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Annealing of gel-spun hot-drawn ultra-high molecular weight polyethylene fibres

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Summary

Gel-spun hot-drawn ultra-high molecular weight polyethylene (UHMWPE) fibres were annealed with fixed fibre ends, at temperatures near the orthorhombic-hexagonal lattice transition temperature. A permanently reduced tensile modulus without loss in tensile strength, i.e. increased elongation at break, was observed upon tensile testing of these annealed fibres. The unchanged tensile strength upon annealing, indicates that the tensile strength is likely to be determined by the entanglement concentration.

Introduction

Gel-spun hot-drawn UHMWPE fibres display material properties that make them suitable as an industrial yarn. Its high tensile strength, upto 7 GPa (1, 2), is higher than any other industrial fibre, and its low density makes it even more attractive for many applications . The tensile modulus, of about 150 to 200 GPa, is near that of the crystal modulus of polyethylene. For some purposes however, especially for usage with high energy absorbance, the high modulus is not desirable. An industrial yarn with high tensile strength and moderate tensile modulus, *i.e.* high elongation at break, would be capable of absorbing enormous amounts of energy.

In the gel-spinning hot-drawing process, the high tensile strength is automatically accompanied by a high tensile modulus. The gel-spun hot-drawn UHMWPE fibre is thought to consist of almost entirely chain extended molecules. Large crystal blocks are interrupted by small disordered domains containing defects like entanglements, chain ends, twists, etc. (3, 4). The tensile strength of the fibre is often thought to be determined by the fraction of load carrying chains, or taut tie molecules (TTM), in the disordered domains (4). The tensile modulus of the fibre is determined by the ratio of crystal-block length to disordered domain length, and the fraction of TTM in the disordered domain (4). Due to this model a high-strength fibre with moderate tensile modulus should have a large TTM fraction and a low ratio of crystal-block length to disordered-domain length.

In this communication some further results on annealing experiments are presented.

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Annealing, at a temperature near the orthorhombic-hexagonal lattice transition, resulted in a remarkable permanent reduction of the tensile modulus and an increase of the elongation at break, while maintaining a high strength level.

Experimental part

Ultra-high strength polyethylene fibres used in this study were obtained by hot-drawing of porous polyethylene obtained by gel-spinning of UHMWPE (Hifax 1900 : $M_w = 4 \cdot 10^6$ kg/kmol, $M_n = 5 \cdot 10^5$ kg/kmol) hot drawn to a ratio of $\lambda = 100$, as described previously (5). Upon tensile testing, the initial (unannealed) fibre displayed a tensile strength of $\sigma = 4$ GPa, a tensile modulus of $E = 150$ GPa and an elongation at break of $\varepsilon = 0.03$.

The gel-spun hot-drawn UHMWPE fibre was wound onto an aluminium cylinder, with both fibre ends glued onto the aluminium surface to prevent fibre shrinkage upon annealing. The cylinder was subsequently placed into a glass container, which was flushed with nitrogen gas in order to keep out oxygen. The glass container was submerged in a thermostated silicone oil bath of the desired temperature.

Tensile tests were performed using an Instron 4301 tensile tester at a crosshead speed of 24 mm/min and a gauge length of 50 mm, at room temperature.

Differential Scanning Calorimetry (DSC) measurements were performed using a Perkin Elmer DSC-7 at a scanning rate of 0.1 °C/min. Constrained melting of the fibres was conducted by winding a piece of fibre, ca. 30 cm in length, tightly around an aluminium frame. The fibre ends were knotted and loose ends were cut off. In this way the length of the fibre was kept constant during heating.

Results and Discussion

In figure 1 the stress-strain curve of a gel-spun hot-drawn UHMWPE fibre annealed at 149 °C for 24 hours is shown. The increase in absorbed elastic energy is indicated by shading the area corresponding to the difference in applied work.

In figure 2 the stress-strain curves of gel-spun hot-drawn annealed UHMWPE fibres are shown. The fibres are annealed for one hour at various temperatures. Annealing experiments below 149 °C did not show any change in mechanical behaviour. Annealing at 149 °C for 24 hours resulted in a decrease in tensile modulus from $E = 150$ GPa to $E = 70$ GPa, and an increase in elongation at break from $\varepsilon = 0.03$ to $\varepsilon = 0.06$. No change in tensile strength was measured upon annealing. The data in figure 2 shows that the annealing effects are very temperature sensitive. The effects of annealing for 24 hours at 149 °C (see figure 1) are comparable with those encoutered after annealing for only 1 hour at 151.4 °C. Figure 2 also shows that annealing at 151.9 °C for 1 hour resulted in a drastic decrease in tensile strength. After cooling down to room temperature, the fibre annealed at this high temperature adheres strongly to the aluminium surface, indicating that the molecular conformation in the fibre had changed completely.

The change in material properties of fibrous material upon annealing was succesfully explained by the microfibrillar model of fibrous structure which was developed by Peterlin (6). Peterlin showed that annealing at temperatures between 60 and 120 °C of fibrous material, obtained by drawing of lamellar polymer, drastically reduced the axial modulus .

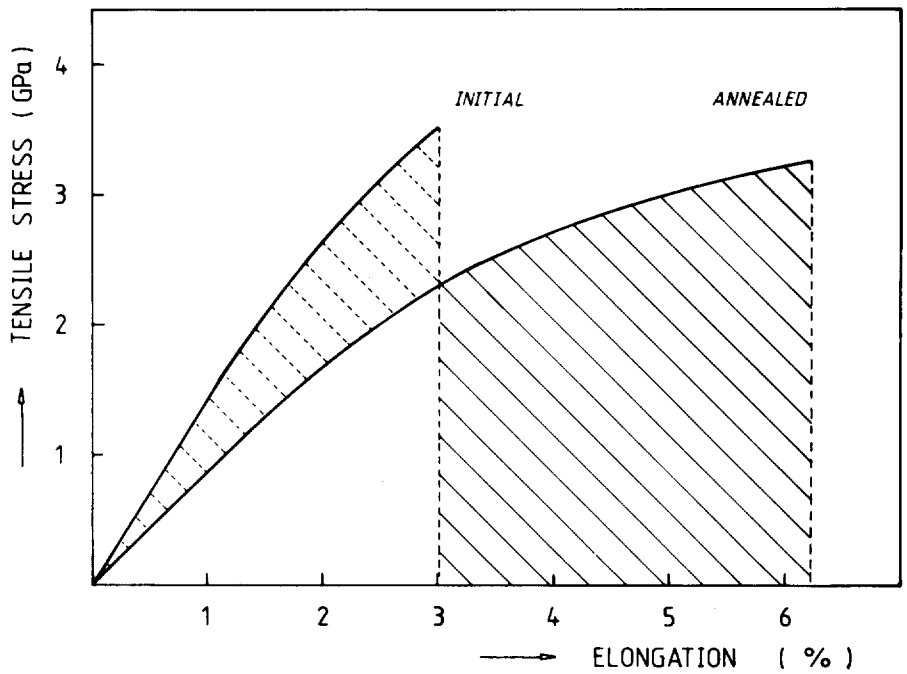

Figure 1 : The stress-strain curve of a gel-spun hot-drawn UHMWPE fibre annealed at 149 °C for 24 hours. The increase in elastic energy absorbance is indicated by shading.

Samples annealed with fixed ends recovered or even surpassed the elastic modulus before annealing, if they stayed for a few hours at room temperature. Tsruta *et al.* (7) showed that folded chain crystals within microfibrils sensitively reorganize on annealing at temperatures above 110 °C .

Our annealing experiments once again emphasize the difference in morphology and material properties between gel-spun hot-drawn and melt-spun hot-drawn polyethylene. At the low annealing temperature of 140°C described previously (8), no change in material properties was recorded for gel-spun hot-drawn UHMWPE fibres. Additionally, the reduction in tensile modulus after annealing at the high temperatures ($149 \leq T \leq 152$ °C) is permanent, *i.e.* it did not recover after staying at room temperature.

Recently Dijkstra and Pennings (4) presented a simple morphological model explaining the material properties of gel-spun hot-drawn UHMWPE fibres. These fibres are thought to be composed of arrays of long crystal blocks, about 70 nm in length, and small disordered domains, of about 4 nm in length. The tensile strength is thought to be determined by the fraction of load carrying chains bridging the crystal blocks, the taut tie molecules (TTM). The elongation of the fibre is determined by the elongation at break of the disordered domains and the elongation of the crystal blocks. In this model, the tensile modulus is determined by the ratio of crystal-block length and disordered-domain length, and the fraction of TTM.

A decrease in tensile modulus without a decrease in tensile strength could be achieved, according to the model, by lowering the ratio of crystal-block length and disordered-domain length. The TTM fraction however, should be maintained unchanged.

Annealing of drawn polyethylene not only results in a healing of the crystal defects or lattice faults from the crystals (9), but it also extends the contour length of the TTM by pulling out of crystal blocks chain sections by which these molecules are anchored in the crystal lattice (6). It is evident that both annealing effects tend to decrease the ratio of crystal-block length to disordered-domain length, thereby reducing the tensile modulus and increasing the elongation at break of the fibres.

The annealing effects on the material properties seem to depend very critically on the annealing temperature. Below 149°C no change in modulus was observed, although De Boer and Pennings (8) reported that gel-spun hot-drawn UHMWPE fibres were less radiation sensitive after annealing for 64 hours at 140°C, *i.e.* a fraction of the TTM relaxed by the annealing treatement (10). Above 149°C the material properties change very rapidly. Near 152°C the molecules seem to disentangle and the number of TTM per disordered domain decreases .

Figure 3 shows the differential scanning calorimetry (DSC) curve of a constrained, *i.e.* with fixed fibre ends, heated gel-spun hot-drawn UHMWPE fibre. As described previously (11, 12), the orthorhombic-hexagonal lattice-transition is observed at 152 °C. In the hexagonal or rotary phase, the molecules can easily slip past one another and disentangle (11).

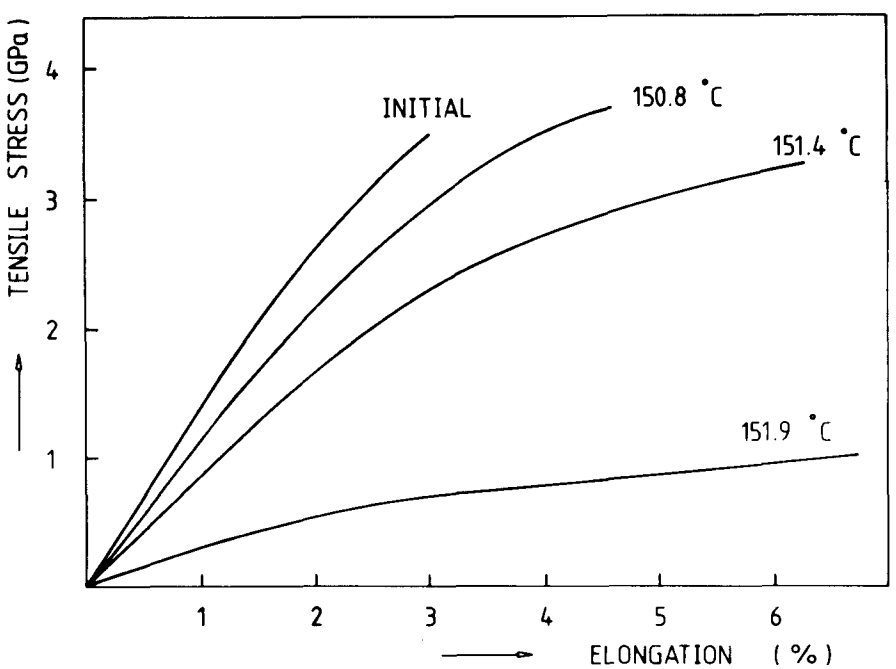

Figure 2 : The stress-strain curves of gel-spun hot-drawn UHMWPE fibres. The curve of the initial fibre is shown together with those of the fibres annealed at 150.8 °C, 151.4 °C and 151.8 °C for one hour.

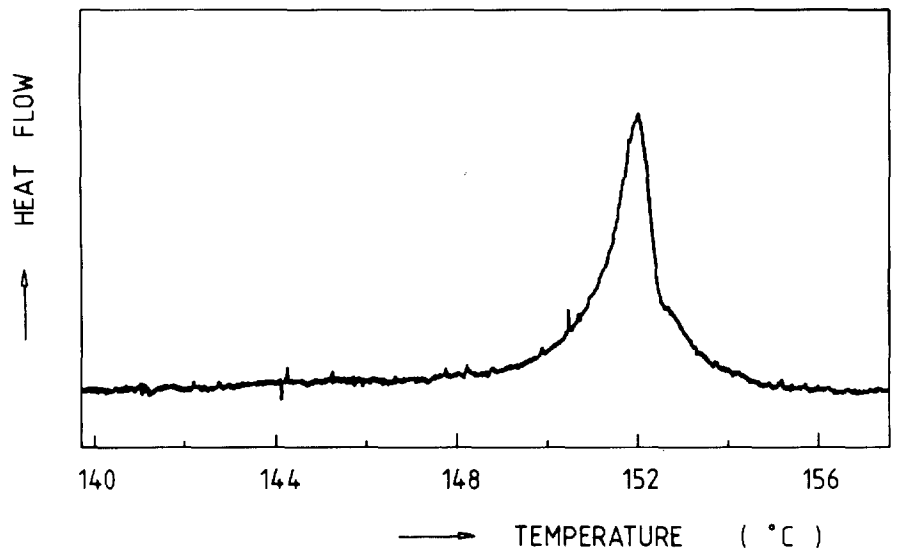

Figure 3 : The constrained melting DSC thermogram of a gel-spun hot-drawn UHMWPE fibre, recorded at a scanspeed of 0.1 °C/min.

The annealing temperatures used in the experiments shown in figure 2 are located in the onset of the phase transition peak shown in figure 3. Thus, it is very likely that the orthorhombic-hexagonal lattice transition plays an important role in the annealing experiments. The rotary phase makes it very easy for TTM to become lax, because the chains can easily slip past one another. The crystal blocks might be too long to be traversed by Reneker defects (13) at temperatures below the lattice transition temperature. In this study, the annealing phenomena are explained by the laxing of TTM. The authors want to emphazise that these phenomena can also be explained by entanglements instead of TTM.

The material properties of polycrystalline polymers are often explained by the assumption that TTM are responsible for the stress transfer in these materials. Recently, Lacher *et al.* (14, 15) pointed out that entanglements between neighbouring lamellae might contribute even more to the stress transfer than TTM do. In favour of the assumption that entanglements initiate fibre failure in the UHMWPE gel-spun hot-drawn fibre, are the following arguments :

- Annealing of gel-spun hot-drawn UHMWPE fibres did not increase the tensile strength of these fibres. Annealing laxes the overstressed TTM , *i.e.* the length distribution of TTM broadens and the tensile strength is expected to increase. The number of entanglements, however, is expected to remain unchanged.
- The number of entanglements per disordered domain in UHMWPE fibres calculated from crazing studies and scaling theories (16) almost equals the number of load bearing chains calculated from irradiation experiments of these UHMWPE fibres (10).
-Fracture studies by Zhurkov *et al.* (17) yielded an energy barrier for fracture of polyethylene substantially lower than the C-C bond energy. Dijkstra and Pennings (18)

showed that this low C-C bond energy may not be attributed to highly overstressed bonds due to residual stresses in the UHMWPE fibres, because such stresses would introduce a reduction of the orthorhombic-hexagonal phase transition temperature, and relaxation would occur.
The energy barrier for the scissioning of entanglements might be substantially lower than for the C-C bond.

Conclusions

The elongation at break of gel-spun hot-drawn UHMWPE fibres can be increased by more than 100 % , without loss in tensile strength, by annealing the fibres with fixed fibre ends at a temperature between 149 and 152 °C.

The orthorhombic-hexagonal lattice transition, at 152°C, is thought to be responsible for this annealing phenomenon. In the hexagonal, or rotary phase, the chains can easily slip past one another, thereby laxing the TTM or entanglements and decreasing the ratio of crystal-block length to disordered- domain length.

The tensile strength of gel-spun hot-drawn UHMWPE fibres does not change upon annealing, meaning that it is more likely that the tensile strength is determined by the number of entanglements in the disordered domains, than by the fraction of taut tie molecules.

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