The Effect of Gamma Ray Irradiation on the Mechanical Properties of Large Cross-Section Oriented Polyethylene Rods

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SYNOPSIS

The effect of gamma irradiation, in acetylene, on large diameter oriented polyethylene has been investigated. The dependency of gel content, melting point, and crystallinity on dose was evaluated. The gel content dose relationship showed two regions, indicating that an effective network is formed at low doses, 60 kGy. Irradiating the oriented rod in acetylene was found to more than double the initial tensile modulus. This improvement in the tensile properties resulted in improved creep–strain resistance for the material. These improvements in the mechanical properties were attributed to crosslinks formed both in the amorphous regions and at the surfaces of the crystalline regions. At high doses > 180 kGy degradation of the oriented polymer resulted in a deterioration in mechanical properties.

INTRODUCTION

High density polyethylene consists of long linear molecules which can be aligned to produce an oriented material with excellent mechanical properties. Several methods have been developed to produce an oriented structure,[1,2] and are currently used to produce high strength and high modulus polyethylene fibers. The production of larger diameter highly oriented polyethylene (HOPE) has also been investigated.[3] Such a product could be used as a reinforcing tendon for earth stabilization, in mining, or for reinforcing concrete where the inherent inertness and low density of polyethylene would be a considerable advantage.

The two main barriers to the engineering application of oriented polyethylene as a reinforcing material relate to:

(i) the ability to transfer load to the oriented polyethylene rod or bar,
(ii) the creep straining and recovery of the material when subject to long term loads.

This report is only concerned with the latter problem.

HOPE is inherently more creep resistant than unoriented polyethylene. Irradiation of unoriented polyethylene with gamma rays, or an electron beam, improves its mechanical properties. The enhancement is due to the formation of crosslinks within the polymer. Woods et al.[4,5] have investigated the effect of irradiating HOPE fibers in an acetylene atmosphere. They found that the creep and recovery behavior of the irradiated fibers was greatly improved and that the acetylene effectively lowered the dose at which these improvements were achieved. The work reported in this paper is concerned with extending the application of gamma irradiation to large diameter (10 mm) HOPE.

EXPERIMENTAL

Material Characterization

The orientation characteristics of several grades of high density polyethylene were investigated and an optimum material was chosen, having an $\bar{M}_n$ of 10×10^3, $\bar{M}_w$ of 12.9×10^4, a melt flow index of 1.6 at 190°C/5 kg, and an initial crystallinity of 72%. The

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molecular weight values in dichlorobenzene were determined at 140°C using a Waters 150C gel permeation chromatograph; a mixture of Irgafos 168 and Irganox 1010 was added as an antioxidant. Side chain lengths and types were determined from the ^{13}C-NMR spectrum of the material. The spectrum was determined at 140°C in trichlorobenzene and standard peak assignments were used.[6,7] This analysis showed that the material had ethyl side chains (0.7C/1000C) and long side chains (1.1C/1000C).

Preparation of Oriented Rod

Raw material billets were produced by extruding molten polymer into a heated cylindrical mold held at 130°C for 2 h before being cooled at 10°C/h to room temperature. With this procedure it was found that void free billets with diameters of up to 150 mm could be produced. Cylindrical specimens were machined from these billets.

HOPE was produced from cylindrical billets using the die drawing technique of Capaccio and Ward,[1] as illustrated in Figure 1. An isotropic cylindrical billet is pulled through a heated conical die. The process of yielding and flow of the material as it passes through the die orients the polyethylene molecules in the direction of travel, the overall reduction in billet cross-sectional area being determined by the drawing speed, temperature, and the material being drawn. The 10 mm diameter rods were produced using a drawing speed of 50 mm/min and an oven temperature of 100°C; the reduction ratio in cross-sectional area was 14. Earlier work in these laboratories had shown these to be the optimum drawing conditions for this material.

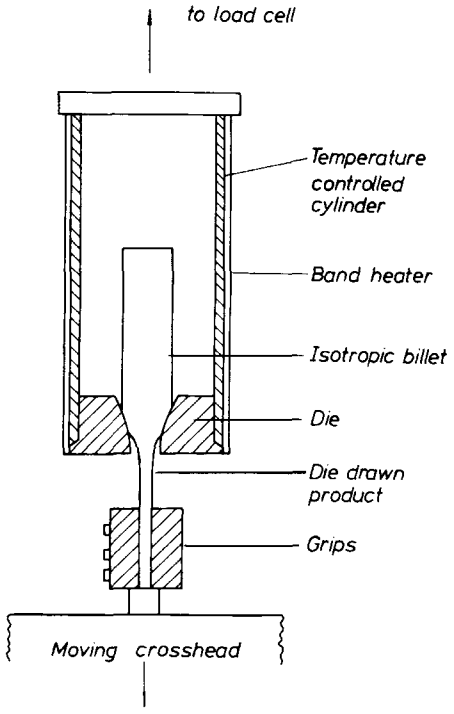

Figure 1 Schematic of the die drawing equipment.

Gamma Ray Irradiation

Irradiation of the Samples

HOPE rods were placed inside glass or aluminium cylinders with a stopcock at one end. The cylinders were evacuated to $< 10^{-4}$ torr and pumping continued for 7 days. Acetylene gas was then introduced to the evacuated cylinders until a slight positive pressure of acetylene was attained (40 cm H_2O above atmospheric), and the stopcock closed. Acetylene was replaced (by evacuation/refilling) daily for 7 days, at which point the samples were left for a further 7 days. After this 21-day period, the filled cylinders were irradiated to doses from 25 to 250 kGy in the flux from a ^{60}Co γ-source. Temperature during irradiation was maintained at 22 ± 3°C. After irradiation, the cylinders were left for a further 7 days prior to removal of samples.

Gel Content

The gel content of the irradiated rods was determined gravimetrically, using a 12-h extraction in refluxing xylene. Small additions of Irgafos 168 and Irganox 1010 were used to inhibit polymer degradation during extraction. Samples of the irradiated polymer, approximately 0.5 g, were cut into fine particles. These were placed into a preweighed and washed stainless steel mesh container. The container was then washed in acetone and dried to constant weight in an oven at 80°C. The gel fraction was calculated by dividing the final weight of polymer by the initial weight.

Differential Scanning Calorimetry

The melting behavior of the polymers was determined in a Mettler TA-3000 differential scanning calorimeter. The temperature range 30–180°C was scanned at a heating rate of 10°C/min, the melting point of the sample being determined from the peak in the endotherm. A typical melting endotherm for an oriented polyethylene sample, irradiated to 100 kGy, is given in Figure 2. The apparent melting enthalpy for each sample was calculated from the area

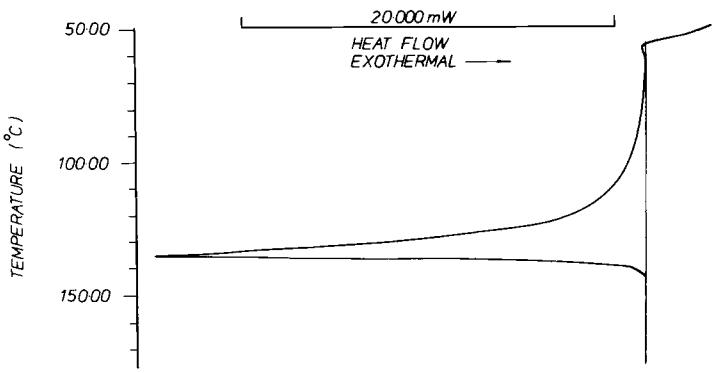

Figure 2 A typical DSC melting endotherm for an irradiated HOPE sample.

under the melting endotherm from which the degree of crystallinity was calculated by division of this value by the theoretical melting enthalpy[8] of 100% crystalline polyethylene, 278 J g^{-1}.

Tensile Testing

The room temperature mechanical properties of the rods were determined in an Instron tensile testing machine at a strain rate of 6.4×10^{-2} s^{-1}. The specimen strain was measured using two standard knife edge extensometers, over an initial gauge length of 25 mm. The extensometers were mounted opposite each other in the center of the test specimen, an arrangement which ensured that slight misalignments of the specimen or bending did not affect the measurement of strain during specimen testing. The specimens were gripped in specially designed cylindrically serrated grips. Previous work by one of the authors has shown that specimen lengths of at least 250 mm between the grips were necessary in order to avoid gripping effects.

Typically nonlinear stress/strain curves for the oriented rod before and after irradiation are given in Figure 3. In order to characterize the mechanical properties of these materials in tension, an initial modulus was calculated from the initial slope of the stress/strain graph.

The Determination of Creep Strain

The room temperature creep strain behavior of the samples was measured using standard cantilever dead loading apparatus. A 500 mm length of the specimen to be tested was gripped using the serrated cylindrical grips developed for tensile testing. The creep extension was measured using two linear variable differential transformers (LVDT) mounted on either side of the specimen. The extension data was collected using a personal computer interfaced to the averaged output of the LVDTs. This extension data was used to calculate true strain as a function of time. An initial gauge length of 10 mm was used.

To ensure that the desired loading was smoothly and reproducibly applied, the loading pan was hydraulically supported during placement of the desired masses/weights and specimen mounting. Time zero was taken from the time the specimen took the full load after gradual release of the hydraulic support. Generally this was 1–2 s after release of the jack. Multiple creep experiments were run for 6 months or to a strain of 5%, whichever occurred first. Replication results showed a variation of 10%.

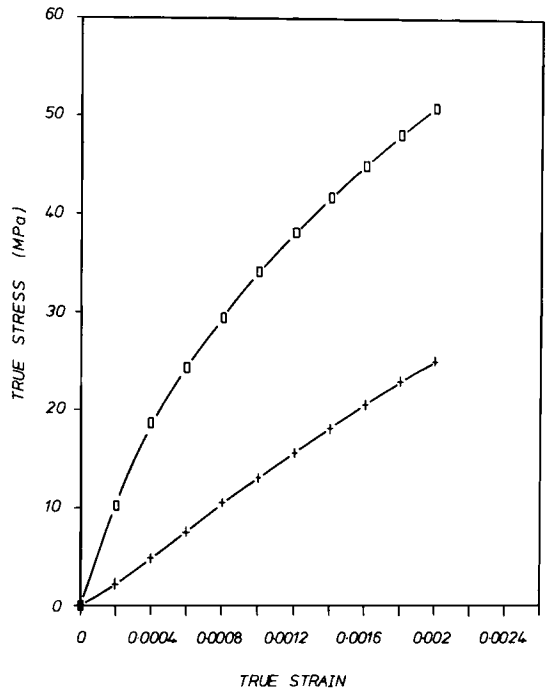

Figure 3 Tensile stress/strain curve for HOPE before (+) and after irradiation: (□) to 170 kGy.

RESULTS AND DISCUSSION

Gelation as a Function of Dose

The gelation data is plotted as a function of dose in Figure 4, the gel content initially increasing until doses above 60 kGy, when the rate of gel content increase slowed. Figure 4 shows that the crosslink network is effectively formed at a dose of 60–80 kGy.

In many polymers the relationship between the soluble fraction of the crosslinked polymer, s, and the dose r, is described by the Charlesby–Pinner equation.[9] This equation is given below:

$$s + s^{1/2} = G(s)/2G(x) + K/G(x) \cdot M_w \cdot r,$$

where $G(s)$ is the number of main chain scission events $G(x)$ is the number of crosslinks produced and K is a constant. This equation predicts that a plot of $s + s^{1/2}$ versus $1/r$ should be linear. The intercept is the ratio $G(s)/2G(x)$ and the slope is proportional to $1/G(x)$. Figure 5 is a Charlesby–Pinner plot for the irradiation of HOPE. At low doses a linear relationship is observed, but as the dose is increased the data become nonlinear, which has been reported previously.[10] A possible explanation relates to the formation of a crosslinked network which effectively increases the value of molecular weight in the Charlesby–Pinner equation. The deviation in the linearity of the Charlesby–Pinner plot occurs in the dose range 60–80 kGy, shown to be the dose range at which the effective network is formed (see Fig. 4). The intercept of the data line on the $s + s^{1/2}$ axis indicates that the probabilities of scission or crosslinking are about equal.

Melting Point and Crystallinity as a Function of Dose

Figure 6 shows the melting point behavior of the specimens as a function of dose. Initially the melting point decreases, and then remains virtually constant at 134°C except in the region 140–180 kGy; there appears to be an increase in melting point, probably associated with superheating of the highly constrained polymer.

The degree of crystallinity of the specimens is plotted as a function of gamma ray dose in Figure 7. Initially crystallinity diminishes, associated with the annihilation of small crystallites and loss of crystallinity at the surface of the larger crystallites. This is in contrast to the reported effect of irradiation on isotropic polyethylene,[11] where an increase in crystallinity with dose was observed. That in-

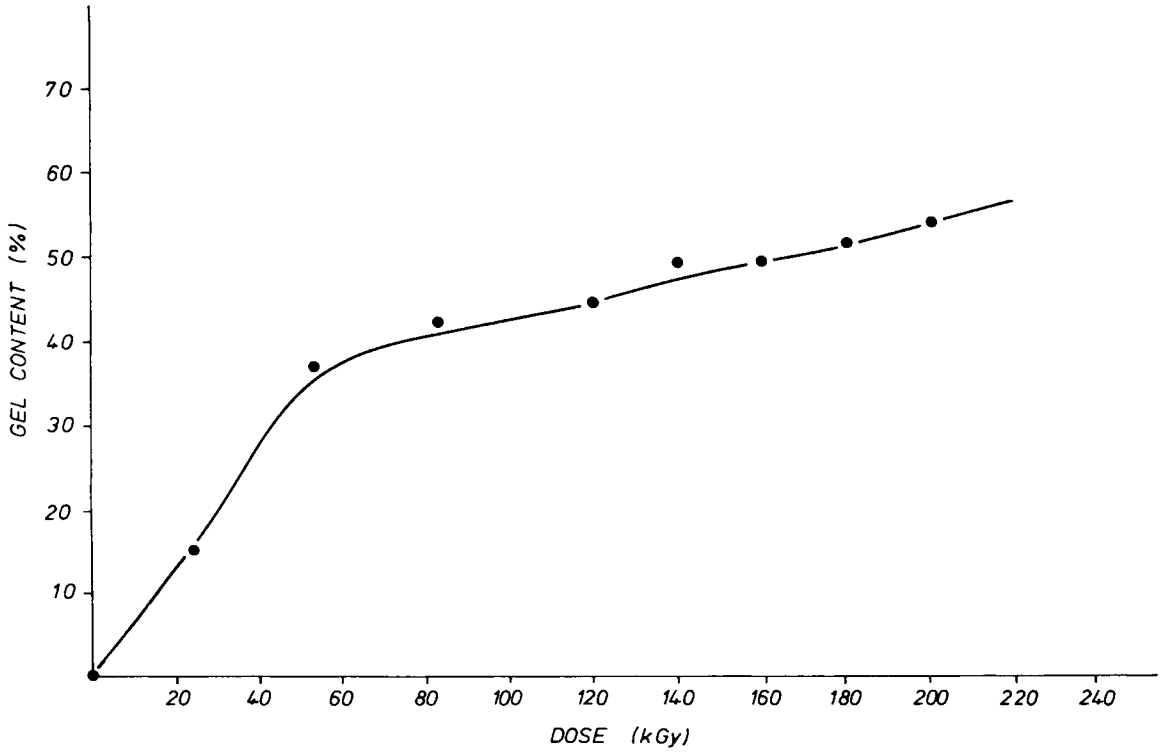

Figure 4 Gel content as a function of dose, for HOPE irradiated in acetylene.

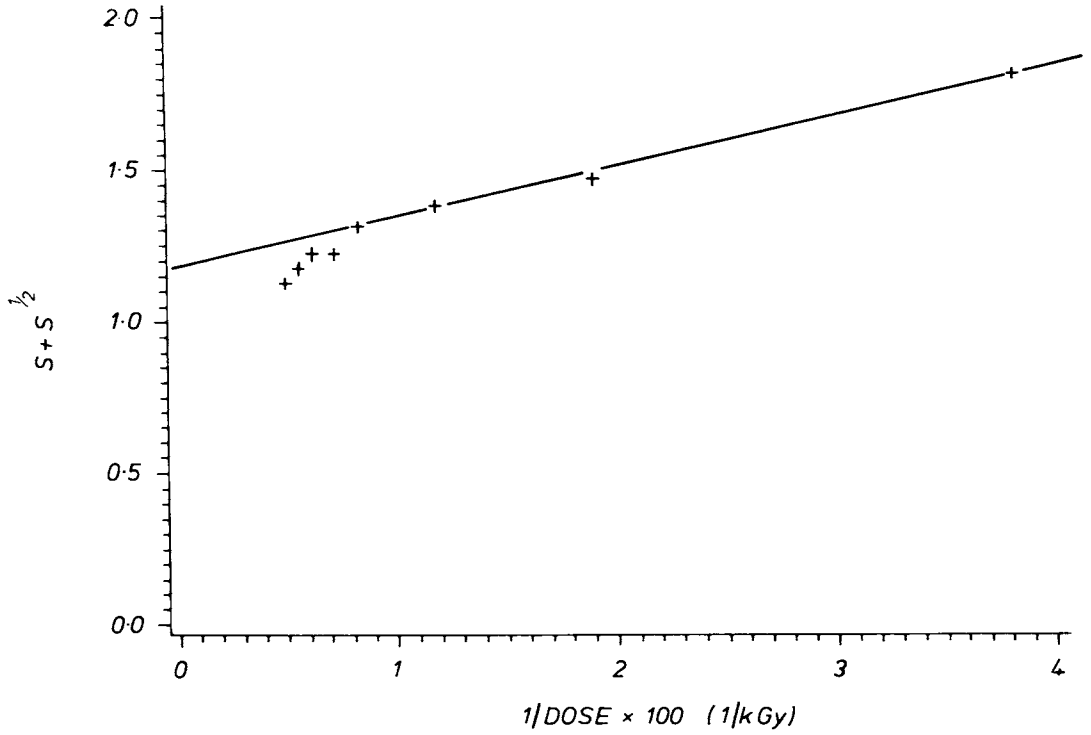

Figure 5 Charlesby–Pinner plot of HOPE irradiated in acetylene.

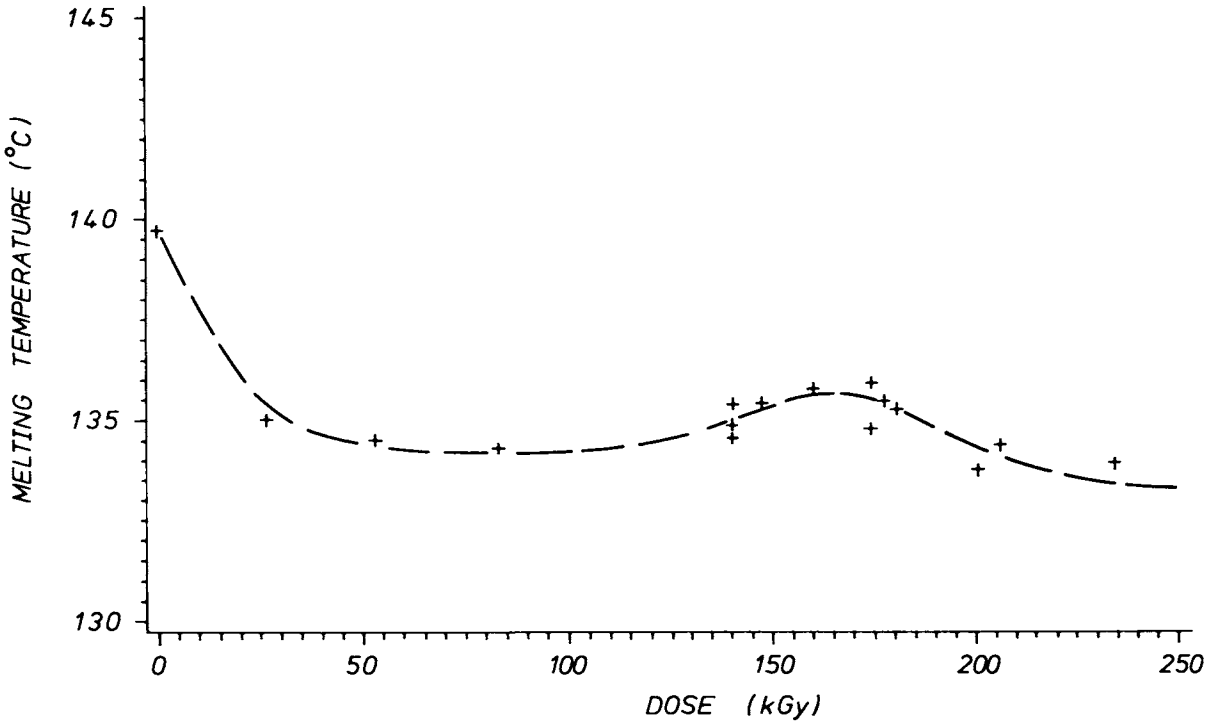

Figure 6 Melting temperature of HOPE, as a function of irradiation dose in acetylene.

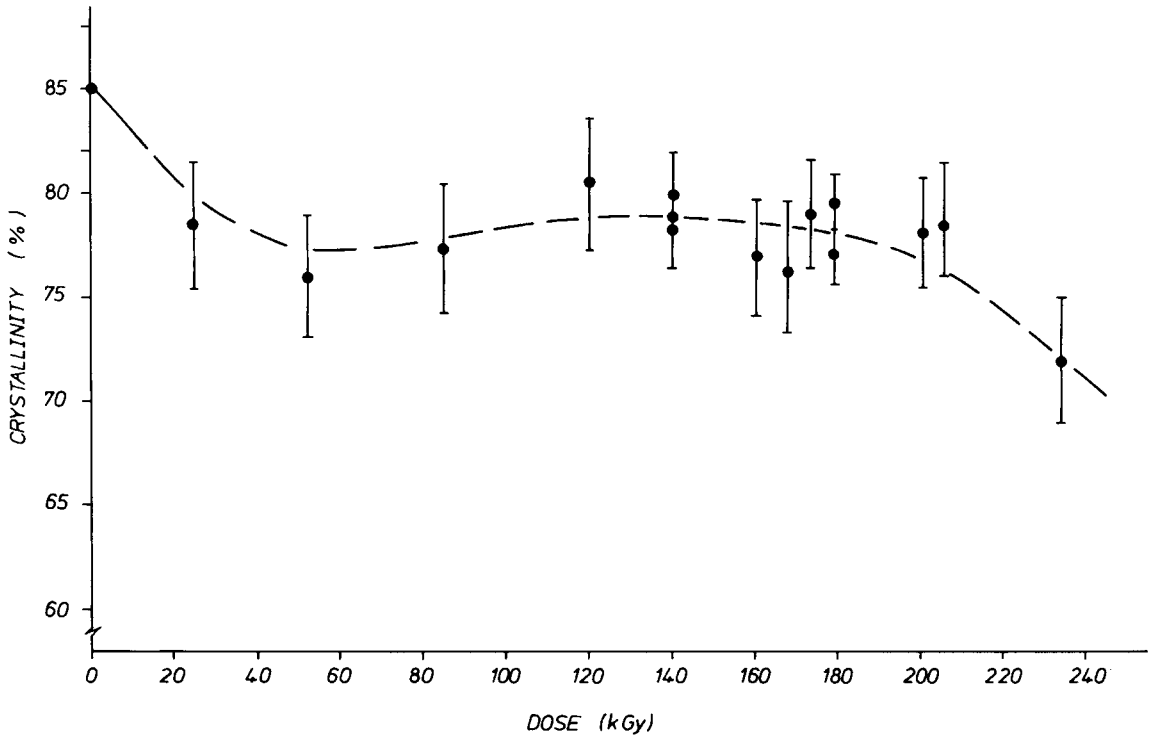

Figure 7 Crystallinity of HOPE as a function of irradiation dose in acetylene.

crease was attributed to chain scission followed by recrystallization. Clearly the results indicate that during the irradiation of HOPE in this work there is no net increase in crystallinity, but it is not possible to ascertain if the rate of recrystallization is equalled by the rate of crystallinity loss or if in fact there is no real change in the structure.

Tensile Modulus as a Function of Dose

The dependence of the tensile modulus on dose is plotted in Figure 8. At low doses there is little change in the tensile modulus. As the dose is increased, the modulus increases and passes through a maximum in the region 140–180 kGy. Higher doses result in a pronounced reduction in tensile modulus value, as chain scission predominates over chain crosslinking. The maximum in the modulus/dose relationship occurs in the same dose region as the observed rise in melting point (see Fig. 6).

The improvement in the tensile mechanical properties reported in this paper could be explained by the formation of crosslinks in the amorphous and crystalline surface regions. These crosslinks effectively stiffen the material by retarding flow in the amorphous regions and inhibiting c-axis slip in the crystalline regions.[12] Alternatively, another stiffening mechanism is that of tie molecule scission followed by recrystallization. This mechanism has been used to explain improvement in the mechanical properties of irradiated unoriented polyethylene.[13] However, the crystallinity-dose studies discussed earlier suggest that this crystallinity-induced enhancement of properties is not occurring.

Creep Strain versus Dose

The creep properties of HOPE fibers have been extensively studied by Wilding and Ward[14–16] and coworkers.[10] The creep behavior has been interpreted using a stress-activated model. At low stresses, creep is envisaged as occurring via a process of molecular rearrangement in the amorphous regions. Conversely, at high stresses creep occurs by slip between the molecular chains in the crystalline regions. Irradiating the polymer results in crosslinking in the noncrystalline regions and chain scission throughout the polymer. The dependence of the high stress process on crystalline slippages results in radiation induced crosslinking becoming less effective at high stresses. Klein et al.[10] found that increasingly high radiation doses were necessary to stiffen the noncrystalline regions and so "shield" the crystalline regions from high stresses.

The tensile creep-strain at 100 MPa as a function of time for specimens with various doses is plotted

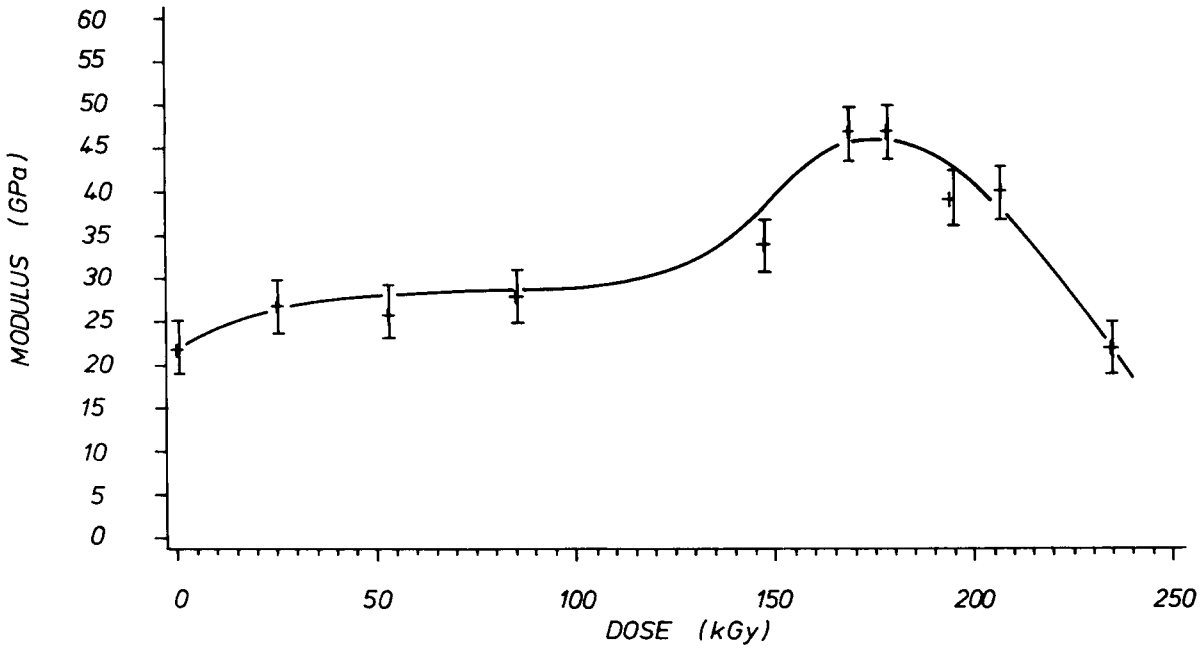

Figure 8 Initial tensile modulus of irradiated HOPE, plotted as a function of dose.

in Figure 9. This figure is typical of the tensile creep–strain behavior of the material for the stress range tested. The creep–strain time data from this Figure 9 is replotted as log(strain rate) versus strain in Figure 10. Although Wilding and Ward[14] have previously reported a leveling off in the strain rate with strain, in all the creep testing carried out on the material under investigation here, leveling off to a

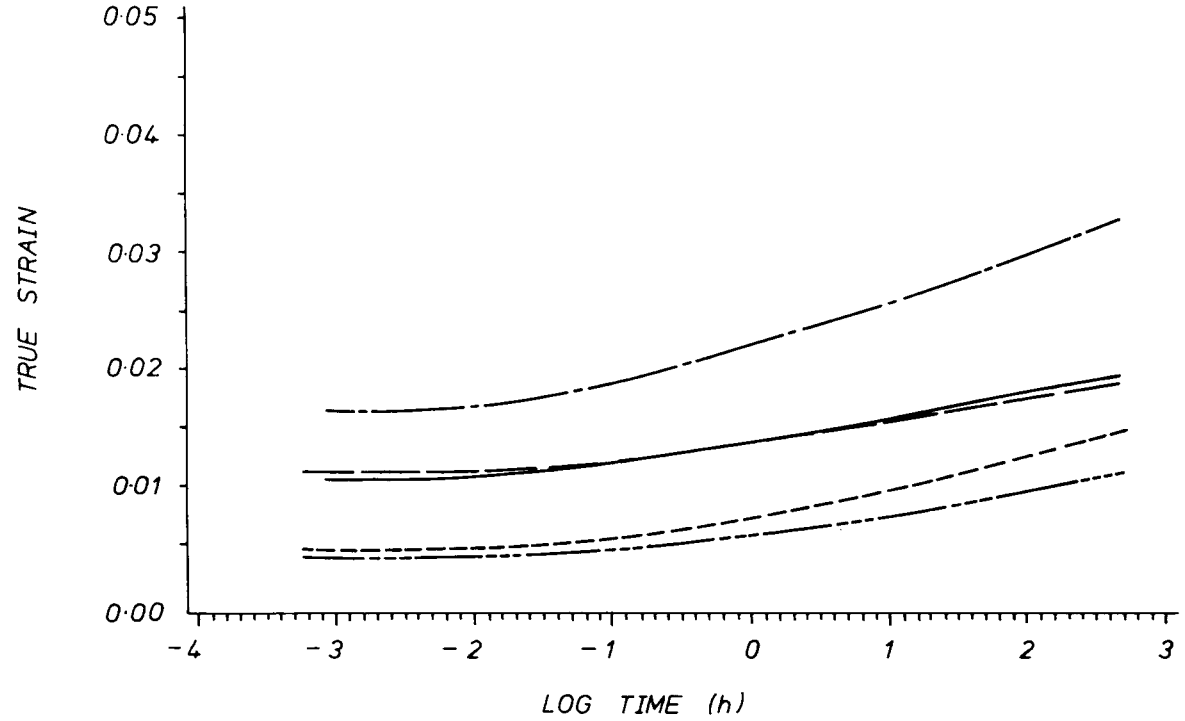

Figure 9 Creep–strain as a function of time at 100 MPa and room temperature. (—·—) 0 kGy; (——) 25 kGy, (– –) 85 kGy; (----) 140 kGy, (— · · · —) 190 kGy.

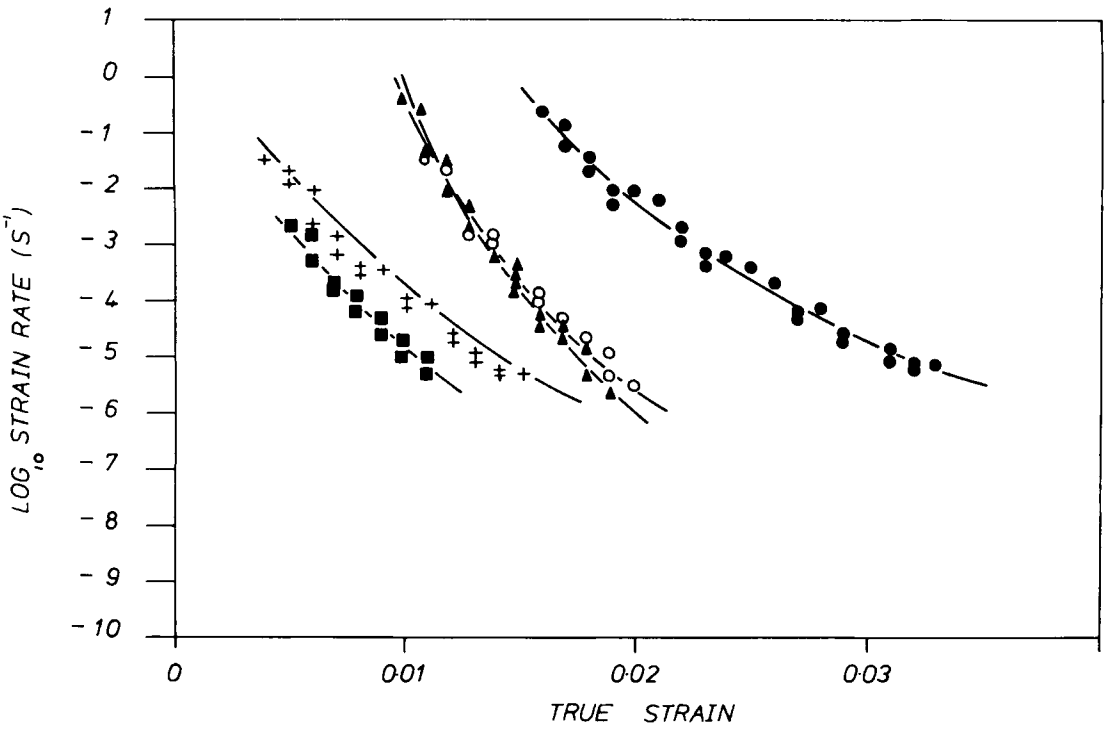

Figure 10 Log strain rate versus strain for the creep–strain time data given in Figure 9: (●) 0 kGy; (▲) 25 kGy; (○) 85 kGy; (■) 140 kGy; (+) 190 kGy.

constant creep rate was not observed, even for tests that were run at 160 MPa for periods up to 10^7 s (6 months). This constant strain rate region may occur at higher stresses, or after longer times. The characterization of the creep behavior of this material is continuing to be investigated, and will be the subject of a future report.

The tensile creep-strain time results shown in Figures 9 and 10 indicate that gamma ray irradiation in acetylene has substantially improved the creep resistance of the material. This improvement is primarily due to the greater stiffness of the material, and results from the enhanced tensile properties as shown in Figure 8. The reasons have been discussed earlier, but effectively result in the molecular relaxations being retarded.

CONCLUSIONS

These investigations have shown that the irradiation of large diameter HOPE rod improves its mechanical properties. Irradiation results in an increase in the tensile modulus which has been attributed to the formation of crosslinks within the amorphous regions and at the crystalline surfaces. These crosslinks retard the short time relaxations in the oriented polymer and result in an improvement in the tensile creep resistance of the material at a constant stress. The improvements in these mechanical properties were found to be dependent on the irradiation dose.

Irradiation of the oriented polymer was found to produce an initial drop in crystallinity and in melting point. These changes were thought to relate to the annihilation of imperfect crystallites.

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