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Suspension Spinning of Ultra-High Molecular Weight Polyethylene

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SUMMARY.

This note deals with the preparation of ultra-high strength polyethylene filaments by suspension spinning and subsequent hot-drawing at 148°C. Suspension spinning involves the flow of stabilized suspensions of high molecular weight polyethylene powder in a solvent mixture through a long heated tube. In the tube, which acts as the spinning apparatus, the polyethylene is dissolved after which the polymer solution is spun in air. Under appropriate conditions of spinning and hot-drawing monofilaments were produced with a tensile strength at break of 3.8 GPa and a Young's modulus of 124 GPa.

INTRODUCTION.

Filament preparation from ultra-high molecular weight polyethylene (UHMWPE) requires spinning from semi-dilute solutions, i.e. gel-spinning, to produce high strength fibres in subsequent hot-drawing(1-4). This technique essentially amounts to the stretching of a dilute entanglement network, formed in the polymer solution by reptation(5), which finally leads to the formation of highly oriented, highly crystalline structures.

A bottle-neck of the gel-spinning procedure is however, that a certain demolition of the entanglement structure in the UHMWPE solutions is unavoidable. Due to the elastic flow behaviour of the long chain molecules, extremely strong Weissenberg effects have to be overcome in the preparation of the UHMWPE solutions, which will inevitably lead to shear degradation of the polyethylene(6). Furthermore the solutions need to be cooled down to form a gel, which has to be cut in pieces to be feedable to an extruder(4). Additionally also the generation of elastic turbulences(4,7,8) in the UHMWPE solutions in the flow field during spinning can cause breakdown of the entanglement network, especially at high spinning rates(4).

Therefore a preliminary investigation was undertaken to prepare the UHMWPE fibres by a new method, i.e. suspension spinning/hot-drawing (22). In this technique the dissolution and the spinning of the polyethylene are combined in a single step, to reduce the mechanical shearing forces exerted on the molecules as much as possible. Suspension spinning comprises the flow of a stabilized suspension of UHMWPE powder in a solvent mixture through a long heated tube, which acts as the spinning apparatus. After spinning the filaments are extracted with n-hexane and subsequently hot-drawn.

It will be shown that fully hot-drawn filaments obtained by suspension spinning, can attain a tensile strength at break up to 3.8 GPa and a Young's modulus up to 124 GPa.

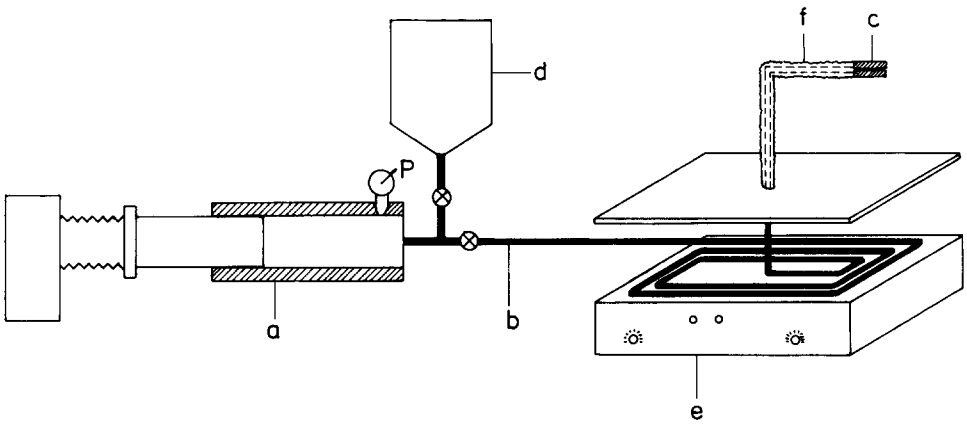

Fig.1. Schematic representation of suspension spinning apparatus.

EXPERIMENTAL.

The spinning of the polyethylene suspensions was conducted in the apparatus as schematically depicted in fig.1. It consists of a plunger pump(a) connected to a long copper tube(b). For the first experiments a spinning capillary(c) was mounted at the end of the tube, but itself could also be employed as a die. In this way flow irregularities, which always occur in the entrance region of the die(9,10) may be avoided.

The plunger pump, which was operated at room temperature, was driven by a strong electromotor, which guaranteed a constant speed of the moving plunger as to produce a constant volume output.The volume output could be varied in the range of 0.2-4.6 ml/min. Filling of the pump occurred from a reservoir(d) by moving the plunger backwards. The copper tube had an inner diameter of 4 mm and a length of 5 m. It was bended in a flat spiral shape, which was placed horizontally on a hot-plate(e), the temperature of which was regulated within 1^{0}C. The temperature of the final vertical part was controlled by means of a heating tape. The spinning temperatures quoted in this note refer to the highest temperature of the polymer solution at the end of the tube. The spinning capillary used throughout the experiments had a length L = 3 cm, a diameter D = 1 mm and an entrance angle of 90^{0}.

The linear polyethylene used was Hostalen Gur with $\overline{M}_w$ = 1.5 x 10^6 and $\overline{M}_n$ = 2 x 10^5. The solvents were paraffin-oil(density ρ = 860 kg/m^3, viscosity at room temperature η = 0.75 P) and 1,2,4-trichlorobenzene (density ρ = 1450 kg/m^3). To prevent oxidative degradation 0.5 wt.% of anti-oxidant 2,6-di-t-butyl,4-methylcresol was added to the spinning suspension.Al-stearate was added to the suspensions to keep the polyethylene powder suspended, since this additive largely increases the solvent viscosity(11). The proper suspension was composed of 5 wt.% polyethylene and 1.25 wt.% Al-stearate in a mixture of 80/20 v/v paraffin-oil/1,2,4-trichlorobenzene.

Stretching of the extrudate during spinning occurred by collecting the molten as-spun fibres on a take-up device at a distance of ca. 1 m from the capillary exit. Spinning draw ratio's were determined as the ratio of free spinning rate and take-up speed. After spinning the gel filaments were extracted in n-hexane and dried in vacuum. Hot-drawing of the porous as-spun filaments occurred at a drawing temperature of 148^{0}C in the appara-

tus described previously(3).

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 room temperature. The cross-sectional area's of the fibres were determined from fibre weight and length, assuming a density of 1000 kg/m^3. The scanning electron micrographs were taken in an ISI-DS 130 microscope operated at 40 kV from gold covered samples.

RESULTS AND DISCUSSION.

Special care had to be taken in the preparation of suspensions of the UHMWPE powder, that they were stable in the complete temperature range from room temperature up to the dissolution temperature. Otherwise plugging up of the spinning tube occurred. For this reason the polyethylene powder was suspended in a mixture of paraffin-oil/1,2,4-trichlorobenzene, such that the density of the mixture was 980 kg/m^3, which about equals the density of the polyethylene. Furthermore 1.25 wt.% Al-stearate was dissolved in the solvent mixture, before the polyethylene powder was suspended. This additive has been found to suppress the occurrence of elastic turbulences as a result of a high local viscosity(4). The polyethylene concentration was 5 wt.%. With this spinning suspension good spinnability was obtained and moreover the spinning apparatus could be entirely cooled down to room temperature and heated up again, without getting plugged up.

At first instance the filaments were freely spun into the ambient air atmosphere, during which gelation of the as-spun fibres occurred ca. 10 cm behind the capillary exit. A constant volume output of 2.6 ml/min was applied throughout all the experiments, which came down to an average residence time of the suspension c.q. solution in the tube of about 30 min. This period of time appeared to be sufficient for the establishment of an equillibrium entanglement network in the polymer solution, as to be expected since even in the highly viscous UHMWPE solutions formation of entanglements by reptation(5) occurs on a time-scale of tens of seconds(12).

In order to produce regularly shaped fibres with a constant diameter, a spinning temperature of at least 190^{0}C had to be applied. At lower spinning temperatures significant die-swell and melt-fracture was encountered, which lowers the tensile properties of the hot-drawn fibres(13). A fibre obtained at a spinning temperature of 175^{0}C and a spinning rate of 0.8 m/min could attain a tensile strength of 2.3 GPa after drawing to a draw ratio of 80. Fibres spun at 190^{0}C and a spinning rate of 1.1 m/min had a tensile strength of 3.8 GPa after hot-drawing to the maximum draw ratio of 100. This value of 3.8 GPa is close to the highest values, achievable through the technique of gel spinning/hot-drawing. This clearly indicates that the proper entanglement network had been established in this suspension spinning experiment.

Fig.2 presents a SEM-micrograph of the morphology of the as-spun filament obtained at 190^{0}C and a spinning rate of 1.1 m/min. It consists of large chain folded lamellae interconnected by several chain extended fibrils, as was also generally observed after free extrusion during gel spinning(4,14). This similarity in the morphology of the as-spun filaments after gel spinning and suspension spinning indicates that the flow patterns in the spinning solution were essentially the same in both techniques. This is because the morphology in the as-spun filaments can be considered to originate from a solidification(15) of the flow units, that were already developed in the flowing UHMWPE solutions during spinning(4). In the flow field the entanglement network is locally stretched, which leads to a splitting up in long flow units, consisting of alternating bundles of

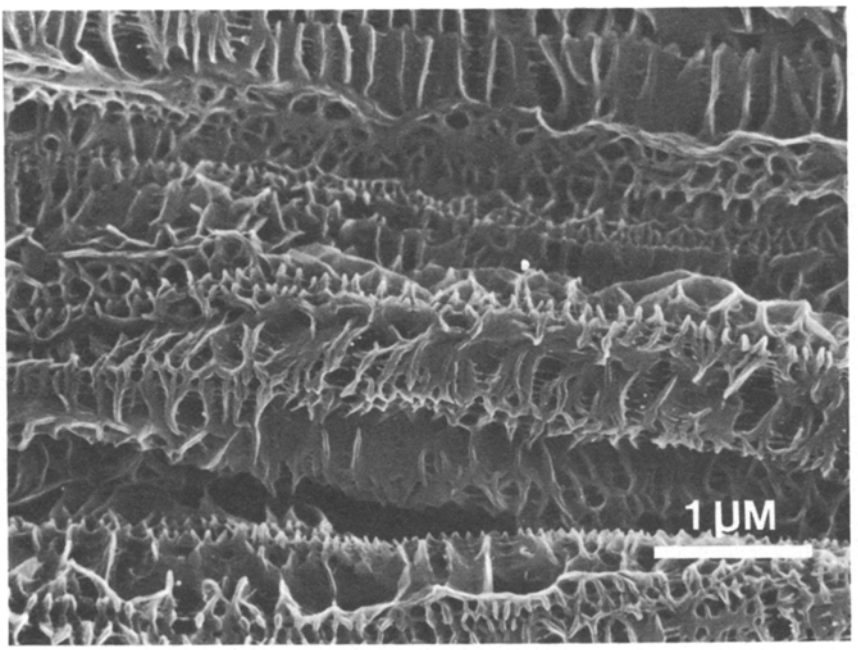

Fig.2. SEM-micrograph of an extracted as-spun filament obtained by suspension spinning at 190°C and a spinning rate of 1.1 m/min.

elongated molecules and clusters of unoriented molecules, analogous to early observations of cluster flow(12,16,17). These clusters, which are connected to the elongated bundles by entanglements, contain in major part elastically inactive loops, dangling chains, trapped entanglements and a few tie molecules. Crystallization of these flow units results in the shish-kebab like entities as shown in fig.2.

Upon hot-drawing the porous structure in the as-spun filaments is converted into a highly oriented, smooth fibrillar structure with outstanding mechanical properties. The high drawability of these porous UHMWPE fibres can be attributed to the reduced entanglement density, as compared to that in fibres processed from the melt(18) and the high drawing temperature of 148°C that can be applied to the fibres(19). This temperature is beyond the melting temperature of the as-spun fibres, which implies that the drawing proceeds by a complex process comprising melting, elongation and recrystallization of the molecules. Entanglements are therefore essential to get the molecules drawn out and to prevent them from recoiling. Drawing is completed if the elastically inactive chain ends and loops in the original lamellae have become fully elongated between entanglements, after which they are trapped in the chain extended orthorhombic crystallites in the fibrils.

The drawability of the porous UHMWPE fibres is thus mainly determined by the entanglement topology in the as-spun fibres. Since this entanglement topology is strongly dependent on the flow conditions during spinning(20), also a set of fibres was collected at different take-up speeds during

suspension spinning, by stretching the filaments directly behind the capillary exit, while they were still in the molten state.

In the course of gel spinning we had noticed that such extrudate stretching resulted in a strong decrease of the ultimate tensile properties after hot-drawing, except when Al-stearate was added to the spinning solution(4,14). If 1 wt.% Al-stearate was present in the gel spinning solution, the ultimate strength after hot-drawing was independent of the winding speed up to 100 m/min. The main effects of this additive were argued to be a strong increase of solvent viscosity(11) and suppression of the polyethylene adsorption onto the die-wall. Due to these effects the entanglement connectedness in the flow units during spinning was preserved.

Since also Al-stearate was added to stabilize the suspensions during suspension spinning, it seemed worthwhile to increase the spinning rate by extrudate stretching. Fig.3 presents a plot of the tensile strength at break σ_b and the Young's modulus E_{mod} after hot-drawing as a function of the spinning draw ratio λ_{spin} during suspension spinning at 190°C (Free spinning rate 1.1 m/min). Despite the presence of 1.25 wt.% Al-stearate in the spinning solution σ_b drops quite rapidly from 3.8 GPa for freely extruded fibres to 2.0 GPa for fibres produced at a take-up speed of 15 m/min. Similar behaviour was observed for the Young's modulus as a function of λ_{spin}. A take-up speed of 15 m/min was found to be the maximum speed that could be applied, since at higher take-up speeds filament fracture occurred. In fig.4 the maximum hot-draw ratio λ_{hd} as well as the overall draw ratio $\lambda_{ov} = \lambda_{hd} \times \lambda_{spin}$ are presented as a function of the spinning draw ratio λ_{spin}. For λ_{hd} we observed a decreasing value as λ_{spin} increased, in accordance with earlier observations during gel spinning(4). The value of λ_{ov} increases from 100 at $\lambda_{spin} = 1$ to about 300 for $\lambda_{spin} = 15$. These values of λ_{ov} during suspension spinning are considerably lower than

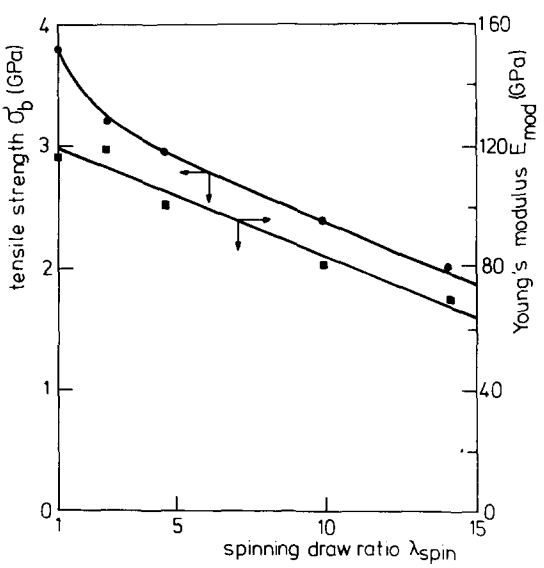

Fig.3 Tensile strength at break σ_b and Young's modulus E_{mod} after hot-drawing as a function of the spinning draw ratio λ_{spin} (Free spinning rate 1.1 m/min, spinning temperature 190°C)

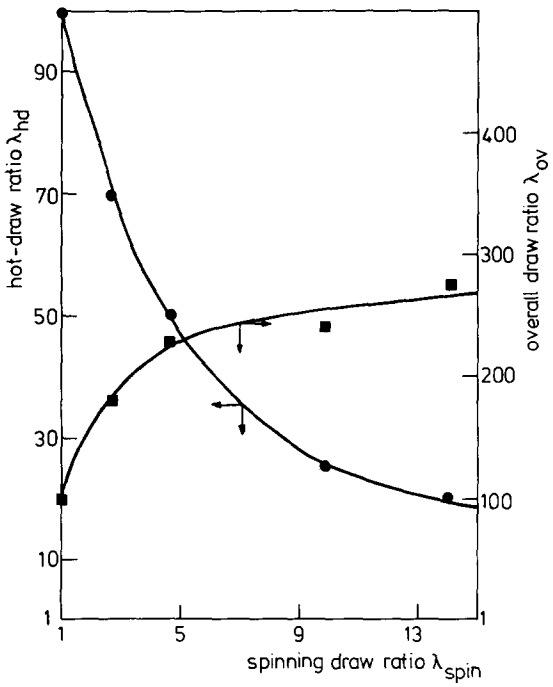

Fig.4. Plot of the maximum attainable hot-draw ratio λ_{hd} and the overall draw ratio λ_{ov} as a function of the spinning draw ratio λ_{spin} after suspension spinning at 190°C

the ones observed during gel spinning in the presence of Al-stearate, where values of λ_{ov} in the range of 1000-1500 were measured, if extrudate stretching was applied.

The strong decrease of σ_b and the relatively low value of λ_{ov} after suspension spinning at increased take up speeds, suggest that in spite of the presence of Al-stearate in the spinning solution, the long flow units are broken at several places by pulling molecules out of entanglement couplings. This may occur especially at those places where the bundles of elongated molecules are connected to the clusters of unoriented molecules, since in particular these entanglements become stressed at high flow rates. Accordingly, an increasing number of elastically inactive chain ends are generated at the end of the flow units, which cannot be effectively elongated in subsequent hot-drawing. This phenomenon that the long flow units in the spinning solution remain intact during gel spinning at high winding speeds, if Al-stearate was added, whereas they are broken down in the suspension spinning experiments, is possibly a consequence of differences in the composition of the spinning solution.

One difference between gel spinning and suspension spinning concerns the presence of 1,2,4-trichlorobenzene in the spinning suspension.The stabilizing effect of the Al-stearate on the flow units may have been reduced by this solvent, due to a strong interaction with the Al-stearate. Moreover a different polyethylene was employed in the suspension spinning experiments, i.e. Hostalen Gur with $\overline{M}_w = 1.5 \times 10^6$. In gel spinning experiments Hi-fax 1900 with $\overline{M}_w = 4 \times 10^6$ was used. The lower molecular weight

of the Hostalen Gur leads on the average to somewhat shorter strand lengths protruding from the entanglements in the spinning solution. Stability or lifetime of entanglements depends on these strand lengths (21). Accordingly it will be easier to pull the molecules out of entanglements during suspension spinning at high flow rates.

After the completion of the present investigation we found that it was also possible to obtain a stable spinning suspension of the UHMWPE powder by suspending it in a solution of 1 wt% EPDM rubber and 1,25 wt% Al-stearate in paraffin-oil. In the first experiment with this suspension a fibre was spun at 190°C and a spinning rate of 1.1 m/min. This fibre, which could be hot-drawn to a draw ratio of 90, had a tensile strength at break of 2.7 GPA. Future experiments will have to clarify whether this or another composition of the spinning suspension allows the generation of high strength fibres at high spinning rates.

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