The effects of short chain branching and molecular weight on the impact fracture toughness of polyethylene*

A. D. Channell† **and E. Q. Clutton**
BP Chemicals, Research and Development Centre, PO Box 21, Grangemouth FK3 9XH, UK
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The impact fracture toughness of eight grades of polyethylene, five homopolymers (high density polyethylene) covering a range of molecular weights from 66 000 to 311 000, and three copolymers (linear low density polyethylene, LLDPE) with branch contents from 15 to 21 per 1000 C, has been evaluated at −20°C. It is proposed that the increased toughness of LLDPE is due to the influence of branches on morphology and tie-molecule concentration. This promotes the formation of a fibrillated damage zone in which greater energy is absorbed to initiate a crack than unbranched polyethylenes. The process for fracture toughening is similar for homopolymers, which demonstrate increasing toughness with molecular weight. The mechanisms are the same as those proposed by others for slow crack growth.

(Keywords: chain branching; molecular weight; impact fracture toughness; polyethylene)

INTRODUCTION

The fracture toughness of linear low density polyethylenes (LLDPEs) has been characterized by Hashemi and Williams[1] using the J-integral method to define the parameter J_c for the onset of cracking. Tests were performed at sub-zero temperatures and values as high as 40 kJ m^{-2} quoted at −20°C. Subsequent investigation of this phenomenon was performed by Mirabella *et al.*[2]. Evidence from temperature rising elution fractionation and scanning electron microscopy (SEM) on etched samples, was interpreted as indicating the existence of a second soft amorphous phase. It was proposed that this acted as a rubber toughening agent and accounted for the high toughness obtained.

Wooster *et al.*[3] investigated the effect of short chain branching distribution (SCBD) on the stress intensity factor for a series of LLDPEs at strain rates of 11.3 s^{-1}, compared with those used by Hashemi and Williams[1], i.e. 2×10^{-4} s^{-1}. It was suggested that fracture toughness correlated with spherulite morphology; this was influenced by the existence of branches and the effect of SCBD on crystallization.

The role of tie-molecules in slow crack growth of copolymers has recently been described by Huang and Brown[4]. Resistance to slow crack growth increased as butyl branch density increased because of the increased number of tie-molecules which result from decreased lamella thickness. However, it was pointed out that the resistance to slow crack growth depends on the yield stress of the material and fibril disentanglement which is determined by the tie-molecules. The former controls the rate of craze initiation, and the latter controls the rate of crack initiation.

Huang and Brown's work is supported by the findings of Barry and Delatycki[5]. Lamella thickness and hence tie-molecule concentration, and the degree of lamella imperfection are described as determining the rate of conversion from voided material to a fibrillated structure. Crack propagation rate is then controlled by the resistance of fibrils to deformation, i.e. strain hardening, and rupture of the fibrils.

EXPERIMENTAL

In this work we attempt to extend the interpretation of the effects of short chain branching and molecular weight on slow crack growth, to crack growth at high strain rates, i.e. impact rates. The fracture mechanics parameter, G, was evaluated for eight commercial polyethylene resins covering a range of molecular weights and branch contents.

Specimen preparation

Specimens were machined from compression-moulded sheets prepared using the semi-positive technique of Cawood and Smith[6]. The required amount of polymer to produce a sheet 12 mm thick was preheated in a press at 180°C for 30 min. Slow cooling was then applied at 2°C min^{-1} until the press was at 120°C when pressure was applied in 5 t increments at each subsequent 5°C cooling interval. Crash cooling was applied when the press temperature reached 80°C.

Bars of $\sim 12 \times 12 \times 100$ mm were then cut from the sheets using a circular saw, which gave a satisfactory surface finish. A multi-toothed cutter was then used to notch each specimen. A range of notch depth to specimen depth ratios from 0.05 to 0.45 were machined in 15 increments. A number of passes were made with the cutter to cut each notch, depending on the depth. The actual notch depth was measured after fracture using a travelling microscope.

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† To whom correspondence should be addressed

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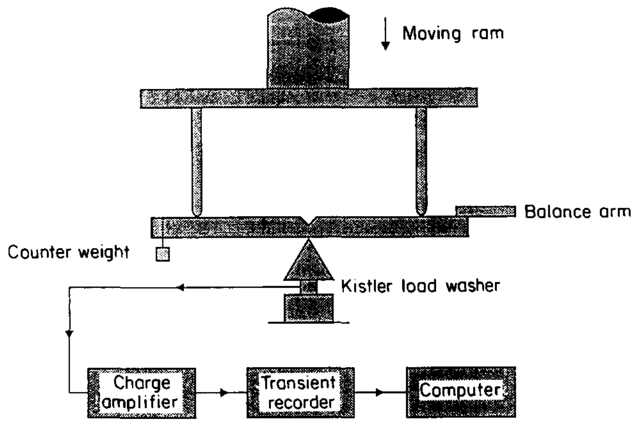

Figure 1 Instrumented impact testing apparatus

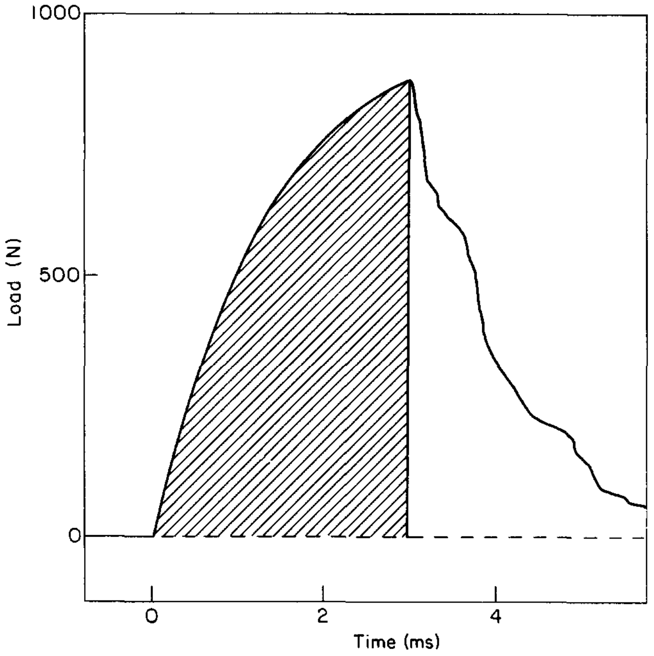

Figure 2 Load *versus* time curve for polyethylene. The shaded area represents the energy absorbed to peak load

Fracture testing

The multiple specimen method for evaluating G as advocated by Plati and Williams[7] was used, based on sharp notched Charpy specimens of varying notch depths. Our instrumented impact technique used a hydraulically driven ram, and an inverted test geometry to improve the signal to noise ratio (*Figure 1*). Load was measured during the impact event by a Kistler quartz piezo-electric load washer, the output of which was converted to a voltage by a charge amplifier and recorded on a transient recorder subsequent to transfer to a computer for analysis. Impact toughness as defined by the energy absorbed to peak load on the load *versus* time curve was denoted by G_p (*Figure 2*). An example of the type of graph obtained is shown in *Figure 3*. Previous work[8] has shown that the energy to peak load is absorbed in initiating the crack, the remainder of the total fracture energy being absorbed in propagation. The test velocity was $1\,\mathrm{m\,s^{-1}}$ to limit dynamic effects and all tests were performed at $-20°\mathrm{C}$.

Damage zone measurement

A damage zone formed at the notch tip during the impact event for all of the materials examined. The maximum length of this zone, which occurred midway through the specimen thickness, was measured using an optical travelling microscope. The zone was defined by the notch tip and a smooth region at the curved front of the damage zone as seen in *Figure 4*. An average value was obtained from at least eight specimens of intermediate notch depth, giving a typical standard deviation of 0.05 mm.

Microscopy

Optical micrographs were taken of the fracture surfaces of specimens with similar notch depths using the Macro viewer attachment on a Reichert-Jung Polyvar microscope and illuminated with incident light. SEM was performed using a Hitachi S/570 SEM. Sections of the fracture surface for specimens of interest were mounted on a stub with epoxy, and sputter coated with gold. A beam voltage of 15 kV was used.

Material parameters

The following material parameters were determined.

Short chain branching level was obtained by acquiring i.r. spectra for each grade on a Nicolet 740 spectrometer. The $1387\,\mathrm{cm^{-1}}$ band was isolated for methyl, ethyl and butyl branching. Isobutyl branching was measured using the absorbance peak at $1384\,\mathrm{cm^{-1}}$. Suitable chain end corrections were made as appropriate.

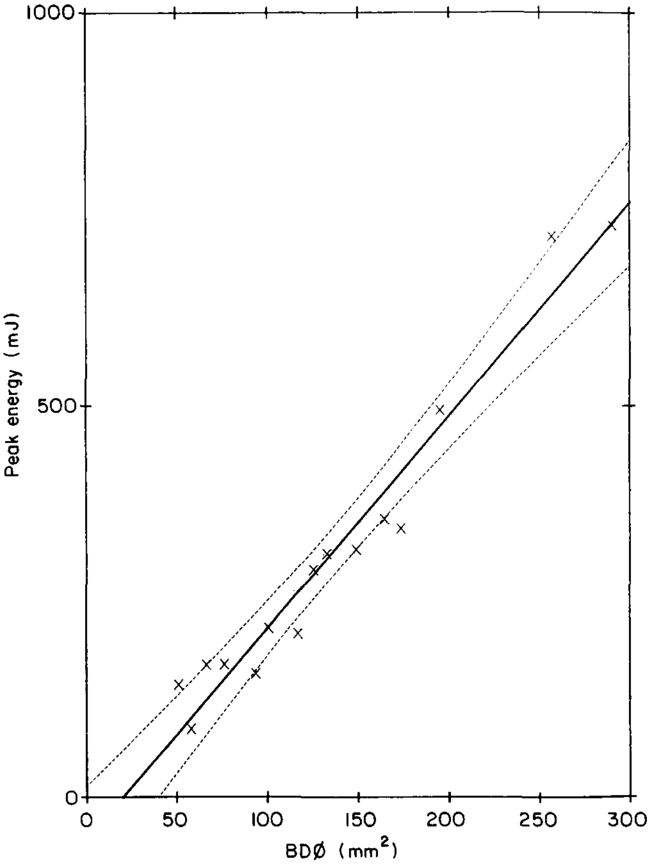

Figure 3 A typical peak energy *versus* BDΦ graph for polyethylene ($G_p = 2.71 \pm 0.16\,\mathrm{kJ\,m^{-2}}$), *BDΦ* as defined in reference 7

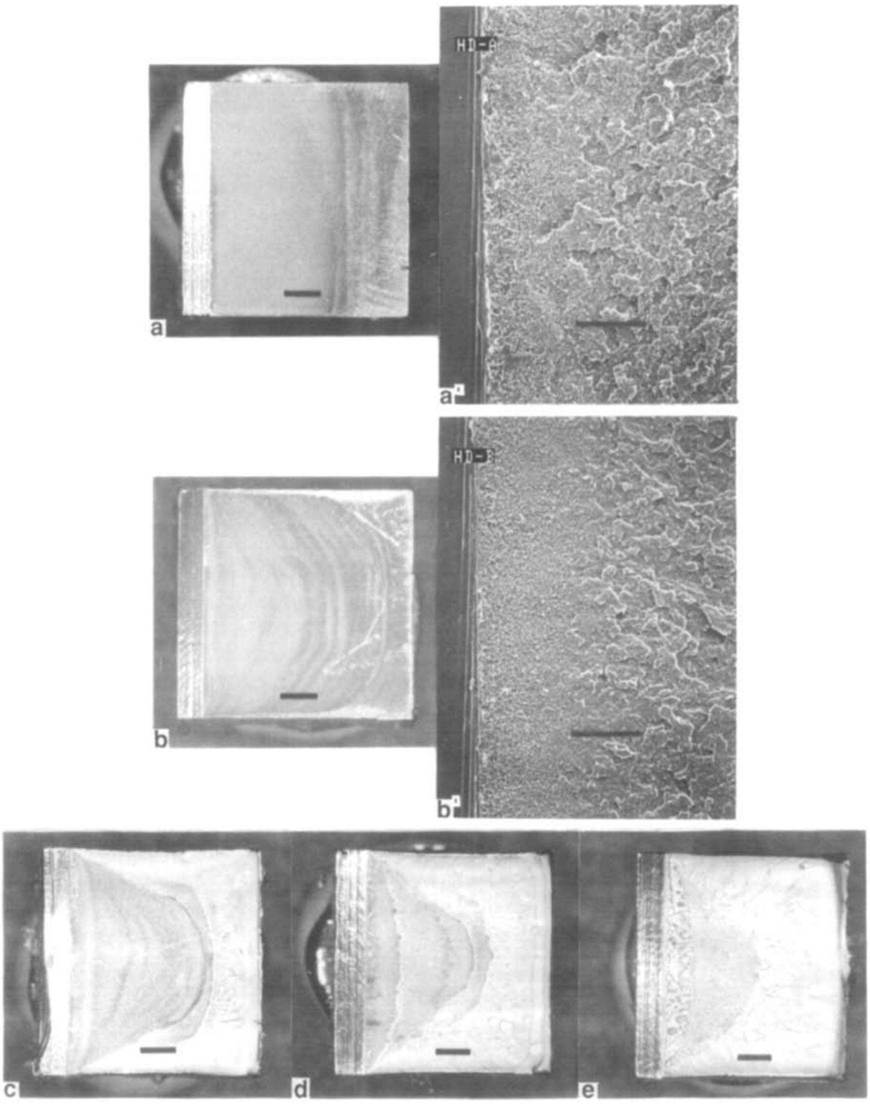

Figure 4 Optical micrographs of the fracture surfaces of the homopolymers (scale bar 2 mm). The damage zone is that immediately ahead of the machined notch (on the left of each micrograph). SEM micrographs (a', b') of the region at the notch tip are included for the two lowest molecular weight materials (scale bar 200 μm): (a) HD-A; (b) HD-B; (c) HD-C; (d) HD-D; (e) HD-E

Molecular weight. A Waters 150C high temperature gel permeation chromatograph was used to analyse each sample and to obtain their molecular weight distributions. A 0.1% solution of each material was prepared by dissolving the material (50 mg) in trichlorobenzene (50 ml). Dissolution was carried out for 2 h at 140°C with slow stirring, followed by 1 h at 160°C, after which the solution was injected into the chromatograph. The dissolution process was carried out to ensure that all the material was fully dissolved. The gel permeation chromatograph was calibrated using 22 narrow polystyrene standards.

Crystallinity was determined using a Perkin Elmer series 7 thermal analysis differential scanning calorimeter. Samples were heated at 10°C min^{-1} to 200°C, then cooled at the same rate to 0°C to remove any process history. The crystallinity was obtained by comparing the latent heat of fusion on a second heating at the same rate with the value for a 100% crystalline polyethylene.

Density was measured in columns prepared to British Standard 2782 from isopropyl alcohol and water. Two columns were prepared covering overlapping high and low density ranges over 70 cm of column height, and calibrated with glass spheres of known density.

RESULTS

The materials were compared on the basis of their G_p values. The G_p values and characterization data are given in *Table 1*.

Micrographs of the fracture surfaces are shown in *Figure 4* for the homopolymers, and in *Figure 5* for the copolymers. Due to the small zone size generated in HD-A and HD-B, SEM micrographs are shown in *Figure 4* of the region at the tip of the notch midway through the specimen thickness. Craze zones are more clearly seen in the micrographs of the other materials.

For the homopolymers G_p was found to increase much as expected with molecular weight (*Figure 6*). Examination of the fracture surfaces revealed two features. First, as the molecular weight increased so did the extent of yielding at the edge of the specimen (shear lips), and yielding associated with hinging of the specimen due to crack arrest (see *Figures 4c*, *d* and *e*). Second, a damage

Table 1 Impact toughness (G_p), characterization and damage zone size data for copolymers and homopolymers

	Copolymers			Homopolymers				
	LL-A	LL-B	LL-C	HD-A	HD-B	HD-C	HD-D	HD-E
G_p (kJ m^{-2})	9.3	9.4	8.9	2.0	2.7	6.7	16.9	18.0
M_w	109000	95000	130000	66000	130000	167000	280000	311000
Polydispersity	4.2	4.1	5.5	4.7	6.8	6.7	10	8.6
Density (kg m^{-3})	920	920	920	964	965	959	961	957
Crystallinity (%)	43.8	43.6	45.0	77.6	77.3	74.0	75.2	72.9
Branch content (per 1000C)	21.3	18.5	15.5	0.5	<0.1	–	–	<0.2
Damage zone (mm)	1.47	1.89	2.43	0.20	0.30	1.23	1.97	2.20

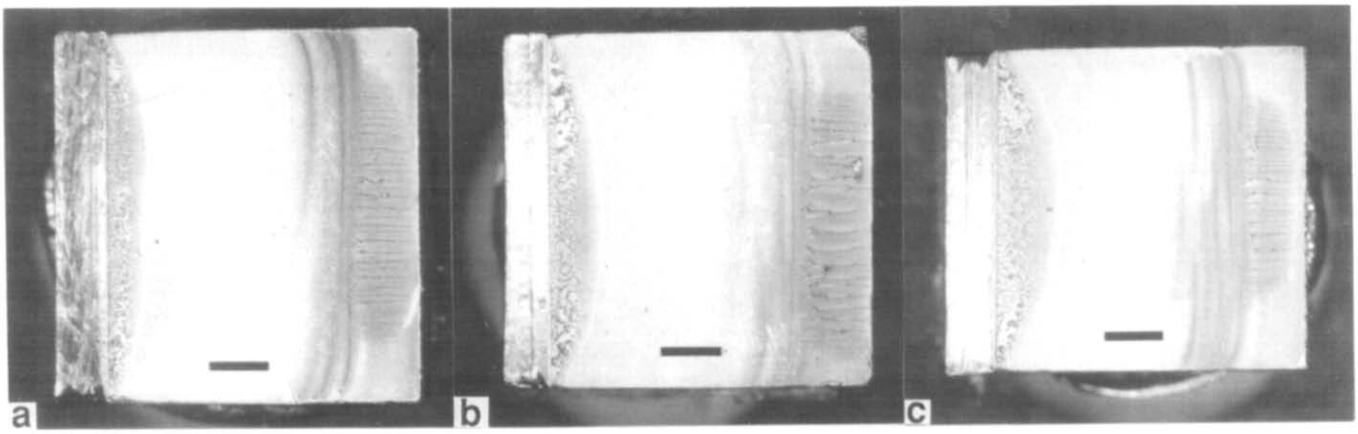

Figure 5 Optical micrographs of the fracture surfaces of the copolymers (scale bar 2 mm). Note the absence of any surface features; shear lips and hinging, except the damage zone itself: (a) LL-A; (b) LL-B; (c) LL-C

zone was observed at the root of the notch. Hemingway *et al.*[8], have shown that this zone forms during the rise in load to its peak value. The parameter G_p characterizes the breakdown of this zone and the initiation of crack growth. In the two lower molecular weight homopolymers, HD-A and HD-B, a zone could not be detected using optical microscopy, but under SEM zones of 200 and 300 μm were measured. The zone size was found to increase with molecular weight for HD-A, B, C, D and E leading to an increasing G_p (*Figure 7*).

By contrast, all the copolymers gave a value of G_p of $\sim$9.2 kJ m^{-2}; the actual values obtained are given in *Table 1*. Again, examination of the fracture surfaces revealed the presence of a damage zone, but the absence of shear lips. It was noticed that there were large differences in zone size despite similarity in molecular weight (*Figure 5*).

DISCUSSION

The findings of Huang and Brown[4] for slow crack growth can be extended to explain the impact behaviour of copolymers and homopolymers seen here. They stated: 'There are two processes that control the rate of slow crack growth: (i) the initiation rate of the craze as it precedes the crack, which is governed by the yield point of the matrix; and (ii) the rate of crack initiation, which is governed by the rate of disentanglement of the fibrils at the base of the craze and which is primarily determined by the tie-molecules as described by us'. It appears that the same processes govern the impact behaviour of

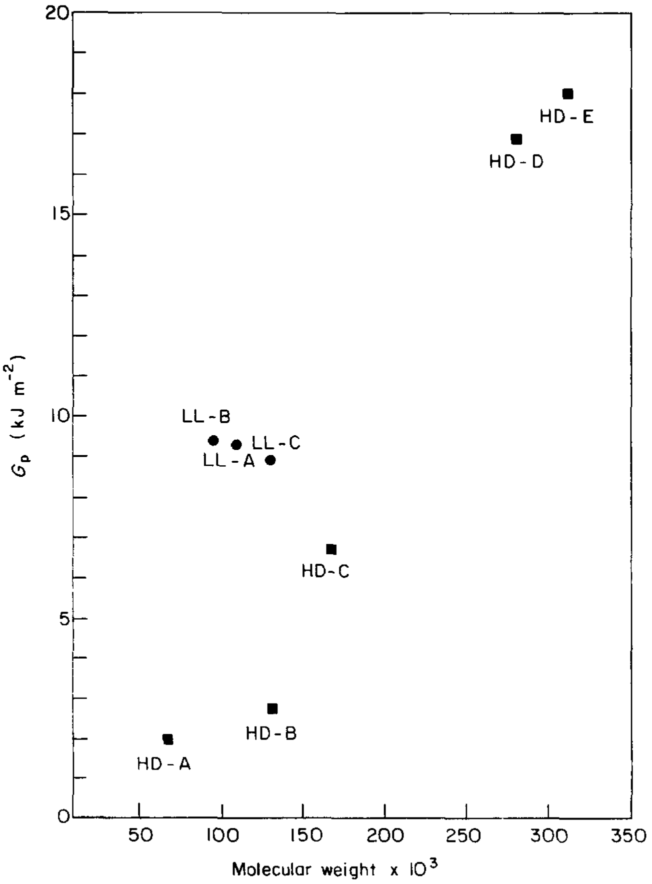

Figure 6 G_p *versus* molecular weight at −20°C for polyethylene homopolymers (■) and copolymers (●)

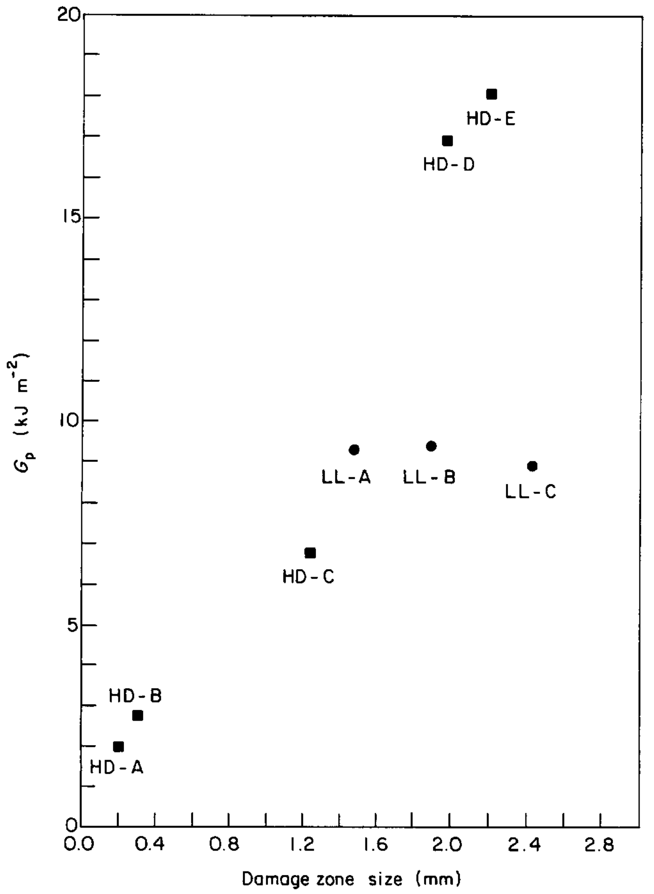

Figure 7 G_p *versus* damage zone size at −20°C for polyethylene homopolymers (■) and copolymers (●)

polyethylene as illustrated by the results for the materials studied here.

In polyethylenes the influence of increasing molecular weight is to increase the concentration of tie-molecules spanning the amorphous regions[9,10]. For the low molecular weight homopolymers, HD-A and HD-B, a small damage zone is formed because of the combination of high yield stress and low tie-molecule concentration. This results in low toughnesses due to the inability of the crazed material to form fibrils with an effective strength, and hence a low energy absorption capability. At higher molecular weights, HD-C, HD-D and HD-E, the formation of a zone is observed in which the material subsequently crazes more effectively prior to crack initiation. This leads to enhanced energy absorption and confers increasing fracture toughness with molecular weight. This is due to the strength of the fibrils in the damage zone as a result of increasing the tie-molecule concentration with molecular weight.

The main feature of copolymers is the presence of branching which reduces crystallinity and increases tie-molecule concentration[11]. The low crystallinity promotes a lower yield stress, making the initiation of a damage zone easier. Once initiated, the damage zone fibrillates and subsequent initiation of a crack is difficult. This is attributed to the drawing ability and strength of the fibrils, which Huang and Brown[4] suggest depends on the rate of disentanglement of the fibrils, controlled by the tie-molecules. Thus more energy will be absorbed in this zone and G_p is increased, compared with a homopolymer of similar molecular weight as illustrated in *Figure 6*.

Based on the process for toughening described, one would expect the copolymer with the highest branch content to be tougher. It would also be expected to form the largest damage zone. However observation of zone size showed that this was not so (*Figure 5*). The fact that similar values of G_p were obtained from the formation and breakdown of a zone of varying size, suggests that these copolymers each require a different energy per unit volume to form a craze before a crack can initiate. At present this phenomenon is not understood and further investigation is warranted.

CONCLUSIONS

1. LLDPE exhibits high values of G_p at impact rates, due to the influence of short chain branching on tie-molecule concentration, through greater energy absorption in a damage zone at the root of the notch.
2. HDPE exhibits increasing toughness with increasing molecular weight, because this also increases tie-molecule concentration.
3. This process is the same as that postulated for slow crack growth and it is proposed that the mechanisms involved can still affect fracture toughness up to the high impact rates used here.

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REFERENCES

1 Hashemi, S. and Williams, J. G. *Polymer* 1986, **27**, 384
2 Mirabella, F. M., Westphal, S. P., Fernando, P. L., Ford, E. A. and Williams, J. G. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 1995
3 Wooster, J. J., Parikh, D. R., Sehanobish, K. and Chum, S. P. *Polym. Prepr.* 1989, **30**, 323
4 Huang, Y. and Brown, N. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 129
5 Barry, D. and Delatycki, O. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 883
6 Cawood, M. J. and Smith, G. A. H. *Polymer Testing* 1980, **1**, 3
7 Plati, E. and Williams, J. G. *Polym. Eng. Sci.* 1975, **15**, 470
8 Hemingway, A. J., Channell, A. D. and Clutton, E. Q. *Plastics Rubber Comp. Proccess. Appl.* 1992, **17**, 147
9 Brown, N. and Ward, I. M. *J. Mater. Sci.* 1983, **18**, 1405
10 Mandelkern, L. *J. Polym. Sci. Symp.* 1975, **50**, 457
11 Alamo, R., Domszy, R. and Mandelkern, L. *J. Phys. Chem.* 1984, **88**, 6587