an unstrained, originally lamellae containing gel-spun fiber, prepared from a 1.5 wt% HifaxB solution at a spinning temperature of 190 °C, a spinning speed/winding speed of 1 m/min and afterwards cold-drawn to various draw ratios λ ; (a) undrawn; (b) $\lambda = 9$; (c) $\lambda = 25$

increasing length of the crystallites leading to higher tensile strengths since, as mentioned before, a creep mechanism is involved in fiber fracture [44, 45]. An additional observation in agreement with this mechanism is the increase of the volume of the crystal lattice of oriented polyethylene fibers with increasing stress found by Slutsker et al. [49].

3.3. Melting behavior of cold-drawn extracted gel-spun polyethylene fibers

Figures 11 and 12 show the change of the DSC behavior upon cold-drawing of two different types of extracted gel-spun polyethylene fibers. For fibers containing shish-kebab structures only low cold-draw ratios up to about 1.3 can be obtained [8, 18, 19]. The melting behavior of such an unstrained fiber cold-drawn to a ratio 1.2 is presented in Fig. 11. As expected, no significant changes in the peak melting temperature and crystallinity could be observed upon cold-drawing these very stiff shish-kebab structures. On the other hand extracted fibers containing a lamellar structure can be cold-drawn to very high draw ratios (up to 25; [18, 19]). DSC curves showing the changes during melting as a function of the cold-draw ratio representative for such an unstrained lamellar structure are presented in Fig. 12. The peak melting temperature shifts to higher melting temperatures and the absolute value of the shift increases with increasing maximum cold-draw ratio for this type of structure. During cold-drawing, at low draw ratios the melting peak broadens

but if high draw ratios can be obtained the peak width decreases again. It is well known from literature that during cold-drawing a lamellar structure is transformed into a fibrillar structure [50–52]. The presence of both structures at low cold-draw ratios may account for the initial broadening of the melting peak. The observation of a melting peak with a shoulder (Fig. 12 b) shows that the cold-drawing is not homogeneous throughout the whole sample but takes place by a multiple necking process [53, 54]. If the fiber can be drawn to a high enough cold-draw ratio the lamellar structure is completely converted into a fibrillar one and the width of the melting peak decreases again. What happens with the amount of crystallinity during cold-drawing is not quite clear because of the small amount of drawn material available for a DSC measurement but there seems to be a tendency for the crystallinity to decrease somewhat at low cold-draw ratios and then to increase again if it is possible to convert the total lamellar structure completely into a fibrillar one without premature breakage. This may point to a local melting/recrystallization mechanism [50]. Compared to the hot-drawing process, cold-drawing shows qualitatively the same unstrained melting behavior although in the case of hot-drawn fibers the shift of the peak melting temperature is somewhat greater. The melting peak width of the hot-drawn fibers drawn to their maximum draw ratio is smaller than the melting peak width of cold-drawn samples pointing to more perfect crystals in the first case.

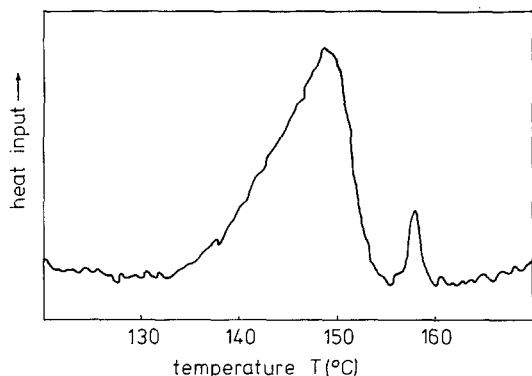


Fig. 13. Thermogram showing the melting behavior of a strained, originally lamellae containing gel-spun fiber, prepared from a 1.5 wt% HifaxB solution at a spinning temperature of 190°C, a spinning speed/winding speed of 1 m/min and afterwards cold-drawn to a draw ratio of 25

This idea is supported by a DSC curve of a strained, originally lamellar containing fiber cold-drawn to a ratio 25. This curve contains a very broad endotherm around 148°C and a small melting peak at 158°C (Fig. 13; compare with Fig. 8 which shows the strained melting behavior of the same starting fiber hot-drawn to a ratio 100). This very broad endotherm is caused by the melting of "unstrained" lamellar/fibrillar material and it may also contain a small contribution of the orthorhombic to hexagonal solid-solid phase transition. This last mentioned contribution is expected since the melting peak at 158°C is ascribed to melting of the hexagonal phase.

4. Summary

We have shown that DSC is an excellent technique to study the morphological differences in polyethylene fibers during different steps of the gel-spinning process. These different morphologies originate from different preparation conditions such as spinning speed, spinning temperature, spinline stretching, polymer concentration, and molecular weight/molecular weight distribution. The melting behavior of the strained extracted gel-spun fibers allows us to distinguish between lamellar and shish-kebab structures. It turns out that after hot-drawing the shish-kebab structure results in relatively weak fibers. Therefore, it is possible to predict, at least semi-quantitatively, the ultimate tensile properties on the basis of these experiments. The melting behavior of the strained hot-

drawn fibers indicates that during hot-drawing the transformation of the shish-kebab structures into fibrillar structures is incomplete. This is probably caused by the presence of regions containing a high entanglement concentration (tight knots). The remaining lamellar fraction bears no load during stress/strain experiments and may therefore partly explain the low tensile strength. Moreover, the increase of the tensile strength with increasing orthorhombic to hexagonal solid-solid phase transition temperature points to an increase of the length of the crystal blocks with increasing tensile strength. Since this phase transition (after which chain slippage can occur) is involved in the fracture mechanism, longer crystal blocks prevent creep failure up to higher stresses. This results in stronger fibers. The changes in the DSC behavior upon cold-drawing gel-spun polyethylene fibers shows the same tendencies as observed for hot-drawn fibers but the transformation into fibrillar material is less perfect.

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