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# Crosslinking of Ultra-High Strength Polyethylene Fibers by Means of $\gamma$-Radiation

## 2. Entanglements in Ultra-High Strength Polyethylene Fibers*

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## Summary

An ultra-high strength polyethylene fiber with an initial tensile strength at break of 3.0 GPa, was irradiated at room temperature under vacuum by means of $^{60}$Co $\gamma$-radiation.

Gelcontent and equilibrium volume degree of swelling of the gel-fraction, were determined as a function of dose. From a plot of the effective network chain density versus dose, it was concluded that the fiber contained about 2 entanglements per number average molecule. Furthermore, a crosslinking efficiency of 0.33 crosslink per 100 eV of absorbed energy was found.

## Introduction

One of the most succesful techniques to produce ultra-high strength polyethylene fibers, consists of the spinning of an ultra-high molecular weight polyethylene gel followed by subsequent hot drawing in a temperature gradient (PENNINGS,1979; KALB, PENNINGS,1980; SMOOK et al., 1980). Such a gel is thought to contain a reduced number of molecular entanglements (FERRY,1961) and therefore, since an entanglement represents a center of increased friction upon deformation, the mobility of the polyethylene chains is greatly enhanced in these systems. Concomitantly, the alignment of polyethylene chains in the direction of the fiber axis upon hot drawing, is much more easily performed, resulting in excellent mechanical properties of the fiber (SMOOK et al., 1980).

The reduction of the entanglement concentration prior to hot drawing is however not without limit. Hot drawing can be considered as the deformation of a time-dependent network, in which entanglements and crystallites act as crosslinks. Without these transient crosslinks, the polyethylene chains would simply slip past each other during hot drawing, rendering a fiber with poor tensile properties (SMOOK et al., 1981). It has been argued that per molecule at least two entanglements are necessary, in order to be able to conduct hot drawing in such a way that ultra-strong fibers are obtained (KALB, PENNINGS, 1980).

In view of all this it seems of great interest to determine the entanglement concentration in an ultra-high strength polyethylene fiber after hot drawing. This can be done in two different manners.

First of all, one could swell the ultra-high strength polyethylene fiber in a suitable solvent. If there are any entanglements left after hot drawing, a swollen fiber will behave as a transient network (HONG et al., 1977; BALL et al., 1981; LIU et al., 1981) and from the degree of swelling the effective network chain density due to entanglements could be calculated (FLORY, 1979; LLORENTE, MARK, 1980). This method

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* Part 1 : cf[5]

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however, has the disadvantage that swelling has to be performed at a temperature where the fiber can still exist without dissolving. At such a temperature some crystallites, also acting as physical crosslinks, may still be present, thus obscuring the determination of the entanglement density (ELDRIDGE, FERRY, 1954; TAKAHASHI et al., 1980).

We have therefore chosen a different approach. In a recent note from this laboratory, it was shown that ultra-high strength polyethylene fibers could be transformed into chemical networks by means of $\gamma$-irradiation (de BOER, PENNINGS, 1981). From measurements of the equilibrium degree of swelling of an irradiated fiber as a function of dose, the effective network chain density can be calculated (FLORY, 1979; LLORENTE, MARK, 1980) and plotted versus dose. Extrapolation of such a plot to zero dose, renders the concentration of physical crosslinks in the system. Since the swelling is performed at high temperatures, crystallites are no longer present and the physical crosslinks are identical with the molecular entanglements (BUECHE, 1956; MULLINS, 1959; LANGLEY, 1968; FERRY, 1970).

In the present paper the determination of the entanglement concentration in a fiber with an initial tensile strength at break of 3.0 GPa is reported. It was found that the number average molecular weight between entanglements was about 70.000. A crosslinking efficiency of 0.33 crosslink per 100 eV of absorbed energy was calculated, in excellent agreement with theoretical predictions.

## 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 $4.10^6$ kg/kmol (HiFax 1900, Hercules), as reported elsewhere (SMOOK et al., 1980). Since stressed chains tend to break preferentially upon irradiation (de BOER, PENNINGS, 1981), the fibers where annealed for 64 hours prior to irradiation to remove stress concentrations (PETERLIN, 1977). Furthermore, annealing may promote gelation of the fibers (KAWAI et al., 1964; SALOVEY, BASSETT, 1964; ORMEROD, 1965). The experimental details of the irradiation procedure were the same as described earlier (de BOER, PENNINGS, 1981). After irradiation, the samples were annealed for 2 hours prior to opening of the irradiation cell, to eliminate any trapped free radicals (DOLE, 1979). All annealing was performed at 140°C at constant fiber length under vacuum.

Extraction of the sol-fraction was performed in boiling p-xylene, containing 0.5 weight-% of anti-oxidant (Ionol CP 0275, Shell). Samples were deswollen in acetone and dried under vacuum at 50°C. Extractions were performed in duplo and average values for the gelcontent were used for further calculations. It needs mentioning that fibers irradiated with high doses retained their fiber shape upon extraction. Fibers irradiated with low doses however, swelled enormously during extraction. The highly swollen parts of such a fiber, displayed a strong tendency to aggregate upon cooling of the extraction mixture after completion of the extraction. This resulted in a lump-like shape of the extracted sample.

Determination of the equilibrium volume degree of swelling was conducted on extracted samples in p-xylene at 120°C, as previously reported (POSTHUMA de BOER, PENNINGS, 1976). The volume degree of swelling reported for each fiber, was averaged over 5 measurements. Average values of this quantity are plotted and were used to calculate the effective network chain density.

## Results and Discussion

A fiber with an initial tensile strength at break of 3.0 GPa was irradiated using $^{60}$Co $\gamma$-radiation. Radiation dose varied from 6 to 70 kGy (1 kGy = 0.1 Mrad). Upon irradiation the gelcontent of the fiber increased from 54 up to 81%, while the equilibrium volume degree of swelling decreased from 64.2 down to 32.3. The results of the reticulation experiments are compiled in the table.

### Equilibrium Volume Degree of Swelling

Networks obtained through irradiation of a polymer can have a large number of dangling chains arising from chain scissions occurring during the crosslinking process (ANDRADY et al., 1981). As upon irradiation of ultra-high strength polyethylene fibers, main-chain scissioning actually occurs (de BOER, PENNINGS, 1981) also in our case a network structure containing pendent chains may be expected. Fortunately, pendent chains have a negligible effect on the equilibrium degree of swelling of a network (BASTIDE et al., 1979; BASTIDE et al., 1981; ANDRADY et al., 1981).

It was found that with increasing radiation dose the equilibrium volume degree of swelling decreased steadily from about 60 down to about 30, in the present situation. The results of the swelling experiments are presented in the table and plotted in figure 1.

### Effective Network Chain Density

The equilibrium volume degree of swelling, q, was used to calculate the effective network chain density in the gel, $\nu_g^*$ (in kmol per dm$^3$ of dry gel), using the recent swelling theory of Flory (FLORY, 1979). From this theory a formula for the effective network chain density was derived (LLORENTE, MARK, 1980), which, if it is assumed that both crosslinks and trapped entanglements contribute to the free energy change associated with distention of the network (CARPENTER et al., 1980), can be written as:

$$\nu_g^* = (\nu_x^* + \nu_e^*) = - \frac{\ln(1 - q^{-1}) + q^{-1} + \chi . q^{-2}}{F_\phi . \bar{V}_1 . v_{2c}^{2/3} . q^{-1/3}} \qquad (1)$$

where $\nu_x^*$ and $\nu_e^*$ are the contributions to the effective network chain density in the gel of the crosslinks and the trapped entanglements, respectively, $\chi$, the Flory-Huggins interaction parameter, is given by $\chi = 0.33 + 0.55 \cdot q^{-1}$ (GENT, VICKROY, 1967), $\bar{V}_1$, the partial molar volume of the diluent, is 136 dm$^3$/kmol and finally $v_{2c}$ represents the weight fraction of polymer succesfully incorporated into the gel. It has been shown that equation (1) for the reticulation density of a network, i.e. $(\nu_x^* + \nu_e^*)$, can also been applied to systems crosslinked in the oriented state (CARPENTER et al., 1980).

The theoretical expression for $F_\phi$ is given by:

$$F_\phi = (1 - \frac{2}{\phi}) \cdot (1 + \frac{\mu}{\xi} \cdot K) \qquad (2)$$

in which $\phi$, the crosslink functionality, equals 4, $\mu$, is the number of crosslinks in the network and $\xi$ represents the cycle rank of the network (DUISER, STAVERMAN, 1965). For a perfect $\phi$-functional network holds:

$$\frac{\mu}{\xi} = 2/(\phi - 2) \qquad (3)$$

TABLE

| Radiation Dose (kGy)[a] | Gelcontent (%) | Equilibrium Volume Degree of swelling,q | $10^3 \cdot \nu_g^*$ [b)] $(\mathrm{mol \cdot dm^{-3}})$ | $10^3 \cdot \nu_o^*$ [c)] $(\mathrm{mol \cdot dm^{-3}})$ |
|---|---|---|---|---|
| 6 | 54 ± 1 | 64.2 ± 1.4 | 2.55 | 1.74 |
| 13 | 61 ± 3 | 60.7 ± 2.0 | 2.59 | 1.86 |
| 26 | 72 ± 2 | 45.3 ± 1.6 | 3.75 | 2.92 |
| 45 | 82 ± 1 | 39.2 ± 1.0 | 4.37 | 3.69 |
| 65 | 83 ± 1 | 31.3 ± 0.1 | 6.21 | 5.29 |
| 70 | 81 ± 2 | 32.3 ± 1.0 | 6.06 | 5.09 |

a) 1 kGy = 0.1 Mrad

b) $\nu_g^*$ : effective network chain density in the gelfraction

c) $\nu_o^*$ : overall effective network chain density

Table : Fiber characteristics after irradiation of a polyethylene fiber with an initial tensile strength at break of 3.0 GPa. Prior to irradiation the fiber was annealed at 140°C under vacuum, at constant length for 64 hours.

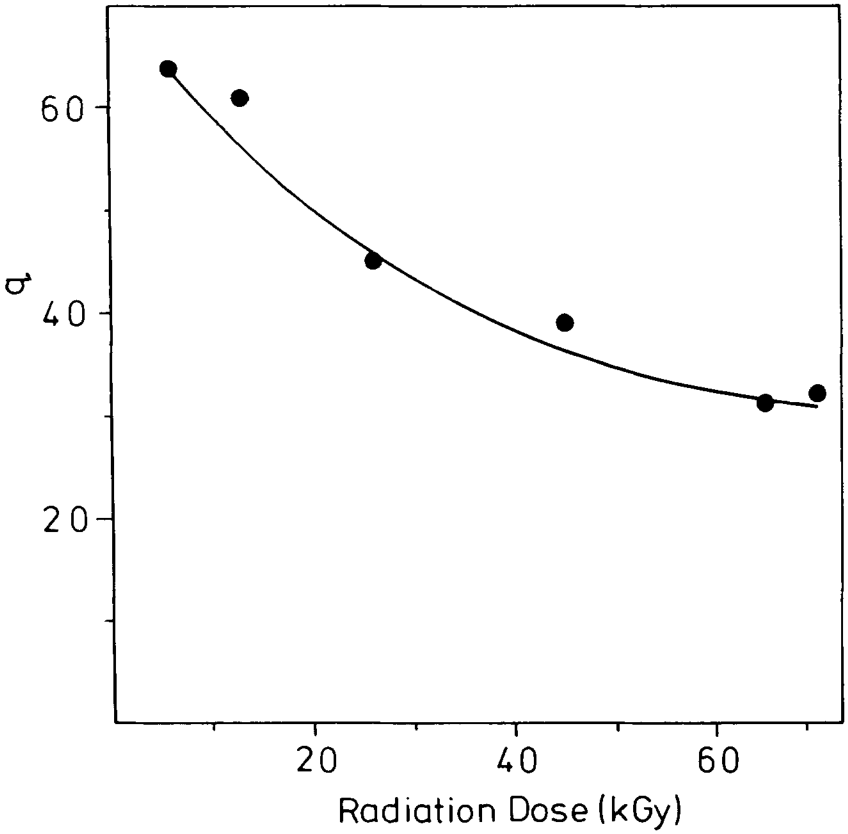

Figure 1 : Equilibrium volume degree of swelling, q, as a function of radiation dose, for a polyethylene fiber with an initial tensile strength at break of 3.0 GPa. Prior to irradiation the fiber was annealed at 140 °C under vacuum, at constant length, for 64 hours.

The quantity K is a function of q and of two network parameters, p and $\kappa$, which specify, respectively, the dependence of the crosslink fluctuations on the strain and the constraints on the crosslinks from the neighbouring chains. Realistic estimates for these quantities are p = 2 and $\kappa$ = 20 (FLORY, 1979; LLORENTE, MARK, 1980).

Combining all this information, $\nu_g^*$, can now be calculated. It was observed that $\nu_g^*$, increased from $2.55 \cdot 10^{-3}$ mol/dm$^3$ up to $6.06 \cdot 10^{-3}$ mol/dm$^3$ upon irradiation. The results of the calculations are shown in the table.

Considering the fact that for all radiation doses used, still a considerable sol-fraction remained after irradiation it was thought appropiate to base the effective network chain density on the total polymer volume rather than just on the volume of the gelfraction alone. Therefore $\nu_g^*$ was transformed into the overall effective network chain density, $\nu_o^*$, i.e. the number of elastically effective chains in the total polymer volume, constituted by both the gel- and the sol-fraction. This can be done using the following equation, which is independent of the initial molecular weight distribution of the irradiated polymer:

$$\nu_g^* = \nu_o^* (1 + s) \qquad (4) \qquad \text{(FLORY, 1975)}$$

in which s represents the weight fraction of sol after irradiation. The thus obtained values of $\nu_o^*$ ranged from $1.74 \cdot 10^{-3}$ mol/dm$^3$ up to $5.09 \cdot 10^{-3}$ mol/dm$^3$, when the radiation dose increased from 6 to 70 kGy. The $\nu_o^*$ -values are compiled in the table and plotted in figure 2.

From figure 2 the following conclusions can be drawn. First of all, as already stated in the Introduction, extrapolation of the plot to zero dose, i.e. absence of crosslinking and absence of main-chain scissioning, yields the number of elastically effective chains due to entanglements. That an intercept is actually found, confirms the conclusion drawn from solubility studies performed on extended chain polyethylene fibers, that ultra-high strength polyethylene fibers contain a residual amount of entanglements (TORFS et al., 1981). After correction for chain-ends the intercept rendered a number average molecular weight between entanglements of 67.000 kg/kmol. With an initial number average molecular weight of the polyethylene of $1.5 \cdot 10^5$ kg/kmol, this implies that about 2 entanglements per molecule were present in the starting material, in excellent agreement with the prediction of Kalb and Pennings (KALB, PENNINGS, 1980), suggesting that ultra-high strength polyethylene fibers contain the minimum amount of molecular entanglements necessary for hot drawing.

Secondly, from the slope of figure 2, a crosslinking efficiency in terms of the so-called G(x)-value, can be derived. The G(x)-value of a system stands for the number of crosslinks produced in the system per 100 eV of absorbed energy. From the slope of figure 2 a G(x)-value of 0.33 was obtained. Ungar (UNGAR, 1981) calculated an upper limit of 0.6 for the G(x)-value of polyethylene irradiated in the crystalline phase, a value that agrees well with our result.

In conclusion we have shown that a fiber with an initial tensile strength at break of 3.0 GPa contains about 2 entanglements per molecule. A crosslinking efficiency for this type of material of 0.33 crosslink per 100 eV of absorbed energy was derived.

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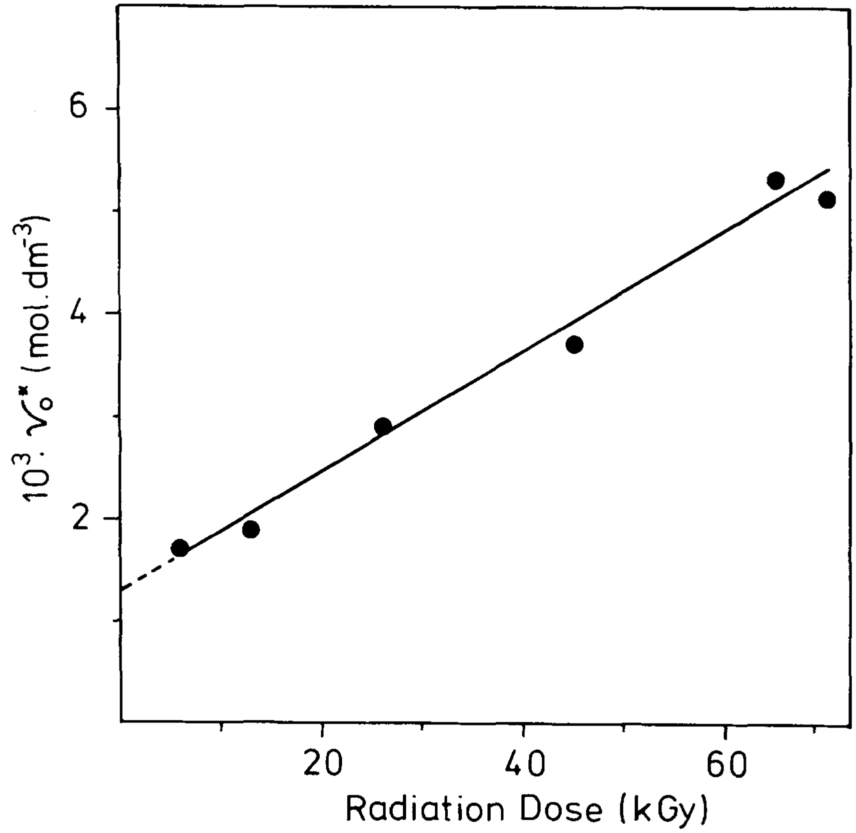

Figure 2 : Overall effective network chain density, $\nu_0^*$, as a function of radiation dose, for a polyethylene fiber with an initial tensile strength at break of 3.0 GPa. Prior to irradiation the fiber was annealed at 140 °C under vacuum, at constant length, for 64 hours.

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References

1. ANDRADY,A.L., LLORENTE,M.A., SHARAF,M.A., RAHALKAR,R.R., MARK,J.E., SULLIVAN,J.L.,YU,C.U.,FALENDER,J.R.,J.Appl.Polym.Sci.,26,1829 (1981)
2. BALL,R.C.,DOI,M.,EDWARDS,S.F.,WARNER,M.,Polymer,22,1010 (1981)
3. BASTIDE,J.,PICOT,C.,CANDAU,S.,J.Polym.Sci.,Polym.Phys.Ed.,17,1441, (1979)
4. BASTIDE,J.,PICOT,C.,CANDAU,S.,J.Macromol.Sci.-Phys.,B19,13 (1981)
5. de BOER,J.,PENNINGS,A.J.,Polym.Bull.,5,317 (1981)
6. BUECHE,A.M.,J.Polym.Sci.,19,297 (1956)
7. CARPENTER,R.L.,KAN,H.-C.,FERRY,J.D.,J.Polym.Sci.,Polym.Phys.Ed., 18,165 (1980)
8. DOLE,M.,Polym.-Plast.Technol.Eng.,13,41 (1979)
9. DUISER,J.A.,STAVERMAN,A.J.,"Physics of Non-Crystalline Solids", Amsterdam, North Holland Publ.Co.,1965,p.376
10. ELDRIDGE,J.E.,FERRY,J.D.,J.Phys.Chem.,58,992 (1954)
11. FERRY,J.D.,"Viscoelastic Properties of Polymers", New York, Wiley, 1961,p.372
12. FERRY,J.D.,"Viscoelastic Properties of Polymers", New York, Wiley, 1970,p.265
13. FLORY,P.J.,"Principles of Polymer Chemistry", Ithaca, Cornell University Press,1975,p.381
14. FLORY,P.J.,Macromolecules,12,119 (1979)
15. GENT,A.N.,VICKROY,V.V.,Jr.,J.Polym.Sci.,Part A-2,5,47 (1967)
16. HONG,S.D.,SOONG,D.,SHEN,M.,J.Appl.Phys.,48,4019 (1977)
17. KALB,B.,PENNINGS,A.J.,J.Materials Sci.,15,2584 (1980)
18. KAWAI,T.,KELLER,A.,CHARLESBY,A.,ORMEROD,M.G.,Phil.Mag.,10,779 (1964)
19. LANGLEY,N.R.,Macromolecules,1,348 (1968)
20. LIU,T.Y.,SOONG,D.S.,WILLIAMS,M.C.,Polym.Eng.Sci.,21,675 (1981)
21. LLORENTE,M.A.,MARK,J.E.,Macromolecules,13,681 (1980)
22. MULLINS,L.,J.Appl.Polym.Sci.,2,1 (1959)
23. ORMEROD,M.G.,Phil.Mag.,12,681 (1965)
24. PENNINGS,A.J.,Makromol.Chem.,Suppl.2,99 (1979)
25. PETERLIN,A.,J.Appl.Phys.,48,4099 (1977)
26. POSTHUMA de BOER,A.,PENNINGS,A.J.,J.Polym.Sci.,Polym.Phys.Ed.,14,187 (1976)
27. SALOVEY,R.,BASSETT,D.C.,J.Appl.Phys.,35,3216 (1964)
28. SMOOK,J.,FLINTERMAN,M.,PENNINGS,A.J.,Polym.Bull.,2,775 (1980)
29. SMOOK,J.,TORFS,J.C.M.,PENNINGS,A.J.,Makromol.Chem.,182,3351 (1981)
30. TAKAHASHI,A.,SAKAI,M.,KATO,T.,Polymer J.,12,335 (1980)
31. TORFS,J.C.M.,ALBERDA van EKENSTEIN,G.O.R.,PENNINGS,A.J.,Eur.Polym.J., 17,157 (1981)
32. UNGAR,G.,J.Materials Sci.,16,2635 (1981)

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