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Ultra-High Strength Polyethylene by Hot Drawing of Surface Growth Fibers

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Summary

Hot drawing at 150°C has been applied to high molecular weight polyethylene fibers produced by flow induced crystallization in a Couette apparatus, referred to as the 'surface growth' technique. A distinct improvement of the tensile properties of the fibers was noticed upon drawing. A tensile strength at break of 4.7 GPa was reached. Drawability is discussed in relation to fiber morphology. The shish-kebab like structure of the 'surface growth' fiber was transformed into a morphology consisting of smooth fibrils upon drawing.

Introduction

High-strength and high-modulus structures of polyethylene are generated by several techniques i.e. drawing (CAPACCIO, WARD, 1974), solid state extrusion (SOUTHERN, PORTER, 1970) and flow-induced crystallization of high molecular weight polyethylene in a Couette-apparatus, referred to as the 'surface growth' technique (ZWIJNENBURG, 1978).

The tensile strength at break of the 'surface growth' fibers may reach values of 4 GPa with a Young's modulus of 105 GPa; the highest values that have been reported for polyethylene (PENNINGS, MEIHUIZEN, 1979). However the experimental conditions for producing fibers of this strength often result in breakage of the growing fiber. Fiber breakage occurs less frequently while growing at lower take-up stresses. Concomitantly the tensile strength at break will also decrease with decreasing take-up stress during growth. This is probably caused by a change in morphology of the macrofibers. Fibers grown at low stresses consist of elementary fibrils of the shish-kebab type. The amount of lamellar overgrowth gradually decreases with increasing stress and crystallization temperature and eventually the fibrils seem to be smooth.

Drawing of shish-kebabs of ordinary molecular weight polyethylene is possible at room temperature to draw ratio's larger than 10 (KRUEGER, YEH, 1972). However drawing high molecular weight polyethylene proceeds much more difficult, in fact it is only recently that drawing of high molecular weight polyethylene to high draw ratio's succeeded, at elevated temperatures (CAPACCIO ET Al., 1976; CLARK, SCOTT, 1974; KALB, PENNINGS, 1979).

Hot drawing of 'surface growth' fibers may be a useful method for improving their tensile properties. The problem of fiber

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breakage occurring so often during 'surface growth' can than be avoided by growing at lower take-up stresses and subsequently applying drawing at elevated temperatures. Preliminary results are reported in this letter. It will be shown that 'surface growth' fibers can be drawn by which tensile strengths at break of 4.7 GPa can be reached. Drawability will be discussed in relation to fiber morphology.

Experimental

The linear polyethylene used in this study was Hi-fax 1900 having a weight average molecular weight of about 4×10^6 Kg/kmol. Drawing experiments were carried out in a double walled glass cylinder of 1.5 m in length, through which hot silicon oil was pumped from a temperature regulated bath to establish a constant temperature within the tube.

In order to prevent oxidative degradation nitrogen was allowed to flow through the tube at a slow rate as not to upset the temperature regulation. The velocity of the fiber entering the tube was 4.2×10^{-3} m/sec. Drawing could be accomplished in two ways. Stress on the fiber could be applied by means of a free suspended wheel positioned in front of the wind-up drum. Secondly drawing was possible by means of different speed of the feed roll and the wind-up drum.

Tensile tests were performed using Zwick Z1.3B tensile tester at a cross-head speed of 2×10^{-4} m/sec and an original sample length of 25 mm at 20°C. Cross-sectional areas were calculated from fiber weight and length assuming a density of 1000 kg/m^3.

X-ray investigations were carried out using Ni-filtered CuKα radiation. A Philips generator was operated at 45 kV and 35 mA. WAXD fiber diagrams were obtained in a flat-film camera with pinhole optics, using a sample-to-film distance of 17.6 mm. SAXS measurements were performed with a Kratky-camera equipped with a 40 μm entrance slit, an electronic step-scanner, proportional counter and pulse height discrimination. The curves were corrected for background scattering.

Results and Discussion

All drawing experiments were carried out at a drawing temperature of 150°C. This appears to be about the optimum temperature for drawing Hi-fax 1900 (KALB, PENNINGS, 1979). Kalb and Pennings reported that a temperature gradient should be applied during drawing in order to avoid neck formation. In our experiments this was not found to be necessary probably due to the high degree of orientation of the 'surface growth' fibers used in these drawing experiments. Some typical results are shown in Table 1. The highly extended 'surface growth' fibers could still be drawn up to a draw ratio of 5. The draw ratio's that could be achieved seemed to be somewhat higher for the drawing by means of different speed of the wind-up drum and the feed roll. A distinct improvement of tensile properties was noticed as is illustrated by stress-strain curves for a series of fibers drawn to increasing draw ratio (set II, fig. 1). Tensile properties for a draw ratio of 5.0 (tensile strength at break of 4.7 GPa, Young's modulus 119 GPa) are even better than the highest values reported for 'surface growth' fibers.

Set	Drawn ratio	Tensile strength (GPa)	Young's modulus (GPa)	Elongation at break (%)	Drawing temperature °C	Cross sectional area (10^{-9} m^2)
I	1.0	2.5	48	6.3	undrawn	2.30
I	2.1	3.3	75	5.6	150	1.20
I	2.6	3.6	89	5.0	150	1.09
I	2.9	4.0	106	5.0	150	0.88
II	1.0	2.7	60	7.2	undrawn	1.62
II	2.2	3.1	69	5.9	150	0.78
II	3.6	4.1	95	6.0	150	0.48
II	5.0	4.7	119	5.2	150	0.33

TABLE 1: Results of Hot Drawing Surface Growth Fibers. Fibers of Set I were drawn by means of a free hanging wheel positioned before the wind-up. Fibers of Set II were drawn by means of different speed of wind-up drum and feed roll.

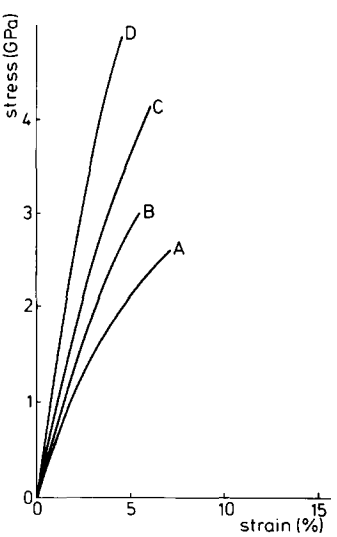

Fig. 1: Stress-strain curves of samples (set II) given in table 1. A: undrawn 'surface growth' fiber, B: draw ratio 2.2, C: draw ratio 3.6, D: draw ratio 5.0.

Where does the improvement of tensile properties upon drawing originate form? This problem is partly been clarified by investigations of the morphology of the fibers before and after the drawing process. The 'surface growth' fibers originally show a shish-kebab like morphology. The shish-kebabs consist of 'backbones' of continuous extended-chain crystals overgrown by a large number of regularly spaced folded-chain lamellae at distances of about 1000 Å. SEM-micrographs (fig. 2) of a fiber before (2 A) and after (2 C) drawing indicate strongly that the lamellar overgrowth has disappeared during drawing. Heat treatment of the fiber, by letting it pass the glass cylinder at 150°C at constant length (2 B), seems to close the structure and no distinguished fibrils can be noticed anymore. However additional information about the drawing mechanism has been revealed by SAXS and WAXD-investigations (fig. 3, 4).

SAXS-patterns of a bundle of macrofibers show that the Bragg-peak that arises from the scattering of the voids between the lamellae in the undrawn sample (3A) is absent when the fiber is drawn to a draw ratio of 3.2 at 150°C (3 B). However the Bragg-peak is also absent, when the fiber is heat treated at 150°C (3 C). This high temperature is sufficient for the vanishing of the Bragg-peak, probably due to agglomerating of the elementary fibrils, by which the voids between the fibrils disappear and thus leads to absence of the void scattering. Therefore also SAXS-patterns were made of the same fiber drawn at 90°C, though the draw ratio that could be achieved at 90°C was only 1.5. In this case the Bragg-peak is still present after heat treatment at 90°C (3 D), but after drawing to draw ratio 1.5 (3 E) the maximum in intensity that arises from the scattering of the voids between the lamellae is absent or has at least shifted to such low angles, which could not be seen with the slit collimator of our camera. The large intensity at small angles indicates that the material has remained porous, thus the absence of the Bragg-peak can not be due to closing of the fibrillar structure.

Further information about the morphology of the fibers is supplied by wide angle X-ray diffraction patterns of an undrawn fiber (4 A), of a fiber that was heat treated at constant length at 150°C (4 B) and of a fiber drawn at 150°C to a draw ratio of 3.2 4 C). The fiber that was given a heat treatment shows a more intense ring which originates from the amount of unoriented material. Because lamellae are not highly oriented, the increase in unoriented material points to a larger amount of lamellar overgrowth. In the drawn fiber on the other hand, the ring due to unoriented material is less intense, indicating the amount of unoriented material has decreased upon drawing. The almost point-like reflections indicate that the orientation of the molecular chains parallel to the fiber axis has markedly increased in comparison to the undrawn sample.

Information given by SEM, SAXS and WAXD reveals that hot drawing of 'surface growth' fibers is accompanied by an increase in orientation of the chains parallel to the fiber axis and by vanishing of the lamellar overgrowth. The smoothening of the fibrils upon drawing must originate from extension of the folded chains of the lamellae. The folded chains of the lamellar overgrowth may become extended by a shearing action of the fibrils past each other due to stretching forced during drawing. A second possibility for

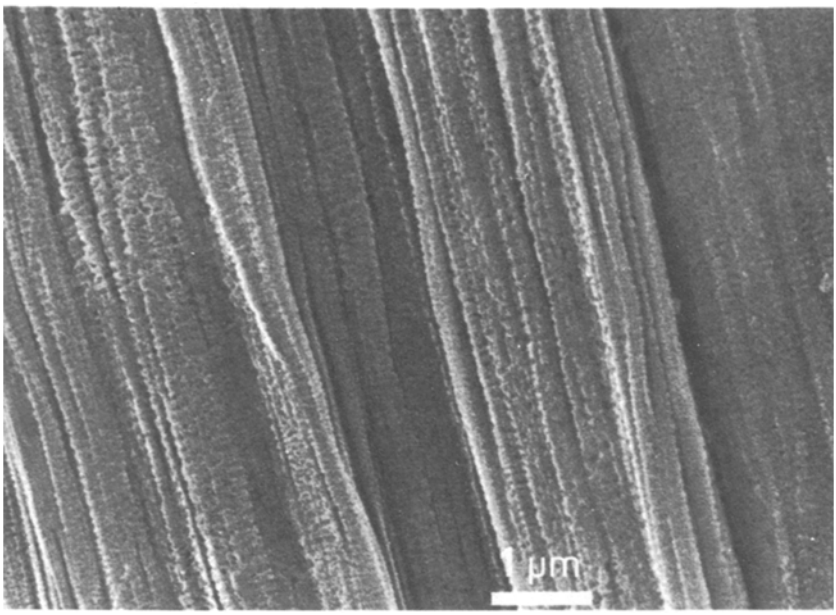

Fig. 2 A: Scanning electron micrograph of a fiber produced by the 'surface growth' technique, revealing a shish-kebab like structure.

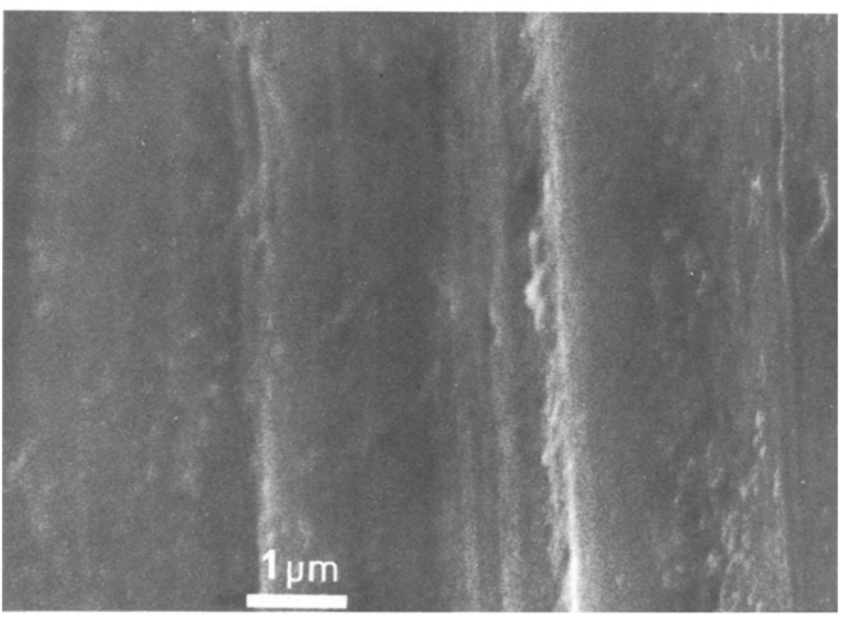

Fig. 2 B: Scanning electron micrograph of a fiber that was heat treated at constant length at 150°C.

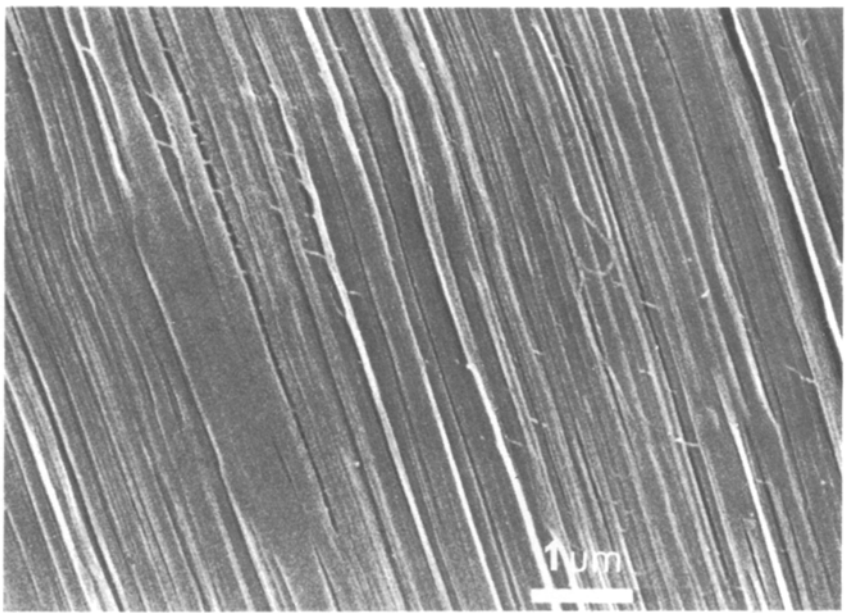

Fig. 2 C: Scanning electron micrograph of a fiber drawn to a draw ratio of 3.2 at 150°C, consisting of smooth fibrils.

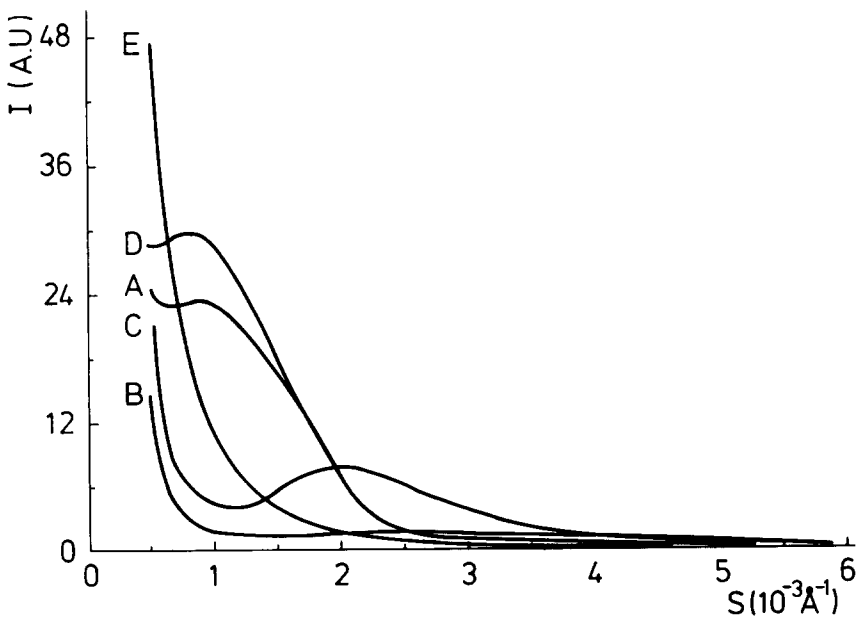

Fig. 3: SAXS-patterns of a fiber produced by 'surface growth' (A), a fiber drawn to draw ratio 3.2 at 150°C (B), a fiber heat treated at 150°C (C), a fiber drawn to draw ratio 1.5 at 90°C (E) and a fiber heat treated at 90°C (D).

extending the folded chains can be explained by the fact that chains of lamellar overgrowth are anchored in the 'backbone'. During drawing chains of the 'backbone' must be going to slip past each other and chains of the lamellar overgrowth that are trapped between 'backbone' chains are going to be pulled into the 'backbone'. Because of trapped entanglements between the chains of the lamellar overgrowth also chains which are not anchored in the 'backbone' will be pulled into the 'backbone'.

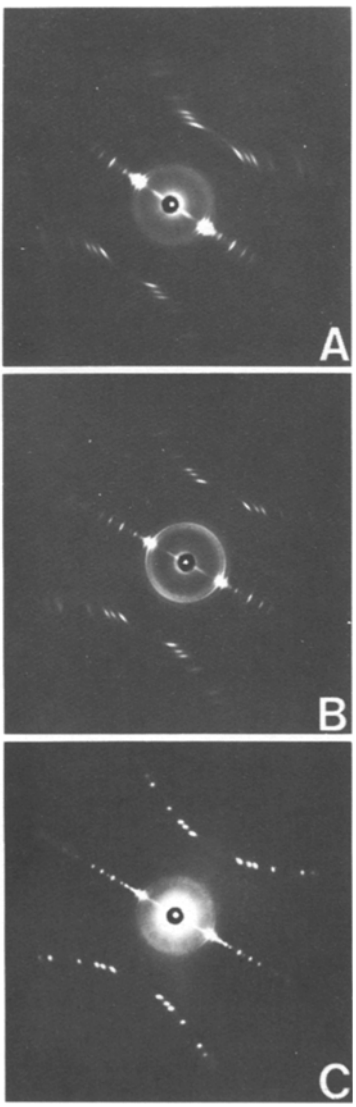

Fig. 4: WAXD-patterns of a fiber produced by 'surface growth' (A), of a fiber that was heat treated at 150°C (B) and of a fiber drawn to a draw ratio of 3.2 at 150°C (C).

The orientation along the fiber axis in the 'surface growth' fibers was already extremely high. Uncomplete orientation in this starting material must arise from defects in the crystal lattice such as trapped entanglements, twist disclinations, chain ends, loops, kinks, jogs, etc. These defects are likely to be responsible for the smaller tensile strength of oriented polymers (PENNINGS, 1979) in comparison with tensile strength at break calculated quantum-mechanically for polyethylene (BOUDREAUX, 1973). This value of 19 GPa is still far beyond the highest experimental values that have been reported for polyethylene. The presence of defects is confirmed by the WAXD-patterns, which show some reflections that are to be ascribed to a triclinic modification of the polyethylene crystal lattice in addition to the reflections of the orthorombic cell. The triclinic modification is due to the presence of twist disclinations, since only a twist of the planar zig-zag chain is needed to transform the orthorombic cell into a triclinic one (HAY, KELLER, 1970; ZWIJNENBURG, 1978). Increase in orientation along the fiber axis must be due to minimising the number of defects e.g. by using high molecular weight polyethylene. So, the increased orientation that has been accomplished during drawing must originate from a removal of defects. This points to slippage of the chains in the 'backbones' past each other. Dissolution experiments of 'surface growth' fibers (TORFS, to be published) demonstrated that

the mobility of the chains strongly increases above 133°C. Above this temperature the mobility of the chains has increased sufficiently as to move through the crystallites. Migration of defects can occur and defects are removed in this way. The WAXD-patterns confirm this, because the reflections that arise from the triclinic modification are less intense in the heat treated and drawn fiber (4 B, C).

A more detailed study on hot drawing 'surface growth' fibers will be presented in the near future.

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