Gel-spun polyethylene fibres

Part 1 Influence of spinning temperature and spinline stretching on morphology and properties

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The tensile strength of gel-spun polyethylene fibres hot-drawn to the maximum draw ratio depends on the spinning conditions such as spinning speed, spinline draw ratio and spinning temperature. High deformation rates during spinning introduce defects and fibres with poor ultimate properties are produced. These defects are already present before the hot-drawing step and can be detected indirectly by wide-angle X-ray scattering, since they are accompanied by preferential c-axis orientation parallel to the fibre axis and a shish-kebab structure. The introduction of flaws such as chain scission and tight knots can be prevented by avoiding spinline stretching and/or increasing the spinning temperature. This is due to the fact that higher spinning temperatures reduce the span of time in which the chains remain entangled and behave like a real network. Due to their lamellar/shish-kebab structure, the extracted fibres show a mechanical behaviour which to some extent is characteristic of composites.

1. Introduction
Gel-spinning of semi-dilute ultra-high molecular weight polyethylene solutions is a by now familiar technique to obtain ultra-high strength polyethylene fibres. Due to the reduction of the number of entanglements compared to more concentrated systems (eg. melt-spinning [1-3] or hydrostatic extrusion [4, 5]) better properties can be obtained [6, 7]. Currently, fibres with a tensile strength of more than 6 GPa and a Young's modulus of 160 GPa can be prepared [8-11]. For an overview of the many different techniques developed for preparing ultra-high strength polyethylene fibres we refer to recently published review papers [12-14].

The method used in our laboratory consists of extruding a solution of 1 to 5 wt% polyethylene in paraffin oil followed by quenching in air. To remove the paraffin oil the gel-spun fibre is extracted with n-hexane and subsequently dried. Then, the extracted fibre is hot-drawn which transforms the lamellar/fibrillar structure into smooth fibrils. During this stage a large improvement of the properties is achieved. The ultimate properties obtained depend strongly on the spinning conditions such as spinning speed, spinning temperature, stretching in spinline, geometry of the die and polymer concentration. It is the aim of this paper to describe the influence of some of these spinning variables on the morphology of the as-spun fibres and to show how they affect the ultimate properties of the polyethylene fibres.

One of the problems encountered during gel-spinning polyethylene solutions is the adsorption of the polyethylene on the wall of the die [15]. This results in fibres with poor properties, because stretching the entanglement network at one end while the other end is anchored by the adsorbed layer on the wall of the die leads to rupturing of the entanglement structure. This problem can be solved in a number of ways. Adding 1 wt% aluminium stearate to the polyethylene solution spun at a rate of 1 m min⁻¹ and a spinning temperature of 170°C suppresses the adsorption [15, 16], as is reflected by higher tensile strengths compared to fibres spun under the same conditions without aluminium stearate. A second way to suppress adsorption is to reduce the residence time of the polymer solution in the spinneret below the time required for adsorption. Indeed, for solutions extruded at a rate of 100 m min⁻¹ instead of 1 m min⁻¹ the effect of the addition of 1 wt% aluminium stearate on the ultimate tensile strength is insignificant [16]. Finally, the adsorption can also be suppressed by raising the spinning temperature [17].

Besides adsorption, stretching of the spinline can also have a deteriorating effect on the ultimate properties of gel-spun polyethylene fibres hot-drawn to the maximum draw ratio. This is in particular true at spinning temperatures of about 170°C and spinning speeds of approximately 100 m min⁻¹ [16]. The tensile strength decreases with increasing take-up speed. The high deformation rate in the orifice and in the spinline creates defects in the transient entanglement network, which on the time-scale of the experiment behaves as a more or less permanent network. At higher spinning temperatures the polymer chains are more flexible and the permanent-network behaviour is lost to some degree. Disturbances introduced by high deformation rates are restored by fast relaxations. The degree of c-axis orientation parallel to the fibre axis introduced
during stretching of the spinline is a measure of the permanence of the entanglement network on the time-scale of the experiment. This type of c-axis orientation is at the same time a measure of the number of defects such as tight knots and chain scissions introduced during this rather crude method of spinning. These flaws determine the ultimate tensile strength obtained after hot-drawing. In this paper the influence of the spinning conditions on the degree of c-axis orientation parallel to the fibre axis will be discussed, and its effects on the mechanical behaviour of the as-spun as well as the hot-drawn fibres will be described. This paper is restricted to polyethylene fibres obtained from a solution of 5 wt % Hifax 1900 dissolved in paraffin oil. In a subsequent paper the influence of the polymer concentration and molecular weight distribution will be considered.

2. Experimental procedure

The linear polyethylene sample used throughout this study was Hifax 1900 with $M_n = 2 \times 10^5$ kg mol$^{-1}$ and $M_w = 4 \times 10^6$ kg mol$^{-1}$. 5 wt % of this polyethylene was dissolved in paraffin oil (containing 0.5 wt % DBPC anti-oxidant) at 150°C and homogenized for 48 h at this temperature. Upon cooling, this solution formed a gel which was fed to the spinning apparatus. The gel was extruded into a filament at temperatures varying from 170 to 250°C with a spinning speed of 1 or 100 mm min$^{-1}$ using a conical die [16] with an exit of 1 mm. The paraffin oil was extracted from these filaments with n-hexane. Afterwards hot-drawing was carried out at 148°C in a nitrogen atmosphere, always to the maximum draw ratio. The mechanical properties of the fibres were investigated with an Instron 4301 tensile tester. For the hot-drawn fibres the original sample length was 25 mm and a tensile speed of 12 mm min$^{-1}$ was used. For the extracted fibres these values were 22 mm and 30 mm min$^{-1}$, respectively. Wide-angle X-ray scattering (WAXS) experiments were carried out with a Statton camera using CuKα radiation ($\lambda = 0.154$ nm) produced by a Philips X-ray generator connected to a closed cooling circuit and operated at 45 kV and 45 mA. Azimuthal scattering intensities were obtained with a densitometer. Scanning electron microscopy (SEM) micrographs were obtained with an ISI DS-130 scanning electron microscope operated at 25 kV.

3. Results and discussion

The organization of this section is as follows. First the influence of the spinning conditions on the ultimate tensile strength of the hot-drawn polyethylene fibres will be discussed. Next, the connection between the ultimate tensile strength and the degree of preferential c-axis orientation parallel to the fibre axis in the extracted fibres not yet hot-drawn will be established. Finally the morphology and mechanical behaviour of these extracted fibres will be considered in relation to the degree of preferential c-axis orientation parallel to the fibre axis.

Fig. 1 shows the tensile strength obtained after hot-drawing as a function of the spinning temperature for freely extruded fibres and fibres drawn in the spinline to a draw ratio of 50. In all cases the extrusion rate was 1 m min$^{-1}$. At a spinning temperature of 170°C the difference in tensile strength observed can be ascribed to the deteriorating effect of adsorption combined with spinline stretching as described before [15–17]. In contrast to freely extruded fibres, the tensile strength of the fibres drawn in the spinline to a ratio of 50 increases considerably with increasing spinning temperature. The tensile strengths are observed to merge at a spinning temperature of about 250°C. This implies that at this temperature the ultimate tensile strength becomes independent of spinline stretching, at least for draw ratios smaller than 50. Higher spinning temperatures imply improved chain flexibility and therefore a loss of permanence of the transient entanglement network on the time-scale of the experiment. The viscosity of the polymer solution becomes too low to build up stresses high enough to create defects. Moreover, even if some defects are introduced, fast relaxations may prevent them from existing long enough to become trapped by solidification. The adsorption of the polyethylene chains on the wall of the die is also suppressed. For freely extruded fibres adsorption has, even at a spinning temperature of 170°C, no effect on the ultimate tensile strength. Stretching of the spinline is necessary for the