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The effect of fibre diameter on the drawing behaviour of gel-spun ultra-high molecular weight polyethylene fibres

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Summary

In the continuous drawing of gel-spun UHMWPE fibres, the diameter of the undrawn fibre appears to have a pronounced effect on its drawing behaviour and on the mechanical properties of the resulting hot-drawn fibres. A highly oriented structure is developed more efficiently upon drawing of thinner fibres, which may be attributed to differences in the deformation mechanism between as-spun fibres of various diameters. By drawing of thin fibres, UHMWPE filaments having a strength of 6.0 GPa and a Young's modulus of 222 GPa can be obtained at a relatively low draw ratio of λ=70.

Introduction

Polymeric fibres with a very high strength and stiffness can be prepared from flexible chain polymers, such as polyethylene. Polyethylene fibres having a strength of $\sigma = 3$ GPa and a Young's modulus of E=100 GPa have been prepared by longitudinal growth of fibrillar crystals from seeds in solutions subjected to a shear flow pattern, the so-called 'surface growth' technique [1]. By solution-spinning of ultra-high molecular weight polyethylene (UHMWPE) and additional hot-drawing, fibres having similar mechanical properties could be produced [2]. The development of this gel-spinning/hot-drawing technique over the past decade has made it possible to obtain UHMWPE fibres with strengths up to 7.2 GPa [3] and Young's moduli up to 265 GPa [4]. The mechanical properties of the fibres obtained are, however, influenced by a number of processing conditions, in particular the concentration of the spinning solution [5], the fibre draw ratio [6] and the temperature and rate of drawing [7,8].
In this study, the effect of a more or less uncommon parameter, namely the diameter of the *undrawn* gel-spun filament, on the drawing behaviour and on the mechanical properties of the resulting hot-drawn fibres is reported. It was observed that hot-drawing more effectively enhances the fibre properties as the diameter of the undrawn, as-spun fibre is smaller. These effects are not related to differences in the physical and morphological properties of the various undrawn fibres, as can be shown by characterization of these fibres by means of röntgen diffraction and thermal analysis. Due to the more efficient improvement of properties observed upon drawing of small-diameter as-spun fibres, UHMWPE fibres with excellent mechanical properties (tensile strength 6.0 GPa, Young's modulus 222 GPa) could be prepared by hot-drawing of thin fibres to a relatively low draw ratio of λ=70.

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Experimental

High-strength UHMWPE fibres were prepared according to the following procedure. Linear polyethylene (Hifax 1900 by Hercules) with M_w=5500 kg/mol and M_n=2000 kg/mol was dissolved in paraffin oil, containing 0.5 % antioxidant (2,6-di-t-butyl-4-methylphenol), by rapid mechanical stirring at 135°C, using a polymer concentration of 1.5 % by weight. The solution was allowed to stand at 150°C for 48 hours under a nitrogen atmosphere. The polyethylene gel, formed upon slow cooling of the solution, was transferred to a piston-cylinder apparatus and was redissolved at 190°C for 3 hours. The solution was subsequently spun at this temperature using a single, tapered spinneret hole of either 0.25 mm, 0.5 mm, 1.0 mm or 2.0 mm exit diameter, where the mass output was adjusted to the die exit diameter to give a fibre exit velocity of 1 m/min in each experiment. The fibres were cooled to ambient temperature by natural air convection and collected at 1 m/min by means of a take-up device. The solvent was removed from the gel-fibres by extraction with n-hexane and subsequent drying at 50°C in vacuo with fixed ends. The as-spun fibres were stretched in a tubular, electrically heated oven at 148°C (under nitrogen atmosphere) between two spools located outside the oven. The draw ratio was determined from the ratio of wind-up and feed velocities of the fibre. A feed velocity of 6.25 mm/min was employed in each drawing experiment.
Tensile properties of all fibres were determined using an Instron 4301 tensile tester, operating at a crosshead speed of 25 mm/min, using a sample gauge length of 50 mm. Digitized stress-strain data were collected at a sampling rate of 20 pts./sec and analyzed using the Instron Series IX Automated Materials Testing Program in order to obtain highly accurate stress-strain data. Strength and modulus values reported in this paper refer to the average values of at least 50 measurements. The diameter of the hot-drawn fibres was determined from the weight and the length of the fibre assuming a density of 1000 kg/m3 for polyethylene. Röntgen diffraction patterns were obtained using a Statton camera producing CuKα radiation with a wavelength of 1.5418 Å. Differential scanning calorimetry was performed on unconstrained fibre samples of 1-5 mg in size, using Perkin Elmer DSC-7 equipment.

Results and discussion

Fibres were spun using spinneret holes of 2 mm, 1 mm, 0.5 mm and 0.25 mm in diameter and the various as-spun fibres are drawn in a one-step, continuous process to a number of draw ratios ranging from λ=30 to λ=90 in a tubular, electrically heated oven of 30 cm in length. In order to minimize the effect of spinneret hole diameter on the physical properties and drawing behaviour of the as-spun fibres, a low spinning speed (1 m/min) is employed. The diameter of the spinneret hole can affect the physical properties of the as-spun in two ways. First of all, the use of small orifices may introduce pre-orientation in the as-spun fibre, which tends to decrease the maximum draw ratio of the fibre and increases the strength at a given draw ratio [9]. In Fig. 1, wide angle X-ray diffraction patterns of as-spun fibres, prepared using 2.0 mm and 0.5 mm orifices, are shown. It is seen that, in both cases, no orientation is introduced during spinning, indicating that the spinning speed employed here is sufficiently low to suppress pre-orientation effects. The diameter of the spinning orifice also affects the cooling rate of the gel-fibre. In the gel-spinning process, it is of importance to preserve the transient entanglement network as it is present in solution, which is achieved by rapid crystallization of the gel-fibre upon cooling to ambient temperature. In thicker fibres, the time required to achieve complete gelation of the fibre is considerably longer than it is in thinner ones, which possibly has an effect on the entanglement topology in the as-spun fibre. From differential scanning calorimetry, the heats of fusion of the as-spun fibres were found to be 241 J/g, 232 J/g and 236 J/g for fibres spun using 2 mm, 1 mm and 0.5 mm orifices respectively. Since the heat of fusion of the fibre may be regarded as a measure of the concentration of entanglements present in the semi-crystalline state [10], the effects of the cooling history of the fibre appear to be negligible. On the basis of these data, we assume that, under spinning conditions employed, the relevant physical properties of

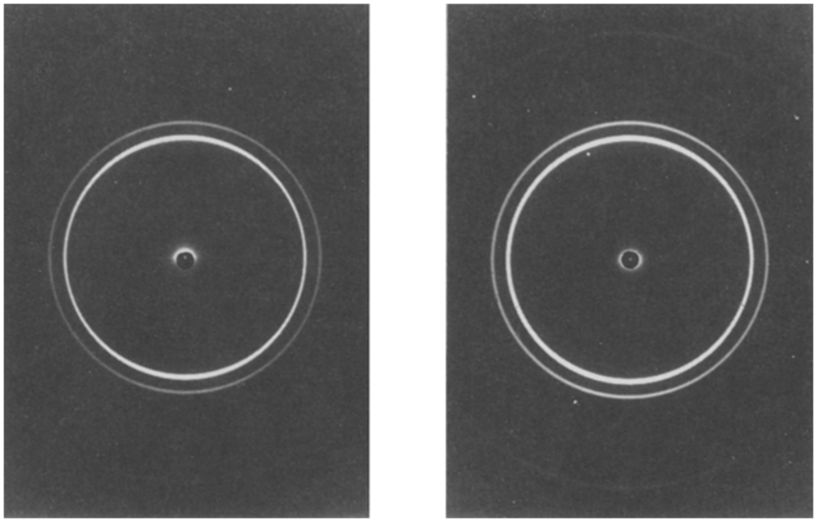

Fig. 1 Wide angle X-ray diffraction patterns of as-spun, extracted UHMWPE gel-fibres, obtained using spinneret holes of 0.5 mm (left) and 2.0 mm (right) in diameter.

the as-spun fibres with respect to their drawing behaviour are not affected by the diameter of the orifice used in the spinning process.

Figs. 2 and 3 show the effect of draw ratio on the tensile strength and Young's modulus of fibres obtained using spinning orifices of 2 mm, 1 mm and 0.5 mm in diameter. In Fig. 2 it can be seen that, at a given draw ratio, thinner fibres are substantially stronger than thicker ones, suggesting a pronounced effect of fibre diameter on tensile strength [11,12]. However, the Young's modulus is found to depend on the diameter of the fibre as well (see Fig. 3). The Young's modulus reflects a number of structural properties of the fibre, such as the degree of chain orientation [13] and the fraction of load-carrying chains [14,15] and therefore it follows from our data that the fibre structure develops more efficiently during hot-drawing as the diameter of the undrawn precursor fibre has a smaller diameter. Since the various as-spun fibres were found to have similar morphologies and physical properties, this effect is caused by differences in their diameter only. These effects are remarkably pronounced, especially at higher draw ratios. For example, at a draw ratio of λ=70, fibres prepared from the 0.5 mm as-spun fibre have an average strength and modulus of 6.0 GPa and 222 GPa respectively, whereas fibres prepared from the 2 mm precursor have an average strength and modulus of 3.7 GPa and 128 GPa respectively.

In order to investigate the effect of initial fibre diameter on the drawing behaviour, the maximum draw ratio, drawing stress and drawing efficiency (i.e. the rate of increase of modulus with increasing draw ratio) were determined for as-spun fibres of various diameters. The results are summarized in Table 1. It is seen that, at a given draw ratio, the drawing stress is remarkably higher when the undrawn fibre is thinner. Since the stress-level in the drawing line reflects the number of chains (per unit area) that becomes extended in the drawing process, fibres produced at a higher stress have a higher fraction of load-carrying chains and, as a consequence, higher moduli and strengths. Kalb et al. [16] indeed found a pronounced dependence

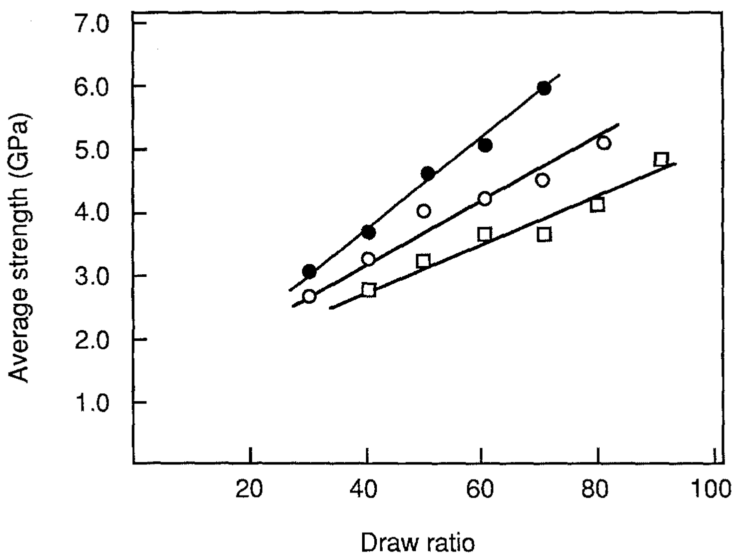

Fig. 2. Effect of draw ratio on the tensile strength of UHMWPE fibres, spun using (•) 0.5 mm, (o) 1.0 mm and (□) 2.0 mm orifices.

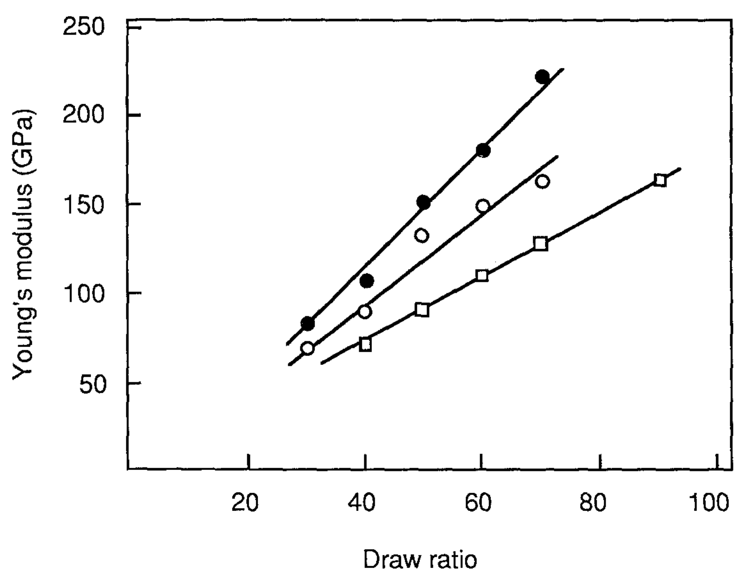

Fig. 3. Effect of draw ratio on the Young's modulus of UHMWPE fibres, spun using (•) 0.5 mm, (o) 1.0 mm and (□) 2.0 mm orifices.

Table 1. Effect of spinneret hole diameter on the drawing behaviour of the as-spun fibres. Drawing is performed at 148°C using a fibre feed velocity of 6.25 mm/min.

Spinneret hole diameter (mm)	Maximum draw ratio	Drawing efficiency* (GPa/λ)	Drawing stress at λ=50 (GPa)
2.0	90	1.9	0.29
1.0	80	2.5	0.54
0.5	70	3.5	0.69
0.25	40	4.1	-

*) Rate of increase of the Young's modulus of the drawn fibre as a function of draw ratio, $\partial E/\partial\lambda$, expressed in GPa/λ

of the strength of hot-drawn UHMWPE fibres on drawing stress. The observed influence of initial fibre diameter on both tensile strength and Young's modulus of the hot-drawn fibre is therefore most likely related to the observed differences in drawing stress. Marked differences in the maximum draw ratios of the various as-spun fibres may also be explained in terms of drawing stress : in thinner filaments, the stress-level required to cause fracture of the drawing line is reached at a lower draw ratio.

The question arises why drawing stress, at a given draw ratio, depends on the initial diameter of the fibre in the drawing line. During drawing experiments carried out in a double-walled, oil-heated glass tube, where the process could be followed visually, it was observed that thick fibres deform homogeneously over the total length of the heated zone (tapered drawing profile), whereas thin fibres deformed in a neck upon hot-drawing. Due to the low thermal conductivity of polyethylene, thick fibres are gradually heated up from the outside, and the outer layers of the fibre will deform first, bringing a new material to the fibre surface that will subsequently be deformed [11]. As a result, thick fibres are deformed over a relatively large distance along their length, whereas thin fibres will deform in a narrow zone, similar to a neck. Thus, the length of the zone in which drawing actually takes place depends on the diameter of the undrawn fibre. The length of the drawing path in a continuous process has a pronounced effect on the local deformation rates and hence affects the drawing stress [17].

We like to emphasize that the effects discussed here relate to continuous drawing processes, in which thermal equilibrium is usually not achieved. Our results demonstrate that under such conditions the properties of drawn fibres can not be related uniquely to draw ratio. When drawing is performed under isothermal conditions, or when the deformation is forced to take place in a neck, which is the case in, for instance, zone-annealing [18] or pin-drawing [19], the effects reported here will be less pronounced.

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References

1 A. Zwijnenburg and A. J. Pennings, *J. Pol. Sci., Pol. Lett. Ed.*, 14 (1976) 339
2 P. Smith, P. J. Lemstra, B. Kalb and A. J. Pennings, *Polym. Bull.*, 1 (1979) 733
3 A. J. Pennings, D. J. Dijkstra, A. R. Postema, M. Roukema, W. Hoogsteen and H. van der Werff, "Frontiers of Macromolecular Science", edited by T. Saegusa, T. Higashimura and A. Abe (Blackwell Scientific Publications,1989) p. 357
4 H. van der Werff and A. J. Pennings, *Coll. Pol. Sci.*, 269 (1991) 747
5 P. Smith, P. J. Lemstra and H. C. Booij, *J. Pol. Sci, Pol. Phys. Ed.*, 19, 887 (1981)
6 A. J. Pennings and J.Smook, *J. Mater. Sci.*, 19, 3443 (1984)
7 G. Capaccio, T. A. Crompton and I. M. Ward, *Polymer Lett. Ed.*, 17, 644 (1976)
8 Y. Termonia, S. R. Allen and P. Smith, *Macromolecules* , 21, 3485 (1988)
9 J. Smook and A. J. Pennings, *J. Mater. Sci.*, 19 (1984) 31
10 A. J. Pennings, *Makromol. Chem., Suppl.*, 2 (1979) 99
11 J. Smook, W. Hamersma and A. J. Pennings, *J. Mater. Sci.*, 19 (1984) 1359
12 H. D. Wagner and L. Steenbakers, *Phil. Mag. Lett.*, 59 (1989) 77
13 P. A. Irvine and P. Smith, *Macromolecules*, 19 (1986) 240
14 A. Peterlin, *Pol. Eng. Sci.*, 19 (1979) 118
15 J. P. Penning, H. van der Werff, M. Roukema and A. J. Pennings, *Polym. Bull.*, 23 (1990) 347
16 B. Kalb and A. J. Pennings, *Polym. Bull.*, 1 (1979) 877
17 A. Ziabicki, "Fundamentals of Fibre Formation", (John Wiley, London, 1976), ch. 6
18 T. Kunugi, S. Oomori and S. Mikama, *Polymer*, 29 (1988) 814
19 M. P. Laughner and I. R. Harrison, *J. Appl. Pol. Sci.*, 33 (1987) 2955

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