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Cross-linking of porous gel-spun ultra-high molecular weight polyethylene by means of electron beam irradiation

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Summary

Porous gel-spun ultra-high molecular weight polyethylene (UHMWPE) fibres, consisting of large folded chain lamellae linked to each other by means of tie molecules, have been irradiated at room temperature by means of high energy electrons.

From a discrepancy in yield of cross-links per unit of absorbed irradiation energy as calculated from sol-gel measurements and equilibrium swelling experiments, it was concluded that the tie molecules are preferentially scissioned, and thereby separating the different lamellae. At high irradiation doses the lamellae are linked again by cross-links between consecutive lamellae.

Introduction

The porous gel-spun UHMWPE fibre is a semi-manufactured article for the production of ultra-high strength polyethylene fibres. These highly oriented fibres are made by hot-drawing the porous polyethylene fibre (1, 2). The porous polyethylene fibre can be deformed to high draw ratios due to the fact that its molecules are connected to each other by only very few chain entanglements (3, 4).

The highly crystalline porous polyethylene fibre, with a crystalline volume fraction of more than 80%, consists of large folded chain lamellae which are connected to each other by trapped entanglements. The difference with normal mel-spun HMWPE is that the gel-spun fibre contains only very few entanglements and the melt-spun fibre, the large number of entanglements limit the number of adjacent reentries as can be seen from Fischer's 'Erstarrungs Modell' (5).

In this communication, preliminary results are presented concerning the sol-gel measurements and equilibrium swelling experiments on these irradiated porous gel-spun UHMWPE fibres.

A large discrepancy between the yield of cross-links per unit of absorbed irradiation energy, as calculated from sol-gel measurements, led to the conclusion that tie molecules are preferentially scissioned by irradiation, and that the large lamellae can be very effectively cross-linked by electron beam irradiation.

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Experimental part

The porous gel-spun polyethylene fibres, used in this study, were obtained by dissolving 5 % by weight of UHMWPE (Hifax 1900 from Hercules, $M_w = 4 \cdot 10^6$ kg/kmol) in 94.5 % by weight of paraffin oil to which 0.5 % by weight of anti-oxidant (2,6-di-t-butyl 4 methylcresol) was added. The polyethylene gel was spun in a cylinder-piston apparatus as described in a previous study (6). The paraffin oil was removed by extraction in n-hexane, which was subsequently removed by drying the fibre under vacuum at 50 °C for one hour.

The irradiation procedure was as follows. The fibre was wound onto an, 0.1 mm thick, aluminium cylinder with the fibre ends glued to the aluminium surface, using araldite glue. The aluminium cylinder was subsequently placed in the electron beam, in a nitrogen atmosphere at room temperature, while being rotated in order to achieve a homogeneous irradiation dose. The Van de Graaff generator accelerated the electrons up to 3 MeV.

Extraction of the sol-fraction was performed with boiling p-xylene, containing 0.5% by weight of anti-oxidant (2,6-di-t-butyl 4 methylcresol) at 130 °C. The degree of swelling was determined from the ratio of weight between swollen and dry polymer.

Results and Discussion

Porous ultra-high molecular weight polyethylene fibres, made by the gel-spinning technique, were analyzed in terms of the Charlesby-Pinner equation (7), relating the sol-fraction, s, to the irradiation dose, r,

$$s + \sqrt{s} = \frac{G(s)}{2 \cdot G(x)} + \frac{9.6 \cdot 10^5}{G(x) \cdot M_w \cdot r} \qquad (1)$$

where G(s) is the number of main chain scissions and G(x) the number of cross-links both produced per 100 eV absorbed irradiation energy and M_w is the weight average molecular weight of the initial polymer.

In figure 1 the sol-gel data are plotted in a Charlesby-Pinner plot. The gel-point was found to be about 2 Mrad. And the extrapolation to infinite irradiation dose, yielded a value of $s + \sqrt{s} = 0$, meaning that G(s) should be zero, *i.e.* no chain scissioning occurs upon irradiation.

If G(s) is zero, then it is possible to calculate the yield of cross-links per 100 eV absorbed irradiation energy from the gel-point and equation 1. A value of G(x) = 0.06 cross-links per 100 eV was found for the molecular weight of $M_w = 4 \cdot 10^6$ kg/kmol of the polyethylene used in this study.

In figure 2, the equilibrium degree of swelling, q, is shown as a function of the irradiation dose. The equilibrium degree of swelling is used to calculate the effective network chain density, using the swelling theory of Flory (8). The value for the parameters used in this calculation are described in reference (9, 10). The

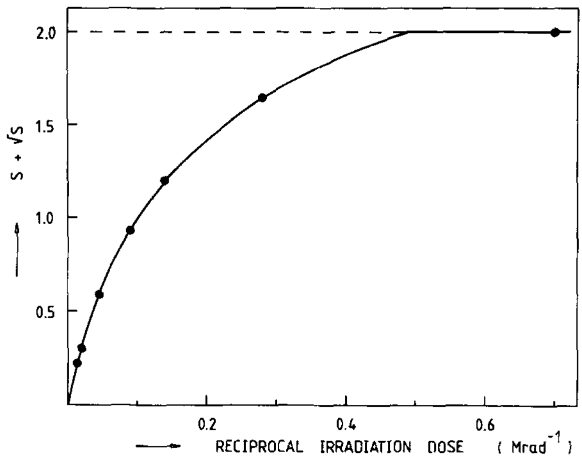

Figure 1 : Charlesby-Pinner plot of irradiated porous gel-spun UHMWPE fibre.

resulting calculated effective network chain density is shown in figure 3.

From scaling arguments it is well known (11) that the molecular weight between entanglements in a gel, M(gel), depends on the volume fraction polymer, φ, like M(gel) = M(melt) $\cdot\ \varphi^{-1.25}$, where M(melt) represents the molecular weight between entanglements in the melt. For polyethylene, M(melt) is known to be about 2000 kg/kmol (12), leading to an effective network chain density of 0.01 mol/dm^3. From figure 3, it can be seen that this density is very small as compared to the values calculated from the equilibrium swelling experiments, *i.e.* the contribution from trapped entanglements in figure 3 can be neglected.

The yield of cross-links per 100 eV absorbed irradiation energy can also be calculated from figure 3. For an irradiation dose of 71 Mrad, there are 0.16 mole chains per dm^3 in the network, *i.e.* 0.08 mole cross-links per dm^3, leading to a cross-link yield of G(x) = 1.3 / 100 eV. This value of G(x) is very much larger than the value found from the sol-gel measurements.

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The G(x) value of 0.06 as found from the sol-gel measurements is very low as compared to value found in previous studies. For polyethylene the values range from G(x) = 0.5 for irradiated ultra-high strength UHMWPE fibres (13) to G(x) = 2.6 for bulk UHMWPE irradiated in the melt (9).

The large differences in G(x) values might be explained, however, if the very special morphology of the porous polyethylene fibre is taken into account. If the entanglements or tie molecules, connecting the large folded chain lamellae, are preferentially scissioned by the radiation, this would separate the lamellae com-

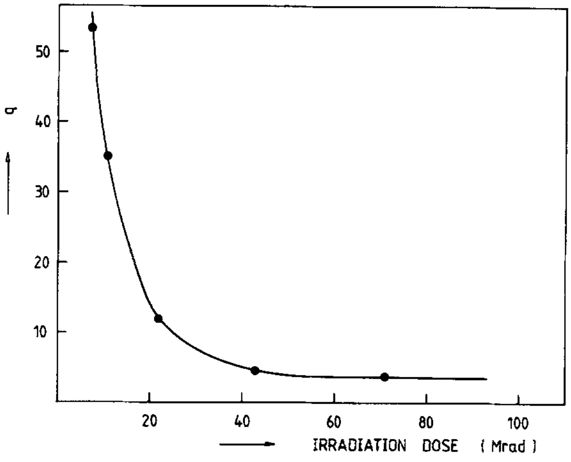

Figure 2 : The equilibrium degree of swelling versus the irradiation dose of irradiated porous gel-spun UHMWPE fibres.

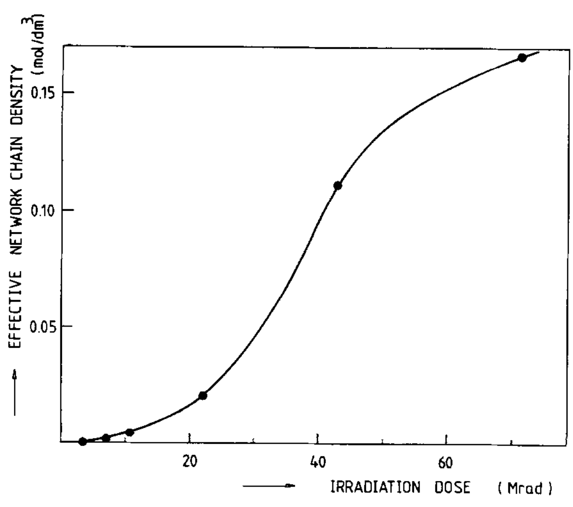

Figure 3 : The effective network chain density, as calculated from the equilibrium degree of swelling, versus the irradiation dose of irradiated porous gel-spun UHMWPE fibres.

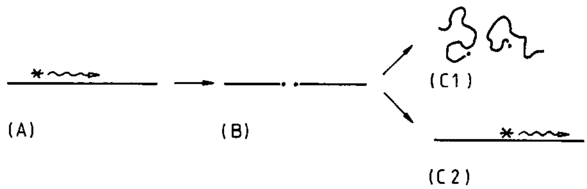

Figure 4 : A schematic model for chain scissioning by means of exciton transfer. In (a) an C-C exciton travels along the polymer chain, resulting in a chain scission shown in (b). If the chains can recoil a permanent scission occurs with two radicals (c1). If, however, no recoiling can occur due to constraints (e.g. chains in a crystal lattice) the radicals will recombine and the reformed exciton travels further along the polymer chain (c2).

pletely from each other and no measurable gel-fraction can be found, although the lamellae might be highly cross-linked. At large irradiation doses the lamellae are likely to be connected again by cross-links between folds in consecutive lamellae. This would also account for the S-shape of the curve in figure 3.

It is often believed that taut tie molecules are preferentially scissioned by high energy irradiation (13, 14) . One should bear in mind that if this is true, an energy migration process should occur, otherwise the energy conservation law would be broken. For example, the average energy absorbed in the taut tie molecules is far less than the energy necessary for bond scissioning, *i.e.* irradiation energy absorbed in the crystalline parts will have to migrate to these taut tie molecules to initiate fracture. Partridge's (15) exciton model seems to be applicable. Due to this model, C-C excitons can travel very efficiently along the backbone of a polyethylene molecule. Now and then a C-C bond is broken. A permanent chain scissioning occurs, however, only if the two radical chain ends can recoil. If not, the two radicals recombine in a cage reaction and the exciton is reformed, and travels further along the polymer chain (see figure 4). This mechanism would not only describe the scissioning of load carrying taut tie molecules or overstressed entanglements, but it would also explain why no chain scissioning in the crystalline parts occurs and how this absorbed energy can migrate to the disordered domains and amorphous parts of the polymeric material.

Conclusions

The results from sol-gel measurements and equilibrium swelling experiments on irradiated porous gel-spun UHMWPE fibres, led to the conclusion that the folded chain lamellae can be cross-linked very effectively, but that at low irradiation doses no gel-fraction can be determined, because the connecting tie molecules between consecutive lamellae have been preferentially scissioned. At larger irradiation doses other connections between these lamellae are installed by means of cross-links, leading to a measurable gelfraction.

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