Crosslinking of ultra-high molecular weight polyethylene in the melt by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne: 2.* Crystallization behaviour and mechanical properties

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Ultra-high molecular weight polyethylene, was crosslinked in the melt at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne. It is shown that crosslinks and entanglements, whether trapped or not, contribute to the same degree to the decrease in crystallinity of the polyethylene upon crosslinking. Crosslinking introduced a very stable type of radical into the polyethylene. It was concluded that an almost completely crosslinked material with high crystallinity and therefore good mechanical properties, could be obtained by using as little as 0.2–0.3 wt% of peroxide.

Keywords Polyethylene; crosslinking; crystallization; entanglement; radical; strength

INTRODUCTION

The aim of the present investigation was to study the influence of crosslinking on the crystallization behaviour and the mechanical properties of ultra-high molecular weight polyethylene. Ultra-high molecular weight polyethylene possesses outstanding engineering properties, such as extreme abrasion resistance and exceptional chemical resistance[1]. However, its use is limited by its low melting point, its solubility in hydrocarbons and its tendency to crack when stressed[2]. Introducing crosslinks into the ultra-high molecular weight polyethylene is known to mitigate these disadvantages.

Since, because of the extremely long chains of ultra-high molecular weight polyethylene, only a few crosslinks are needed to cause gelation[3], the loss of crystallinity due to the crosslinking may be small[4]. Therefore crosslinking ultra-high molecular weight polyethylene can result in a material with good material properties at room temperature, whereas at higher temperatures polymer flow is precluded[5].

In a recent paper from this laboratory it was reported that ultra-high molecular weight polyethylene can be crosslinked in the melt at 180°C by means of the bifunctional peroxide 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne[6]. The present paper deals with the effect of crosslinking on the crystallization behaviour and the tensile properties of ultra-high molecular weight polyethylene. From end melting temperature and heat of fusion data it was concluded that crosslinking caused only a slight disturbance of the polymer crystallinity. Furthermore, electron paramagnetic resonance spectroscopy proved the existence of a very persistent type of radical in the polyethylene networks. Finally, tensile properties, such as tensile strength at break and Young's modulus, of the ultra-high molecular weight polyethylene, showed a tendency to decrease with increasing peroxide content.

EXPERIMENTAL

The ultra-high molecular weight polyethylene, with a weight average molecular weight of 4.10^6 kg/kmol (HiFax 1900; Hercules), was mixed with 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne (Luperox 130; Wallace, Tiernan) and crosslinked in the melt at 180°C (pressure ≃30 atm.) as described previously[6,7].

Extraction of the crosslinked polyethylene was performed in boiling *p*-xylene, containing 0.5 wt% of antioxidant (Ionol CP 0275; Shell). Samples were deswollen in acetone and dried under vacuum at 50°C. The gelfraction was taken as the ratio of the weight of the extracted to the non-extracted network. Calculation of the effective network chain density, from measurements of the equilibrium degree of swelling at 120°C in *p*-xylene, was reported elsewhere[6].

Melting point depression and heat of fusion were measured on extracted and afterwards carefully dried samples, using a Perkin-Elmer D.S.C.-2, equipped with a Perkin-Elmer Scanning AutoZero unit. Scans were conducted from 323 up to 453 K. Indium was used for temperature calibrations (Indium: melting temperature = 429.6 K[8]). The heat of fusion was determined by comparing the area under the melting endotherm with the area of fusion of an Indium sample, with a known heat of fusion of 6.8 cal/g[9]. Before first scanning every polyethylene sample was kept at 453 K for half an hour, to provide an initial random melt. The

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* Part 1: cf[6]

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Table 1 Network characteristics of ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne

Wt % of peroxide	Gelcontent (%)	$10^2 \cdot \nu^{*a}$ (mol dm^{-3})	$10^5 \cdot (\bar{M}_c)^{-1b}$ (kmol kg^{-1})	$10^2 \cdot \nu_c{}^c$ (mol dm^{-3})	$T_m{}^d$ (K)	ΔH^e (kJ kg^{-1})	$10^5 \cdot \frac{(T_m^0 - T_m)}{T_m^0 \cdot T_m}$ (K^{-1})^f
–	–	–	–	–	403.0	159	0
0.048	25.5	0.2	1.6	0.27	402.8	155	0.123
0.078	60.4	1.1	2.6	1.40	403.2	158	–0.123
0.110	79.8	5.6	7.9	7.48	402.3	154	0.430
0.150	85.0	8.3	11.0	11.04	402.7	139	0.185
0.196	91.8	11.0	14.2	14.67	401.1	136	1.175
0.258	96.4	12.6	16.0	16.80	400.0	132	1.861
0.373	97.8	13.0	16.6	17.33	399.0	134	2.488
0.488	97.9	13.7	17.4	18.27	398.0	128	3.117
0.911	99.3	16.1	20.1	21.47	393.1	115	6.249
1.571	100.0	19.2	23.8	25.60	391.2	109	7.485

[a] ν^*, effective network chain density
[b] $\bar{M}_c$, molecular weight between crosslinks
[c] ν_c, concentration of intermolecular crosslinked units
[d] T_m, end melting temperature
[e] ΔH, heat of fusion
[f] T_m^0, end melting temperature of non-crosslinked polyethylene

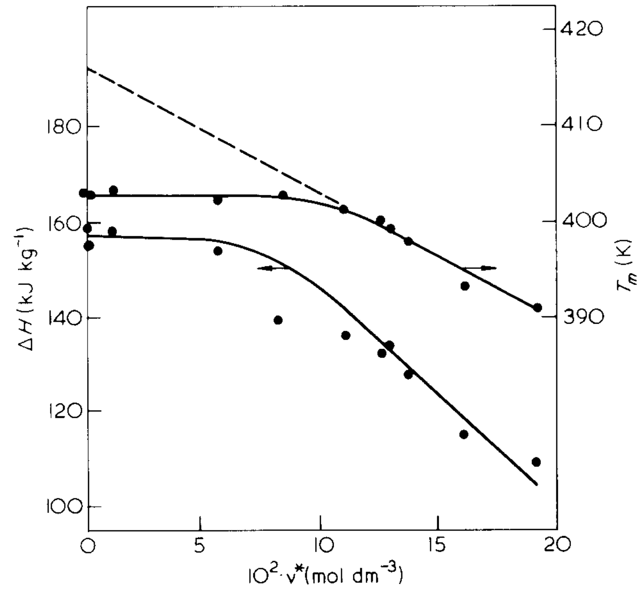

Figure 1 End melting temperature, T_m, and heat of fusion, ΔH, as a function of the effective network chain density, ν^*, for ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne

samples were crystallized from the melt at a cooling rate of 5 K min^{-1}. The end melting temperature and the heat of fusion were determined as a function of scan-speed and plotted against the square root of the scan-speed[10,11]. The end melting temperature data given, were obtained by extrapolating to zero scan-speed, whereas the heat of fusion was independent of the scan-speed.

Electron Paramagnetic Resonance (e.p.r.) spectra were obtained with a Varian E4 EPR spectrometer. Spectra were taken from the same network sample after different treatments and recorded at room temperature.

Tensile tests were performed using a Zwick Z1-3B tensile tester at a cross-head speed of 2.10^{-4} m s^{-1}, on dumb-bell shaped non-extracted samples (dumb-bell type: A.S.T.M. D1708.59T). The samples were cut from compression moulded network sheets. For every peroxide concentration, five tensile tests were carried out; the average results of the tests are reported. The tensile tests were conducted at room temperature. Specimen cross-sections were determined by means of a micrometer. No substantial macro-necking was observed.

The Scanning Electron Micrographs (*SEM*) were taken using an I.S.I. DS-130 scanning electron microscope. The fracture surfaces were obtained by cooling the samples down in liquid nitrogen and subsequent breaking.

RESULTS AND DISCUSSION

The amount of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne, abbreviated as DDPHY, used to crosslink the ultra-high molecular weight polyethylene, abbreviated as UHMWPE, was varied from 0.048 up to 1.571 wt%. The gel content of the polymer increased from 25.5% to 100%, while the effective network chain density increased from $0.2 \cdot 10^{-2}$ mol dm^{-3} up to $19.2 \cdot 10^{-2}$ mol dm^{-3}.[6] The results of the curing experiments are summarized in *Table 1*.

Crystallization behaviour

The first subject to be discussed is the crystallization behaviour of the crosslinked UHMWPE. The end melting temperature (T_m) and the heat of fusion (ΔH) of the semi-crystalline networks were determined as a function of the effective network chain density (ν^*). Both quantities showed the same dependence on ν^*. Up to a certain value of ν^*, T_m and ΔH remained constant, while upon exceeding this critical value of ν^*, T_m and ΔH decreased linearly with ν^*. The results of the crystallization experiments are presented in *Table 1* and *Figure 1*.

In the previous paper[6] it was shown that entanglement trapping was complete at a peroxide content of 0.258 wt% or higher, i.e. starting from an effective network chain density of $12.6 \cdot 10^{-2}$ mol dm^{-3}. Remembering this we now concentrate on the T_m *versus* ν^* plot in *Figure 1*, and notice that T_m starts decreasing in the ν^*-region, where entanglement trapping due to the crosslinking is complete. To analyse this phenomenon further we first discuss the general theory underlying the crystallization of crosslinked systems.

The melting temperature of the crystallites in a cross-

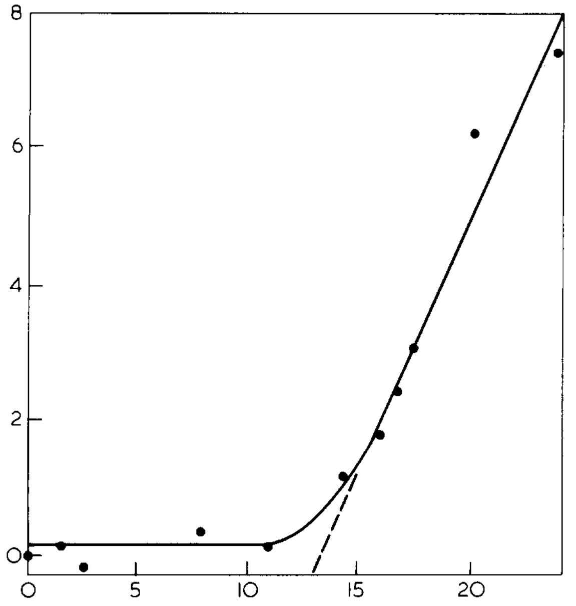

Figure 2 Melting point depression *versus* reciprocal molecular weight between crosslinks for ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne

linked system is usually lower than that of the uncrosslinked material. This melting point depression can, according to Flory[12,13], be explained as a result of a reduction of the concentration of segments of a length suitable for crystallization, just as for the crystallization of copolymers. Akana and Stein[14] obtained an expression for the melting point depression of a crosslinked polymer that can be written as:

$$\frac{T_m^\circ - T_m}{T_m^\circ \cdot T_m} = \frac{A}{\bar{M}_c} \tag{1}$$

where T_m° and T_m are the equilibrium melting temperatures of the uncrosslinked and the crosslinked material respectively, A is a positive constant and $\bar{M}_c$ is the molecular weight between crosslinks. According to equation (1), a plot of $\frac{T_m^\circ - T_m}{T_m^\circ \cdot T_m}$ *versus* $(\bar{M}_c)^{-1}$ should yield a straight line. Such a plot is shown in *Figure 2* (see also *Table 1*). $(\bar{M}_c)^{-1}$ was calculated from ν^*.

At low values of $(\bar{M}_c)^{-1}$, i.e at low peroxide concentrations, the melting point depression is negligible, whereas at high values of $(\bar{M}_c)^{-1}$ a straight line with a positive slope was obtained. The value of $(\bar{M}_c)^{-1}$, where melting point depression was first observed, was derived by extrapolating the linear part of the $\frac{T_m^\circ - T_m}{T_m^\circ \cdot T_m}$ *versus* $(\bar{M}_c)$ plot at high $(\bar{M}_c)^{-1}$-values, to a $\frac{T_m^\circ - T_m}{T_m^\circ \cdot T_m}$-value of zero, and corresponded to a $\bar{M}_c$-value of 7600. The thus obtained value of $\bar{M}_c$ is close to the value of 7000, which is the molecular weight between entanglements, derived from a plot of the effective network chain density against the peroxide concentration[6].

Firstly, these results confirm the idea that upon peroxide curing the entanglement sites are preferentially crosslinked, i.e. entanglement trapping occurs. Furthermore they suggest that entanglements and chemical crosslinks contribute to the same extent to the melting point lowering of UHMWPE on the time scale of our experiments. That melting point lowering only occurs after the complete conversion of entanglements into chemical crosslinks, offers an interesting method to determine the entanglement concentration in a polymer system.

Equation (1) considers only the influence of crosslinks on the melting point depression of a crosslinked system. A more realistic treatment would also have to include the influence of network flaws as e.g. loops, chain-ends and entanglements. Such an analysis will be the next subject of interest.

As the UHMWPE was crosslinked in the melt the concentration of intermolecular crosslinks (loops) is expected to be low, whereas the high molecular weight of the polymer reduces the amount of chain-ends. We have already reported that the chemical modification of the polyethylene due to the crosslinking was small[6]. Therefore we think it justified to consider only the influence of intermolecular crosslinks and entanglements on the crystalline melting point of the networks. Posthuma de Boer and Pennings derived an equation for the melting point depression of a crosslinked system, accounting for the influence of crosslinks as well as entanglements[4]. This equation reads:

$$\frac{T_m^\circ - T_m}{T_m^\circ \cdot T_m} = \frac{R}{\Delta H_f}(K \cdot \nu_c + 2 \cdot \delta \cdot \varepsilon) \tag{2}$$

in which, R, the gas constant equals 8.3143 J K^{-1} mol^{-1}, ΔH_f, the heat of fusion per unit volume, is $2.5 \cdot 10^5$ J dm^{-3} (70 cal g^{-1}[11]), ν_c is the concentration of intermolecular crosslinked units, ε, the entanglement concentration is $5.54 \cdot 10^{-2}$ mol dm^{-3} and finally K and δ are the weight factors for the different kinds of chain units in equation (2).

Before we can now make a plot of the melting point depression *versus* ν_c, we first have to calculate ν_c. In doing so we have to consider the following. Each decomposing DDPHY-molecule can yield 4 radicals[15], each of them capable of abstracting hydrogen from polyethylene[15]. As the crosslinking reaction is thought to proceed through the so-called cage mechanism[7,16], each peroxide molecule may yield two tetrafunctional crosslinks within the same cage, i.e. in close vicinity of each other. Upon elastic deformation, such as swelling, the two tetrafunctional crosslinks will behave as one hexafunctional crosslink, when the chain inbetween the two crosslinks becomes too short to be elastically active[17], as was discussed earlier[6]. Therefore the effective network chain density, ν^*, was calculated assuming a crosslink functionality of six, in the present network. Crystallization however is not elastic deformation and therefore we have to treat the crosslinks as tetrafunctional implying that every hexafunctional crosslink changes into two tetrafunctional crosslinks. As there are two crosslinked units per tetrafunctional crosslink we can now derive ν_c from ν^* (see *Table 1*).

A plot of $\frac{T_m^\circ - T_m}{T_m^\circ \cdot T_m}$ against ν_c is presented in *Figure 3*. At low ν_c-values the melting point depression is about zero and $K = 0$. This again is the region where crosslinking preferentially takes place at entanglement sites. When all entanglements are trapped a straight line with a positive slope is found, from which a K-value of 20 was calculated,

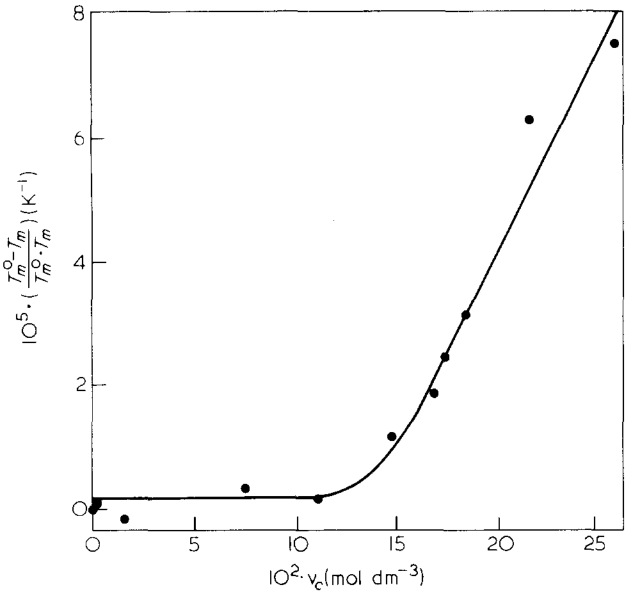

Figure 3 Melting point depression as a function of the concentration of intermolecular crosslinked units, ν_c, for ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne

implying that per crosslinked unit, 20 CH_2-units are excluded from crystallization. This number is of the same order of magnitude as the value found by Akana and Stein[14], namely $K = 10$ polybutadiene units. For solution crosslinked polyethylene it was reported that K was equal to 60[4]. These networks suffered however from considerable chemical modification due to the crosslinking, which may result in too high a value of K.

Equation (2) shows that δ can be derived from the intercept on the $\frac{T_m - T_m}{T_m \cdot T_m}$-axis of a plot of the melting point depression as a function of ν_c. However *Figure 3* shows that no such intercept exists. Therefore we return to the plot of T_m *versus* ν^* from *Figure 1*. We have already reasoned that the linear part of the plot at high ν^*-values, reflects the lowering of the melting point solely due to the crosslinks. Extrapolating this linear part to $\nu^* = 0$, a T_m-value of 416.7 K was derived. In spite of the high crystallization rate, the high melt viscosity and the presence of network flaws, this value is surprisingly close to $T_m = 418.7$ K, which is considered to be the equilibrium melting temperature of an ideal polyethylene crystal of infinite size[11]. If we attribute the melting point lowering from 416.7 to 403.0 K, the melting point of non-crosslinked polyethylene (see *Table 1*), completely to the presence of entanglements, a δ-value of 22 can be calculated, i.e. about 20 CH_2-units are prevented from crystallization per entangled unit. For a trapped entangled unit a value of 30 was found[4]. Considering the close agreement between these two δ-values, we feel that we can now conclude, what was already suggested, namely that an entanglement, chemically fixed or not, contributes to the same degree to the melting point depression of melt crystallized UHMWPE, crystallized from the melt at a cooling rate of 5 K min^{-1}.

DiMarzio *et al.*[18] demonstrated that polymer chains disentangle while crystallization takes place. In contrast to this, Yoon and Flory[19], remarked that extensive configurational reorganizations do not take place when a high molecular weight polymer crystallizes. Due to the high relaxation rates in molten high molecular weight polymers the high entanglement concentration that exists in the melt will be largely retained during crystallization. Therefore the structure of a crystal produced by rapid cooling of a high molecular weight polymer melt, will be related to that of this precursing melt[20,21]. Our results support this last point of view and they may be understood if we realize that we are dealing with a highly viscous melt, that contains almost the equilibrium concentration of entanglements[6]. In such a surrounding even an untrapped entanglement has already a very limited spatial freedom and therefore contributes significantly to the melting point depression. How severe the constraints on the crystallizing chains are can be seen from the fact that K and δ are of the same order of magnitude in the present case. However, a more pronounced difference between K and δ may arise at lower crystallization rates.

The heat of fusion exhibits more or less the same behaviour as a function of ν^* as T_m (see *Figure 1*) so this does not require a modification of the ideas presented. The ΔH measurements offer an extra check upon the validity of the K- and δ-values obtained. Therefore the concentration of chain-units excluded from crystallization was calculated, from both the decrease in heat of fusion and from the melting point depression. Calculations were performed using $K = 20$, $\delta = 22$ and $\varepsilon = 5.54 \cdot 10^{-2}$ mol dm^{-3}, for those samples in which all entanglements were trapped. The results of the calculations are summarized in *Table 2* and it is seen that there is an excellent agreement between the concentration of chain-units excluded from crystallization derived by the two methods, implying the correctness of the weight factors from equation (2). There is a slight discrepancy at high peroxide concentration, which may be explained by the fact that we have neglected the chemical modification of the chains during the crosslinking process.

Electron paramagnetic resonance (e.p.r.) spectroscopy

E.p.r. spectra were taken of a network synthesized by means of 0.110 wt% DDPHY. The spectra are presented in *Figure 4*. The first spectrum, denoted A, was recorded three weeks after curing, using an unextracted sample that received no special treatment after the synthesis. As the sample was prepared for e.p.r. spectroscopy by cutting slices from the original compression moulded network sheet, it may have contained mechanically induced radicals. To assure removal of these surface radicals, the sample was annealed under vacuum at 120°C for 17 h.

Table 2 Concentration of chain units excluded from crystallization, N_{ex}, as a function of peroxide content for ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne

Wt % of peroxide	N_{ex}, calculated from the decrease in heat of fusion (mol dm^{-3})	N_{ex}, calculated from the melting point depression (mol dm^{-3})
0.258	5.6	5.8
0.373	5.2	5.9
0.488	6.4	6.1
0.911	9.1	6.7
1.571	10.4	7.6

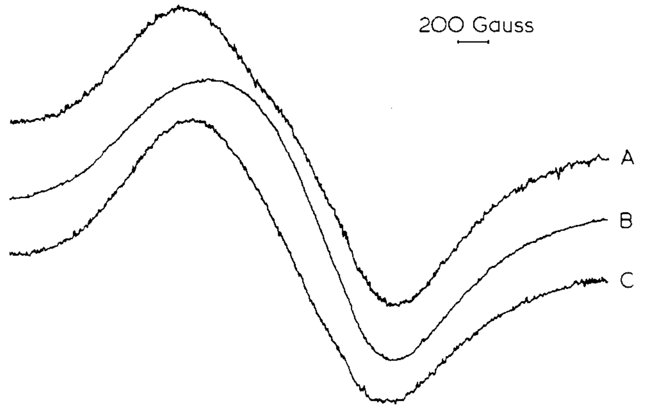

Figure 4 Electron paramagnetic resonance spectra of ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 0.110 wt % 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne. A, Spectrum recorded 3 weeks after curing; B, spectrum recorded after subsequent annealing at 120°C for 17 h; C, spectrum recorded after annealing at 120°C for 17 h and subsequent extraction for 20 h

Afterwards spectrum B was recorded. Spectrum B is less broad than spectrum A but apart from that, not much difference can be detected. Finally, the sample was extracted in boiling *p*-xylene for 20 h, but although spectrum C has again narrowed in comparison to spectrum B, no further changes can be seen.

All spectra were recorded using the same amount of material and the same amplification. As the intensity of the spectra does not seem to change, it can be concluded that the radical concentration remains constant.

From spectrum B it can be concluded that the radicals are not mechanically induced surface radicals, as annealing would have extinguished those. That even after extraction radicals are still present implies that the radicals are actually on the polyethylene chains otherwise they would have been washed out. The reader may remark that radicals would easily have to be able to recombine in the swollen state, as here the chain mobility has increased enormously. We have to remember though, that the polyethylene chains are separated by solvent molecules, which are thus hindering the recombination reaction.

We also have to consider the influence of the anti-oxidant used during the extraction. The persistence of the radicals however cannot be attributed to the anti-oxidant present, as anti-oxidant is known to stabilize radicals, not to prevent them from recombination reactions.

Evaluating all this information, it is evident that we are dealing with a very persistent type of radical, which is stuck on the polyethylene chains. Whether all radicals have the same structure cannot be said, but it is clear that the radicals are unable to move along the chains to find a suitable partner for a recombination reaction. This immobility is in accordance with the cage mechanism[7,16]. Finally, the enormous width of the spectra can be understood as a consequence of the random orientation of the radicals in the semi-crystalline materials investigated[22].

How can the presence of the radicals be explained? In order to answer this question we have to discuss the several stages during the crosslinking process, i.e. during the compression moulding at 180°C for 3 h. At first the polyethylene powder mixed with the peroxide, is heated under pressure. Above the melting temperature, which is about 400 K, the chain mobility increases. As at this temperature the decomposition rate of the DDPHY is still low[23], crosslinking at this stage can be neglected.

The motion of molecules in polymer melts has been extensively studied by several methods such as nuclear magnetic resonance spectroscopy[24,25] and neutron scattering[26]. The results of these studies are usually interpreted by means of the reptation-model, i.e. a model that assumes a snake-like movement of a polymer chain along its own contour. This concept was introduced by de Gennes[27] and later extended by Doi and Edwards[28-30]. In the Doi and Edwards treatment a chain in a polymer melt is thought to be confined to a tube by the surrounding chains. In the case of a polyethylene melt Graessley[31] calculated a tube diameter of about 34 Å, illustrating the severity of the constraints on a polyethylene chain in the melt, in agreement with the conclusions drawn from our crystallization study (see previous section).

In the present case, the polyethylene chains from all molten powder particles, will try to form an equilibrium entanglement network, through reptation. Klein and Ball[32] studied the crystallization kinetics of polyethylene crystallized from the melt. Using their results Hoffman[33] derived the following expression for the rate of reptation in a polyethylene melt:

$$r \simeq 30.7/n \qquad (3)$$

where r is the reptation rate in cm s^{-1} and n equals the number of CH$_2$-units in the polyethylene chain. In our case this would imply, using a number average molecular weight of $1.5 \cdot 10^5$ kg kmol^{-1}, a reptation rate of about 10 cm h^{-1}. This high reptation rate will enhance the formation of an equilibrium entanglement network in an early stage of the crosslinking process. The high rate of reptation is in agreement with the observation of Schreiber and Bagley[34], who reported a partial re-establishment of the entanglement network in fractionated high molecular weight polyethylene in 1 h at 190°C.

A factor that may even promote the formation of an entanglement network in the underlying case, is the irregular shape of the initial HiFax 1900 powder particles, which is illustrated in *Figure 5*. The irregular shape gives

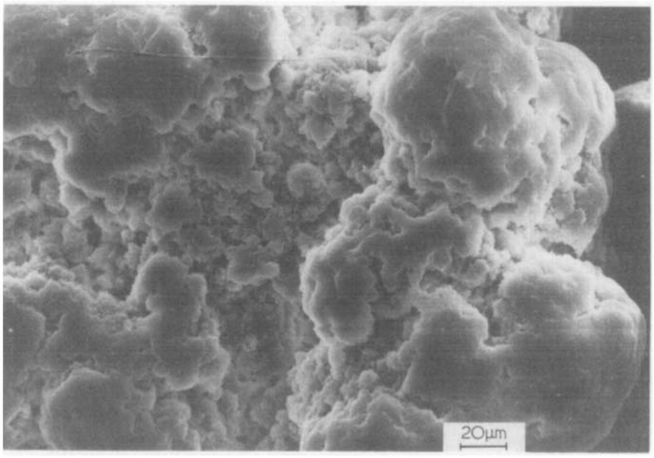

Figure 5 A *SEM* micrograph of an ultra-high molecular weight polyethylene (HiFax 1900) powder particle. The powder was used as received

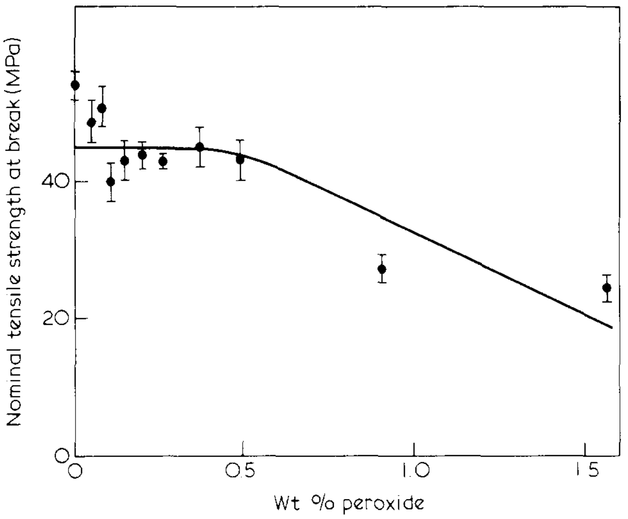

Figure 6 Nominal tensile strength at break as a function of peroxide content for ultra-high molecular weight polyethylene (HiFax 1900) cross-linked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne

rise to enormous shear stresses due to the applied pressure above the melting point of the polymer, thus favouring the homogeneous mixing of the polyethylene chains from the individual powder particles.

To illustrate further the fast reptation in our case, eight compression moulded HiFax 1900 polyethylene sheets were packed on top of each other and again compression moulded at 180°C for 3 h. After cooling one solid had been formed that could not be separated into the original sheets, not even by severe mechanical loading.

The reptation is hindered however by the very high melt viscosity of HiFax 1900, resulting in the 'shape' stability of the HiFax 1900 powder particles. When heated under a microscope with a hot stage attachment, it is seen that the powder particles retain their original shape up to 493 K. Only above this temperature the polymer starts to flow spontaneously, a phenomenon which is pared to extensive polymer degradation[35]. This 'shape' stability is consistent with the limited intergrain diffusion reported by McKenna *et al.*[36], observed with compression moulded UHMWPE sheets. Furthermore, the crosslinks formed during the crosslinking process, reduce the chain mobility in the melt and with that, the interpenetration of the various polymer chains. Therefore the initial fast reptation is hindered by the parameters mentioned, resulting in only a partial establishment of an equilibrium entanglement network. This agrees with the fact that we derived a molecular weight between entanglements of 7000[6], instead of 4000, which is considered to be the equilibrium molecular weight between entanglements in a polyethylene melt[37].

As already mentioned, the introduction of crosslinks in the polyethylene reduces the chain mobility and some polyethylene radicals, resultant from the reaction of polyethylene with the peroxide fragments, become trapped, unable to recombine with other radicals. These trapped radicals give rise to the spectra in *Figure 4*. The presence of the unreacted radicals may explain the low crosslinking efficiency for this system[6]. Furthermore, the free radicals detected, disturb the view that all crosslinks would behave as hexafunctional crosslinks under elastic deformation. Therefore it seems likely that some crosslinks with other functionalities, e.g. four, may also be present in the network. It is difficult to estimate from e.p.r. spectroscopy the free radical concentration in these semi-crystalline materials.

The enormous stability of the radicals offers the opportunity to study the molecular motion of the radical sites from the width of the e.p.r. spectra[38,39], without using a so-called spin trapping agent. Together with results obtained from nuclear magnetic resonance spectroscopy[40] this could give information of chain fluctuations in semi-crystalline UHMWPE.

Finally, free radicals may affect the mechanical properties of the material. The tensile properties are studied next.

Mechanical properties

Usually, mechanical testing of UHMWPE is concerned with such properties as abrasion resistance and impact strength. We have therefore focussed our attention on a different set of mechanical properties, including nominal tensile strength at break, Young's modulus, elongation at break, nominal yield stress and finally elongation at the yield point.

The tensile properties were measured as a function of peroxide content and the results of the tests are presented in *Figures 6, 9, 10, 11* and *12*. Although the lines drawn may suffer from subjective interpretation, the general tendency seems to be clear.

Figure 6 shows that at low peroxide concentration the nominal tensile strength at break is not influenced much by the crosslinking reaction. As in compression moulded polyethylene the tensile strength at break is largely determined by the sample crystallinity[41], this is in accordance with the observation that up to a certain degree of crosslinking the polyethylene crystallinity does not change (see *Figure 1*). At higher peroxide concentration the crystallinity drops and with that the nominal tensile strength at break, in accordance with the results of Manley and Qayyum[2].

It was also observed that with increasing peroxide content the strain-hardening at high elongations was less pronounced. As strain-hardening is caused by strain-induced crystallization[42], it is also likely that this type of crystallization is hindered by the crosslinks.

The change in fracture behaviour with crosslinking can also be seen from *SEM* micrographs taken of the fracture surfaces of non-crosslinked and densely crosslinked polyethylene samples. These *SEM* micrographs are shown in *Figures 7* and *8*, respectively. During breaking of the samples, it was found that the non-crosslinked sample broke brittle, while the dense crosslinked sample exhibited a more ductile fracture behaviour. This difference is further illustrated with *SEM* micrographs. *Figure 7* shows a rough fracture surface (brittle fracture, high crystallinity) whereas *Figure 8* shows a smooth fracture surface (ductile fracture, low crystallinity). *Figure 8* also reveals a layered-like structure and the presence of bubble-like cavities. Kunert *et al.*[43], also reported cavities in crosslinked polyethylene and these authors ascribed them to the presence of more or less dense crosslinked phases in the network. It is also conceivable that in our case the bubbles are due to the development of gases, such as methane and acetone, which are known to be produced when DDPHY-fragments react with polyethylene[15]. Unfortunately, the formation of these micro-cavities may have a negative influence on the network tensile properties.

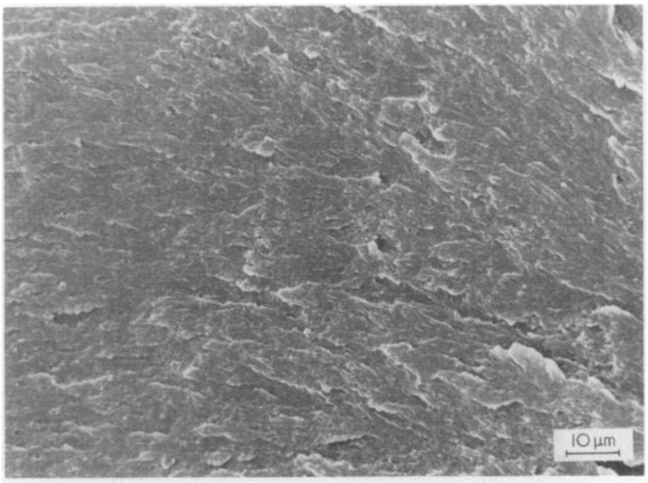

Figure 7 A ***SEM*** micrograph of the fracture surface of compression moulded ultra-high molecular weight polyethylene (HiFax 1900), cooled down in liquid nitrogen and subsequently broken

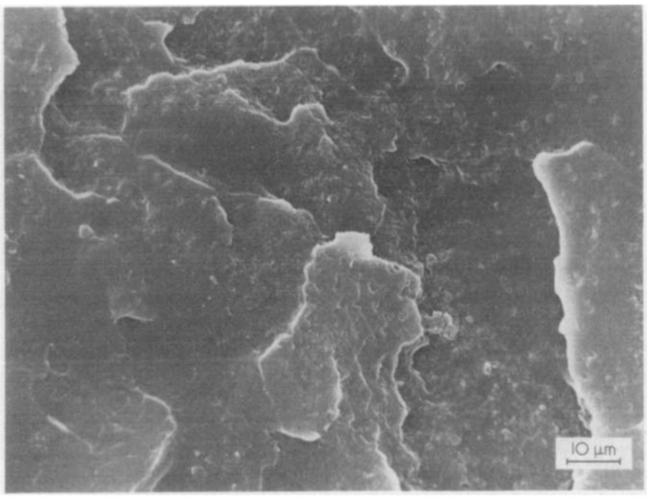

Figure 8 A ***SEM*** micrograph of the fracture surface of ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 1.571 wt % 2,5-dimethyl-2,5-bis (tert-butyldioxy)-3-hexyne, cooled down in liquid nitrogen and subsequently broken

Figure 9 represents the Young's modulus as a function of the amount of DDPHY used to crosslink the UHMWPE. The Young's modulus is decreasing with increasing wt% peroxide, a behaviour that is in agreement with the data of Kunert *et al.*[41,44] Although the Young's modulus variation is not as clearly parallel with the changing of the sample crystallinity as was the case for the behaviour of the nominal tensile strength at break, we do hold the decrease in crystalline content, concomitant with a softening of the material, responsible for the decrease of the initial modulus due to the introduction of the crosslinks.

The elongation at break (see *Figure 10*) is independent of the degree of crosslinking. The molecular process taking place during extension of a semi-crystalline polymer beyond the yield point, is the unfolding of lamellar-like folded chain crystals[45,46]. As only little crosslinks were needed to gelate UHMWPE[6], this unfolding is not too much hindered by the introduction of the crosslinks, implying a constant elongation at break. This result seems to be in sharp contrast with the findings of Kunert[41] and Lyons and Vaughn[47], who reported a decrease in the elongation at break of polyethylene upon crosslinking. Let us examine their results more closely.

Kunert[41] crosslinked low molecular weight polyethylene by means of a peroxide. Because of the short polymer chains in low molecular weight polyethylene, a considerable crosslink density will be needed to cause gelation[3]. Due to this high crosslink density, the polyethylene chain mobility will decrease, thus hindering the unfolding process and resulting in a decrease of the elongation at break. Lyons and Vaughn[47] prepared networks by irradiation of polyethylene at room temperature. It seems now generally accepted that upon irradiation of polyethylene in the solid state, crosslinking preferentially takes place in the amorphous part of the material[48]. Therefore a network thus synthesized will have a structure which differs completely from that of a network obtained by means of peroxide curing high above the melting temperature, as in our case. Furthermore, irradiation may induce main-chain scissioning[49], a

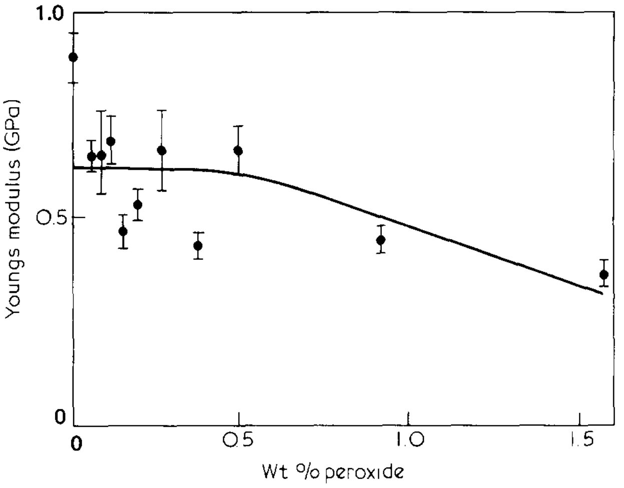

Figure 9 Young's modulus as a function of peroxide content for ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne

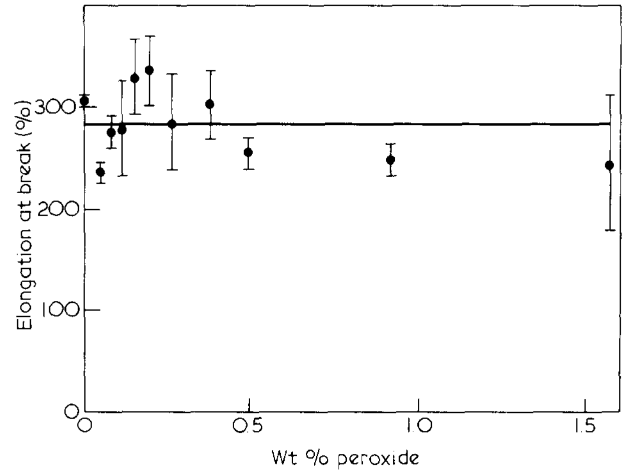

Figure 10 Elongation at break as a function of peroxide content for ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis (tert-butyldioxy)-3-hexyne

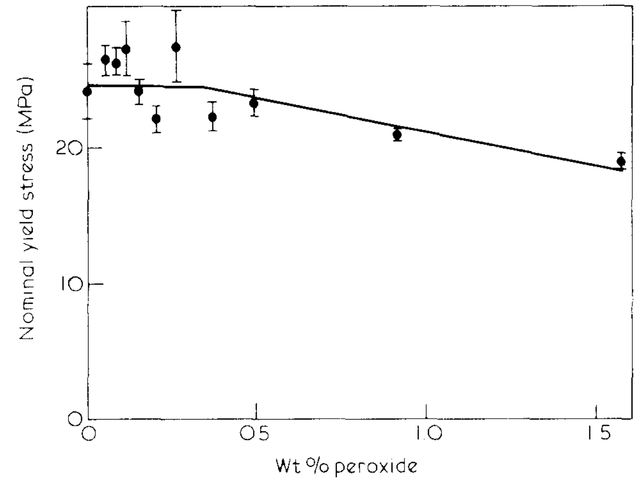

Figure 11 Nominal yield stress as a function of peroxide content for ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis (tert-butyldioxy)-3-hexyne

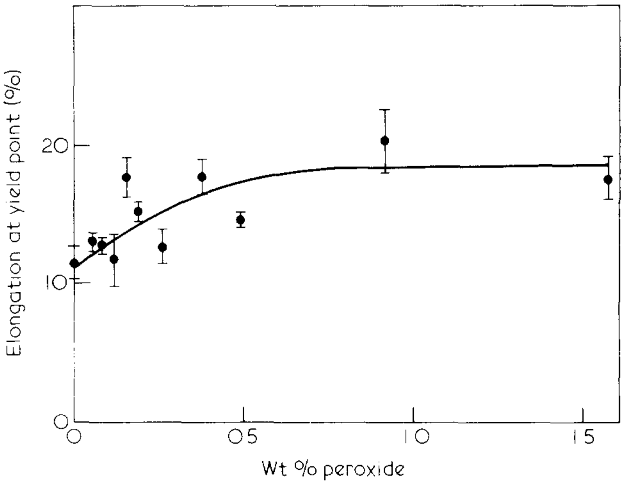

Figure 12 Elongation at the yield point as a function of peroxide content for ultra-high molecular weight polyethylene (HiFax 1900) crosslinked in the dry state at 180°C by means of 2,5-dimethyl-2,5-bis(tert-butyldioxy)-3-hexyne

phenomenon that was not observed in the present study[6]. Combining all this information it may be expected that irradiation of polyethylene renders a different dependence of the elongation at break on the crosslink density.

In *Figures 11* and *12* the yielding phenomena are considered as a function of crosslinking agent content. The nominal yield stress is practically insensitive to peroxide-curing as shown in *Figure 11*. The little variation that does present itself again more or less coincides with the change in sample crystallinity upon crosslinking (see *Figure 1* and *Table 1*). We would like to compare this behaviour with the results of Lawton *et al.*[50] and of Capaccio *et al.*[51], who observed an increase in both yield stress and the amount of strain hardening upon radiation crosslinking of polyethylene at room temperature. In order to explain this difference, we first have to realize that radiation crosslinking below the melting temperature results in a specific type of network, as mentioned earlier. Furthermore, the above authors explain their findings as the result of the increasing chain-connectivity due to irradiation, i.e. an increase in the effective molecular weight of the material. As in our case the starting polymer already had an extremely high molecular weight, a somewhat different behaviour of the yield stress and the amount of strain hardening with crosslink density may be expected.

Finally, *Figure 12* demonstrates a tendency for the elongation at the yield point to increase with increasing wt% peroxide. As the Young's modulus decreases and the nominal yield stress remains constant with increasing peroxide concentration, this is to be expected.

The radicals detected (see *Figure 4*) will especially affect the long-term mechanical properties of the network (e.g. oxidative degradation). An investigation into this sort of properties is however beyond the scope of this paper.

It is well known that the interpretation of the mechanical properties of a semi-crystalline polymer, is a difficult matter. All kinds of factors as e.g. strain-rate, initial sample length and the presence of surface cracks, are considered to be of influence. On top of that the molecular origin of the tensile properties is often not well understood. We are well aware that we have not given a complete account of the relation between mechanical properties on one side and sample structure on the other side. To point out the similarity between the mechanical properties as a function of peroxide content and the sample crystallinity as a function of peroxide content, was our only intention. The poor correlation between the mechanical properties and the peroxide concentration, common for these kind of experiments[2], does not allow the drawing of any further conclusions.

CONCLUSION

We have shown that only a small amount of peroxide, i.e. in the range of 0.2 up to 0.3 wt%, is sufficient to cause complete gelation of the ultra-high molecular weight polyethylene (see *Table 1*). Thus polymer flow is prevented above the melting point, whereas at low temperatures the decrease in crystallinity is limited, resulting in good mechanical properties at room temperature.

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