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Property modification of polyethylene tapes by acetylene-sensitized gamma irradiation

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Gamma-irradiation techniques for improving the creep performance of polyethylene tapes (draw ratio 6.5) have been investigated. With acetylene present during irradiation, the optimum dose required for maximum suppression of yielding under tensile stress coupled with minimum embrittlement was found to be 5–10 kGy. This is one-tenth that required for irradiation in vacuum. Creep performance was also improved at 100 °C. Creep experiments at higher loads have shown that the optimum acetylene-sensitized treatment is more effective in reducing creep rate than the optimum vacuum-irradiation treatment.

1. Introduction

Polyolefin tapes are commercially produced by drawing extruded film either in a hot-air oven or over hot rollers to give a product with a relatively high tensile strength and modulus in the draw direction. Coupled with the low cost and chemical inertness of stabilized polyolefins, this property has led to a wide variety of applications. Under the rapid drawing conditions, which are used for commercially economic reasons, the draw ratio achievable is in the range 6–12, the so-called natural draw ratio. Much higher draw ratios can be achieved, and in fact are achieved commercially in the gel-spun polyethylene fibres, by specialized drawing techniques developed over recent years [1, 2]. These are often called the ultra-high-modulus polyolefins (e.g. UHMPE) owing to their extremely high modulus and strength in the draw direction.

Although the drawn tapes and fibres are said to have good and excellent tensile properties, respectively, this is only true in tests and situations involving rapidly applied forces. Their ability to withstand stress over an extended time period, even in the draw direction, is a much less attractive property. This creep problem becomes progressively worse at higher temperatures. Cross-linking by high-energy irradiation (or by chemical means) is a possible method of improving creep performance [3] but previous work has shown that coincident chain scission, which occurs to varying extents in the irradiation of all polyolefins, can be critical in the case of drawn polyethylene [4, 5] in that, under some conditions, loss of strength can overide any improvement in creep performance. The reason is that the high tensile strength and modulus of drawn polyolefins depends to a large extent on the presence of taut tie molecules, which are particularly vulnerable to chain scission during free radical attack in the irradiation process. One method of improving the ratio of cross-linking to chain scission in the gamma irradiation of polyolefins is to perform the irradiation in the presence of acetylene [6–9].

In this paper we describe experiments designed to optimize the conditions for the creep improvement of polyethylene tapes, draw ratio 6.5. Creep experiments can be extremely slow in providing information under ambient temperature conditions. We have found it convenient and informative also to investigate creep at higher temperatures. Irradiations have been performed both in vacuum and in an acetylene atmosphere for comparative purposes and the influence of dose and irradiation temperature have been studied.

2. Experimental procedure

2.1. Materials

All experiments were carried out on a single stock sample of polyethylene tape with a draw ratio of 6.5 which was kindly supplied by ICI Australia. It was prepared by extrusion from stock, code COMPOL HDPE 6905 and drawn in a hot-air oven at 260 °C (MW by GPC: $M_n = 21.8$, $M_w = 119\,kg\,mol^{-1}$, dimensions: 2.7×0.05 mm).

2.2. Irradiation procedures

All irradiations were carried out at the ANSTO gamma pond facility, Lucas Heights, Sydney. The dose rate was $1.2\,kGy\,h^{-1}$. Samples were irradiated in sealed ampoules either evacuated to 10^{-4} torr (or better) or filled to 101 kPa pressure with acetylene following evacuation. All samples (including unirradiated controls) were heated for 1 h at 100 °C prior to opening the ampoules in order to remove residual free-radical species.

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2.3. Gel contents

These were determined by comparing the sample masses before and after refluxing in xylene for 24 h.

2.4. Mechanical properties

Creep, stress–strain and shrinkage–stress experiments were carried out on the Flexitest, an instrument designed and built in our laboratories. It is a computer-controlled instrument designed to measure any combination of the variables stress (transducer output), strain (transducer output), time and temperature ($\pm$ 0.5 °C) applied to a sample. The computer controls the selected test and collects and analyses the data as required. Prior to each tensile creep, stress–strain or shrinkage–stress test, a conditioning program was applied to the sample in order to straighten out kinks and minimize grip effects. The sequence included the application of a 600 g mass at ambient temperature for 10 s followed by a recovery period of 5 min with no applied load. Shrinkage stress experiments were commenced by the application of a mass of 10 g to the samples at 30 °C. The strain was then held constant whilst the stress was monitored as the sample was heated through a temperature programme of 5 °C min^{-1}.

Owing to the restricted available number of irradiated samples, only one or two experiments were possible for each test. Thus the absolute magnitude of the mechanical properties, particularly break stresses and strains, do not have statistical support.

Initial sample lengths in all mechanical tests were 100 mm.

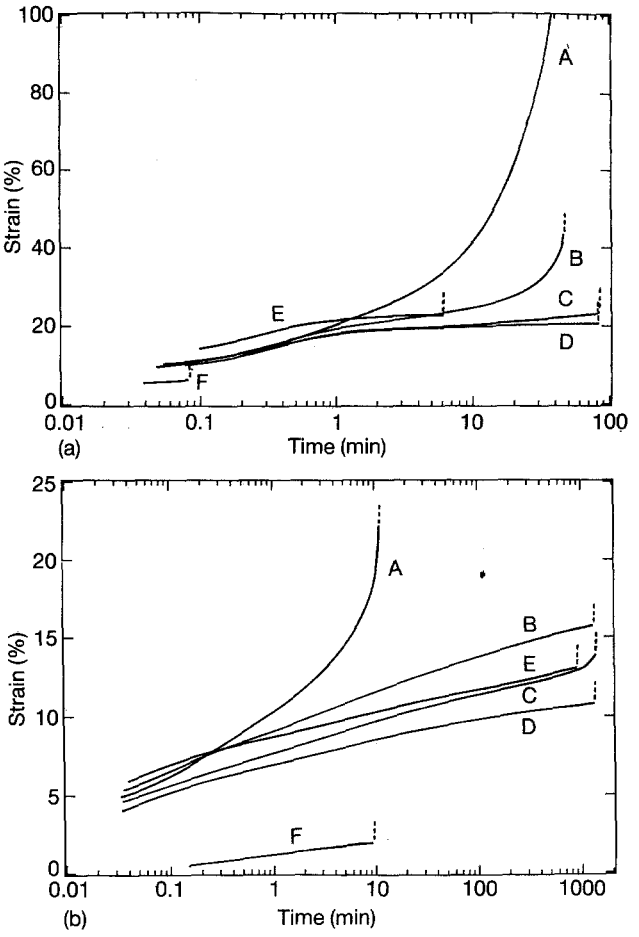

Figure 2 Creep curve of PE tapes irradiated in acetylene. Conditions of creep test: (a) 2.4 kg, 30 °C; (b) 0.4 kg, 100 °C. A, unirradiated control; B, 2 kGy; C, 5 kGy; D, 10 kGy; E, 20 kGy; F, 100 kGy.

3. Results and discussion

3.1. Influence of irradiation dose

The amount of cross-linking, as indicated by the gel content, as a function of irradiation dose is shown in Fig. 1. The observed enhancement of cross-linking by the presence of acetylene during the irradiation is in agreement with previous observations on polyethylenes [5–8] and polypropylene [9]. When acetylene is present, less than one-tenth the dose is required to produce the same gel content as produced by 100 kGy irradiation in vacuum.

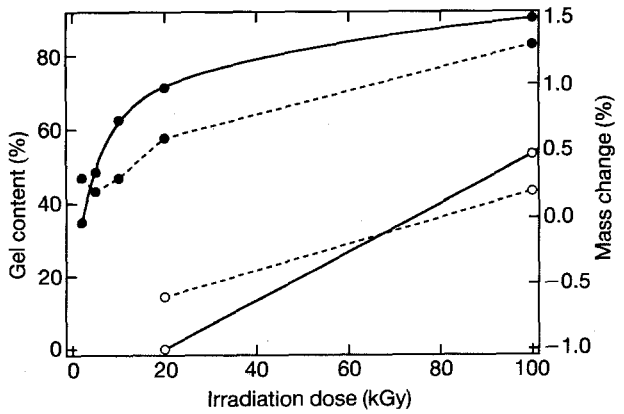

Figure 1 Gel content (——) and mass changes (– – –) as a function of irradiation dose for irradiation of PE tape in (●) acetylene and in (○) vacuum.

The sample mass increases slightly during irradiation in acetylene, see Fig. 1, indicating that acetylene is incorporated in very minor amounts in the polyethylene structure. In contrast, there is a slight loss or negligible change in mass observed during irradiation in vacuum. Undrawn polyethylene [6] and undrawn polypropylene [9] have also been observed to undergo small mass increases when irradiated in acetylene.

The creep curves of samples irradiated to various doses in the presence of acetylene for loads of 2.4 kg at 30 °C and 0.4 kg at 100 °C are compared with those of the unirradiated control sample in Fig. 2. The control samples had been subjected to identical thermal treatments to those experienced by the irradiated samples, to remove any differences due to thermal history. The response of the sample in a creep experiment can be considered in two stages. First, the short-term response reflects the elastic nature of the samples and relates to the flexibility of the amorphous regions of structure and their ability to respond to stress. Doses of 2–20 kGy in acetylene do not significantly affect the short-term creep at either 30 or 100 °C, although the short-term creep strain of the 20 kGy sample slightly exceeds that of the control at both temperatures, indicating a slight weakening of amorphous structure. However, there is a very marked decrease in creep strain for the sample given a 100 kGy dose, indicating significant stiffening of the amorphous regions. Unfor-

tunately, this desirable feature is accompanied by brittleness, as indicated by early sample fracture, see later.

In the longer term of the creep experiment, a sharp increase in creep rate indicates the commencement of lamellar breakdown by chain unfolding, i.e. yielding. With a load of 2.4 kg at 30 °C this occurs after about 5 min in unirradiated tape. This is delayed to about 20 min by 2 kGy irradiation in acetylene and suppressed completely by 5 kGy or higher doses. Similar effects are observed in the creep experiments at 100 °C with a load of 0.4 kg except that even the 2 kGy samples did not yield before 16 h (experiment terminated). Under these conditions, the unirradiated control is undergoing plastic flow from the start of the experiment. These findings are fully consistent with earlier suggestions [9] that acetylene preferentially causes cross-links to be formed in the defect structure at the surface of lamellae, thereby essentially locking the structure and inhibiting the chain-unfolding process.

It is also important to consider whether the irradiation process causes brittleness. In the creep experiments at 30 °C, the time to break is shown as a function of dose in Fig. 3. Time to break in a creep experiment provides a reasonable measure of relative brittleness as long as the extension at break is not excessive. At large extensions, the constant load applied in the creep experiment translates into increased sample stress. The time to break under such conditions is not comparable with values obtained at low extensions. Of the samples represented in Fig. 3, only the 2 kGy sample had a break strain $> 25\%$. Its break strain was 40%. Thus the time to break for this sample and also the unirradiated control sample, which did not break in the creep experiment, can only be regarded as minimum values. It is clear from Figs 2 and 3 that the optimum dose in terms of minimum brittleness combined with maximum suppression of plastic flow is 5–10 kGy in the presence of acetylene.

Similar information can also be observed from the results of stress–strain tests. These have also been run at 30 and 100 °C at a constant strain rate of 50% min^{-1}, see Fig. 4. The strain-hardening effect induced by the irradiation is not so clearly observed at 30 °C as in the creep experiments. However, it is very obvious at 100 °C, where the unirradiated sample undergoes yielding easily with a yield stress of only 40 MPa. The break stress of the sample with the optimum dose of 10 kGy in acetylene is 114 MPa, almost three times the yield stress of the unirradiated sample. Irradiation at lower doses has a detrimental effect on the initial modulus, see Table I, which relates in structural terms to the slight decrease in short-term creep strain observed for the sample irradiated to 20 kGy in acetylene, described above. At the optimum dose of 10 kGy the initial modulus decreases by about 24% at 30 °C and about 40% at 100 °C. The initial modulus increases with higher doses. With 100 kGy in acetylene, for example, the initial modulus is 6% greater at 30 °C and 52% greater at 100 °C than that of the unirradiated sample. These increases are accompanied by decreased break stresses owing to brittle fracture, as also observed in the creep experiments.

3.2. Influence of irradiation temperature

The effects of temperature of irradiation on the mechanical properties of the tape, given the optimum dose of 10 kGy, were investigated by experiments at 0 and 60 °C. The creep performance of both samples was very similar to that irradiated at 35 °C, although that irradiated at 0 °C exhibited the longest time to break.

The data for stress–strain experiments are given in Table I. Again the performance is similar to that of the sample irradiated at 35 °C (10 kGy in acetylene) and, in agreement with the creep results, the break stress of the sample irradiated at 0 °C is greatest. In conclusion, although irradiation temperature in the range 0–60 °C does not have a major effect, the tapes exhibit maximum strength when irradiated at 0 °C.

3.3. Comparison of optimum irradiation treatments in vacuum and in acetylene

The mechanical property improvements for samples irradiated under optimum conditions in acetylene (10 kGy) and in vacuum (100 kGy) have been compared by investigating creep behaviour at higher loads. Such test conditions are more discriminating but, of course, are only useful for samples which can take the loads. Differences can be most easily observed by Sherby–Dorn [10] graphs of creep strain rate

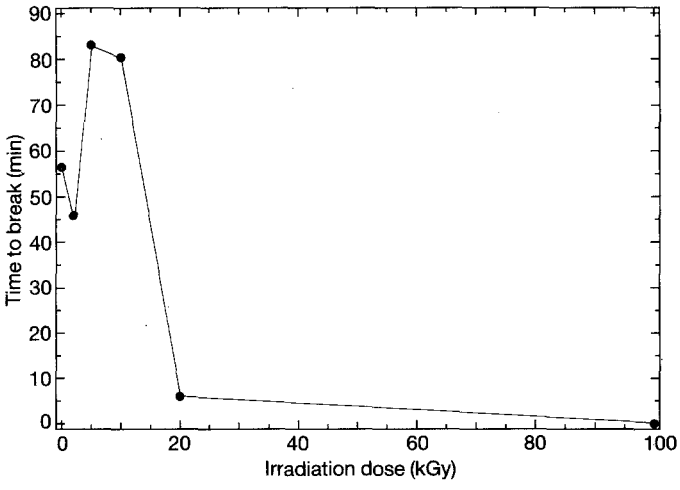

Figure 3 The time to break in creep experiments at 30 °C as a function of irradiation dose. Load 2.4 kg.

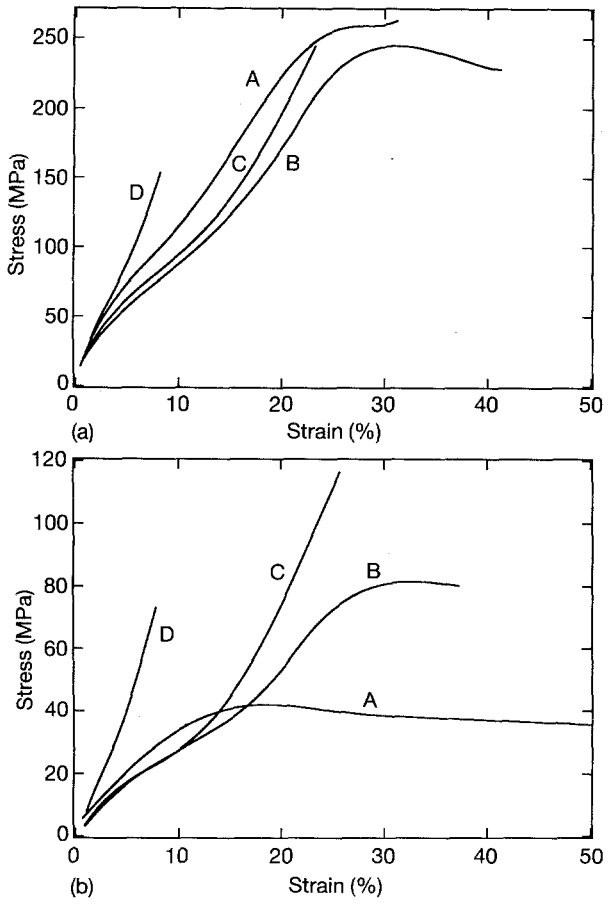

Figure 4 Stress–strain curves of PE tapes irradiated in acetylene. Test conditions: (a) 50% min^{-1} at 30 °C; (b) 50% min^{-1} at 100 °C. A, unirradiated control; B, 2 kGy; C, 10 kGy; D, 100 kGy.

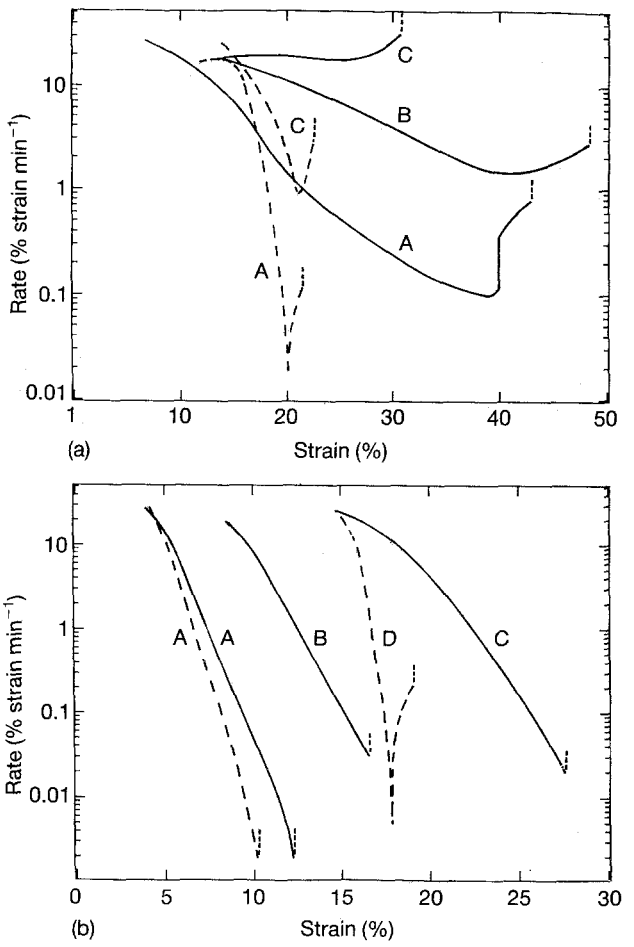

Figure 5 Creep curves, plotted as creep strain rate versus creep strain, of PE tapes irradiated in vacuum to 100 kGy (——) and in acetylene to 10 kGy (– – –). Test conditions: (a) 30 °C, A, 2.4 kg; B, 2.8 kg; C, 3.2 kg; (b) 100 °C, A. 400 g; B, 500 g; C, 800 g; D, 1 kg.

TABLE I Stress–strain data for PE tape irradiated in the presence of 1 atm acetylene under various conditions. Strain rate: 50% min^{-1}

Test temp. (°C)	Irradiation		Initial modulus (GPa)	Break	
	Dose (kGy)	Temp. (°C)		Stress (MPa)	Strain (%)
30	Control		17	262	31
	2	35	9	225	41
	10	35	12	243	23
	100	35	17	156	8
	10	0	12	282	23
	10	60	16	275	27
100	Control		4.7	< 23 (43)[a]	> 163 (18)[a]
	2	35	3.1	80	37
	10	35	2.8	114	26
	100	35	7.3	74	7
	10	0	3.8	121	21
	10	60	3.5	111	21

[a] Yield stress and strain.

versus creep strain. The results of creep tests at 30 °C for the two samples at loads of 2.4 and 3.2 kg (equivalent to 77% and 98% of the break stress of the unirradiated sample, respectively) and at 100 °C with various loads, are shown in Fig. 5.

At 30 °C, application of the loads initially results in similar strain rates. The strain rates of the sample irradiated in acetylene decrease much more rapidly than those of that irradiated in vacuum. The superiority of the sample irradiated in acetylene is more easily seen under high stress conditions where the creep strain rate of this sample reduces by a factor of 20 at a strain of about 20%, once it has borne the load, whereas the sample irradiated in vacuum never really bears the load as it proceeds to fracture at 32% strain with a strain rate always greater than 15% min^{-1}. At 100 °C, the similarity of creep behaviour of the two samples with a load of 0.4 kg is clearly shown in Fig. 5, although the creep rate of the sample irradiated in acetylene becomes increasingly less than that of the vacuum-irradiated sample. Again higher loads discriminate effectively between the performance of the two samples as illustrated in Fig. 6 by a graph of the strain at which the strain rate has decreased to 1% min^{-1} versus the applied load.

3.4. Break strains of irradiated samples

The break strains in creep experiments performed on a range of samples are shown in Table II. Coupled with the break strain observed in the stress–strain experiments listed in Table I, it can be seen that all values for samples irradiated to 5 kGy or greater in the presence of acetylene lie in the range 18%–26%,

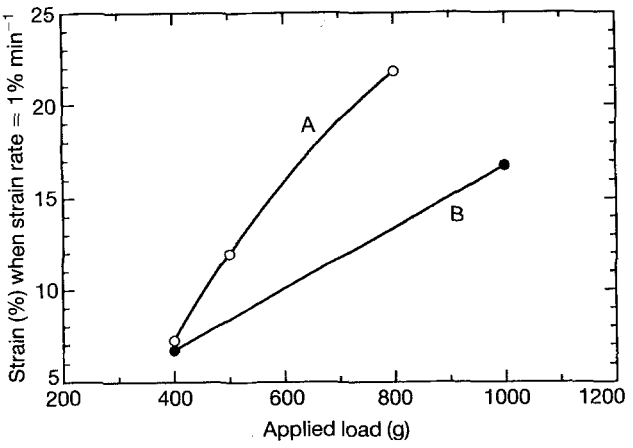

Figure 6 Effect of applied stress on the strain reached when the creep strain rate has reduced to 1% min^{-1} at 100 °C of PE tapes irradiated to (A) 100 kGy in vacuum, (B) 10 kGy in acetylene.

TABLE II Values of break strains in creep experiments at 30 °C

Irradiation			Test Load	Break	
Dose (kGy)	Temp. (°C)	Atm: Ac/V[a]	(kg)	Strain (%)	Time (min)
Control			2.4	> 100	> 30
2	35	Ac	2.4	40	45
5	35	Ac	2.4	23	85
10	35	Ac	2.4	20	80
20	35	Ac	2.4	23	6
100	35	Ac	2.4	7	0.1
10	60	Ac	2.4	21	8
10	0	Ac	2.4	> 18[b]	> 100
10	35	Ac	3.2	22	3
100	35	V	2.4	42	105
100	35	V	2.8	49	11
100	35	V	3.2	31	1

[a] Atmosphere: Ac = acetylene; V = vacuum.
[b] Sample had not broken at the termination of the experiment.

except where premature fracture occurred in the case of the sample irradiated to 100 kGy. The yield strain of the unirradiated sample is not greatly influenced by test temperature or applied load and lies in the range 13%–14% [11]. The fact that the break strain of the samples irradiated in acetylene slightly exceeds this suggests that either the suppression of chain unfolding under stress is not completely achieved by the cross-linking process or that there is some structural loosening in the amorphous regions due possibly to chain scission. The observations on early creep strain and modulus suggest the latter is the more important factor. The break strains observed for the samples given 100 kGy of irradiation in vacuum are significantly greater and, because the initial creep strain rates are similar to those of the acetylene-irradiated samples (Fig. 5), it appears the vacuum-irradiation process is much less efficient in suppressing chain unfolding under stress, even after 100 kGy.

3.5. Shrinkage–stress behaviour

Shrinkage–stress experiments give an indication of the strength of the polymer network in a sample. The

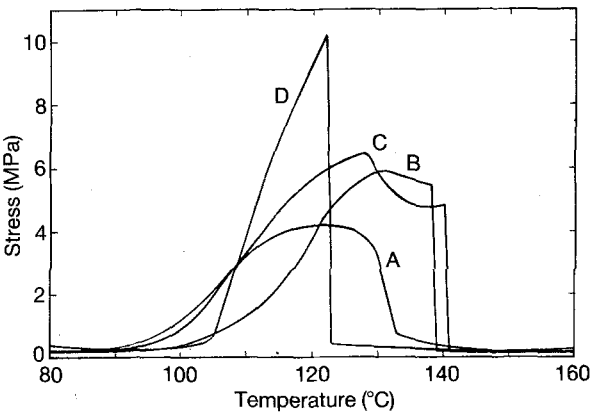

Figure 7 Effect of irradiation dose on the shrinkage stress responses of PE tape irradiated in acetylene. A, unirradiated control; B, 2 kGy; C, 10 kGy; D, 100 kGy. Heating rate 5 °C min^{-1}.

effect of irradiation dose on the development of internal stress as each sample is heated through a temperature program whilst being held at constant strain is shown in Fig. 7. The maximum stress which develops within the sample increases with irradiation dose. The effect could not be due to direct strengthening of the network because that was set before the polymer was drawn and is the source of the retractive force causing the shrinkage stress. New cross-links would retard the action of the network.

The increase is probably due to the cross-links inhibiting structural reorganization which would normally move to relieve the stress build-up. The stress build-up is so severe after 100 kGy irradiation that the sample fractures prior to melting. On the other hand, after doses of 2 and 10 kGy, a residual stress persists to about 140 °C, i.e. well above the melting point, showing that a new weak amorphous network has formed which is capable of maintaining the integrity of the sample, when the crystalline structure has gone, if only for a short time.

4. Conclusion

This work has shown that polyethylene tapes drawn to their "natural draw ratio" can be given improved creep performance by gamma-irradiation techniques. When acetylene is present during irradiation, the optimum dose required is in the range 5–10 kGy, one-tenth that required if the irradiation is performed in vacuum. The irradiation treatment leads to suppression of plastic flow (sample yielding) and consequently low creep rates over extended time periods. This is a particularly important improvement for higher temperature application. Creep experiments with higher loads have shown that the optimum acetylene-sensitized treatment is more effective in reducing creep rate than the optimum vacuum-irradiation treatment.

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