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On the theoretical strength of gelspun/hotdrawn ultra-high molecular weight polyethylene fibres

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Summary

The fraction of load carrying chains in various gelspun/hotdrawn ultra high molecular weight polyethylene (UHMWPE) fibres was evaluated on the basis of a recent morphological model. A linear relation was found between the strength of the fibre and the fraction of load carrying chains, calculated by this method. By extrapolation of this relation to a fraction of load carrying chains of unity, a theoretical strength of 30±3 GPa was estimated for polyethylene.

Introduction

For the production of high modulus/high strength fibres, ultra high molecular weight polyethylene (UHMWPE) is an excellent starting material, because of its high theoretical modulus and strength [1,2]. In order to achieve high strength fibres, the technique of gelspinning and subsequent hotdrawing of the gelspun fibre is a very succesful method, leading to fibres with strengths up to 7 GPa [3]. Compared to the theoretical strength of a single polyethylene chain however, this is a relatively low value, especially when is taken into account that the moduli of these fibres approach values upto 80% of the theoretical modulus of polyethylene.

Estimations of the theoretical strength of polymers can be made using, for instance, the kinetic theory of fracture [2] or Morse potential calculations [4,5], i.e. by considering the single polymer chain only. An estimation of the theoretical strength of polymers from extrapolation of experimentally obtained results seems more desireable, since this approach provides a better understanding of the origin of the strength of oriented polymer samples. In this way, Smook et al. [6] found a theoretical strength of 26 GPa for polyethylene, from extrapolation of fibre strength to the limit where the fibre has zero diameter, thus eliminating the effect of surface irregularities on the strength of the fibre.

The aim of this study is to estimate the theoretical strength of polyethylene fibres by extrapolation of the fraction of load carrying chains in the fibre to unity. This fraction will be calculated for gelspun/hotdrawn UHMWPE fibres from physical properties on the basis of a recent morphological model [7], that has been proven to be succesful for the interpretation of the mechanical properties of these fibres.

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Experimental

The preparation of the high strength fibres, examined in this study, is descibed in detail in a previous publication [8]. Two grades of polyethylene were used throughout this study, one with $M_w=4\times10^6$ kg/kmol and $M_n=2\times10^5$ kg/kmol, referred to as Hifax-A, and one with $M_w=5.5\times10^6$ kg/kmol and $M_n=2.5\times10^6$ kg/kmol, referred to as Hifax-B. Fibres used for drawing experiments were spun from solutions, containing 5 % by weight Hifax-A or solutions containing 1.5 % by weight Hifax-B in paraffin oil.

Mechanical properties of the drawn fibres were determined using an Instron 4301 tensile tester. Tensile tests were performed using a crosshead speed of 12 mm/min and a sample gauge length of 32 mm. At least six separate determinations were made to calculate the strength of each fibre. The cross-sectional area of the fibre was determined from the weight of a piece of fibre of known length, assuming a density of 1000 kg/m^3. The crystallinity of a fibre was determined by differential scanning calorimetry (DSC), using a Perkin Elmer DSC-7 calorimeter, operating at a scanspeed of 10^oC/min. The crystallinity of the sample was calculated from the heat of fusion, taking a heat of fusion of 292.8 J/g for perfectly crystalline polyethylene [9].

Results and discussion

By spinning of semi-dilute solutions of ultra high molecular weight polyethylene (UHMWPE), fibres with high drawability are obtained. Upon hotdrawing, the loosely connected lamellar structure of these fibres is gradually transformed into a fibrillar morphology, with excellent mechanical properties. The basic element of this structure is the microfibril, that is thought to consist of an almost infinite sequence of crystalline blocks, interrupted by disordered domains, in which imperfections like chain entanglements are collected [10]. According to Peterlin [11], the high axial modulus and strength of the microfibril arises from the presence of taut tie molecules (TTM), that form the connection between adjacent crystalline blocks, in the disordered domains (see fig. 1).

Abstract mechanical models of the Takayanagi-type [12], based on the structure of the microfibril described above, have been applied succesfully in the past to explain the dynamic modulus behaviour of fibrous materials. In explaining the strength of these materials however, the theory is in disagreement with experimental data [13].

A recent model, proposed by Dijkstra et al. [7], accounts for the relatively low strength, compared to the high axial moduli, of gelspun/hotdrawn UHMWPE fibres, by emphasizing the ratio of the length of the disordered domains (L_d) to the length of the crystalline blocks (L_c) in the microfibril (see fig 1). Furthermore, the elongation at break of highly drawn fibres that was calculated by the model, assuming that fibre failure is accomplished by rupturing of TTM in the disordered domains, appeared to be in perfect agreement with experimental data. On the basis of this fracture mechanism, a relation between the strength of the fibre and the TTM fraction may be expected. Sample failure will occur, when the TTM in the disordered domains are stressed to fracture, and therefore the strength of the fibre will be $\sigma_f=\sigma_{th}\times\beta$, where σ_{th} represents the theoretical strength of the polyethylene chain. Consequently, we can estimate the theoretical strength of polyethylene from this relation.

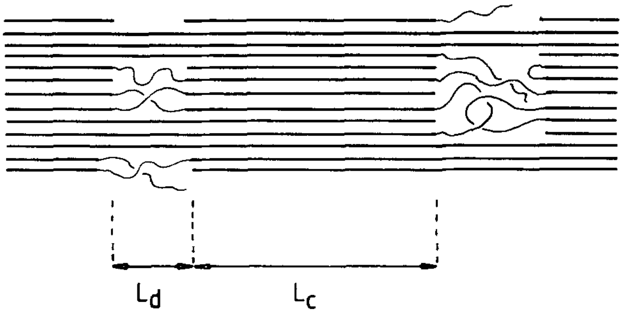

Fig. 1. Schematic representation of the elementary microfibril, showing crystalline blocks with length L_c and disordered domains with length L_d.

According to the model, the modulus of the fibre is related to the fraction of TTM in the disordered domains, β, and the ratio of the disordered domain length to the length of the crystalline blocks in the microfibril, L_d/L_c, through

$$E = E_c \times \frac{1+(L_d/L_c)}{1+(1/\beta)\times(L_d/L_c)} \qquad \text{(eqn 1)}$$

where E_c represents the theoretical modulus of polyethylene and E represents the modulus of the fibre that is found in tensile testing. From spectroscopic techniques, the theoretical modulus of polyethylene is estimated at 350 GPa [1].

In order to calculate the TTM fraction of fibres with various moduli from this equation, L_d/L_c must be known for these fibres. Assuming that all amorphous material in the fibre is located in the disordered domains, and that TTM are segregated to form crystalline bridges between adjacent crystalblocks, this ratio can be calculated from the crystallinity (χ) of the various fibres, through

$$(L_d/L_c) = (1-\chi)/(\chi-\beta) \qquad \text{(eqn 2)}$$

Inserting this equation into (1), and assuming a theoretical modulus of 350 GPa for polyethylene, we can calculate the TTM fraction β for various fibres from experimentally obtained modulus and crystallinity data.

High strength fibres were obtained by hotdrawing of two different gelspun fibres, referred to as fibre A and fibre B respectively. Fibre A was prepared from a spinning solution containing 5% by weight Hifax-A. The maximum draw ratio that could be achieved by drawing this fibre in a two-step drawing process was $\lambda=100$, giving a fibre with a tensile strength of 4 GPa. Fibre B was prepared from a more dilute solution, containing 1.5% by weight of Hifax-B, which has a higher molecular weight and a narrower molecular weight

Table I Physical properties of some gelspun/hotdrawn UHMWPE fibres.

	Draw ratio	Modulus (GPa)	Crystallinity	TTM fraction	Strength (GPa)
Fibre A	10	10	0.47	0.019	0.7
	25	60	0.63	0.092	2.3
Fibre B	80	161	0.80	0.170	5.3
	150	210	0.87	0.195	5.9

distribution than Hifax-A. The lower concentration of the spinning solution, from which fibre B was prepared, resulted in a higher drawability of this fibre. The maximum strength that could be achieved by hotdrawing of fibre B in a two-step process was 6 GPa at a draw ratio of λ=150.

From modulus and crystallinity data of the fibres, that were drawn to various ratios, the TTM fractions in these fibres were calculated according to the procedure discribed above. Table I shows the results for a selected number of fibres. Crystallinity data were calculated from the ratio of the heat of fusion of the sample to the heat of fusion of perfectly crystalline polyethylene. The crystallinity values reported should therefore be interpreted with caution, since this method does not take the contributions of surface free energy to the heat of fusion into account [14].

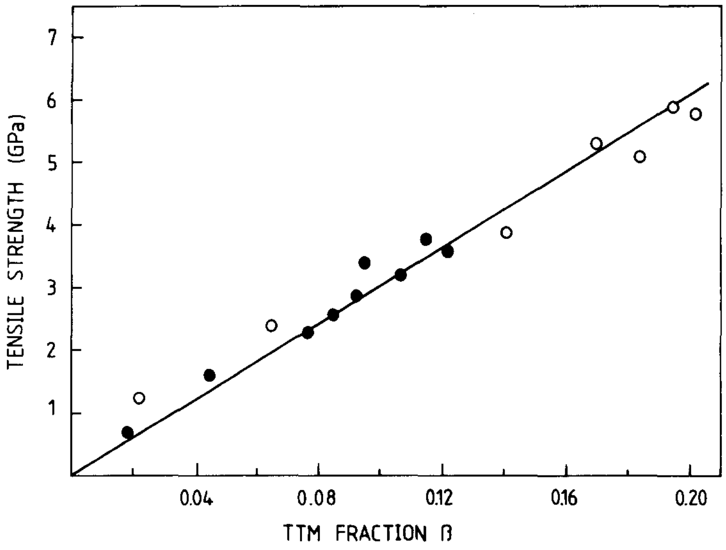

Fig. 2. The strength of various hotdrawn fibres as a function of the taut tie molecule (TTM) fraction. Open and closed circles refer to fibres prepared by hotdrawing of Fibre B and Fibre A respectively.

In figure 2, the strength of various hotdrawn fibres is plotted as a function of the TTM fraction, calculated according to the method described above. A linear relation is found, with a maximum deviation from data points of approximately ten procent. Upon tensile testing, an experimental error of the same order of magnitude is usually encountered, due to failure of the sample at the spots where it is clamped. Experimental errors in modulus and crystallinity determination will result in an experimental error in the TTM fractions calculated. This experimental error may be especially large for samples with high crystallinity, since the experimental error in the crystallinity might approach the value of $(1-\chi)$, from which the ratio of the disordered domain length to the length of the crystalline blocks is calculated (see eqn. 2). Taking this into account, the correlation between experimentally obtained strength data and TTM fractions is very good.

The slope of the line equals 30±3 GPa, i.e. extrapolation of the line to $\beta=1$ yields a theoretical strength of gelspun/hotdrawn UHMWPE fibres of 30±3 GPa. This value is in very good agreement with the theoretical strength polyethylene that is found by other methods. From Morse potential calculations a value of 33 GPa is obtained [4,5], where the kinetic theory of fracture estimates the theoretical strength of polyethylene at 32.5 GPa [2]. It should be noted, that extrapolation to $\beta=1$ implies that we extrapolate to 100% crystallinity and infinite molecular weight, since crystal imperfections and chain ends interrupt the crystal continuity, that is inherent to a TTM fraction of unity. It is remarkable that hotdrawn fibres, prepared from polyethylene samples with different molecular weight characteristics using spinning solutions having different polymer concentrations obey the same relation between strength and TTM fraction.

The results indicate that the strength of a gelspun/hotdrawn UHMWPE fibre is solely determined by the fraction of TTM created upon hotdrawing. The process of formation of TTM during drawing is, however, extremely complicated, and will be affected by a number of parameters, e.g. the molecular weight characteristics of the polymer sample used and the initial morphology of the as-spun fibre. The maximum strength that can be achieved by spinning a solution containing 1.5 % by weight Hifax-B and subsequent hotdrawing of the as-spun fibre is 7.2 GPa. According to the model, this corresponds to a TTM fraction of 0.24. Higher strengths might be achieved by applying higher draw ratios, which requires spinning from more dilute solutions, since a lower concentration of entanglements in the spinning solution enhances the maximum attainable draw ratio of the as-spun fibre [3]. Concomitantly, polymer samples with a higher molecular weight will have to be used, in order to retain the fibre forming properties of the spinning solution.

The results demonstrate that the simple morphological model provides a straightforward method for interpreting the mechanical properties of gelspun/hotdrawn UHMWPE fibres.

Conclusions

The strength of gelspun/hotdrawn UHMWPE fibres is directly related to the fraction of TTM , that connect adjacent crystalline blocks in the microfibril. A linear relation was found between the strength of the fibres and the TTM fraction, that was calculated on the basis of a simple morphological model. By extrapolation of this linear relation to a TTM fraction $\beta=1$, a theoretical strength of 30±3 GPa was found for polyethylene, which is in very good agreement with the theoretical strength of polyethylene, calculated by other methods. This implies that fracture of these high strength fibres, under testing conditions used throughout this study, arises from rupturing TTM in the disordered domains in the fibre structure. The strength of the fibre is therefore strongly depressed by the presence of small disordered domains. Since these disordered domains are very small compared to the long crystalline blocks in the microfibril, the modulus of these fibres may reach a value, close to the theoretical modulus of polyethylene.

Acknowledgement

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