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Crosslinking of Ultra-high Strength Polyethylene Fibers by Means of γ-Radiation

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Summary

Ultra-high strength polyethylene fibers, with a tensile strength at break varying from 1.6 up to 3.5 GPa, were irradiated, at room temperature under vacuum by means of ^{60}Co γ-radiation. Sol-gel analysis showed a ratio of crosslinking to main-chain scissioning of about 1. The tensile strength at break decreased upon irradiation . The decrease of tensile strength at break depended on initial fiber strength and could be attributed to main-chain scissioning. It was concluded that stressed chains break preferentially upon irradiation. "Fiber" networks exhibited a deformation ratio of 16 during stress-strain measurements.

Introduction

The aim of the present investigation was to synthesize networks of ultra-high strength polyethylene fibers by γ-irradiation and to examine the influence of irradiation on the mechanical properties of the fibers. Ultra-high strength polyethylene fibers, produced by the gel-spinning technique (SMOOK ET AL., 1980), are likely to contain a minimum amount of topological defects, such as entanglements and loops. Accordingly, crosslinking of this material results in networks with a reduced number of so called network defects. Therefore these networks should enable us to perform experimental studies to verify recent developments of rubberlike elasticity theories (RONCA, ALLEGRA, 1975; FLORY, 1976) and of oriented crystallization (POSTHUMA DE BOER, PENNINGS, 1979). Furthermore crosslinking of an ultra-high strength polyethylene fiber may reduce the amount of creep in the fiber, whereas crosslinked fibers can find practical applications at temperatures far above 145°C.

Crosslinking ultra-high strength polyethylene fibers, without destroying the fiber structure, can only be performed using high-energy electrons or γ-radiation. Unfortunately high-energy radiation causes, apart from crosslinking, main-chain scissioning (UNGAR, KELLER, 1980).

Preliminary results of the ^{60}Co γ-irradiation of ultra-high strength fibers of polyethylene with a weight average molecular weight of 4×10^6 kg/kmol, are presented in this paper. Decrease of the tensile strength at break upon irradiation was found to depend on the initial fiber strength and could be correlated to main-chain scissioning. It is shown that stressed chains break

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preferentially. Stress-strain measurements demonstrated that these "fiber" networks allow high deformation ratios up to 16.

Experimental

Ultra-high strength polyethylene fibers, used in this study were obtained by hot-drawing of porous fibers of polyethylene, with an initial weight average molecular weight of 4 x 10^6 kg/kmol, as described previously (SMOOK ET AL., 1980). The irradiation procedure was as follows. The fiber was wound into a helical groove, which was etched into a glass cylinder. This was done to avoid contact between different parts of the fiber during annealing at high temperatures. Fiber ends were glued onto the glass-surface, using araldite glue (AVM138M/MV998, Ciba-Geigy), to prevent the fiber from shrinking, while annealing takes place. The glass cylinder was subsequently placed in a glass vessel, with a constant wall-thickness of 2.3 ± 0.1 mm. The vessel was sealed using Torr Seal high-vacuum glue (Varian Associates, Vacuum Division). After evacuation the fiber was irradiated by means of ^{60}Co γ-radiation, at room temperature. The dose rate was varied between 1.5 and 4.8 kGy per hour (1 kGy = 0.1 Mrad). The irradiation intensity was corrected for absorption of the glass vessel-wall and for fiber thickness (DOLE, PATEL, 1977), taking the fiber diameter as the thickness of the sample. After irradiation the samples were annealed at 140°C for 15 minutes to eliminate any trapped free radicals. Radical elimination was checked by Electron Paramagnetic Resonance spectroscopy, taking the fiber direction perpendicular to the magnetic field.

Extraction of the sol-fraction was performed in boiling p-xylene, containing 0.5% by weight of anti-oxidant (Ionol CP 0275, Shell). Samples were deswollen in acetone and dried under vacuum at 50°C. Tensile tests were performed using a Zwick Z1.3B tensile tester at a cross-head speed of 2 x 10^{-4} m/sec and an original sample length of 25 mm at 20°C. Cross-sectional areas were calculated from fiber weight and length, assuming a density of 1000 kg/m^3.

Results and Discussion

Ultra-high strength polyethylene fibers, with an initial tensile strength at break ranging from 1.6 to 3.5 GPa, were irradiated using ^{60}Co γ-radiation. The radiation dose was varied from 7 to 91 kGy. Gelcontent increased with radiation dose up to 85%, while tensile strength at break decreased approximately 40%. The results of the irradiation experiments are compiled in Table 1.

The first subject to be discussed is the gelation of ultra-high strength polyethylene fibers due to γ- irradiation. The gel-fraction of a fiber with an initial tensile strength at break of 3.4 GPa, was determined as a function of dose (see Table 1).

TABLE 1

Dose (kGy)'	Reciprocal dose (10^{-2}kGy^{-1})	Gel content (%)	$s+s^{\frac{1}{2}}$''	Tensile strength at break (GPa)	Decrease of tensile strength at break(%)	
					measured	calculated
7	14.0	33	1.49	2.6	23	4
8	12.5	48	1.24	2.5	26	5
17	5.9	65	0.94	2.4	29	10
35	2.9	78	0.69	2.4	29	20
56	1.8	81	0.63	2.3	32	32
91	1.1	85	0.54	2.0	41	52

' 1 kGy = 0.1 Mrad

'' s = sol fraction

TABLE 1: Fiber characteristics after irradiation of a fiber with an initial tensile strength at break of 3.4 GPa.

Since irradiation of polyethylene causes both crosslinking and main-chain scissioning, it is pertinent to analyse the sol-gel data in terms of the well-known Charlesby-Pinner equation, yielding quantitative information about both chemical modifications of the polymer. According to the Charlesby-Pinner equation, the sol fraction, s, for a polymer with initially a random molecular weight distribution and undergoing simultaneous random crosslinking and random main-chain scissioning, is related to the radiation dose, r, as follows:

$$s + s^{\frac{1}{2}} = \frac{G(s)}{2G(x)} + \frac{1.602 \times 10^{-18} \times N_A}{G(x) \times \bar{M}_w \times r} \quad (1)$$

(CHARLESBY, PINNER, 1959)

where G(s) is the number of main-chain scissions and G(x) the number of crosslinks, both produced per 100 eV absorbed energy, $\bar{M}_w$ is the initial weight average molecular weight of the irradiated polymer and N_A is Avogadro's number. If this theory is applicable, a plot of $s + s^{\frac{1}{2}}$ versus the reciprocal dose should give a straight line. Such a plot is shown in Figure 1 and a straight line was indeed obtained, although the initial molecular weight distribution in our case was not a random one ($\bar{M}_w/\bar{M}_n \simeq 20$, $\bar{M}_n$ being the initial number average molecular weight of the polymer). By extrapolation of the Charlesby-Pinner plot of Figure 1 to infinite dose, i.e. 1/r = 0, an intercept on the $s + s^{\frac{1}{2}}$-axis was found, indicating that main-chain scissioning actually occurs when ultra-high strength polyethylene fibers are irradiated using γ- radiation. When 1/r = 0, equation (1) reduces to:

$$s + s^{\frac{1}{2}} = \frac{G(s)}{2G(x)} \quad (2)$$

therefore making it possible to calculate G(s)/G(x) from the intercept of the Charlesby-Pinner plot at infinite dose.
From Figure 1 and using equation (2), a G(s)/G(x)-value of 1.00 was calculated, indicating that per 100 eV absorbed energy, the amount of main-chain scissioning equals the amount of crosslinking.

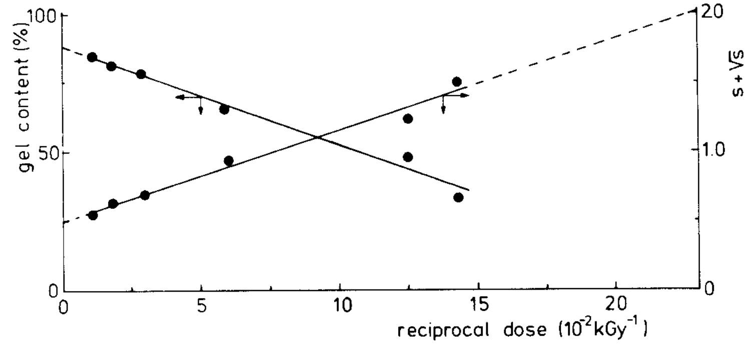

Figure 1: Gelcontent (%) and $s + s^{\frac{1}{2}}$ versus reciprocal dose of an irradiated polyethylene fiber, with an initial tensile strength at break of 3.4 GPa.

An estimation of the ratio of main-chain scissioning to crosslinking can also be made, using the so-called Inokuti-equation (INOKUTI, 1963), which is independent of the initial molecular weight distribution of the irradiated polymer. The Inokuti-equation relates the maximum obtainable gelfraction upon irradiation, $(1-s)_{max}$, to the ratio G(s)/G(x):

$$(1-s)_{max} = \tfrac{1}{2} \times \{1 - \frac{G(s)}{G(x)} + (1 + 2\,\frac{G(s)}{G(x)})^{\frac{1}{2}}\} \quad (3) \quad \text{(DOLE, 1974)}$$

In order to determine $(1-s)_{max}$, a plot of the gelcontent (%) as a function of the reciprocal dose is also presented in Figure 1. The plot yields a straight line, which made it possible to perform an accurate extrapolation to infinite dose ($1/r = 0$), rendering a maximum obtainable gelfraction of 88%. According to equation (3) this corresponds to a G(s)/G(x)-ratio of 0.93, which is in excellent agreement with the value of 1.00, obtained from the Charlesby-Pinner analysis. Furthermore, both values are in good agreement with a G(s)/G(x)-ratio of 1.01, which was previously found for the γ-irradiation of bulk polyethylene at 30°C (MITSUI, HOSOI, 1973), in spite of the completely different morphology of bulk polyethylene.

By extrapolation of the Charlesby-Pinner plot from Figure 1, to a $s + s^{\frac{1}{2}}$-value of 2, i.e. zero gelcontent, corresponding to the gelpoint dose, a gelpoint dose of 4.4 kGy was obtained.

Finally, from the slope of the Charlesby-Pinner plot and using equation (1), G(x) can be calculated. With $\overline{M}_w = 4 \times 10^6$ kg/kmol a G(x)-value of 0.37 was found. As upon irradiation of solid state polyethylene, crosslinks are thought to be preferentially formed in the disordered domains of the polymeric solid, the low G(x)-value may be attributed to the high degree of crystallinity of ultra-high strength polyethylene fibers. The large distance between adjacent chains and the low movability of the chains in the polyethylene crystal, make crosslinking less likely to occur in the crystalline part of the fiber (UNGAR, KELLER, 1980). That, in spite of the low G(x)-value, a low gelpoint dose was found, is probably caused by the extremely high molecular weight of the polyethylene used in this study.

The next subject to be discussed, is the decrease of tensile strength at break upon irradiation of the fibers. It is known that generally irradiation of polymers causes an improvement of the tensile properties (LANZA, 1964; LYONS, VAUGHN, 1967; PERKINS ET AL., 1978). This improvement is explained as an increase of the connectivity of the polymer chains, i.e. an increase of the effective molecular weight, resulting in reduced stress-cracking.

As the initial polyethylene used in this study, already has an extremely high molecular weight, a somewhat different behaviour may be expected.

Fibers, with a different tensile strength at break before irradiation, were irradiated with a radiation dose of 20 kGy. Tensile strength at break decreased during irradiation. The decrease was found to depend on the initial tensile strength at break of the fiber. Stronger fibers were in this respect more sensitive towards irradiation then relatively weaker fibers. Results are summarized in Table 2.

TABLE 2

Tensile strength at break (GPa)		Decrease of tensile strength at break (%)
before irradiation	after irradiation	
1.6	1.5	6
2.9	2.5	14
3.5	2.6	26

TABLE 2: Decrease of tensile strength at break as a function of initial fiber strength. In all cases the radiation dose was 20 kGy.

The decrease of tensile strength at break as a function of radiation dose of a fiber with an initial tensile strength at break of 3.4 GPa, is presented in Table 1. The decrease appeared to be most pronounced at relatively low doses.

How can the decrease of tensile strength be explained? Reduction of the degree of crystallinity of the fibers was ruled out as a possible reason as it is believed, that in the dose range used here the crystallinity of the polyethylene does not change (UNGAR, KELLER, 1980). Therefore it was attempted to correlate the decrease in tensile strength to the amount of main-chain scissioning, due to irradiation, calculated by means of the G(s)-value. First of all we have to understand what happens when a fiber breaks. Fiber failure can be seen as the propagation of a fracture path, throughout the fiber. As chain-ends represent parts of the fiber with a low resistance towards fracture path propagation, the fracture path will preferentially pass these discontinuities in the structure (PREVORSEK, 1971). Irradiation induces main-chain scissioning, concomitantly increasing the number of chain-ends. Therefore the increase of the number of chain-ends, calculated using G(s), relative to the initial number of chain-ends, calculated using $\bar{M}_n$, could be an indication for the relative decrease of strength of the fibers upon irradiation.

If we focus our attention to the 3.4 GPa fiber, it was already shown from the Charlesby-Pinner analysis, that $G(s)/G(x) = 1.00$, indicating that $G(s) = 0.37$. With $\overline{M}_n = 1.5 \times 10^5$ kg/kmol, the relative decrease of strength could now be calculated. At high dose there was a fair agreement between the calculated decrease and the experimental one, whereas at low doses the discrepancy was much larger. Comparison between experiment and calculation is presented in Table 1 en Figure 2.

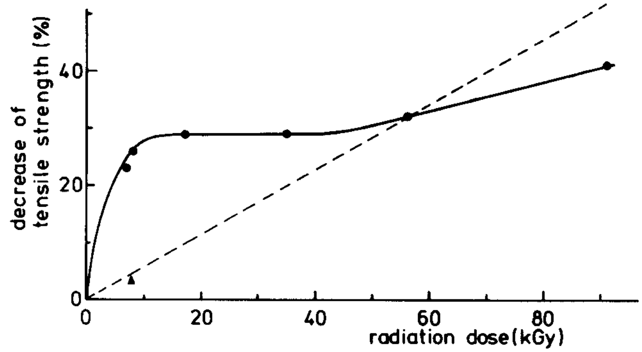

Figure 2: Decrease of tensile strength at break (%) versus radiation dose of an irradiated polyethylene fiber, with an initial tensile strength at break of 3.4 GPa. Solid line (o): experimental values; broken line: calculated decrease in strength. Triangle (Δ) indicates a decrease in strength, when the fiber was annealed prior to irradiation.

The large difference between calculation and experiment at low dose, could be due to the preferential scissioning of stressed chains in the fiber, which are crucial for determining the fiber strength. In order to check this hypothesis a fiber with an initial tensile strength at break of 3.5 GPa was annealed, prior to irradiation, at 140°C for 64 hours, at constant length and under vacuum. Annealing of polymer crystals tends to raise the gelcontent of the crystal upon irradiation, therefore one of the effects of annealing may be the improvement of contact between adjacent crystals (KAWAI ET AL., 1964; SALOVEY, BASSETT, 1964; ORMEROD, 1965). The observation that elementary fibrils, constituting the ultra-high strength polyethylene fibers, aggregate to form a solid like structure upon annealing at 140°C (VAN HUTTEN, PENNINGS, 1980), supports this observation. Furthermore, annealing may establish the removal of stressed chains, consequently reducing the decrease of strength upon irradiation at low doses.

Annealing reduced the tensile strength at break of the fiber by 3% to 3.4 GPa. Subsequent irradiation, with a radiation dose of 8 kGy, rendered a fiber with a strength of 3.3 GPa, implying a decrease in tensile strength of only 3% due to irradiation. This is in excellent agreement with the calculated decrease, as is indicated by the triangle in Figure 2. It was therefore concluded, that main-chain scissioning plays an important role in decreasing the tensile strength at break of ultra-high strength polyethylene fibers, when they are irradiated by means of ^{60}Co γ-radiation. Furthermore stressed chains tend to break preferentially.

We are well aware of the fact that the treatment given here is a simplified one. We have for instance neglected the influence of crosslinks on the fiber strength. It is obvious that when a crosslink is introduced inside the polyethylene crystal lattice, it will cause a local increase in density and comcomitantly a stress concentration, reducing the tensile strength at break of the fiber (GUIU, SHADRAKE, 1975).

The next point of interest is the type of radicals introduced in the ultra-high strength polyethylene fiber by the irradiation proces. In order to obtain information about the nature of the radicals, an Electron Paramagnetic Resonance signal was recorded of an irradiated fiber, which received no post-irradiation treatment,24 hours after irradiation. The initial fiber strength was 3.5 GPa. The fiber was not annealed prior to irradiation. The spectrum is shown in Figure 3 and was recorded taking the fiber direction perpendicular to the magnetic field. The spectrum was believed to be due to allyl-radicals (DOLE, 1972).

The absence of peroxy-radicals indicates that, as the allyl-radicals are trapped inside the crystal lattice, the rate of oxygen diffusion into the crystal, after opening the irradiation cell, is low.

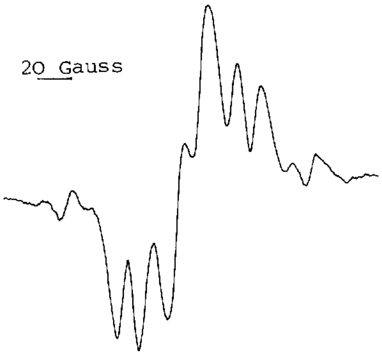

Figure 3: Electron Paramagnetic Resonance signal of an irradiated polyethylene fiber, with an initial tensile strength at break of 3.5GPa. The radiation dose was 52 kGy.

Finally we would like to report preliminary stress-strain measurements using a "fiber" network obtained from a fiber with an initial tensile strength at break of 1.6 GPa. After irradiation, with a radiation dose of 20 kGy, the gelcontent was 81% and the tensile strength at break 1.5 GPa. At 165°C, this "fiber" network exhibited a deformation ratio of 16, which is unusually high, especially for polyethylene networks. It is our intention to report more detailed stress-strain measurements in near future.

In summary, we have shown that, in spite of the high degree of crystallinity and the high degree of orientation, ultra-high strength polyethylene fibers can be crosslinked, using ^{60}Co γ-radiation. The decrease of the tensile strength at break due to irradiation could be explained in terms of main-chain scissioning. "Fiber" networks showed remarkable elastic behaviour.

Although irradiation using ^{60}Co γ-radiation has proved to be a very useful technique to crosslink ultra-high strength polyethylene fibers, the applicability of the proces could be greatly expanded, when high energy electrons are used. In combination with radiation induced surface grafting of the fibers (YAMAKAWA, 1976), it may be possible to obtain fibers, which are highly suitable to reinforce composite materials.

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