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Influence of chemical crosslinking on the creep behavior of ultra-high molecular weight polyethylene fibers

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Abstract: In this study, the effect of chemical crosslinking on the creep behavior of high-strength fibers, obtained by gel-spinning and subsequent hot-drawing of ultra-high molecular weight polyethylene (UHMWPE), is examined. In the first part of the paper, the general aspects of the creep behavior of these fibers are discussed. The second part deals with UHMWPE fibers that are crosslinked by means of a) chlorosulfonation and b) dicumyl peroxide treatment followed by UV irradiation. The latter technique leads to an improvement of the creep resistance of the UHMWPE fibers without affecting their high tensile strengths. In spite of the fact that the network formation is fairly high, the creep cannot be completely removed. The results indicate that the creep process in UHMWPE fibers is associated with a deformation mechanism in the crystalline regions of the fiber, which are not affected by chemical crosslinking.

Key words: Creep – UHMWPE fibers – solution-spinning – crosslinking – chlorosulfonation – dicumylperoxide – UV-irradiation

1. Introduction

Over the past decades, a variety of techniques has been developed in order to produce high-modulus fibers from linear polyethylenes. These methods include solid state extrusion [1], hydrostatic extrusion [2], flow-induced crystallization [3], gel-spinning followed by hot-drawing [4], drawing of single-crystal mats [5], drawing of "virgin" polyethylene [6] and swell-drawing [7]. The highly oriented polyethylene fibers that are obtained in this way offer a combination of a very high stiffness and strength [8] and a low specific gravity, which makes these materials particularly suitable for application in fiber-reinforced composites. The low creep resistance of polyethylene is, however, a disadvantageous property in this respect. In the present study, we wish to discuss some general aspects of the creep behavior of high-modulus fibers, obtained by gel-spinning and subsequent hot-drawing of ultra-high molecular weight polyethylene (UHMWPE), and to investigate the possibilities of improving the creep resistance of these fibers.

The creep behavior of high-modulus polyethylene fibers has been studied in detail by Ward and coworkers [9–13]. The results of these studies indicate that the creep behavior of polyethylene fibers depends strongly on molecular weight and polymer composition, as well as on structural factors which are mainly controlled by the fiber draw ratio. On the basis of their results, Wilding and Ward [10, 12] proposed a model which adequately describes the experimentally observed creep behavior of high-modulus polyethylene fibers, and, in particular, the dependence of the creep rate on the applied stress. This model also allows an interpretation of the creep process in terms of structural parameters. Another interesting result of these studies is that solution-spun fibers show a very different creep behavior from

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melt-spun and drawn fibers, which may be related to the fundamental differences in structure between the two kinds of high-modulus polyethylene [12].

It is well-known that the creep behavior of polymeric materials may be improved by means of crosslinking. Crosslinking of polyethylene is usually achieved by means of γ-irradiation [14, 15] or by vulcanization using organic peroxides [16]. Other methods include photochemical crosslinking [17, 18] and oxidative crosslinking by means of chemical reagents such as chlorosulfonic acid and sulfuric acid [19]. Treatment of UHMWPE according to these methods may, however, give rise to several side reactions, including main-chain scission, which has an adverse effect on the mechanical properties of the fiber. It is known, for instance, that γ-irradiation of highly oriented UHMWPE fibers is accompanied by a considerable amount of chain scissioning, which leads to a decrease of the fiber strength and to an increase of the creep rate [13, 20, 21]. Crosslinking by means of organic peroxides, on the other hand, has been shown to occur without main-chain scission [16, 22], and this method may therefore provide a route to improvement of the creep resistance of UHMWPE fibers without sacrificing their high tensile strengths. A preliminary experiment by de Boer et al. [23] showed that high-strength UHMWPE fiber networks would be obtained by peroxide treatment followed by ultra-violet (UV) irradiation of the drawn filaments.

In the present study, the possibilities of improving creep resistance of gel-spun/hot-drawn UHMWPE fibers by means of chemical crosslinking will be discussed. The general aspects of the creep behavior of these fibers will be discussed first, in relation to the effects of the preparation history and fiber structure. Subsequently, the crosslinking of hot-drawn UHMWPE by means of chlorosulfonic acid and dicumylperoxide will be described. It will be shown that treatment of gel-spun/hot-drawn UHMWPE fibers with dicumyl peroxide followed by UV-irradiation leads to an effective network formation and a reduction of the creep rate under constant load, without a reduction of the initial tensile strength of fiber. The oxidative treatment of UHMWPE fibers using chlorosulfonic acid also leads to a considerable improvement of the creep resistance, but this is accompanied by a loss of tensile strength.

2. Experimental

Fiber preparation

The UHMWPE fibers used in this study were prepared according to the following procedure. Linear polyethylene (Hifax 1900 by Hercules) with $M_n = 2.5 \cdot 10^6$ kg/kmol and $M_w = 5.5 \cdot 10^6$ kg/kmol was dissolved in paraffin oil, containing 0.5 wt% anti-oxidant (Ionol; 2,6-di-*t*-butyl-4-methylephenol), by rapid mechanical stirring at 135 °C. A polymer concentration of 1.5 wt% was used throughout the experiments, unless stated otherwise. The solution was allowed to stand at 150 °C for 48 h under a nitrogen atmosphere. The polyethylene gel, formed upon slow cooling of the solution, was transferred to a piston-cylinder apparatus and kept at 190 °C for 3 h. The solution was subsequently spun at this temperature using a single tapered spinneret hole with a 1-mm exit diameter at a fiber exit velocity of 1 m/min and collected at the same speed by means of a take-up device. The solvent was removed from the gel-fibers by extraction with *n*-hexane and subsequent drying at 50 °C under vacuum with fixed ends. The as-spun fibers were stretched in an electric oven at 148 °C between two spools located outside the oven. A feed velocity of 6.25 mm/min was employed in each drawing, and the draw ratio was varied via the speed of the take-up device.

Crosslinking of the monofilaments

Chlorosulfonation of both as-spun and hot-drawn fibers was carried out by immersing the fibers, in an unconstrained fashion, in 25% (v/v) solutions of p.a. chlorosulfonic acid (HSO_3Cl) in p.a. dichloroethane at 45 °C for different periods of time. The fibers were washed for 20 min with p.a. chloroform and p.a. acetone, respectively, and subsequently dried for 1 h at 50 °C under vacuum.

For peroxide crosslinking experiments, the hot-drawn fibers were wound loosely onto glass frames, which were then immersed in a 12 wt% solution of dicumylperoxide ($[C_6H_5C(CH_3)_2]_2O_2$) in p.a. cyclohexane at 60 °C for 120 to 135 h. Dicumylperoxide was recrystallized from methanol prior to use. After immersion in the peroxide solution, the fiber was dried in air and placed in a quartz tube through which a moderate nitrogen flow could be maintained. Crosslinking was brought

about by irradiation with UV-light. To this end, the quartz tube was placed in a Rayonet RPR-100 photochemical reactor, equipped with 16 low pressure mercury lamps, producing UV-radiation with a wavelength of 253.7 nm. The temperature in the reactor was kept constant at 50 °C. The fibers were in this way exposed to UV-radiation for different periods of time, varying from 0 to 150 h.

Fiber characterization

Tensile tests were performed using an Instron 4301 tensile tester, equipped with pneumatic action grips. Digitized stress-strain data were collected at a speed of 20 pts/s and analyzed using the Instron Series IX Materials Testing program. The fibers were tested at a gauge length of 50 mm, using a cross-head speed of 25 mm/min. The filament diameter was determined from the weight of a piece of fiber of known length, assuming a fiber density of 1000 kg/m^3. For creep experiments, a dead weight was attached to the lower end of a vertically mounted fiber sample of approximately 10 cm in length, and the strain was measured as a function of time using a linear displacement transducer coupled with an x-*t*-recorder. In this way, the strain could be measured with a 0.02% accuracy. A dead-load corresponding to 50% of the breaking load (as determined during tensile testing) was used throughout the experiments, unless mentioned otherwise.

Gel-fractions of the crosslinked fibers were determined by means of extraction in boiling *p*-xylene (138 °C) for 24 h. Anti-oxidant (Ionol) was added to the extraction solvent at a concentration of 0.5 wt% in order to prevent oxidative degradation. The extracted fibers were de-swollen in acetone for 15 h and dried under vacuum at 50 °C for 24 h. The gel-fraction was calculated from the weight of the fiber before and after extraction.

Scanning electron microscopy was performed on gold-covered samples, using an ISI-DS 130 microscope, operating at 40 kV.

3. Results and discussion

3.1 General aspects of the creep behavior of solution-spun UHMWPE fibers

In order to study the creep behavior of gel-spun/hot-drawn UHMWPE fibers, a number of fibers having draw ratios ranging from $\lambda = 20$ to $\lambda = 150$ have been prepared from 1.5 wt% spinning solutions. Creep curves were obtained by applying a dead weight to the fiber, corresponding to 50% of the breaking load as measured in a conventional tensile test, and monitoring the strain as a function of time. A typical creep curve obtained in this way is given in Fig. 1 for a fiber having a draw ratio of $\lambda = 60$. Three stages of deformation are observed: primary creep (Regime I) where the creep rate decreases, secondary creep (Regime II) characterized by a constant creep rate, and tertiary creep (Regime III) where the creep rate accelerates until fiber failure occurs. In Fig. 1, the accelerated process is only partially shown, and for a typical UHMWPE fiber, this regime extends up to $t \approx 40 \cdot 10^3$ s and strains of $\varepsilon \approx 35\%$, where failure occurs. The creep strain at break of $\varepsilon = 35\%$ is very high, taking into account that the fibers fail at strains of about 3–4% in a conventional tensile test. The main part of the total creep deformation takes place in the accelerated regime of the creep process, and it has been shown [9, 10] that deformation in this regime is almost completely irreversible.

It is well-known [9, 10, 24] that the creep behavior of high-modulus polyethylene fibers is very sensitive towards the applied stress. The typical three-stage creep behavior, however, is observed over a wide range of stresses. It is therefore convenient to express the creep behavior in terms of

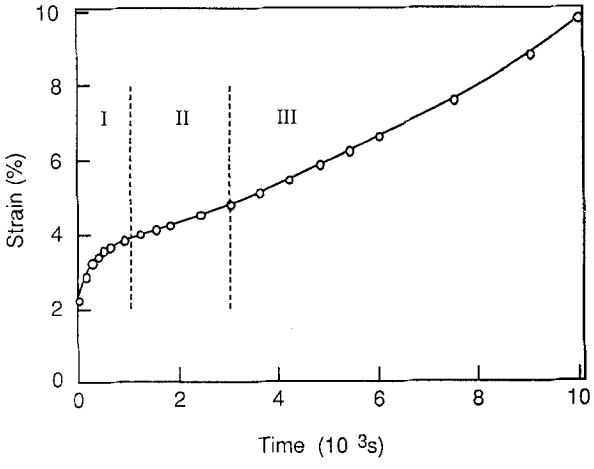

Fig. 1. Typical creep curve of an UHMWPE fiber ($\lambda = 60$) having a tensile strength of 3.8 GPa, at an applied stress of 1.9 GPa

the constant deformation rate occurring in Regime II, the so-called plateau creep rate $\dot{\varepsilon}_p$. The stress-dependence of the plateau creep rate can be evaluated in terms of the Eyring equation of flow [25]

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp\left(-\frac{\Delta H}{kT}\right) \sinh\left(\frac{\sigma v}{kT}\right), \quad (1)$$

where ΔH and v are the activation energy and the activation volume, respectively, and $\dot{\varepsilon}_0$ is a pre-exponential factor. At high stress σ, where the back-flow term can be neglected, this equation reduces to

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp\left(-\frac{(\Delta H - \sigma v)}{kT}\right). \quad (2)$$

On the basis of this equation, a linear logarithmic dependence of $\dot{\varepsilon}_p$ on applied stress σ is expected. In Fig. 2, the dependence of the constant creep rate $\dot{\varepsilon}_p$ on the applied stress is shown for an UHMWPE fiber with $\lambda = 100$ (data from Ref. [24]). At high stresses ($\sigma > 1.5$ GPa), a linear relation between log ($\dot{\varepsilon}_p$) and σ, as predicted by Eq. (2), is indeed observed. However, it is seen that at low stress-levels the plateau creep rate falls with decreasing stress more rapidly that this linear relation would imply. This behavior has also been observed by Ward et al. [12] for melt-spun and drawn polyethylene fibers, and a satisfactory representation is given by the superposition of two thermally activated processes that are acting in parallel. It is assumed that one process (process 1) has a relatively large activation volume v_1, whereas the second process (process 2) has a smaller activation volume v_2. This representation can be expressed by the equation

$$\sigma = \frac{kT}{v_1}\left[\ln \dot{\varepsilon}_p - \ln\left(\frac{\dot{\varepsilon}_0}{2}\right)_1\right] + \frac{kT}{v_2} \sinh^{-1}\left[\frac{\dot{\varepsilon}_p}{(\dot{\varepsilon}_0)_2}\right]. \quad (3)$$

The subscripts 1 and 2 refer to process 1 and 2, respectively, and the pre-exponential factors $(\dot{\varepsilon}_0)_1$ and $(\dot{\varepsilon}_0)_2$ include the temperature-dependent $\exp(\Delta H/kT)$ terms. It has been suggested that the process 2 with the smaller activation volume relates to a deformation process in the crystalline regions of the fiber, whereas process 1 is associated with the (transient) molecular network.

Typical values for v_1 and v_2 obtained by Ward et al. by fitting the creep data of high-modulus melt-spun and drawn polyethylene fibers to this equation are $v_1 \approx 500$ Å^3 and $v_2 \approx 100$ Å^3, respectively [12]. By fitting the creep data presented in Fig. 2 to the two-process model, one finds $v_1 = 30$ Å^3 and $v_2 = 15$ Å^3 for the gel-spun/hot-drawn UHMWPE fiber. The values are very small as compared with the results of Ward et al. for melt-spun and drawn polyethylene. This indicates that the activated events are very localized, which is consistent with the high degree of crystal continuity in hot-drawn UHMWPE fibers. The results presented here are in line with the findings of Ward et al. concerning the creep behavior of solution-spun fibers, and confirm the idea that the structure of these fibers differs fundamentally from that of melt-spun and drawn polyethylene.

In the gel-spinning/hot-drawing process of UHMWPE, the draw ratio is one of the key parameters with respect to the mechanical properties of the resulting fibers. In order to investigate the effect of draw ratio on the creep behavior of gel-spun UHMWPE fibers, the plateau creep rate was determined for a number of fibers having draw ratios in the range $\lambda = 20$–150. Since the mechanical properties of the fiber drastically improve with increasing draw ratio, all creep

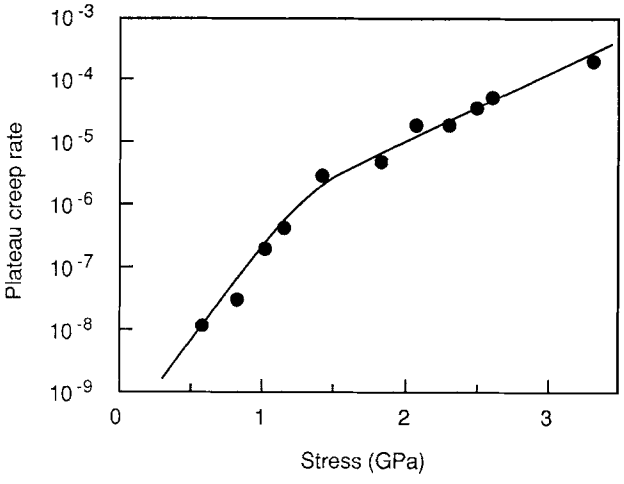

Fig. 2. Dependence of the plateau creep rate (s^{-1}) on the applied stress for an UHMWPE fiber with $\lambda = 100$ (data from Ref [24]. The solid line was calculated according to Eq. (3) using $(\dot{\varepsilon}_0)_1 = 3.4 \cdot 10^{-10}\,s^{-1}$; $(\dot{\varepsilon}_0)_2 = 3.0 \cdot 10^{-6}\,s^{-1}$; $v_1 = 30$ Å^3 and $v_2 = 15$ Å^3

measurements were performed at a stress-level corresponding to approximately 50% of the breaking stress determined in tensile testing (see Table 1). Thus, the creep data obtained provide a measure of the creep resistance of the fiber relative to its overall mechanical behavior. The results are presented in Fig. 3, which shows that there is a great improvement of the relative creep resistance of UHMWPE fibers upon hot-drawing. The plateau creep rate decreases from approximately $5 \cdot 10^5 s^{-1}$ at $\lambda = 20$ to a nearly constant value of $3 \cdot 10^{-6} s^{-1}$ for draw ratios above $\lambda = 120$, i.e., an improvement by a factor 15. The improvement of the creep resistance is most pronounced at low draw ratios ($\lambda \leq 40$) and levels off at higher values of λ. It is assumed [26, 27] that during the initial stage of the drawing process, the polymer chains are gradually pulled taut between entanglement junctions that constitute the macromolecular network. Further drawing is accomplished by chain slippage, which removes topological defects and leads to an improvement of the crystal perfection. It is therefore conceivable that the relatively fast creep process in moderately drawn fibers involves the deformation of chains that are not fully stretched between entanglements. In fibers with higher draw ratios, the creep process appears to be governed by very localized events, and the gradual decrease of the creep rate at higher draw ratios is most likely related to the improvement of the crystalline phase of the fiber. Thus, there is an equivalence between drawing and creep in that both processes reflect the state of the entanglement network.

So far, we have discussed the creep properties of UHMWPE fibers prepared from 1.5 wt% spinning solutions. At this point, it seems interesting to investigate the effects of the concentration of polymer in the solution from which the fibers are spun, since this parameter is known to have

Table 1. Mechanical properties and creep behavior of UHMWPE fibers with various draw ratios

Draw ratio	Strength (GPa)	Modulus (GPa)	Creep stress (GPa)	Plateau creep rate (s^{-1})
20	1.70	30	0.88	$4.8 \cdot 10^{-5}$
30	2.07	59	1.06	$1.0 \cdot 10^{-5}$
40	2.96	89	1.51	$1.4 \cdot 10^{-5}$
50	3.77	120	1.92	$1.3 \cdot 10^{-5}$
60	3.84	129	1.90	$6.7 \cdot 10^{-6}$
80	4.31	162	2.30	$6.3 \cdot 10^{-6}$
100 [a])	3.97	163	1.99	$3.9 \cdot 10^{-6}$
120 [a])	4.50	194	2.25	$3.1 \cdot 10^{-6}$
150 [a])	4.34	180	2.17	$2.9 \cdot 10^{-6}$

[a]) Fibers prepared in a two-step drawing process

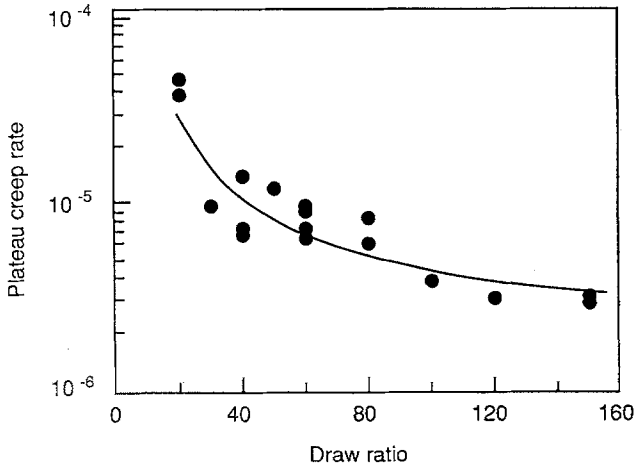

Fig. 3. Influence of the draw ratio on the creep rate (s^{-1}) for an UHMWPE fiber prepared from a 1.5 wt% spinning solution. All creep measurements were performed at an applied stress corresponding to 50% of the breaking stress as determined in tensile testing

a significant effect on the deformation behavior of solution-spun fibers [28–30]. These effects are usually explained in terms of chain entanglements, which are present in the semi-dilute spinning solution and are transferred into the solid state upon crystallization [29, 31]. A high entanglement density in the solidified polymer impedes large deformations, which explains the well-known phenomenon that fibers spun from more concentrated solutions exhibit a reduced drawability. From this point of view, it is conceivable that the state of entanglements in the solid polymer also has an effect on its creep behavior.

In order to investigate these effects, a number of fibers was prepared by spinning from solutions containing 1.5 wt%, 3.0 wt%, and 5.0 wt% UHMWPE and subsequent drawing to a ratio of $\lambda = 35$. The mechanical properties of these fibers are summarized in Table 2. It follows from these data that the short-term mechanical behavior of UHMWPE fibers, at a given draw ratio, is hardly affected by the concentration of the spinning from which they are produced. A similar result was obtained recently by Bastiaansen [32]. The creep properties of these fibers were determined at a stress-level of 1.50 GPa, which corresponds to 50% of their breaking stress. The relevant creep data are collected in Table 2, and the plateau creep rate $\dot{\varepsilon}_p$ is plotted as a function of the spinning concentration in Fig. 4. These data show very clearly that there is a pronounced effect of spinning concentration on the creep properties of gel-spun/hot-drawn UHMWPE fibers. First of all, the plateau creep rate decreases from $5.4 \cdot 10^{-6}\,s^{-1}$ to $8.2 \cdot 10^{-7}\,s^{-1}$ when the spinning concentration is increased from 1.5 wt% to 5.0 wt%. Furthermore, the creep strain at break is lower for fibers spun from more concentrated solution, indicating that the fiber structure containing a higher concentration of entanglements is less deformable, even at the time-scale of the creep experiment. It should also be noted that the fiber spun from a 5.0 wt% solution can sustain the applied stress over a much longer period of time than fibers obtained from more dilute solutions. The results emphasize the importance of the entanglement network with respect to the creep behavior of solution spun UHMWPE fibers. In this sense, there is a similarity between the effects of draw ratio and spinning concentration on the creep properties. Since an increase of the spinning concentration leads to a reduction of the maximum draw ratio, the fiber obtained from a 5 wt% solution is, at the given draw ratio of $\lambda = 35$, much closer to its maximum draw ratio than fibers obtained from more dilute solutions.

3.2 Improvement of the creep properties of UHMWPE fibers by means of crosslinking

In this section, the effect of crosslinking on the crosslinking on the creep behavior of solution-spun UHMWPE fibers will be discussed. As

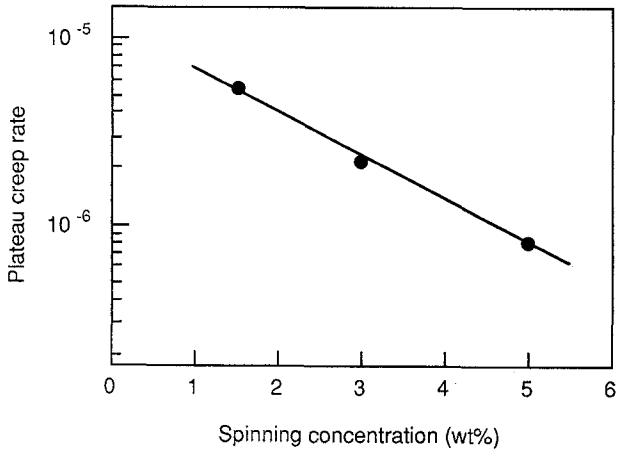

Fig. 4. Effect of the spinning concentration on the plateau creep rate (s^{-1}) of UHMWPE fibers with $\lambda = 35$. Applied stress 1.50 GPa

Table 2. Mechanical properties and creep data of UHMWPE fibers with a draw ratio of $\lambda = 35$, spun from different spinning solutions. The creep data were determined at an applied stress of 1.50 GPa.

Spinning concentration (wt%)	Strength (GPa)	Modulus (GPa)	Plateau creep rate (s^{-1})	Creep strain at break (%)	Time to failure (10^3 s)
1.5	3.01	113	$5.4 \cdot 10^{-6}$	36	38
3.0	3.04	100	$2.2 \cdot 10^{-6}$	28	40
5.0	2.95	110	$8.2 \cdot 10^{-7}$	21	200

pointed out above, crosslinking of these fibers by means of irradiation with high-energy electrons is accompanied by substantial main-chain scissioning, and it has been established that this technique leads to a reduction of both tensile strength and creep resistance [13, 20, 21]. Crosslinking by means of chemical agents, however, might provide an improved route to creep-resistant UHMWPE fibers, since the problem of main-chain degradation may be avoided in this way. It is important, however, that the crosslinking agent is thoroughly mixed with the filament so as to achieve a sufficient crosslink density. The hot-drawn fibers used in this study possess a highly crystalline structure, which is rather inaccessible to chemical substances, and a homogeneous mixing with the crosslinking agent is difficult to achieve. In general, two approaches can be adopted to overcome these problems. The fiber can be treated with the crosslinking agent prior to drawing, when a highly crystalline fiber structure has not yet developed and the fiber is more accessible to chemical substances. Alternatively, the crosslinking treatment can be carried out using hot-drawn fibers in the presence of a swelling agent, so as to increase the permeability of the fiber structure [33]. It should be kept in mind that crosslinks formed prior to drawing might impede the formation of a highly oriented structure and, in this way, limit the maximum strength of the fiber after hot-drawing [23], which evidently restricts the usefulness of this method. In this study, various possibilities for the crosslinking of UHMWPE fibers are investigated, using chlorosulfonic acid and dicumylperoxide crosslinking agents.

Chlorosulfonation: All chlorosulfonation experiments were carried out at 45 °C in a 25% solution of chlorosulfonic acid in dichloroethane, which acts as a swelling agent for polyethylene. In order to examine the effects of chlorosulfonation, two different UHMWPE fibers, both obtained from a 1.5 wt% spinning solution and referred to as Fiber A and Fiber B, respectively, were used. Fiber A was prepared by hot-drawing of the untreated as-spun fiber to a ratio of $\lambda = 40$. Fiber B was obtained by treating the as-spun fiber with chlorosulfonic acid for 10 min and subsequent hot-drawing to $\lambda = 40$. The maximum draw ratio of the as-spun fiber reduced from $\lambda_{max} = 80$ to $\lambda_{max} = 40$ after this short chlorosulfonation treatment, indicating that the crosslinking reaction is quite effective in the undrawn material.

In Fig. 5, the effect of chlorosulfonation on the plateau creep rate is shown for the two different fibers. It is seen that, in the case of Fiber A, chlorosulfonation does not lead to an improvement of the creep properties of the fiber. This is probably related to the poor accessibility of the hot-drawn fiber. The weight increase of Fiber A after prolonged treatment ($t \geq 140$ h) was about 8%, indicating that the extent of the reaction is very small, even in the presence of the swelling agent. In the case of Fiber B, however, a more pronounced effect of the chlorosulfonation treatment is observed. It is seen that there is an initial decrease of the creep rate from $\dot{\varepsilon}_p = 6.0 \cdot 10^{-6}\,s^{-1}$ to $\dot{\varepsilon}_p = 2.2 \cdot 10^{-6}\,s^{-1}$ as a result of the chlorosulfonation prior to hot-drawing. Upon further treatment of Fiber B, an additional decrease to $\dot{\varepsilon}_p = 3.8 \cdot 10^{-7}\,s^{-1}$ is observed, which corresponds

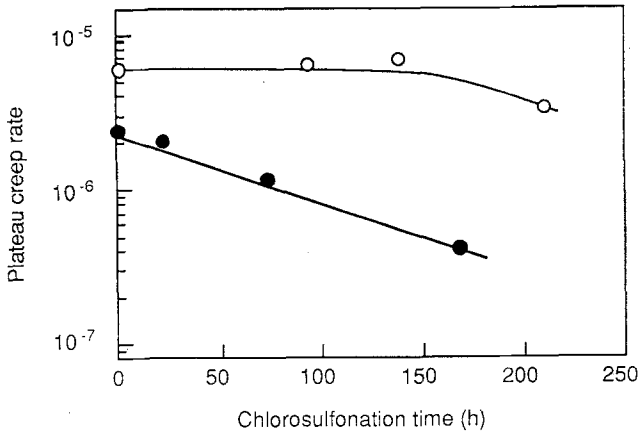

Fig. 5. Effect of chlorosulfonation on the creep rate (s^{-1}) of two different UHMWPE fibers; (○) fiber with $\lambda = 40$ (Fiber A) and (●) fiber with $\lambda = 40$, treated for 10 min with chlorosulfonic acid prior to drawing (Fiber B).

to an improvement of the creep resistance by a factor 16 with respect to Fiber A. The maximum weight increase for Fiber B was approximately 40%. The tensile strength data of Fibers A and B treated for different periods of time are collected in Fig. 6, which shows very clearly that the chlorosulfonation treatment is accompanied by an undesirable loss of fiber strength. These effects are more pronounced for Fiber B, where the chlorosulfonation reaction was found to take place more effectively, due to the additional treatment prior to drawing. Figure 7 shows the surface of Fiber B, treated for 170 h with chlorosulfonic acid. Apparently, the loss of tensile strength upon chlorosulfonation under the reaction conditions employed here cannot be accounted for in terms of environmental stress-cracking phenomena, which have been observed previously [34]. The decrease in tensile strength may rather be related to a more brittle fracture behavior resulting from the chemical modification of the polymer taking place upon chlorosulfonation.

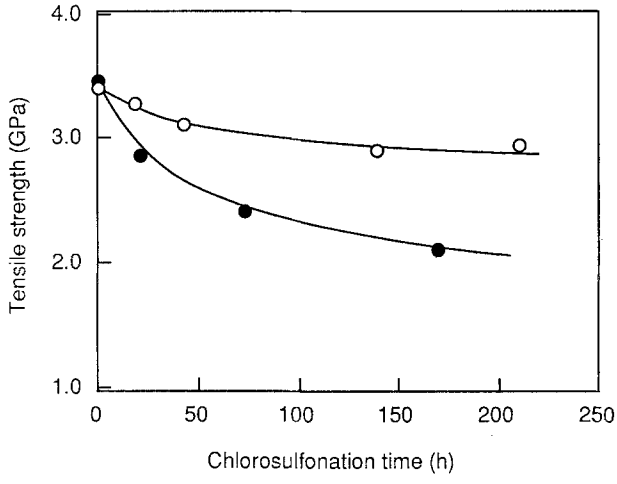

Fig. 6. Effect of chlorosulfonation on the tensile strength for Fiber A (○) and Fiber B (●)

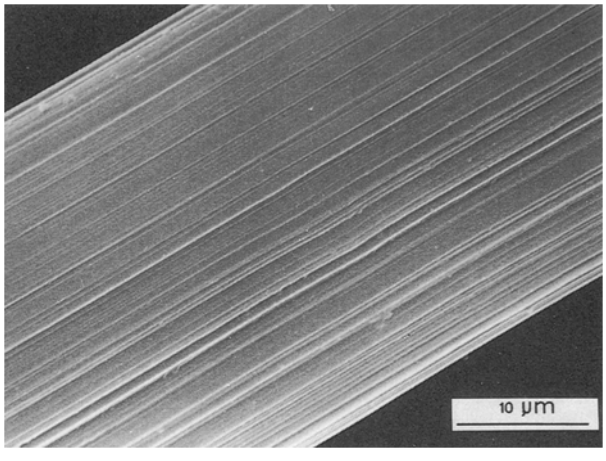

Fig. 7. Scanning electron micrograph of the surface of Fiber B after chlorosulfonation treatment for 170 h

Peroxide crosslinking: Crosslinking of polyethylene by means of organic peroxides has been found to occur without main-chain scissioning [16, 22]. Therefore, the use of peroxides may provide an improved route to crosslinked, high-strength fibers as compared with γ-irradiation and chlorosulfonation where crosslinking is accompanied by a reduction of tensile strength. The crosslinking of UHMWPE in the oriented state by means of dicumylperoxide (DCP) has been studied in detail by de Boer et al. [23] and by Matsuo and Sawatari [35]. In these experiments, the peroxide was introduced into the fiber prior to drawing in order to obtain a high content of the crosslinking agent in the polymer. De Boer found that decomposition of DCP during hot-drawing at 150 °C drastically reduced the drawability of the material, resulting in fibers with rather poor tensile properties. These effects can be suppressed by drawing at a lower temperature, but this also leads to a reduction of the maximum draw ratio and, more importantly, less effective curing of the fiber. In the context of the objectives of the present study, i.e., to obtain high-strength and creep resistant UHMWPE fibers by means of chemical crosslinking, it seems appropriate to extend de Boer's and Matsuo's experiments by using hot-drawn fibers for peroxide crosslinking experiments.

A fiber with $\lambda = 60$, having an initial strength and Young's modulus of 3.8 GPa and 129 GPa respectively (see Table 1), was used for the crosslinking experiments. The peroxide was mixed with the fiber by immersion for 120 to 135 h at 60 °C in a 12% solution of DCP in cyclohexane, which acts as a swelling agent for polyethylene. Subsequent network formation was brought about by UV-irradiation at 50 °C for different periods of time. Norrish and Searby [36] found that DCP radicals, formed by UV-photolysis of DCP, are able to abstract a proton from hydrocarbons at temperatures as low as 20 °C. This method

therefore avoids the use of an additional high-temperature treatment, which is required to bring about thermal decomposition of DCP. Annealing of the drawn filament at high temperatures has been shown to lead to a decrease of the Young's modulus of the fiber [23, 37] due to a partial disorientation of the fiber structure.

The network formation resulting from UV-irradiation of DCP-treated UHMWPE fibers is illustrated in Fig. 8, where the gel-content of the fiber is plotted as a function of the irradiation time. It is seen that a negligible amount of crosslinking has taken place as a result of the DCP treatment prior to irradiation (initial gel-content 2.0%). An effective network formation takes place initially upon irradiation, but the gel-content levels off at a value of about 80% after prolonged exposure. In this context, it is pertinent to mention that the peroxide crosslinking technique applied by de Boer resulted in fiber networks with a gel-content up to 100%. This difference may be due to main-chain scission arising from the exposure of the fiber to UV radiation. Analysis of the sol-gel data in terms of the Charlesby–Pinner equation [38] may help to elaborate on this point. For photoprocesses this equation can be written [17].

$$s + s^{1/2} = \frac{G(s)}{2\,G(x)} + \frac{1}{G(x)\,M_w\,I_a}, \qquad (4)$$

where s is the weight fraction of the soluble part of the fiber after an irradiation time t, $G(s)$ and $G(x)$ are the number of scissions and crosslinks formed, respectively, and I_a is the intensity of light absorbed by the fiber during time t. Thus, a plot of $s + \sqrt{s}$ vs. the reciprocal irradiation dose should give a straight line with an intercept (infinite irradiation dose) corresponding to $G(s)/2G(x)$. In Fig. 9, such a plot is presented for our sol-fraction data, where it is assumed that I_a is directly proportional to the irradiation time t. From this plot, a value of $G(s)/G(x_1) = 1.03$ is obtained, implying that the number of chain scissions per amount of light-intensity absorbed is approximately equal to the number of crosslinks formed.

In a different approach, the sol-gel data may be analyzed in terms of the Inokuti relation [39]

$$(1 - s)_{max} = \frac{1}{2}\left[1 - \frac{G(s)}{G(x)} + \left(1 + \frac{2\,G(s)}{G(x)}\right)^{1/2}\right], \qquad (5)$$

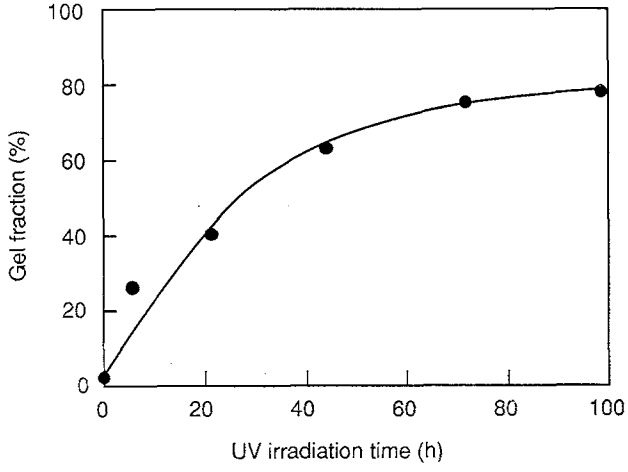

Fig. 8. Effect of UV irradiation on the gel fraction of an UHMWPE fiber with $\lambda = 60$, treated with DCP for 120 h

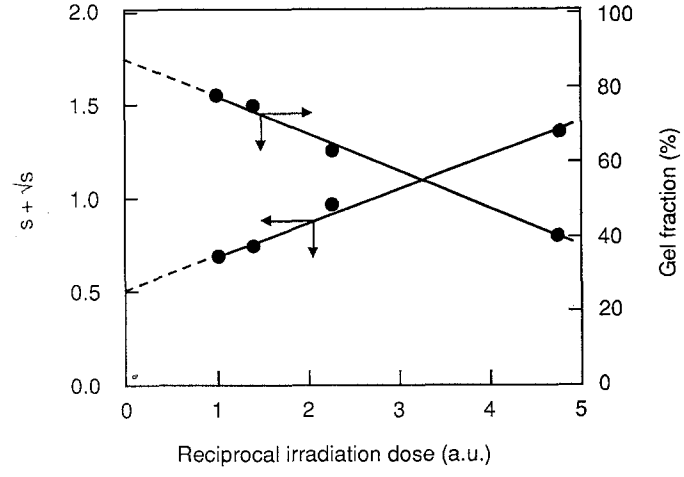

Fig. 9. Gel-content and $s + \sqrt{s}$ as a function of the reciprocal UV irradiation dose (see text for explanation)

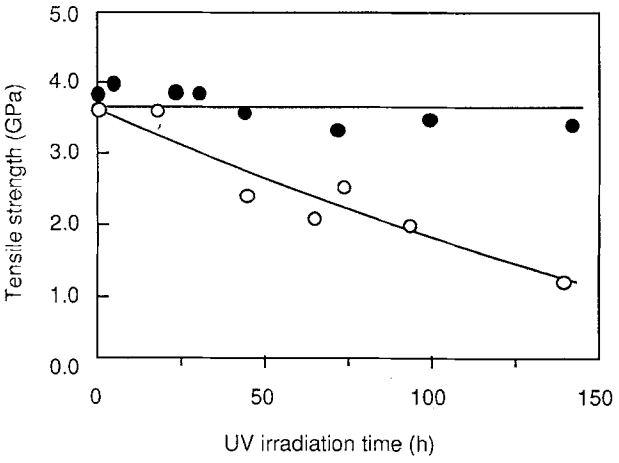

Fig. 10. Tensile strength vs. UV irradiation time for an UHMWPE fiber with $\lambda = 60$ (○) and for the same fiber after treatment with DCP for 120 h (●)

which relates the maximum obtainable gelfraction $(1 - s)_{max}$ to the scission-to-crosslink ratio $G(s)/G(x)$. In order to determine $(1 - s)_{max}$, a plot of the fiber gel-content against the reciprocal irradiation dose is presented in Fig. 9. Extrapolation of the linear relation that is obtained in this way leads to a maximum attainable gel fraction of 88.0%. This value is somewhat higher than is expected on the basis of Fig. 8. A scission-to-crosslink ratio of $G(s)/G(x) = 0.93$ is calculated from $(1 - s)_{max}$ using the Inokuti relation, which is in reasonable agreement with the value obtained from the Charlesby–Pinner analysis.

Figure 10 shows the tensile strength of DCP-treated fibers subjected to UV irradiation for different periods of time. It is seen that the tensile strength of the fiber is hardly affected by the UV irradiation treatment. This is very important, because it shows that crosslinked UHMWPE fibers with a high tensile strength can be conveniently prepared by using this method. However, the retention of tensile strength is quite remarkable in the light of the results of the Charlesby–Pinner and Inokuti analyses, which suggest that chain scissioning takes place upon UV irradiation. In the case of high-strength fibers, chain scissioning is expected to give rise to a reduction of the tensile strength, since it will preferentially break taut tie molecules which transfer stresses in the fiber [20, 21]. When a control fiber that is not treated with DCP is subjected to UV irradiation, gelation of the fiber is observed (after an irradiation time of 139 h, the gel-content of the control fiber was 80%), but in this case irradiation is actually accompanied by a decrease in tensile strength from 3.7 to 1.2 GPa. These results indicate that DCP plays an important role in the processes involved in the UV irradiation of UHMWPE filaments. From this point of view, it is questionable whether the network formation in the system studied here can be adequately described using the Charlesby–Pinner and Inokuti equations.

In connection with the observed preservation of the tensile strength of UHMWPE fibers upon UV-induced peroxide crosslinking, it is of interest of examine the fracture morphology of the crosslinked fibers. In Fig. 11, the fracture surfaces of the uncrosslinked starting fiber ($\lambda = 60$) and the same fiber after DCP treatment and subsequent UV irradiation for 23 h are compared. The two fibers show very similar stress-strain characteristics: a strength of 3.88 GPa and 3.84 GPa, a Young's modulus of 134 GPa and 129 GPa, and a strain at break of 4.3% and 4.0% for the crosslinked and the uncrosslinked fibers respectively. The uncrosslinked fiber displays a highly fibrillar fracture surface (Fig. 11a) indicating that the individual fibrils in the fiber structure have little lateral coherence. The crosslinked fiber, on the other hand, does not show such an extensive fibrillation (Fig. 11b), which points to an increased connectivity between the fibrils. We like to emphasize that the observed differences in fracture morphology between crosslinked and uncrosslinked fibers are in no way related to a change in fracture behavior from ductile to brittle, since the strength and strain at break of the two fibers shown in Fig. 11 are virtually identical. The result merely suggests that longitudinal splitting of the fibrillar structure is hampered by covalent bonds formed between individual fibrils as a result of crosslinking.

Figure 12 shows the effect of the crosslinking treatment on the creep behavior of the fiber. It is seen that the initial stage of the network formation results in a steady decrease of the plateau creep rate from $\dot{\varepsilon}_p = 6.7 \cdot 10^{-6} s^{-1}$ to $\dot{\varepsilon}_p = 1.1 \cdot 10^{-6} s^{-1}$ after 25 h of irradiation. Continuation of the process beyond this point does not lead to a further improvement of the creep resistance, which is quite remarkable since the gel-content of the fiber increases continuously with irradiation dose. Thus, the introduction of crosslinks is only partially effective as far as the reduction of the creep rate is concerned.

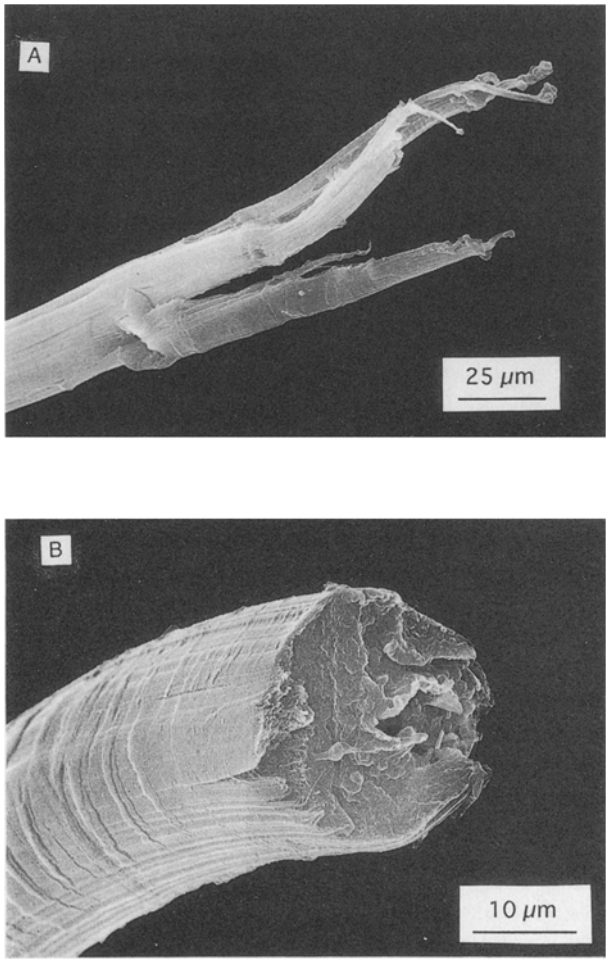

Fig. 11. Fracture surfaces of a) the initial, uncrosslinked UHMWPE fiber ($\lambda = 60$) and b) the same fiber after DCP treatment followed by 23 h of UV irradiation. Both fibers were tested at an initial deformation rate of 0.5 min^{-1} and had a tensile strength of 3.8 GPa

Although our knowledge of the formation and structure of the UHMWPE fiber networks studied here is yet far from complete, it is attractive to speculate that this phenomenon is related to the high crystallinity and the microfibrillar structure of the hot-drawn filaments. First of all, it is likely that the crosslinking agent will diffuse into the fiber via the interfibrillar regions, so that crosslinks are predominantly formed at these sites. Furthermore, it has been pointed out by Patel and Keller [40] that, in the case of polyethylene, a crosslink can never be formed inside the crystal lattice, because the chains are too far apart (4.1 Å) to be linked together by a covalent bond (1.5 Å), Crosslinking will therefore only affect chains in the amorphous domains in the fiber structure, whatever technique is applied. Thus, flow processes associated with the crystalline phase, i.e., inside the microfibril, cannot be completely arrested by means of crosslinking. The analysis of the general creep behavior of UHMWPE fibers in terms of the Ward–Wilding model [12] indicated that creep in these fibers is governed by such crystalline deformation processes. From this point of view, it will be very difficult, if not impossible, to remove the creep of high-strength UHMWPE fibers and, at the same time, preserve the highly crystalline fiber structure and extraordinary short-term mechanical properties.

4. Concluding remarks

The experimental data concerning the general creep behavior of gel-spun/hot-drawn UHMWPE

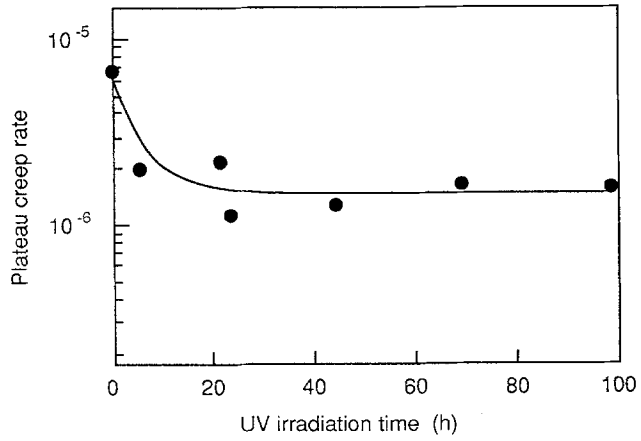

Fig. 12. Plateau creep rate (s^{-1}) vs. UV irradiation time for an UHMWPE fiber with $\lambda = 60$, treated with DCP for 120 h

fibers presented here show a good qualitative agreement with the results of Ward et al. [12] for melt-spun and drawn polyethylenes. The creep behavior of both materials can be satisfactorily described by two thermally activated processes acting in parallel. The kinetic parameters of the creep process in solution-spun fibers, however, differ very appreciably from what is commonly found for other types of high-modulus polyethylene. The activation volumes, obtained from the analysis of the creep in terms of the two-process model, are $v_1 = 30$ Å^3 and $v_2 = 15$ Å^3, respectively, for the solution-spun fiber, which is substantially lower than the approximate values of $v_1 \approx 500$ Å^3 and $v_2 \approx 100$ Å^3 found for melt-spun and drawn polyethylene. In this connection, it is interesting to note that the yield behavior of solution-spun and drawn UHMWPE fibers is also characterized by a very small activation volume of $v = 66$ Å^3, as was determined by van der Werff et al. [8]. Although the kinetic data presented here are clearly not sufficient to permit a thorough interpretation of the creep process in UHMWPE fibers, it is evident that the activated events are extremely localized.

In the light of the experimental data presented here, the identification of the two thermally activated processes with the molecular network (process 1) and the crystalline regions of the fibre (process 2) is not very obvious in the case of solution-spun UHMWPE fibers. The activation volumes determined here correspond approximately to the volume of a single methylene unit, suggesting that the creep is mainly related to deformation processes in the crystalline regions of the fiber structure. On the other hand, there is a pronounced effect of the spinning concentration on the creep behavior of the solution-spun fibers, indicating that the non-crystalline molecular network does affect the long-term deformation behavior of the material.

The above considerations also related to the effects of chemical crosslinking on the creep properties of UHMWPE fibers. As already mentioned above, crosslinking will only affect chains in the amorphous domains in the fiber structure. Although the results of this study show that the creep resistance of UHMWPE fibers can be improved considerably by means of chemical crosslinking, it has become clear that the creep cannot be completely removed upon crosslinking, even when the extent of the network formation is fairly high. This points to some kind of "intrinsic" flow process that is not affected by the presence of crosslinks. As already mentioned above, it is conceivable that this intrinsic flow process is associated with the crystalline domains in the fiber structure.

In order to speculate on the mechanisms involved in the creep process of UHMWPE fibers, the following points deserve some attention. Although the morphology of UHMWPE fibers is obviously very complex, the mechanical properties have been successfully interpreted in terms of a simplified model of the microfibril, which is assumed to be the basic element of the fiber structure [8, 21, 41]. The microfibril is thought to consist of successive crystalline blocks that are interrupted by small disordered domains, where entanglements and chain ends are collected. Stresses are transferred from one crystal block to the next by (taut) tie molecules, which are therefore of great importance with respect to the strength and stiffness of the fibre [42]. It has been derived by Kausch [43] that the maximum force that a tie molecule can exert on the surrounding crystalline lattice corresponds to 7.5 GPa. The strength of a covalent bond is estimated at approximately 30 GPa, which implies that when a sufficient stress is applied to a tie molecule, it would be pulled out of the crystal lattice rather than break. Since the tie molecules in the disordered domains experience a high stress concentration, this process may commence even at moderate macroscopic stress-levels. It is very well conceivable that the intrinsic flow process is related to such a gradual pull-out of load carrying chains out of the crystal blocks and can, therefore, be associated with the crystalline-amorphous entity as it exists at the level of the microfibril. If crosslinks are formed selectively in the interfibrillar regions, as suggested above, crosslinking will only suppress that part of the creep process that involves sliding of individual (micro) fibrils past each other, but will leave the deformation processes inside the microfibril unaffected.

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