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Preparation of Ultra-High Strength Polyethylene Fibres by Gel-Spinning/Hot-Drawing at High Spinning Rates

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SUMMARY

The addition of 1 wt.% Al-stearate to the spinning-solution of ultra-high molecular weight polyethylene in paraffin-oil allows take-up speeds of the extrudate of 270 m/min. These as-spun filaments could still be hot-drawn, resulting in a tensile strength of 2.8 GPa. The overall draw ratio's encountered after spinning and hot-drawing are of the order of 1500 suggesting a resemblance between these flow phenomena and superplasticity.

INTRODUCTION

Ultra-high strength polyethylene fibres with a tensile strength at break up to 4.1 GPa and a Young's modulus up to 120 GPa can be produced by the rather simple gel-spinning/hot-drawing technique (KALB, PENNINGS, 1980; SMOOK et al., 1980). This method essentially amounts to the stretching of an entanglement network, formed in a semi-dilute solution of ultra-high molecular weight polyethylene (UHMWPE), which finally leads to the formation of highly oriented, highly crystalline fibrillar structures. In practice this is accomplished by the preparation of porous as-spun fibres via extrusion of the polymer solution, followed by extraction of the solvent. In a subsequent step these fibres are hot-drawn at 148°C to the maximum draw ratio of 70 or larger.

In a recent publication from our laboratory (SMOOK et al., 1980), it was found that the manufacturing of high tenacity filaments by this method seemed to be limited to very low extrusion rates (< 1.5 m/min). Stretching of the extrudate directly behind the extruder by collecting it with a wind-up speed of 12.5 m/min resulted in a dramatic decrease of the strength of the polyethylene fibres after hot-drawing. It is the purpose of this note to demonstrate that the wind-up speed of the as-spun filaments during gel-spinning can be greatly enhanced by the use of additives in the spinning solution. The addition of 1 wt.% Al-stearate to the spinning solution, consisting of 5 wt.% UHMWPE in paraffin-oil, made it possible to produce as-spun filaments at a take-up speed of 270 m/min during gel-spinning, which still had a tensile strength of 2.8 GPa after hot-drawing.

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EXPERIMENTAL

The linear polyethylene used in the present study was Hi-fax 1900 with $\bar{M}_w$ = 4 x 10^6 kg/mol and $\bar{M}_n$ = 2 x 10^5 kg/kmol. The experimental procedure for the preparation of the UHMWPE solutions and the gel-spinning has been described in detail elsewhere (SMOOK et al., 1980). Stretching of the spinning-line occurred by collecting the extrudate on a take-up device at a distance of 1.5 m from the die-exit. The take-up velocity could be continuously varied up to 400 m/min. Extrusion draw ratio's were determined as the ratio of take-up speed and free extrusion rate. Hot-drawing was carried out at a drawing temperature of 148°C. Further details of this technique have been previously described (SMOOK, PENNINGS, 1982). The mechanical testing apparatus used was a Zwick Z1,3B tensile tester operated at a cross-head speed of 12 mm/min and an original sample length of 25 mm at 20°C. The cross-sectional areas of the fibres were calculated from fibre weight and length, assuming a density of 1000 kg/m^3.

RESULTS AND DISCUSSION

In the course of gel-spinning UHMWPE solutions, severe limitations arise from the occurrence of extrusion instabilities, such as die-swell and melt-fracture (RAM, 1969; PAUL, SOUTHERN, 1975). The onset of elastic turbulence, which is clearly related to the presence of entanglement couplings in the flowing polymer solution (LEBLANC, 1981, BUSSE, 1967), will consequently take place much faster with increasing molecular weight of the polymer. In fact, it was only possible to obtain smooth filaments during the gel-spinning of 5 wt.% UHMWPE solutions in paraffin-oil under conditions of free extrusion in air, if a long conical die (entrance angle ca. 6°, length L = 10 cm, exit diameter D = 0.8 or 1.8 mm) was used at extrusion rates less than ca. 1.5 m/min (TORDELLA, 1956). As-spun filaments obtained under these conditions, can readily be drawn to 70 times their original length, resulting in fibres with tensile strengths exceeding 3 GPa.

Fig.1 shows a SEM-micrograph of a porous as-spun filament obtained from a 5 wt.% solution of UHMWPE in paraffin-oil at an extrusion rate of 0.75 m/min. The morphology of this fibre consists of large lamellae which are loosely interconnected by several fibrils protruding from each lamella. Apparently some orientation is already developed during spinning due to the converging flow lines in the die. The entanglement network is stretched out in the spinning-solution at several places, presumably especially at the areas where the drawing-stress is transmitted through the network, i.e. at long-lifetime entanglement sites, from which long chain ends are protruding. After crystallization the drawn out molecules become fixed in the fibrils, whereas the unoriented material will crystallize as lamellae. Accordingly the most essential prerequisite for a highly drawable filament cannot be seen in the present micrograph, since it is the existence of an entanglement network underlying the crystalline texture of the material. By starting from semi-dilute solutions of the UHMWPE the number of entanglements per molecule is already strongly reduced, as compared to the melt.Upon hot-drawing of the filament at 148°C individual molecules are slipping past each other (SMOOK, PENNINGS, 1982), until the molecules become fully extended between entanglements, after which they are anchored by the

orthorhombic crystallites. In the course of this process again a few entanglements slip off, but a minimum number of 2 achoring points per molecule, i.e. 2 entanglements, is preserved throughout the hot-drawing (DE BOER, PENNINGS, 1982).

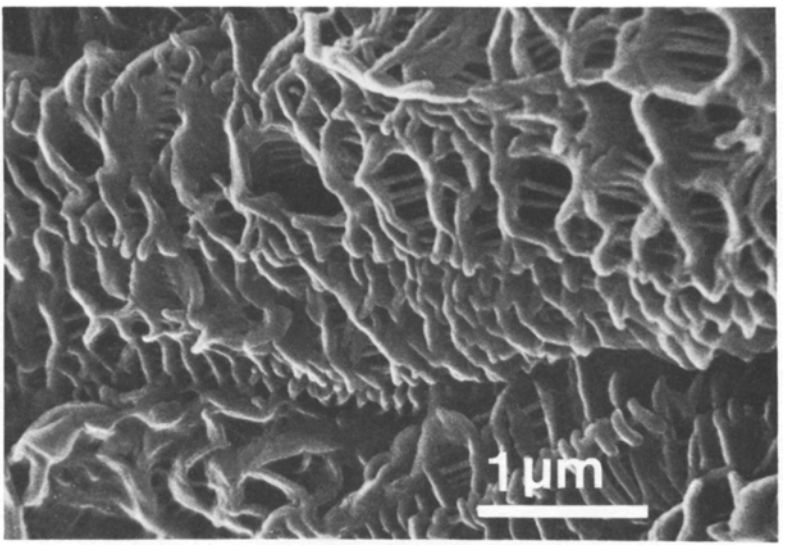

Fig.1. SEM-micrograph of an extracted as-spun filament obtained from a 5 wt.% solution of ultra-high molecular weight polyethylene in paraffin-oil (extrusion rate 0.75 m/min)

Elongation of the extrudate, by collecting it on a take-up device directly behind the extruder, is an effective means of suppressing elastic turbulence (HAN, 1976), while at the same time the production rate is increased. However, filaments prepared in such a way, showed only a poor drawability and poor tensile properties (SMOOK et al., 1980) as is shown in fig.2 (curve A). Fibres that were obtained at a take-up speed of 20 m/min (free extrusion rate 1 m/min) only had a tensile strength of about 0.5 GPa after hot-drawing. At higher take-up speeds the strength after hot-drawing is even stronger reduced.

The explanation for this phenomenon may be found in a complete disruption of the entanglement network upon stretching of the spinning-line. Due to the reduced viscosity in the molten state of the polymer solution a great many entanglements can slip off while the network is being elongated, after which the molecules will immediately recoil. Accordingly the coherence of the network structure is completely lost in the as-spun filaments, resulting in poor drawing properties. In this context we should make note of the fact that the stretching of the extrudate is actually accompanied by a removal of the gel from the interior of the die, except for a thin strongly adsorbed layer in the direct vicinity of the die-wall.

After the addition of a lubricant to the spinning solution, i.c. 1 wt.% Al-stearate, the deformation of the extrudate occurred comple-

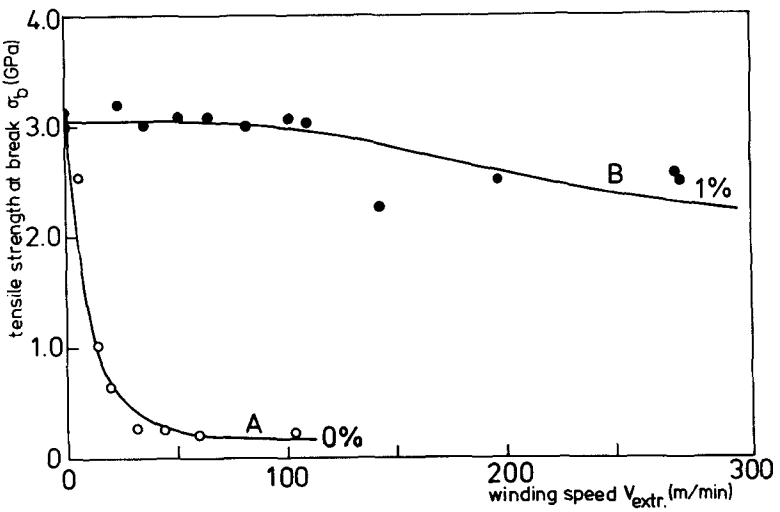

Fig.2. Tensile strength at break after hot-drawing vs. take-up speed during gel-spinning for a spinning solution without (A) and with 1 wt.% Al-stearate (B)

tely outside the extruder. More surprisingly we observed that the addition of 1 wt.% Al-stearate had a tremendous effect on the tensile strength-take-up speed relationship, as is shown in fig.2(curve B). Filaments collected with a take-up speed of 270 m/min still had a tensile strength level of about 3 GPa after hot-drawing.

The addition of Al-stearate to the spinning solution presumably greatly suppresses the adsorption of the polymer molecules in the die and also raises the solvent viscosity to quite an extent (STEPHENS, 1971). This implies that upon stretching of the entanglement network in the extrudate a great deal of the entanglements are prevented from slipping off. Furthermore it may be so that the increased viscosity suppresses the occurrence of elastic turbulence. Nevertheless we observed that the overall draw ratio's, i.e. the product of extrusion draw ratio and hot-draw ratio, are about 1500, if Al-stearate is added to the spinning-solution. This clearly demonstrates that the drawing behaviour cannot be accounted for by an entire affine deformation of the entanglement network, but it must involve viscous flow of the molecules. There may be an analogy with the "superplasticity" as it was observed in metal alloys and which has been related to an apparent Newtonian flow behaviour (KRAUSZ, EYRING, 1975).

The morphology of a quickly spun "stearate"-filament consists of a shish-kebab structure as can be seen in fig.3, which shows a SEM-micrograph of a porous as-spun filament produced at a take-up speed of 54 m/min (extrusion draw ratio = 54). The appearance of such a morphology suggests that during the stretching of the spinning-line, the molecules start to be drawn out at stable entanglement sites, after

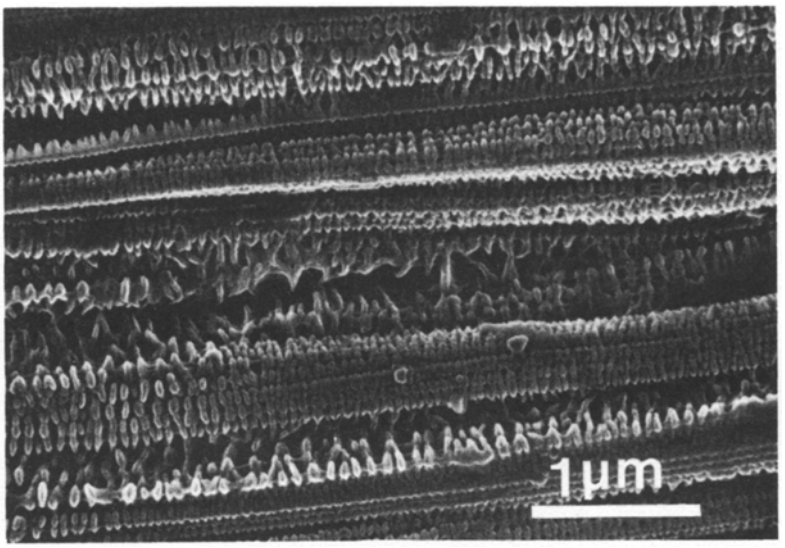

Fig.3. SEM-micrograph of an extracted as-spun filament from a solution with 1 wt.% Al-stearate spun at a winding speed of 54 m/min (free extrusion rate 1 m/min)

which flow units are developed consisting of bundles of more or less extended molecules. The large clusters of unoriented molecules between these bundles, which were responsible for the formation of the large lamellae in fig.1, will break up due to a shearing motion of the bundles of elongated molecules past each other (PECHHOLD, 1980). Presumably these clusters of unoriented molecules contain in majority less stable entanglements, i.e. entanglements with relative short chain-ends protruding from it. Accordingly these clusters can easily break up in smaller units due to the fact that these entanglements slip off. There may be close resemblence to flow units proposed by Mooney (MOONEY, 1958) and the "cluster flow" suggested by Busse (BUSSE, 1967). The thus deformed entanglement network will evidently result in the formation of a shish-kebab morphology after crystallization. Furthermore in the course of this stretching process the most stable entanglement couplings are preserved, which are a prerequisite for an effective stretching of the molecules during hot-drawing.

The appearance of a shish-kebab morphology in the quickly spun filaments as an intermediate between the porous lamellar network after slow gel-spinning and the fully aligned, smooth fibrillar structure after hot-drawing suggests there is a basic analogy in the fiber formation process during gel-spinning/hot-drawing and the so-called "surface growth" technique (TORFS, PENNINGS, 1980). In fact a shish-kebab morphology is generally observed as an intermediate structure, even during the hot-drawing of slowly spun gel-filaments. Also in the "surface growth" process a shish-kebab morphology of the fibres was observed as a general feature, while also in this process the fibre formation was explained by the stretching of an entanglement network in a gel-layer adsorbed on the rotor surface of the inner rotor of a Couette-apparatus.

Additional experimental evidence and a more detailed description concerning the "stearate" effect during gel-spinning/hot-drawing of UHMWPE will be presented in a forthcoming paper (SMOOK et al., to be published).

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