JOURNAL OF MATERIALS SCIENCE 19 (1984) 31–43

Elastic flow instabilities and shish-kebab formation during gel-spinning of ultra-high molecular weight polyethylene

JAN SMOOK, ALBERT J. PENNINGS
Department of Polymer Chemistry, State University of Groningen, Nijenborgh 16,
9747 AG Groningen, The Netherlands

The flow behaviour during gel-spinning of semi-dilute solutions of ultra-high molecular weight polyethylene in paraffin oil was investigated in relation to fibre strength and morphology. Shish-kebab morphologies observed in the as-spun filaments originate from a solidification of long flow units already developed in the polymer solution during spinning. These flow units consist of alternating bundles of elongated molecules and highly entangled clusters of unoriented molecules. Extrudate stretching leads to a demolition of these long flow units by elastic flow instabilities. As a result, the tensile properties after hot-drawing of the fibres are strongly reduced. The inclusion of 1 wt % aluminium stearate in the spinning solution preserves the long bundle-like flow units even at high take-up speeds during extrusion. This additive suppresses the adsorption of the polyethylene on the die-wall and avoids the generation of elastic turbulences. Filaments with a strength between 2.5 and 3.0 GPa can be obtained from these doped solutions after hot-drawing, in spite of high winding speeds up to 300 m min^{-1} in the spinning process.

1. Introduction

The use of ultra-high molecular weight polyethylene is a prerequisite for the preparation of fibres having not only a high modulus, but a high strength as well [1]. The relationship between strength and the reciprocal of the number average molecular weight was already pointed out by Flory as early as 1945 [2]. The processibility and orientation of ultra-high molecular weight polyethylene is however restricted to limited conditions due to the existence of a very effective entanglement network in the flowing melt or solution. Chain entanglements, whose frequency and efficiency increase with molecular weight, promote the storage of elastic free energy [3]. As a result elastic flow instabilities are encountered in the spinning of ultra-high molecular weight polyethylene solutions already at low flow rates [4].

This paper presents an explorative study concerning the occurrence of elastic turbulences during gel-spinning of ultra-high molecular weight polyethylene (UHMWPE) and the suppression of this phenomenon by the use of additives. Emphasis will be placed on fibre strength and morphology in relation to the flow conditions during spinning. UHMWPE filaments with outstanding mechanical properties may be obtained by spinning from semi-dilute solutions [5–8]. Fibre preparation involves extrusion of a 5 wt % solution of UHMWPE in paraffin oil, followed by extraction of the solvent in *n*-hexane. On subsequent hot-drawing of the dried porous as-spun fibres, tensile strengths at break up to 4.1 GPa and Young's moduli up to 160 GPa can be achieved. The manufacturing of such high tenacity fibres however is restricted to low spinning rates of 1.5 m min^{-1}. At higher extrusion speeds the onset of elastic flow instabilities, e.g. melt fracture, die swell, etc., takes place.

It will be shown that the addition of 1 wt % aluminium stearate to the spinning solution permits a substantial enhancement of the take-up speeds during gel-spinning, while a high strength

0022–2461/84 $03.00 + .12

level is maintained. A flow model is presented that accounts for the observed morphologies noticed in the as-spun fibres. It comprises the formation of long bundle-like flow units in the flowing polyethylene solution, which seem to be the precursors of the shish-kebab-like entities, commonly observed in the as-spun filaments after crystallization.

2. General background

2.1. Some aspects of elastic turbulence

The occurrence of extrusion instabilities, such as melt-fracture, shark-skin effects, etc., are highly undesirable phenomena in any fibre spinning operation. Melt fracture leads to non-uniform diameters of the fibres and thus inevitably lowers the strength [9]. Although there is still no general agreement about the main causes of extrusion instabilities, it seems to be well accepted now, that the onset of elastic turbulence is related to a critical wall shear stress in the die [10, 11], which is inversely proportional to the molecular weight of the polymer [12, 13]. Upon spinning of polymer solutions it has been noticed [14, 15] that the critical value of the wall shear stress is also proportional to the second power of the polymer volume fraction, ψ^2, if the molecular weight was larger than M_c, the critical value for coil overlap. Therefore it need not be surprising that the UHMWPE solutions are highly sensitive to the onset of melt-fracture. Elastic turbulence can be avoided to some extent by taking a large L/D ratio of the spinning capillary [10] with a conical entrance region. This will reduce the shear components of the elongational flow field, that is produced by the converging flow lines in the die. The transverse velocity gradient in shear flow will produce rotation of large entities, whereas the velocity in extensional flow, which increases in the direction of the flow, makes the molecules effectively elongated. Probably for similar reasons, pulling of the extrudate behind the die exit is an effective means of avoiding the formation of structurized fibres [11]. Drawing of the spinning-line also creates a pure elongational flow field in the filaments. Additionally, the use of fillers in the extrusion of polymers has been found to be of practical interest. Carbon black in elastomers reduces extrudate swell and the intensity of extrudate distortion [3]. Similar effects were noticed for the addition of small amounts of polyethylene during the extrusion of polystyrene [11].

It is pertinent to note that elastic turbulence cannot be accounted for in terms of a fully turbulent flow, as is common in Newtonian liquids above a Reynold's number of about 2100. In viscoelastic liquids, such as the ultra-high molecular weight polyethylene solutions, vortices may be generated at a much smaller Reynold's number of about 1 [16], as was pointed out by Giesekus [4, 17]. Such vortices arise from the elastic nature of the liquid and are not being caused by inertia forces. In fact, these elastic vortices will rotate in the opposite direction to, for example, Taylor vortices [18], which result from centrifugal forces in a Couette-flow between rotating cylinders.

The rotating units in the elastic vortices may be envisaged by the formation of clusters, a concept originally introduced by Mooney [19]. Williamson and Busse [20] and Busse [21] proposed the formation of highly entangled, rotating clusters of molecules at high shear rates. These clusters adopt an ellipsoidal form in shear flow [22], which will lead to a periodic stretching of the rotating molecules, if they are directed along the long axis of the ellipsoid and a recovery at the short axis. The formation of entangled aggregates upon shearing of high molecular weight polymer solutions has been recognized by several other authors [23–28]. Shearing of such solutions at a constant shear rate is characterized by an upturn effect in the viscosity as a function of time, before a steady state value of the viscosity is reached. Upon starting of the shearing motion additional entanglements will be formed leading to an increased viscosity. Subsequently the viscosity decreases due to the formation of separated entangled aggregates in the solution. Finally a dynamic equilibrium between entanglement formation and breakdown is reached, leading to a steady state value of the viscosity.

Vinogradov [29] has pointed out that with increasing shear rate a situation will be reached, where the breakdown of entanglement networks is no longer compensated by recovery of entanglements. It is conceivable that this will result in irregular flow patterns. The stretched molecules will snap back to the random coil conformation, when they are pulled out of entanglement couplings, thereby generating elastic turbulences.

For a far more complete treatment of the subject we refer to salient reviews as given by Han [11], White [30], Leblanc [3], Tordella [31], Bagley and Schreiber [32].

2.2. Some aspects of fibril formation in oriented polymers

A common feature in many oriented, crystalline polymers is the presence of a highly fibrillated morphology. Fibril formation is however also observed after deformation in glassy amorphous polymers leading to crazes. The generation of fibrous material is the result of stretching the long polymer molecules, if the requirement of a minimum rate of deformation is fulfilled [9, 33]. Subsequently the oriented state needs to be trapped, to prevent the oriented molecules from recoiling. This generally takes place by means of oriented crystallization. The extended chain conformation may however also be frozen in between entanglement couplings, which occurs upon craze formation in glassy amorphous polymers. In fact, the extension ratio of the fibrils in such polymers is directly related to the molecular weight between entanglements, as was recently demonstrated by Donald and Kramer [34]. In both crystalline and glassy polymers the fibrils have usually the same morphology, with lateral dimensions in the range of 5 to 30 nm. It has been noticed in crystalline polymers, that the lateral dimensions of the fibrillar entities were reduced when crystallization occurred at lower supercoolings [35]. This implies that the dimensions of the fibrils are more likely to be determined by the flow field in which they are formed rather than by crystallization. Due to the effective orientation of the molecules in the flow field, the free energy of the polymer is raised, primarily as a result of the storage of elastic free energy [36], which permits crystallization to occur at much lower supercoolings [27]. It seems also conceivable that a phase separation occurs at high deformation ratio's of the molecules after which crystallization is induced [37]. Frenkel and Ginzburg [38] noticed in polymer solutions subjected to elongational flow, that above a critical deformation rate, excess solvent is squeezed out.

Although the generation of fibrillar entities is brought about by the flow field, the flow phenomena that are responsible for fibril formation may widely differ in different polymer systems. Fibril formation in glassy polymers was recently [39] argued to be due to a phase transition locally to a rubbery phase. This permits locally a rapid length increase to occur, that is not compensated for by a corresponding area decrement in surrounding regions, thus leading to void formation.

In low concentrated polyethylene solutions fibrillar crystallization is induced at high shear rates in a Couette apparatus [40]. This phenomenon was ascribed to the generation of regions of extensional flow between Taylor vortices [18]. Fibril formation in polymer solutions has also been associated with deformation of droplets in a shear flow field [22, 41].

In more concentrated solutions beyond the point of coil overlap, entanglements start to play a dominant role in the flow behaviour. In such solutions secondary flow phenomena of the inertia type are not likely to occur [4, 17] and fibril formation may be associated with the onset of cluster flow [19–21]. A question that remains to be answered is, why is there a tendency in these originally isotropic solutions to split up into bundle-like flow units if they are subjected to an elongational flow? The answer may again be found in the salient work of Taylor [42]. Taylor showed that the meniscus of a liquid or the interface between two fluids, streaming between parallel plates and on which a negative pressure gradient is working, can break up into "fingers" if a periodic disturbance occurs at the fluid surface (meniscus instability). Also, Glansdorff and Prigogine [43] pointed to the fact that certain hydrodynamic instabilities may lead to a splitting of the fluid front. A similar event may take place at entanglement clusters in flowing concentrated polymer solutions. Recently this work of Taylor [42] was also utilized to account for the fibrillation in crazes in glassy amorphous polymers [44, 45]. According to these investigators [44, 45] fibril diameters are related to the deformation rate during stretching, and higher deformation rates lead to smaller fibril diameters.

Recent reviews on the subject are given by McHugh [46], Barham and Keller [47] Pennings *et al.* [48] and Mackley and Sapsford [49].

3. Experimental details

The linear polyethylene used in the present study was Hi-fax 1900 (from Hercules) with weight average molar mass, $\bar{M}_w = 4 \times 10^6$ and number average molar mass, $\bar{M}_n = 2 \times 10^5$. The following procedure was adopted for the preparation of the polyethylene solutions. The Hi-fax powder and 0.5 wt % antioxidant (i.e. 2,6-di-t-butyl, 4 methylcresol) were added to the paraffin-oil ($\rho = 860\,\mathrm{kg\,m^{-3}}$, viscosity at 20° C of about $7.5 \times 10^{-2}\,\mathrm{Pa \cdot sec}$) at room temperature. Addition of aluminium stearate, if so, also occurred at room temperature. Then, under continuous stirring, the suspension was slowly heated to 150° C. Special care was taken to keep the suspension as homogeneous as possible and to avoid clogging. When the viscosity had sufficiently increased the stirring was stopped to avoid the occurrence of a Weissenberg effect and the solution was kept at 150° C for about 48 h under nitrogen atmosphere. Subsequently the solution was allowed to form a gel by slowly cooling to room temperature and the gel was cut into small pieces prior to extrusion.

Spinning was performed in a Reifenhauser S013-25 extruder through a long conical die ($L = 14.5$ cm, entrance angle $= 6°$, exit diameter $D = 0.8$ or 1.8 mm) at a spinning temperature of 170° C. The filaments were quenched behind the extruder by the surrounding air atmosphere. Stretching of the spinning-line occurred by collecting the as-spun filament on a take-up device at a distance of 1.5 m from the spinneret orifice. The take-up velocity could be varied continuously up to 800 m min^{-1}. Extrusion draw ratio's were determined as the ratio of winding speed and free extrusion rate.

Prior to hot-drawing the solvent was extracted from the gel-filaments in *n*-hexane and the fibres were dried in vacuum. This was found necessary in order to obtain good drawability. Wet-drawing of the fibres was almost impossible due to premature breakage. The extraction procedure with *n*-hexane did not fully remove aluminium stearate from the filaments. With the aid of an analytical reagent, alizarine-red-S dissolved in ammonia [50], it was possible to detect the presence of some aluminium stearate in the extracted as-spun fibres. Hot-drawing was carried out at the optimum drawing temperature of 148° C [8]. Further details of this technique are described elsewhere [7, 8].

The mechanical testing apparatus used was a Zwick Z13B tensile tester operated at a crosshead speed of 12 mm min^{-1} and an original sample length of 25 mm at 20° C. The cross-sectional areas of the fibres were determined from fibre weight and length assuming a density of 1000 kg m^{-3}. Differential scanning calorimetric measurements were conducted on extracted polyethylene gels with a Perkin Elmer DSC II operated at a scan speed of 5° C min^{-1}. The melting temperatures quoted in this paper refer to the end melting temperatures of the thermograms. Scanning electron microscopy was performed with an ISI-DS 130 microscope operated at 40 kV.

4. Results and discussion

The tenacity of oriented polymeric fibres is very sensitive to macroscopic as well as microscopic irregularities, such as diameterfluctuations, entanglements, chain ends, etc. The severeness of flow instabilities during gel-spinning of UHMWPE may therefore be reflected in a reduction of the mechanical properties of the ultimately oriented structures. In the first section the dependence of the strength of the UHMWPE fibres on spinning conditions will be dealt with. In the second part morphological aspects of the as-spun fibres obtained at different flow rates are described. Finally a flow model is presented that accounts for the observed morphologies.

4.1. Tensile strength in relation to spinning flow rates

4.1.1. Free extrusion

The manufacturing of UHMWPE fibres with a strength of 3 to 4 GPa after extraction and hot-drawing, required extrusion speeds of less than about 1.5 m min^{-1} during free extrusion. Higher extrusion speeds resulted in discontinuities in the output and melt fracture. Fig. 1 presents a scanning electron micrograph (SEM) of a typical example of a structurized fibre due to melt fracture. This filament was obtained at an extrusion rate of 3 m min^{-1}.

The most suitable gel concentration to be employed in spinning was 5 wt % polyethylene in paraffin oil. With lower concentrations extensive backflow of solvent was encountered in the extruder. Higher gel concentrations resulted in a reduced strength of the filaments after hot-drawing. Nevertheless fibres with a strength of

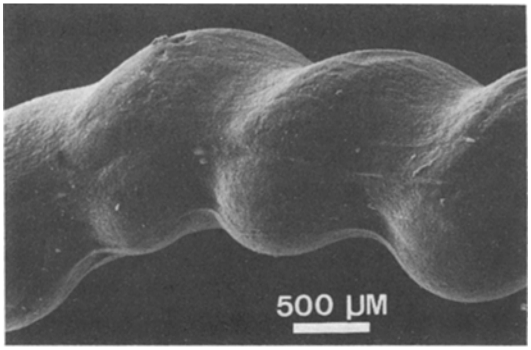

Figure 1 SEM micrograph of an as-spun polyethylene filament revealing melt fracture, produced from a 5 wt % solution of ultra-high molecular weight polyethylene in paraffin oil at a free extrusion rate of 3 m min^{-1}.

2.4 GPa after hot-drawing at 148°C to a draw ratio of 104 could be generated from a 20 wt % solution. This high draw ratio could be accomplished in a two-stage drawing process, i.e. drawing to an initial draw ratio of 35, followed by the maximum additional stretch ratio of about 3 in a second step. However the larger residual entanglement density as compared to filaments from a 5 wt % solution, will limit the strength of these hot-drawn fibres from a 20 wt % solution, in spite of the high draw ratio [8].

4.1.2. Extrudate stretching

Higher spinning rates may be accomplished by elongation of the filaments in the molten state directly behind the extruder. In this way the appearance of melt fracture, at least macroscopically, is avoided [11]. Upon spinning of 5 wt % solutions of UHMWPE in paraffin oil (free extrusion output about 1 m min^{-1}) smooth filaments were obtained by stretching the spinning line with winding speeds up to 60 m min^{-1}. Higher take-up speeds resulted in fracture of the spinning line. With a 20 wt % solution elongation of the extrudate was impossible as a result of immediate fracture of the filaments. Unfortunately the properties of the hot-drawn fibres, that were initially elongated during spinning, are of a minor quality as is shown in Fig. 2. This presents a plot of the tensile strength at break after hot-drawing, σ_b, as a function of the winding speed during extrusion. The tensile strength strongly decreases with increasing take-up speeds, notwithstanding the fact that the overall draw ratio, i.e. during extrusion and hot-drawing together, was not affected by the winding speed. Fig. 3 shows a graph of the extrusion draw ratio λ_{ext} against the maximum attainable ratio λ_{hd} in hot-drawing for UHMWPE fibres spun from a 5 wt % solution. Although a higher take-up speed during spinning strongly reduces the maximum draw ratio in subsequent hot-drawing, the overall draw ratio remains more or less constant at a value of about 150.

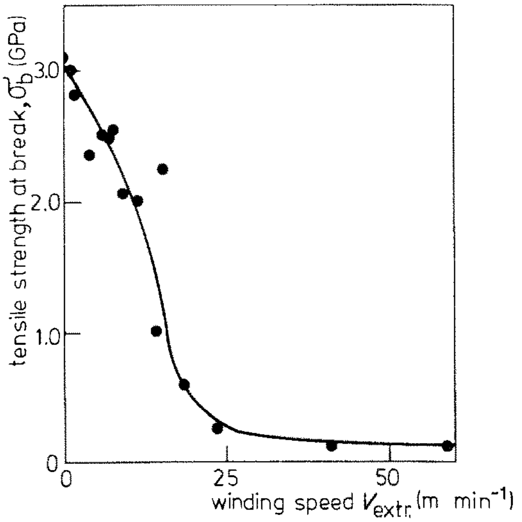

Figure 2 Tensile strength at break, σ_b, after hot-drawing as a function of the winding speed during extrusion of 5 wt % solutions of UHMWPE in paraffin oil.

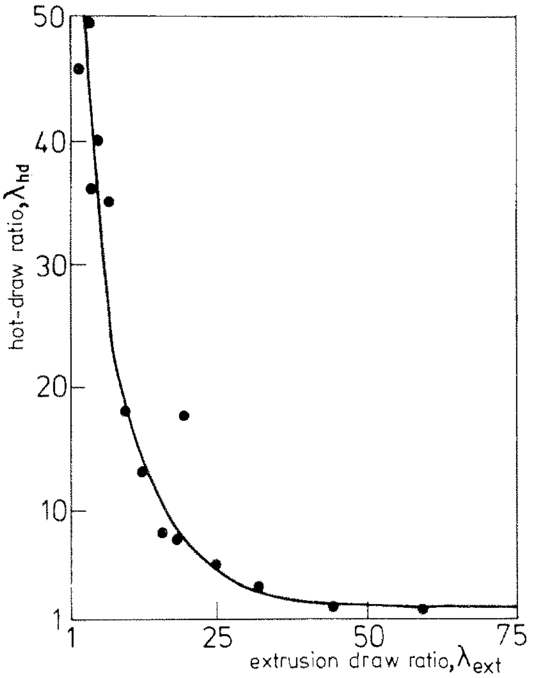

Figure 3 Plot of the extrusion draw ratio λ_{ext} against the maximum attainable draw ratio λ_{hd} in hot-drawing of 5 wt % solutions of UHMWPE in paraffin oil.

We often noticed that after a few minutes of spinning at high take-up speeds filament fracture occurred, after which the extruder output almost stopped. This phenomenon seems to be attributable to the formation of a conically shaped hollow space in the polymer solution just before the die exit. Only a small gel layer alongside the die wall remained present. This situation is schematically depicted in Fig. 4. Such a conically shaped hole was also observed if extrudate stretching had been conducted behind a conventional die with a large entrance angle ($\alpha = 90°$) and an exit diameter of 2 mm. These observations suggest that upon extrudate stretching the filaments are being pulled from the interior of the die, because the supply of new gel material to the die cannot keep up with

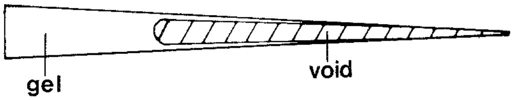

Figure 4 Schematic representation of a longitudinal cross-section of the gelled material in the conical die after fracture of the spinning line had occurred and the extruder was cooled down to room temperature.

the removal of material. The fact that a thin gel layer on the die wall is not removed, indicates that adsorption of the polyethylene molecules on the die wall may play a dominant role in determining the limited transport of gel material in the extruder. This view is corroborated by the fact that after cooling down the extruder the UHMWPE gel heavily stuck to the screw and the die wall.

The very high molecular weight polyethylene will be bound to the die wall according to the train-loop-tail model [51]. The loops of the molecules in this first adsorbed layer act as favourable entanglement sites for other molecules. In such a way an entanglement network is built up with the longest entanglement lifetimes in the direct vicinity of the die wall. The mobility in this entanglement network will thus increase going from the wall to the centre of the die. A similar event will take place in the extruder itself, as a result of which the transport of the UHMWPE solution in the extruder is inhibited. On applying extrudate stretching the molecules in the middle of the die are most easily pulled out of it. These molecules are however connected to the strongly adsorbed, immobile layers alongside the die wall, which guarantees an effective stretching of the entanglement network. On the other hand the relatively low viscosity in the molten state enables the molecules to slip easily out of an entanglement coupling, after which they immediately recoil. This sudden recoiling of molecules may lead to the generation of elastic turbulences [3] and the entanglement structure in the quickly spun filaments will be completely disrupted. Accordingly, no anchoring points are left between the molecules to get them drawn out in subsequent hot-drawing and poor tensile properties are the result. This is in sharp contrast to the hot-drawing of slowly spun filaments, during which the molecules are elongated with entanglements serving as junction points [8]. In this process the extended chain conformation between entanglements is trapped by the orthorhombic crystallites.

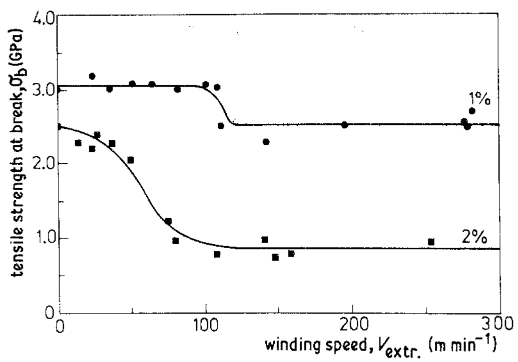

Figure 5 Tensile strength at break, σ_b, after hot-drawing against take-up speed during gel-spinning of UHMWPE at different concentrations of aluminium stearate (wt %) in the spinning solution (Die: $L = 14.5$ cm, $\alpha = 6°$ and $D = 1.8$ mm).

4.1.3. The effect of aluminium stearate

The use of low molecular weight additives can be effective in suppressing extrusion instabilities of polymers [3]. Fig. 5 shows the strength–winding speed relationship for fibres obtained from 5 wt % UHMWPE solutions to which 1 resp. 2 wt % aluminium stearate was added. (Free extrusion output was about 1 m min^{-1}. Aluminium stearate $Al(OOCC_{17}H_{35})_3$ is a widely used lubricant. The presence of 1 wt % aluminium stearate in the spinning solution made it possible to collect gel-filaments with take-up speeds up to 100 m min^{-1}, which still had a strength of 3.0 GPa after hot-drawing. After spinning at higher take-up speeds between 100 and 300 m min^{-1}, the strength of the polyethylene fibres was still 2.5 GPa.

In the course of spinning the aluminium stearate solutions, we noticed that high take-up speeds during extrudate stretching could be maintained for prolonged times without breakage of the spinning line. The tendency to form a conically shaped hole in the die was strongly reduced and the elongation of the spinning line proceeded from a neck region located a few centimetres behind the die exit. Furthermore the gelled materials did not adhere at all to the screw, when the extruder was cooled down. Hence the adsorption of the polyethylene molecules must have been strongly reduced by the aluminium stearate. Presumably the metal ions in the aluminium stearate have a much stronger interaction with the metal surface of the die [52]. Accordingly an adsorbed aluminium stearate layer will be formed between the flowing polymer solution and the die wall. This will promote a more regular flow of the solution with a reduced chance of elastic flow instabilities to be brought about. Moreover, also the solvent viscosity will be substantially increased by the addition of aluminium stearate to the spinning solution. In a more viscous medium the slippage of polyethylene chains through entanglements will be inhibited. The viscosity increasing effect of the aluminium stearate is illustrated by the dissolution of merely aluminium stearate in paraffin oil. Such solutions [52] can already be set to gelate at concentrations higher than 1.5 wt %.

Not only the solvent viscosity is affected by the amount of aluminium stearate in the spinning solution, but also the appearance of the polyethylene gels. Probably for this reason the effect of aluminium stearate on the strength-winding speed relation is bound to an optimal concentration of about 1 wt %. With 2 wt % aluminium stearate in the spinning solution the strength of the hot-drawn polyethylene fibres again decreased with increasing take-up speed, though to a smaller extent than for gel filaments without stearate.

Polyethylene gels containing 2 wt % or more aluminium stearate consisted of poorly coherent, grain-like material. On the other hand at lower concentrations the gels showed a very coherent character. Due to the reduced solvent quality at high stearate concentrations, the interpenetrating action of the polyethylene molecules in solution is inhibited [53]. Concomittantly an entanglement topology results after cooling with far more intramolecular entanglements that are not effective in stretching the molecules. Furthermore, the rate of shear degradation is faster in poor solvents [54]. Presumably for similar reasons, i.e. an ineffective entanglement topology as a result of poor solvents, rather low tenacity values were achieved in the early phase-separation spinning experiments of Zwick [55].

Enlargement of the die exit from 1.8 to 3 mm again led to a decrement in the strength of the quickly spun filaments in spite of the presence of 1 wt % aluminium stearate in the spinning solution (Fig. 6). This may be caused by the delayed quenching of the filaments, due to the large fibre diameters, which promotes a more extensive slippage through entanglements.

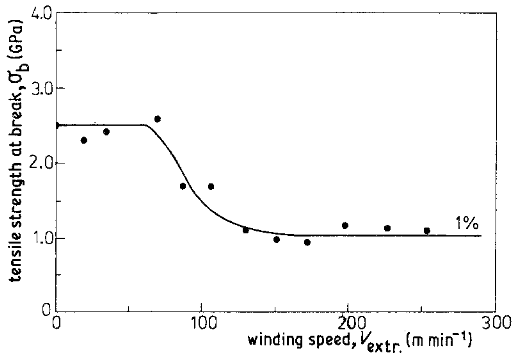

Figure 6 Strength-winding speed relation for 5 wt % UHMWPE solutions containing 1 wt % alumium stearate (Die: $L = 10$ cm, entrangle angle $\alpha = 6°$ and exit diameter $D = 3$ mm).

All the curves in Figs. 5 and 6 reveal a critical winding speed above which the strength attainable after hot-drawing quite suddenly decreases. The nature of this transition is still unknown to us. It may correspond to a point above which the entanglement breakdown increases drastically [29], but also the possibility of a phase-separation at high take-up speeds, e.g. the occurrence of a nematic mesophase [37, 38, 56], is still conceivable. Nevertheless this behaviour must be associated with the fact that extremely high draw ratios could be realized during the spinning and hot-drawing from "stearate" solutions. The overall draw ratios $\lambda_{hd} \times \lambda_{ext}$ were all in the range between 1000 to 1500, as can be seen in Fig. 7, which shows a plot of λ_{nd} as a function of λ_{ext} for UHMWPE solutions containing 1 and 2 wt % aluminium stearate. These high draw ratios are

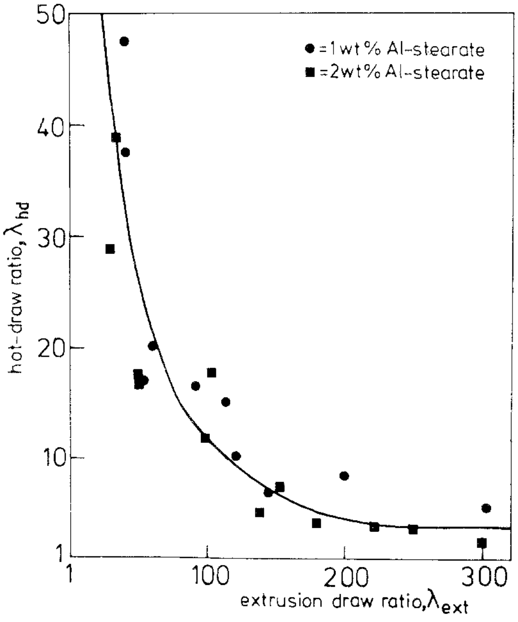

Figure 7 Extrusion draw ratio λ_{ext} against the maximum draw ratio in hot-drawing λ_{hd} for 5 wt % solutions of UHMWPE with 1 resp. 2 wt % aluminium stearate.

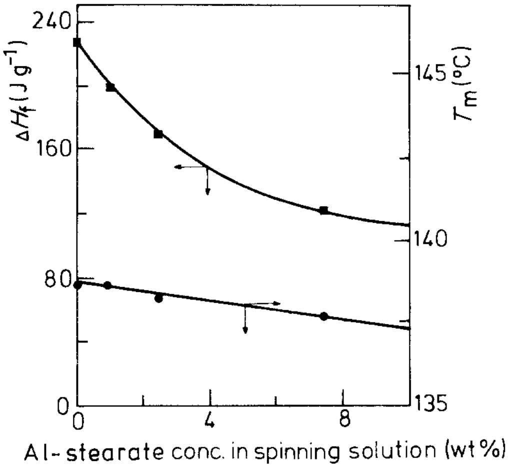

Figure 8 Heat of fusion ΔH_f and end melting temperature of UHMWPE in extracted gels as determined from DSC for different concentrations of aluminium stearate in the spinning solution.

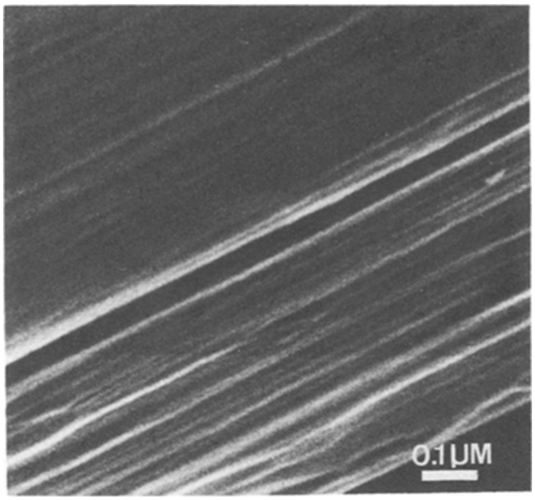

Figure 9 SEM micrograph of a fully hot-drawn fibre ($T_{dr} = 148°$ C) comprising a highly oriented, smooth fibrillar structure.

even very much higher than the ratio of fully extended chain length to the radius of gyration of the random coil molecules [6]. Accordingly, the deformation behaviour cannot be accounted for by an affine deformation of the entanglement network in the filaments and it implies that the flow units, however they may look like, cannot be continuous on a molecular scale, but must have a finite length. Finally it should be remarked that also the crystallinity of the as-spun filaments is reduced by the aluminium stearate. Fig. 8 shows a plot of the heat of fusion ΔH_f and the melting temperature of the UHMWPE as a function of the aluminium stearate concentration in the spinning solution. The melting endotherms were obtained from polyethylene gels that were extracted with *n*-hexane. The reduced crystallinity, due to the aluminium stearate, may be favourable in hot-drawing as it will decrease the resistance towards deformation.

4.2. Morphological features of the as-spun filaments

In this section attention will be paid to the morphological aspects of the polyethylene filaments, produced at different flow conditions during spinning.

The morphology of fully hot-drawn fibres seems to be quite the same, irrespective of the spinning conditions and only highly oriented, smooth fibrillar structures can be seen in scanning electron microscopy. A typical example of a smooth fibre is shown in the scanning electron micrograph of Fig. 9.

The flow conditions during spinning appear to have however a marked effect on the morphology of the as-spun filaments. Fig. 10 shows an SEM micrograph of an extracted as-spun filament obtained from a 5 wt% UHMWPE solution produced at an extrusion rate of 0.75 m min^{-1}, further on referred to as filament A. The structure of this fibre consists of large lamellae interconnected by several fibrils, which illustrate the degree of orien-

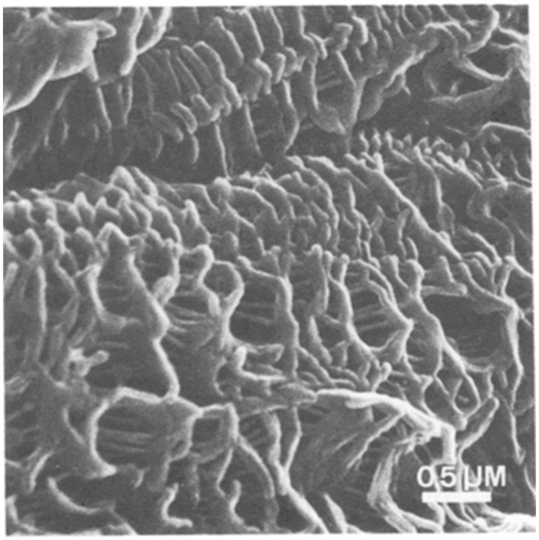

Figure 10 SEM micrograph of an extracted as-spun fibre obtained from a 5 wt% solution of UHMWPE in paraffin oil (extrusion rate 0.75 m min^{-1}).

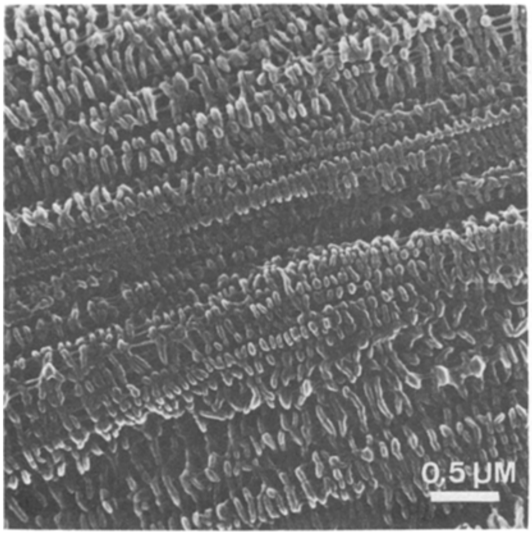

Figure 11 SEM micrograph of an as-spun fibre produced at an extrusion rate of 0.8 m $\min^{-1}$, but elongated to a $\lambda_{ext} = 4$ during spinning.

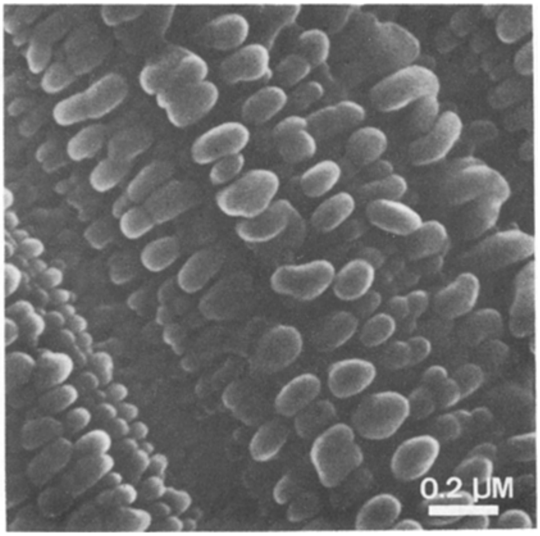

Figure 12 SEM micrograph of an extracted as-spun filament produced at a take-up speed of 18.8 m $\min^{-1}$ without aluminium stearate.

tation that is already accomplished during spinning. Slightly higher deformation rates during spinning already lead to profound changes in the morphology of the as-spun filaments. Fig. 11 presents an SEM micrograph of a fibre that was collected with a take-up speed of 0.8 m $\min^{-1}$, but it was elongated to a $\lambda_{ext} = 4$ during spinning. As compared to the structure of Fig. 10 the lateral dimensions of the lamellae have been strongly reduced, while the interlamellar distances seem to be quite similar.

It should be emphasized at this point that the shish-kebab-like morphologies in the as-spun fibres must have been developed already in the flowing polymer solution during spinning. In the course of the spinning operation quench crystallization was applied. If elongation of the filaments had taken place after crystallization, this would have resulted in increased interlamellar distances, as was recently observed in our laboratory [57]. The crystalline texture in the as-spun filaments should therefore be considered as a solidification of a heterogeneous structure that was already formed in the flowing polyethylene solution.

Since extrudate stretching to high draw ratios without aluminium stearate being present in the spinning solution, strongly reduced the maximum strength attainable in subsequent hot-drawing, we were anxious to see how the morphology in the quickly spun filaments looked like. Fig. 12 shows the morphology of an extracted as-spun filament produced at a winding speed of 18.8 m $\min^{-1}$ ($\lambda_{ext} = 19$). This filament reveals roundly shaped lamellae, whereas almost no separate fibrillar entities can be distinguished. This fibre will further on be referred to as filament B.

Finally, in Fig. 13 the morphology is present of an as-spun fibre, filament C, spun from a solution containing 1 wt % aluminium stearate at a winding speed of 55 m $\min^{-1}$ ($\lambda_{ext} = 55$). Again a shish-kebab structure, can be seen, consisting of a central backbone overgrown with lamellar platelets.

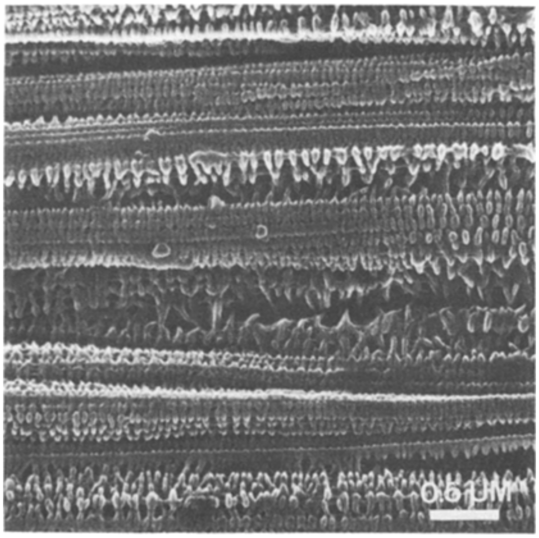

Figure 13 SEM micrograph of an extracted fibre spun from a solution with 1 wt % aluminium stearate at a winding speed of 55 m $\min^{-1}$.

Such shish-kebab morphologies appear to be a general feature in the deformation of entangled UHMWPE solutions [58], since they were also generally observed in stirring-induced fibres [40] and "surface-growth" fibres [59].

Though all the filaments in Figs. 10 to 13 reveal a shish-kebab-like morphology a distinct difference concerns the nature of the backbone material. In the electron micrograph of filament B (Fig. 12) no fibrils can be discerned, while filament A (Fig. 10) reveals fibrillar entities with average lateral dimensions of about 35 nm. The fibre of Fig. 11 shows fibrils with an average width of about 10 nm, and in fibre C (Fig. 13) the width of the fibrils is about 13 nm. This observation implies that the lateral dimensions of the fibrils are inversely proportional to the deformation rate during spinning. Upon craze formation in polycarbonate it was also noticed that the widths of the fibrils formed in the crazes decreased if the samples had been elongated with a larger deformation rate [44, 45]. It supports the view that the dimensions of the structural units in the as-spun filaments are primarily determined by the flow field during spinning and not necessary alone by crystallization.

Upon hot drawing the shish-kebabs in the as-spun fibres are converted into smooth fibrils. Hot-drawing of surface growth shish-kebab fibres also revealed the transformation of the lamellar overgrowth into extended chain fibrils [60]. Hence one would expect the filaments which show the largest amount of lamellar material to be drawn out to the highest draw ratio. Hot-drawing or even drawing at room temperature shows, however, quite opposite results. Fig. 14 presents the stress–strain curves at room temperature of fibres A, B and C. Both the filaments A and C could be elongated about 350%, whereas filament B already fractured at an elongation of 5%. Hot-drawing of filament A showed a maximum draw ratio of 100, for filament B, λ_{hd} was 11 and for filament C a λ_{hd} of 20 was noticed. Accordingly the hot-drawing behaviour cannot be accounted for simply in terms of the crystalline texture of the material. The main factor determining the drawability is presumably the topology of the entanglement network underlying the crystalline texture in the as-spun fibres, which is strongly affected by the flow conditions in the extruder.

4.3. Cluster flow

In the previous section it was concluded that the shish-kebab structures in the as-spun fibres originate from a heterogeneous structure in the UHMWPE solutions during spinning. This phenomenon needs further consideration, in particular since it suggests a possible mechanism underlying the formation of shish-kebabs.

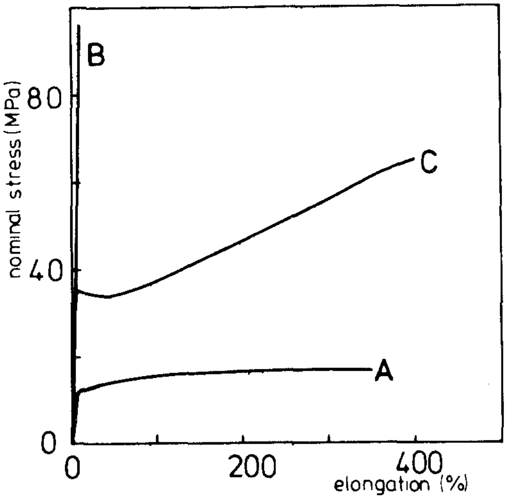

Figure 14 Stress–strain curves of as-spun filaments at room temperature. Filament A was spun at an extrusion rate of 0.75 m min^{-1}, filament B was spun at a take-up speed of 18.8 m min^{-1}. Both fibres A and B were spun from 5 wt % UHMWPE solutions without stearate. Filament C was spun at a winding speed of 55 m min^{-1} from a UHMWPE solution containing 1 wt % Aluminium stearate.

At first we will focus the formation of entangled clusters in the polyethylene solutions. In that respect we should point to the resemblance with early work concerning cluster flow [19–21] and entangled aggregates in polymer solutions subjected to shear flow [23–28]. In the UHMWPE solutions an entanglement network will be formed with a distribution of life-times of the chain-entanglements, mainly dependent on the strand length protruding from an entanglement [61]. Moreover a number of exceptionally long life-time entanglements are formed in the direct vicinity of the die wall, where the polyethylene molecules are strongly adsorbed. Upon free extrusion, even at low flow rates, the entanglement network is already effectively elongated due to the converging flow lines in the die and the attachment of the molecular network to the die wall by adsorption. In this process the molecules will be set in motion especially at those places where the stress is transmitted through the network, i.e. at entanglement sites. Particularly short life-time entanglements can easily migrate through the network, whereas

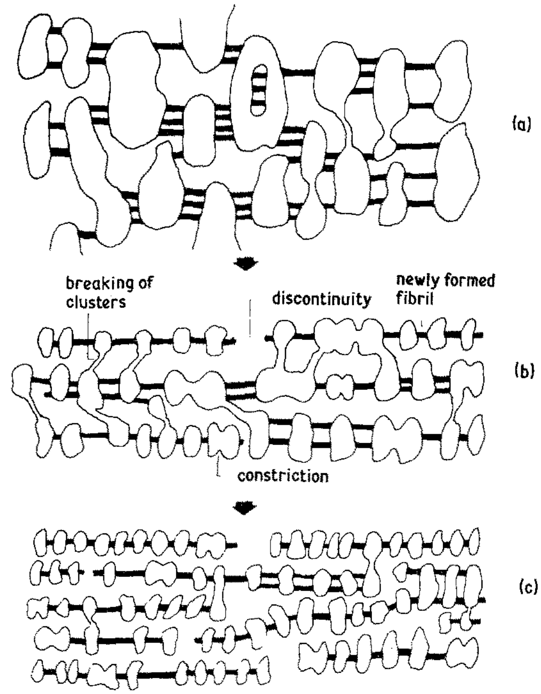

Figure 15 Flow scheme of UHMWPE solutions during gel spinning at increasing flow rates, involving flow units of alternating bundles of elongated molecules and clusters of unoriented molecules.

strongly entangled molecules show a high resistance towards deformation.

Concomittantly the network is locally stretched, during which bundles of molecules are elongated by pulling them out of clusters of unoriented molecules. The entanglements, originally involved in the stretched molecules migrated towards the clusters of unoriented molecules in the course of the stretching process. In such a way an anisotropic structure is developed in the flowing polyethylene solution as is schematically depicted in Fig. 15a. This structure consists of several bundles of elongated molecules protruding from each cluster of unoriented molecules. The elongated bundles are connected to the clusters by entanglement couplings.

The splitting up of the entanglement network being subjected to elongational flow in several bundles of elongated molecules, may possibly proceed by a mechanism analogous to the "meniscus instability", as originally proposed by Taylor [42]. This theory [42] could also account for the observation that the width of the bundles decrease with increasing deformation rate [44, 45]. The large clusters of unoriented molecules may be envisaged as strongly entangled aggregates of elastically inactive loops, dangling chains or loose chain ends and a few tie molecules [61], bridging the cluster to the next elongated bundle. Obviously, the solidification of this heterogeneous structure by crystallization results in a morphology such as is shown in Fig. 10.

Concerning the crystallization in these structures it should be remarked, that the elongated bundles may already have crystallized in the flow field at high temperatures. Due to their extension the conformational entropy of these molecules is strongly reduced [36], while also solvent may be squeezed out of the bundles [38]. As a result oriented crystallization may occur even at temperatures not far below the spinning temperature of 170°C. On subsequent quench crystallization the structure will immediately be completely solidified. On increasing the flow rate, especially the entanglements which connect the unoriented clusters with the oriented bundles, become more and more stressed. However at moderate flow rates these entanglements, in the majority, can resist the drawing forces due to oriented crystallization in the elongated bundles at a short distance behind the die exit. Under such circumstances it will be more easy to deform the unoriented clusters. The solvent that is squeezed out of the bundles of elongated molecules will induce an osmotic pressure in the clusters. As a result these clusters will swell more strongly in the solution and the molecular mobility in the clusters is greatly enhanced. The clusters or unoriented molecules, covering more than one bundle, can thus easily break up in smaller units, due to a sliding motion of the long bundle-like flow units past each other. Additionally new bundles of elongated molecules will be generated by a constriction of the clusters, analogous to the deformation of droplets in a shear flow field, which proceeds by the formation of dumb-bell shaped entities [22]. Furthermore it seems probable that at some places the entanglement connections, between the clusters and the oriented bundles will be broken. This implies flow units of a finite length, that can slide past each other. The adaption of the flow units to increasing flow rates is schematically depicted in Figs. 15b and c. The resulting morphology in the as-spun filaments corresponds to that of Fig. 11.

If extrudate stretching was applied during gel spinning to generate high flow rates in the spinning line, we noticed that the filaments were, to a great extent, pulled from the interior of the die. In the die itself, the temperature is so high that oriented crystallization presumably does not take place, otherwise the die would be plugged up. As a result the flow units, consisting of alternating clusters of unoriented molecules and elongated bundles, will break down more and more. This is because the relatively low viscosity in the molten state, in combination with the high stretch ratios, makes that the molecules in the elongated bundles are easily pulled out of an entanglement, with which they are connected to the unoriented clusters. If such a stretched molecule is pulled out of an entanglement, it will immediately snap back to its random coil conformation, which leads to the generation of elastic turbulences [4, 17]. Additionally, the elastic inhomogeneities caused by the sudden recoiling of molecules can give rise to stress concentrations in neighbouring molecules. Therefore not only disentangling, but also chain scission will take place to some extent [12, 13]. In this way the entanglement connectedness in the as-spun fibres is largely destroyed, which manifests itself in the morphology of the filaments by the absence of separate fibrillar entities (Fig. 12). As a result such fibres show poor drawing properties due to a lack of coherence, since there are no anchoring points left to get the molecules drawn out.

At this point we will concentrate the discussion on the effect of aluminium stearate on the flow behaviour of the UHMWPE solutions. The addition of aluminium stearate to the spinning solution strongly reduced the adsorption of the polyethylene molecules onto the die wall, which means that the flow of the polymer solution approaches more of a plug flow type of behaviour. Consequently the extrudate stretching in these cases occurred completely behind the die exit and thus the extrudate is simultaneously cooled in air, which will promote the trapping of the bundle-like entities by crystallization. Furthermore the solvent viscosity is quite extensively raised in the doped solutions. All these factors make it much more difficult for the elongated molecules in the bundles to slip out of an entanglement, with which they are connected to the unoriented clusters. Accordingly, much longer flow units of alternating randomly oriented clusters and highly oriented bundles of molecules, are preserved in the doped solutions even at extremely high flow rates. The flow in the aluminium stearate doped solutions at high flow rates must proceed by an extensive slippage of these long flow units past each other in view of the extremely high overall draw ratios ranging from 1000 to 1500. The aluminium stearate and solvent located between these long flow units will act as a lubricant in this slippage process, providing a low friction between the bundle-like entities moving past each other. This flow behaviour may be somewhat analogous to the "superplasticity" in metal alloys, which was associated with an apparent Newtonian flow behaviour [63]. In the doped solutions the entanglement connectedness is thus preserved to a great extent even at high flow rates. On subsequent hot-drawing of these as-spun fibres there are sufficient anchoring points left between the molecules to get them fully drawn out, after which the extended chain conformation is trapped by the orthorhombic crystallites [8]. Concomittantly it is possible to make strong fibres from these doped solutions even after spinning at high take-up speeds.

Finally it will be clear that the flow units in the spinning solution upon solidification will give rise to shish-kebab structures in the as-spun fibres. We noticed that higher deformation rates during spinning result in a reduction of the lateral dimensions of both the lamellae and the fibrils. The interlamellar distance alongside the backbones was not affected by the spinning rate. This is in sharp contrast to the elongation of the shish-kebab filaments in the crystalline state, upon which the interlamellar distances are extensively increased [57].

Acknowledgements

This study was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the advancement of Pure Research (ZWO). The authors wish to express their gratitude to Drs E. van der Wilt and H. B. Savenije for their assistance in the experimental work. They would also like to thank B. A. Klazema for his assistance in the SEM experiments. We are indebted to Drs L. Dijkema and Professor Dr Ir. A. A. H. Drinkenburg for their valuable comments.

References

1. W. H. CAROTHERS and J. W. HILL, *J. Amer. Chem. Soc.* **54** (1932) 1557.
2. P. J. FLORY, *ibid.* **67** (1945) 2048.
3. J. L. LEBLANC, *Rubber Chem. Technol.* **54** (1981) 905.
4. H. GIESEKUS, *Rheol. Acta* **5** (1966) 239.
5. P. SMITH, P. J. LEMSTRA, B. KALB and A. J.

PENNINGS, *Polym. Bull.* **1** (1979) 733.
6. B. KALB and A. J. PENNINGS, *J. Mater. Sci.* **15** (1980) 2584.
7. J. SMOOK and M. FLINTERMAN and A. J. PENNINGS, *Polym. Bull.* **2** (1980) 775.
8. J. SMOOK and A. J. PENNINGS, *J. Appl. Polym. Sci.* **27** (1982) 2209.
9. A. SIABICKI, "Fundamentals of Fibre Formation" (J. Wiley and Sons, London, 1976) p. 62, 97.
10. J. P. TORDELLA, *J. Appl. Phys.* **27** (1956) 454.
11. C. D. HAN, "Rheology in Polymer Processing" (Academic Press, New York, 1976) pp. 304–28.
12. A. HAM, "Rehology" Vol. 4, edited by F. R. Eirich (Academic Press, New York, 1967) p. 251.
13. D. E. HANSON, *Polym. Eng. Sci.* **9** (1969) 405.
14. J. H. SOUTHERN and D. R. PAUL, *Polym. Eng. Sci.* **14** (1970) 560.
15. D. R. PAUL and J. H. SOUTHERN, *J. Appl. Polym. Sci.* **19** (1974) 3375.
16. J. A. BRYDSON, "Flow Properties of Polymer Melts" (George Godwin Ltd, London, 1981) p. 89.
17. H. GIESEKUS, *Rheol. Acta* **4** (1965) 85.
18. G. I. TAYLOR, *Phil. Trans.* **A223** (1923) 289.
19. M. MOONEY, "Rheology" Vol. 2, edited by F. R. Eirich (Academic Press, New York, 1958) p. 181.
20. R. B. WILLIAMSON and W. F. BUSSE, *J. Appl. Phys.* **38** (1967) 4187.
21. W. F. BUSSE, *J. Polym. Sci.* **A2, 5** (1967) 1261.
22. H. L. GOLDSMITH and S. G. MASON, "Rheology" Vol. 4, edited by F. R. Eirich (Academic Press, New York, 1967) p. 85.
23. A. PETERLIN and D. T. TURNER, *J. Polym. Sci., Polym. Lett.* **3** (1965) 517.
24. A. PETERLIN, C. QUAN and D. T. TURNER, *J. Polym. Sci., Polym. Lett.* **3** (1965) 521.
25. P. MUNK and A. PETERLIN, *Trans. Soc. Rheol.* **14** (1970) 65.
26. K. A. NARH, P. J. BARHAM and A. KELLER, *Macromolecules* **15** (1982) 464.
27. A. J. PENNINGS, *J. Polym. Sci., Polym. Symp.* **59** (1977) 55.
28. F. C. FRANK, A. KELLER and M. R. MACKLEY, *Polymer* **12** (1971) 467.
29. G. V. VINOGRADOV, *Polymer* **18** (1977) 1275.
30. J. L. WHITE, *Appl. Polym. Symp.* **28** (1973) 155.
31. J. P. TORDELLA, "Rheology" Vol. 5, edited by F. R. Eirich (Academic Press, New York, 1969) p. 57.
32. E. B. BAGLEY and H. P. SCHREIBER, "Rheology" Vol. 5, edited by F. R. EIRICH (Academic Press, New York, 1969) p. 93.
33. G. MARRUCCI, *Polym. Eng. Sci.* **15** (1975) 229.
34. A. M. DONALD and E. J. KRAMER, *J. Polym. Sci., Phys. Ed.* **20** (1982) 899.
35. A. ZWIJNENBURG, P. F. VAN HUTTEN, A. J. PENNINGS and H. D. CHANZY, *Coll. Polym. Sci.* **256** (1978) 729.
36. G. VERSTRATE and W. PHILOPPOFF, *J. Polym. Sci., Polym. Lett.* **12** (1974) 267.
37. S. YA. FRENKEL, "Macromolecular Microsymposia XII and XIII", edited by B. Sedlacek (Butterworths, London, 1973) p. 117.
38. S. YA. FRENKEL and B. M. GINZBURG, Probl. Fiz.–Kim. Mekh. Voloknistykh Poristykh Dispersnykh Struktur, lecture presented at Mater. Konf. Riga (1965).
39. T. JUSKA and I. R. HARRISON, *Polym. Eng. Sci.* **22** (1982) 766.
40. A. J. PENNINGS, J. M. A. A. VAN DER MARK and H. C. BOOIJ, *Kolloid-Z. u.Z. Polymere* **236** (1970) 99.
41. W. GEORGE, *Appl. Polym. Symp.* **27** (1975) 159.
42. G. I. TAYLOR, *Proc. Roy. Soc. Lond.* **A201** (1950) 192.
43. P. GLANSDORFF and I. PRIGOGINE, "Thermodynamic Theory of Structure, Stability and Fluctuations" (Wiley Interscience, London, 1971).
44. A. S. ARGON and M. M. SALAMAR, *Mater. Sci. Eng.* **23** (1950) 219.
45. E. PAREDES and E. W. FISCHER, *Makromol. Chem.* **180** (1979) 2723.
46. A. J. MCHUGH, *Polym. Eng. Sci.* **22** (1982) 15.
47. P. J. BARHAM and A. KELLER, *Plast. Rubber Int.* **6** (1981) 19.
48. A. J. PENNINGS, J. SMOOK, J. DE BOER, S. GOGOLEWSKI and P. F. VAN HUTTEN, *Pure Appl. Chem.* in press.
49. M. R. MACKLEY, G. S. SAPSFORD, "Development in Oriented Polymers-1", edited by I. M. Ward (Applied Science Publishers, London, 1982) p. 201.
50. J. ATACK, *J. Soc. Chem. Ind.* **34** (1915) 936.
51. M. A. COHEN STUART, thesis, Agricultural University, Wageningen, The Netherlands (1980).
52. J. H. BANNON, US Patens 2 766 224 (1956).
53. N. H. LADIZESKY, *J. Lamb. Polym.* **23** (1982) 1765.
54. J. KLEIN, *Macromolecules* **11** (1978) 852.
55. M. M. ZWICK, *Appl. Polym. Symp.* **6** (1967) 109.
56. L. H. SAWYER and W. GEORGE, *J. Polym. Sci., Polym. Lett. Ed.* **16** (1978) 193.
57. C. E. KONING, P. F. VAN HUTTEN and A. J. PENNINGS, *Makromol. Chem. Rapid. Commun.* in press.
58. P. F. VAN HUTTEN, A. J. PENNINGS and A. M. KIEL, *J. Mater. Sci.* **17** (1982) 3525.
59. J. C. M. TORFS and A. J. PENNINGS, *J. Appl. Polym. Sci.* **26** (1981) 303.
60. J. SMOOK, J. C. M. TORFS and A. J. PENNINGS, *Makromol. Chem.* **182** (1981) 3351.
61. F. BUECHE, *J. Chem. Phys.* **48** (1968) 4781.
62. A. PETERLIN, *J. Mater. Sci.* **6** (1971) 490.
63. A. S. KRAUSZ and H. EYRING, "Deformation Kinetics" (J. Wiley and Sons, London, 1975) p. 357.

*Recieved 21 March
and accepted 30 March 1983*