The Effect of γ Radiation on the Physical Structure and Mechanical Properties of Ultrahigh Molecular Weight Polyethylene

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Synopsis

Ultrahigh molecular weight polyethylene has been irradiated using a cobalt 60 source to give received dose between zero and 50 Mrad. Irradiated specimens were subjected to tensile characterization, dynamic mechanical analysis, and differential scanning calorimetry. Changes in tensile and dynamic mechanical properties following irradiation arise from both molecular rearrangement and from increased crystallinity following scission of long interlamella tie chains. The effects of post-irradiation aging on mechanical properties are associated with increasing crystallinity resulting from decomposition of metastable groups formed in the amorphous region during irradiation. Irradiated materials have been subject to sinusoidal stressing between 0.275 and 0.55 of yield stress for 100,000 cycles, and changes in mechanical and physical properties measured. Increased resistance to creep during stressing was observed with the irradiated materials, behavior which is consistent with previously observed changes in crystallinity and crosslink density. Overall property changes measured following stressing were small compared with those induced by the initial irradiation.

INTRODUCTION

The designation of polyethylenes as ultrahigh molecular weight is accepted as indicating a material with an average molecular weight greater than 2 million as measured by light scattering. The technical advantages offered by these materials over conventional polyolefins are superior wear and creep characteristics,[1] which taken in conjunction with physiological inertness has encouraged their use for medical prostheses. Some important differences exist between the behavior of the ultrahigh molecular weight grades and conventional polyethylenes, principally arising from the effects of hindered molecular mobility due to chain entanglement. These behavioral differences may be expected to influence the response of the material to γ radiation.

Exposure of all polyolefins to γ radiation results in both chain scission and crosslinking processes,[2,3] with consequent changes in mechanical behavior. Increase in modulus is usually associated with predominance of the crosslinking reaction, while changes in elongation at break are associated with a reduced ability to undergo plastic deformation as crosslink density increases. Most work on irradiation effects has concentrated on standard mechanical testing immediately after irradiation; however, a number of studies have shown the importance of aging affects in irradiated material.[4-6] In particular, it has been suggested that peroxide linkages play an important part in the aging of materials irradiated in the presence of air.[4] Technologically, long-term

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postirradiation aging is important, and observation of such effects ought to form part of any comprehensive study of radiation-induced changes. Similarly, in many practical applications behavior of materials under dynamic loading is important. Dynamic stressing must result in energy dissipation by molecular damping processes, which may lead to chemical and morphological changes. For this reason the effect of cyclic stress loading on the properties of materials that have been subjected to irradiation ought to be of interest but has received little experimental attention.

EXPERIMENTAL

The material used in this investigation was Hostalen GUR, which has a number average molecular weight of 3–4 million. Extremely high melt viscosity precludes the use of injection molding for sample preparation and therefore tensile specimens, after BS2782, were machined from compression-molded block. Irradiation was carried out in air, using a cobalt 60 source at a dose rate of 0.156 Mrad h^{-1} to give received doses between 0 and 50 Mrad.

Tensile characterization was performed using standard test methods. Dynamic mechanical analysis was carried out using a DuPont 982 resonant frequency instrument and specimens for this were machined from the central parallel section of the tensile dumbbell. Percentage crystallinity and melting temperature were measured by differential scanning calorimetry, a DuPont 910 instrument being used. Samples were taken from the parallel section of the tensile specimens before and after cyclic stressing. Previous work on irradiated polymers[7] has shown a double scan procedure to be of value. All crystallinity values quoted are the average of at least three individual determinations.

Dynamic stress loading was performed on a Dartec M1000/RD servohydraulic test frame with a 9500 microprocessor system programmed to provide sinusoidal tension–tension loading with a frequency of 5 Hz. Upper stress limit was 0.55 of yield stress and lower load limit was 0.275 of yield stress as established by tensile testing. Energy input can be calculated from the standard viscoelastic relationship:

$$\text{energy loss per cycle} = \sigma_0 \cdot \epsilon_0 \cdot \tan \delta$$

where σ_0 is the peak stress amplitude, ϵ_0 the peak strain amplitude, and $\tan \delta$ is loss tangent. This indicates a total energy dissipation of approximately 3.7 kJ per specimen for 100,000 cycles. Temperature increase in the specimen during testing was found to be less than 2°C. Maximum strain per cycle was monitored to provide dynamic creep information.

In view of the importance of long-term aging effects in polyolefins irradiated in air, all testing, other than experiments specifically investigating aging, were carried out within 25 days of irradiation.

RESULTS AND DISCUSSION

The effect of postirradiation aging on material that had received 10 Mrad dose is detailed in Table I. Aging results have been considered in detail elsewhere[4] and have been interpreted as arising from a general mechanism of

TABLE I
Variation in Crystallinity with Post-Irradiation Aging[a]

Aging time (days)	Crystallinity (%)
3	52.1
11	51.0
25	53.2
50	53.2
150	56.1
335	57.8

[a] Dose received 10 Mrad.

breakdown of metastable peroxy and hydroperoxy groups formed during the initial irradiation. The increase in crystallinity is associated with structural rearrangement following the time-dependent scission process. The results obtained provide a reference against which the effects of dose and cyclic stressing can be judged. Percentage crystallinity values at various dose levels, and following cyclic stressing, are detailed in Table II. Considering the dose-dependent data, certain trends can be identified. First, there is an increase in percentage crystallinity with dose. This arises from the tie chain scission process previously observed in this material[8,9] and reflects the increase in crystal perfection as the released chains rearrange into the lamellae, thus increasing lamellae thickness and reducing disorder on the surface. This observation also reinforces the proposal[10] that scission and crosslinking processes are confined to the amorphous phase.

Rescan results show a reduction in percentage crystallinity irrespective of received dose. The difference for the unirradiated material, which is 3.4%, can be accounted for in terms of the differences in cooling rate between the initial material and the rescan. The compression-molded blocks were cooled at a rate of 1.5°C min^{-1}, while the recrystallization in the calorimeter occurs at a mean rate of 3°C min^{-1}. However, the differences in crystallinity between the

TABLE II
Effect of Dose and Cyclic Stressing on Crystallinity

Dose received (Mrad)	Crystallinity (%)	
	Original	Following stressing
0	44.2	49.3
Rescan	40.8	47.0
2.5	50.8	51.2
Rescan	45.8	45.1
5.0	51.6	50.6
Rescan	44.5	43.9
10	53.2	50.5
Rescan	47.1	41.5
20	56.7	51.7
Rescan	44.9	41.7
50	55.3	52.7
Rescan	43.5	40.7

original and rescanned samples show a general increase with dose received. This suggests that during the melting and recrystallization process used in the rescan technique, radiation-induced crosslinks are effective to hindering molecular diffusion processes. This trend is again evident in the results of the material examined after dynamic stressing.

The initial increase in percentage crystallinity following dynamic stressing is assumed to arise from mechanical scission of the interlamella tie chains and is an equivalent process to time-dependent tie chain scission observed in aging studies. The reduction in crystallinity at higher dose levels following stressing is difficult to explain, as the strain level experienced by the material is below that expected to have a significant disruptive effect on the crystal lamellae.

The changes in yield stress and elongation at break with dose are given in Figure 1. Previous work[9] at low irradiation dose has shown these properties to be most sensitive to structural change. The mechanical properties of the

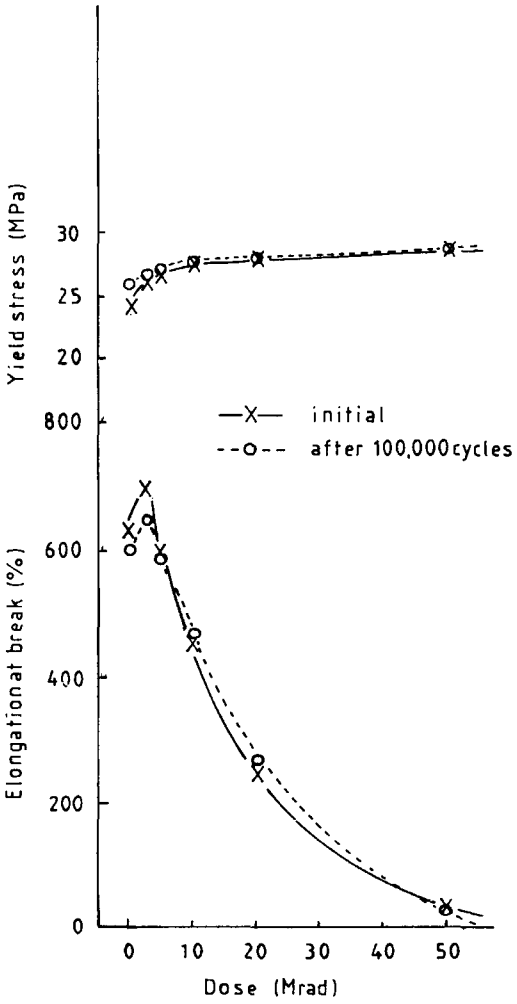

Fig. 1

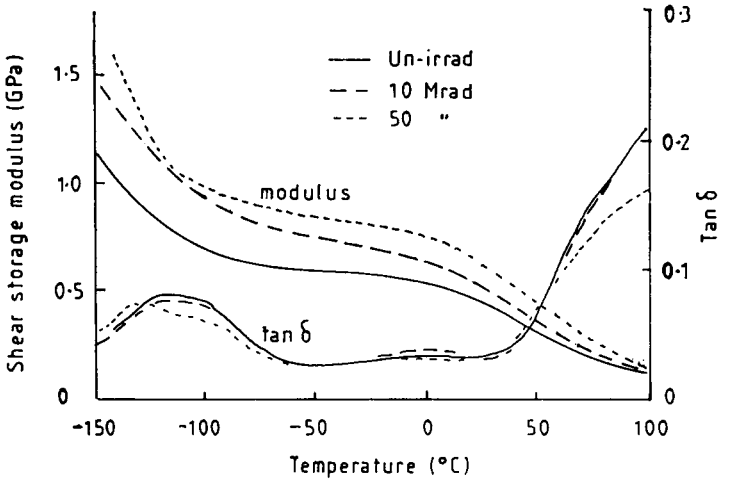

Fig. 2

material after dynamic stressing are also shown in this figure. Dynamic mechanical behavior of unirradiated and 10 and 50 Mrad materials are illustrated in Figure 2. Relative changes in strain observed during the dynamic creep tests are shown in Figure 3.

The results obtained from tensile testing of the initial irradiated materials are generally similar to those obtained previously.[9] The high sensitivity of elongation at break to dose received is presumed to arise from an increasing

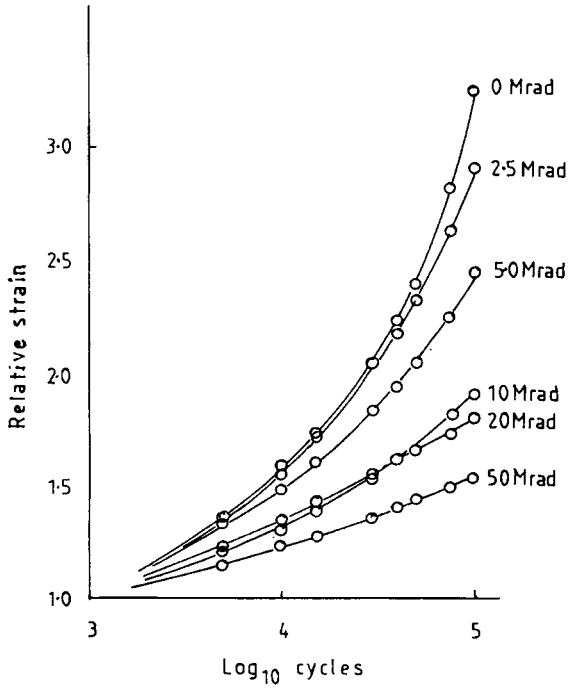

Fig. 3

TABLE III
Effect of Dose on Dynamic Mechanical Properties

Dose received (Mrad)	Original		Following stressing	
	Shear storage modulus (GPa)	tan δ	Shear storage modulus (GPa)	tan δ
0	0.407	0.036	0.492	0.029
2.5	0.482	0.039	0.505	0.030
5.0	0.514	0.032	0.508	0.030
10	0.538	0.031	0.555	0.028
20	0.555	0.030	0.578	0.030
50	0.599	0.030	0.652	0.032

inability to undergo plastic deformation and flow as crosslink density increases with dose received. The changes in crosslink density, or the onset of crosslinking in linear systems, can be expected to affect the ratio of the viscous to elastic response of the material with subsequent changes in dynamic mechanical behavior. However, the tan δ results at 20°C, detailed along with the shear shortage moduli in Table III, remain relatively constant regardless of dose or stress history.

Comparing shear storage modulus with percentage crystallinity, for both original and stressed materials, shows a linear correlation within each set of data. This confirms the important role of the crystallinity change in determining the stiffness of these materials.

Elongation at break shows no significant change following stressing. As this property is known to be sensitive to small structural changes, it must be concluded that the mechanical energy imparted to the material by cyclic stressing has caused little additional structural alteration in the amorphous region of the polymer.

The creep data in Figure 3 may be usefully analyzed as a power law relationship[11] in which the natural logarithm of relative strain is plotted against the natural logarithm of number of cycles. The power indices obtained from linear regression analysis, as shown in Table IV, give a relative measure of the tendency of the material to creep under the cyclic stress conditions used.

A progressively increasing resistance to creep with dose is observed throughout the range examined. This behavior is consistent with both the progressive increase in crystallinity, as tie chain cleavage occurs, and with the development of crosslinks between chains in the amorphous region.

TABLE IV
Variation in Power Law Index with Received Dose

Dose (Mrad)	0	2.5	5	10	20	50
Index	0.284	0.247	0.203	0.156	0.127	0.094

CONCLUSIONS

The results obtained emphasize the importance of the interlamella tie chains in determining the physical and mechanical response of UHMWPE to irradiation. While there is no reason to believe that there are any substantial chemical differences in behavior at the molecular level between different types of polyethylene, the extremely high molecular weight of the tie chain molecules in UHMWPE permits morphological modification processes that are not available to lower molecular weight materials. This leads to significant behavioral differences after irradiation.

Following energy input from mechanical stressing, only minor changes in the mechanical and physical properties of the material were observed. This indicates that in practical applications the changes in material properties arising from in-service dynamic loading are likely to be negligible when compared with changes arising from chemically initiated aging processes.

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