Tensile strength of solution-spun, ultra-drawn ultra-high molecular weight polyethylene fibres: 1. Influence of fibre diameter

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The influence of fibre diameter on the tensile strength of solution-spun, ultra-drawn, ultra-high molecular weight polyethylene (UHMW-PE, $M_w > 10^3$ kg mol^{-1}) fibres was investigated. Fibres with a wide range of diameters were produced by varying the polymer concentration in solution and by applying a drawdown to the fibres. The tensile strength of drawn fibres is compared at a constant Young's modulus in order to eliminate the influence of morphological parameters, such as degree of chain orientation and extension, on the fracture behaviour. It is shown that the tensile strength of UHMW-PE fibres is independent of the fibre diameter. In accordance with previous studies, it is found that fibre fracture is initiated by molecular events, such as chain scission.

(Keywords: tensile strength; fibre; fibre diameter)

INTRODUCTION

In the late 1970s it was discovered that, in contrast to melt-crystallized ultra-high molecular weight polyethylene (UHMW-PE, $M_w > 10^3$ kg mol^{-1}), solution-spun UHMW-PE can be drawn in the solid state to high draw ratios[1–5]. Based on this discovery a process was developed for the production of high modulus (100–150 GPa) and strength (3–5 GPa) polyethylene fibres.

Several studies have been performed concerning the fracture behaviour of solution-spun, ultra-drawn UHMW-PE fibres[4–8]. Two different approaches have been used. The influence of morphological parameters on the tensile strength of UHMW-PE fibres has been studied extensively[4–6]. It was shown that the tensile strength of polyethylene fibres depends on their draw ratio, Young's modulus and on the molecular weight and polydispersity of the polymer. Also, empirical relationships between the Young's modulus of ultra-drawn fibres, the molecular weight of the polymer and the tensile strength were derived[4–6]. In a second set of studies the relationship between macroscopic dimensions and the tensile strength of UHMW-PE fibres is emphasized[7,8]. In these studies it is claimed that the tensile strength (σ_t) of UHMW-PE fibres is inversely proportional to the square root of the fibre diameter (d):

$$\sigma_t \propto d^{-0.5}$$

These two approaches seem to contradict each other, i.e. they focus on different parameters to model the fracture behaviour of polyethylene fibres. Therefore an additional study was performed concerning the influence of fibre diameter on the tensile strength of UHMW-PE fibres.

EXPERIMENTAL

A UHMW-PE grade with weight average molecular weight, $M_w \approx 2 \times 10^3$ kg mol^{-1} and polydispersity, $Q = M_w/M_n \approx 10$ was used in this study.

UHMW-PE was dissolved in decalin at 170°C at nominal concentrations of 2, 4 and 10% w/w. Prior to the dissolution procedure 2% w/w of an antioxidant (d-butyl-*p*-cresol) was added to the polymer and the polymer–solvent mixtures were degassed at room temperature. After complete dissolution, which took approximately 2 h, the solutions were transferred to a fibre extrusion device (*Figure 1*). Fibres were spun at 170°C. Two different spinning procedures were used. In a first set of experiments the initial polymer concentration in solution was varied to obtain fibres with different diameters. The extrusion rate (v_1) and wind-up rate (v_2) of the fibres were equal, i.e. drawdown, $\lambda_1 = v_2/v_1 = 1$. In a second set of experiments a constant polymer concentration of 4% w/v was used. In these experiments the ratio of wind-up rate to extrusion rate was increased stepwise in order to obtain fibres with a different diameter.

Solid-state drawing of dried, solution-spun UHMW-PE fibres was performed at 120°C on thermostatically controlled hot shoes. The draw ratio was determined by measuring the weight of 20 cm of fibre prior to and after drawing.

Nominal stress–strain curves of ultra-drawn UHMW-PE fibres were recorded on a Zwick Tensile Tester equipped with fibre clamps. The original length of the fibres was 0.25 m and a constant crosshead speed of 0.025 m min^{-1} was used.

RESULTS AND DISCUSSION

The prime objective of this study is to investigate the influence of fibre diameter on the tensile strength of solution-spun, ultra-drawn UHMW-PE fibres. Two different procedures were used to obtain fibres with different diameters.

First, the initial polymer concentration in solution was varied. *Figure 2* shows that the polymer concentration,

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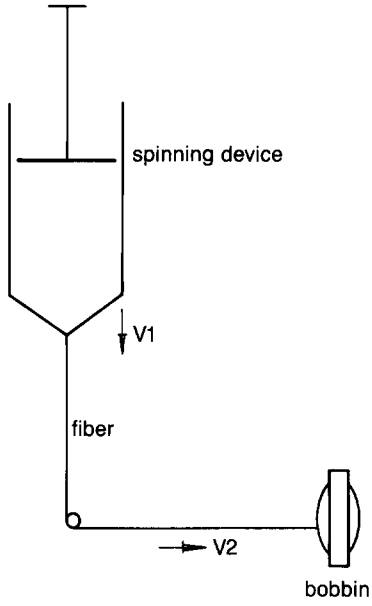

Figure 1 Schematic drawing of the spinning equipment

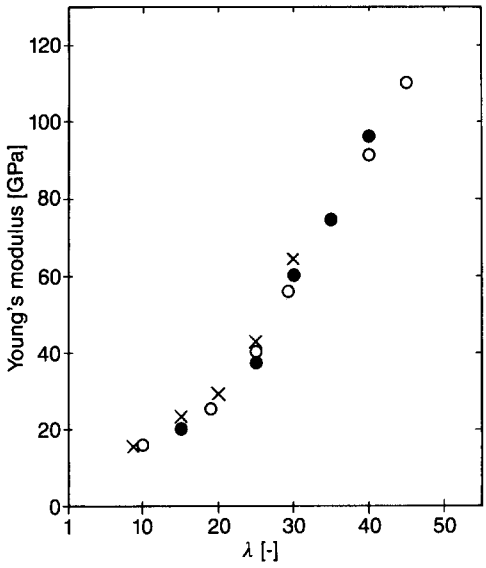

Figure 2 Young's modulus of UHMW-PE fibres as a function of the draw ratio (λ). Concentration (% w/w): ○, 2; ●, 4; ×, 10

at a constant draw ratio (λ), hardly influences the Young's modulus of UHMW-PE fibres. Moreover, in *Figure 3* it is shown that the tensile strength of drawn fibres is also independent of the initial polymer concentration in solution.

In the second set of experiments the ratio of wind-up rate and extrusion rate (drawdown, $\lambda_1 = v_2/v_1$) is increased stepwise (see Experimental section). In other words, the fibres are predrawn in solution during the spinning procedure. In *Figures 4* and *5*, the Young's modulus and tensile strength of these fibres are plotted as a function of the draw ratio in the second drawing step. It is shown that the slope of both the Young's modulus and tensile strength *versus* draw ratio curves increase with increasing drawdown which indicates that pre-orientation is generated.

A variety of studies has been performed concerning the parameters which determine the Young's modulus of drawn polyethylene fibres[9–13]. In general, it is assumed that the Young's modulus is uniquely determined by the degree of chain orientation and extension. However, this degree of chain orientation and extension also influences the tensile strength of fibres[1–5]. Consequently, to investigate the effect of fibre diameter on the fracture behaviour, the influence of chain orientation and extension has to be eliminated. This is achieved by comparing the tensile strength of UHMW-PE fibres at a constant Young's modulus.

The room temperature tensile strength of ultra-drawn UHMW-PE is plotted in *Figure 6* as a function of the Young's modulus. Experimental data from both sets of experiments (*Figures 2–5*) are included in this figure.

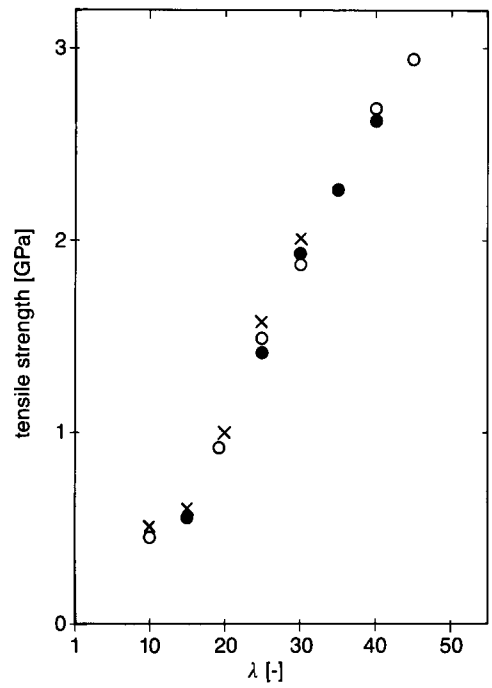

Figure 3 Tensile strength of UHMW-PE fibres as a function of the draw ratio (λ). Concentration (% w/w): ○, 2; ●, 4; ×, 10

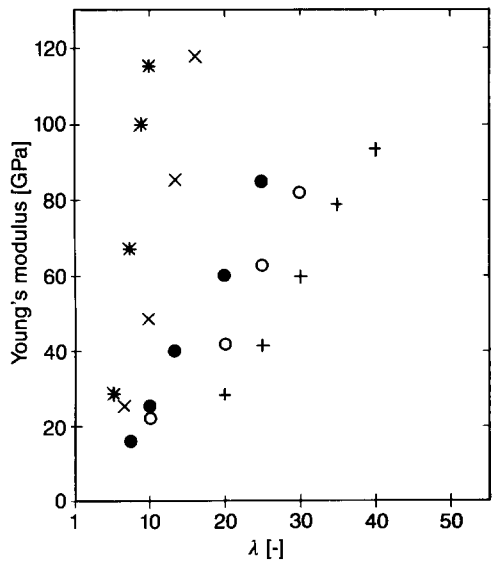

Figure 4 Young's modulus of UHMW-PE fibres as a function of the draw ratio (λ). Drawdown (λ_1) value: +, 1; ○, 5; ●, 19; ×, 32; ✳, 65

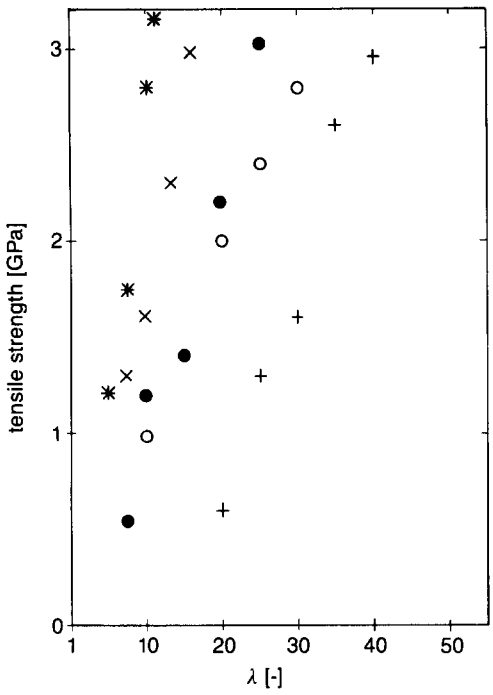

Figure 5 Tensile strength of UHMW-PE fibres as a function of the draw ratio (λ). Drawdown (λ_1) value: +, 1; ○, 5; ●, 19; ×, 32; ✳, 65

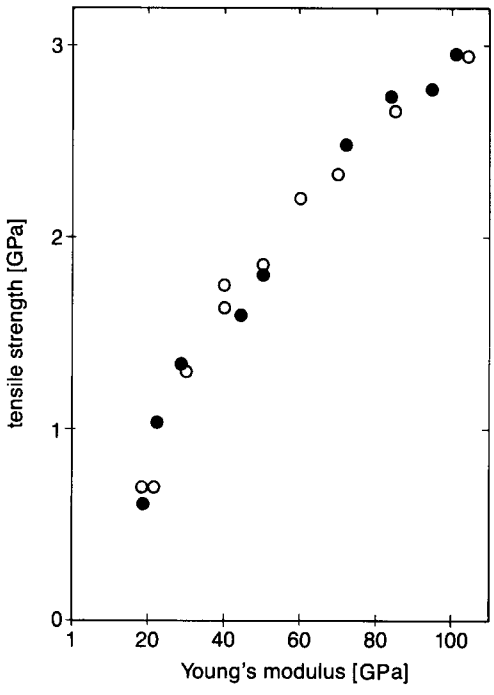

Figure 6 Tensile strength as a function of Young's modulus. ○, Data from *Figures 2* and *3* (concentration = 2, 4 and 10% w/w); ●, data from *Figures 4* and *5* (λ_1 = 1, 5, 19, 32, 65)

Apparently, the tensile strength of UHMW-PE fibres is independent of both the initial polymer concentration in solution and the drawdown. The tensile strength of UHMW-PE fibres, at a constant Young's modulus (75 GPa), is plotted in *Figure 7* as a function of the fibre diameter. It is shown that the tensile strength of UHMW-PE fibres is virtually independent of the fibre diameter, if proper corrections are made for differences in Young's modulus.

Previously, linear elastic fracture mechanics (LEFM), or related theories, were used to model the fracture behaviour of UHMW-PE fibres[7,8]. In LEFM it is assumed that solids are isotropic and fully elastic[14]. A geometry-dependent correction factor is introduced into these models[14] and it is predicted that the tensile strength scales with the fibres diameter to the power −0.5. In *Figure 7*, it is shown that a large discrepancy exists between the experimental data and the theoretical predictions (dashed line). Of course this is hardly surprising because UHMW-PE fibres are highly anisotropic and exhibit pronounced non-elastic effects[15–17].

The experimental observation that the tensile strength of fibres is independent of the fibre diameter indicates that fibre fracture is probably controlled by molecular events such as chain scission or intermolecular chain slippage[4–6,18]. However, at this point it is unknown whether chain scission or chain slippage (creep) initiates the fibre fracture process. This subject will be dealt with in a forthcoming study[19].

A few critical remarks are in order with respect to the tensile strength measurements in this study. First, drawn UHMW-PE fibres with a low Young's modulus (<20 GPa) exhibit a yield stress in the stress–strain curve. These fibres were excluded from this study. The experimental data are limited to UHMW-PE fibres which fracture in a (pseudo-) brittle fashion. Secondly, the tensile tests were performed at room temperature and at a high strain rate. It is well known that the mechanical properties of UHMW-PE fibres are strongly dependent on the time scale and temperature of testing[15–17]. The influence of these parameters on the fracture mechanism of drawn UHMW-PE fibres is discussed in part 3 of this series[20].

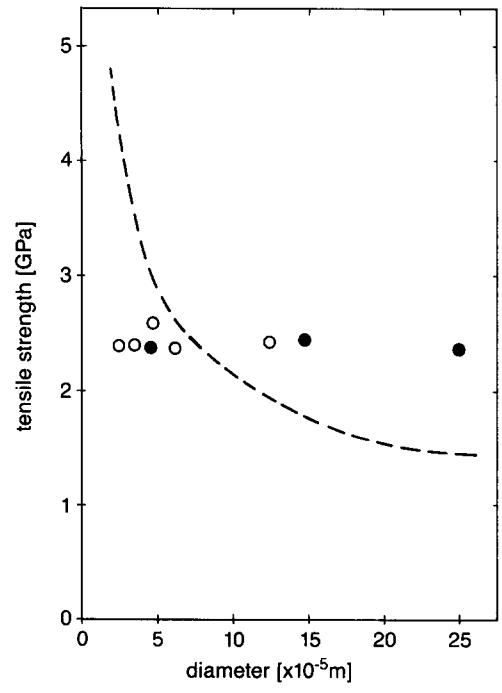

Figure 7 Tensile strength of UHMW-PE fibres as a function of the fibre diameter at a Young's modulus of 75 GPa. ○, Data from *Figures 2* and *3* (concentration = 2, 4, 10% w/w); ●, data from *Figures 4* and *5* (λ_1 = 1, 5, 19, 32, 65)

CONCLUSIONS

The tensile strength of solution-spun, ultra-drawn UHMW-PE fibres, at a constant Young's modulus, is independent of the fibre diameter. This experimental observation indicates that the tensile strength of UHMW-PE fibres, at a constant molecular weight and polydispersity, is mainly determined by morphological parameters such as the degree of chain extension. In accordance with previous studies, it is therefore concluded that the fracture process of UHMW-PE fibres is mainly controlled by molecular events such as chain scission or intermolecular chain slippage.

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