Hardness and creep of cross-linked polyethylene

P. J. Henderson* and A. J. Wallace
Department of Materials Technology, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

Vickers microhardness, tensile and compression tests and creep experiments have been performed at 22°C on electron beam irradiated high density polyethylene (HDPE). The microhardness and compression strengths were found to increase progressively with increasing dose in the range 0–500 kGy but the tensile strength was relatively constant. The time dependence of the creep moduli at low stresses can be described by the time dependence of the microhardness values.

INTRODUCTION

Hardness tests have been successfully applied to metallic materials for nearly 60 years[1], but it is only recently that the hardness or microhardness test has emerged as a useful means of characterizing polymers (see, for example, References 2–9). For metals, the hardness values can be taken as a measure of resistance to permanent deformation; the hardness of polymers is more difficult to define. Hardness tests are usually performed at 22°C; at this temperature many polymers will creep under load but most metals (with the exception of indium and lead) will not. Therefore, the hardness of polymers is time dependent and there is also some time dependent elastic recovery. Most hardness tests on polymers have involved the load being applied for a short and constant time, although time dependence has been investigated to a limited extent[3,5,9,10], showing that hardness values decrease with increasing time under load. This paper investigates the time dependence in greater detail than previous studies, and in addition creep modulus experiments have been carried out on the same samples over the same time span as the microhardness tests.

For metals, which are treated as rigid perfectly plastic solids, the mean contact pressure or hardness, H, can be related to the yield stress in compression, Y_c, such that[11]:

$$H/Y_c \simeq 3 \qquad (1)$$

and conveniently Y_c is equal to the yield stress in tension Y_t. Therefore, for metallic materials:

$$H \simeq 3Y_t \qquad (2)$$

The simple relationship of Equation (2) has been applied by polymer scientists and engineers. Correlations have been found between hardness and tensile yield strength on a wide variety of polymers[12] and microhardness tests have been carried out for 6 s to give microhardness numbers of $3Y_t$ in polyethylene[6]. However, for polymers, Y_c is always greater than Y_t because their yield strengths are affected by hydrostatic pressure, some polymers being

more affected than others[13,14]. Therefore, more correctly, the hardness of polymers should be related to Y_c. The variation of H with Y_c has also been investigated in this study.

The microhardness of polyethylene has previously been investigated with respect to crystalline content[3], lamellar thickness[4] and draw ratio[5]. It was found to increase with these three variables. In the present investigation the crystallinity of the samples remained constant but the structure was affected by electron beam irradiation, which causes an increase in molecular weight at low radiation doses and cross-linking at higher doses[15].

The hardness values reported in this paper were obtained from Vickers microhardness tests in which the size of the indentation is measured after the load has been removed. Time dependent recovery at the indentation has not been taken into account but it is felt that this approach is justified because a previous study[9] showed that after periods in excess of one month the lengths of the diagonals of Vickers indentations were the same as those measured immediately after the load was removed. This effect has been confirmed by a more recent investigation where interference microscopy was used to show that most of the recovery occurred in the depth of the indentation and not in the length of the diagonals[16]. Therefore, the length of the diagonals can be taken as a measure of time dependent deformation occurring under load and the effects of recovery on the Vickers hardness values can be considered negligible.

EXPERIMENTAL

Granules of an injection moulding grade of high density polyethylene (HDPE) were compression moulded at 150°C into sheets approximately 6 mm thick, which were slow cooled at a rate of 2°C min^{-1}. The sheet material was then irradiated in air at room temperature with a high energy beam of electrons at a constant dose rate to total doses of 20, 50, 100, 200 and 500 kGy. Some HDPE was retained in the original, unirradiated condition.

Molecular weights were determined by RAPRA Technology Limited using high temperature gel permeation chromatography (g.p.c.). Densities were

---

measured at 22°C in a density gradient column consisting of propan-2-ol and etnane-diol and the percentage crystallinity was also estimated from the melting peaks produced by differential scanning calorimetry (d.s.c.) at a heating rate of $10°C \min^{-1}$. Gel contents were determined by extracting the soluble fraction from samples suspended in stainless steel mesh containers exposed to refluxing xylene and purged with nitrogen to avoid oxidation. Dynamic mechanical testing was carried out on unirradiated and 500 kGy samples at a frequency of 1 Hz and a heating rate of $2°C \min^{-1}$.

Samples for tensile and creep testing were approximately 3 mm thick and were taken from the centre of the 6 mm sheet by milling 1.5 mm from both surfaces and then grinding and polishing the milled surfaces to a 6 μm finish. The samples were taken from the centre of the sheet because the gel content was reduced at the surfaces (see results). The reduction in gel content has been attributed to oxidation during irradiation, which causes chain scission, so hindering crosslinking and resulting in a reduction in tensile strength due to the occurrence of brittle fracture rather than yielding[17]. Tensile testing was carried out according to ASTM D638 at 22°C with a crosshead speed of 5 mm min^{-1}. Three samples were tested for each type. Young's modulus was measured at 5 and 0.5 mm min^{-1} with a clip gauge extensometer and taken as the tangent to the stress–strain curve at 0.1% strain.

Uniaxial tensile creep modulus experiments were performed at 22°C using a lever-arm creep machine. The load was applied smoothly using a damper–piston and dashpot assembly. Extensions were measured by two super linear variable capacitor transducers attached either side of the specimen between two sets of knife-edges initially 50 mm apart. The transducers were clamped to the lower set of knife-edges and were lightly sprung to ensure that the tip of the shaft maintained contact with the upper set. A digital display gave a strain resolution of 2×10^{-5} and a continuous analogue output could also be produced on a chart recorder. Each creep test lasted 1000 s and the samples were allowed to recover for at least 10 000 s before the next load was applied.

Compression tests were performed to BS2782 (Method 345A Type 4) with a cross-head speed of 2 mm min^{-1}. The samples were right square prisms 10 mm high and with a slenderness ratio of 6–7. A problem with compression tests is the lack of an observable yield point. In this case the yield stress was taken as the engineering stress required to cause permanent deformation (a permanent reduction in height) as assessed immediately after the test. In all tests this corresponded to a change in slope on the load *versus* reduction in height plots (also on true stress *versus* true strain plots) and is shown schematically as load point B in *Figure 1*.

Vickers microhardness measurements were taken from material in the centre of the sheets and the surfaces to be tested were ground and polished to 1 μm. A load of 20 g (i.e. 0.196 N) was applied for times up to 1000 s and the Vickers pyramid number (VPN) was calculated from

$$VPN = \frac{2P \sin (\alpha/2)}{d^2} \qquad (3)$$

where P is the applied load in newtons, α is the included angle of the pyramid (136°) and d is the average diagonal of the residual indentation measured in millimetres, thus
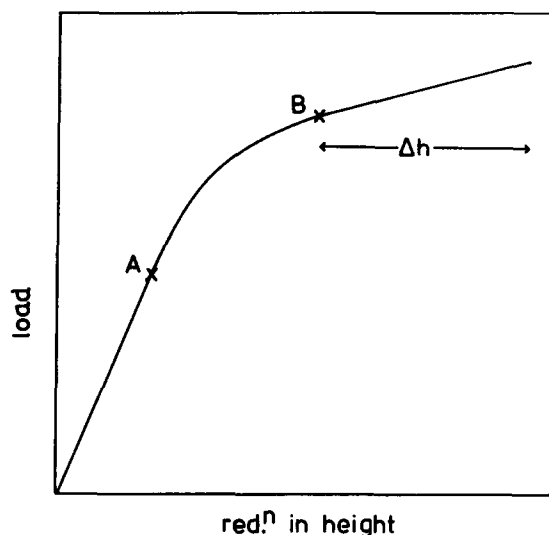
red.^{n} in height

Figure 1 Schematic load *versus* reduction in height plot obtained from compression tests. A represents the load at which deviation from linearity first occurred. B is the load at which linearity reoccurred and Δh is the permanent reduction in height measured after the test. In all cases it was found that B coincides with Δh. B was taken as the load at yield

Table 1 Density and crystallinity

Dose (kGy)	Density (kg m^{-3})	Crystallinity $\pm 0.2\%^a$ (vol%)	Crystallinity by d.s.c.^{b} (vol%)
0	968.1	77.1	78.5 $\pm$ 2
20	971.2	79.6	79.5 $\pm$ 2
50	971.6	79.9	82 $\pm$ 6
100	971.2	79.6	84 $\pm$ 4
200	972.0	80.2	77 $\pm$ 4
500	970.5	79.0	77 $\pm$ 3

^{a} Volume percentage crystallinity calculated using: density of crystalline phase $= 997.2$ kg m^{-3} (ref. 29); density of amorphous phase $= 870.0$ kg m^{-3} (ref. 15)
^{b} Volume percentage crystallinity calculated using latent heat of fusion of 100% crystalline phase $= 277.68$ J g^{-1} (ref. 30)

giving a VPN in megapascals. Indentations were separated by a distance of at least $3d$.

RESULTS

The densities and calculated crystalline contents of the samples are given in *Table 1*. The volume fraction crystallinity V_c/V was obtained from

$$\frac{V_c}{V} = \frac{\rho - \rho_a}{\rho_c - \rho_a} \qquad (4)$$

where ρ, ρ_a and ρ_c respectively are the densities of the whole sample, the amorphous region and the crystals. There is no evidence to suggest that irradiation had substantially altered the crystalline content of the material. The variation in gel content through the thickness of the 500 kGy sheet is shown in *Figure 2*. The gel content (and molecular weight) was reduced at the edges, which is why creep and tensile samples were cut from the central 3 mm thick section. The average gel contents of the central section of each sheet are given in *Table 2*. Gel was formed at doses of 100 kGy and above.

The variation of weight average molecular weight $\bar{M}_w$ in the central 2 mm thick section of the 0 to 100 kGy sheets is shown in *Table 3*. The effect of the radiation at
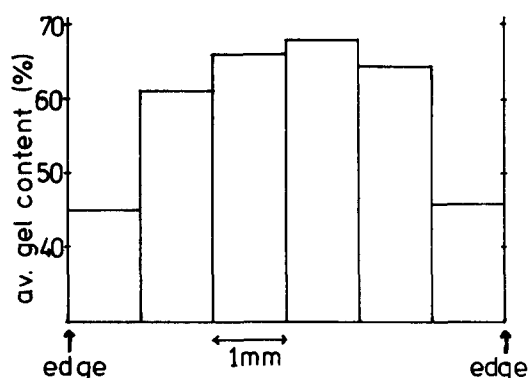
Figure 2 Variation in weight percentage gel through the thickness of the 500 kGy sheet

Table 2 Average gel content of samples used in creep and tensile testing

Dose (kGy)	0, 20, 50	100	200	500
Gel (wt%)	0	12	36	66

Table 3 Variation of weight average molecular weight, $\bar{M}_w$, in the centre of the sheets

Dose (kGy)	0	20	50	100
$\bar{M}_w$	57 500	71 600	78 600	50 000[a]

[a] Cross-linking had occurred at this dose

values increase progressively with increasing dose. This trend was found for all microhardness values from 10 to 900 s. Failure in compression occurred (after yielding) by cracking at 45° to the applied stress in samples receiving a dose of 100 kGy and above. Failure in other samples occurred by barrelling or buckling.

The variation of microhardness with time for the six HDPE samples and metallic lead are shown in *Figure 7*; irradiation increased the hardness number and also reduced the time dependence. At very short times (< 10 s, not shown in *Figure 7*) there was considerable scatter in the hardness values. For loading times of $\approx$ 1 s *VPN* readings were in the range 73–77 MPa for the unirradiated HDPE and 96–103 MPa for the 500 kGy material. Preliminary hardness tests using different loads applied for various times showed that, for the same

Table 4 Young's modulus taken as the tangent to the stress–strain curves at 0.1% strain

Dose (kGy)	E at 0.5 mm min^{-1} (GPa)	E at 5 mm min^{-1} (GPa)
0	2.13	2.46
20	2.25	2.61
50	2.12	2.53
100	2.29	2.70
200	2.18	2.57
500	2.16	2.43

Figure 3 Variation in tan δ with temperature. – – –, Unirradiated HDPE; ——, 500 kGy sample
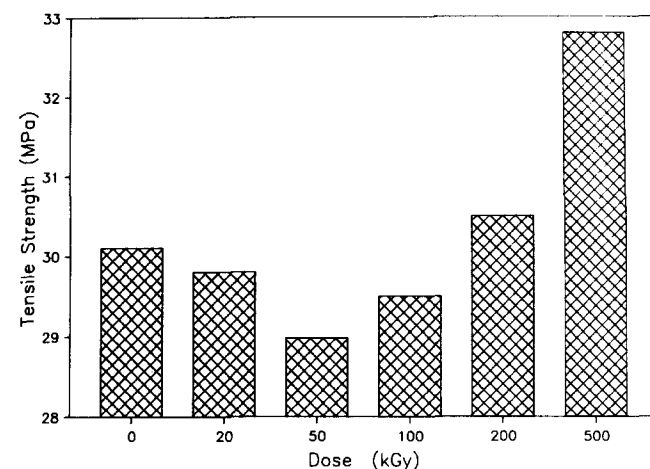
Figure 4 Variation of tensile yield strength with dose

lower doses was to increase the molecular weight. At doses of 100 kGy and above crosslinking had occurred, which is manifested as an insoluble gel. Because g.p.c. provides information only on the uncrosslinked, soluble fractions of a polymer this leads to an apparent decrease in $\bar{M}_w$ above the gel point. The dynamic-mechanical-thermal analysis (DMTA) damping peaks are shown in *Figure 3* as the variation in tan δ with temperature. The peaks present indicate γ, α and α' relaxations at -110, 50 and 130°C, respectively. Irradiation has reduced the δ relaxation peak and considerably affected the α' relaxation.

Young's modulus values obtained from tensile tests are tabulated in *Table 4*. These were not affected by radiation dose. The tensile and compressive yield strengths and some microhardness values are displayed in *Figures 4–6*. The tensile yield stresses remain relatively constant, increasing marginally at the highest dose, whereas the compression yield stresses and microhardness
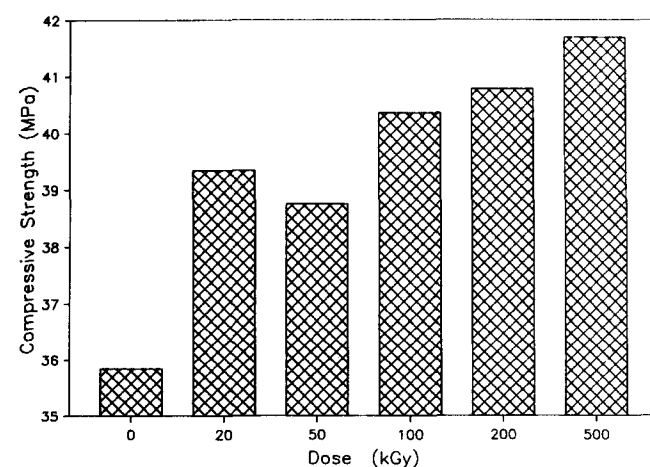

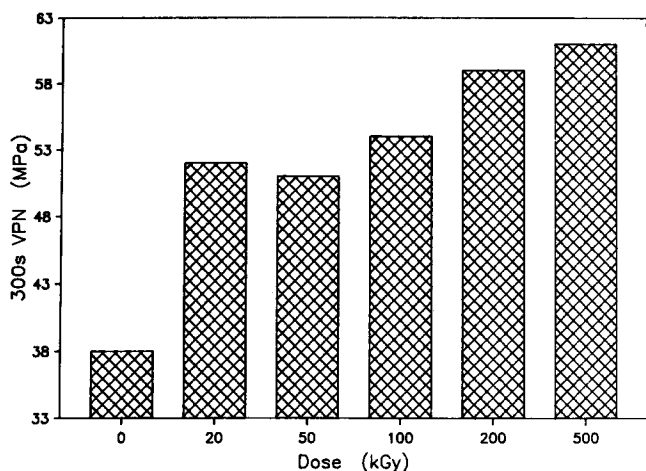**Figure 5** Variation of compressive yield strength with dose

Figure 6 Variation in microhardness values with dose. The load of 20 g was applied for 300 s
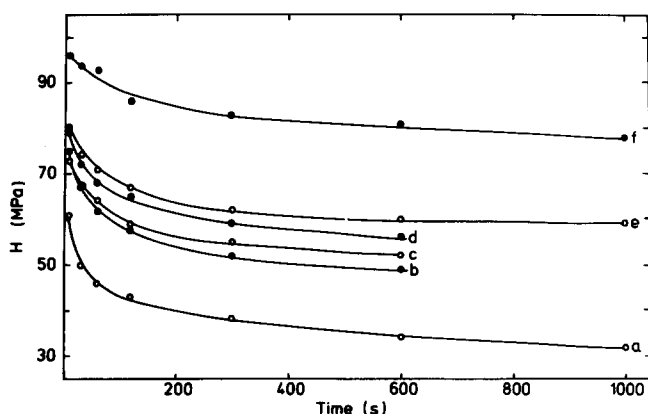

Figure 7 Variation of microhardness with time for: a, 0; b, 20; c, 100; d, 200; e, 500 kGy. Curve f is for lead

material and indentation time, the hardness values were independent of load for loads of 10 g and above. A load of 20 g was chosen for all subsequent microhardness tests because it produced indentations of a size that could be easily measured after short indentation times but remained totally contained within the field of view after long times.

Examples of creep curves are given in *Figure 8*; irradiation increased the creep resistance of the HDPE.

DISCUSSION

Young's modulus and yield stresses

Irradiation of polyethylene in the absence of oxygen causes, at low doses, an increase in side-branching and molecular weight and, at higher doses, crosslinking to form an insoluble network[15]. Crosslinking is thought to occur preferentially within the amorphous phase or at the crystal chain fold surfaces[18-20] but not within the crystal lattice[19,20]. This is confirmed by the DMTA results, which showed that the radiation reduced the γ relaxation peak (which is associated with the glass transition of the amorphous phase)[21] and reduced the α' peak (or shifted it to higher temperatures). For the unirradiated material there is no distinct α peak, probably because of interference from the α' relaxation. The α relaxation has been shown[21], to be due to processes within the crystal lamellae, but the α' relaxation is due

to slip at the chain fold surfaces. At room temperature the elastic modulus of HDPE is dominated by the modulus of the crystalline phase, but this property is not likely to be changed by irradiation if the crosslinks are at the crystal surfaces[21].

A study of ultra high molecular weight polyethylene (PE) $(M_w > 2 \times 10^6)$ and high molecular weight PE $(M_w = 207\,000)$ that had been electron beam irradiated found that both E and Y_t increased with dose[22] but this was shown to be caused by a radiation-induced increase in crystallinity[23]. No such effect was found in this study, but the HDPE used had been slowly cooled from the melt and probably contained the maximum amount of crystallinity before irradiation.

The compressive yield strength Y_c, unlike Y_t, progressively increased with increasing dose. The reason for this is not well understood but could be related to the variation in hydrostatic pressure dependence with molecular weight and crosslinking.

Microhardness and creep

Previous work (e.g. References 6 and 12) has related the hardness, H, of polymers to E or Y_t. However, these two quantities are often interdependent. For example, an increase in crystallinity in PE will produce an increase in E or Y_t (presumably also in Y_c) and an increase in H. In the present case, the increase in H with dose scales with the increase in Y_c; E and Y_t are relatively invariant.

The hardness values decreased very rapidly with time in the first 60 s and, therefore, measurements taken at short times will be subject to considerable error. The results support Crawford's recommendation[10] that loads should be applied for ≥ 120 s.

The hardness values are time dependent because the material creeps under load at the temperature of test. *Figure 7* shows that the hardness of metallic lead is also time dependent at 22°C, which is about half the absolute melting temperature $(T_m$ in Kelvins) for lead. As a general rule, thermally activated processes such as creep predominate at temperatures $\geq 0.5\,T_m$ in crystalline
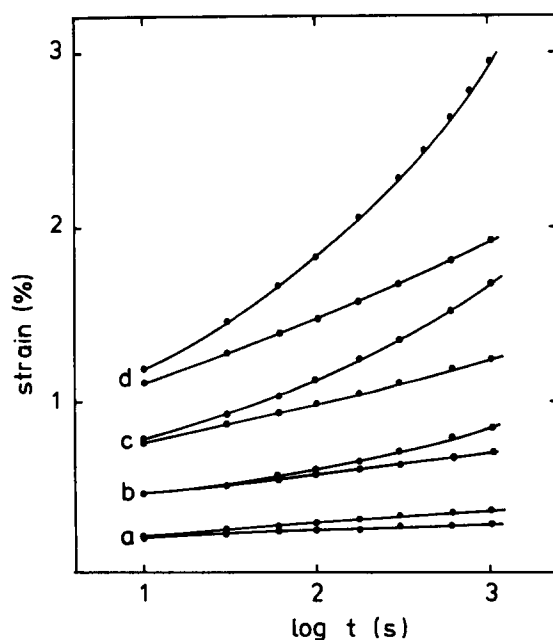

Figure 8 1000 s creep curves for 0 (upper curve of each pair) and 500 kGy (lower curve) PE at 22°C. Curve a, 4; b, 8; c, 12; d, 16 MPa
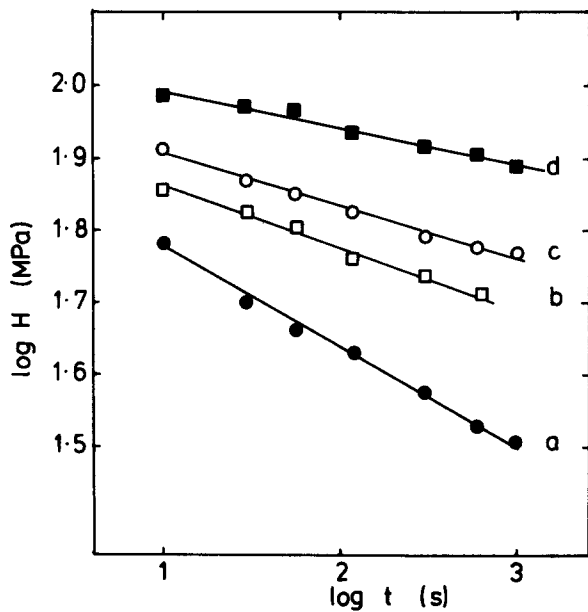
Figure 9 Log hardness (H) versus log time (t) for: a, 0; b, 100; c, 500 kGy; d, lead
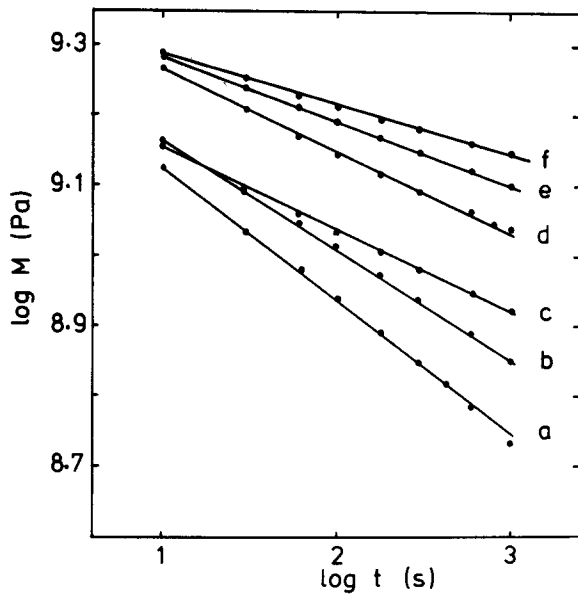

Figure 10 Log creep modulus (M) versus log time (t). Applied stress (MPa): a–c, 16; d–f, 4. Curves a, d, 0; b, e, 100; c, f, 500 kGy

materials. For HDPE, which melts at 140°C, the test temperature is $0.7 \, T_m$. For totally amorphous polymers it could be expected that at temperatures $\geqslant 0.5 \, T_g$, where T_g is the absolute glass transition temperature, the hardness values will also be time dependent. (Hardness measurements made on PMMA at about $0.7 \, T_g$ were found to decrease with increasing time[10]).

The variation of hardness with time for metals at temperatures $\geqslant 0.5 \, T_m$ has been found[24] to follow the relationship

$$H = At^{-h} \qquad (5)$$

where A and h are constants and t is the time under load. Such a relationship was found to exist for the microhardness of drawn PE[5] and also applies to the irradiated HDPE (see *Figure 9*). The gradients of the lines in *Figure 9* give some indication of the relative creep resistance of the PE. The values of h are 0.076, 0.094 and

0.143 for doses of 500, 100 and 0 kGy, respectively. Clearly the 500 kGy material deforms less under load than the unirradiated polymer (see also creep curves in *Figure 8*) and this could be attributed to the reduction in the creep of the amorphous phase and the reduction in slip at the crystal boundaries.

The creep modulus M shows the same time dependence as H, namely

$$M = At^{-m} \qquad (6)$$

but the values of m (obtained from the gradients in *Figure 10*) vary with stress and dose. The stress at which m becomes equal to h in Equation (5) is between 4 and 8 MPa, being nearer to 4 MPa for doses of 500 and 100 kGy and nearer to 8 MPa for the unirradiated material. Clearly, if the time dependence of H is equal to the time dependence of M at low stresses then hardness or microhardness tests could be used to determine the creep moduli under service stresses of small volumes of materials.

For all the HDPE samples the H/Y_c ratio was $\ll 3$, given by Equation (1). However, Equation (1) applies to metallic materials where the elastic modulus E is 100–1000 times Y_c. For materials with E/Y_c ratios in the range 10–100 (e.g. polymers) the H/Y_c ratio has been derived or measured[25–28] and found to follow the general form

$$H/Y_c = B + C \, \ln(E/Y_c) \qquad (7)$$

where B and C are constants. In the present treatment E has been replaced by M, the creep modulus, in order to take time dependent effects into consideration. Therefore, the hardness after time t, H_t can also be related to the creep modulus after time t, M_t, through the equation
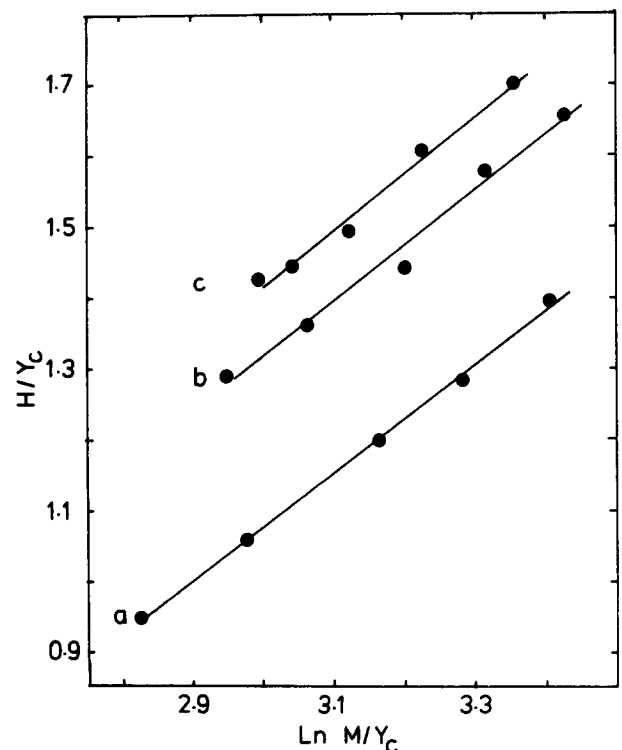
$$H_t/Y_c = B + C \, \ln(M_t/Y_c) \qquad (8)$$

Figure 11 H/Y_c versus ln M/Y_c. H is the hardness at any time t; M is the corresponding creep modulus at the same time t and 16 MPa; Y_c is the compression yield stress. Curve a, 0; b, 100; c, 500 kGy
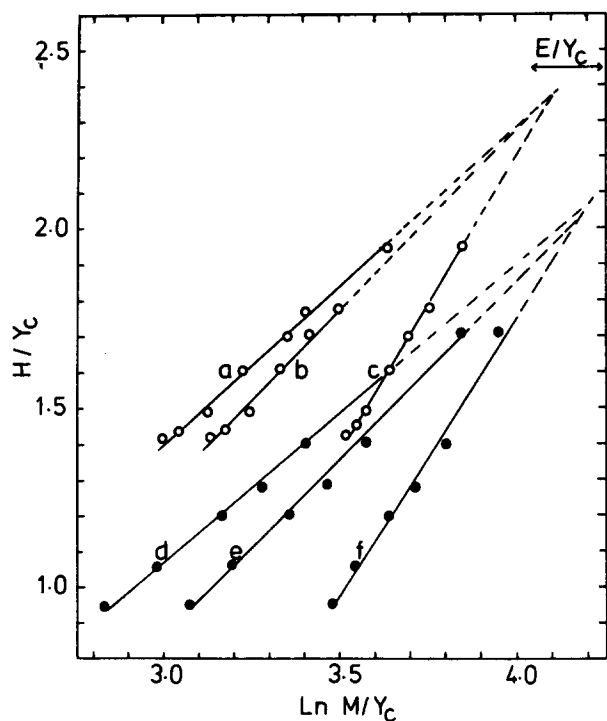
Figure 12 H/Y_c versus ln M/Y_c. Curves a, b, c, 500 kGy at 16, 12, 4 MPa, respectively; d, e, f, 0 kGy at 16, 12, 4 MPa, respectively. The range of values of E/Y_c (where E is the elastic modulus in a 500 mm min^{-1} tensile test) is also shown

A plot of H_t/Y_c versus ln (M_t/Y_c) for 0, 100 and 500 kGy tested at 16 MPa is shown in *Figure 11*. The gradient C is independent of dose, but varies with the applied creep stress. *Figure 12* shows plots for 0 and 500 kGy materials tested at stresses of 4, 12 and 16 MPa. The gradient C at these stresses is about 1.5, 1.0 and 0.8, respectively.

The difference in creep modulus with stress increases as the time under load increases (see *Figure 10*). At very short times M would be expected to be independent of stress for each material and to become equal to the elastic modulus measured in a tensile test at a relatively fast crosshead speed. In practice, it is not possible to measure M at short times because the piston and dashpot assembly ensure that the load is applied smoothly over a period of 2–3 s. However, it is not surprising that the plots in *Figure 12* converge at ln(M/Y_c) values of 4.1–4.2 (M/Y_c of 60–67), which fall within the range of E/Y_c values for the HDPE, where E is the elastic modulus measured at 0.1% strain in a 50 mm min^{-1} tensile test. The corresponding H/Y_c values give *VPN* measurements of 75 MPa for the unirradiated HDPE and 96 MPa for the 500 kGy material and can be identified as the hardness values expected at very short loading times ($t \approx 1$ s).

CONCLUSIONS

The Vickers microhardness of HDPE crosslinked by irradiation varies with the yield stress in compression, but does not depend on the tensile yield strength. The

time dependence of the hardness can be related to the time dependence of the creep modulus at low stresses (4–8 MPa). Hardness or microhardness tests could therefore be used to assess the creep moduli of small volumes of material.

Hardness values decrease rapidly at short loading times, leading to considerable errors in measurements. It is recommended that where hardness values are being used to assess microstructural variations (using constant load and time) the indentation time should be $\geqslant 30$ s.

REFERENCES

1 O'Neill, H. 'Hardness Measurement of Metals and Alloys', Chapman and Hall, London, 1967
2 Bowman, J. and Bevis, M. *Colloid Polym. Sci.* 1977, **255**, 954
3 Baltá-Calleja, F. J. *Colloid. Polym. Sci.* 1976, **254**, 258
4 Baltá-Calleja, F. J. and Bassett, D. C. *J. Polym. Sci.* 1977, **58**, 157
5 Baltá-Calleja, F. J., Rueda, D. R., Porter, R. S. and Mead, W. T. *J. Mater. Sci.* 1980, **15**, 765
6 Baltá-Calleja, F. T. *Adv. Polym. Sci.* 1985, **60**, 119
7 Martinez Salazar, J., Garcia Tijero, J. M. and Baltá-Calleja, F. J. *J. Mater. Sci.* 1988, **23**, 862
8 Covas, J. A. *Plast. Rubber Proc. Appl.* 1988, **9**, 91
9 Eyerer, P. and Lang, G. *Kunststoffe* 1972, **62**, 322
10 Crawford, R. J. *Polym. Test.* 1982, **3**, 37
11 Tabor, D. 'The Hardness of Metals', Clarendon Press, Oxford, 1951
12 Selden, B. R. and Gustafson, C. G. ANTEC 84, 'Plastics in a World Economy', Society of Plastics Engineers, p. 573
13 Mears, D. R., Pae, K. D. and Sauer, J. A. *J. Appl. Phys.* 1969, **40**, 4229
14 Rabinowitz, S., Ward, I. M., Parry, J. S. C. *J. Mater. Sci.* 1970, **5**, 29
15 Charlesby, A. 'Atomic Radiation and Polymers' Pergamon, London, 1960
16 Lorenzo, V., Pereña, J. M., Fatou, J. M. G., Mendez-Morales, J. A. and Aznarez, J. A. *J. Mater. Sci. Lett.* 1987, **6**, 756
17 Aboutorabi, A. A., Bowman, J. A. and Henderson, P. J. in preparation
18 Jenkins, H. and Keller, A. *J. Macromol. Sci. Phys.* 1975, **B11**, 301
19 Patel, G. N. and Keller, A. *J. J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 303
20 Patel, G. N. and Keller, A. *J. J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 323
21 McGrum, N. G. and Morris, E. L. *Proc. R. Soc. Lond.* 1966, **A292**, 506
22 Bhateja, S. K. and Andrews, E. H. *Polymer* 1983, **24**, 160
23 Bhateja, S. K., Andrews, E. H. and Young, R. J. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 523
24 Mulhearn, T. O. and Tabor, D. *J. Inst. Metals.* 1960, **89**, 7
25 Bishop, R. F., Hill, R. and Mott, N. F. *Proc. Phys. Soc.* 1945, **57**, 147
26 Marsh, D. M. *Proc. R. Soc. Lond.* 1964, **A279**, 420
27 Hirst, W. and House, M. G. J. W. *Proc. R. Soc. Lond.* 1969, **A311**, 429
28 Johnson, K. L. *J. Mech. Phys. Solid* 1970, **18**, 115
29 Young, R. J. 'Introduction to Polymers', Chapman and Hall, London, 1983
30 Billmeyer, F. W. 'Textbook of Polymer Science', 2nd Edn., Wiley, New York, 1971