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High modulus filaments of polyethylene with lamellar structure by melt processing; the role of the high molecular weight component

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In a previous work it was shown that, by appropriate melt processing, oriented filament polyethylene plugs could be produced such as possessed ultra-high modulus in spite of containing predominantly lamellar structures, the advantageous properties being due to the parallel and interlocking arrangement of the lamellae. In the present work it is demonstrated how the extreme high end of the molecular weight distribution is instrumental in the attainment of such structures. The longest chains, even if present in very small amounts, produce fibrous crystals during extrusion which are inadequate to influence the properties in themselves but by serving as nuclei for lamellar crystallization determine the detailed arrangements and hence the mechanical effectiveness of the lamellar texture. We show examples of how sensitively these structures and the resulting properties can be influenced by slight variations in the high molecular weight content of the material. In fact, materials which otherwise would not produce the desired effect can be made to do so through prior blending with a few percent of ultra high molecular weight material. By judicious creation of bimodal distributions, however, the previous batch production of high modulus plugs with lamellar structures can be turned into a continuous spinning process, thus for the first time achieving the production of oriented, high modulus filaments in the course of a single-step continuous extrusion.

1. Background

The present work has its origin in the attainment of a special kind of oriented polyethylene in these laboratories several years ago [1]. That work indicated new potential for producing polymers with enhanced mechanical properties by controlling the morphology during crystallization; the work reported here extends those ideas by producing a similar morphology in continuously spun polyethylene, yielding fibres with improved mechanical properties compared to normal as-spun polyethylene fibres. For an adequate appreciation of how this was achieved, the background needs recapitulating.

The original work by Odell *et al.* [1] produced oriented plugs (or short fibres) of polyethylene, ~ 5 cm long and 0.8 mm diameter. Briefly, this was achieved by extruding polyethylene just above the melting point through a capillary, and blocking the die exit with a needle valve at a critical temperature and flow velocity, thereby causing crystallization of the melt in the die due to the rapid increase in pressure (see Fig. 1a). These oriented polyethylene plugs (extracted from the die after cooling) had ultra high modulus, ranging between ~ 10 and 100 GPa without, however, possessing the fibrillating behaviour and thermal shrinkage which usually accompanies the attainment of high modulus by a process such as fibre drawing. Even more remarkable was the underlying structure which was found to be essentially lamellar with the lamellae oriented normal to the plug or fibre axis. A largely lamellar structure, representing chain-folded crystallization can, in fact, produce high modulus materials, in contrast to the usual belief that the attainment of high

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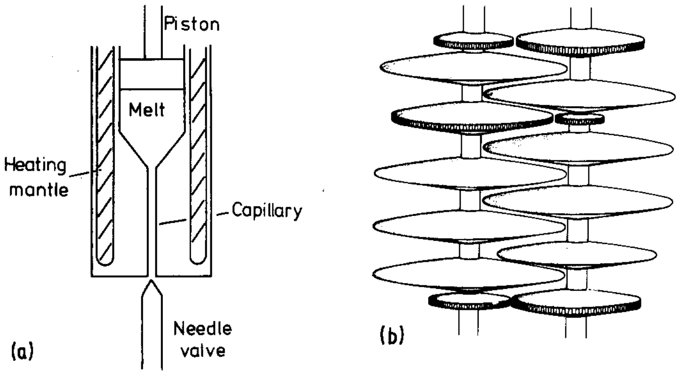

Figure 1 (a) A capillary rheometer with a needle valve to block the die exit was used for preparing oriented plugs of polyethylene. After cooling under pressure, the plug can be pulled out of the die [1]. (b) A diagram of the interpenetrating shish-kebab morphology (the zip fastener structure) consisting of chain extended cores and tapering lamellar overgrowths. Computer generated from experimental data [1].

modulus requires a high level of chain extension. In fact, neutron scattering studies confirmed the essentially unextended overall trajectory of the chains as is to be expected from chain-folded lamellae [2]. The new principles referred to above, relate to the ability of such a largely chain-folded arrangement to produce mechanical properties normally associated with a high degree of chain extension.

1.1. The structure

The parallel lamellar nature of the morphology of these plugs has been mentioned. This in itself is partially the cause of substantial stiffening along the lamellar normal direction (i.e. plug or fibre axis) for if the lamellae are wide enough, the disordered material between the crystal layers (fold surface, interlamellar ties etc.) is unable to contract laterally. Thus, provided the chain stems within the lattice are parallel to the plug axis, we benefit from the high modulus of the oriented chain coupled in series with the bulk modulus of the disordered amorphous material, which is much bigger than the tensile and/or shear modulus usually considered in treating amorphous–crystalline composites. The parallelism of the lamellae, however, is not the full picture. These lamellae are actually overgrowths on central cores created during extrusion and consist of extended chain material; that is, they are the familiar shish-kebabs. The extended chain cores themselves need only be a negligible volume fraction of the total sample and so will not significantly contribute to the modulus; their function is to provide a framework for the oriented parallel growth of the lamellae which satisfy further requirements described below.

Lamellae grown from unoriented melts usually acquire skew molecular configurations (the basal planes slope with respect to the chain stems) and if sufficiently developed laterally, they will start twisting, as they do in spherulites. Both effects are detrimental to stiffness as the former induces shear either on the lamellar or chain level, or both, while the latter destroys the preferential chain orientation itself. Nucleation by a judiciously chosen or created arrangement of core fibrils can avoid both the deleterious effects. If the cores are sufficiently close, the lateral development of the lamellae will remain confined to the direction normal to the cores; conversely if the separation of cores is too wide, growing lamellae will have a chance to twist and diverge. If, in addition, the supercooling of the melt increases during lamellar growth, the lamellar thickness will decrease according to the well known relation between fold length and supercooling [3], resulting in tapering in thickness of the lamellae. The tapering lamellae centred on adjacent cores will thus intermesh (see Fig. 1b) producing a kind of zip fastener effect, to the benefit of the mechanical properties: stiffness along the fibre axis and lateral cohesion are promoted. The overall structural principle can, therefore, be stated as follows: a small amount of parallel oriented core material when favourably spaced, together with the appropriate programming of the crystallization temperature can ensure a particular morphological development of the overwhelming majority of the material growing in lamellar form which is conducive to good mechanical properties.

1.2. Production of the structure of Fig. 1b

The first step in the process is achieved by extruding the melt through a capillary. The extensional flow at the orifice entry produces chain alignment and if the temperature of the melt is in the vicinity of the crystallization temperature, fibrous chain extended crystals are formed in the flowing melt. The essential points in controlling the situation are that there should be such fibrils, they should not melt outside the elongational flow field (for example in the die), they should not be too abundant which leads to blockage of the flow but they should be sufficiently closely spaced to satisfy the structure criterion stated above. The second step is the control of the formation of the lamellar overgrowths. These form in the die, after blockage of the capillary exit, from chains which have either relaxed before crystallization or have never become extended. The gradually increasing supercooling required to produce the tapering of lamellae was achieved by raising the pressure by blocking the die exit while the original elevated temperature of the melt was retained (in this work, we have also achieved the same result alternatively by thermal quenching, instead of pressure quenching).

We add that owing to the higher melting points of fibrous crystals compared to lamellar crystals, pre-existing fibrous polyethylene crystals can be added to the system from without to serve as core fibres for the formation of the structure of Fig. 1b. This technique, which will not be utilized in the present work, is described elsewhere [4].

Although not to feature specifically in the present work, we add for completeness that in structures such as in Fig. 1b there is a very slow subsequent crystallization that proceeds at room temperature after the sample has cooled (or conversely, the first melting starts at unusually low temperatures on heating). We associate this "physical ageing" effect with the crystallization of the last traces of material within the interstices (the lamellar tips), which in turn can have a disproportionate effect on mechanical properties, producing considerable further stiffening on storage of the specimen [1, 4]. We believe, that this may well be the general explanation of the rather surprising 'self stiffening' effects observed under different circumstances in oriented materials [5]; the rather special texture of Fig. 1b has helped to identify its morphological origin.

2. Objectives – plan of work

Our principal objective was to convert the batch process in the previous work [1] into a continuous one capable of technological exploitation, an aim which we achieved eventually. The principal single factor to emerge is that the highest molecular weight component of the distribution can have an effect on the processability, final structure, and properties which is out of proportion to the fraction of material involved. The development of this work has proceeded through three distinct stages which is reflected in the subdivision of the present paper.

1. We found that the original experiment [1] was not reproducible with the same batch of starting material, but has become so on using a fresh batch of material of similar designation of recent manufacture. This experience made us aware of the extreme sensitivity of the whole effect to the presence of the longest molecules, as clearly the latter must have been affected on storage.

2. As a result of (1) we deliberately enhanced the high molecular weight content by suitable blending, which, as we observed, considerably promoted the effect (still as tested on discontinuously produced plugs) in a highly favourable way for our purpose.

3. We utilized the recognition under (2) to develop the attainment of the desired product through a continuous fibre spinning process. It will be stated here that the optimum properties of the batch produced plugs have not yet been achieved (though improvement compared with the usual one stage spinning process is considerable) yet the underlying morphologies have. The latter combined with the new recognition of the extremely sensitive role of the molecular weight distribution raises the promise that further improvement relying on the principles now recognized should only be a matter of development. This should have consequences not only for spinning but for all processes involving extrusion.

The techniques applied for assessment were as before: tensile testing, electronmicroscopy, DSC, X-rays and the polarizing microscope. Concerning electron microscopy, in the previous work samples were etched in chloro-sulphonic acid (the Kanig etch, [6]) and thin sections directly examined in the TEM. Here, we have used the permanganic etch of Olley *et al.* [7] and prepared replicas of the cut interior surfaces for examination by TEM.

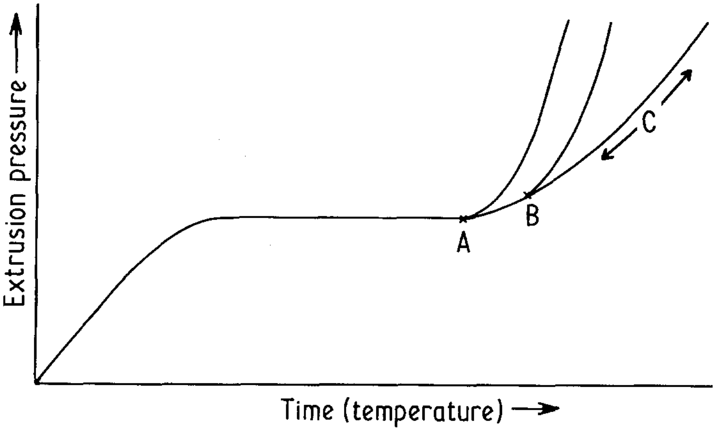

Figure 2 Variation of extrusion pressure with time, as temperature is allowed to drop during extrusion of polyethylene. A: Blocking the die at point A, anticipating pressure rise at the temperature when chain extended fibrils are just formed gives the best, oriented plugs. B: Blocking the die at point B gives a plug which is more oriented and transparent at the die entrance and less so at the die exit end. C: Self-blocking in the absence of external blocking of the die as the temperature drops. The pressure rise rate is slower, hence the quenching rate is not as rapid. The plug is white with little orientation.

For those interested in microscopy, we will be publishing a separate note comparing the advantages and disadvantages of the Olley *et al.* and Kanig etching techniques, using our polyethylene with the shish-kebab morphology to illustrate the differences.

3. The oriented plug experiment repeated

3.1. Materials

The experiment was repeated first with pellets of our old stock of BP Rigidex 9 and subsequently with the new BP grade Rigidex 006-60 as a substitute.

3.2. Experimental details

3.2.1. Method of production of oriented plugs

Pellets of polyethylene were melted in an Instron capillary rheometer at ~ 155° C. The barrel diameter was 0.9 cm, the diameter of the die was 0.85 mm and its length 5 cm. The molten polymer was extruded using piston velocities of 1,2,5 and 10 mm min^{-1}.

The extrusion pressure initially increases followed by a plateau of constant pressure, when the melt is extruding at constant velocity (see Fig. 2). Now, if the temperature is allowed to drop, after a certain time a critical temperature will be reached at which the pressure will start to rise again (Fig. 2). At this stage crystallization of oriented fibrils is taking place increasing the effective melt viscosity and leading to the rise in extrusion pressure. Furthermore, maximum die swell is obtained at this critical point, the extrudate diameter swelling to ~ 3 mm. If nothing further is done, the pressure will continue to rise as all the melt crystallizes leading to self blocking of the die (route C in Fig. 2); the plug left in the die is opaque and unoriented. If the die exit is blocked with a needle valve at point A in Fig. 2 (as soon as the natural rise in pressure is detected) and the piston velocity raised, the consequent rapid rise in pressure leads to pressure-induced crystallization of the rest of the capillary contents in a controlled fashion. If the die exit is blocked slightly later at point B in Fig. 2, the resultant strand will be oriented and stiff at the die entrance end and less oriented and stiff at the die exit end. The reason for this is that the polymer near the exit end of the die solidifies first by self blocking so that the beneficial effects of crystallization under conditions of increasing supercooling do not occur at the bottom of the capillary. In the current experiments the blocking of the die exit was usually in the region of point B, as it is difficult to block precisely at point A. The barrel was cooled to room temperature under 200 MPa pressure and the solidified plug was pulled out of the die, which was lined with a stainless steel tube to prevent adhesion. The most transparent and rigid plugs were those obtained at the highest extrusion velocity (10 mm

min^{-1} piston velocity). The more transparent and rigid end of the plug was used in all cases for comparing morphology.

3.2.2. Morthological examination

This was conducted by transmission electron microscopy. We shall not include the micrographs in this part of the work, but we will merely say whether we obtained the shish kebab morphology of Fig. 1b.

3.3. Results and discussion

We found that our old sample of Rigidex 9 invariably gave plugs that were translucent and not very stiff. Translucency indicates light scattering and points to a morphology of twisting lamellae and this was corroborated by electron microscopy: unlike the previous work with this polymer, the structure of Fig. 1b was not obtained. Since we had used the same conditions as in the previous successful work, we concluded that the most probable reason for this is the degradation of the polymer due to oxidation possibly induced by exposure to light. The degradation, particularly of the high molecular weight end of the distribution can affect the formation of the chain extended cores, necessary for producing the shish-kebab morphology.

On the other hand, when the newer sample of Rigidex 006-60 was substituted for Rigidex 9, we obtained the former satisfactory results of [1], namely stiff and transparent oriented plugs, which showed the tapered shish-kebab morphology of Fig. 1b. Thus we have highlighted the importance not only of using the right molecular weight of polyethylene, but also a fresh batch of the polymer.

4. Effect of high molecular weight on chain extension and pressure crystallization

4.1. Introduction

Studies on chain extension, which have been principally conducted in dilute solutions, show that first the nature of the velocity field in the liquid is important: chain extension takes place significantly in longitudinal velocity gradients, but in transverse velocity gradients, chain extension competes with rotation of the molecule [8–14]. In our system, there is little chain extension in the capillary itself, because of the transverse velocity gradient present. However, in the region where the rheometer barrel tapers into the die, a longitudinal velocity gradient exists and it is here where most of the chain extension occurs. The oriented fibrils that make the backbone of the shish-kebabs are formed in this region, but if the melt is continuously extruded under constant conditions, these backbones contract and remelt when the liquid reaches atmospheric pressure. Secondly, studies have shown that the total strain as well as the strain rate is important in achieving chain extension [8]. The strain in this system is the ratio of the barrel to die diameters. The importance of the strain-rate criterion is as follows: the process of chain extension is competing with the process of chain relaxation, characterized by a relaxation time, τ, and in dilute solution, one condition to be met for high chain extension is $S\tau > 1$, where S is the strain rate or the magnitude of the longitudinal velocity gradient [8, 14].*

Now τ, the relaxation time, depends on the molecular weight. Short molecules have short τ and long molecules longer τ. Thus for a given strain rate, only a certain fraction, the high molecular weight component, will be fully stretched out; for the remaining lower molecular weight component, τ is shorter and hence S may not be sufficiently high to cause chain extension [8, 14]. In the melt, the molecules have longer relaxation times compared to the dilute solution state. One of the ways of increasing the proportion of molecules undergoing chain extension is to increase the strain rate by increasing the extrusion rate. However, this creates problems because high extrusion velocities result in higher melt pressures which would necessitate higher melt temperatures to avoid self blocking of the die. Higher melt temperatures mean shorter relaxation times, so that chain relaxation can become competitive with extension. Furthermore, any extended chain fibrils are even more likely to contract and melt when they come out of the exit at higher temperatures.

Another method of increasing the proportion of molecules undergoing chain extension is to increase the molecular weight. The highest molecular weight linear polyethylenes currently available have $\bar{M}_w$ in the range of $\sim 5 \times 10^6$. However, it is

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*This relaxation time, τ, is that characteristic of small perturbations from the random coil configuration and does not refer to relaxation from the highly extended state, which is expected to be a much slower process [18].

not possible to work directly with such high molecular weight polyethylene as it does not extrude satisfactorily below its degradation temperature. Thus, in this experiment we have kept our standard polyethylene Rigidex 006-60 ($M_w = 130\,000$) but introduced a small amount (~ 3%) by weight of the super high molecular weight ($\bar{M}_w = 5 \times 10^6$) Hostalen GUR 415 to provide extendable material for the nucleating cores in a controlled fashion. This was achieved by forming a solution of the two polymers in xylene and quenching the solution to produce a blend.

Our ideal would be to increase the number of chain extended cores in the cross-section of the capillary and further, we would like these to be distributed uniformly. From our previous work, interbackbone separations of $\leqslant 150$ nm are required for producing the interlocking shish-kebab structure of Fig. 1b. At the moment, we do not know how to control the distribution of cores in a given cross-section of the plug. Even though we have good reason for expecting an addition of an extra high molecular weight component to augment the number of fully extended molecules, we do not know *a priori* whether this will lead to many more cores of the previous thickness (as obtained before with Rigidex 006-60 and Rigidex 9) or to an increase in the thickness of the cores instead of their number.

To show the effect of the addition of the extra high molecular weight to normal Rigidex 006-60, we have first deliberately extruded Rigidex 006-60 at such a low strain rate that very few extended chain cores are formed and then extruded and formed a plug under the same strain rate from the Rigidex 006-60 with the added high molecular weight.

4.2. Materials

An approximately 3% blend of polyethylene Hostalen GUR 415 in polyethylene Rigidex 006-60 was made as follows: 150 mg Hostalen GUR 415, 5 g Rigidex 006-60 pellets and antioxidant were dissolved in 500 m xylene. The mixture was refluxed with stirring at ~ 115 to 120° C for 15 min in an oil bath. Then the solution was taken out and the flask immersed in ice-cold water. After attaining room temperature, the suspension was filtered to remove the solvent. The polyethylene was dried by first squeezing out the solvent between filter papers in a press followed by drying in a vacuum oven at 70° C for 24 h. The dried blend was melted and extruded to form a plug as described in the ensuing section.

4.3. Experimental details and results

4.3.1. Preparation of the plugs

The blend melted and extruded at a piston speed of 2 mm min^{-1} (extrusion speed of 4×10^{-3} m sec^{-1}) in the Instron capillary rheometer. The capillary used was the same as in the previous section. One immediate difference noted due to the presence of the added high molecular weight was an increase in viscosity, necessitating higher temperatures for extrusion in order to prevent self blocking. For example, the rise in extrusion pressure (Fig. 2) due to formation of cores occurs at 148° C for polyethylene Rigidex 006-60 extruded at 10 mm min^{-1} piston speed (melt speed of 2×10^{-2} msec) but for the 3% high molecular weight blend, this occurs at 152° C even when extruded at 2 mm min^{-1} piston speed. The die exit was blocked as before with a needle valve at this critical temperature (152° C) and the pressure was rapidly raised to 200 MPa. The plug was pulled out of the capillary after cooling the rheometer under high pressure to room temperature.

4.3.2. Electron microscopy

Electron micrographs obtained from replicas from the middle of the plug are shown in Fig. 3. The rigid end of the plug was shaved longitudinally in a microtome until its centre was reached and then etched in permanganic acid and shadowed with Pt/Pd. The etching conditions [7] employed were: 1.66 g $KMnO_4$ dissolved in 15 ml sulphuric acid was placed in a test tube with a ground glass stopper and the samples were etched at 60° C in an oil bath for 1 h.

After etching, the sample was washed in dilute sulphuric acid followed by hydrogen peroxide, distilled water and acetone. After drying, the sample was shadowed at an angle of ~ 45° with Pt/Pd and then coated with carbon. Next, a layer of polyacrylic acid was placed on the etched and shadowed surface and then dried in a vacuum oven at room temperature. The solidified polyacrylic acid layer can be peeled off with the help of a razor blade when dry, thereby obtaining a replica of the etched surface. When these peelings are placed in distilled water, the polyacrylic acid dissolves. The replicas with attached carbon film are left floating on the water and can be picked up on microscope grids.

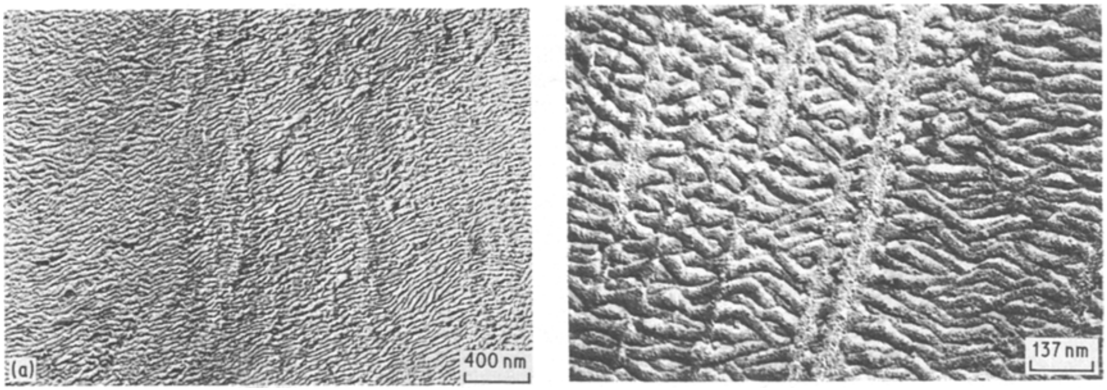

Figure 3 (a) Typical morphology of Rigidex 006-60 plug, formed by extruding at a low strain rate (melt velocity of 4×10^{-3} m $\sec^{-1}$. Replica from central cross-section of strand, prepared after etching in permanganic acid. (b) Addition of ~ 3% high molecular weight GUR 415 to Rigidex 006-60 produces a typical shish-kebab morphology in a plug formed at the same extrusion rate as in (a).

4.4. Discussion

The plug from the high molecular weight blend was stiff and quite transparent. This must be contrasted with a Rigidex 006-60 plug formed by extrusion at the same piston velocity of 2 mm $\min^{-1}$ and a temperature of 144° C. Such a sample is not rigid and is translucent. The shish-kebab morphology of Fig. 1b can of course be made to predominate by extruding the Rigidex 006-60 melt at higher extrusion speeds than used here and this has been described in the first part of this work.

In the Rigidex 006-60 plug formed here by extrusion at low velocity, it is difficult to find any shish-kebabs and the sample has predominantly disoriented lamellar morphology, as shown in Fig. 3a. In contrast, a plug made at the same low extrusion speed from the high molecular weight doped Rigidex 006-60 blend show extensive areas containing shish-kebabs as in Fig. 3b. The low strain rate employed when extruding at 2 mm $\min^{-1}$ piston speed is clearly not sufficient to produce many chain extended crystals in Rigidex 006-60, but is evidently sufficient to extend just the high molecular weight component of the blend. Once again, the cores appear to be randomly distributed, with intermeshing of lamellae where the cores are less than 150 nm apart.

Our belief that it is the high molecular weight tail of the molecular weight distribution that becomes extended and forms the chain extended areas is borne out by the dramatic difference in morphology (Fig. 3) between Rigidex 006-60 plugs and the ~ 3% high molecular weight–Rigidex 006-60 blend plugs produced under the same strain rates. Thus the introduction of a very small amount of very high molecular weight into the distribution drastically alters polymer processing as well as the end product, to an extent hitherto unsuspected. This opens an area of research on the effect of the natural high molecular weight tail in a bulk synthetic polymer, as well as the effect of introducing a sharply differing high molecular weight component separately. In the next part of the work, we look at the effect of the added high molecular weight component on one polymer processing technique, fibre spinning, and indicate that the artificial creation of a bimodal molecular weight distribution can enable the continuous spinning of fibres with the morphology of Fig. 1b together with the beneficial effects upon mechanical properties that ensue from it.

5. Continuous spinning of an oriented fibre from polyethylene with added high molecular weight fraction

5.1. Introduction

So far, we have dealt with the production of high modulus plugs of polyethylene and explained the properties by the interpenetrating shish-kebab morphology [1]. Although the process yields a desirable product in terms of mechanical properties, it is laborious and discontinuous. On the other hand, flexible chain polymer melts have been previously extruded continuously into filaments but have usually resulted in little orien-

TABLE I Spinning conditions

Polyethylene	Melt extrusion speed (m sec^{-1})	Wind-up speed (m sec^{-1})	Self blocking temperature (° C)	Spinning temperature (° C)	Comments
Rigidex 006-60	4×10^{-3}	–	145.5	146.5	Die swell, but extrudate cannot be wound up as melt will not sustain tension.
	4×10^{-3}	$\gg 4 \times 10^{-3}$ Rigidex 006-60	145.5	150	Melt draws down; fibre diameter $\ll$ die diameter. Fibre has little orientation.
3% Hostalen GUR 415/Rigidex 006-60	4×10^{-3}	$\sim 4 \times 10^{-3}$	152	153	Die swell. Filament can sustain high tension. Spinning is stable. Fibre diameter slightly less than die diameter.
3% Hostalen GUR 415/Rigidex 006-60	10^{-2}	$\sim 10^{-2}$	152	153	Die swell. Filament can sustain high tension. Spinning is stable. Fibre diameter slightly less than die diameter.

tation in the as-spun product [8, 15]. But as Marrucci indicates [15] in an article on extensional flow, there is no *a priori* reason for not producing an as-spun oriented fibre. Chain extension takes place in the region of the capillary entrance and it is a matter of retaining the orientation and crystallizing it in the filament. Hitherto, spinning temperatures and cooling conditions that are practical have led to loss of orientation. If the temperature is too high, no extended chain fibrils form, or if they do, they rapidly melt. As we have seen chain extended fibrils do form during extrusion if the temperature is low enough (just above self blocking) and by rapid quenching (by increasing pressure) a morphology conducive to high tensile modulus is obtained.

It is natural to attempt extruding conventional molecular weight distribution polyethylene just above the self blocking temperature, winding up the product and using a temperature quench instead of a pressure quench to help retain the orientation. However, we found it proved impossible to retain any significant orientation in the extrudate. We felt there was a chance of retaining the shish-kebab morphology in the as-spun fibre by melt spinning the ~ 3% Hostalen GUR 415/Rigidex 006-60 blend just above self-blocking temperature and cooling with a stream of cold air. Our reasoning is based on a well known property of highly oriented fibrous crystals: owing to their superheatability, they melt at ~ 160° C, which is 20 to 25° C higher than normal [16]. Our optical microscope observations of the oriented strands made from the high molecular weight blends had also shown that the cores survive (the birefringence does not disappear) at temperatures up to about 160° C.

In what follows we describe the spinning of fibres from both Rigidex 006-60 and the special high molecular blends used previously.

5.2. The method of spinning

The melt was extruded through the Instron capillary rheometer with a die, 0.85 mm diameter and 5 cm long. The filament was passed over a pulley and then wound up on a motor driven drum. The thread was quenched by cold air from a pipette directed ~ 2 cm from the die exit. The extrusion conditions are shown in Table I.

Conventional Rigidex 006-60 was extruded at just above the self blocking temperature (see Table I) at a melt speed of 4×10^{-3} m sec^{-1}. There is maximum die swell just before self blocking and we know from the previous experiments that chain extended fibrils are present, for if the die is blocked with a needle valve at this point shish-kebabs are retained in the plug in the capillary. However, when we attempted to pull the extrudate in order to spool it on the wind-up system, we invariably found that it would not draw or sustain a tension, highlighting the difficulties of spinning conventional molecular weight distribution polymers near the self-blocking temperature (145.5° C). When the temperature is raised to 150° C (Table I) and the melt extruded, there is less die swell. Now the melt can be pulled, spooled and wound up. If the take-up drum speed is increased above the melt exit velocity, the fibre will draw down to a diameter smaller than the die diameter. The spinning line is invariably slack and increasing the tension will cause the fibre to draw down in diameter until it breaks. This, of course, is conventional fibre spinning. The as-spun fibre is white, has little orientation and has low modulus (Table II). In conventional fibre spinning the chain extension produced by the longitudinal velocity gradient at the die entrance [8] is invariably lost by the time of exit at practical spinning temperatures. When the fibre is drawn down below the die diameter during spinning, there is a subsidiary axial extensional flow present from the die exit to the point where the fibre solidifies. However, not much orientation is produced in this way as the draw ratios (die diameter to final fibre diameter) are low; before high draw ratios can be attained the fibre breaks owing to the increase in melt tensile stress.

In contrast to the above, there is a marked difference in the spinning behaviour of the high molecular weight blend. Once again, there is maximum die swell just above self-blocking temperature but due to the increase in viscosity, the self-blocking temperature is much higher for the same extrusion rate compared to Rigidex 006-60. The most important difference is that whereas Rigidex 006-60 melt cannot be pulled without breaking if extruded just above the self-blocking temperature, the blend melt can sustain a very high tension and can be pulled and wound up. As the wind up motor speed is increased the die swell is lost and the filament thins down to approximately the die diameter. (If wind up speed is increased further, the filament will not reduce much more in diameter, the tension on the line increases and finally it ruptures.) At this stage the fibre is translucent. However, if now a stream of cold air is directed at the taut fibre as it is wound up, through a pipette, ~ 2 cm below the die exit, the fibre becomes transparent. It is this as-spun fibre with a high degree of transparency and orientation that we have used for further analysis.

During the spinning of the blend, close monitoring of the operational variables is necessary. The blend may be extruded very close to the self-blocking temperature, provided a tension is maintained on the extrudate; otherwise the extrusion pressure creeps up causing solidification of the polymer in the capillary. If a tension is maintained on the fibre the extrusion pressure will not rise, and self blocking will not occur. For high spinning speeds, it is most practical to start with a low extrusion rate, spool the fibre first and then increase the piston velocity. The extrusion pressure will momentarily rise, and the die swell increases as the fibre goes slack; however, if the take-up speed is increased immediately, so that there is renewed tension on the line, the extrusion pressure will settle down and there will not be any blockage problems. To sum up, for successful spinning of a relatively transparent and stiff fibre, three conditions have to be met: (i) the blend is extruded at or slightly above self-blocking temperature; (ii) the filament is wound up taut with no die swell left; and (iii) the filament is cooled during spinning.

5.3. Morphology and properties of fibres spun from high molecular blends

The electron micrograph shown in Fig. 4 of the fibre spun from the blend clearly indicate the presence of shish-kebabs which are similar to the ones from the oriented plugs. Again intermeshing of lamellae occurs when the cores are far apart. This structure is different from the morphology of as-spun Rigidex 006-60, where no shish-kebabs are present. We have succeeded in our aim of continuously producing a filament

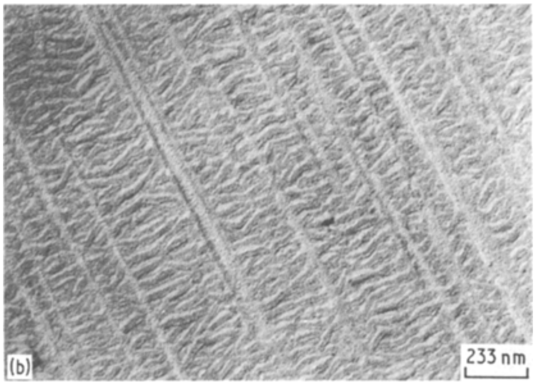

Figure 4 Typical interpenetrating shish-kebab morphology (cf. Fig. 1b) of as-spun fibre from ~ 3% high molecular weight/Rigidex 006-60 blend. This is a replica taken from a central cross-section of the fibre after etching in permanganic acid. On the left, the cores are sufficiently close together so that the lamellar overgrowths taper and interpenetrate but from the middle to the right of the picture, the cores are far apart leading to lamellar twisting and disorientation.

TABLE II Extensional moduli of as-spun polyethylene fibres

Polyethylene	Gauge length (cm)	Extensional modulus ($\mathrm{N\,m^{-2}}$)	Comments
Rigidex 006-60	10	$(5\text{-}7) \times 10^8$	Spun at 150° C Little orientation; see Table I
3% Hostalen GUR 415/Rigidex 006-60	10	3×10^9	Fibre was extruded at $4 \times 10^{-3}\,\mathrm{m\,sec^{-1}}$; see Table I
3% Hostalen GUR 415/ Rigidex 006-60	10	10^{10}	Fibre was extruded at $10^{-2}\,\mathrm{m\,sec^{-1}}$; see Table I

Note: Owing to slight non-uniformity of fibres, the cross-sectional area was determined by weighing the gauge length and using a density of $0.93\,\mathrm{g\,cm^{-3}}$.

of polyethylene that retains the shish-kebab morphology.

Transparency of the fibre is often reduced by an outer sheath of less oriented material. This transcrystalline exterior is apparent when thin sections of the fibre are viewed in the polarizing microscope. Hot-stage microscopy showed three stages in the melting of these fibres. Between 130 and 135° C, the outer transcrystalline sheath melts and interference colours appear at ~ 135° C. The value of the birefringence, determined from thin central sections of the fibre, was 0.04 which is close to that expected from completely oriented polyethylene (0.06). Between 135 and 140° C the birefringence decreases through many orders as the lamellar overgrowths melt leaving at 140° C a small retardation (a low order white) due to fibrils composed of aggregates of cores. The residual retardation is approximately 3% of the initial value, which is consistent with our belief that the cores are composed of essentially all the added high molecular weight component. This residual birefringence usually persists up to temperatures of 160° C, but sometimes it can remain until 200° C as the apparent melting point of the fibrils is influenced by the constraints preventing the sample from shrinking. If the fibre is heated up to a temperature where all birefringence is lost (usually higher than ~ 160° C), and then cooled, it will crystallize spherulitically; on the other hand, if the fibre is heated to 140 to 150° C and then cooled, first the interference colours reappear at ~ 127° C as the birefringence increases when the lamellar overgrowths grow back on to the cores and then the transcrystalline surface layer grows as the temperature drops. The melting behaviour of these figures is distinctly different from conventional as spun Rigidex 006-60 fibres which melt at 133 to 136° C and crystallize spherulitically afterwards.

The melting behaviour of the as-spun fibres was also studied with a differential scanning calorimeter (Perkin and Elmer DSC IIB) and the relevant traces are shown in Fig. 5. Fig. 5a shows the melting behaviour of the Rigidex 006-60 with added high molecular weight, immediately after solution preparation, filtering and drying. There is only one broad melting peak, similar to the one observed with pellets of Rigidex 006-60. However, after spinning this high molecular weight blend into an oriented fibre, the melting behaviour invariably shows two peaks consisting of one main peak formed from the melting of the lamellae and a subsidary peak at a higher temperature (Fig. 5b), which can be attributed to the melting of the cores. If the sample is cooled after heating to 180° C and remelted (Fig. 5c), only one broad peak remains; clearly the shish-kebab morphology is largely lost during recrystallization after heating above 160° C.

We also draw attention to the fact that the presence of two melting peaks was shown by the oriented plugs made previously from Rigidex 9 and now from Rigidex 006-60. Details of the melting behaviour of the plugs was described in the previous publication [1] and will not be repeated here. In contrast, the largely unoriented, low modulus, as-spun fibres made from Rigidex 006-60 (see Table II for spinning conditions) which have no shish-kebab morphology only show one broad melting peak (Fig. 5d). Thus a two-peak melting behaviour seems to go hand-in-hand with a shish-kebab morphology, as shown by the oriented Rigidex plugs and also by the as-spun fibre made

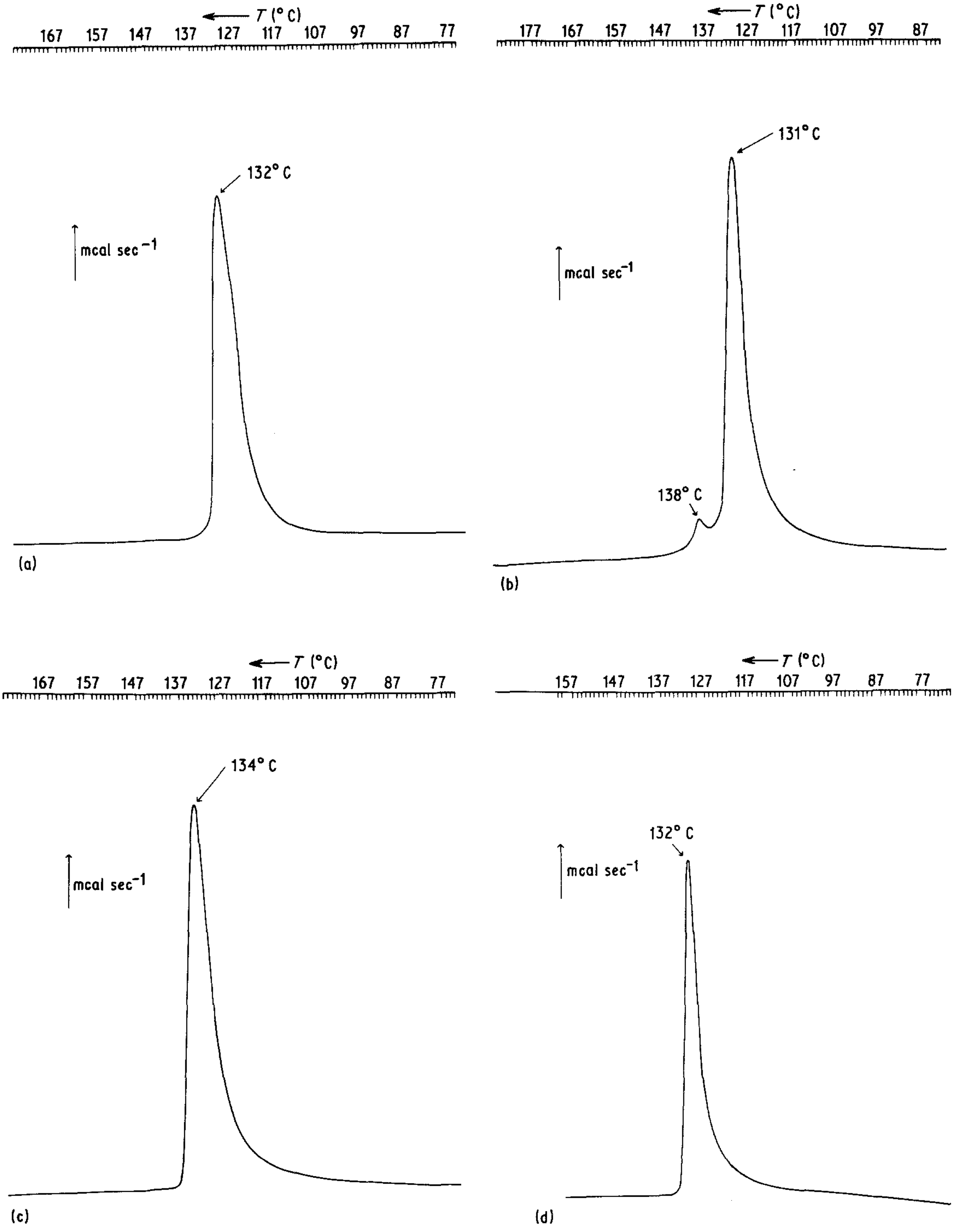

Figure 5 DSC endotherms of melting. The heating rate was 10° C min^{-1} (a) The melting endotherm of ~ 3% Hostalen GUR 415/Rigidex 006-60 blend after preparation from solution and before spinning. (b) The melting of the as-spun fibre made from the 3% Hostalen GUR 415/Rigidex 006-60 blend, showing two peaks resulting from the melting of the lamellar overgrowths (131° C) and from the melting of the cores (138° C). (c) The sample of (b) was cooled to 25° C at 10° C min^{-1} and remelted. Only one peak is now obtained, as the cores have been melted out. (d) The melting endotherm of a typical as spun fibre from conventional Rigidex 006-60. The shish-kebab morphology is absent and only one broad peak is obtained.

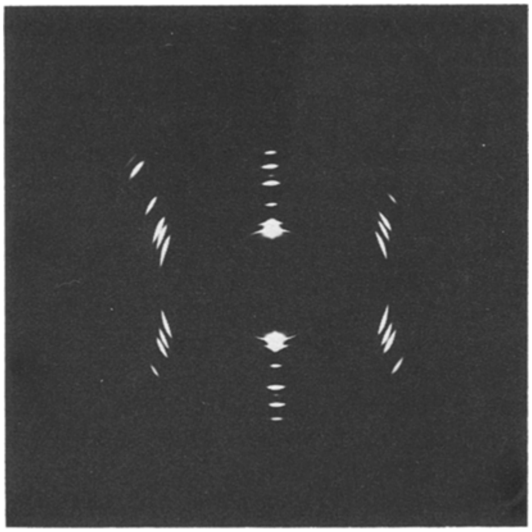

Figure 6 Wide-angle X-ray diffraction pattern of as-spun fibre from ~ 3% Hostalen GUR 415/Rigidex 006-60 blend. Fibre axis is vertical.

from the Rigidex with added high molecular weight. (NB Increasing heating rates only broadens the DSC peaks but does not change their relative sizes. Thus annealing effects are not prominent.)

The wide-angle X-ray diffraction pattern of the as-spun fibre from the high molecular weight blend shown in Fig. 6 displays arcs from the oriented regions superimposed on rings from the disoriented regions. The latter presumably include the unoriented outer sheath of the fibre, as well as the regions where there is lamellar twisting when the cores are more than 1500 nm apart.

The mechanical properties of the fibre shown in Table II tie in with the other information. The unoriented as-spun Rigidex 006-60 fibre has tensile modulus of (5 to 7) $\times 10^8\,\mathrm{N\,m^{-2}}$. The as-spun 3% high molecular weight Rigidex 006-60 fibres have moduli of $\sim 3 \times 10^9$ to $10^{10}\,\mathrm{N\,m^{-2}}$. Thus, the as-spun fibre from the blend is more rigid than an as-spun fibre of ordinary Rigidex by a factor of 5 to 20, but lower by a factor of 10 compared to the tensile moduli of the oriented plugs. The strength of the fibres was not measured because the fibre invariably broke at the grips or at spinning defects, but we have reason to believe that the fibres from the blend have enhanced strength; some of these fibres were unbreakable by hand, whereas fibres of similar diameter from Rigidex 006-60 can be easily broken.

6. Discussion and conclusion

We started this work by checking the reproducibility of the blocked plugs experiment which was originally done several years ago; we found that a batch of polyethylene that had aged did not yield plugs with the desired interlocking shish-kebab morphology, but a new batch of polyethylene that was similar in molecular weight yielded the desired morphology. We then went on to definitely identify the high molecular weight component as the key constituent of the extended chain cores. We observed that by adding ~ 3% by weight of extremely high molecular weight ($\bar{M}_w = 5 \times 10^6$) polyethylene to the bulk polyethylene ($\bar{M}_w = 1.3 \times 10^5$) and extruding at a low strain rate (where the ordinary polyethylene gave a largely lamellar, unoriented material), a stiff and transparent plug was formed that showed a profusion of shish-kebabs. In this way, the formation of cores can, for the first time, be controlled.

Ordinary fibre spinning from commonly used grades of polyethylene does not generally yield an oriented fibre. Nor is it feasible to use the very high molecular weight grades of polyethylene, like Hostalen GUR 415, as they are not extrudable. However, we have shown that it is sufficient to use a polyethylene with a small amount of added high molecular weight to produce an as-spun fibre that retains a substantial degree of orientation. The level of stiffness achieved in this one step process is comparable to that attained by two-stage commercial spinning and drawing. Although the stiffness is not as great as the ultra high modulus obtained from gel drawn polyethylene fibres [17] or from the blocked plugs [1], intermediate modulus/strength fibres have been produced in a single continuous step.

The key to success lies in forming chain extended core fibrils in the extensional flow field of the die entrance and preventing these from retracting on exit by putting tension on the filament. The remainder of the melt will be nucleated by the chain extended cores to give the shish-kebab morphology. With the high molecular weight polyethylene blends, there are two factors that promote the formation of the desirable shish-kebab morphology. Firstly, the chain extended core fibrils formed chiefly by the high molecular weight component superheat and, therefore, survive in the die at spinning temperatures of 153° C. Secondly, the melt strength of the high molecular weight blend just above the self-blocking temperature is much greater than that of conventional polyethylene, so that a tension can be successfully put on the extrudate, to prevent contraction of the cores which would normally take place at the temperatures used for spinning here.

There are many experimental parameters that remain to be investigated and which, we expect, will further enhance the mechanical properties of our fibres. Thus, in the immediate short run, we are pursuing fibre spinning of blends with the aim of improving the properties by looking at the effect of blend constitution (molecular weight composition), flow and quenching conditions.

The most important scientific point is the effect on polymer processing of the highest molecular weight component of the distribution, either natural or added separately. It is unexpected and remarkable that a small quantity such as 3% of added high molecular weight can have a disproportionate effect on processing and the end product. In effect, a special composite morphology can be produced in plugs and fibres, where the extended chain cores are predominantly high molecular weight polyethylene in a matrix of its own material, the lower molecular weight polyethylene. These extended chain cores, though minority consituents can, if present in just the right number, set the pattern for the lamellar crystallization of the rest of the material, producing the overall morphology and advantageous properties described in this paper. This in itself should be of consequence for any extrusion process, as, for example, in the batch type process of injection moulding, where by fine tuning the molecular weight distribution at its high end, and for a given molecular weight distribution, by careful control of processing conditions (pressure, melt temperature and cooling rate) the properties of the final product can be dramatically improved. It is a further significant development that as the result of the last section of the present work, all the above considerations have become applicable also to production methods relying on continuous processing.

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