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The role of taut tie molecules on the mechanical properties of gel-spun UHMWPE fibres

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Summary

Gel-spun hot-drawn UHMWPE fibres are known to display a high tensile modulus and strength. These properties are treated in a simple morphological model, explaining the approach of nearly the crystal modulus for fibres attaining only a fraction of the theoretical tensile strength and elongation at break.

Creep experiments on irradiated gel-spun UHMWPE fibres serve as an additional test for the application of the model.

Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is one of the most promising polymeric materials to produce high tenacity fibres, because of the high crystal modulus of 210 to 350 GPa (1-4), the theoretical strength of about 30 GPa (5), and the theoretical elongation at break of 30 % (6).

Industrially made gel-spun hot-drawn UHMWPE fibres, with a tensile strength of 2.6 GPa and tensile modulus of 117 GPa (7), are already available. In laboratries tensile strengths up to 7 GPa and tensile muduli up to 200 GPa have been achieved (8-10) for gel-spun UHMWPE fibres and tapes.

Chains connecting the crystal blocks in the fibre, called taut tie molecules (TTM), are often thought to determine the tensile strength (11-13). Recently, irradiation experiments on gel-spun UHMWPE fibres confirmed the dependence of the tensile strength on the number of TTM in the intercrystalline disordered domains (14).

In this paper a model is presented explaining the high tensile modulus of gel-spun, hot-drawn UHMWPE fibres, in spite of the relatively low tensile strength and elongation at break as compared to the theoretical limits.

As an additional test for the model, creep measurements were performed in a dead-load apparatus and in a tensile tester. In spite of the high crystallinity and the ultra-high molecular weight polyethylene used, still some creep could be measured. It must be noted that creep levels for gel-spun hot-drawn UHMWPE fibres are substantially below those encountered with conventional polyethylene, or the specialized high-modulus fibres from the melt-spinning processes and solid-state extrusion (7, 15).

Dead-load experiments on irradiated gel-spun UHMWPE fibres revealed an increase in creep rate with increasing irradiation dose, just as reported very recently by Klein, Woods and Ward (16). The increase in creep rate up on irradiation, predicted by the model from the number of scissioned TTM, is in good agreement with the experimental values.

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Experimental

Gel-spun UHMWPE fibres, used in this study, were obtained by hot-drawing of porous polyethylene, with an initial weight average molecular weight of $4 \cdot 10^6$ kg/kmol (Hifax 1900, Hercules) as described previously (17) . Cross-sectional areas of the filaments were determined from fibre weight and length assuming a density of 1000 kg/m^3 .

For the dead-load measurements, a piece of fibre, 50 cm in length, was clamped at both ends. One of the clamps had a fixed position, the other was freely suspended and had various weights attached. The movement of the latter was recorded by means of a linear displacement transducer coupled with a x-t recorder. Tensile tests were performed using an Instron 4301 tensile tester at various crosshead speeds. Both dead- load experiments and tensile tests were performed at room temperatuur.

The irradiation procedure was as follows. The fibre was wound onto an, 0.1 mm thick, aluminium cylinder. Fibre-ends were glued onto the aluminium surface. The aluminium cylinder was subsequently placed in the electron beam, in a nitrogen atmosphere, while being rotated in order to achieve a homogenious irradiation dose.

The Van de Graaff generator accelerated the electrons up to 3 MeV, an energy most suitable for irradiation experiments as the linear energy transfer (LET) is almost constant from 1 to 3 MeV (18).

Extraction of the sol- fraction, for the determination of the cross-link efficiency, was performed with boiling p-xylene, containing 0.5 wt. % of anti-oxidant (2,6-di-t-butyl 4 methylcresol). Samples were deswollen in aceton and dried under vacuum at 50 ° C.

Tabel 1

Irradiation dose (Mrad)	Gel-fraction (%)	$\sigma(R)/\sigma(0)$	$\dot{\varepsilon}(R)/\dot{\varepsilon}(0)$ measured	$\dot{\varepsilon}(R)/\dot{\varepsilon}(0)$ calculated
1	4.6	1.06	3.1	1.4
3	39.3	1.19	7.7	2.9
10	64.3	1.82	26.3	40.0

Results

Tensile tests on gel-spun hot-drawn UHMWPE fibres, with an initial strength of 3.5 GPa, were performed at different deformation rates. Figure 1 shows that the deformation rate influences the stress-strain curve. At low deformation rates the stress reaches a plateau, after an initial increase with strain. The high strain rates are normaly used to determine the tensile strength and initial tensile modulus.

In figure 2 a stress-strain curve, recorded at low strain rate, was stopped after a certain amount of strain and the cross-head was returned. Then the stress-strain curve was again recorded at a much higher strain rate. The stress in the first part of the second curve was zero, indicating that a large part of the strain in the first curve was plastic deformation. No influence was seen from the first curve on the tensile strength and initial modulus in the second curve.

Dead-load tests were performed to determine the deformation creep rate as a function of the load. An extremely load sensitivity of the creep rate was found. In figure 3 these data are shown together with the stress and deformation rate values of the tensile testing. Dead-load testing, for loads greater than 2 GPa was not possible, because of the short lifetime of the fibre under such circumstances. Smook, Hamersma and Pennings (19) measured the lifetime of gel-spun UHMWPE fibres in dead-load tests, and found an exponential dependence between lifetime and applied load.

Cross-linking is often recommended to improve creep-resistance (20-22). For this reason we irradiated the UHMWPE fibre with high-energy electrons. The results of

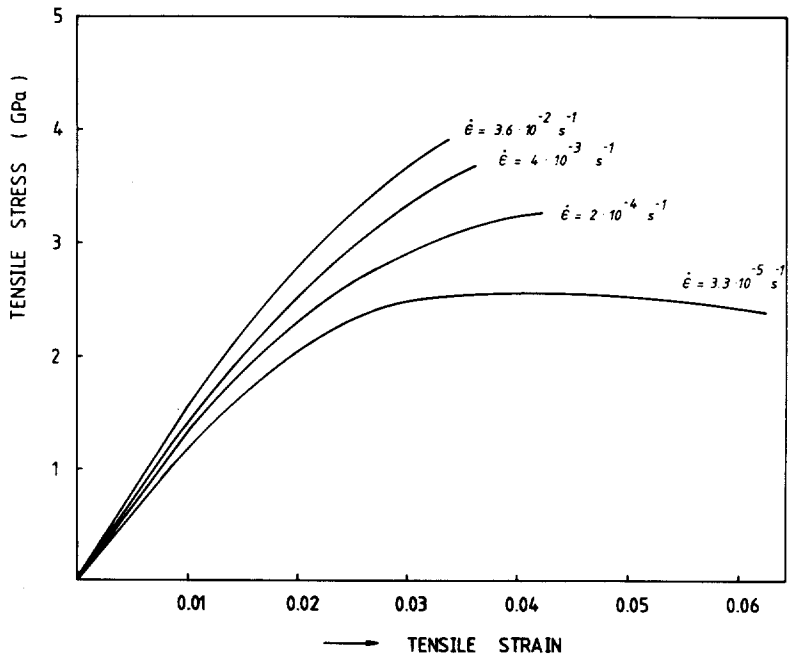

Figure 1 : Stress-strain curves at room temperature for a gel-spun hot-drawn (λ= 100) UHMWPE fibre at various deformation rates, $\dot{\epsilon}$.

the gel-sol measurements, an indication for the cross-link density(23) , are shown in tabel 1.

Dead-load tests at a stress level of 1 GPa on these cross-linked fibres revealed the opposite of the expected reduced creep rates. Creep-resistance of gel-spun hot-drawn UHMWPE fibres is not enhanced by irradiation (see figure 4) , just as Klein, Woods and Ward (16) found very recently.

Dead-load experiments on fibres with a hot-draw ratio of λ = 50 and λ = 80 yielded creep rates that fitted perfectly in figure 3, i.e. for a fibre with draw ratio λ = 100.

Discussion

The extraordinary material properties of fibrillar UHMWPE encouraged many scientists to find an explanation for these properties, and to forecast its ultimate properties. Peterlin (12) treats three of the most generally applied models in an excellent review artical on the mechanical properties of fibrous structures. Peterlin's microfibrillar model (11), Prevorsek's Swiss cheese model (27) and the composite model of Barham and Arridge (24).

Fibres made by gel-spinning (9, 25 , 17), surface-growth (26) and drawing of virgin polymer (27) are known to display material properties quite different from those made by melt-spinning (28) or solid-state extrusion (29).

Peterlin's model describes the melt-spun hot-drawn polyethylene fibres quite well, the ultra-high modulus of the gel-spun hot-drawn UHMWPE fibres however can not be explained by this model. The composite model of Barham and Arridge yields a more realistic value for the tensile modulus of these fibres, but annealing experiments cannot be explained. Very recently Zachariades and Kanamoto (30) discussed a new morphological model based on the tensile modulus and tensile strength to the macrofibrillar dimen-

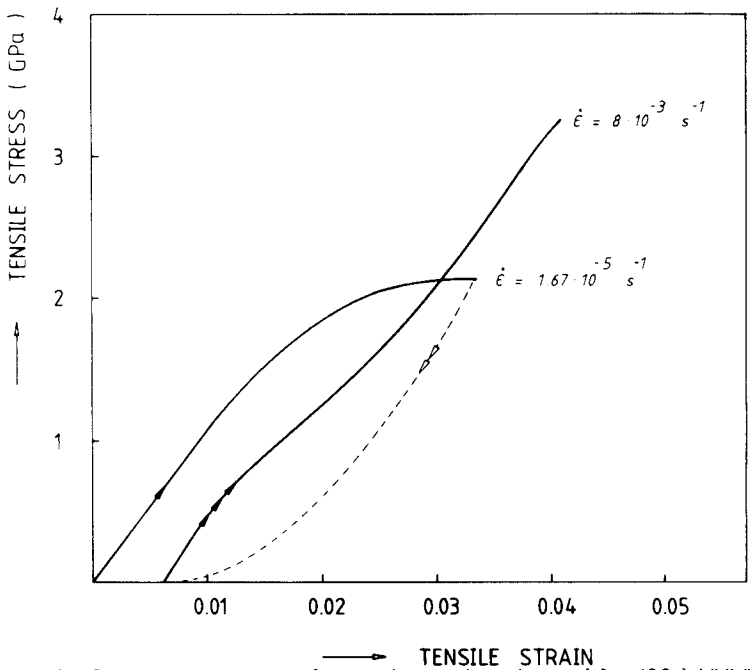

Figure 2 : Stress- strain curve for a gel-spun hot-drawn ($\lambda = 100$) UHMWPE fibre. First deformation rate $\dot{\varepsilon} = 1.67 \cdot 10^{-5}\ s^{-1}$, after cross-head return ,second deformation rate $\dot{\varepsilon} = 8 \cdot 10^{-3}\ s^{-1}$.

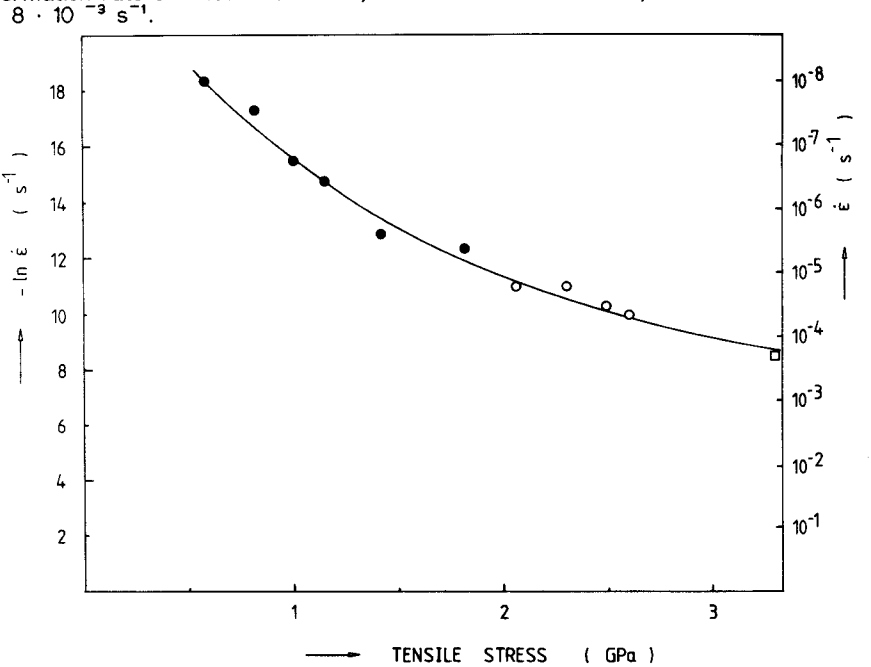

Figure 3 : Creep-rates as a function of the tensile load for a gel-spun hot-drawn (λ=100) UHMWPE fibre. ● dead-load experiments , ○ tensile tests, □ extrapolated tensile test.

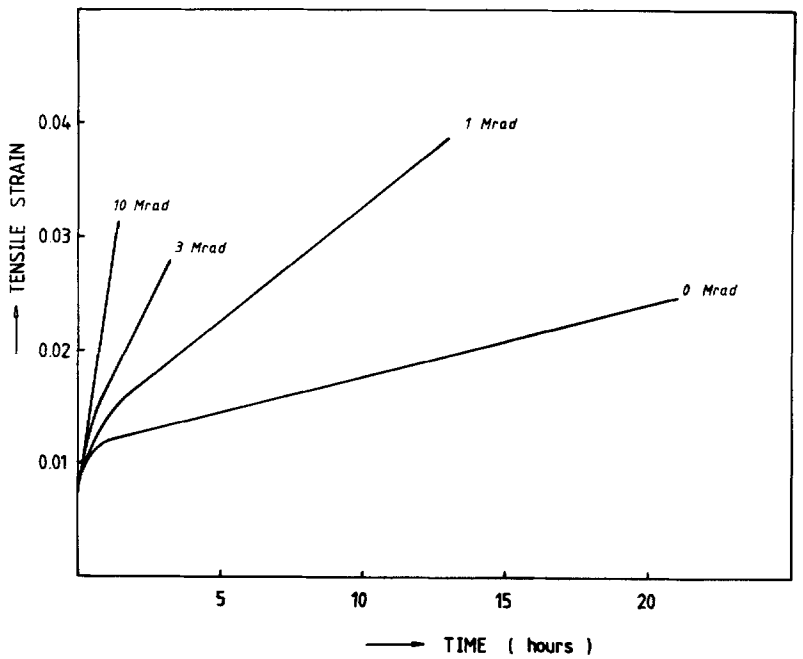

Figure 4 :Strain-time creep curves for a gel-spun hot-drawn (λ=100) UHMWPE fibre, at different irradiation doses.

sions. The deformed crystals are thought to be connected by taut tie molecules and intercrystalline connections. The experimental results of Zachariades are very promising, but the UHMWPE samples examined are very different in structure compared to the gel-spun fibre. Zachariades' sample preparation yields finite crystal dimensions connected by tie molecules. Gel-spun and surface-growth fibres are believed to consist of infinite structures in the direction of the fibre axes. The detection of macrofibril ends has never been effectuated.

The lack of a model explaining satisfactorily the material properties of gel-spun or surface-growth UHMWPE fibres, led us to a new simplified model. The gel-spun and surface-growth UHMWPE fibres consist of macrofibrils of about 0.5 μm in diameter, just as in many other kinds of fibres (31). These macrofibrils are thought to consist of microfibrils of about 20 nm in diameter (32). Dark-field electron-microscopy and WAXS experiments (33) revealed that these microfibrils consist of crystal blocks of at least 70 nm in length connected by disordered domains of about 4 nm in length. In the disordered domains the physical entanglements, chain ends and other imperfections, as well as TTM, are thought to be collected. From the entanglement density (34) in a 5 wt.% gel, assuming that no entanglements are lost during gel- spinning and hot-drawing, and the molecular weight , a number of about 110 entanglements per disordered domain can be calculated, and a number of chain ends of about 15 (32). From irradiation experiments (14) the number of TTM was calculated to be 150 per disordered domain for a fibre with a tensile strength of 3.5 GPa .

Morse- potential calculations on the C-C bond (34) and infra-red experiments (6) on polyethylene estimated the bond-strength at about 25-30 GPa and the elongation at break at about 30-35 %. In our model the stress in the microfibril is transfered by the TTM and the entangled chains in the disordered domains. The disordered domain is the weakest spot in the microfibril, i.e. the elongation at break of the disordered domain, of length l_a, may be about 35 %. The elongation of the crystalline block, of length l_c, is determined by the crystalline modulus, E_c , and the tensile stress at break, σ_b . The elongation at break of the fibre must be the sum of both (see figure 5):

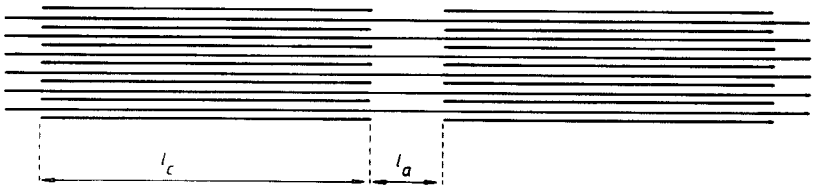

Figure 5 : Schematic model of the gel-spun h0t-drawn UHMWPE fibre, consisting of crystal blocks with length l_c and disordered domains with length l_a .

$$\varepsilon_b = \frac{\Delta l}{l} = \frac{\frac{\sigma_b}{E_c} \cdot l_c + 0.35 \cdot l_a}{l_c + l_a} \qquad (1)$$

For a fibre with a tensile strength of 3.5 GPa, equation (1) yields an elongation at break of 3 % , exactly the experimental value (see figure 1). The tensile modulus is now given by equation (2)

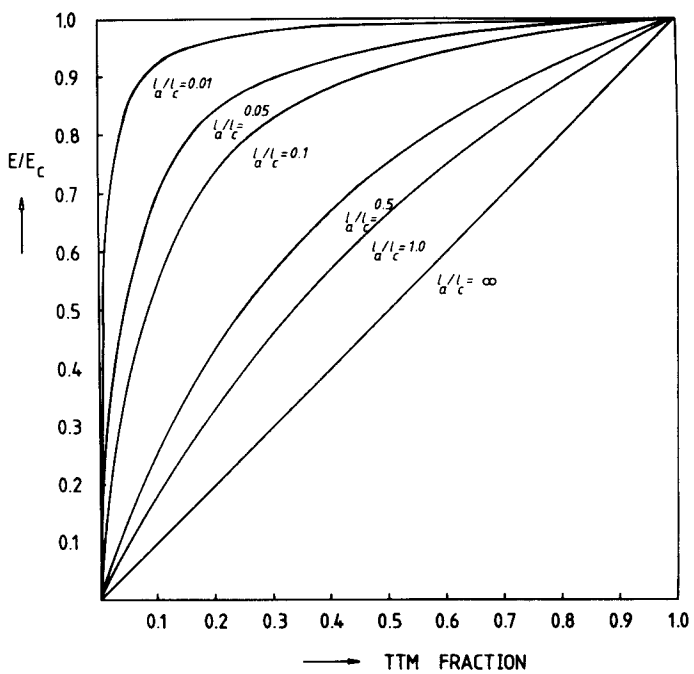

Figure 6 : The tensile modulus as a function of the taut tie molecule (TTM) fraction, for various length ratios of the crystalline blocks and amorphous domains.

$$E = \frac{\sigma}{\varepsilon} = E_c \cdot \frac{1 + (l_a / l_c)}{1 + 1 / \beta \cdot (l_a / l_c)} \qquad (2)$$

Where β is the fraction of load carrying TTM in the disordered domain (see figure 5). Equation (2) can also be deduced from the Takayanagi model (36, 37), but the quintessence of our model lies in the ratio of crystal-block length to disordered-domain length, and not in the crystalline fraction. In figure 6 the tensile modulus is shown as a function of the fraction of TTM, β . For the ratio of crystal-block length to disordered-domain length in the gel-spun hot- drawn fibre, $l_a/l_c \approx 0.05$, at a TTM fraction of only 10 %, the tensile modules has already achieved 70 % of the crystal modulus , i.e. at only 10 % of the theoretical strength, the tensile modulus is already 70 % of the crystal modulus.

Our model gives not only a very simple explanation for the relatively low elongation at break and high modulus for a given tensile strength, but it also accounts for the increase in creep rate with increasing irradiation dose. TTM are thought to be preferentially scissioned in irradiation experiments (14). Both ends will immediately recoil, separating the two radicals over such a distance that recombination is rather unlikely. In tensile testing the stress must be transfered by the chains that are left, i.e. the stress in these chains is increased. Irradiation experiments showed that 6 % of the load carrying chains per Mrad irradiation dose are scissioned in gel-spun UHMWPE fibres (14). From figure 6 the creep rate can be calculated for the increase in internal stress. In tabel 1 these creep rates are compared with the measured creep rates of the irradiated samples (see figure 3). In view of the precision of the creep-rate measurements, since a small variation in fibre diameter results in a large creep rate deflection, and neglecting interfibrillar TTM and contributions of trapped entanglements, the agreement between experiment and calculation is very good.

Conclusion

The microfibrils in gel-spun hot-drawn UHMWPE fibres are thought to consist of large crystal blocks connected by small disordered domains. In tensile testing the stress in the disordered domains is supposed to be transfered by TTM and entangled chains. The tensile strength is determined by the fraction of load carrying chains in the disordered domains. The elongation at break and the tensile modulus are largely determined by the ratio of disordered-domain length to crystal-block length.

This model explaines very adequately :

- the tensile strength of the fibre
- the high tensile modulus for fibres with relatively low elongation at break and tensile strength
- the elongation at break for a given tensile strength
- the increase in creep rate with irradiation dose

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