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Cross-linking of ultra-high strength polyethylene fibres by means of electron beam irradiation

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Summary

Ultra-high strength polyethylene fibres, with a tensile strength at break of 3.0 and 3.4 GPa, were irradiated, at various temperatures in a hydrogen atmosphere, by means of high energy electrons. When the fibres were not annealed, the tensile strength at break was found to decrease upon irradiation, while the Young's modulus remained unchanged. A maximal obtainable tensile strength of 22 GPa was calculated from the decrease in tensile strength and the gel-sol measurements. Gel contents upto 100% were obtained for fibres irradiated in the hexagonal phase.

Introduction

Ultra-high strength polyethylene fibres, composed of practically fully oriented very long chains and containing only a few trapped entanglements, seem to be especially suitable for synthesizing networks by irradiation, using either high energy electrons or, as in previous work (1) a Co^{60} γ source. Very high irradiation dose rates can be achieved with electron beam irradiation. Leading to instantaneous cross-linking and short irradiation times, making electron beam irradiation industrially more actractive than Co^{60} γ irradiation. Cross-links can improve various material properties such as creep-resistance, compressive strength, high temperature stability, flexural fatigue, abrasion resistance and anti-fibrillation. Cross-linked fibres can also be used to study the fibre morphology, rubber-elasticity and oriented crystallisation. They might even be useful as a precursor for carbon fibres. Small doses of ionizing radiation are sufficient for sterilisation purposes.
The aim of this communication is to present some interesting preliminary results on the irradiation of ultra-strong polyethylene with high-energy electrons.
It has been found that the Young's modulus remained unchanged whereas the tensile strength at break decreases with increasing irradiation dose if the fibres were not annealed. Gel contents upto 100% have been realized in high-temperature irradiation experiments. Elongations at break of these fibres amounted upto 25%.
Comparing the number of main-chain scissions as obtained from the gel-sol measurements with those from the decrease in tensile strength due

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to load-carrying main-chain scissions, leads to a calculated maximal obtainable tensile strength for polyethylene fibres of 22 GPa.

Experimental

Ultra-high strength polyethylene fibres, used in this study were obtained by hot-drawing of porous fibres of polyethylene, with an initial weight average molecular weight of 4.10^6 kg/mol, as described previously (2). 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, using araldite glue, to prevent the fibre from shrinking while irradiating or heating. The aluminium cylinder was subsequently placed in the electron beam, in a nitrogen atmosphere, while being rotated in order to achieve a homogeneous irradiation dose. The Van de Graaff generator accelerated the electrons upto 3 MeV, an energy suitable for irradiation experiments as the linear energy transfer (LET) is almost constant from 1 to 3 MeV (3).
The irradiation temperature was measured by means of a thermocouple, in the nitrogen atmosphere, outside the radiation bundle. The extra temperature increase caused by the irradiation energy absorbed by the aluminium cylinder is measured indirectly in this way, leading to an uncertainty in temperature of about ± 10°C. Extraction of the sol-fraction was performed with boiling p-xylene, containing 0.5% by weight of anti-oxidant (2,6-di-t-butyl 4 methylcresol).
Samples were deswollen in acetone and dried under vacuum at 50°C.
Tensile tests were performed using an Instron 4301 tensile tester at a cross-head speed of 2.10^{-4} m/s and an original sample length of 25 mm at 20°C. Cross-sectional areas were calculated from fibre weight and length, assuming a density of 1000 kg/m³.

Results and discussion

Ultra-high strength polyethylene fibres, with an initial strength of 3.0 and 3.4 GPa, were irradiated using electrons accelerated to 3 MeV by means of a Van de Graaff generator.
The initial fibre showed a highly ductile fracture behaviour in tensile testing (see fig. 1).
A change from ductile to brittle fracture mechanism was found with increasing irradiation dose (see fig. 2, 3).
The tensile strength at break as a fuction of irradiation dose for a fibre with initial tensile strength at break of 3.0 GPa is presented in fig. 4. It was quite remarkable to see that the Young's modulus at zero strain remained unchanged upon irradiation.
The gel-sol measurements were analyzed in terms of the Charlesby-Pinner equation (4), relating sol fractions, s, to radiation dose, r,

$$s + \sqrt{s} = \frac{G(s)}{2G(x)} + \frac{9.6 \cdot 10^5}{G(x).\overline{M}_w.r} \qquad [1]$$

where G(s) is the number of main-chain scissions and G(x) the number of cross-links, both produced per 100 eV absorbed energy and $\overline{M}_w$ is the weight average molecular weight of the initial polymer.
Equation [1] holds strictly for random distributions, whether or not main-chain fracture occurs simultaneously with cross-linking, and also holds at high doses for other distributions, providing cross-linking is accompanied by fracture. Innokuti (5) derived an equation giving

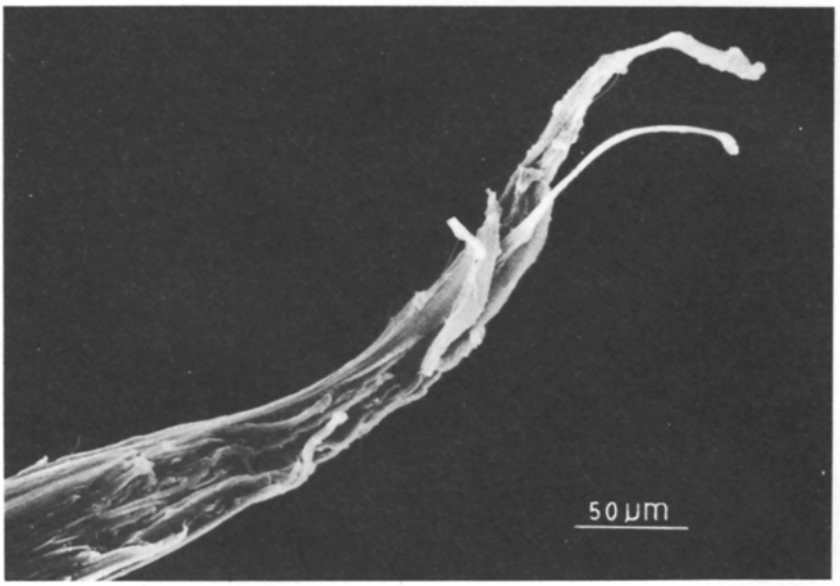

Fig. 1. A SEM-micrograph of the fracture surface of the initial fibre.

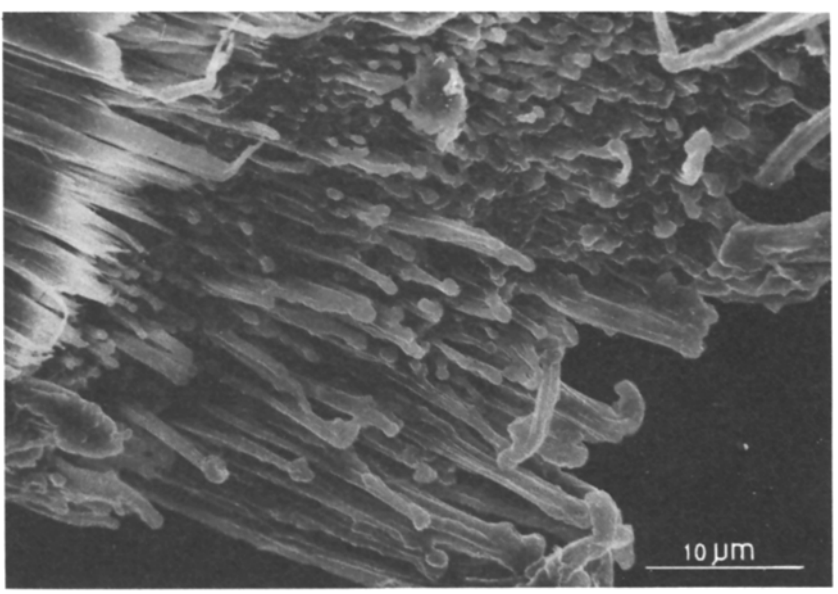

Fig. 2. A SEM-micrograph of the fracture surface of an (30 Mrad) irradiated fibre.

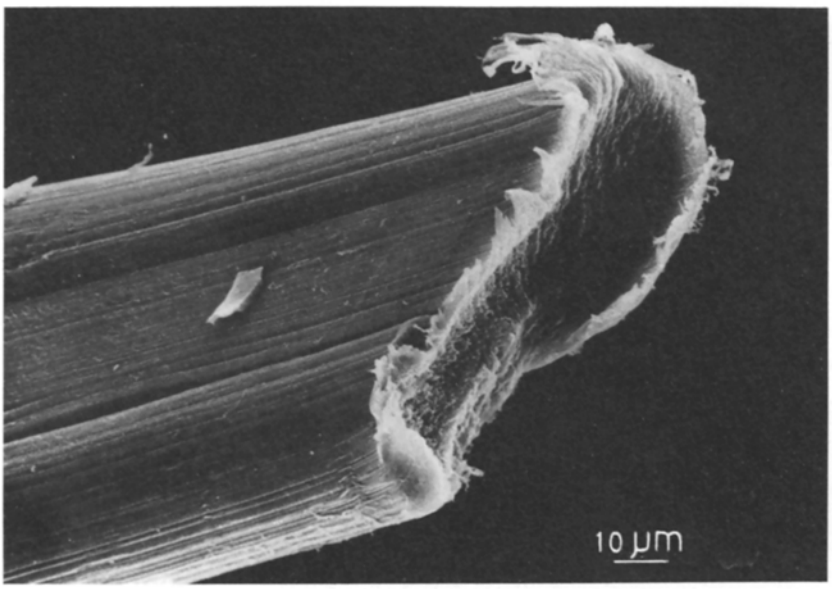

Fig. 3. A SEM-micrograph of the fracture surface of an (100 Mrad) irradiated fibre.

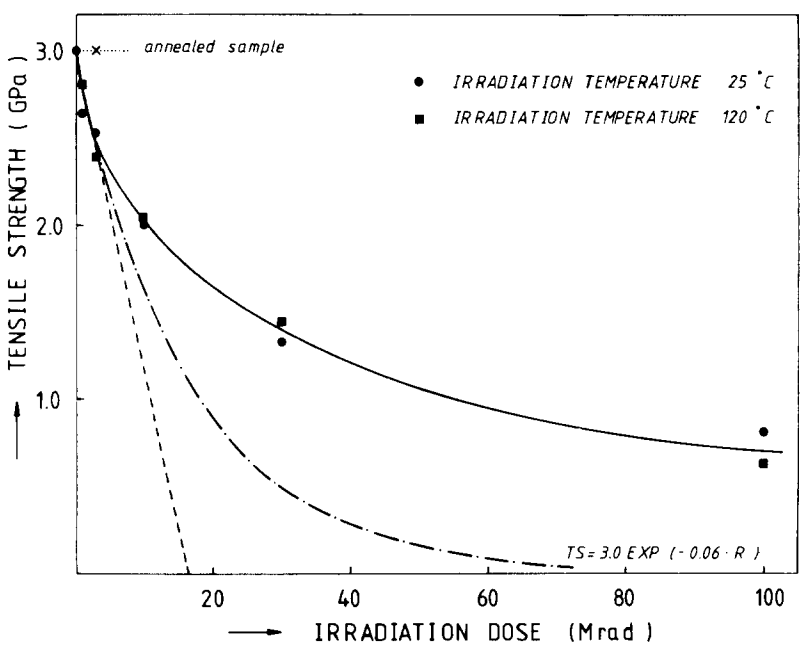

Fig. 4. The tensile strength at break versus radiation dose of a polyethylene fibre, with an initial tensile strength at break of 3.0 GPa.

the sol fraction of polymers undergoing simultaneous cross-linking and scission for an arbitrary initial molecular size distribution, leading to a convex curve in the Charlesby-Pinner plot for the weight to number average of 19 for the polyethylene used (see fig. 5).
From figure 5 a pronounced decrease in G(s)/G(x) value was found by increasing the irradiation temperature from below to above 150°C, probably due to the increase in molecular mobility when the lattice changes from the orthorhombic to the hexagonal phase (6).

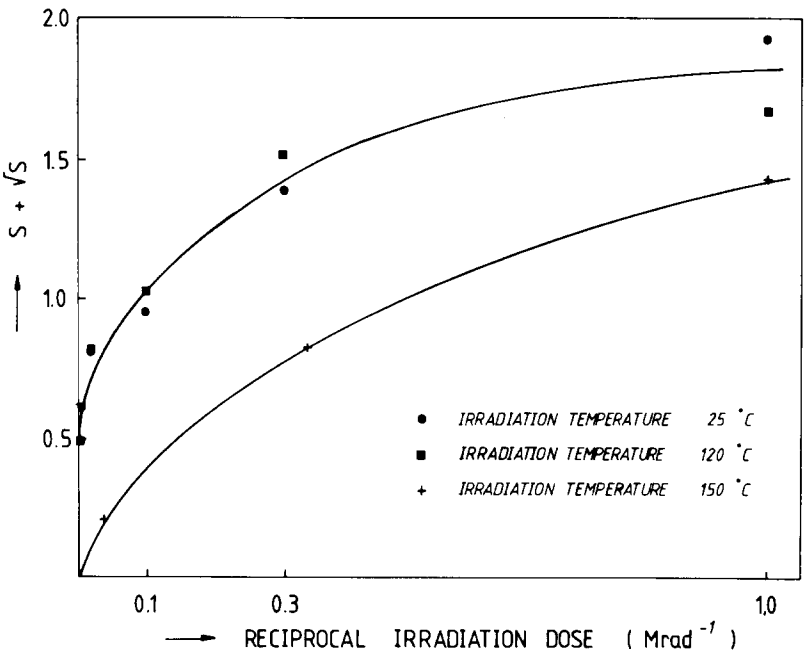

Fig. 5. Charlesby-Pinner plot of polyethylene fibres irradiated at various temperatures.

Ungar and Keller reported a higher radiation sensitivity of the hexagonal phase in paraffins (8). Because of fibre fracture, it is not possible to irradiate far above 150°C, but when a small first irradiation dose is given at a lower temperature, a second dose can be given even at temperatures higher than 200°C, leading to gel-contents of 100% for a total irradiation dose of 10 Mrad.
Fibres irradiated above 150°C revealed an increase in elongation at break, upto 25% for the two step irradiation experiment.
No decrease in tensile strength at break was found for fibres first annealed at 90°C and irradiated with a dose of 3.3 Mrad at 50°C.
How can the decrease in tensile strength and the constant Young's modulus upon irradiating be explained?

The ultra-high strength polyethylene fibres are composed of nearly fully oriented very long chains. The elementary fibrils might be visualized as an array of large crystalline blocks of length 70 nm (at least) and width 20 nm, interrupted by disordered domains with a length of approximately 4 nm (10).
Let us assume that the stress at break is proportional to the number of load-carrying molecules in a cross-section of the fibre, N. Much the same way as Peterlin (9) explains the axial elastic modulus mainly by taut tie molecules (TTM) which bridge the disordered domains between consecutive crystal blocks. Each main-chain scissioning of load bearing TTM reduces the number of them, i.e.

$$dN = -\lambda.N.dr \qquad [2]$$

or

$$N = N_o \exp\{-\lambda.r\} \qquad [3]$$

Where λ is the probability of main-chain scissioning of load-bearing TTM per Mrad, calculated with [2] from figure 4 to be 0.06 $Mrad^{-1}$.
For large irradiation doses a considerable deviation from this simple model occurs (see fig. 4), as expected because almost no TTM are left.
The number of scissions in one crystallite and disordered block is

$$G(s)/100\ eV \cdot 6.25 \cdot 10^{19} eV/g \cdot 1\ g/cm^3 \cdot 3.10^{-17} cm^3 \simeq 18 \cdot G(s)$$

per Mrad. Where $6.25 \cdot 10^{19} eV/g$ is the energy absorbed of a Mrad and $3.10^{-17} cm^3$ is the volume of a crystallite and disordered domain. The slope of the Charlesby-Pinner plot and the gelpoint (see fig. 5) yield a G(s) value of 0.5. These 9 scissions per Mrad in one crystallite and disordered block should lead to a reduction in tensile strength, i.e. concentration of TTM, of 6%, from which a total of 150 TTM per disordered domain can be calculated. From the chain cross-section in the crystallite of ca. 0.18 nm^2 (10) it follows that 13.5% of the cross-section of the disordered domain is occupied by TTM in the 3 GPa fibre (if we assume that each molecule comprises a cross-section of about twice the value of 0.18 nm^2 due to backfolding in entanglements (10)). Leading to a maximal obtainable tensile strength of 22 GPa, which is in very good agreement with the theoretical strength in polyethylene of about 25 GPa, as estimated from Morse potential calculations on the C-C bond strength in polyethylene (11). This result might justify the assumption that all scissions occur in the disordered domains and that they affect preferentially TTM.
The Young's modulus is expected, according to Peterlin's model, to decrease when taut tie molecules are fractured by radiation. But surprisingly no decrease was found. The Young's modulus at zero strain remains constant, 105 GPa for the fibre with initial strength of 3 GPa irradiated at room temperature.
When overstressed taut tie molecules are fractured by radiation, both ends will immediately recoil. Separating the two radicals over such a distance that recombination is rather unlikely.
Annealing the fibre at high temperatures allow Reneker-defects (12) to migrate from the crystalline parts to the overstressed taut tie molecules, and convert them into lax tie molecules. When lax tie molecules are fractured by radiation, recombination of the radicals should be possible, especially at higher temperatures, i.e. higher molecular mobility. This model could explain why the sample annealed before irradiating revealed no decrease in tensile strength upon irradiating.

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