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# Post-gamma irradiation cross-linking of polyethylene tape by acetylene treatment

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The feasibility of enhancing cross-linking in drawn polyethylene tape by a two-stage process involving first irradiation and second exposure to acetylene gas, has been established. A number of variables have been investigated; a dose of 50 kGy gamma irradiation in vacuum at − 196 °C followed by exposure to 1 atm acetylene for 36 h results in a cross-linked product with far superior creep performance to that of the untreated tape without loss of tensile modulus or strength. The treatment is particularly effective for the improvement of creep performance at 100 °C. It is also shown to be slightly superior to both irradiation in vacuum and irradiation in an acetylene atmosphere, each under optimum conditions.

## 1. Introduction

In a recent paper [1] we have described the advantages of acetylene-sensitized irradiation cross-linking of polyethylene tape for the improvement of creep performance. Unfortunately, the combined hazards of irradiation by either gamma rays or electron beam and the presence of potentially explosive acetylene gas are likely to prohibit commercial application of this process. Post-irradiation grafting has been known and utilized for many years and we have shown that post-irradiation cross-linking with acetylene is a viable process for use with polypropylene film [2]. Recently, Klein *et al.* [3] have shown that post-irradiation techniques are also effective in the cross-linking of highly drawn PE fibres. They utilized a number of techniques to compare the structure and morphology of samples cross-linked by irradiation in an inert atmosphere, by irradiation in an inert atmosphere followed by exposure to acetylene, and by irradiation in an atmosphere of acetylene followed by exposure to acetylene. One conclusion was that the latter method results in the highest gel content. However, they did not report the mechanical properties of the cross-linked samples.

We describe here the results of an investigation into the viability and optimization of cross-linking drawn polyethylene tapes by a two-step process involving irradiation in an inert atmosphere followed by exposure to acetylene gas. The separation of the two hazardous processes would improve the commercial viability.

The control of post-irradiation reactions of polymers with gases requires consideration of a number of variables. The conditions of the irradiation process need to be optimum for the production of long-lived free radicals, which, although relatively inert during irradiation and storage, will react to form effective cross-links when exposed to acetylene gas. Irradiated samples need to be stored prior to post-irradiation reactions at low temperatures to prevent premature radical decay. The temperature of exposure of pre-irradiated polymer to acetylene gas will be critical, because cross-linking reactions will always be in competition with free radical decay by alternative routes. In addition, sufficient time is required to allow complete diffusion of acetylene to reactive sites in the polymer.

Previous work on the grafting of polyethylene undrawn film [4] has suggested that pre-irradiation might be effective if carried out in air. This, of course, would be an added advantage at a commercial level.

This work covers a study of some of these variables on the production of cross-linked polyethylene tapes. Cross-linking has been monitored by gel content and mechanical property measurements.

## 2. Experimental procedure

### 2.1. Material

The polyethylene tape was the same as that described in the preceding paper [1]. It was kindly supplied by ICI Australia, draw ratio, 6.5; $M_n = 21.8$, $M_w = 119\ \mathrm{kg\,mol^{-1}}$; dimensions, 2.7 mm × 0.05 mm.

### 2.2. Cross-linking procedure

Irradiations were carried out at the ANSTO gamma pond facility, Lucas Heights, Sydney. The dose rate was $1.2\ \mathrm{kGy\,h^{-1}}$. Samples were irradiated in ampoules, fitted with break seals, evacuated to $10^{-4}$ torr (or better) either at pond temperature (about 35 °C) or at − 196 °C. Following transport and storage at − 196 °C, the ampoules were sealed to a vacuum line,

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brought to 0 °C, evacuated and filled with acetylene gas at 1 atm pressure to the break seal and, finally, after breaking the internal seal, the ampoule was brought to the appropriate post-irradiation temperature for 36 h. Before the samples were removed, the ampoule was re-evacuated and heated at 100 °C for 1 h to allow any remaining free radicals in the sample to decay.

In one experiment, the sample was irradiated in an open ampoule at pond temperature. Thereafter, it was treated in the same way as vacuum-irradiated samples.

### 2.3. Gel contents

These were determined by comparing the sample masses before and after immersion inside stainless steel mesh baskets in boiling xylene for 24 h.

### 2.4. Mechanical properties

Creep and stress–strain experiments were carried out on the Flexitest, an instrument designed and built in our laboratories. Details are given in the preceding paper [1].

## 3. Results and discussion

### 3.1. Conditions of irradiation

In experiments designed to find the optimum conditions of irradiation, the first stage of the process, our previous experience with the post-irradiation grafting of polypropylene film [2] was used to indicate suitable conditions for post-irradiation cross-linking, the second stage. These were: storage at − 196 °C between irradiation and reaction, followed by contact with acetylene at 1 atm pressure for 36 h at 40 °C. The gel content of samples given various irradiation doses, temperatures and atmospheres, all with the above post-irradiation treatment are shown in Table I. Post-irradiation cross-linking certainly occurs for samples pre-irradiated in vacuum, because the gel dose for the vacuum-irradiated tapes without the second stage is between 20 and 50 kGy and even after a dose of 100 kGy in vacuum, the gel content is only 53%. Thus post-irradiation exposure to acetylene has caused considerable increase in the gel content. The temperature of sample irradiation (− 196–35 °C) has had negligible effect on the gel content achieved after the second stage, indicating that it is the long-lived radicals with stability above 35 °C which are effective in the second stage. On the other hand, pre-irradiation in air at 35 °C was found to be completely ineffective, as no effective cross-links were formed after this treatment and post-irradiation exposure to acetylene.

The effects of irradiation dose on the mechanical properties are shown in Figs 1 and 2. The stress–strain behaviour at both 30 and 100 °C shows how the post-irradiation cross-linking treatment is completely effective in inhibiting the yielding ability, whilst not causing any reduction in break stress or initial modulus, see Table II. The treatment is particularly effective at 100 °C where the untreated sample has a low yield stress, whilst the treated samples exhibit considerable

TABLE I Gel contents and mass changes of PE tape following irradiation under various conditions and post-irradiation treatment: 36 h exposure to acetylene at 1 atm and 40 °C

| Irradiation | | | Gel content (%) |
|---|---|---|---|
| Temp. (°C) | Dose (kGy) | Atm[a] | |
| − 196 | 20 | V | 55.6 |
| − 196 | 50 | V | 66.4 |
| − 196 | 100 | V | 70.9 |
| 35 | 50 | V | 63.6 |
| 35 | 50 | A | 0 |

[a] Atmosphere inside ampoule: V = vacuum, A = air.

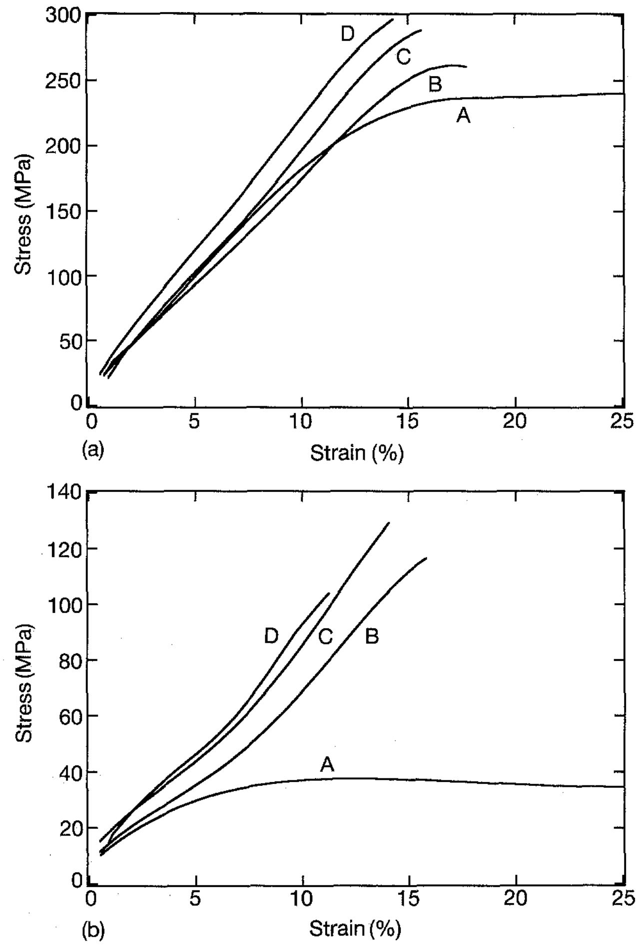


*Figure 1* Stress–strain curves for PE tape after various doses of irradiation at − 196 °C in vacuum followed by post-irradiation treatment of exposure to 1 atm acetylene for 36 h at 40 °C. Test conditions: (a) 50% min$^{-1}$ at 30 °C, (b) 50% min$^{-1}$ at 100 °C. A, unirradiated control; B, 20 kGy; C, 50 kGy; D, 100 kGy.

strain hardening on extension. The creep curves in Fig. 2 confirm that yielding is completely inhibited in the treated samples at both 30 and 100 °C. With a load of 2.4 kg (stress of 174 MPa) the time to break of the tape given a pre-irradiation dose of 50 kGy is over 300 min at 30 °C, i.e. greater than a five-fold increase over that of the untreated sample. The relative performance at 100 °C is even better. From the times to break in the creep experiments at 30 °C and the break stresses observed in the stress–strain experiments at 100 °C, the optimum dose appears to be 50 kGy. On the other hand, a dose of 100 kGy resulted in slightly

TABLE II Stress–strain data for PE tape before and after various post-irradiation treatments. Acetylene pressure = 1 atm, exposure time = 36 h, strain rate = 50% $min^{-1}$

| Test temp. (°C) | Irradiation | | PI temp. (°C) | Initial modulus (GPa) | Break | |
|---|---|---|---|---|---|---|
| | Dose (kGy) | Temp. (°C) | | | Stress (MPa) | Strain (%) |
| 30 | Control | | | 19.1 | 249 | 46 |
| | | | | | 229[a] | 15[a] |
| | 20 | − 196 | 40 | 18 | 263 | 18 |
| | 50 | − 196 | 40 | 21 | 290 | 16 |
| | 100 | − 196 | 40 | 22 | 297 | 14 |
| | 50 | − 196 | 0 | 21 | 266 | 15 |
| | 50 | − 196 | 80 | 19 | 242 | 18 |
| 100 | Control | | | 4.4 | < 18[b] | > 160[b] |
| | | | | | 38[a] | 13[a] |
| | 20 | − 196 | 40 | 5.5 | 117 | 16 |
| | 50 | − 196 | 40 | 7.1 | 130 | 14 |
| | 100 | − 196 | 40 | 8.6 | 105 | 11 |
| | 50 | 35 | 40 | 5.6 | 117 | 18 |
| | 50 | − 196 | 0 | 6.6 | 124 | 14 |
| | 50 | − 196 | 80 | 4.7 | 113 | 23 |

[a] Yield stress and strain.
[b] Did not break in the experiment.

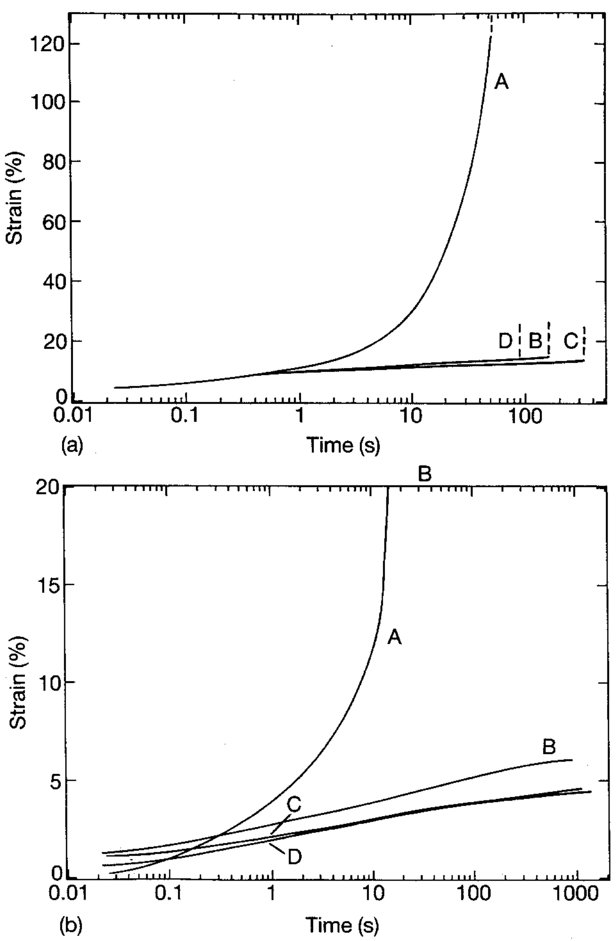


*Figure 2* Creep curves for PE tape (a) at 30 °C with load 2.4 kg and (b) at 100 °C with load 0.4 kg. For treatment and captions, see Fig. 1.

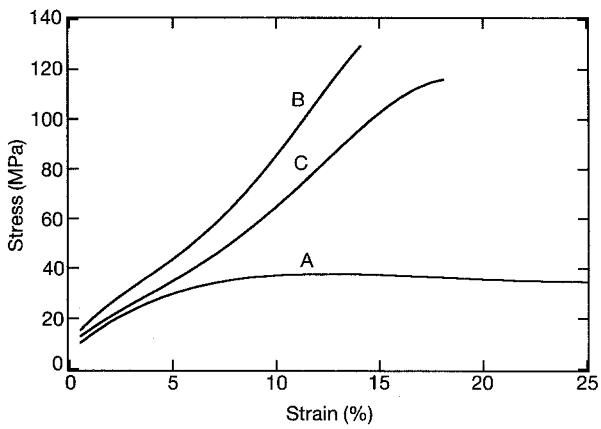


*Figure 3* Stress–strain curves for PE tape after 50 kGy irradiation at − 196 °C (Curve B), 35 °C (Curve C) in vacuum followed by post-irradiation treatment of exposure to 1 atm acetylene for 36 h at 40 °C. Test conditions: 50% $min^{-1}$ at 100 °C. Curve A: unirradiated control.

higher modulii and slightly lower initial creep strains suggesting that a dose between 50 and 100 kGy may be more beneficial. The properties do not critically depend on dose in this range, however.

The effect of irradiation temperature on the mechanical properties of the tapes is shown in Figs 3 and 4. Irradiation at − 196 °C results in slightly better performance than that at 35 °C where the time to break in the creep experiment at 30 °C is reduced by about 50% and the break strength and modulus in the stress–strain test at 100 °C are also inferior.

## 3.2. Conditions of post-irradiation treatment

Irradiation to 50 kGy at − 196 °C followed by storage at − 196 °C was used as the optimum set of conditions in a study of the influence of post-irradiation temperature on the efficiency of the overall process. The gel contents for temperatures of 0, 40 and 80 °C were 64.2, 66.4 and 59.4%, respectively, indicating that post-irradiation temperature is not a critical variable for cross-link formation in this process. This contrasts with the post-irradiation grafting behaviour of polypropylene with butadiene [5], where it was

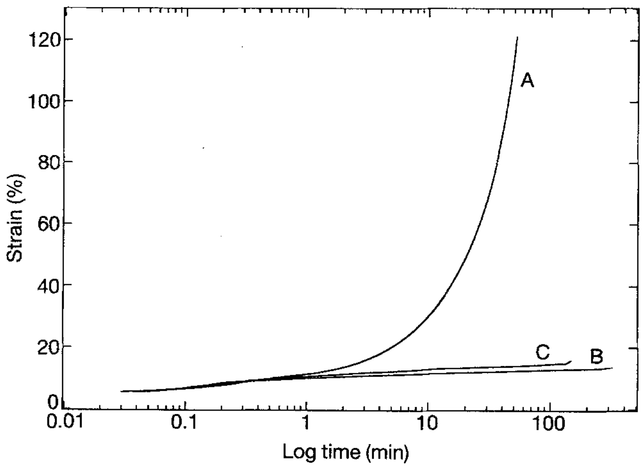


*Figure 4* Creep curves for PE tape at 30 °C with a load of 2.4 kg. For treatment and captions, see Fig. 3.

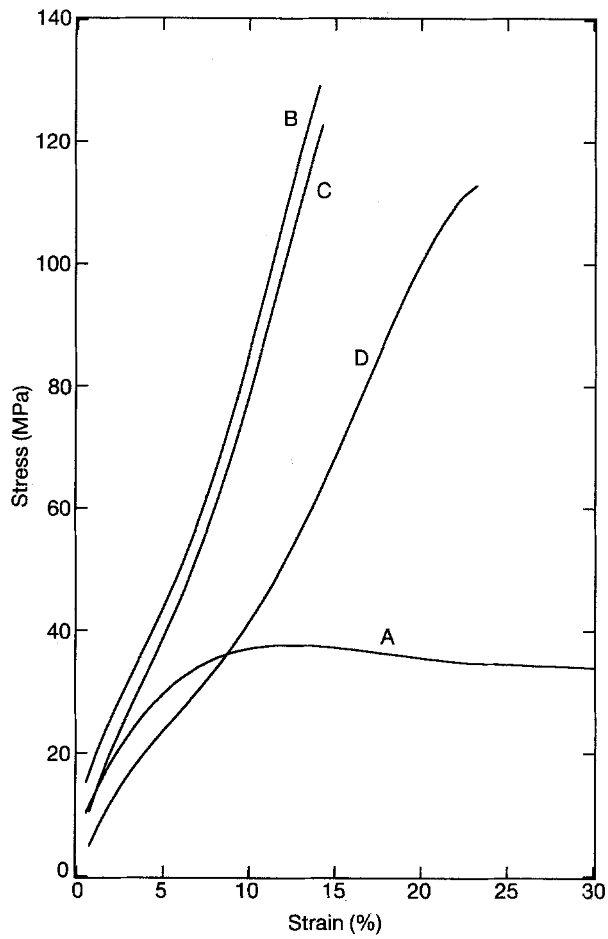


*Figure 5* Stress–strain curves for PE tape after 50 kGy irradiation at − 196 °C in vacuum followed by exposure to 1 atm acetylene for 36 h at 0 °C (B); 40 °C (C); 80 °C (D). Unirradiated Control: Curve A.

found that the grafting rate was very slow at 0 °C, optimum at about 45 °C, and did not compete well with radical decay at 80 °C, i.e. post-irradiation temperature was a more critical factor in that system.

The stress–strain and creep performance of samples cross-linked with different post-irradiation temperatures and otherwise constant conditions of cross-linking treatment are shown in Figs 5 and 6. Some stress–strain data are also listed in Table II. These show that, despite the similarity in gel content achieved, cross-linking is less effective in the modification of mechanical properties when the post-irradiation treatment is carried out at 80 °C than when carried out at lower temperatures. The creep strain is consistently and significantly higher in creep experiments at both 30 and 100 °C, the time to break at 30 °C is lower and in the stress–strain experiments the initial modulus and break stress are lower at both 30 and 100 °C. The difference between the properties of the samples given post-irradiation treatment at 0 and 40 °C is minor. The former is slightly superior in creep strain, modulus and break stress at 100 °C, whereas the latter is slightly superior in terms of time to break (creep 30 °C) and break stress at 30 °C.

### 3.3. Comparison of post-irradiation cross-linking with one-stage irradiation cross-linking

The stress–strain behaviour at 100 °C of samples cross-linked by (i) irradiation *in vacuo*, (ii) irradiation in acetylene gas, and (iii) post-irradiation treatment (labelled PI sample below), all under optimum conditions are compared with that of untreated polyethylene tape in Fig. 7. Whilst all irradiation treatments result in improved tensile properties, the post-irradiation treatment produces the most significant effect. The PI sample exhibits a higher initial modulus than the unirradiated control, whereas both other irradiated samples exhibit lower values. This suggests that chain scission in the amorphous regions is minimal in the PI sample because it has been argued [1] that the slight decrease in initial modulus and slightly increased initial creep strains observed for vacuum- and acetylene-irradiated samples is due to some structural loosening in the amorphous regions, i.e. the regions most critical in sample response to low stress levels. The loosening could only be caused by some chain scission. Also, the break strain for the PI sample is the least of all samples, and similar in value to the yield strain of the untreated sample. This indicates that the post-irradiation treatment is the most effective in locking the crystallites by the formation of cross-links on the crystallite surface and thereby preventing lamellar unfolding when a tensile stress is applied.

The corresponding creep curves, see Fig. 8, also illustrate the superiority of the post-irradiation technique for creep improvement. Creep strain is always less for the PI sample than for both the vacuum-irradiated and the acetylene-irradiated samples at both temperatures. The time to break at 30 °C with a load of 2.4 kg is also greater by about a factor of 4. In creep experiments at 100 °C, none of the treated samples broke.

## 4. Conclusion

This work has shown that irradiation cross-linking of drawn polyethylene tape is most effective when carried out in a two-stage process involving irradiation with gamma rays in vacuum followed by treatment with acetylene gas. When carried out under optimum

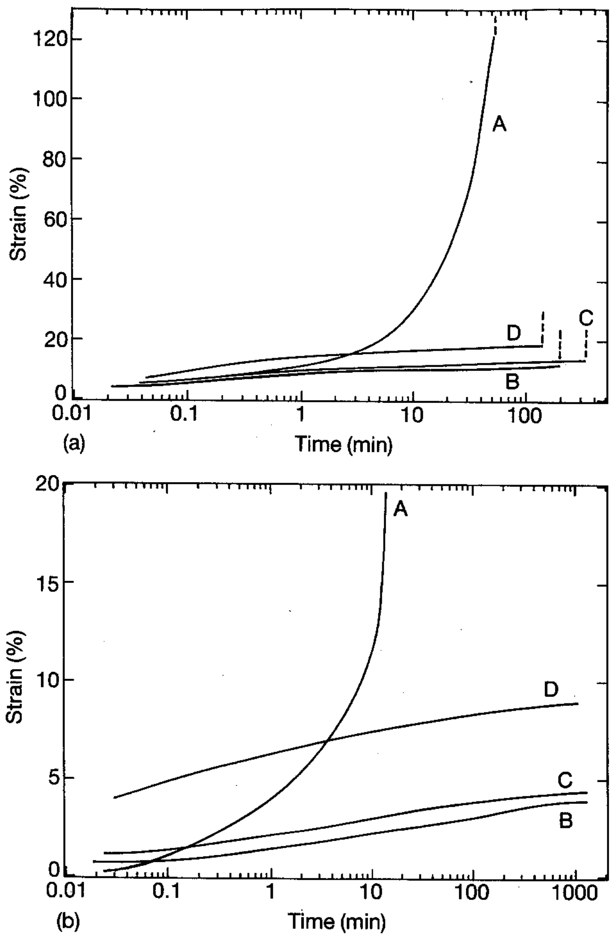


*Figure 6* Creep curves for PE tape (a) at 30 °C with a load of 2.4 kg and (b) at 100 °C with a load of 0.4 kg. For treatment and captions, see Fig. 5.

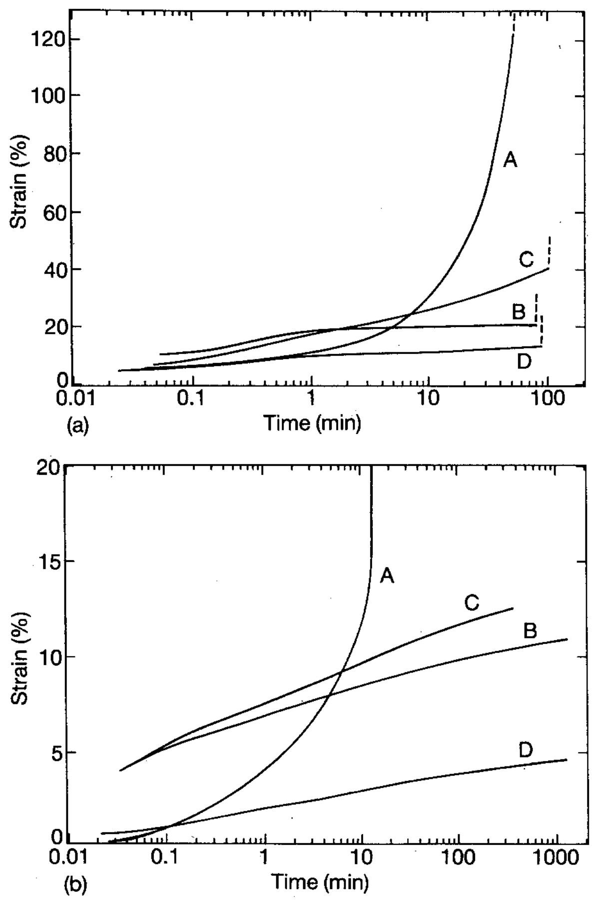


*Figure 8* Creep curves for PE tape (a) at 30 °C with a load of 2.4 kg and (b) at 100 °C with a load of 0.4 kg. For treatment and captions, see Fig. 7.

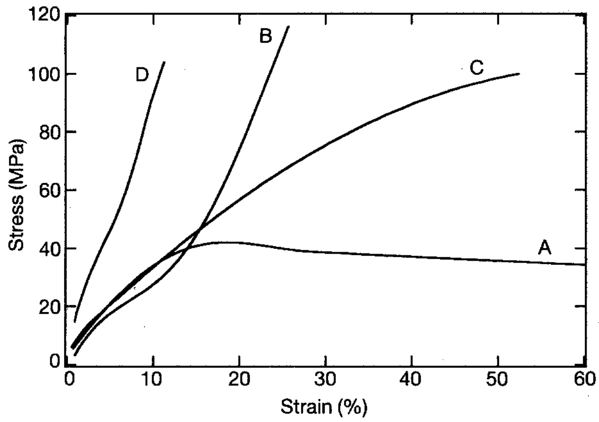


*Figure 7* Stress–strain curves for PE tape given various cross-linking treatments. A, Unirradiated control; B, 10 kGy irradiation at 35 °C in 1 atm acetylene; C, 100 kGy irradiation at 35 °C in vacuum; D, 100 kGy irradiation at − 196 °C in vacuum followed by 36 h exposure to acetylene at 40 °C. Test conditions: 50% $min^{-1}$ at 100 °C.

conditions the treatment improves the creep performance remarkably without any decrease in modulus or break stress. Plastic flow under stress (yielding) is completely suppressed and the residual creep rate is significantly less than that of samples cross-linked by irradiation in vacuum or in an acetylene atmosphere. The time to break under load at both 30 and 100 °C is increased many times over that of untreated tape.


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