Effect of high-energy radiation on the uniaxial tensile creep behaviour of ultra-high molecular weight linear polyethylene

S. K. Bhateja*
354 Building, Saran Converted Products Research, The Dow Chemical Company, Midland, Michigan 48640, USA

and E. H. Andrews
Department of Materials, University of London, Mile End Road, London E1 4NS, UK
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The tensile creep (and other tensile) properties of ultra-high molecular weight polyethylene (UHMW PE) have been determined before and after electron beam irradiation and compared with similar results on normal molecular weight high-density polyethylene (NMW PE). In both polymers, irradiation increases the tensile modulus and the yield stress whilst reducing creep. The major effects occur over the first 20 MRad irradiation dose, though creep strain continues to diminish with dose in UHMW PE up to 64 MRad. Most of the effects can be attributed to crosslinking in the amorphous phase, though the rise in yield stress seems to require crosslinking in the crystalline phase, and the initial rise in modulus in UHMW PE seems to reflect a rise in crystallinity. Comparison with other polymers shows that the creep behaviour of UHMW PE remains relatively poor, even after irradiation. The improvements obtained may, however, be significant in applications where creep resistance is of secondary importance compared with, say, impact and wear resistance, in which UHMW PE excels.

Keywords High-energy radiation; uniaxial tensile creep behaviour; polyethylene; tensile properties

INTRODUCTION

Various aspects of the creep behaviour of polyethylene have been discussed in the literature, some of which are briefly reviewed below. The tensile creep of both low-density polyethylene (LDPE)[1-6] and high-density polyethylene (HDPE)[5,7-11] has been investigated, attention being given to the effects of both internal and external variables. For instance, the influence of density[7,8], melt flow index[7], molecular weight[12,13] and temperature[8,14-16] on the tensile creep behaviour of polyethylene has been examined.

The long-term creep behaviour of polyethylene has also been studied. For instance, tensile creep data for both LDPE and HDPE up to 10000 h (approximately one year) has been presented[17], while LDPE has been studied for up to 16 years[2,3,6]. Attempts have also been made to extrapolate and predict the long-term creep behaviour from a small number of short-term experiments[18,19].

Oriented polyethylenes have received some attention[20-25]. The tensile creep behaviour of uniaxially oriented LDPE[20-22] and of ultra-drawn, ultra-high modulus HDPE filaments[25] has been examined, and the temperature dependence of the tensile creep compliance of uniaxially[23] and biaxially [24] oriented HDPE can be predicted by simple, mechanical models of the type proposed by Takayanagi[26].

Although creep measurements are most easily made under tension, creep data under several other stress states have also been reported (compression[27], superimposed hydrostatic pressure[28-30], and other stress states[31,32]). Several different non-linear theories, used to describe the creep response of HDPE under multiaxial loading, have been evaluated and compared[33].

Creep failure and fracture behaviour of polyethylene were studied by Goldfein[9], who described the creep and rupture of polyethylene by an equation involving only one material constant, and by Zapas and Crissman[10,11], who related the tensile creep and failure of HDPE to the applied stress level, the molecular structure and the environment.

Despite all the work presented in the literature, no work on the creep behaviour of UHMW PE was reported until recently[34,35]. The influence of molecular weight and its distribution on the creep and stress-relaxation behaviour of polymers has been discussed in general terms by Nielsen[12] and Martin *et al.*[13], but none of the data or the discussion pertains to UHMW PE. Limited data on the tensile, compressive and flexural creep behaviour of UHMW PE as a function of temperature are available in ref. 34. Also, the uniaxial tensile creep response of UHMW PE at 23°C was examined by the present author and compared with that of normal molecular weight linear polyethylene (NMW PE)[35]. It was found that, at all the stress levels examined, the creep deformation at a given time was substantially higher in UHMW PE than that in NMW PE.

UHMW PE has been reported[36-38] to have a unique combination of good properties, such as wear and abrasion resistance, impact and impact–fatigue resistance, etc., which makes it a good candidate for many different applications, such as gears, sprockets, wear

* New address 201-2E-08, 3M Center, St. Paul, MN 55148, USA

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Table 1 Materials employed, together with some of their physical and mechanical properties

Material[a]	Reported intrinsic viscosity (dl g^{-1})	Density of moulded sheets (g cm^{-3})	Differential scanning calorimetry (d.s.c.)		Crystallinity calculated from		Young's modulus	
			Peak melting temperature (°C)	Heat of fusion (cal g^{-1})	Density (%)	Heat of fusion (%)	(x10^{-5} psi)	(GPa)
UHMW PE	19.8[b]	0.928	134	32.6	48.6	46.8	1.0	0.69
NMW PE	2.7[c]	0.962	136.5	49.0	72.9	70.3	1.7	1.17

[a] Supplied by Dow Chemical Co.
[b] The intrinsic viscosity measured in decalin at 135°C; although the molecular weight is difficult to measure precisely, weight average molecular weight, $M_W > 2 \times 10^6$; melt index = 0
[c] $M_W \sim 207\,000$, as measured by g.p.c.; melt index ~0.3

plates, and liners for conveyers and ball mills, etc.[39,40]. However, the poor creep response of UHMW PE could impose limitations on the use of this material. Potential means of improving the creep behaviour of UHMW (e.g. by increasing the crystallinity, introducing crosslinks, or using fillers or reinforcements) were proposed earlier[35], and the present paper examines the use of one such technique. In particular, the effect of electron beam radiation on the uniaxial tensile creep behaviour of UHMW PE is evaluated and compared with that of NMW PE and other polymers.

MATERIALS

The two materials examined, together with some of their relevant physical, thermal and mechanical properties, are listed in *Table 1*. The densities of the moulded sheets were measured in a density–gradient column using toluene and chlorobenzene as the two miscible liquids. The thermal data (i.e. the peak melting temperature and the heat of fusion) were obtained on a Perkin–Elmer DSC-2 instrument using a scan speed of 20°C min^{-1}. The NMW PE resin used in the present work is the same as that in ref. 35, and the UHMW PE resin is the same as UHMW PE-'A' in the same paper.

EXPERIMENTAL

Sheets, 0.32 mm in thickness, were compression moulded in a steam-heated Pasadena Hydraulics Press. A pre-weighed quantity of polyethylene powder was placed in the picture-frame mould, held between two lubricated aluminium foils and back-up ground steel plates, and subjected to the following moulding cycle:

Moulding temperature	~200°C
Time at 0.25 MPa (~50 psi) nominal pressure	~5 min
Time at 6.9 MPa (~1000 psi)	~8 min
Water-cool the press-platens to ~25°C	~4 min
During cooling, gradually increase pressure to 8.6 MPa (~1250 psi) to avoid sink marks	

These sheets were crosslinked by exposure at ambient conditions (air, room temperature) to electron beam radiation in a Van de Graaff accelerator. The sheets were irradiated with 2 meV electrons with a beam current of 250 μA, delivering a dose of 0.5 MRad per pass through the beam. Radiation doses of 0, 4, 16, 64 and 128 MRad were employed.

Creep measurements were made on 1.27 cm wide and 10 cm long specimens machined out of the moulded and irradiated sheets. These specimens were loaded in tension to three different *nominal* (based on original cross-sectional area) stress levels: 6.9 MPa (~1000 psi), 10.3 MPa (~1500 psi) and 11.7 MPa (~1700 psi). Elongations on a 5 cm gauge-length were monitored at various times, up to 1000 h, with a strain-gauge extensometer and fed directly into a computer. Elongations over 8% (the limit of the extensometer) were measured with a cathetometer having an accuracy of ± 0.005 mm. For each material, one fresh specimen was tested at each different stress level and irradiation dose. All test specimens were preconditioned for 48 h at the testing conditions (23°C and 50% relative humidity).

The uniaxial tensile load–elongation behaviour of different specimens was also evaluated according to ASTM Standard D-638. The tensile creep data for both materials are presented in the form of *nominal* (based on the original length) strain *versus* time plots. The data were automatically recorded and plotted by the computer at fairly close time intervals; for each decade of time, 36 data points at regularly spaced time intervals were collected. In fact, for any given specimen, the data points were so close that they almost appeared to form a continuous curve. However, the computer plots were not dark enough to be reproduced satisfactorily and, thus, had to be redrawn. In redrawing the plots, the individual data points were purposely omitted for convenience; instead, the data are represented by smooth, continuous curves.

EXPERIMENTAL RESULTS AND DISCUSSION

Effects of irradiation on initial modulus and yield stress

The initial moduli of both NMW PE and UHMW PE increase with irradiation dose as shown in *Figure 1*. The yield stresses (defined as the peak values of stress at the onset of yield) undergo a similar variation (see *Figure 2*). These effects are expected from previous experience[41,42] and reflect the structural changes produced in the materials by irradiation. These structural changes include crosslinking in the amorphous phase[43], crosslinking in the crystalline phase or at the lamellar surfaces[44,45] and chain scission. These effects, in turn, give rise to mechanical consequences as indicated below.

The rise in modulus with increasing radiation dose can be attributed to crosslinking in the amorphous phase. The amorphous modulus is increased, of course, but this itself would not produce changes of the magnitude observed, since at ambient temperature the non-crystalline phase is

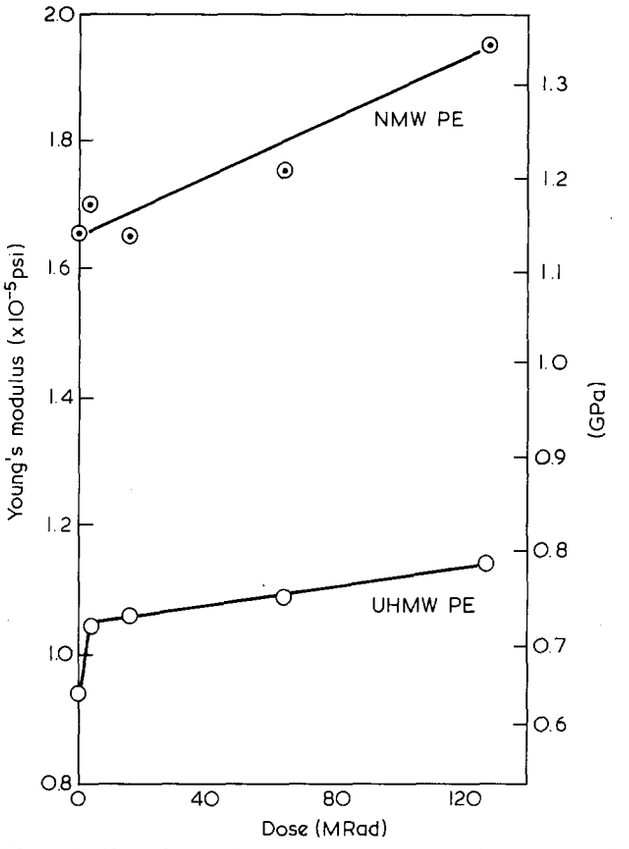

Figure 1 Young's modulus *versus* irradiation dose for both materials

above its glass transition, and the relevant modulus contributes only slightly to that of the crystalline/amorphous 'composite'. The initial modulus of a spherulitic polymer probably arises from the flexure of a network of lamellar crystals bound together by tie molecules. These tie molecules exert their greatest effects at 'weld' points where different lamellae lie in contact or approach one another closely[46]. The viscoelastic amorphous matrix imparts pre-yield time-dependence, whilst the relatively open crystalline network, together with a certain amount of reversible dislocation movement in the crystals themselves, leads to a modulus much lower than the appropriate rule-of-mixtures value for the crystalline/amorphous composite.

Crosslinking in the amorphous phase increases the effective concentration of tie chains and thus stiffens the 'open' crystalline network. At the same time, inhibition of *c*-axis slip[45] hardens the crystals themselves and renders the network less flexible. These two effects are sufficient to account for the modulus rise in NMW PE with dose. In UHMW PE, there is an initial jump in modulus which may be caused by a third effect. We have shown elsewhere[47] that irradiation of this material results in increased crystallinity. This was attributed to the breakage of the long tie chains that are to be expected in UHMW PE, removing an inhibition to further lamellar growth. This effect was most marked at doses up to 20 MRad and is, therefore, the likely cause of the initial rise of modulus observed here.

The effect of irradiation on yield stress has been explained previously[45,46] in terms of the suppression of *c*-axis slip in the lamellar crystals by crosslinking. In this case, the crosslinks must be either internal to the lamellae or at their surfaces. Although the bulk yield stress is low compared with that of the single crystal, it was shown that the former was controlled by the latter, bulk yield being observed when localized crystalline yielding takes place.

The effect of irradiation on creep

The large deformation and extreme non-linearity of UHMW PE in creep are shown in *Figure 3*, where the strain *versus* log time plots are given for three stress levels. These levels are, admittedly, relatively high, covering a range from about one-third to two-thirds the yield stress, but they represent the kind of loading to which

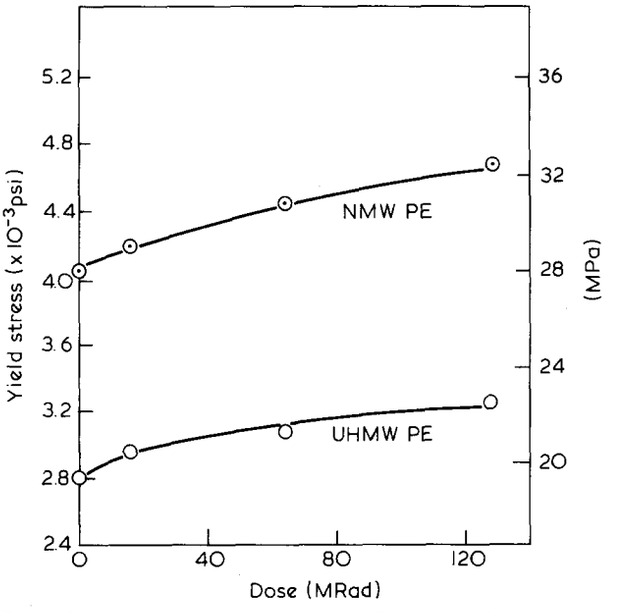

Figure 2 Tensile yield stress *versus* irradiation dose for both materials

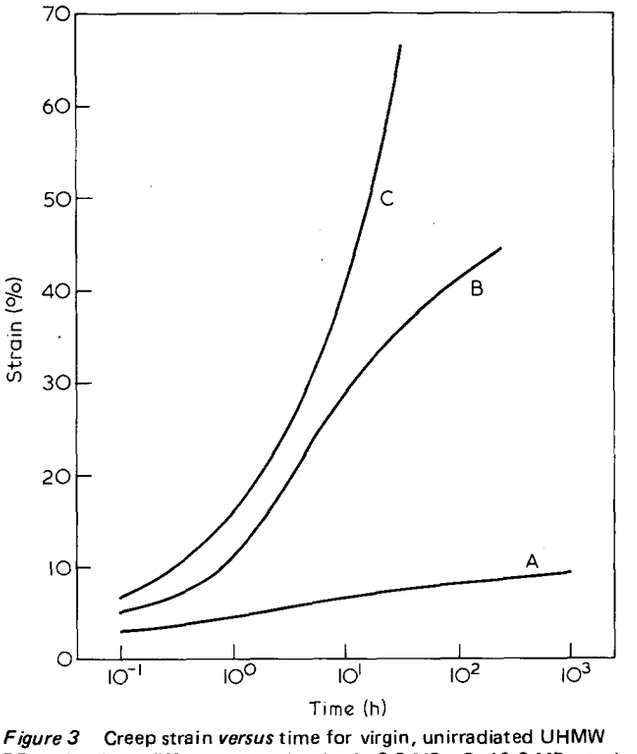

Figure 3 Creep strain *versus* time for virgin, unirradiated UHMW PE at the three different stress levels: A, 6.9 MPa; B, 10.3 MPa; and C, 11.7 MPa

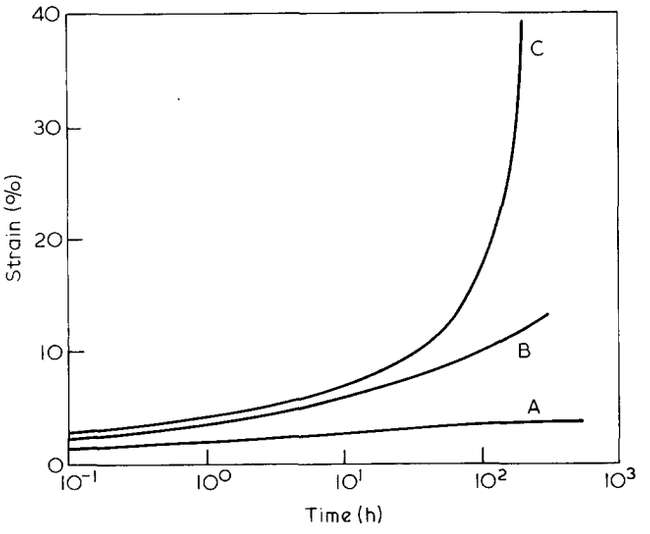

Figure 4 Creep strain *versus* time for virgin, unirradiated NMW PE at the three different stress levels: A, 6.9 MPa; B, 10.3 MPa; and C, 11.7 MPa

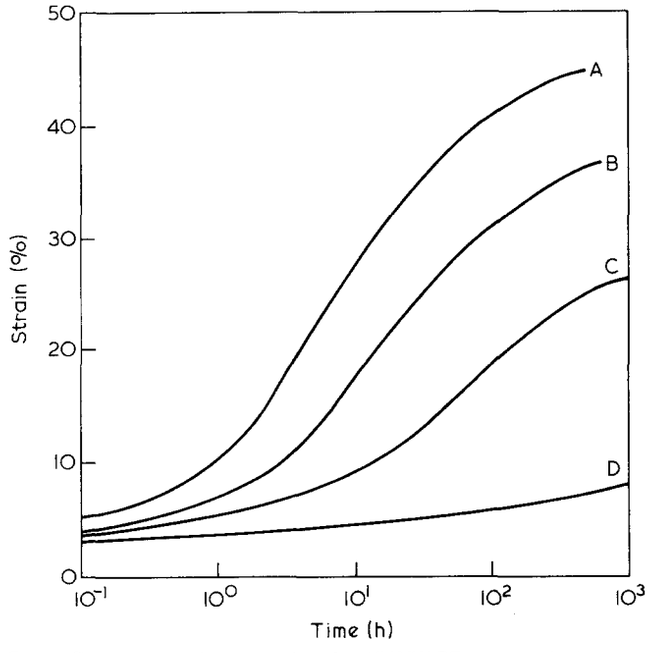

Figure 5 Creep strain *versus* time for UHMW PE at a nominal stress of 10.3 MPa: A, 0 MRad; B, 4 MRad; C, 16 MRad; and D, 64 MRad

engineering polymers may well be subjected. Above about 1500 psi, the creep rate increases continuously with log time and rapidly achieves levels which represent 'failure' in an engineering sense. NMW PE, though still prone to creep, is marginally better at the lower loads and impressively so at the higher ones, as shown in *Figure 4*.

These results are not surprising, since UHMW PE has a much lower degree of crystallinity than NMW PE, while in both materials the amorphous phase is, in effect, an uncrosslinked elastomer with the structural and mechanical properties of a viscous liquid. The question of interest is how far the creep properties can be modified by radiation crosslinking. The answer to this question is found in *Figures 5* and *6* which show, respectively, the creep curves at 1500 psi for UHMW PE and NMW PE, before and after radiation doses of 4, 16 and 64 MRad. In both cases, creep is reduced progressively as irradiation dose rises, the effect being to shift the creep curve to longer times. That is, all the creep curves have the same essential form, but are shifted to longer times *and* stretched out along the log time axis, as radiation dose is increased. Thus, it is not possible to obtain a master curve by shifting the data along the log time axis, even though the qualitative effect of irradiation is to increase the apparent retardation times.

In practical terms, the accumulated creep strains are reduced by as much as five-fold in UHMW PE after 64 MRad, and by similar factors in NMW PE. Irradiation does not therefore produce a significantly greater relative improvement in one material than in the other, and this suggests that the creep properties of both polymers derive only from the amorphous phase, and that this phase is modified by irradiation to a similar degree in both materials. This simple picture is further supported by plots of the strain at a fixed time *versus* the radiation dose. *Figures 7* and *8* show such curves for 1 h and 500 h, respectively. To a first approximation, these curves can be explained on the basis that UHMW PE contains about three times as much 'mobile' material in its amorphous phase as does NMW PE, but that otherwise the amorphous phases behave similarly in all respects. Reference to *Table 1* shows that the amorphous contents of the two polymers are not in this ratio, being some 28% in NMW PE and some 53% in UHMW PE. If, however, we suppose that 15% of the polymer is present as non-mobile amorphous material (fold surfaces and tie chains, for example), the discrepancy vanishes.

Returning to the shape of the creep curves, we have already pointed out that the qualitative effect of crosslinking by irradiation is to increase and spread the retardation times rather than simply remove 'mobile' material. This may be a simple consequence of the presence of permanent crosslinks in the amorphous phase, increasing the viscosity of the medium. It may also involve more subtle effects, such as the establishment of highly load-bearing tie molecules which relieve the stress on the network once they become extended as a result of creep deformation. This would help to explain why high irradiation doses produce a similar effect upon the shape

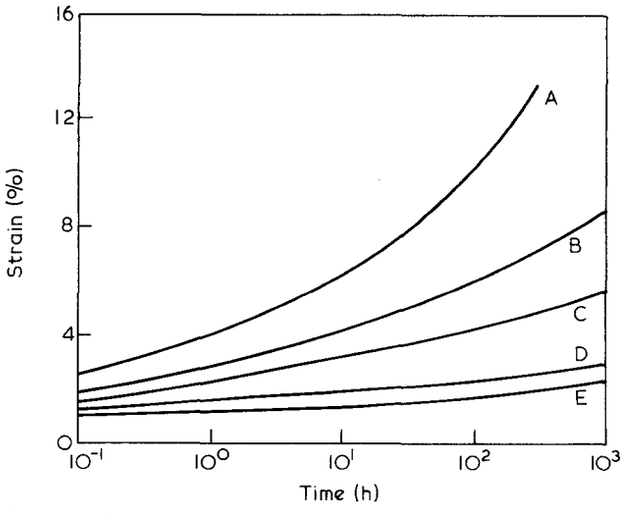

Figure 6 Creep strain *versus* time for NMW PE at a nominal stress of 10.3 MPa: A, 0 MRad; B, 4 MRad; C, 16 MRad; D, 64 MRad; and E, 128 MRad

of the creep curve as does a reduction in stress (compare *Figures 3* and *5*). At present, these comments must remain qualitative and, to some extent, speculative, but they provide a rational interpretation of the general features displayed by the data.

COMPARISON OF THE CREEP RESPONSE OF IRRADIATED UHMW PE WITH THAT OF OTHER POLYMERIC MATERIALS

The data on irradiated UHMW PE and NMW PE were converted to the form in which creep data on other polymers are available[48]. These are presented in *Table 2* as apparent creep modulus calculated from the total strain at the times indicated. Identical data on a range of other polymers (both amorphous and crystalline) were compiled from ref. 48 and are given in *Table 3*. The applied nominal stress level for all materials in both the tables is approximately 1500 psi.

Comparison of *Tables 2* and *3* reveals that, as far as the tensile creep response is concerned, irradiated NMW PE approaches PP, while irradiated UHMW PE only approaches NMW PE. Thus, irradiation does not make UHMW PE a good creep-resistant material. All the materials in *Table 3* are substantially better in tensile creep behaviour than UHMW PE. In fact, if creep resistance were the primary consideration, one would not employ any of the polymers listed in *Table 3*, since other polymers have a markedly superior creep response[48]. As pointed out earlier, however, UHMW PE is used primarily in applications which exploit its exceptional properties, such

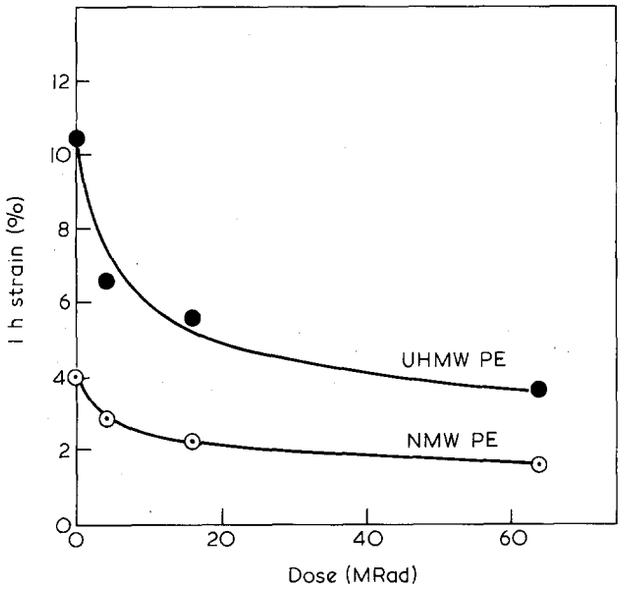

Figure 7 Creep strain (at a nominal stress of 10.3 MPa) after 1 h as a function of irradiation dose for both materials

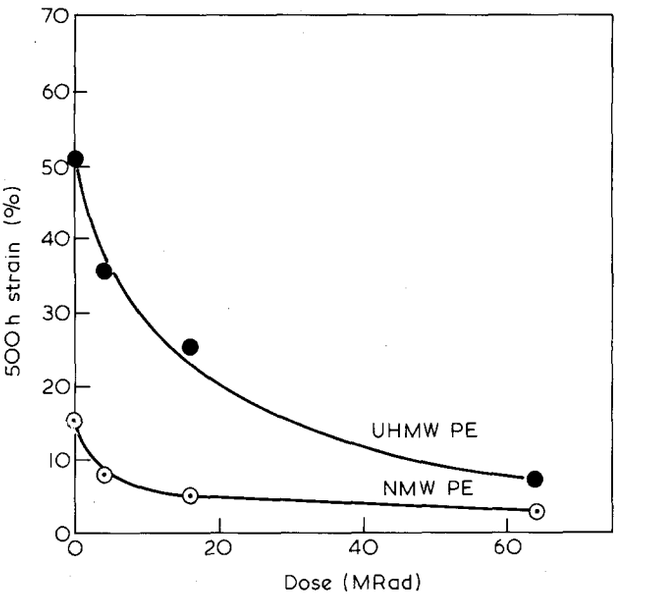

Figure 8 Creep strain (at a nominal stress of 10.3 MPa) after 500 h as a function of irradiation dose for both materials

Table 3 Tensile creep data for several different polymers (taken from ref. 48)

Material	Apparent creep modulus (x10^{-3} psi*) calculated from total creep strain at following test times (h)					
	1	10	30	100	300	1000
PMMA	402	361	354	326	–	–
ABS	284	278	273	263	254	240
PP	104	77	66	58	52	46
POM	390	360	340	280	270	240
Nylon-6,6 (dry)	420	395	380	340	290	–
(equilib. with 50% RH)	160	130	120	115	105	100
PET (1422 psi)	484	469	455	440	412	384

* 1 psi ~6.89 x 10^{-3} MPa

Table 2 Tensile creep data for UHMW PE and NMW PE as a function of irradiation dose

Material	Radiation dose (MRad)	Apparent creep modulus (x10^{-3} psi*) calculated from *total* creep strain at following test times (h)					
		1	10	30	100	300	1000
UHMW PE	0	13.6	5.6	4.2	3.6	3.3	–
	4	23.1	9.1	6.3	4.8	4.3	4.0
	16	29.7	18.8	12.5	8.3	6.5	5.8
	64	44.1	37.5	30.0	28.3	25.0	21.4
NMW PE	0	37.5	25.0	20.0	14.7	11.5	–
	4	55.5	37.5	31.9	25.9	21.7	17.0
	16	68.2	50.0	44.1	37.5	31.3	28.9
	64	100.0	83.3	75.0	68.2	60.0	53.6
	128	130.0	107.2	93.8	81.1	75.0	68.2

* 1 psi ~6.89 x 10^{-3} MPa

as wear and abrasion resistance, impact and impact–fatigue resistance. Thus, in applications where creep resistance is significant but of secondary importance, irradiated UHMW PE could obviously be used to advantage.

FINAL DISCUSSION

The improvement upon irradiation of the creep resistance of UHMW PE and NMW PE reported in this paper can be explained in terms of the stiffening of both the amorphous and the crystalline phases. Stiffening of the amorphous phase is caused by radiation crosslinking, which in polyethylene has been suggested to occur preferentially in the amorphous phase[43,49]. Another viewpoint places the crosslinks either at the fold surfaces[50,51] or within the crystallites[52,53], and in both these cases *c*-axis slip will be prevented, resulting in stiffening of the crystalline phase[44,45].

The effect of γ-radiation on the creep behaviour of HDPE has also been reported by Awatani and Minegaki[54]. These authors explained the improvement in creep resistance upon irradiation in terms of crosslinking. They also noted that specimens irradiated in vacuum showed higher creep resistance than those irradiated in air. In fact, they claimed that irradiation in air did not change the creep properties in a regular fashion and explained this in terms of surface degradation. However, as can be seen from the data presented in the present paper, irradiation in air does cause a systematic improvement in the creep resistance of UHMW PE, even though the possibility of surface degradation cannot be ruled out.

Another feature of the data presented is that UHMW PE, which exhibits higher creep strain (at any given time, stress level and irradiation dose) than NMW PE, also has the lower density or crystallinity of the two materials (see *Table 1*). The inverse relation of the magnitude of creep strain with density or crystallinity has been reported earlier[7,8,35,55,56] and was explained[57–61] to result from two major causes: first, the rigid crystallites act as filler particles, and secondly, the crystallites immobilize many chain segments and thus essentially serve as physical crosslinks. This general picture is supported by the present data, as discussed earlier.

It should be pointed out that crosslinking does not have to be achieved by exposure to radiation. It could, for instance, be achieved during fabrication by suitable chemical agents. Radiation crosslinking, however, offers an advantage which could be quite significant for an intractable polymer such as UHMW PE, namely that it can be employed as a post-fabrication step which will not hinder fabrication. However, the feasibility of irradiation as a means of improving the creep resistance of UHMW PE will ultimately depend, amongst other things, on how it affects the properties for which this material is especially known, e.g. wear, abrasion resistance, impact and impact–fatigue resistance.

CONCLUSIONS

(1) Exposure to electron beam radiation substantially improves the tensile creep resistance of UHMW PE and NMW PE, even at relatively low irradiation levels.

(2) At any given time and stress level, the tensile creep strain decreases monotonically with increasing irradiation dose, with most of the decrease occurring over the first 20 MRad of irradiation dose.

(3) Despite the significant improvements observed, irradiation does not make UHMW PE a good creep-resistant material. By improving creep response, it may, however, render UHMW PE of use in applications where creep is of secondary importance to other factors, such as impact strength and wear, in which UHMW PE excels.

(4) Radiation crosslinking can be employed as a post-fabrication treatment which will not hinder the fabrication process itself. For an intractable polymer such as UHMW PE, this could be a significant advantage.

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