# Crosslinking of ultra-high molecular weight polyethylene in the oriented state with dicumylperoxide

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Dicumylperoxide was used to crosslink ultra-high molecular weight polyethylene in the oriented state. Completely gelated fibre-networks with a tenacity up to 1.4 GPa were obtained. Storage at 195°C for 1 h left the tensile properties of the crosslinked filaments at room temperature practically unchanged, and vulcanization avoided fibre fibrillation upon failure. It was concluded that to combine high strength with high gel content, crosslinking should be peformed after the polyethylene chains have attained a high degree of orientation.

**Keywords** Polyethylene; crosslinking; fibre; hot-drawing; strength; ultra-violet radiation

## INTRODUCTION

Ultra-high strength polyethylene fibres, with a tensile strength at break of 4.1 GPa and a Young's modulus up to 120 GPa, can be obtained by the gel-spinning technique[1,2]. This technique consists of the spinning of an ultra-high molecular weight polyethylene gel, followed by subsequent hot-drawing. However, the range of applications of these fibres is limited by their low melting point[3,4]. Crosslinking the ultra-high strength polyethylene fibres may overcome this disadvantage[5].

Crosslinking ultra-high strength polyethylene fibres, without destroying the specific fibre structure, can be performed using $\gamma$-irradiation[6,7]. Unfortunately, apart from crosslinking $\gamma$-irradiation causes main-chain scission, thus reducing the tenacity of the filaments[6]. Dicumylperoxide is known to crosslink polyethylene without chain rupture[8]. Since dicumylperoxide decomposes at an appreciable rate only at high temperatures, the idea was conceived to simultaneously hot-draw and vulcanize the as-spun fibres. If dicumylperoxide can be introduced into as-spun polyethylene filaments, hot-drawing may result in both the alignment of the polyethylene molecules in the direction of the fibre axis, as well as the fixation of this highly extended chain conformation with the aid of the chemical crosslinks, resulting in a crosslinked fibre of high tenacity.

The present paper is concerned with the crosslinking in the oriented state of porous as-spun ultra-high molecular weight polyethylene filaments with dicumylperoxide. It will be shown that fibre networks with a tensile strength at break up to 1.4 GPa can be obtained, without the occurrence of main-chain scission. The maximum attainable draw ratio and concomitantly the tensile strength at break were found to decrease with increasing peroxide concentration. Furthermore it was observed that crosslinking prevented the fibre from fibrillation upon fracture at room temperature and that crosslinked filaments could be kept at 195°C for prolonged time without significantly influencing the tenacity of the fibre at 20°C. Finally, it is pointed out that drawing of dicumylperoxide-containing fibres at a low temperature followed by ultra-violet irradiation is a most promising technique for the production of strong gelated filaments.

## EXPERIMENTAL

The polyethylene used in this study was ultra-high molecular weight polyethylene with a weight average molecular weight of $4 \times 10^6$ kg kmol$^{-1}$ (HiFax 1900 from Hercules). Porous as-spun fibres were prepared by spinning a solution of 5% (w/w) HiFax 1900 in paraffin-oil at a spinning temperature of 170°C. After spinning the solvent was extracted from the fibres through extraction at room temperature by means of n-hexane[1,2].

Dicumylperoxide (DiCup R from Hercules) was purified prior to use by repeated recrystallization from methanol. Introduction of the peroxide into the as-spun fibres was performed by swelling the fibres in a solution of dicumylperoxide in n-hexane for 6 h at 50°C. After removal of the fibre from the swelling medium, the fibre was dried under vacuum at room temperature. Fibre peroxide content was taken as the ratio of the increase of the dry weight of the fibre due to the swelling procedure, to the dry fibre weight before swelling. The reproducibility of the mixing technique was found to be rather good. Peroxide-containing fibres were stored under a nitrogen atmosphere to avoid premature rupture of the fibres during the crosslinking process.

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Drawing experiments were carried out in a double-walled glass cylinder 1.5 m in length through which hot silicone-oil was pumped from a temperature-regulated bath[9]. A small stream of purified nitrogen was led through the pipe to eliminate polymer degradation and to establish a temperature gradient in the tube during the hot-drawing experiment. The latter was found to be essential in order to achieve homogeneous deformation during hot-drawing[1,2]. Crosslinking was brought about by leading the peroxide-containing filaments through the tube at high temperature, defining the draw ratio as the ratio of the velocity of the wind-up drum to the velocity of the feed-roll; the fibre entered the drawing tube at a constant speed of $2.1 \times 10^{-4}$ m s$^{-1}$ and was drawn up to its maximum attainable draw ratio. Subsequent to the hot-drawing at 150°C, the networks were annealed at constant length at elevated temperature to complete the vulcanization reaction and to eliminate any trapped free radicals. Electron paramagnetic resonance spectroscopy was employed to check completion of the radical decay. In some experiments, instead of annealing, crosslinking was continued by continued by irradiating the hot-drawn filament with ultra-violet radiation with a wavelength of 253.7 nm, produced by two low-pressure mercury lamps, each with an intensity of 1.5 W (Rayonet Photochemical Reactorlamp RPR 2537 Å).

Extraction of the sol fraction was performed in boiling *p*-xylene, containing 0.5 wt% antioxidant (Ionol CP 0275 from Shell). Samples were deswollen in acetone and dried under vacuum at 50°C. The gel fraction was taken as the ratio of the weight of the extracted to the non-extracted network.

Tensile tests were performed using a Zwick Z1.3B tensile tester at a crosshead speed of $2 \times 10^{-4}$ m s$^{-1}$ and an original sample length of 25 mm at room temperature. Cross-sectional areas were calculated from fibre weight and length, assuming a density of 1000 kg m$^{-3}$. For every peroxide concentration, eight tensile tests were carried out; the average results of the tests are reported.

Scanning electron microscopy (SEM) was conducted using a I.S.I. DS-130 scanning electron microscope. Fracture surfaces of the crosslinked fibres were obtained by breaking the fibres in a tensile test experiment at room temperature.

Melting endotherms of the networks were determined, using a Perkin–Elmer DSC-2, equipped with a Perkin–Elmer Scanning Auto-Zero unit. Baselines were recorded by scanning empty sample pans. Scans were conducted from 323K up to 473K at a heating rate of 5K min$^{-1}$. Indium (melting temperature[10] = 429.6K) was used for temperature calibrations. The temperatures at the maximum of the endotherms were taken as the melting points of the samples. The heat of fusion was determined by comparing the area under the melting endotherms with the area of fusion of an indium sample, with a known heat of fusion[11] of 28.6 kJ kg$^{-1}$. Calculation of the network crystallinity was based on a heat of fusion of 294 kJ kg$^{-1}$ for an ideal polyethylene crystal. All thermograms were obtained from non-extracted networks, cut to a length of about 1 mm.

Infra-red spectroscopy was performed using a Pye Unicam SP3-300 infra-red spectrophotometer. Spectra were taken from fibres that were wound on a glass frame (15 × 15 mm) in such a way that the frame was covered with a monolayer of filament, each winding carefully being placed next to the other.

## RESULTS AND DISCUSSION

### *Mixing of dicumylperoxide with polyethylene filaments*

Recent studies have emphasized that in order to achieve homogeneous curing it is essential that polymer and curing agent are thoroughly mixed[12-14]. Adequate mixing may be performed, for example, by swelling the polymer in the pure or diluted crosslinking agent[15]. This technique, however, can only be successful if the liquid curing resin is totally compatible with the polymer, otherwise segregation may occur, leading to a non-random dispersion of crosslinks in the final network.

The main objective of the present investigation was to synthesize densely crosslinked, strong polyethylene fibres. Therefore, at first we tried to vulcanize a fibre, with a tensile strength at break of 3.1 GPa, obtained by hot-drawing of an as-spun filament at 150°C to a draw ratio of about 70. In order to introduce the dicumylperoxide, abbreviated as DCP, into the high tenacity filament, the fibre was placed in undiluted DCP for 3 days at 50°C. At this temperature the peroxide is a liquid and peroxide decomposition can be neglected[16], so DCP may now diffuse into the high tenacity filament without any chemical reaction. However, after removing the fibre from the liquid no increase in fibre weight could be detected, i.e. no DCP had entered the system. Thus, subsequent curing of the fibre, e.g. by annealing at elevated temperatures, never resulted in a gel. It is our belief that this result is similar to a phenomenon described by Marshall *et al.*[17] and can be explained by the high degree of orientation and crystallinity of ultra-high strength polyethylene fibres. DCP will preferentially enter the fibre through the disordered domains, since the crystal lattice is too densely packed to facilitate easy peroxide penetration. In the case of a hot-drawn polyethylene filament, the amount of amorphous material is minimal, resulting in a low rate of diffusion of low molecular weight compounds, such as DCP, into the 3.1 GPa filament.

Following this line of reasoning, it is evident that the DCP should be introduced into the filaments before it attains a high degree of crystallinity, i.e. prior to hot-drawing. Therefore, as-spun polyethylene fibres, which are highly porous, were swollen in solutions of DCP in n-hexane. Now, after swelling and drying, the fibre weight had increased due to the introduction of DCP. A plot of the amount of DCP in the fibre *versus* the concentration of DCP in the solution is shown in *Figure 1* and it is seen that as the amount of DCP in the solution is raised from 0 to 30 wt%, the weight percentage of peroxide in the filaments increases linearly from 0 to 50. This illustrates that, in comparison to the solution, there is an enrichment of DCP in the fibre, indicating a good compatibility between the polyethylene and the peroxide.

### *Crosslinking of DCP-containing polyethylene filaments*

Hot-drawing of DCP-containing as-spun porous fibres can be regarded as the deformation of a time-dependent entanglement network, during which vulcanization takes place. Since molecular mobility increases with temperature, high temperature conditions will favour the orientation process[18]. Furthermore, peroxide decomposition and concomitantly crosslinking is enhanced if the temperature is raised. All this suggests that the hot-drawing/crosslinking procedure should be conducted at high temperatures.

Smook *et al.*[9] reported that hot-drawing of polyethylene could not be conducted at temperatures exceeding 150°C. At 150°C the orthorhombic crystal lattice is transformened into a hexagonal one, in which the mobility of the polyethylene chains has increased strongly, resulting in easy slippage of chains and concomitant fibre failure[9]. However in the present case introduction of the crosslinks may to some extent prevent chain slippage and hot-drawing above 150°C may very well be possible.

DCP-containing filaments could actually be drawn above 150°C, although relatively low draw ratios were obtained, implying poor fibre tensile properties[1,2]. For example, at 160°C the maximum attainable draw ratio was 25 and at 200°C this parameter was equal to 10. These experiments indicate that the maximum draw ratio decreases with increasing temperature. It seems to us that these observations may be explained by the high rate of crosslinking at these extremely high temperatures. Too many crosslinks are introduced into the fibre in a rather short period of time, resulting in a random connectedness of the polyethylene chains and thus inhibiting chain alignment in the direction of the fibre axis during hot-drawing.

Therefore 150°C was chosen as the drawing temperature, since it was found to be the optimum drawing temperature for ultra-high molecular weight polyethylene with regard to the mechanical properties[9,18].

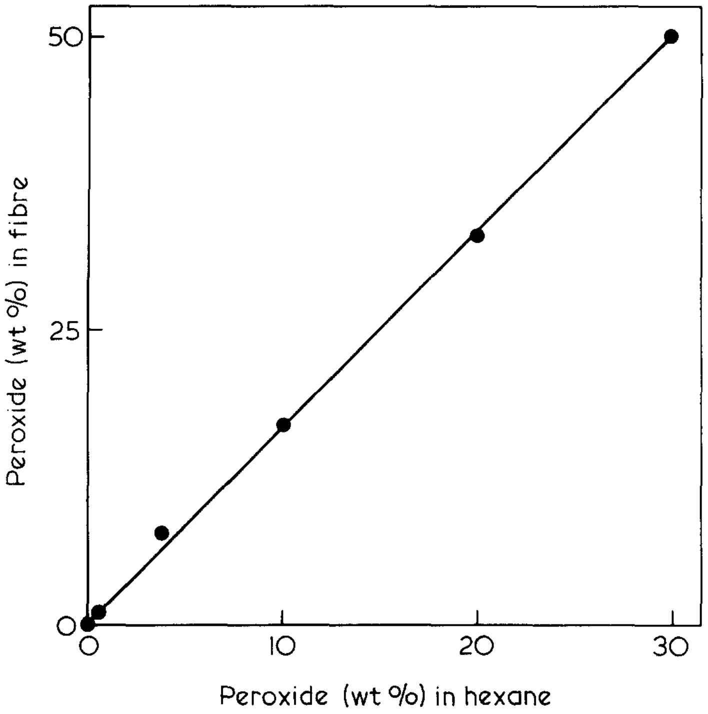

**Figure 1** Peroxide concentration in as-spun polyethylene fibres as a function of the DCP content of the swelling medium

The half-life[16] of the DCP at 150°C is about 20 min. The residence time of the fibre in the drawing tube during hot-drawing was estimated to be on average about 3 min. Accordingly the vulcanization reaction is not completed during hot-drawing. Therefore, subsequent to the hot-drawing, the fibres were annealed at 180°C for a period of time equal to five times the half-life of the DCP at 180°C To illustrate the effect of the annealing, we report that for a filament containing 50 wt% of DCP, annealing after hot-drawing increased the fibre gel content from 79 to 100%.

The results of the curing experiments are summarized in *Table 1*. It was found that, as the weight percentage of peroxide in the as-spun fibres increased from 1 to 50, the gel content of the final network increased from 16–100%. Starting from a DCP content of 17 wt%, curing always resulted in complete gelation. The observation that complete gelation can be attained implies that the possibility of chain fracture during crosslinking is excluded[19].

Upon extraction in boiling *p*-xylene the networks shrunk but the networks retained their fibre shape. The percentage shrinkage, defined as:

$$\frac{l_0-l}{l_0}\times 100 \tag{1}$$

where $l_0$ and $l$ are the fibre length prior to and after extraction respectively, was considered as a measure of the degree of crosslinking of the gels. Raising the fibre peroxide content from 1 to 50 wt%, the shrinkage was found to decrease from 93 to 59%, implying the production of more dense crosslinked networks as peroxide content increases.

In the range of peroxide contents used, it was observed that the maximum attainable draw ratio at 150°C decreased steadily from 105 to 65 with increasing DCP concentration, as is depicted in *Figure 2*. This decrement of the draw ratio was accompanied by a steady drop in fibre tenacity from 2.5 to 1.1 GPa, illustrated in *Figure 3*. The proportionality between draw ratio and fibre strength is in agreement with the work of Smook *et al.*[2] and confirms the idea that the establishment of a high degree of chain alignment in the direction of the filament axis, achieved during hot-drawing, is essential for producing high strength fibres[20]. The observation that vulcanization diminishes fibre drawability, a phenomenon also noticed by DeCandia *et al.*[21], can be understood if we realize that crosslinking increases the

**Table 1** Network characteristics of polyethylene fibres crosslinked with dicumylperoxide

| Amount of DCP in fibre (wt%) | Gel content (%) | Fibre shrinkage upon extraction (%) | $\lambda_{max}$[a] | Tensile strength at break (GPa) | $T_m$[b] (K) |
|---|---|---|---|---|---|
| – | – | – | 105 | 2.8 | 419 |
| 1 | 16 | 93 | 105 | 2.5 | 418 |
| 8 | 69 | 91 | 90 | 1.7 | 415 |
| 17 | 100 | 75 | 80 | 1.4 | 414 |
| 33 | 100 | 68 | 68 | 1.2 | 414 |
| 50 | 100 | 59 | 65 | 1.1 | 413 |

[a] $\lambda_{max}$ = maximum draw ratio at 150° C
[b] $T_m$ = peak melting temperature of unconstrained molten sample

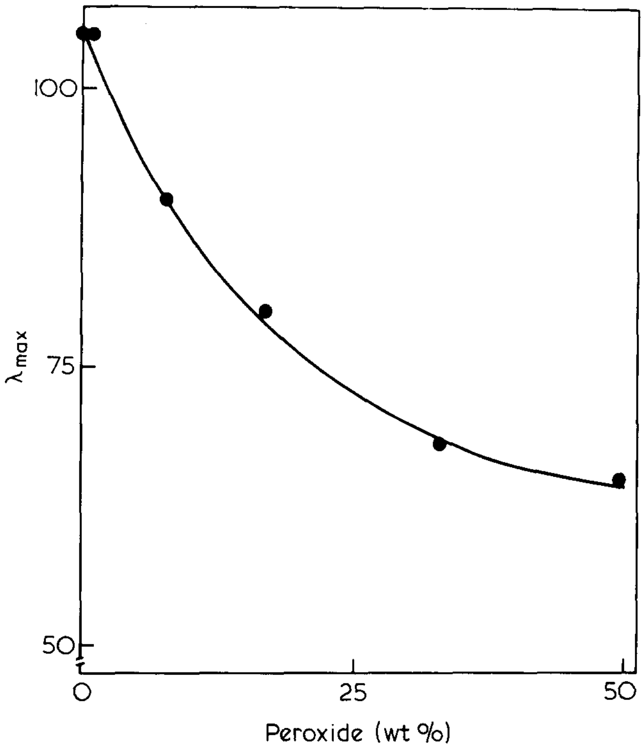

**Figure 2** Maximum attainable draw ratio at 150°C, $\lambda_{max}$, of DCP-containing as-spun polyethylene filaments *versus* peroxide content

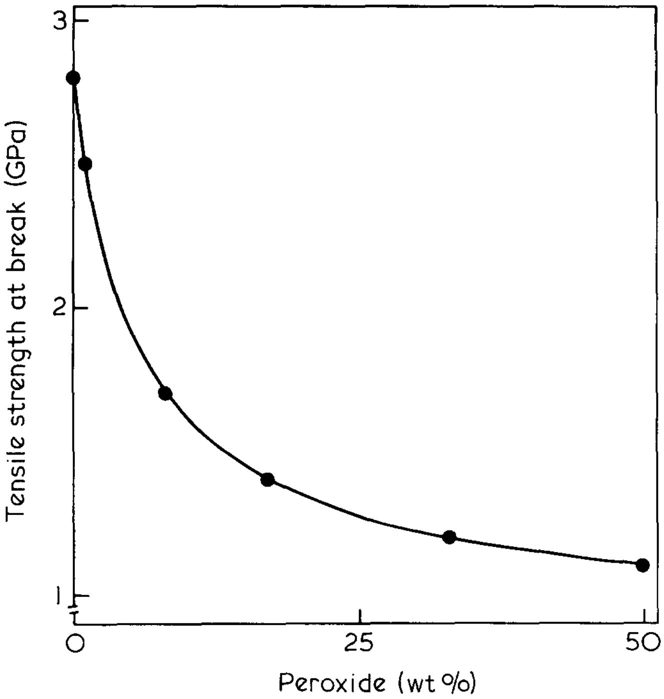

**Figure 3** Tensile strength at break *versus* peroxide concentration for filaments crosslinked with DCP

connectivity of the polyethylene molecules in the filaments and thus hampers chain movements during hot-drawing. This increased connectivity is illustrated by the SEM micrograph of *Figure 4*, which displays the fracture surface of a filament crosslinked with 50 wt% DCP. The fracture surface indicates brittle failure, and no fibrillation can be detected. Normally, non-crosslinked ultra-high strength polyethylene fibres fibrillate strongly upon breaking at room temperature[3,22]. So, we may conclude that crosslinking has connected the chains, thus preventing slippage of the polyethylene molecules past each other and concomitantly avoiding fibrillation upon failure. Finally, with regard to the decrement in fibre strength with increasing peroxide content, we wish to remark that each crosslink represents a stress concentration in the crystal lattice, and therefore introduction of crosslinks may also influence the tenacity of the crystalline fibres in an unfavourable way[23]. The reduced draw ratio is however thought to represent the main cause for the decrease in strength with increasing DCP content.

The idea that crosslinks act as stress concentrations in a crystal lattice is also reflected in the melting behaviour of the gels. Increasing the weight percentage of DCP from 1 to 50, the peak melting temperature of the networks decreases from 418 to 413K (see *Table 1*), and the degree of crystallinity dropped steadily from 70 to 40%, as is illustrated in *Figure 5*. The influence of crosslinking on the melting behaviour of a crystalline network has been extensively discussed in previous papers from our laboratory[24,25]. In the present case, however, we also have to consider the effect of chain contamination. An analysis by means of infra-red spectroscopy demonstrated the presence of a substantial amount of cumyloxy groups on the polyethylene chains after vulcanization. These bulky cumyloxy groups are also likely to hamper network crystallization, but their influence is believed to be low in comparison to the effect of crosslinks[24]. Furthermore, it needs mentioning also that the decrement in drawability with increasing DCP content (see *Figure 2*) may lead to a lower melting point and a lower crystalline content of the final fibre network.

Network characterization should also include determination of the amount of pendant chains, i.e. those chains connected with only one end to the gel, in the network. de Boer *et al.*[26] demonstrated by means of constrained melting of the fibre networks that the present

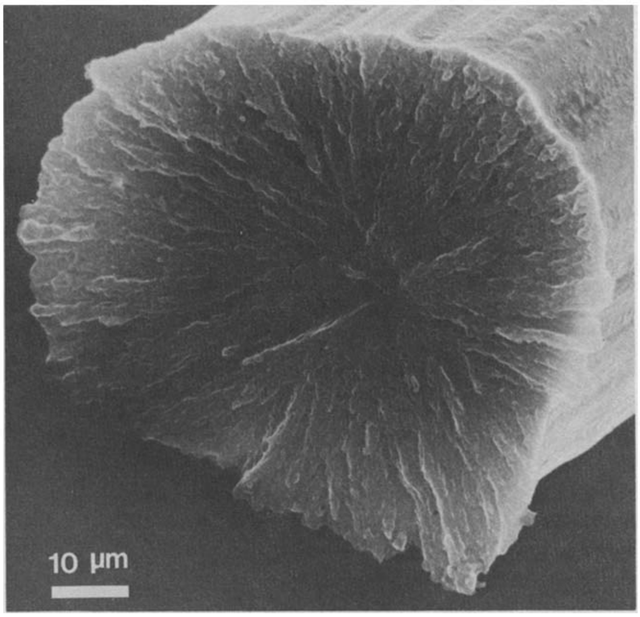

**Figure 4** *SEM* micrograph of a fracture surface obtained by breaking a fibre, crosslinked with 50 wt% of DCP, in a tensile test experiment at room temperature

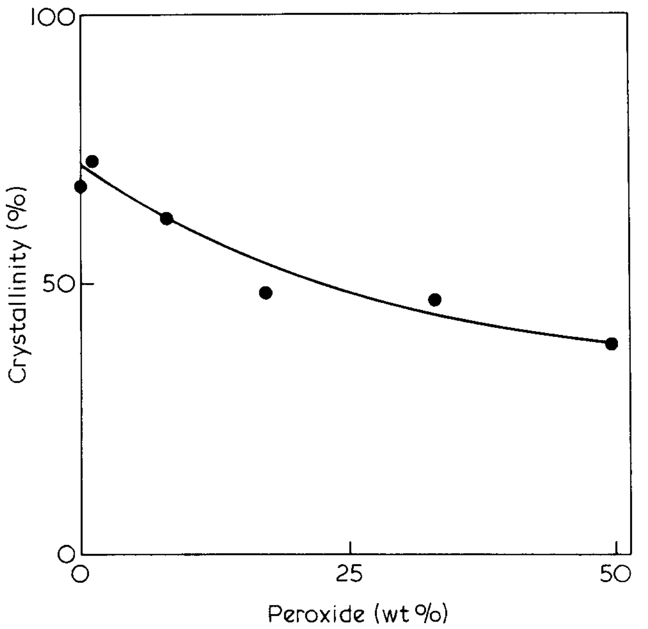

**Figure 5** Crystalline content calculated from heat of fusion *versus* peroxide concentration for filaments crosslinked with DCP

crosslinking technique renders networks with a low weight percentage of pendant chains.

*Force–strain behaviour of crosslinked filaments at 195°C*

For investigating the force–strain behaviour at elevated temperature, a fibre obtained by crosslinking an as-spun filament with 50 wt% DCP was clamped in a dynamometer, of which the technical details were previously reported[27]. Subsequently, the fibre was heated to 195°C in a nitrogen atmosphere. During heating the fibre shrunk. At 195°C the sample was continuously elongated at a constant rate of $2.1 \times 10^{-4}$ m s$^{-1}$ and the force was recorded as a function of the extension.

A typical rubberlike behaviour was observed[28], as is depicted in *Figure 6*. At a strain of 250% an onset of non-Gaussian behaviour was detected. This phenomenon may be attributed to both the limited chain extensibility of the network chains as well as the presence of a hexagonal crystal phase in highly oriented polyethylene above 150°C[4]. At an extension of 370% and a force of about 0.4 N, network failure occurred. It is quite interesting to note that the sample length at which fracture was observed was equal to the initial length of the sample prior to heating. This indicates a severe fixation of the chains in the fibre network and supports the idea that fibre drawability during hot-drawing is limited by the introduction of the crosslinks.

*High temperature resistance of crosslinked filaments*

To study the high temperature resistance of the crosslinked fibres, a fibre crosslinked with 50 wt% of DCP was kept under a constant force of 0.1 N at 195°C for 1 h under nitrogen conditions. Prior to heating the filament possessed a tensile strength at break of 1.1 GPa, a Young's modulus of 22 GPa and an elongation at break of 7% (*Figure 7*, curve A). After heating and subsequent cooling, the tenacity was now equal to 0.9 GPa, the Young's modulus was 14 GPa whereas an elongation at break of 11% was found (*Figure 7*, curve B).

These experiments show that there is only a slight drop in the tenacity due to the heating/cooling cycle. The change in modulus and elongation at break is however more significant, leading to the conclusion that due to the storage at 195°C some disorientation of the fibre chain has taken place, resulting in an overall decrease in the tensile properties of the filament. Nevertheless, we feel confident

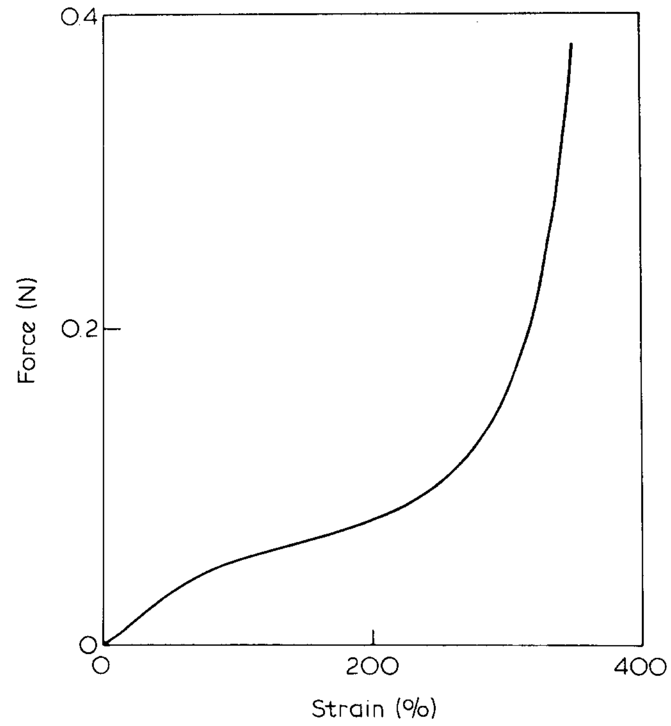

**Figure 6** Plot of the force *versus* the strain at 195°C, for a fibre crosslinked with 50 wt% of DCP

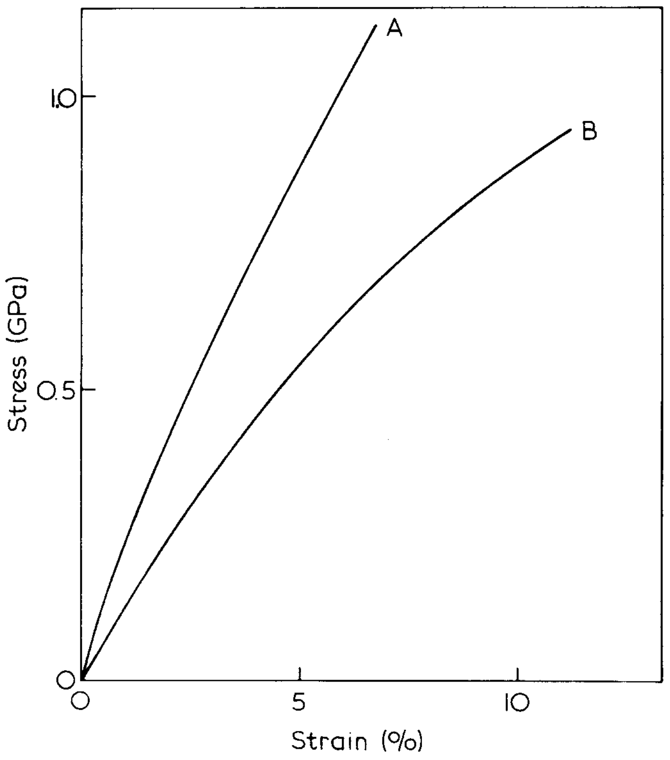

**Figure 7** Stress–strain curves obtained at room temperature from a fibre crosslinked with 50 wt% of DCP, prior to (curve A) and after (curve B) fibre storage for 1 h at 195°C

to state that during the heating/cooling procedure, the mechanical properties were well preserved. The extent of the improvement of the high temperature resistance of the filaments upon crosslinking is even more appreciated if we realize that non-crosslinked ultra-high strength polyethylene fibres cannot even exist at temperatures[3,4] as high as 195°C.

Finally, it is reported that crosslinking improved the lifetime behaviour of the high tenacity polyethylene fibres. Smook *et al.*[3] found that, with a comparable load, crosslinked fibres displayed a much higher time to failure than the non-crosslinked equivalent. A detailed discussion of this subject is however beyond the scope of the present paper, and is postponed to a future publication.

### *Hot-drawing followed by ultra-violet irradiation*

Earlier it was pointed out that the introduction of crosslinks hinders the drawing process and concomitantly reduces the fibre strength. It is evident that the rate of crosslinking can be diminished by lowering the drawing temperature. This favours the chain alignment, but reduces the fibre gel-content. Therefore, subsequent to hot-drawing, completion of the vulcanization process has to be realized. Instead of annealing, we now chose to continue the gelation process through ultra-violet irradiation of the DCP-containing drawn fibre. Ultra-violet radiation activates DCP[29,30], accordingly ultra-violet irradiation may result in a high rate of gelation as well as an increase of the crosslinking efficiency of the DCP.

At this point it is pertinent to mention the work of Norrish and Searby[29], who found that DCP radicals, resulting from ultra-violet photolysis of DCP molecules, are able to abstract hydrogen from compounds such as hexane at temperatures as low as 20°C. Accordingly, hydrogen abstraction from polyethylene by the DCP radicals is very unlikely to become a rate determining step in the proposed vulcanization process.

Hot-drawing followed by ultra-violet irradiation was performed in the following way. An as-spun fibre, containing 17 wt% of DCP, was hot drawn at 130°C up to its maximum draw ratio of 80. At 130°C the peroxide decomposition rate is low[16] and hot-drawing will mainly result in the transformation of lamellae into chain extended crystallites, the hot-drawing process not being hindered by the introduction of a large amount of crosslinks. After hot-drawing, extraction experiments showed that no gel was obtained. However, when an ultra-violet source was placed between the end of the drawing tube and the wind-up drum, a fibre network with a gel content of 64% and a tenacity of 1.8 GPa was produced, i.e. a drastic improvement of the crosslinking efficiency of the DCP was achieved.

The experiments indicate that a combination of hot-drawing at a relatively low temperature followed by ultra-violet irradiation can result in strong, partially gelated filaments. In this way vulcanization is largely postponed until after the hot-drawing process, thus promoting the chain alignment.

It may be clear that in order further to understand and optimize this promising technique, a more extensive set of experiments is needed. Increasing the intensity of the ultra-violet source may, for example, raise the gel content of the fibres, whereas variation of the drawing temperature may lead to even higher filament strengths. In this respect one may also consider the use of benzophenone[31] as an ultra-violet sensitizer for the gelation process.

## CONCLUSIONS

In conclusion we have shown that ultra-high molecular weight polyethylene can be crosslinked in the oriented state with dicumylperoxide. Densely crosslinked fibre networks with a strength of about 1.1 GPa and containing no sol fraction were synthesized. In sharp contrast to non-crosslinked ultra-high strength polyethylene fibres, crosslinked filaments displayed a non-fibrillating fracture surface and a good resistance towards high temperatures. It was concluded that, in order to pair high filament strength to extensive gelation, the fixation of the polyethylene chains by means of crosslinks should be postponed until the polyethylene molecules already possess a high degree of orientation. This may be realized by a combination of drawing at a relatively low temperature and subsequent ultra-violet irradiation of the peroxide-containing filaments.

We are well aware that more experiments are essential for exploring the presented crosslinking technique in greater detail. Moreover, the obtained networks may be of scientific interest with regard to studies of rubberlike elasticity and oriented crystallization. It is our intention to conduct such investigations in the near future.

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