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Stiff and strong polyethylene with shish kebab morphology by continuous melt extrusion

Z. BASHIR, J. A. ODELL, A. KELLER
H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Tyndall Av, Bristol BS8 1TL, UK

In a previous work, it was shown that highly oriented fibres with 10 GPa modulus could be obtained by continuous single-stage melt extrusion of a medium molecular weight polyethylene to which 3% ultra-high molecular weight ($\bar{M}_w \sim 3$ to 5×10^6) material had been added by solution blending. It was demonstrated that a special interlocking shish kebab structure was responsible for the favourable mechanical properties. In the present work, we succeeded in achieving the same effect from an unblended polyethylene by choosing starting materials with an inherently suitable molecular weight distribution. Both the high and low molecular weight tails of the distribution are very influential: the high tail contributes to the formation of extended-chain fibrils (which constitute the backbones of the shish kebabs), while the low tail affects melt extrudability and strength. Melt strength is important because unusually high tensile stresses are required during wind-up. The wind-up stress was measured and found to be an order of magnitude greater than that encountered in conventional melt spinning – where no shish kebabs are formed. The implications of the above findings for polymer processing, crystal morphology and melt rheology are discussed.

1. Background and introduction

In two recent publications [1, 2], we described the production of ultra-high modulus (50 to 100 GPa) plugs and high modulus (~ 10 GPa) fibres from largely lamellar polyethylene. Normally, lamellar polyethylene is associated with low stiffness and various drawing techniques are used to increase the modulus by extending chains [3–6]. However, in our work it was shown that if a special interlocking shish kebab morphology was formed, it was possible to attain high stiffness from a largely lamellar melt-crystallized material. In the first work [1], we showed the formation of highly oriented stiff plugs (5 cm in length) which brought to light this special morphology. In the subsequent work [2], we demonstrated that the high tail of the molecular weight distribution was important, as it was responsible for the formation of the small number of extended-chain core fibrils, which subsequently acted as nuclei for the lamellar crystallization of the remainder of the material. In this second work [2], we deliberately modified the polymer molecular weight distribution by adding 3% ultra-high molecular weight polyethylene (Hostalen GUR 415, $\bar{M}_w \simeq 3$ to 5×10^6) to Rigidex 006-60, a conventional polyethylene with $\bar{M}_w = 130\,000$, and showed that this promoted shish kebab formation. Further, we showed that by extruding this blended polyethylene at a critical temperature and by winding up the extruded filament taut, it was possible to produce the interlocking shish kebab morphology of the plugs in a continuously spun fibre. Conventional melt-spinning yields a largely unoriented fibre with a low modulus of typically 1 GPa; this is subsequently drawn to improve its mechanical properties. With our process, we showed that fibres with moduli of 10 GPa or higher can be extruded in a single-stage, continuous operation [2].

The main drawback of adding Hostalen GUR 415 to conventional molecular weight polyethylene was that it had to be done by solution blending [2]. As this is neither convenient nor practical, we decided to search for polyethylene grades that naturally have the extended high molecular weight tail. Hence the first part of this work looks at the extrusion of various grades of suitably chosen polyethylenes. In the second part, we consider the surprisingly high melt tensile stresses involved during wind-up when shish kebabs are produced. We measure the wind-up stresses during extrusion, and explain the unusual results by using a fibre composite model. Finally, we reassess the molecular weight criteria and establish that the melt spinning of shish kebab fibres is determined in quite a complex way by the detailed molecular weight distribution, especially by the content of both extreme high and low molecular weight tails.

2. Continuous extrusion of high-modulus fibres from polyethylene with an inherent high molecular weight tail

2.1. Materials

The following polyethylenes were selected for initial trials: two ultra-high molecular weight grades Hizex 240M and Hizex 340M (Mitsui Petrochemical Industries), a BP Chemicals Ltd Polymer Grade R, and two commercial grades, Rigidex H020-54P (BP Chemicals Ltd.) and Hostalen GM 9255F (Hoescht). These were chosen on the basis of possessing an extended high molecular weight tail. The molecular weights and distribution curves of these polyethylenes are shown in

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TABLE I Properties of polyethylenes

Polyethylene	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Manufacturer	Comments
Rigidex 006-60	130	19.2	5.9	BP Chemicals Ltd	
Rigidex H020-54P	350	24.4	14.3	BP Chemicals Ltd	A film grade; has high molecular weight tail
Hostalen GM 9255F	282	18.0	15.7	Hoechst	A film grade; has high molecular weight tail
Polymer R	411	73.5	5.6	BP Chemicals Ltd	Has high molecular weight tail
Hizex 240M	1974	226	8.74	Mitsui	An ultra-high molecular weight grade
Hizex 340M	2153	361	6.00	Mitsui	An ultra-high molecular weight grade
Hostalen GUR 415	5000	–	–	Hoechst	An ultra-high molecular weight grade; the exact molecular weight is not known – it is at the limits of the GPC technique
3% GUR 415 + 006-60	205	18.1	11.4		Used by Bashir *et al.* [2]; prepared by solution blending
0.4% GUR 415 + Polymer R	430	91.0	4.73		Solution blended

Table I and Fig. 1. Rigidex 006-60, which has a lower molecular weight and cannot be used by itself to continuously extrude the fibres with the shish kebab morphology [2], and Rigidex 006-60 with added 3% Hostalen GUR 415, have been included in Table I.

2.2. Experimental procedure

Most of the details have been presented before [1, 2] but we will briefly reiterate the method of fibre production. The polyethylene was first sintered in an Instron capillary rheometer (to minimize trapped air bubbles in the extrudate), then melted and extruded at a piston speed of 2 mm min^{-1}. The barrel diameter was 0.9 cm and the capillary had a diameter of 0.85 mm. The capillary length has been shortened here, from the previously used 5 cm [1, 2], to 1 cm. The entrance to the capillary was tapered, as before, with a half cone angle of 45°

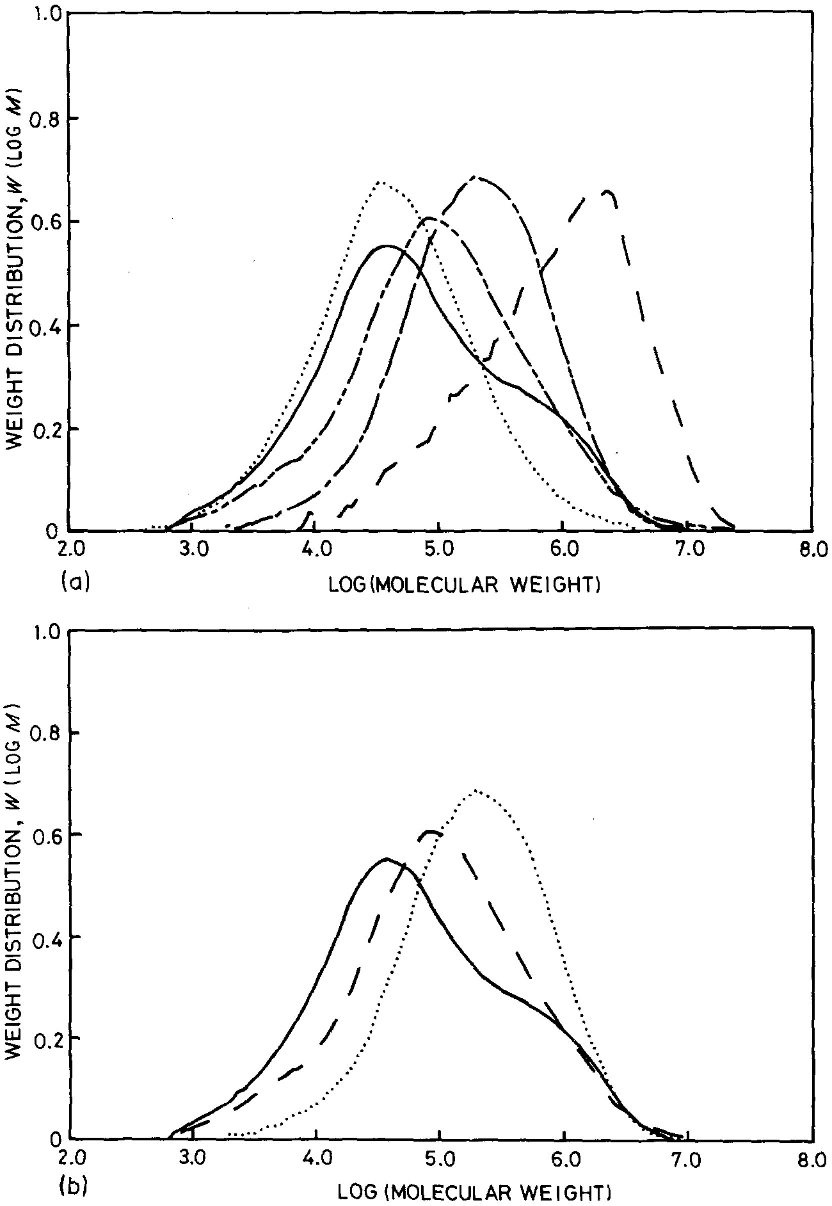

Figure 1 (a) Molecular weight distributions of the polyethylenes used in the extrusion trials. (——) Hostalen GM 9255F, (– – –) Hizex 240 M, (· · ·) 006-60, (- - - -) H020-54P, (–·–) Polymer R. (b) Three of the polyethylenes with extended high molecular weight are presented separately for clarity. (——)Hostalen GM 9255F, (– – –) H020-54P, (· · ·) Polymer R.

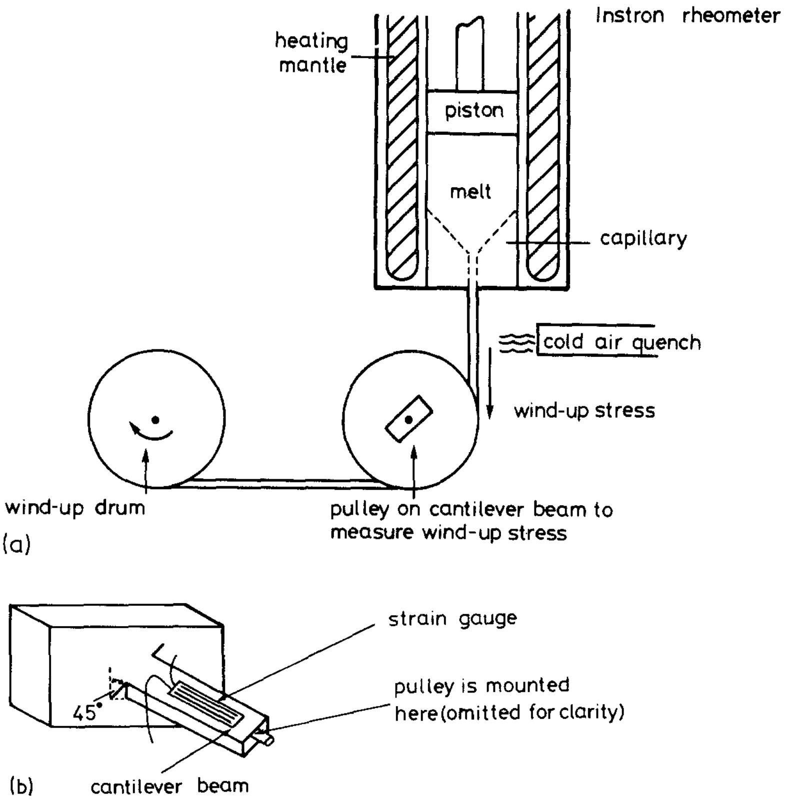

Figure 2 (a) Schematic diagram of extrusion and wind-up apparatus. The resultant force from the combination of extrudate drag and wind-up force is exerted on the cantilever beam on which the pulley is mounted (see b). (b) The deflection of the cantilever due to the resultant force is measured by strain gauges attached to the top and bottom surfaces of the beam. The cantilever was machined from a single block of aluminium and is at 45° to the vertical, so that the resultant force is normal to the surfaces on which the strain gauges are attached.

Initially, the polyethylene was extruded as a smooth filament at 148° C, several degrees above the "self-blocking temperature" [2].* The extrudate was passed over a pulley mounted on a cantilever beam aligned at 45° to the vertical, and was wound up on a drum (Fig. 2). The stress due to the winding up of the filament deflected the cantilever beam, and this deflection was monitored by strain gauges connected to a strain-gauge bridge. The stiffness of the beam had been previously established by a spring balance attached to a wire passed over the pulley in a manner similar to the extruded filament. Hence, we could continuously monitor the force on the fibre as it was wound up; we then used the cross-sectional area of the cooled fibre to convert the wind-up force into a maximum wind-up stress. When the polyethylene was initially extruded at 5 to 10° C above the self-blocking temperature, the wind-up stresses were always low. Then, as the fibre was being wound up, the temperature of the barrel and die was allowed to drop. As the self-blocking temperature was approached, the wind-up stress increased dramatically as the fibre became taut [2]. A steady temperature was chosen for the remainder of the extrusion, where the highest possible wind-up stress could be obtained without filament breakage. The stiffest fibres were obtained under such conditions. For convenience, the wind-up speed was such that there was a spin-line draw ratio of ~ 3 × (this is the ratio of the cross-sectional area of the die to that of the final fibre; thus a draw ratio of 1 × here means that the fibre diameter equals the die diameter).

2.3. Results

2.3.1. Hizex 240M and 340M

Neither of these ultra-high molecular weight polyethylenes (Fig. 1a, Table I) would extrude at

TABLE II Extrusion conditions and mechanical properties of extrudates of various polyethylenes; the die used had a diameter of 0.85 mm and a length of 1 cm, and the extrusion speed was 2 mm min^{-1} piston speed

Polyethylene	Extrusion temperature (° C)	Wind-up stress (MPa)	Fibre Young's modulus (GPa)	Comments
Polymer R	142	50	10 ± 1	Short lengths of 20 GPa modulus fibre were obtainable; fibres had high strength (1 GPa) and were transparent
H020-54P	148	17	3 ± 1	Filament prone to breaking on wind-up; fibres had low strength
GM 9255F	144	10	1.5 ± 1	Filament very prone to breaking on wind-up; fibres had low strength
006-60	138	–	–	Filament cannot be pulled (at this temperature) without breaking [2]
Hizex 240M	135 to 150	–	–	Could not be extruded under these conditions
Hizex 340M	135 to 150	–	–	Could not be extruded under these conditions

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*This is the temperature at which the extrusion pressure starts rising, leading eventually to polymer solidification and blockage of the die. It is 5 to 10° above the ambient melting point of the polymer, under the present extrusion conditions.

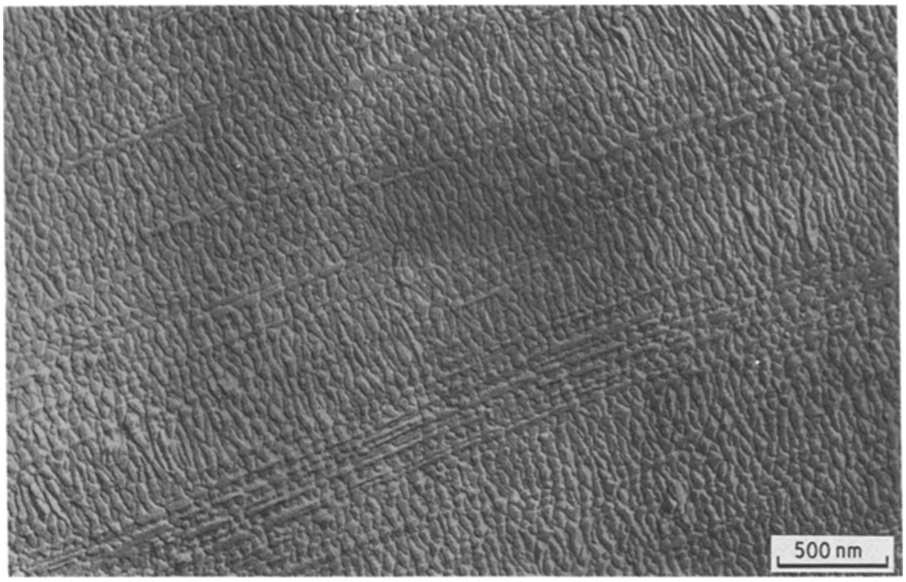

Figure 3 Shish kebabs in a Polymer R fibre with 10 GPa modulus. When the cores are sufficiently close, the lamellar overgrowths taper and intermesh like a zip, which contributes to the high modulus of samples with this morphology. The core direction is from the bottom left to the top right-hand corner. The electron micrograph is from a replica from the central cross-section of the fibre. The replica was prepared after etching the cut fibre in permanganic acid and shadowing with Pt–Pd.

$2\,\mathrm{mm\,min^{-1}}$ piston speed within the range of temperatures explored here (Table II). These grades will extrude at higher temperatures ($\sim 160^\circ$ C) and lower piston speeds, but their behaviour is different and outside the scope of the present work.

2.3.2. *Polymer R*

This polyethylene was the most successful. Fig. 3 shows the typical interlocking shish kebab morphology obtained from Polymer R fibres. Table II presents the spinning conditions of the various polyethylenes together with the mechanical properties of the extrudates. Fig. 4 shows the typical multiple-peak melting endotherms of Polymer R extrudates with the shish kebab morphology. The endotherms were recorded on a Perkin-Elmer Differential Scanning Calorimeter (DSC). Apart from the normal crimping of DSC pans, the fibres were not constrained in any special manner for the DSC. Increasing the heating rate only broadens the peaks slightly. Fig. 5 shows a wide-angle X-ray pattern from a fibre with a modulus of 10 GPa.

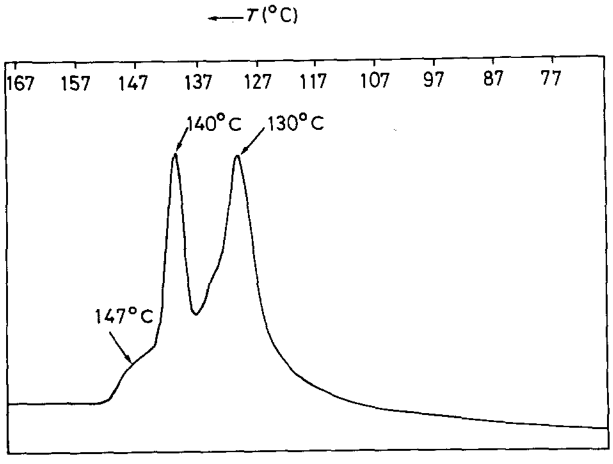

Figure 4 DSC melting endotherm of an as-spun Polymer R fibre with 10 GPa modulus. 3 mm lengths of fibre were cut and placed in pans which were crimped. The fibre is partially constrained and typically shows two or more peaks. After cooling and remelting, only one peak at 130° C is obtained.

2.3.3. *Rigidex H020-54P and Hostalen GM 9255F*

These polyethylenes have built-in extended high molecular weight tails as shown in Fig. 1, and on this basis we expected these to succeed. Although they performed better than 006-60 on its own, neither gave a stiff fibre (see Table II). Unlike Polymer R, these polyethylenes appeared to have low melt strength which led to frequent filament breakage at low stresses near the self-blocking temperature. Electron microscopy showed relatively few shish kebabs, which is consistent with the mechanical properties of these fibres (Table II).

2.4. Discussion

We have succeeded in producing a fibre with a Young's modulus of at least 10 GPa from an unblended polyethylene by a continuous, single-step

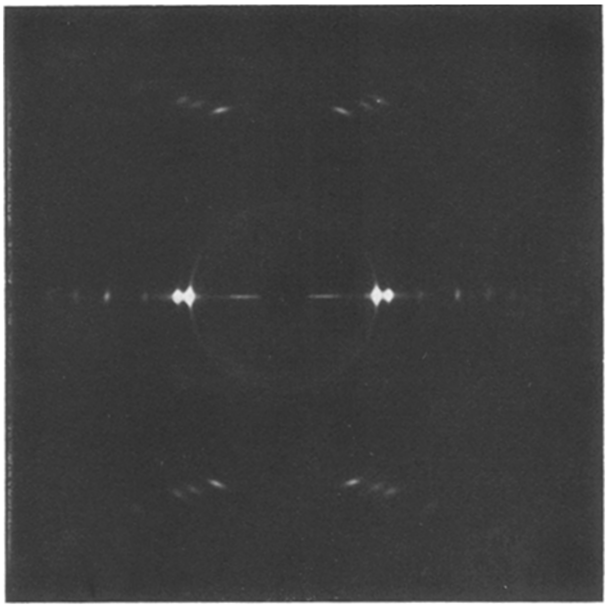

Figure 5 Wide-angle X-ray fibre pattern from as-spun Polymer R fibre with 10 GPa modulus. The pattern is consistent with a fibre where the inner part is densely packed with shish kebabs and the outer skin is less oriented. Fibre axis is vertical. Strongest reflection 1 1 0, spacing 0.413 nm.

melt-extrusion process. This is a considerable advance over the previous work where a small amount of high molecular weight had to be added by solution blending [2].

The fibres from Polymer R were very similar in properties to the fibres made from 3% GUR 415 + Rigidex 006-60 blends in our previous work [2]. They were transparent, stiff, strong and uniform in cross-section. Electron microscopy showed a profusion of shish kebabs (Fig. 3) in the centre of the fibre; once again, the lamellae taper which leads to a zip-like intermeshing when the cores are the optimum distance apart ($\lesssim 150$ nm) [1, 2]. 100 μm thick sections of the fibre viewed under the polarizing microscope showed that the outer skin of the fibre was less oriented than the interior, which probably accounts for the fact that the continuously hauled-off fibres had a lower modulus, in the range 10 to 20 GPa, rather than in the range of 50 to 100 GPa obtained from the plugs [1]. This combination of a highly oriented interior and a less oriented exterior gives the X-ray pattern shown in Fig. 5.

Care has to be taken in the interpretation of the multiple peaks seen in the DSC results in Fig. 4. In our previous work [2], we attributed the higher melting peak to the melting of the extended-chain fibrils and the lower melting peak to the lamellae; the higher melting peak was ~ 3% of the total area of the melting endotherm, and since we added 3% Hostalen GUR 415 to Rigidex 006-60 the conclusion arrived at seemed reasonable. Here, Polymer R oriented fibres show at least two and sometimes three distinct peaks (Fig. 4). However, the areas of the two sharp peaks are approximately equal and if we followed our original interpretation, then these fibres would contain 50% extended-chain core material. But electron micrographs show that this is not the case and that the maximum volume content of cores is less than 5%, the remainder of the material being lamellar. It appears now that our original interpretation was erroneous and based on a fortuitous coincidence. Survey of the literature [7] as well as the experience accumulated in our laboratory [8] indicates that in highly oriented polyethylene, multiple peaks may often be obtained, depending principally upon the constraints put on the sample to prevent contraction. A fibre with shish kebab morphology will show a peak at 130° C and one or more peaks at ~ 140° C or higher (as in Fig. 4) if the fibre is cut into 3 mm long pieces and simply crimped in the DSC pan. The size of the peaks at 140 and 147° C (Fig. 4) can be altered by changing the constraints. For example, winding the fibre round a pin before crimping constrains the fibre from contraction more effectively than simple crimping and markedly increases the size of the peak at 147° C. Hence, there appears to be no simple correlation between the size of the high melting peaks and the number of extended-chain cores. In contrast, an ultra-drawn, well-constrained polyethylene fibre which does not have shish kebabs shows several peaks between 137 and 156° C, but no peak at 130° C. On second melting, all fibres irrespective of initial morphology show one broad peak at 130° C.

In summary, endothermic peaks at ~ 140° C and above are indicators of the presence of highly chain-extended structures but their number, size and position are affected by externally imposed constraints in the course of measurement. A shish kebab morphology such as ours will also show a peak at 130° C (due to the lamellar material), beside the peaks at 140° C and above. Hence, for routine purposes, the DSC trace can still be used as a simple and quick guide to whether a shish kebab morphology is present.

In the next section we will consider the extremely high wind-up stresses encountered when shish kebab fibres are produced from Polymer R. Then, in the last part of the work, we will examine the origin of the seemingly anomalous low melt strength of H020-54P and GM 9255F, which prevented the attainment of the spinning conditions required for the extrusion of shish kebab fibres from these polyethylenes.

3. The tensile stresses during wind-up of the fibre

3.1. Variation of wind-up stress with temperature

For the process to be successful, invariably high wind-up stresses are required. The stiffness of the final fibre increases with increasing wind-up stress, and electron microscopy indicates that the fibres spun at the highest wind-up stresses have the highest number of shish kebabs. Fig. 6 shows the wind-up stress for various polyethylenes plotted as a function of extrusion temperature. Ten degrees above the self-blocking temperature, when there are no extended-chain fibrils present in the melt, the wind-up stress is low, typically less than 5 MPa. However, as the self-blocking temperature is approached, all polyethylenes show a rise in wind-up stress (Fig. 6). The temperature where this rise occurs corresponds to the formation of chain-extended fibrils. In the case of Rigidex 006-60 and Hostalen GM 9255F, the rise leads to filament breakage at very low stresses (~ 10 MPa). Rigidex H020-54P is capable of sustaining higher stresses for short times (dotted line in Fig. 6) but is still prone to breakage. Polymer R, on the other hand, can safely be wound up at 50 MPa wind-up stress. It can be seen from Fig. 6 that a sharp rise in wind-up stress occurs within a small temperature band of ~ 5° C. As it is desirable to spin the fibre at the highest wind-up stress, it therefore proves necessary to accurately control the corresponding optimum temperature within 1 to 2° C.

This phenomenon has not been noticed before for several reasons. For example Ziabicki's treatise [9] on fibre spinning quotes values of wind-up stress of no more than 5 MPa for a variety of polyolefins and polycondensate polymers. His studies refer to standard melt-spinning procedures where polyethylene was extruded at 275° C and a wind-up velocity of 1667 cm sec^{-1} was used, which is many times higher than ours. Clearly, when our Polymer R filament can sustain an extraordinary tensile stress such as 50 MPa it is not behaving like a conventional melt, but rather like a stiff rubber.

Ziabicki [9] found that viscoelastic and aerodynamic forces were the principal contributors to the

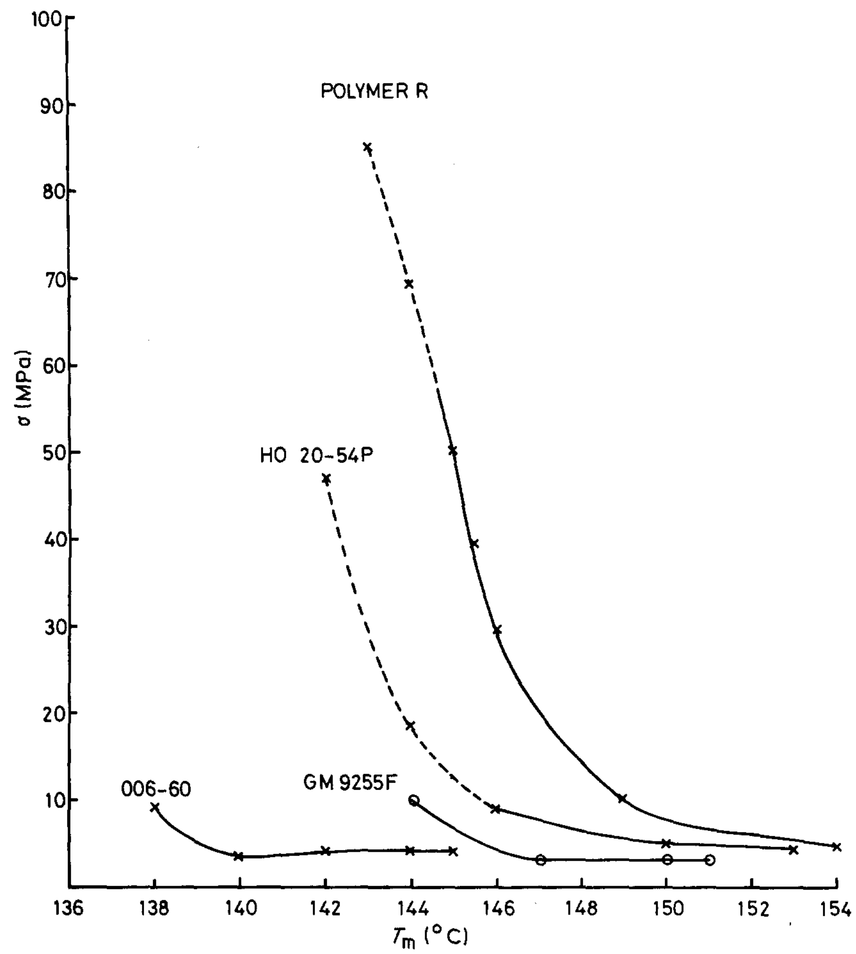

Figure 6 The variation of wind-up stress with extrusion temperature. As the self-blocking temperature is approached, extended-chain fibrils are formed in the melt and the wind-up stress increases. 006-60 and GM 9255F extrudates break at low stresses, while H020-54P can sustain higher stresses for short times. Polymer R extrudates can be wound up continuously at a high wind-up stress of 50 MPa. In dashed regions the extrudate is prone to breaking.

wind-up stress, while the other drag terms (surface and inertial) were negligible; the wind-up stress could be changed by varying parameters such as wind-up velocity. However, in his work the observed wind-up stresses are always less than one-tenth of our values. Fig. 6 shows that even 10° C above the self-blocking temperature, the maximum stresses have been reduced to values comparable to those quoted by Ziabicki at 275° C. This comparatively narrow low-temperature operating band is one of the reasons why these high wind-up stresses, and the consequent products, have not been previously reported. Most past studies of polyolefin extrusion have been carried out at high temperatures specifically to avoid die blockage problems.

We emphasize that even though we are working close to the self-blocking temperature, our process is not a high-temperature solid-state extrusion. Solid-state extrusion processes have been extensively studied. In such studies [10], the die is blocked by solidified polymer and extrusion occurs due to the very high pressures (200 MPa) used thereafter. In contrast the extrusion pressures used in our case are much lower, typically 5 MPa. Further, we observe that die swell occurs when no wind-up is applied, which confirms that the extrudate is largely a melt. The extrusion velocities achieved in solid-state extrusion are also very low [10] compared to ours ($5 \times 10^{-5}\,\mathrm{m\,sec^{-1}}$ versus $4 \times 10^{-3}\,\mathrm{m\,sec^{-1}}$). Finally, the morphology of the extrudate from a solid-state extrusion is similar to that of a highly drawn fibre and is very different from the special shish kebab morphology of our extrudates.

Thus, just above the self-blocking temperature, we believe we have a special situation: we have a filament which is largely molten but one which contains a small concentration ($\sim 2\%$) of extended-chain crystals. The formation of fibrils in a melt subjected to extensional flow was observed optically in our laboratory many years ago [11]. However, the orientation induced was inevitably lost in the final extrudate, and in retrospect we believe that this was because the extrudate was not wound up taut. From our present experience, it is likely that with the low molecular weight polyethylene used in the earlier studies [11], the extrudate could not be pulled near the self-blocking temperature without breaking.

In our continuous process, when the polyethylene reaches the die exit, it is at atmospheric pressure and at temperatures around 142° C. Under these circumstances the extended-chain fibrils will contract and melt, unless the filament is pulled and wound up taut. The high wind-up stresses required are mostly due to the forces needed to counter the contraction of the fibrils.

3.2. The effect of filament draw-down

In the extrusion trials described in the last section, a spin-line draw ratio of $\sim 3\times$ was used. Our intention is to make clear that the orientation produced in our process is due to the formation of fibrils in the extensional flow field at the die entrance, and not due to draw-down of the filament during wind-up.

If we extrude Polymer R under the conditions described before, winding up with a wind-up stress of 50 MPa and a spin-line draw ratio of $3\times$, and then reduce the wind-up speed suddenly so that the spin-line draw ratio is 2 ×, then the wind-up stress drops immediately from 50 MPa to ~5 MPa. However, within 5 min the stress starts to rise again, and not only attains the former value of 50 MPa but exceeds it, reaching values of ~60 MPa; the final extrudate attains a modulus of 12 to 15 GPa and a remarkably high strength of ~1 GPa. In other words, a stiffer and stronger product is obtained by winding up with a lower spin-like draw ratio. Thus, it seems that not only does spin-line drawing not produce much orientation; it even appears to be detrimental. This is probably because excessive draw-down after removal of the die swell causes rupture of the core fibrils.

However, there are problems that can occur if the fibre is wound up too slowly. The extrusion pressure is higher during slow wind-up, and small fluctuations in temperature sometimes cause blockage problems. Hence, for operational convenience, it is best to wind up with some draw-down.

3.3. The extrudate as a fibre composite

In order to account for the high wind-up stresses encountered during wind-up of the filament under our special spinning conditions, we have treated the filament as a fibre composite consisting of extended-chain fibrils embedded in a molten matrix. If the matrix was purely viscous then the extrudate would flow under low tensile stresses. In order to account for the stiffness of the extrudate we must ascribe an elastic response to the molten matrix. The changeover from viscous to elastic response for any entangled polymeric material depends upon the shear rate. In our composite this depends on the length and separation of fibrils. Electron microscopy shows that the length of the fibrils, L_c, is greater than 5 μm whilst the interfibrillar separation ranges from 50 to 150 nm. Such long fibrils and their close separation would imply large local shear rates in the matrix, so that one may assume the matrix behaviour to be primarily elastic. With this assumption, we can use the Cox model [12] for composites and calculate a composite modulus for the extrudate:

$$E_{\text{composite}} = cE_c\left(1 - \frac{\tanh x}{x}\right) + (1 - c)E_{\text{matrix}} \qquad (1)$$

where

$$x = \frac{L_c}{r_c}\left(\frac{G_m}{E_c \ln 2\pi(3c)^{-1/2}}\right)^{1/2}$$

Here $E_c \simeq 300$ GPa = theoretical longitudinal Young's modulus of the crystal [13]; $G_m \simeq 1$ GPa = shear modulus of the matrix [12]; $E_{\text{matrix}} \simeq 3$ GPa = Young's modulus of the matrix (i.e. 3 times shear modulus); L_c is length of fibril; r_c is radius of fibril; $c \simeq 0.02$ = volume fraction of fibrils, estimated from electron micrographs.

Since $E_{\text{matrix}} \ll E_c$, the second term in Equation 1 may be dropped – in other words, we assume that the matrix carries negligible load even though it is the principal constituent of the composite. Thus Equation 1 can be simplified to

$$E_{\text{comp}} = cE_c\left(1 - \frac{\tanh x}{x}\right) \qquad (2)$$

If the fibres are infinitely long, then $(\tanh x/x) \rightarrow 0$ and the equation becomes simply $E_{\text{comp}} = cE_c$. However, L_c/r_c is not infinite. Electron micrographs show that L_c/r_c is often about 200; for $L_c/r_c \simeq 200$, $[1 - (\tanh x/x)] = 0.4$, so that the composite modulus becomes $E_{\text{comp}} \simeq 0.4cE_c$. Inserting values gives $E_{\text{comp}} \simeq 2.4$ GPa as the predicted composite modulus. This is comparable to the modulus of a stiff rubber, which is at least consistent with the observed behaviour of our melt. It should however be noted that the value $E_c \simeq 300$ GPa refers to the room-temperature value, while the actual crystal modulus near the melting point should be lower. Thus the value used for E_c could lead to an overestimate of E_{comp} in our simplified calculation.

Nevertheless, the composite model adequately accounts for the behaviour of the filament in the two regimes. At temperatures much above the self-blocking temperature, $c = 0$ and Equation 2 is inappropriate. That is, in the absence of fibrils, shear rates are low and the matrix behaves as a conventional viscoelastic melt. However, just above the self-blocking temperature, the presence of a very small concentration of extended-chain fibrils is sufficient to make the filament behave like a composite with a modulus comparable to a stiff rubber.

4. The low molecular weight tail

We come back now to the "unsuccessful" polyethylenes, Rigidex H020-54P and Hostalen GM 9255 F, which were expected to succeed because they had an extended high molecular weight tail (Fig. 1b). Fig. 6 shows that there is an upturn in the wind-up stress near the self-blocking temperature. Core fibrils are formed, but the limiting factor is the frequent filament breakage as the wind-up stress increases. In other words, the melt strength of these polyethylenes is much lower than that of Polymer R. Re-examination of the molecular weight distribution (Fig. 1b) shows that H020-54P, GM 9255F and Polymer R all have high molecular weight tails, but the first two also have an extended low molecular weight tail. After careful scrutiny of all the molecular weight parameters and cumulative molecular weight distributions of successful and unsuccessful polyethylenes, we arrived at the hypothesis that the low molecular weight tail is detrimental to melt strength. In what follows, we describe a series of experiments devised to test this hypothesis.

4.1. Extrusion of H020-54P and GM 9255F with the low molecular weight tail removed

In this experiment, our aim was to remove the low molecular weight tail from the unsuccessful polyethylenes to see it this resulted in increased melt strength. The low molecular weight tails were removed by fractionation. Pellets of polyethylene were dissolved with antioxidant in xylene, then cooled to 90°C and crystallized for 6, 8 and 12 h. The low molecular weight material remains in solution at 90°C while the remainder slowly crystallizes. The crystallized material is removed by hot filtration at 90°C. By changing the crystallization temperature and time, various

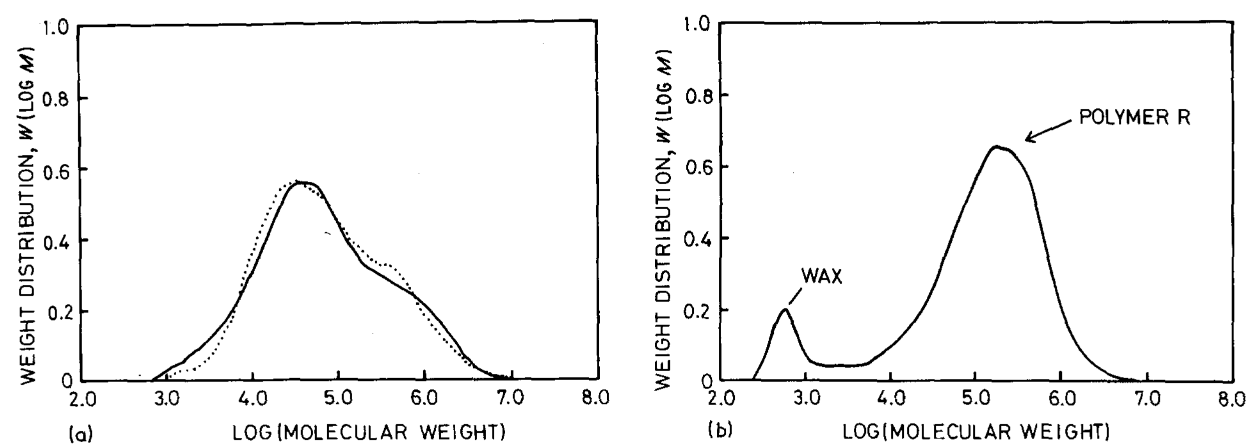

Figure 7 (a) Molecular weight distribution of GM 9255F and GM 9255F fractionated for 8 h at 90° C (dotted line). Some of the low molecular weight material has been removed. Note that the degradation of some high molecular weight material also occurs during fractionation. (b) Molecular weight distribution for 9% paraffin wax + Polymer R blend. The small peak at $M \simeq 600$ is due to the wax. See Fig. 1b for distribution of Polymer R.

amounts of low molecular weight material could be removed.

Extrusion of GM 9255F fractionated at 90° C for 8 h showed that the sustainable wind-up stress increased from 6 MPa (for unfractionated GM 9255F) to 25 MPa and the modulus of the final product increased from 1.5 to 4.9 GPa. The molecular weight distribution curves of the fractionated and unfractionated GM 9255 F are shown in Fig. 7a. Similar results are obtained from H024-54P fractionated at 90° C for 8 h. Wind-up stresses as high as those from Polymer R (~ 50 MPa) were however not obtainable. This is probably due to the fact that the fractionation method, involving holding the polymer in solution at elevated temperatures for several hours, degrades some of the high molecular weight material. This is evident in specimens fractionated at 90° C for 12 h or more; there is significant degradation, which is apparent in the yellowish colour of the filtered polyethylene. On the other hand, with H020-54 P fractionated for 6 h at 90° C we ran into an unexpected problem of a different kind: extrusion occurred in an oscillatory mode, where the die was first blocked temporarily, leading to a rise in extrusion pressure, and was subsequently unblocked by a spurting of polymer. The extrusion pressure oscillated as the die blocked and unblocked repeatedly. This effect, which is most marked with high-density polyethylene (HDPE), has been observed before [14]. With HDPE, the critical shear rate for the onset of oscillatory flow decreases with increasing $\bar{M}_w$, while broadening the molecular weight distribution markedly increases this critical shear rate [14]. In our H020-54P fractionated for 6 h, we have increased the $\bar{M}_w$ and narrowed the molecular weight distribution by removing the low molecular weight, so the oscillatory extrusion behaviour we observed is in accordance with past experience.

4.2. Effect of adding low molecular weight material to a successful polyethylene

In this corollary experiment, 9% paraffin wax ($M \simeq 600$) was added to Polymer R by solution blending, to see if this had the opposite effect to the removal of low molecular weight from the unsuccessful polyethylenes. The molecular weight distribution of the blended polyethylene is shown in Fig. 7b. As expected, the melt strength was decreased and the maximum sustainable wind-up stress was halved from ~ 50 MPa for Polymer R to 25 MPa for the blend. In addition, the blend could be extruded as a smooth filament at higher extrusion velocities than was possible with Polymer R, which indicates that the low molecular weight aids smooth extrusion.

Thus it is evident that the low molecular weight tail is also an influential component of the distribution. Its effect is, however, more complex than we anticipated: presence of the low molecular weight material below $M = 1000$ (essentially the "waxy" component) lowers the melt strength, but on the other hand its presence facilitates smooth extrusion.

4.3. Criteria for choosing a successful polyethylene

It is clear that for the continuous process, the choice of polyethylene is important. We need to consider the unsuccessful polyethylenes in the framework of our fibre composite model. With Polymer R, we assumed that the nature of the matrix did not matter, but for unsuccessful polyethylenes it clearly does. What actually matters is the relative concentration of extended-chain fibrils and the nature of the matrix.

The viscoelastic matrix will exhibit principally elastic behaviour at high strain rates and viscous behaviour at low strain rates. As the molecular weight of the matrix material is decreased, higher strain rates would be required in order to produce an elastic response. Higher strain rates, in this context, can only be realised by an increased fibril concentration, which requires a longer high molecular weight tail.

Table III sums up the qualitative behaviour of various polyethylenes near the self-blocking temperatures and relates it to the concentration of fibrils, the nature of the matrix and the high and low molecular weight tails.

A high molecular weight tail promotes fibril formation while a low molecular weight tail implies low matrix strength. Rigidex 006-60 does not have a high tail, but has a low tail; hence it forms few cores, the matrix does not have a significant shear modulus and consequently it cannot be pulled near the self-blocking temperature [2]. Addition of 3% GUR 415 to 006-60 increases the concentration of fibrils, so that the extrudate can sustain a high tension [2]. Thus, a low molecular weight matrix can support a high tensile stress providing the concentration of fibrils is sufficiently high. Polymer R gives a moderate concentration of fibrils (estimated from micrographs), yet the matrix is "stiffer" as no low tail is present; consequently, the extrudate behaves like a stiff rubber. H020-54P and GM 9255F also produce a moderate number of fibrils as they have as much high molecular weight tail present as Polymer R, but the matrix here is "soft" because of a low molecular weight tail; the concentration of fibrils is not as high as the 3% GUR 415 + 006-60 blend (a system which also has a soft matrix) and so the extrudate breaks easily.

The performance of an already successful polyethylene such as Polymer R can be enhanced by the addition of ultra-high molecular weight Hostalen GUR 415. Smooth extrusion of Polymer R could be obtained after addition of $\sim 0.4\%$ GUR 415 and the extrudate had improved mechanical properties, particularly in terms of strength; for example, strengths of more than 1.2 GPa were attained from these fibres which is quite remarkable because ultra-drawn polyethylenes with 100 GPa moduli have strengths only 3 to 4 times greater [15]. Presumably the intermeshing shish kebab structure promotes high strength because it reduces interfibrillar shear and hinders crack propagation.

We are now in a position to state the molecular weight requirements for choosing a successful polyethylene for the continuous process. Such a polyethylene should have (i) a high molecular weight tail extending beyond 10^6 to 10^7, even though only a low concentration (typically $\sim 3\%$) is needed (the high tail can benefit from "fine tuning" and the presence of a tail in the range of 10^7 to 10^8 is beneficial); (ii) melt strength is an important factor, and this would require the absence of a low molecular weight tail; and (iii) smooth extrusion is of course desirable, but this is not quite so straightforward as it depends on the relative balance of high and low molecular weight tails.

5. Conclusions

The aim of this work has been to continuously extrude high-modulus and high-strength polyethylene without the requirement of prior solution blending, which was a major drawback of our previous work [2]. We have achieved this and hence increased the practical potential of the process.*

In view of the preceding work [2], polyethylenes which intrinsically possessed a high molecular weight tail were chosen for extrusion trials. The original contention that the high molecular weight tail controls the formation of chain-extended fibrils which form the shish kebab backbone remains valid, but these trials show that the high molecular weight tail is a necessary but not a sufficient condition.

For the continuous process, it has become apparent that the low molecular weight tail is also an important factor. The contraction and melting of fibrils is prevented by winding up the filament taut without die-swell. Exceptionally high wind-up stresses are required to prevent this contraction and so melt strength is crucial. The low molecular weight tail has two opposing effects: its presence is generally undesirable because it adversely affects melt strength, but its removal can sometimes pose problems because it could lead to irregular "spurt" extrusion; smooth extrusion depends on the relative balance of high and low molecular weight tails. Thus, the three important and mutually related factors – formation of chain-extended fibrils, melt strength and extrudability – are determined by the high and low molecular weight tails.

We have made it clear that our process is a melt extrusion and not a solid-state extrusion, as the processing conditions and the morphology of the end-product are very different. However, our work differs from conventional melt-spinning procedures described by many workers. In ordinary melt-spinning, the conditions employed are such that the chain extension produced at the die entrance is not preserved at the exit and any orientation that is subsequently produced is due to "spin-off" drawing of the filament, Ziabicki [9] indicates that moderate orientation can be induced by spin-line drawing in the polycondensate polymers like nylon, but very little

TABLE III Behaviour of the filament as a composite (extended chain fibrils in a molten matrix) near the self-blocking temperature. The low molecular weight tail determines the nature of the matrix, while the concentration of fibrils is determined by the amount and extent of the high molecular weight tail. Generally, a soft matrix will lead to low filament strength but this can be compensated by having a higher concentration of fibrils as in the case of 3% GUR + 006-60

Polyethylene	High molecular weight tail	Low molecular weight tail	Concentration of fibrils	Nature of matrix	Filament (composite) strength
006-60	No tail	$M = 560$ present	Low	"Soft"	Low
006-60 + 3% GUR 415 [2]	High tail is introduced	Low tail still present	High	"Soft"	High
Polymer R	High tail present	No low tail; $M < 2000$ not present	Moderate	"Stiff"	High
H020-54P	High tail present	Low tail; $M = 900$ present	Moderate	"Soft"	Low
GM 9255F	High tail present	Low tail; $M = 700$ present	Moderate	"Soft"	Low

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*The matter discussed in this publication is the subject of a patent application in the name of BP Chemicals Ltd.

can be achieved from the higher viscosity polyolefin melts. In fact, the philosophy of melt-spinning has usually been to spin a fibre with little orientation, which is then drawn to produce a typically 10 GPa modulus fibre. Our guideline, on the other hand, has been to create extended-chain fibrils from the extensional flow at the die entrance and use these to create an oriented morphology in the final product. The conventional view on fibre spinning and morphology given in the current textbooks on the subject is embodied in the following extract from Peterlin [16]: "... the orientational effects in fibre spinning must not be overestimated. As a consequence of rather high temperature the orientation of crystallites in a freshly spun fibre is so small that in many cases, particularly at smaller spinning rates, the fibre can be considered as practically unoriented. That means that also the orientation and uncoiling of the macromolecules is hardly sufficient for formation of extended chain crystals and even for markedly influencing the crystallization process. Very probably the main effect of the hydrodynamics of the spinning process is a partial chain alignment which eases the nucleation. The crystals and their superstructure however are not substantially different from those obtained in crystallization from a liquid at rest". Our work clearly counters this conclusion.

The principles outlined here are general and not limited to fibre spinning. It applies to any melt-extrusion process such as injection-moulding, film blowing and the formation of rods where the flow-field during extrusion induces chain extension. For a discontinuous process such as injection moulding (this is similar to the blocked-plug experiment [1]) the high molecular weight tail will be important, but we predict that the low molecular tail will not be critical as the need to support tensile stresses does not arise.

When oriented fibrils are present in the flow, the melt has mechanical properties similar to that of a stiff rubber rather than an ordinary melt. Tensile stresses sustained by the filament are an order of magnitude greater than encountered under normal high-temperature melt-spinning, and have not been observed in previous rheological studies. By using a fibre composite model, we have shown that a small volume fraction of very stiff and very long fibres acting as reinforcing agents can significantly alter the melt behaviour, changing the usual viscous fluid into a stiff rubber.

Regarding future prospects, we have grounds to believe that it is possible to improve processing so as to eventually attain an ultra-high modulus (50 to 100 GPa) in the final extrudate. We have already been able to attain 20 GPa modulus for 10 cm lengths of fibre. The longitudinal tensile strength of 1 GPa already attained with our extruded fibre is perhaps more remarkable. The transverse strength also appears to be favourable as the fibre does not cleave or fibrillate, unlike many ultra-drawn fibres. This surely is a favourable property of the interlocking shish kebab morphology.

We are currently investigating the effects of higher extrusion velocities, of die geometry and of further fine tuning of the molecular weight distribution.

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