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X-linked ultra high strength polyethylene fibres

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Abstract: The present work was aimed to improve further upon the mechanical proper-
ties of gel spun polyethylene fibres of ultrahigh modulus and tenacity. Cross-links were
introduced by electron irradiation of the gels *before* drawing. Under the present cir-
cumstances this resulted in much more favourable creep properties, of the fibres and
tapes and also to retention of much of their strength after holding at 200 °C, without,
however, significantly affecting drawability and the resulting high modulus and strength.

Key words: Polyethylene, ultra streng fibre, X-link, property.

Introduction

As well known, fibres of polyethylene possessing
exceptional stiffness and strength can be obtained by
drawing of gels prepared from ultra high molecular
weight polyethylene (UHMW-PE), the so called gel
drawing technique, developed in different variation
(e.q. 1, 2) in recent years. Fibres or tapes prepared by
this method had several advantageous properties com-
pared to similar high modulus high strength products
obtained along other routes. For example when con-
strained, these tapes did not melt up till 156 °C; they
also showed lower tendency to creep [3] compared to
melt spun and subsequentally hot drawn high modu-
lus fibres of normal grade PE [4]. It was considered
that crosslinking could be used to improve these
favourable properties of gel spun fibres even further.

Perkins et al. [5] used ultra oriented filaments of
linear polyethylene ($\bar{M}_w = 59.000$) prepared by the
solid state extrusion technique and irradiated them at
various doses up to 60 Mrad. They found that, with
increasing radiation dose both the Young modulus and
the tensile strength of the fibres first increased slightly
and then levelled off with the tensile strength levelling
off at higher doses. The maximum strength of the
fibres using the optimum dose was 0.5 GPa. More
recently Pennings and his coworkers [6, 7, 8] were
crosslinking highly drawn UHMW-PE fibres prepared
using the gel spinning technique [1, 2]. Using γ radia-

tion for crosslinking they [6] found that the strength of
the fibres was reduced by the irradiation: even at a dose
as low as 2 Mrad the decrease in strength could amount
to 30 %. This decrease in the strength was attributed to
chain scission. It is well known [9] that apart from
cross-linking, high energy radiation also causes main
chain scission. Charlesby and Pinner's work [10] on
the relative amounts of cross-link and chain scission
for polyethylene implies that at a given dose the num-
ber of cross-links formed within the sample is approxi-
mately three times that of the number of bonds bro-
ken. However, the efficiency of the radiation in form-
ing mechanically effective cross-links depends on the
polymer morphology [11]. This is attributed to the fact
that intermolecular (as opposed to intramolecular)
cross-linking efficiency decreases with increasing
degree of crystallinity. This seems to be associated
with the deduction that at low doses hardly any cross-
linking occurs in the crystal lattice [11]. Gel drawn
UHMW-PE fibres are highly crystalline and contain
very few topological defects (entanglements, folds).
Thus on irradiation most cross-links are intramolecu-
lar and main chain scission acts to increase the number
of chain ends. The broken chains decrease the continu-
ity between the extended microfibrils, hence the
decrease in the strength of the fibre.

In a different study de Boer et al. [12] used chemical
cross-linking through the agency of dicumyl peroxide

without causing chain rupture [13]. The peroxide was introduced into the as spun gel fibre through swelling in a solution of dicumyl peroxide in n-hexane. The fibre was then dried and drawn at 150 °C. During the drawing process the peroxide decomposed and the cross-links formed. The maximum attainable draw ratio and tensile strength at break decreased with increased peroxide concentration. By the time 70 % of the material became part of a cross-linked network the strength decreased by up to 40 %.

More recently Woods et al. [14] showed that the efficiency of intermolecular cross-linking by electron radiation can be increased if irradiation is performed in the presence of a sensitizing agent, acetylene gas.

The present paper is concerned with irradiation cross-linking using electrons prior to drawing of dried solution cast films and solution spun fibres of UHMW-PE for a dose range of 0–15 Mrad and, the drawing behaviour, and following this the mechanical properties, of the resulting products were investigated. Modulus and creep measurements were carried out on films, and strength measurements on fibres for reasons of practicality.

Experimental

Preparation of solution cast films

UHMW-PE powder Hostalen Gur 412 with $\bar{M}_n = 2 \times 10^5$ $\bar{M}_w = 1.5 \times 10^6$ was received in the form of a fine powder. First the powder was suspended in xylene at room temperature at a nominal concentration of 1.5 % wv^{-1} with 0.02 % wv^{-1} anti-oxidant Irgafos-168/Topanol-CA (ratio: 1/1) added. Air trapped by the powder particles was removed by the application of vacuum. Subsequently, the flask containing the deaerated suspension was transferred into a silicon oil bath and heated under continuous stirring at 125 °C. Stirring was maintained until the occurrence of the Weissenberg effect, whereafter the solution was kept under stationary conditions until it became clear. It was then cast in stainless steel trays at room temperature. Upon cooling the solution turned opaque and became gel like. After solvent evaporation at room temperature films of uniform thickness were obtained. Stabilizers and solvent were removed by soaking the films in trichloroethylene.

Solution spinning

A solution of 2 % wv^{-1} UHMW-PE in decalin was prepared as described above but at a dissolution temperature of 160 °C. The solution was transferred to a spinner while at 160 °C. The capillary used has a diameter of 1 mm. A screw driven piston pushed the solution through the capillary at a speed of 0.1 mm min^{-1} into a bath containing cold water. The resulting filaments were wound around a drum and the take up speed was adjusted to avoid draw down. Stabilisers and the solvent were extracted by immersing the filaments in trichloroethylene.

Irradiation process

The samples were sealed in glass tubes under vacuum. Irradiation was performed using high energy electrons from a Van der Graff generator. The typical dose rate ws 0.5 Mrad sec^{-1}. Various doses were given from 1 to 5 Mrad.

Gel content measurements

The percentage of insoluble material after irradiation was measured using a Soxhlet apparatus. Approximately 50 mg of sample wrapped in glass fibre mesh was exposed to refluxing xylene until it attained constant weight which usually took 20 hours. The samples were dried in vacuum oven at 100 °C overnight and the weight of the gel was measured.

Swelling measurements

Swelling measurements were carried out on the irradiated films after removal of the uncross-linked part by Soxhlet extraction. After the extraction the gel was dried in a vacuum oven at 100 °C for 1 day. The gel was then transferred to a bath of para-xylene at 120 °C where it was swollen to reach equilibrium, whereafter it was placed in a sealed container and weighed. Polymer volume fraction was calculated from the weights of the dry and the swollen gel assuming equal densities for polyethylene and p-xylene at the swelling temperature.

Drawing process

The drawing operation was performed by stretching the films on thermostatistically controlled hot shoes slowly by hand. The draw ratios were determined by measuring the displacement of ink marks placed 5 mm apart on the specimens prior to drawing. (Draw ratio = λ = final length/initial length).

Modulus and strength measurements

The Young modulus and strength of the samples were measured at room temperature using a Zwick tensile tester at a constant speed. Corresponding to an initial strain rate of 0.1 min^{-1} the Young modulus was calculated at 0.1 % strain. Cross sectional area used for calculating the stress were obtained from the mass and the length of the samples, assuming a crystal density of lg cm^{-3}.

Dynamic measurements were carried out using a Rheovibron at 11 Hz in the temperature range from −160 °C to 150 °C.

Creep measurements

The experiments on creep were performed using a dead loading apparatus. The samples were clamped between two grips. Weights were hung from the bottom grip in order to obtain a particular desired stress. The sample length was chosen to be 7 cm. The aspect ratio was sufficiently high to ignore the end effects. The sample extension was found from the displacement of the bottom grip by means of a linear displacement transducer. The signal from the transducers were fed into a 12 point chart recorder and recorded as a function of time. (The transducers themselves were kept at constant temperature within a thermostatically controlled box). The creep

measurements were carried out at fixed temperatures under constant load.

Results and discussion

Crosslinking of the dried cast films

The extent of cross-linking in the cast films, irradiated with various doses, was examined using the Soxhlet extraction technique. The results are shown in Table 1. Here it can be seen that the gel content of the samples rapidly increases becoming almost constant at higher doses showing behaviour typical of polyethylene.

Crosslink density in the irradiated samples was estimated from the extent of swelling in p-xylene using the Equation (9):

$$\frac{\varrho V}{M_c} \left(\frac{X}{2} - X^{1/3} \right) = \ln (1 - X) + X + \omega X^2$$

where ϱ is the polymer density (9.2 g cm^{-3}), M_c the average molecular weight between the cross-links, V is the molar volume of the solvent (138 cm^3 mole^{-1} for p-xylene), X is the polymer volume fraction (X^{-1} of course represents the swelling ratio). The parameter ω is the dimensionless heat of mixing, and for polyethylene in p-xylene at 120 °C it is given by $0.33 + 0.55 X$ [15]. The results of the swelling measurements are tabulated in Table 1. It can be seen that, as expected, the density of the crosslinks increases with increasing dose. It is a common practice to express the radiation induced changes in terms of the G value which should be a constant for a given material. The G value for crosslinked units (G_c) is given by

$$G_c = 0.48 \times 10^6 \frac{1}{M_c r}$$

where r is the radiation dose in Mrads.

G_c values for the samples are shown in Table 1. These are on the low side of the range of G_c values (0.1–2) reported [16] for polyethylene. G_c is supposed to be constant for a particular polymer. However, because most methods of determining the number of cross-links formed rely on indirect measurements [11] (elalstic modulus, swelling, gel content) it is usually only the inter-molecular cross-links which are determined. Since the value of $G_c = 0.12 \mp 0.02$ found here is 20 times lower than the highest value reported in the literature then, if G_c is truly invariant it must follow that most cross-links formed in the irradiated gel films are intramolecular. Alternatively our results would

mean that G_c is not a constant for polyethylene and the true number of cross-links itself is lower for our sample type, or that a combination of both effects, i. e. a lowered G_c and large amount of intramolecular cross-links, apply. This issue is discussed in Reference [11].

Drawing behaviour and the subsequent mechanical properties of the cross-linked films and fibres

Drawing of the solution cast films was performed manually using hot shoes at various temperatures. Figure 1 shows how the ultimate draw ratio (λ_{max}) of a 1.5 % wv^{-1} film at various drawing temperatures (including one with two stage drawing method) varies with irradiation dose. Here it can be seen that λ_{max} decreases with increasing dose. This confirms the previous result and shows that cross-link density increases with increasing dose. In this figure it is also clear that higher draw ratios were obtained when the samples were drawn at 90 °C until necking was complete and then further, at 130 °C until break. In all the following experiments this two stage drawing procedure was applied.

Figure 2 shows the plots of the Young modulus (E) against draw ratio (λ) for tapes prepared from films irradiated at various doses. In this figure it can be seen that apart from slight variations in modulus at high
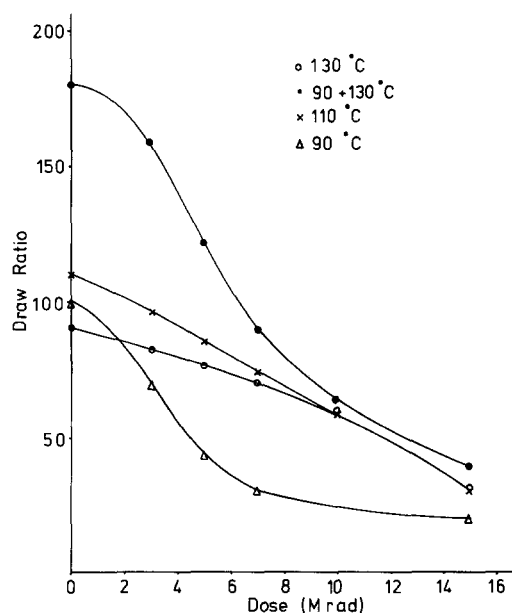
Fig. 1. Maximum attainable draw ratio as a function of dose for films, at various drawing temperatures
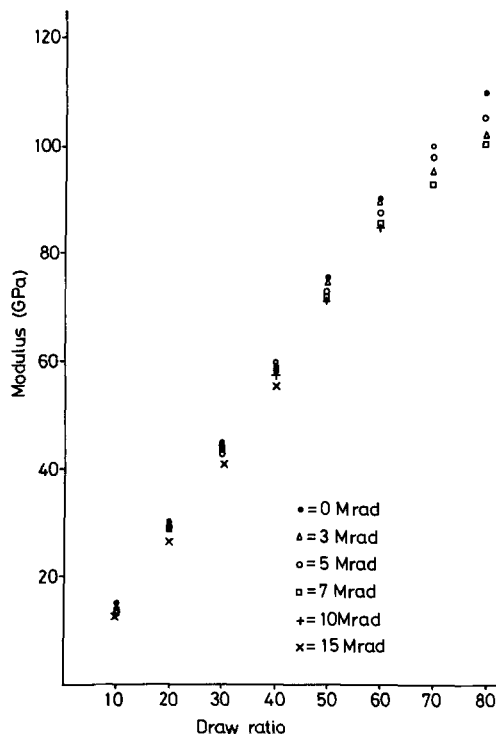
Fig. 2. Young's modulus as a function of draw ratio for films irradiated with various doses
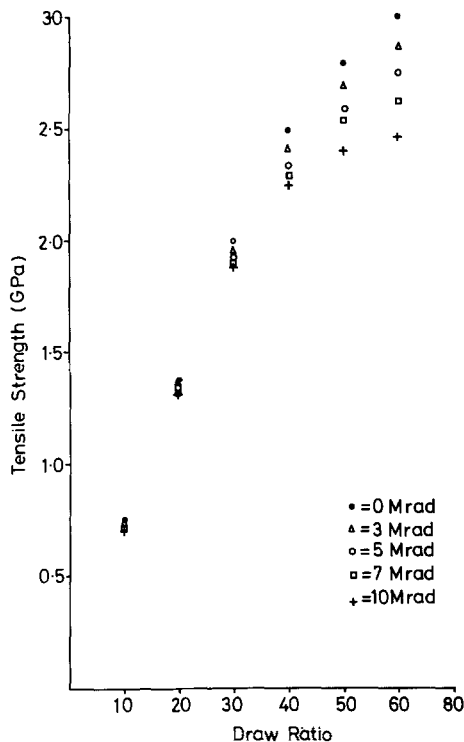

Fig. 3. Tensile strength as a function of draw ratio for fibres irradiated with various doses

draw ratios the *E-λ* curve remains largely unchanged by irradiation. Tensile strength as a function of draw ratio, for the fibres drawn from solution spun filaments irradiated with various doses, are shown in Figure 3. In this figure it can be seen that at draw ratios up to thirty the strength of the fibres remains largely unchanged by irradiation. At draw ratios higher than thirty, at a given

draw ratio, the strengths of the fibres show some decrease with increasing dose. This decrease in strength may be attributed to the cross-links which cause stress concentrations within the fibre.

The results of the dynamical measurements using samples with a draw ratio of sixty prepared from films irradiated with 0 and 7 Mrad are shown in Figures 4
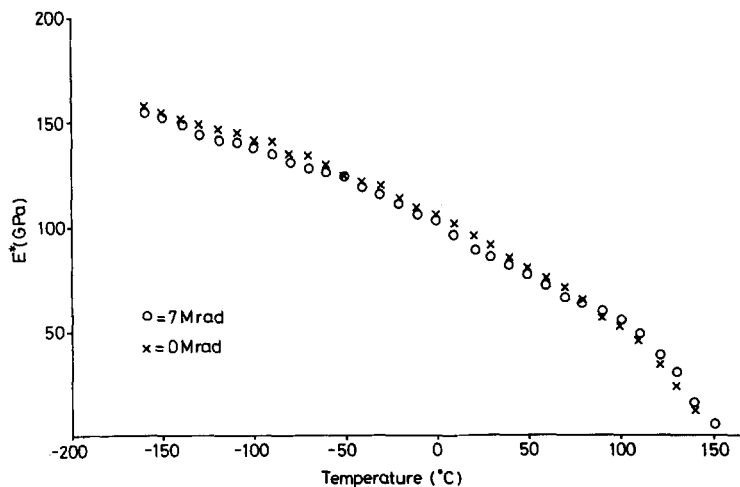

Fig. 4. The complex modulus as a function of temperature for samples with a draw ratio 60 prepared from films irradiated with the doses shown . . .
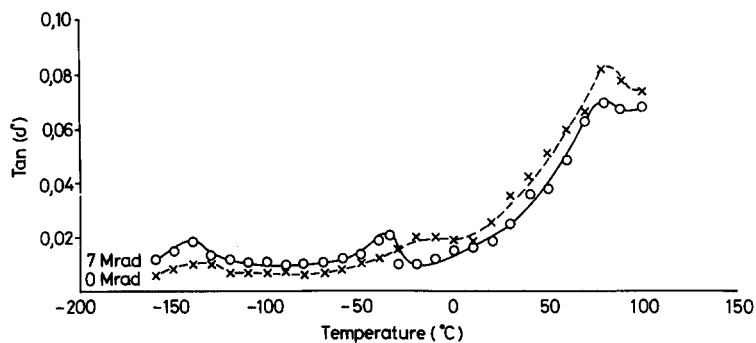
Fig. 5. The loss tangent as a function of temperature for samples with a draw ratio 60 prepared from films irradiated with the doses shown

and 5. In Figure 4 the complex moduli as a function of temperature for the two samples are plotted. Here it can be seen that both samples behave in a similar manner. Figure 5 shows the plots of loss tangent (tan δ) as a function of temperature (T). In this figure no data above 100 °C are given because the creep rate was too high to permit accurate measurements of tan δ. Peaks in the tan $\delta - T$ curves are usually associated with the relaxation behaviour of the molecules. The peak around 80 °C in Figure 5 for both samples is characteristic of polyethylene and is termed the α relaxation peak. This α relaxation is associated with that of the CH$_2$ units and is envisaged as a process within the crystal involving simultaneous relaxation and translation of the molecules [17]. In the $-$ 50 to 0 °C region no distinct peaks for the unirradiated sample could be observed. The 7 Mrad sample, however, displayed a peak around $-$ 40 °C. This peak was reproducible and it may be associated with the relaxation of the side groups (β relaxation). As should be expected for linear polyethylene, a β relaxation peak was not observed for the unirradiated sample, therefore its presence in the irradiated sample must be associated with the cross-links. Finally the humps which appear in both samples around $-$140 °C may be due to a relaxation of polyethylene which is sometimes associated with a glass transition.

For the creep measurements samples with a draw ratio sixty were prepared from films irradiated with various doses, used. The samples were loaded with constant weights and the strain was recorded as a function of time. It was found that for all the stresses used, after some initial time, the samples elongated at constant rates corresponding to the constant rate of creep. At given temperature this constant creep rate shows a linear logarithmic dependence on stress as shown in

Figure 6 for $T = 23$ °C. This is consistent with the description of the constant creep behaviour in terms of a thermally activated process leading to the so called simplified Eyring Equation (18)

$$\dot{\varepsilon}_c = \dot{\varepsilon}_o \exp\left[\frac{(\sigma V - \Delta H)}{kT}\right].$$

Here $\dot{\varepsilon}_c$ is the constant creep rate, σ the nominal applied stress, ΔH is the activation energy, V the activation volume, T the absolute temperature, and k is the Boltzmann's constant.

Figure 6 shows that at a given stress the creep rate decreases as a function of irradiation dose, and that a reduction in the creep rate as high as ten folds could be achieved with a dose of 10 Mrad[1]). Gradients of the lines were used to find the activation volumes for the samples. The results are tabulated in Table 2. Here it can be seen that the activation volume decreases with increasing dose. It has been shown that the activation volume decreases with increasing crystal continuity [4]. Since cross-links may be expected to reduce the crystal continuity they can cause an increase in the activation volume: hence the increase in the activation volume with increasing dose. In Figure 7 log $\dot{\varepsilon}_c$ against $1/T$ for the samples at $\sigma = 0.4$ GPa is plotted. Points in this figure fall on straight lines obeying the above equation. Here again it can be seen that at a given temperature $\dot{\varepsilon}_c$ decreases with increasing dose. Gradients of the lines give a value of 32 $\pm$ 2 kcal mol^{-1} for the activation energy. The activation energy within the experi-

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[1]) All creep data are based on tapes obtained by drawing cast films 60 x with Young modulus of about 90 GPa. Since the creep rate is dependent on M, E etc. the data cannot be compared with those of gel spun UHMW-PE fibres.

Table 1. Cross-linking efficiency expressed in terms of gel content, swelling ratio, molecular weight between cross-links and G_c values for films irradiated with various doses

Dose Mrad	Gel content (%)	X^{-1}	$\bar{M}_c$	G_c
1	35	69	9.3×10^5	0.17
5	62	65	8.2×10^5	0.12
7	70	54	5.7×10^5	0.12
10	74	48	4.6×10^5	0.10

Table 2. Activation energies and volumes of the tapes with a draw ratio 60 prepared from films irradiated with various doses

Dose (Mrad)	Activation Volume (Å^3)	Acitvation Energy cal. mol^{-1}
0	48	32
3	55	32
5	55	32
7	58	33
10	64	33

mental error is independent of the irradiation dose. It is widely believed this activation energy is related to the α relaxation process [19]. Accordingly, since Figure 5 shows the α relaxation peak to be unchanged by irradiation, it is not surprising that the value for ΔH from the creep measurements is also unaffected by irradiation.

Heat treatment of cross-linked tapes

The changes in the constrained cross-linked tapes upon heating to high temperatures were investigated

using WAXS and birefringence techniques. When heating the tapes in vacuo under contraint it was found that at around 144 °C the usual orthorhombic crystal form transforms into the hexagonal phase. Figure 8 shows WAXD patterns of a tape irradiated with 10 Mrad then drawn 60 x. Figure 8a recorded at 23 °C shows a diffraction pattern corresponding to the orthorhombic structure of polyethylene. The diffraction pattern recorded at 150 °C (Fig. 8b) corresponds to a hexagonal packing of the chains in the a–b plane. The absence of higher layer line reflections in this
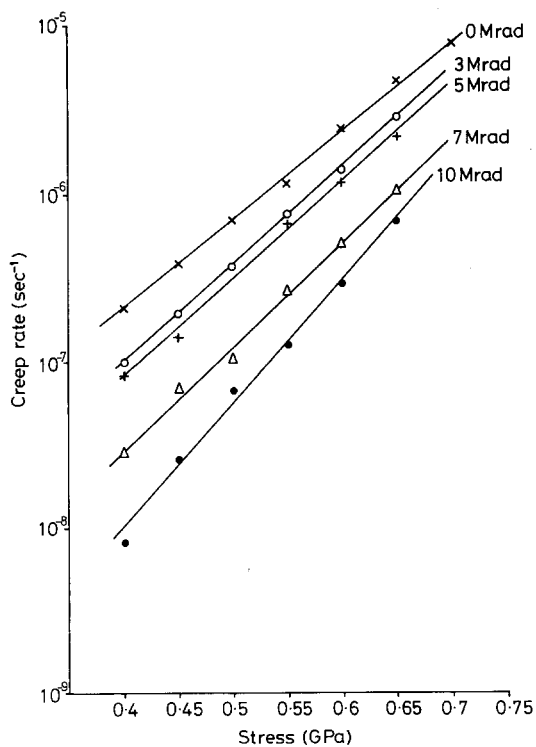

Fig. 6. Constant creep rate versus stress level ($T = 23$ °C) for tapes with a draw ratio 60 prepared from films irradiated with the doses shown
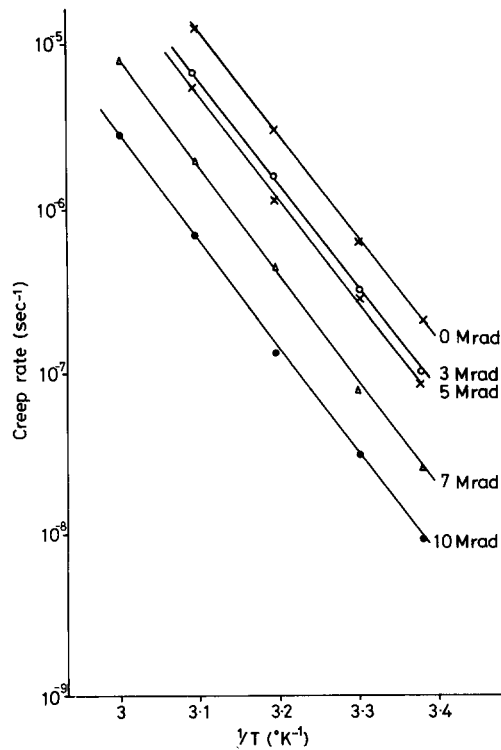

Fig. 7. Constant creep rate versus inverse temperature measured at a stress level of 0.4 GPa for tapes with a draw ratio 60 prepared from films irradiated with the doses shown

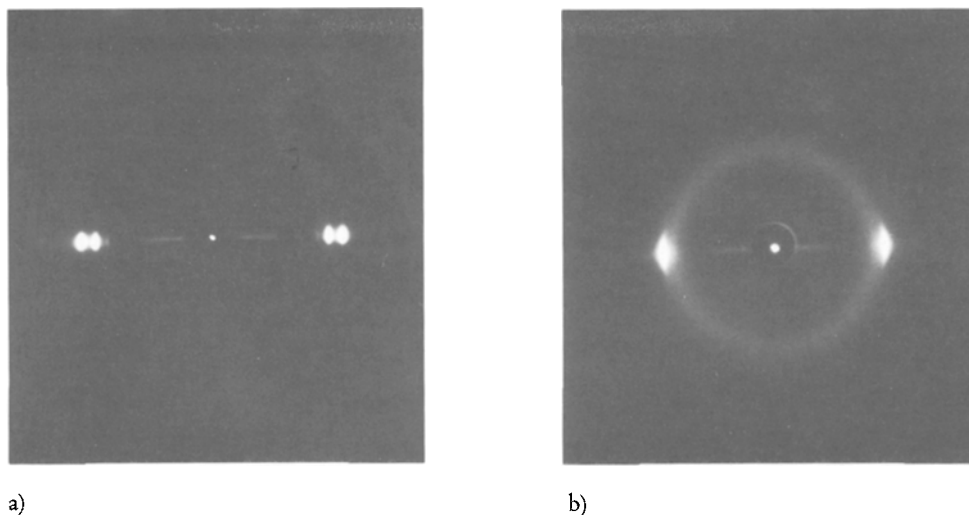a)   b)

Fig. 8. X-ray diffraction patterns recorded at the temperatures shown for a tape with a draw ratio 60 prepared from a film irradiated with
10 Mrad. Sample edge-on to X-ray beam, draw direction vertical. a) taken at 23 °C; b) at 150 °C

figure indicates that there is no register between the different chains regarding their periodicity along the c axis. The equatorial reflections seen in Figure 8b disappear upon heating to 200 °C. At this temperature the material remains highly oriented and birefringent. Upon cooling back to room temperature the material reverts back to the orthorhombic phase preserving its c axis orientation along the film direction, of which more will be said elsewhere [20].

The above high temperature resistance of the cross-linked tapes as opposed to uncross-linked ones, which disintegrate at around 160 °C, can make them a candidate for application as reinforcing agents in resins which need to be cured at elevated temperatures. With the latter in view the structure and mechanical properties of the cross-linked tapes were investigated further. For this study tapes with a draw ratio of forty prepared from films irradiated with 10 Mrad, were used. The tapes were tightly wound around steel rods to which the tape ends were knotted to prevent further movement. The rods were then stored under high vacuum at 200 °C for twenty four hours after which the samples were quenched in air to room temperature.

The structure of the tapes was studied by electron microscopy. Figure 9a shows an electron micrograph of a surface replica, together with its selected area electron diffraction pattern. This micrograph displays very well oriented shish kebab structure, where by the diffraction pattern, the c-axis is oriented along the fibre direction. This type of structure is very common in polyethylene crystallized from the melt under stress [21]. Previous diffraction studies at elevated temperatures, investigating the formation of the crystalline phase in stressed polyethylene, demonstrated consecutive formation of two types of texture consistent with fibrous, extended chain type crystals forming first which then act as nuclei for chain folded lamellar growth, such as is known gave rise to shish kebab structures [22]. Applying this interpretation of the X-ray patterns in References [21] to the cross-linked tapes of the present study, a model for the shish kebab structure could be postulated where the stretched out chains between the cross-links act as nucleation sites for lamellar crystallization (Fig. 9b).

Modulus and the strength measurements of the heat treated samples were performed both at room temperature. It was found that the modulus of the sample was reduced from 60 GPa to 25 GPa after annealing at 200 °C. The strength of the tape was reduced from 2 GPa to 1.1 GPa. Since the tapes always broke in the clamps of the Instron tensile tester it is possible that the true strength values are higher.

Conclusions

The results here presented have implications both for the fundamental understanding of ultraoriented polyethylene fibres and tapes and for their technological application, the principal conclusions being:

a)   b)
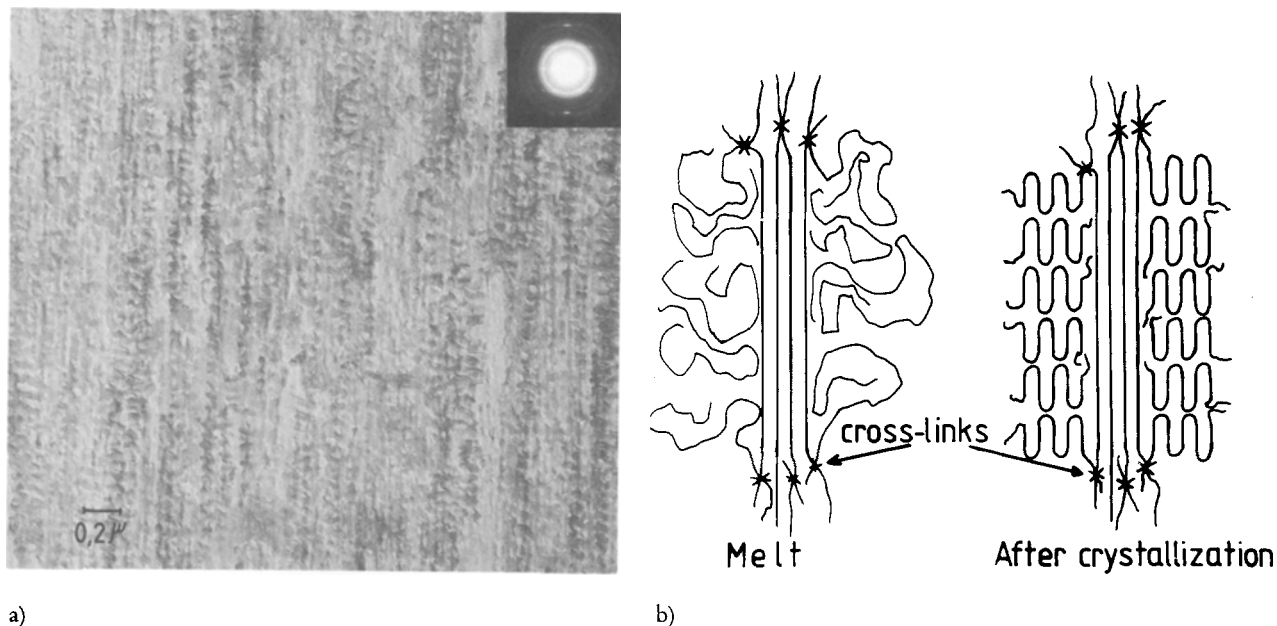
Fig. 9. a) Electron micrograph and electron diffraction pattern of a tape with a draw ratio 40 prepared from a film irradiated with 10 Mrad which was then annealed at 200 °C for 24 hours in vacuum. b) Schematic representation of shish-kebab structure formation

1. Dried solution cast films can be cross-linked by high energy radiation with little loss in the drawability.

2. Upon drawing, the cross-linked gels result in high-modulus, high-strength tapes and fibres.

3. Irradiation reduces creep, this reduction increasing with dose; up to ten fold improvement on the creep properties of the tapes has so far been achieved.

4. When constrained, the cross-linked types do not break at temperatures up to 200 °C in vacuo and retain some of their strength and modulus upon recrystallization at room temperature.

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