Effect of High Energy Radiation on the Stress-Relaxation of Ultra-High Molecular Weight Linear Polyethylene

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Synopsis

Stress–relaxation behavior was studied in ultra-high and normal molecular weight linear polyethylenes (UHMWPE and NMWPE) as a function of radiation dose over the range 0–128 Mrad. Irradiation up to 16 Mrad raises the crystallinity in both types of PE, as demonstrated previously,[1] and thus increases the initial modulus. Also, the initial modulus of NMWPE is higher than that of UHMWPE because the former has a higher crystallinity. Consequently, the initial stress at a constant imposed strain of 1% varies greatly between the two materials. To eliminate the effect of this initial difference on relaxed stress, the stress–relaxation data were normalized with respect to the initial stress and plotted as the fraction, retained stress after time t/initial stress. The normalized plots show no significant difference between NMWPE and UHMWPE in their stress–relaxation behavior. For both materials stress retention improves progressively with increasing radiation dose, the percentage improvement being greatest at long times (50% at 50 h and 64 Mrad, compared with 6% at 10^{-2} h). These results are interpreted to indicate that radiation crosslinking in the amorphous phase is independent of molecular weight and preferentially retards those molecular motions responsible for short relaxation times. The motions in question could involve molecular flow in the amorphous phase or "pull out" of tie molecules from the crystalline lamellae.

INTRODUCTION

Stress–relaxation in solid polymers, together with the associated phenomenon of creep, is one of the major problems facing their use in engineering applications. The incorporation of fillers and fibers is effective in reducing the time dependence of mechanical properties, but the residual behavior of the matrix polymer cannot be eliminated. High levels of crystallinity or of crosslinking (thermosetting polymers) also improve time-dependent behavior, indicating that stress–relaxation and creep occur primarily by molecular relaxations in the amorphous phase.

The radiation crosslinking of thermoplastics after they have been formed to their final shape is therefore an obvious method to improve resistance to stress–relaxation. It is known that such crosslinking occurs preferentially in the amorphous phase[2–4] though, in PE at least, the crystals are also affected.[5] Too much radiation also causes deterioration of bulk properties through

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TABLE I
Some of the Physical and Mechanical Properties of the Two Polyethylenes Examined

Material	Intrinsic viscosity[a] (dL/g)	Molded sheet density (g/cm^3)	Young's modulus (psi)	Yield stress (psi)
UHMWPE	19.8	0.928	1.0×10^5	2.8×10^3
NMWPE	2–4	0.962	1.7×10^5	4.1×10^3

[a] M_w for the NMWPE was approximately 2×10^5 and its melt index was around 0.3. These data were not available for the UHMWPE.

photooxidation and chain scission, so that there is a practical limit to the attainable improvement.[5]

UHMWPE has poorer creep/stress-relaxation behavior than NMWPE, but otherwise exhibits some outstanding mechanical properties. The possibility exists, therefore, of seeking to reduce time dependence in UHMWPE by radiation crosslinking without sacrificing its excellent toughness characteristics. The purpose of the work described here was to investigate this possibility using electron irradiation from a Van de Graaff machine. NMWPE was also studied as a "control" material.

The tensile creep and stress–relaxation behavior of NMWPE has been extensively reported,[6-19] but this is not the case for UHMWPE. This is in spite of the fact that UHMWPE has been reported in the trade literature to have a unique combination of mechanical properties and to be an ideal material for many engineering applications.[20]

MATERIALS AND EXPERIMENTAL PROCEDURES

The materials used in this study were a Dow experimental UHMW linear polyethylene and a commercial NMW linear polyethylene. Some of the properties of these materials are listed in Table I.

All specimens were compression molded in a Pasadena Hydraulics steam-heated press using a preweighed quantity of PE powder in a 1/8-in. picture-frame mold between aluminum foil sheets. The molding cycle was as follows:

Molding temperature	200°C
Time at 50 psi	5 min
Time at 1000 psi	8 min
Water-cool platens to 20°C (during cooling the pressure was gradually increased to 1250 psi to avoid sink marks)	5 min

The compression-molded sheets were exposed to radiation with 2 MeV electrons at a beam current of 250 μA in a Van de Graaff accelerator, yielding a radiation dose of 0.5 Mrad per pass through the beam. Radiation doses of 0, 4, 16, 64, and 128 Mrad were employed.

Specimens were machined from the irradiated sheets in the form of 8 $\times 1/2 \times 1/8$ in. parallel sided strips. These specimens were loaded in tension

in an Instron testing machine to a strain of 1% on a 6-in. gauge length at a crosshead speed of 10 in./min and held at that strain. The load was monitored over a period of 70 h. Specimens were preconditioned for at least 48 h at 23°C and 50% RH before testing under these same conditions.

EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1 and 2 show the stress-relaxation data for UHMWPE and NMWPE, respectively, for various levels of irradiation. As expected, the stress decays with the passage of time, and the curves of stress vs. log (time) can each be represented reasonably well by two linear regions with a transition from "fast" to "slow" decay between 0.1 and 1.0 h for most specimens.

In UHMWPE (Fig. 1), the stress at 10^{-3} h rises slowly with the degree of irradiation from 720 to 840 psi, but a much larger irradiation effect is seen at long times where the stress retention is doubled (from 240 to 580 psi at 70 h) as the dose increases from 0 to 128 Mrad.

In NMWPE (Fig. 2), the stress at 10^{-3} h is some 50% greater than in UHMWPE, reflecting the higher Young's modulus of the higher density material. The stress at 10^{-3} h is also more strongly affected by irradiation, rising from 1100 to 1450 psi as dose increases from 0 to 128 Mrad. This is larger both absolutely and proportionately than the corresponding rise observed in UHMWPE. This effect of irradiation on retained stress can be attributed to the increase in crystallinity known to occur in PE after irradiation.[1] Scission of tie molecules by electron bombardment allows the amorphous regions to undergo fresh crystallization, giving rise to a higher modulus.

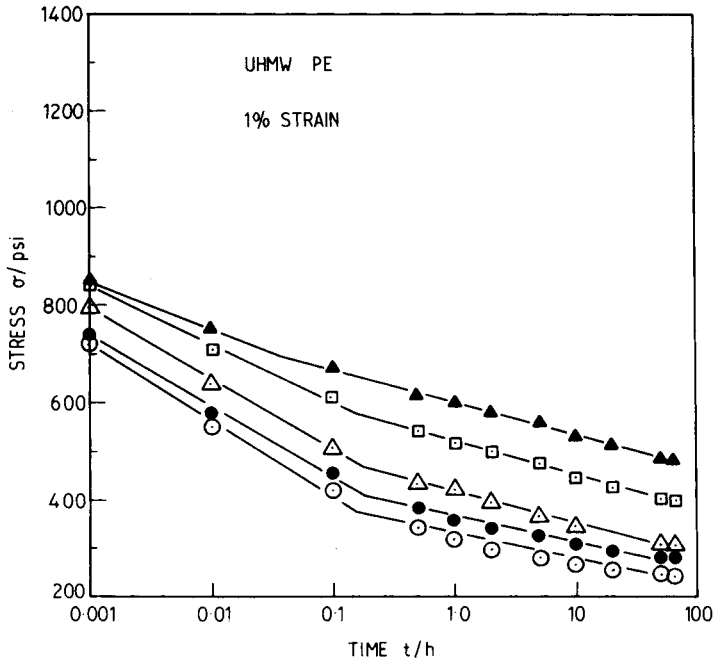

Fig. 1. Stress-relaxation data for UHMWPE at varying levels of radiation dose: (⊙) virgin; (●) 4 Mrad; (△) 16 Mrad; (⊡) 64 Mrad; (▲) Mrad.

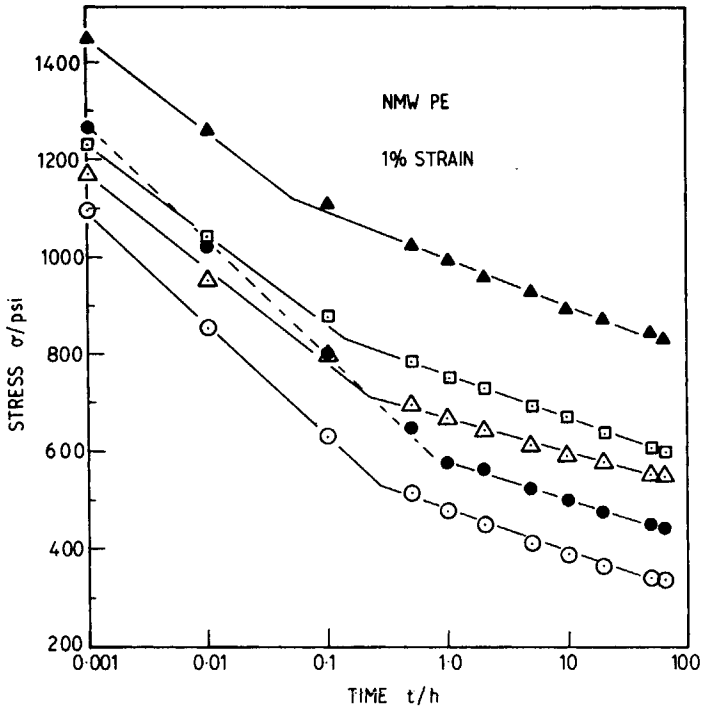

Fig. 2. Stress–relaxation data for NMWPE at varying levels of radiation dose: (⊙) virgin; (●) 4 Mrad; (△) 16 Mrad; (⊡) 64 Mrad; (▲) Mrad.

However, this cannot be the whole story, since increased crystallinity was only observed for the first 16 Mrad dose,[1] whereas the increase in initial stress (Figs. 1 and 2) continues up to 128 Mrad. This is specially noticeable for NMWPE, but less so for UHMWPE.

These observations can be explained by a combination of increased crystallinity and crosslinking in the amorphous phase. Since there is relatively less amorphous material in the NMWPE, the effect of amorphous crosslinking is more pronounced; fewer crosslinking events are needed there to create a network due to the greater proximity of crystal lamellae which also "anchor" amorphous chains. The deformations in PE up to the yield point occur largely in the amorphous phase,[21] and thus the formation of a crosslinked network in this phase raises the modulus of the "composite" of crystalline and amorphous materials.

The changes in initial stress confuse the stress relaxation data. For example, in Figure 2 it appears that the "fast" decay of stress at short times is independent of radiation dose because the stress vs. log (time) curves are (mostly) parallel in this region. This, however, obscures the fact that the stress is decaying *proportionately* more slowly at high irradiation doses.

In order, therefore, to clarify the nature of the stress–relaxation process and the effects of irradiation, the data have been replotted in Figures 3 and 4 in a normalized manner. The normalized stress is defined as $\sigma(t)/\sigma(0)$, where $\sigma(t)$ is the stress after time t and $\sigma(0)$ is the stress at *time zero*, which is defined in Figure 5.

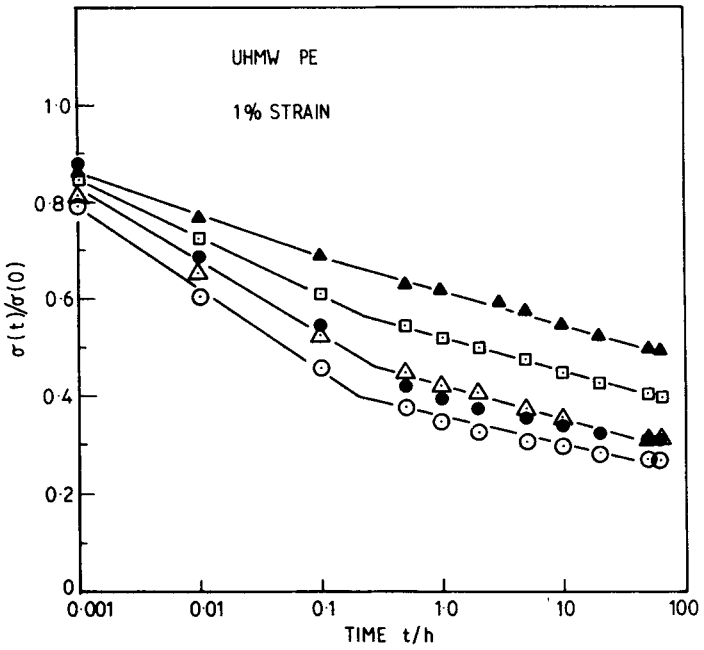

Fig. 3. Normalized stress–relaxation data for UHMWPE at varying levels of radiation dose: (⊙) virgin; (●) 4 Mrad; (△) 16 Mrad; (⊡) 64 Mrad; (▲) Mrad.

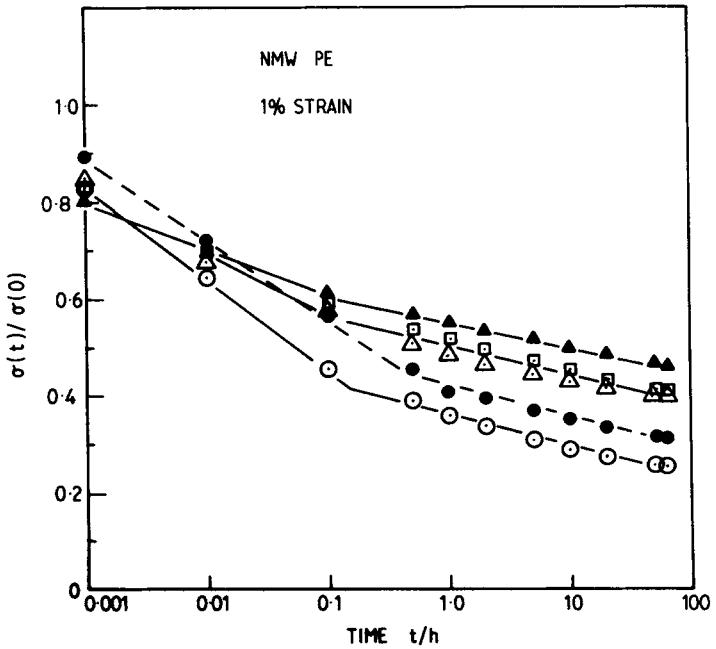

Fig. 4. Normalized stress–relaxation data for NMWPE at varying levels of radiation dose: (⊙) virgin; (●) 4 Mrad; (△) 16 Mrad; (⊡) 64 Mrad; (▲) Mrad.

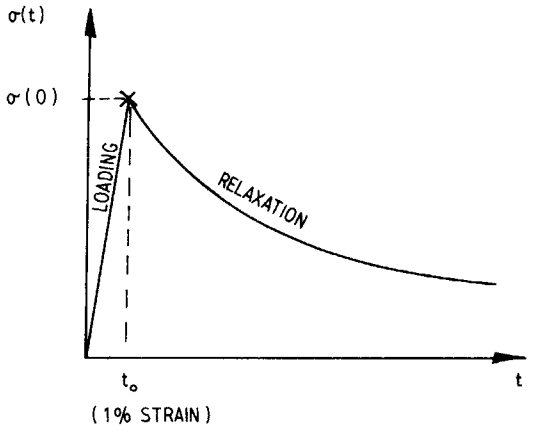

Fig. 5. Schematic diagram showing the present stress–relaxation experiment including a definition of "zero time."

Figure 3 is the normalized plot for UHMWPE and shows clearly the significant retardation of stress–relaxation caused by progressive irradiation. It is also apparent that the major effect of irradiation is upon the "fast" relaxation region at short times (< 0.1 h). At the highest dose of 128 MRad the stress decay becomes almost linear over the whole time range. The same is true of the NMWPE (Fig. 4), irradiation progressively suppressing whatever relaxation mechanism is responsible for the "fast" decay process at short times. There is some evidence (comparing Figs. 3 and 4) that, at the highest dose of 128 MRad, stress–relaxation is more severe in NMWPE than in UHMWPE, and this could be a molecular weight effect (UHMWPE being less damaged by the chain scission process that accompanies radiation crosslinking, for example, because of its initially high molecular weight). Overall, however, the behavior of the two polyethylenes is remarkably similar in the normalized plots. To a first approximation, therefore, there is no obvious molecular weight dependence of stress–relaxation in either unirradiated or irradiated materials. This conclusion is further supported by the "crossplot" of the data shown in Figure 6. Here we have plotted the normalized stress against radiation dose for both materials at two selected times—namely 10^{-2} and 50 h. The data for UHMWPE and NMWPE superimpose very well except at low irradiation doses where some variability is found. There might even be a small peak in normalized stress in the region of 10 Mrad, but there are insufficient data to resolve this point. The scatter in the data occurs in the same range of doses as does the growth in crystallinity, and, although the primary effect of this process has been factored out by normalization, there could be secondary effects of an unspecified kind, giving rise to unexpectedly high normalized stress at 5–15 Mrad dose.

Proportionately, normalized stress is increased by irradiation much more at long times than at short times. Stress retention at 50 h is improved by 50% at 64 Mrad and nearly 100% at 128 Mrad, while stress retention at 10^{-2} h improves only 6–10% at 64 Mrad and 10–25% at 128 Mrad. At first sight, this would suggest that it is mechanisms with long relaxation times that are being suppressed by irradiation, but the earlier data (Figs. 3 and 4) demonstrate

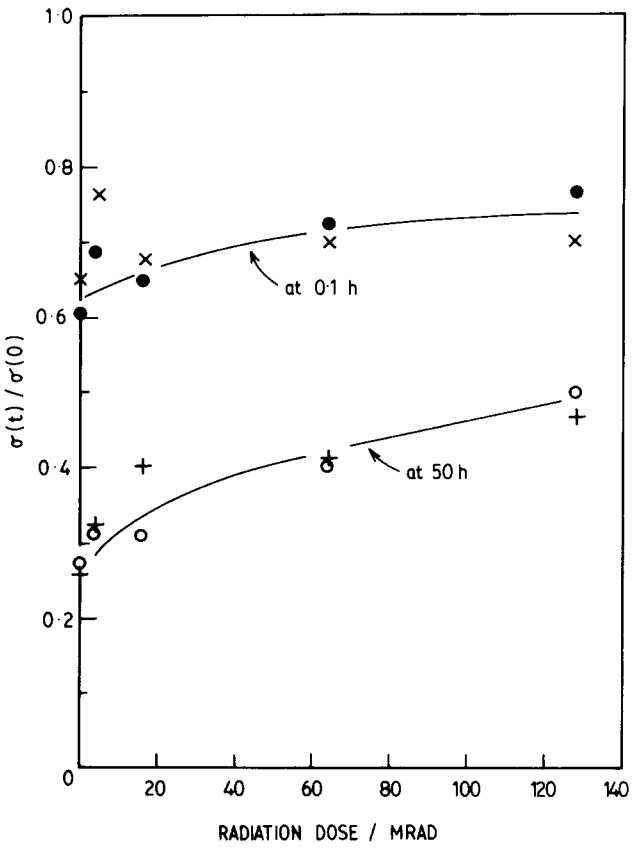

Fig. 6. Variation of the normalized retained stress with radiation dose for both UHMWPE (●, ○) and NMWPE (×, +).

that the opposite is the case. In irradiated material the steep decay of stress at short times is prevented while decay rates at long times are similar for all doses. It seems evident that the creation of a rubberlike network in the amorphous phase by irradiation crosslinking inhibits flow processes responsible for short-term relaxation, leaving only long-term viscoelastic network relaxations to control stress decay. Phenomenologically, this progressively transforms the material from one with a broad (or bimodal) relaxation spectrum to one with a narrow (or monomodal) relaxation spectrum.

The short-term flow processes inhibited by crosslinking are most likely to be taking place in the amorphous phase due to the presence of free molecules (as opposed to tie molecules). Low molecular weight material is expected to be found in the intercrystalline regions but the similarity in behavior between NMWPE and UHMWPE discourages any attempt to explain the flow processes in terms of short molecules. A possible alternative explanation is that the short term flow processes are associated with *c*-axis slip in the crystal lamellae themselves. When the specimen is stressed, short tie molecules impose large local stresses on the lamellae to which they are attached (we have argued elsewhere that most of the load is carried by such tie molecules in preyield deformation). It has been established experimentally that irradiation

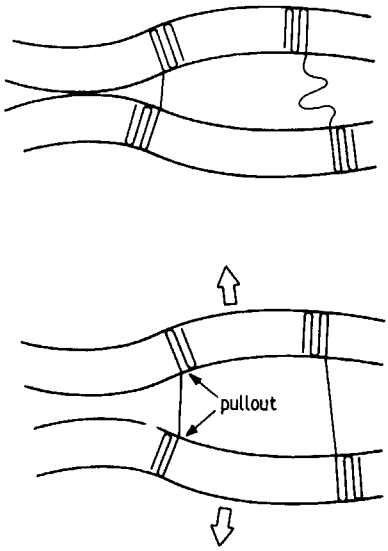

Fig. 7. A schematic diagram showing the deformation process in which the short tie molecules "pull out" of the crystal lamellae to more evenly distribute the load.

of single crystals of polyethylene strongly inhibits *c*-axis slip.[21] The flow mechanism which we observe to be suppressed may, therefore, be a process in which short tie molecules "pull out" from the crystal lamellae until the load is more evenly distributed over a larger population of tie molecules (see Fig. 7).

One advantage of this explanation is that a crystallographic deformation mechanism is very fast compared with viscoelastic relaxations, and this would account for the preferential suppression of short-time processes observed in this study. It also avoids the difficulty of explaining why "flow" should have shorter relaxation times than network deformation in the *absence* of low molecular weight fractions.

We must leave open which of the two proposed "flow" mechanisms is really operative.

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