The gel and rheological behaviour of radiation-crosslinked linear low-density polyethylene

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Linear low-density polyethylene (LLDPE) was irradiated with electron beam radiation at room temperature and in the melt. It was found that the gel point, as measured by an insoluble fraction in boiling xylene, occurred at a slightly lower radiation dose for melt irradiated samples. The melt radiation-crosslinked samples showed different melt rheological properties from the room-temperature radiation-crosslinked samples, as exemplified by the stress relaxing more slowly in a step strain experiment (relaxation modulus) for the former at a given radiation dose. The relaxation modulus could be fitted to a power-law expression consisting of two parameters, which, when plotted against each other, resulted in a single master curve for both irradiation temperatures. The curve showed two distinct regions of differing slope, which intersect at a point argued to represent a pseudogel point.

(Keywords: linear LDPE; electron beam irradiation; melt rheology)

INTRODUCTION

High-energy irradiation of polymers is used to control the strength of polymeric insulation cables, to increase vulcanization of sheet rubber and to increase the stress-work resistance of plastics. Irradiation produces controlled structural changes to the polymer network to yield these property changes. Randall *et al.*[1,2] noted that increasing irradiation temperature increased the effective amorphous regions in the melt, and subsequently increased the effects of irradiation. It must, therefore, be noted that irradiation temperature along with radiation dose will affect the final properties.

Recently, work by Andreucetti *et al.*[3] and Vallés *et al.*[4] has shown the effects of gamma radiation on the rheological properties of linear low-density polyethylene (LLDPE). In particular, Vallés *et al.* have demonstrated that at a certain radiation dosage the polymer melt's rheological properties are consistent with the generalized gel rheological model of Chambon and Winter[5]. This model is written mathematically for shear flows as:

$$\sigma_s(t)=S\int_{-\infty}^{t}(t-t')^n\dot{\gamma}_s\,\mathrm{d}t' \qquad (1)$$

where σ_s is the shear stress, $\dot{\gamma}_s$ is the shear rate, t is the present time, S is the gel strength parameter and n is the relaxation exponent. The parameters S and n are characteristic parameters for each gel and n must be greater than 0 and less than 1. Equation (1) is similar to the model proposed by Larson[6] for a power-law distribution of relaxation times. The only difference is that Larson includes non-linear behaviour in his model by including a damping function.

Here, specifically, the effects of radiation dose and irradiation temperature will be investigated in terms of their effect on the melt rheology of LLDPE. This will be critically examined in light of the results of Randall *et al.* mentioned above. Also, the validity of the power-law model developed by Chambon and Winter for dynamic shear properties will be examined.

EXPERIMENTAL

Materials

The grade of LLDPE used was Dowlex 2045E (pure grade, no additives) from Dow Australia. The polymer was characterized by high-temperature (140°C) gel permeation chromatography in 1,2,4-trichlorobenzene to produce the following molecular-weight information ($\mathrm{g\,mol^{-1}}$): $M_n=29\,200$, $M_w=110\,000$, $M_z=361\,000$, and $M_w/M_n=3.77$. The pellets were placed between two photographic metal plates to reduce sticking and then into a press heated to 150°C. A nitrogen purge was used to reduce degradation and a sheet of approximately 1 mm thickness was formed. Discs were then punched from the sheet for radiation treatment and subsequent testing.

The polymer was stated by the manufacturer to be a copolymer of octene with ethylene. This was independently confirmed by n.m.r. spectroscopy of a 15% w/v solution of the polymer dissolved in 80% dichlorobenzene and 20% perdeuterated benzene using a single pulse (Bloch decay) experiment. This was performed with a Bruker AMX500 spectrometer with the sample at 120°C. It was determined that there were 18 side chains per 1000 main-chain carbon atoms based on the ratio of the areas of the branched (nB6) to main-chain ($-CH_2-$) signals.

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Sample irradiation

The electron beam irradiation was performed with a 3 MV Van de Graaff accelerator (Interuniversity Reactor Institute, The Netherlands) at irradiation temperatures, T_I, of 25 and 150°C. Radiation dose levels were 0.1, 0.5, 1, 5 and 10 Mrad. All samples were dried in a vacuum oven for 1 h at 70°C and then evacuated in sealed tubes for 24 h prior to radiation treatment. After exposure to radiation, the samples were placed in a vacuum oven for 1 h at 105°C to quench radicals.

Rheological characterization

The dynamic shear properties were determined at 170°C with a modified Rheometrics RFS rheometer with the parallel-plate geometry[7]. Dynamic rate sweeps were performed from 0.1 to 100 rad s^{-1} at 5% strain to measure the storage modulus, G', and phase angle lag, δ. Step strain tests were also performed at 5% strain to determine the relaxation modulus, G. This level of strain ensured that the measurements were in the linear viscoelastic region.

Other tests

Differential scanning calorimetry (d.s.c.) tests were performed on a Perkin–Elmer DSC-7 station with 1–5 mg of sample sealed in aluminium pans under a nitrogen atmosphere. Temperature profiles from 50 to 170°C at 20°C min^{-1} were conducted to measure the onset (T_{mo}) and peak (T_{mp}) melting temperatures, heats of melting (H_m) and endotherm shapes. Percentage crystallinity was determined by the ratio of H_m to that of 100% crystalline polyethylene.

Gel fraction tests were performed on irradiated LLDPE to determine the fraction of insoluble gel and amount of solvent absorbed by the gel. Samples of polymer were weighed before and after 8 h in boiling xylene at 140°C. Over this time soluble fractions of LLDPE dissolve in the xylene. Samples were then dried in a vacuum oven at 70°C overnight to determine the amount of gel and amount of solvent in the gel.

RESULTS AND DISCUSSION

Before beginning this section proper, it should be noted that both gamma and electron beam radiations were used to irradiate samples at room temperature. O'Donnell and Sangster[8] have noted that these two types of radiation may influence the final properties owing to differing penetration depths. However, Halley[9] has shown that there is no significant difference between the two types in terms of the physical and melt rheological properties of LLDPE samples, probably due to the samples being relatively thin (ca. 1 mm). Some differences in the physical and rheological properties do exist though.

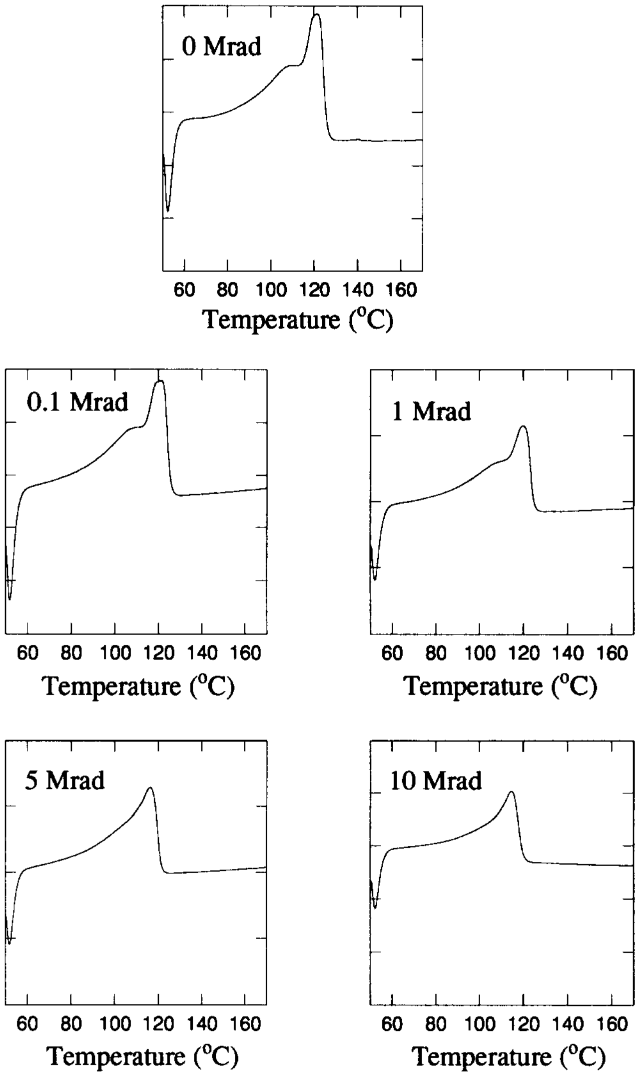

Figure 1 Effect of electron beam radiation dose on the d.s.c. endotherms of LLDPE at an irradiation temperature of 25°C

D.s.c. analysis

Examples of the d.s.c. endotherms are shown in *Figure 1* for various levels of irradiation, where the sample was irradiated at 25°C. Similar shapes are obtained when the irradiation temperature was 150°C. It can be seen that with increasing radiation dose the endotherm becomes broader and loses the double-valued peak characteristic of untreated LLDPE. These results are consistent with those of Whittaker[10], who found broader single-peaked endotherms with increasing radiation dose for a similar LLDPE. The endotherm also shifts to lower temperatures and becomes smaller with increasing radiation dose.

The effect of radiation dose and irradiation temperature on T_{mo}, T_{mp} and H_m is shown in *Figure 2*. Clearly, the melting temperatures (T_{mo} and T_{mp}) and heat of melting decrease with increasing radiation dose for both irradiation temperatures. We first consider the effect of radiation when irradiated at room temperature.

The results agree with those of Whittaker[10], who found a decrease in T_{mp} and H_m with increasing radiation dose when the irradiation was performed at room temperature. Whittaker attributed the reduction in T_{mp} to inhibiting crosslinks formed at the crystallite surface and the decrease in H_m to a decrease in crystalline regions.

The reduction in crystallinity for LLDPE 2045E with radiation dose was quantified from the H_m data based on equation (2)[9–11] and is shown in *Table 1*:

$$\text{Crystallinity (\%)} = \frac{H_m}{H_m(100\%) = 288\ \text{J g}^{-1}} \times 100 \quad (2)$$

One can see initially that there is a reduction in the crystallinity of LLDPE with increasing levels of irradiation, which indicates a growth in the amorphous region through increased crosslinking. This is in agreement with Tabata[12] and Nikolova *et al.*[13], who found that the amorphous regions were crosslinked preferentially to the

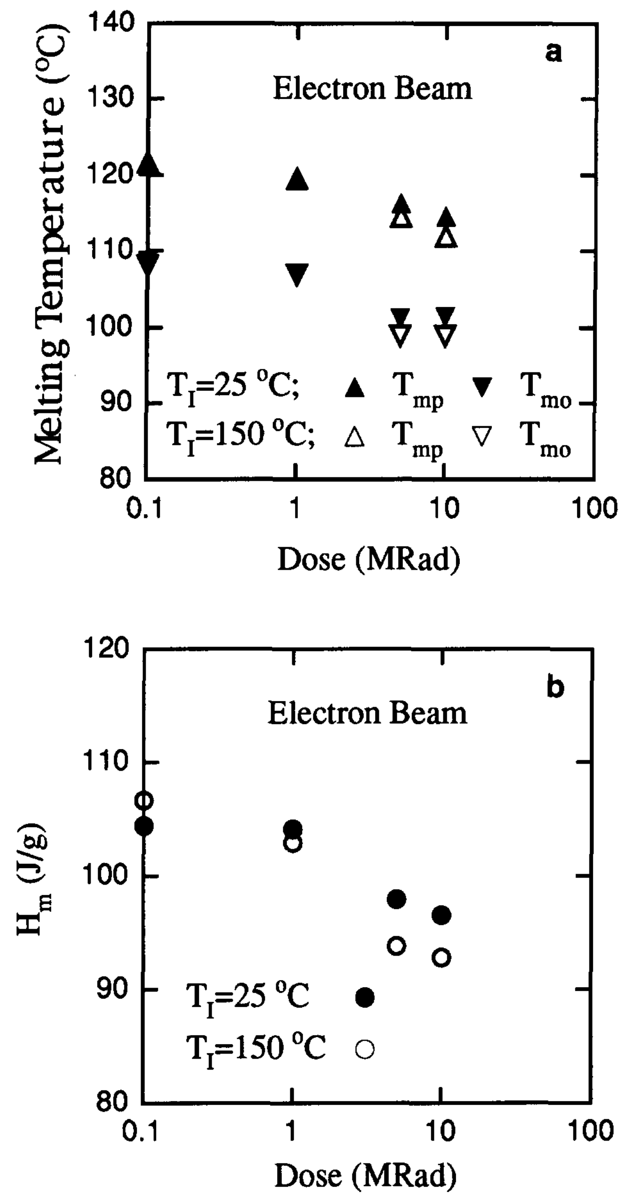

Figure 2 Electron beam radiation dose and irradiation temperature effects on (a) melting temperatures and (b) heat of melting of LLDPE

Table 1 Effect of irradiation temperature, $T_{\rm I}$, on percentage crystallinity of LLDPE for electron beam irradiation at $T_{\rm I}$ of 25 and 150°C

	Crystallinity (%)	
Dose (Mrad)	$T_{\rm I}=25$°C	$T_{\rm I}=150$°C
0	35.0 ± 0.8	–
0.1	36.2 ± 0.2	37.0 ± 0.2
1	36.1 ± 0.3	35.7 ± 0.2
5	34.0 ± 0.2	32.6 ± 0.1
10	33.5 ± 0.2	32.3 ± 0.2

crystalline regions. Dole[14] and Randall *et al.*[1] correlated this preference to the availability of alkyl radical groups in the amorphous region. It is interesting to note that there is an apparent increase in the crystallinity from the virgin sample when irradiated with low doses. We believe that this is due to sample variations, as the virgin sample was prepared from a different heat-pressed sheet of polymer than those sent to The Netherlands for irradiation.

It is seen that at low doses (0.1 and 1 Mrad) there is no effect of irradiation temperature on $T_{\rm mo}$, $T_{\rm mp}$, $H_{\rm m}$ and degree of crystallinity. However, at higher doses (5 and 10 Mrad) a higher irradiation temperature further decreases the melting temperatures, heat of melting and crystallinity. This effect is due to the increased mobility of the polymer at the higher irradiation temperature (150°C), which provides a greater 'effective' amorphous phase that can be increasingly affected by radiation.

Gel fraction

Gel fraction tests were performed on the samples by dissolving the soluble fraction of each sample in boiling xylene at 140°C for 8 h. The insoluble gel fraction remaining and the amount of solvent adsorbed per amount of gel was then measured as a function of radiation dose and is presented in *Table 2*.

There was no evidence of gel formation for radiation doses of 0.1 and 1 Mrad for either irradiation temperature; however, after 5 Mrad of radiation exposure 60–70% of the irradiated LLDPE had formed a gel. This indicates that the gel point of LLDPE 2045E is between 1 and 5 Mrad. Vallès *et al.*[4] determined that the gel point for their LLDPE sample occurred at approximately 7 Mrad. Since $M_{\rm w}$ for the LLDPE sample used here ($110\,000\,{\rm g\,mol^{-1}}$) is greater than that used by Vallès *et al.* ($50\,000\,{\rm g\,mol^{-1}}$), it requires less dose to form a highly crosslinked, infinite gel. In fact, by assuming that the product of $M_{\rm w}$ times the radiation dose for a gel to form is a constant, the gel point for our sample may be calculated to occur at 3.2 Mrad, which is intermediate between 1 and 5 Mrad. Vallès *et al.* irradiated their samples at room temperature, so the calculated amount of radiation required to reach the gel point above is expected to correspond to our room-temperature irradiated sample. Because the gel fraction is greater at equivalent radiation doses for the melt irradiated samples, we expect that the gel would occur at lower doses. These results are in agreement with the d.s.c. results presented above, which show that a lower degree of crystallinity is present for the melt irradiated samples.

The mass of solvent adsorbed per mass of gel decreases for increasing radiation dose and irradiation temperature (see *Table 2*). This indicates that these two factors produce a 'tighter' or more densely crosslinked gel that has a minimal voidage for absorption of solvent. This result will be discussed below when the rheological properties are presented.

Melt rheological properties

Vallès *et al.*[4] have shown that the melt rheological properties change drastically with radiation dose for a similar LLDPE. Equation (1) predicts at the gel point

Table 2 Effect of irradiation temperature, $T_{\rm I}$, on gel properties of LLDPE for electron beam irradiation at $T_{\rm I}$ of 25 and 150°C

	Gel fraction (g/g, %)		Solvent/gel (g/g, %)	
Dose (Mrad)	$T_{\rm I}=25$°C	$T_{\rm I}=150$°C	$T_{\rm I}=25$°C	$T_{\rm I}=150$°C
0.1	0	0	n/a[a]	n/a
1	0	0	n/a	n/a
5	63 ± 1	69 ± 2	21 ± 3	14 ± 2
10	81 ± 2	86 ± 1	7.0 ± 0.5	6.0 ± 0.5

[a] Not available

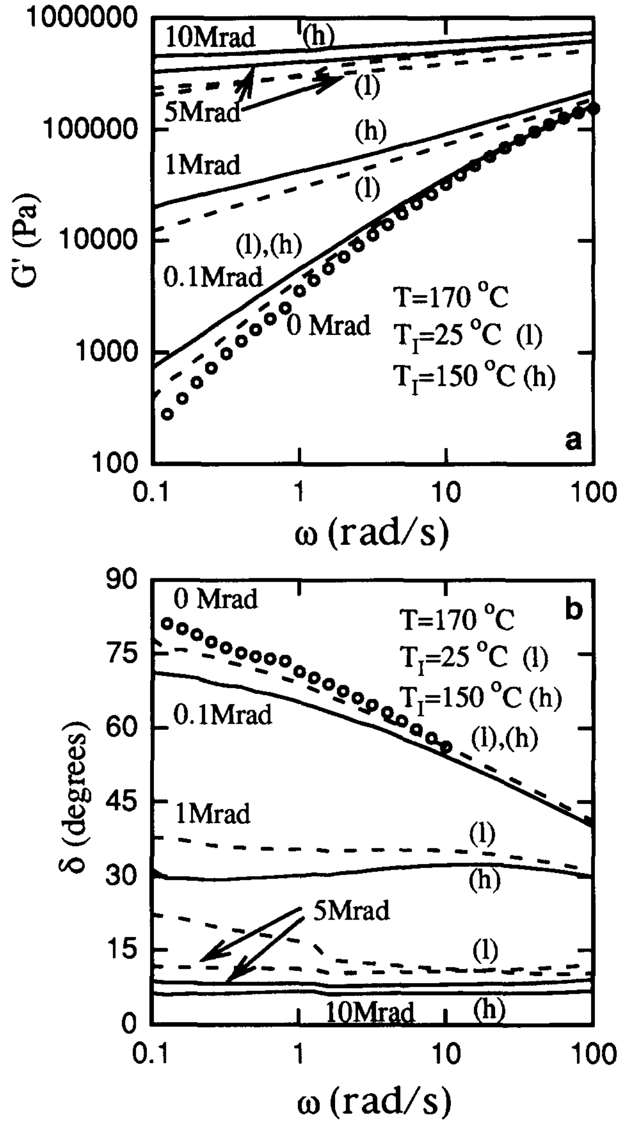

Figure 3 (a) Dynamic storage modulus and (b) phase angle lag for LLDPE at 170°C irradiated at 25 and 150°C for various radiation doses

that the phase angle lag, δ, in dynamic shear should be independent of frequency and equal to $n\pi/2$. Also, the relaxation modulus, G, in step strain should be given by:

$$G(t)=St^{-n} \tag{3}$$

What is interesting is that equation (1) as well as equation (3) hold true within a rather large region of the gel point in terms of the radiation dose[4].

The dynamic shear properties are presented in *Figure 3*. One can see that increasing radiation dosage increases the storage modulus (*Figure 3a*) and decreases the phase angle lag (*Figure 3b*) for a given frequency, in agreement with previous results[4]. The differences are most clearly seen at lower frequencies, where larger vibrational modes are excited. The melt irradiated samples show an increased modulus and decreased phase angle lag for a given frequency at all doses. Gel strength, as measured by the amount of solvent absorbed where a tighter gel occurs with less solvent absorption, is in agreement with these results (see *Table 2*).

The phase angle lag is approximately independent of the frequency for radiation doses above 1 Mrad. The gel point was estimated to occur for a dose of 3.2 Mrad; thus, prior to and after the gel point the dynamic shear properties approximately follow the gel model in agreement with previous results[4]. Note that the sample irradiated to a dose of 10 Mrad at room temperature shows anomalous behaviour at low frequencies, which may be due to increased chain scission of very-high-molecular-weight species.

The relaxation modulus was measured in step strain and the results are shown in *Figure 4*. These results concur with those gathered in dynamic shear, in that increased radiation dose and irradiation temperature increase the solid-like behaviour of the polymer. A Fourier transform of the data to the frequency domain produces good agreement between the transformed and originally gathered data. These results are not shown in *Figure 3* for clarity.

The modulus data for times less than 1 s (*Figure 4*) were fitted to the power-law expression (equation (3)) to determine the constants S and n. These results are shown in *Figure 5*. The relaxation strength parameter, S, shown in *Figure 5a*, increases with increasing radiation dose and irradiation temperature, in agreement with those results discussed above.

Vallés *et al.*[4] and Scanlon and Winter[15] have investigated the relation between S and n to arrive at an equation of the form:

$$S=G_0\lambda_0^n \tag{4}$$

So, equation (3) can be rewritten as:

$$G(t)=G_0(t/\lambda_0)^{-n} \tag{5}$$

where G_0 is a characteristic modulus and λ_0 is a characteristic time. When $n=0$, then the stress cannot relax and S as well as G_0 may represent the plateau modulus[15]. If $n=1$, then S may represent the viscosity. Scanlon and Winter did find good agreement between G_0 and the plateau modulus for poly(dimethylsiloxane) (PDMS). Equation (4) suggests that a master curve should result for log(S) *versus* n (refs. 4, 15) and is demonstrated in *Figure 5b*. The results agree well with those of Vallés *et al.* despite the grade of LLDPE having a lower molecular weight and their measurements being carried out at 177°C.

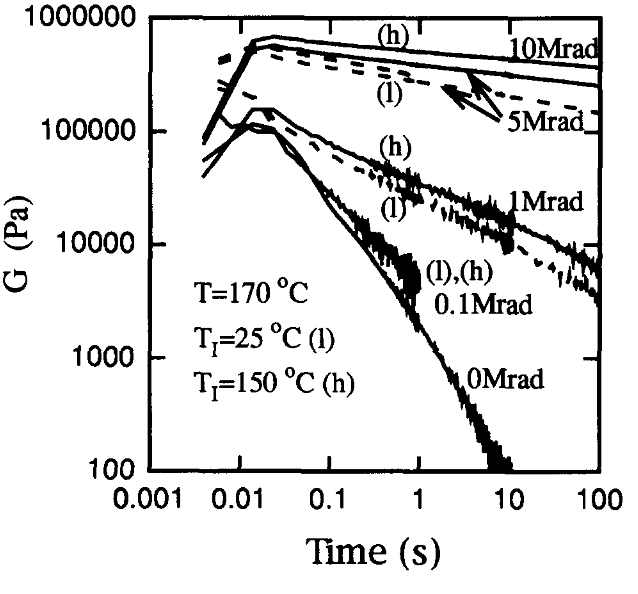

Figure 4 The relaxation modulus of LLDPE at 170°C irradiated at 25 and 150°C for various radiation doses

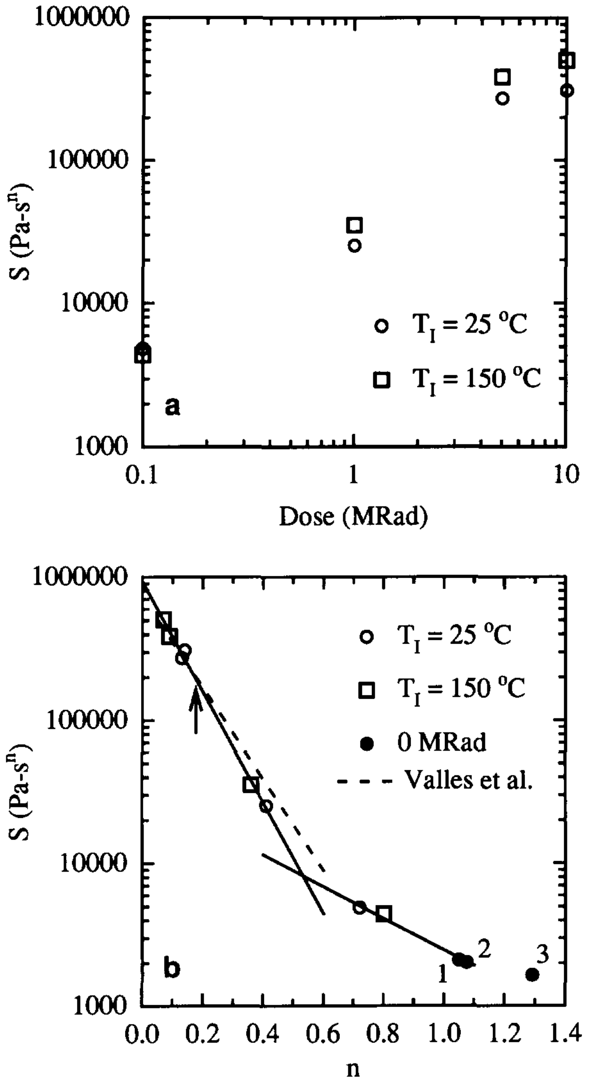

Figure 5 Plots of (a) the power-law gel strength parameter S *versus* radiation dose and (b) log(S) *versus* the relaxation exponent n determined from the relaxation modulus. The results of Vallès *et al.*[4] are also shown for comparison (broken line). The full lines are a fit of equation (4) to the two regions discussed in the text. The vertical arrow near $n = 0.2$ is the likely position of the true gel point. The points labelled 1, 2 and 3 represent empirical curve fits of the relaxation modulus for the virgin polymer for times less than 0.1, 1 and 5 s, respectively

Table 3 Fits of equation (4) to the log(S)–n data shown in *Figure 5b*. Also given are the results of Vallès *et al.*[4] for a similar LLDPE

Region	G_0 (Pa)	λ_0 (s)
Low-slope	3.3×10^4	7.5×10^{-2}
High-slope	9.3×10^5	1.4×10^{-4}
High-slope[4]	7.4×10^5	6.4×10^{-4}

The interesting result shown in *Figure 5b* is that S is clearly different for a given radiation dose when irradiation is carried out in the melt than at room temperature (see *Figure 5a*, this is also true for n), yet a master curve is obtained in S–n space for both irradiation temperatures. In fact, there appear to be two distinct regions, one of greater slope than the other. Equation (4) was fitted to the log(S)–n data shown in the figure for the region of greater slope, yielding the values of G_0 and λ_0 given in *Table 3*. These values agree reasonably well with those of Vallès *et al.* with G_0 close to the plateau modulus of high-density polyethylene (HDPE) (2×10^6 Pa as given in Ferry[16]). One expects that the plateau modulus of LLDPE would be less than that of HDPE as short side-chain branches tend to lower its value. Unfortunately, the plateau modulus could not be determined owing to frequency and torque limitations of the rheometer[9].

One can lend further credence to the fact that G_0 is the plateau modulus by examination of the theory of Rubinstein *et al.*[17] for the relaxation dynamics of polymers near the gel point. Using an asymptotic expansion one can arrive at (see their equations (3.8) and (3.9); we note an error in the exponent where $\sqrt{\gamma}$ should be used rather than γ):

$$G(t) \approx G_N^0 \left(\frac{t}{T_\infty} \right)^{-4/(\alpha\sqrt{\gamma})} \tag{6}$$

where G_N^0 is the plateau modulus, T_∞ is a time constant, α is a constant related to the number of entanglements between crosslinks and γ is a constant that is dependent on the coordination number of the Bethe lattice ($\gamma = 16$ for a coordination number of 3). This equation is valid only for times much shorter than T_∞. This theory clearly shows that G_0 is equal to G_N^0. Further testing of the equivalence between G_0 and G_N^0 is needed.

A linear regression of log(S) with n was also performed for the region of smaller slope with the parameter values shown in *Table 3*. The points labelled 1, 2 and 3 in *Figure 5b* represent various maximum times used in the regression to determine S and n for the virgin polymer. These are only empirical fits as n cannot be greater than 1 as this would make, for example, the phase angle lag greater than $\pi/2$ radians. One can see that any of the three points would be within the extrapolation of the two parameter value pairs, and point 2 was used in the regression.

The two linear regressions for the high- and low-slope regions were extrapolated and their intersection was found to occur at $n = 0.53$ or at a radiation dose of 0.5–0.6 Mrad. This indicates that the virgin polymer and the samples irradiated to doses less than 0.5 Mrad are in a similar rheological state with regard to S–n space. However, for higher doses the rheological state changes and a different slope is followed. This is despite the fact that a true gel, as determined by insoluble fraction being present, does not occur until much larger radiation doses are reached, ~3.2 Mrad, as indicated by the vertical arrow in *Figure 5b*.

The value of n at the true gel point is approximately equal to 1/5, which is in agreement with the value given by Vallès *et al.*[4] and determined for a chemically crosslinked PDMS with balanced stoichiometry with the prepolymer above the critical entanglement molecular weight[15]. However, there appears to be a pseudogel point for this system where the rheological properties change in S–n space at n approximately equal to 1/2. When $n = 1/2$ then excluded volume is taken into account, which is important in a melt of clusters[18,19]. The relaxation exponent n is related to the fractal dimension d_f of the gel by[18]:

$$n = \frac{d_f}{d_f + 2} \tag{7}$$

So, when $n = 1/2$ then the fractal dimension of the gel is 2, which is an easily explainable dimension (i.e. it lies in the physically realizable range $1 \leqslant d_f \leqslant 3$; see ref. 15). The dimension of the gel falls to 1/2 when $n = 1/5$ according to equation (7). Yet, this result can also be explained by the theory of Muthukumar[20] to yield fractal dimensions in the physically realizable range.

Although one can explain the value of 1/5 for the relaxation exponent when the true gel point is reached, we wish to hypothesize why a distinct transition is seen in S–n space. The classic definition of a gel point is when the linear size of a cluster diverges to infinity or more accurately fills the 'reaction vessel'. Thus, one will have an insoluble fraction of polymer. However, this definition may be too restrictive when a rheological test is performed, as trapped entanglements or dangling entangled 'arms' may create a pseudogel in terms of rheological timescales involved in the test. Besides trapped entanglements, persistent regions of high segment density may also be responsible for this behaviour[21]. Regardless of the mechanism, we hypothesize that from a rheological point of view a pseudogel is achieved, which creates rheological properties consistent with the gel model for the timescale considered. This hypothesis also explains how the master curve results in S–n space, as there must be some other factor that allows gels of different 'tightness' to lie on the same curve, and that the rheological behaviour consistent with the gel model (equation (1)) occurs over quite a large range of radiation doses.

CONCLUSION

Electron beam irradiation at room temperature and in the melt was used to alter the structure of LLDPE in a controlled manner by increasing the crosslinking of polymer chains. Increased radiation dose decreased the melting temperature, heat of melting and hence crystallinity of the sample for both irradiation temperatures. The gel point, as measured by an insoluble fraction in boiling xylene, was found to be between 1 and 5 Mrad, and this was independent of irradiation temperature. However, it was demonstrated that the gel point occurred at a lower dose for the melt irradiated sample. The melt irradiated sample also absorbed a smaller amount of xylene at an equivalent dose, indicating a tighter network.

The increased network tightness was also seen in the melt rheological properties, where the stresses relaxed more slowly after step strain for melt irradiated samples. The relaxation modulus was fitted to the power-law model of Chambon and Winter[5] to determine the gel strength parameter, S, and the relaxation exponent, n. It was found that a single master curve for both irradiation temperatures resulted when S was plotted against n. Two distinct regions of differing slopes were seen in the master curve, which intersected at a value of n approximately equal to 1/2. The value of n at the gel point determined by an insoluble fraction was approximately 1/5, in agreement with Vallés *et al.*[4]. We hypothesize that the intersection of the two curves represents a pseudogel point, which results from trapped entanglements, dangling arms, or regions of high segment density[21].

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