The effect of molecular structure and polymer morphology on the fracture resistance of high-density polyethylene

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The fracture resistance of a range of polyethylenes was examined. The tearing modulus, T, was used as a measure of the resistance of the polymer to crack propagation. The values of the tearing modulus were calculated from the gradient of the J-integral *versus* crack extension lines, $J(\Delta a)$. Strain rates in the range from 10^{-7} s^{-1} to 0.1 s^{-1} were tested. The strain rate dependency of crack initiation and crack propagation have been correlated with the composition and morphology of the polymers. The thickness of the lamellae, side chain concentration and degree of order in the crystalline regions have been shown to influence the resistance of the polymer to crack initiation, $J_c(\dot{e})$. The tearing modulus appears to be influenced mainly by changes to the morphology that are due to short side chain branches.

(Keywords: polyethylene; crack initiation; crack propagation; morphology; strain rate dependency)

INTRODUCTION

High-density polyethylene (HDPE) is being used increasingly in piping for gas and water distribution systems. Understanding the fracture properties of this material is important if safe and economical design criteria are to be developed. The future development of fracture-resistant HDPE grades will be advanced if a better understanding of the influence of the elements of the polymeric structure on its fracture resistance is developed.

The resistance of HDPE to crack initiation has been characterized by using the stress intensity factor[1] K, the J-integral[2], the strain energy release rate[2,3] G and crack opening displacement[4,5] *COD*. The resistance to propagation has been determined by measuring the tearing modulus[6] T. In previous papers the authors analysed crack initiation in pipe-grade HDPE[7,8]. The analysis has now been extended to include crack initiation and propagation by using standard three-point bending tests. This fracture behaviour was correlated with the morphology and structure of the polymer. The reader is referred to the nomenclature section at the end of the paper for definitions of the symbols used.

MATERIALS

Several grades of HDPE were tested (see *Table 1*). Polymers 1 to 4 were polymerized using a Ziegler–Natta type catalyst, while polymers 5 and 6 were produced with a Phillips type catalyst. All were pipe-grade materials.

The morphology of the materials was characterized extensively. Nuclear magnetic resonance, infrared spectroscopy and flow properties were used to characterize side chain branching. The structure of the crystalline and amorphous regions and the degree of crystallinity were determined by using wide- and small-angle X-ray analysis. Density was measured according to ASTM D 792–Method B. These results are shown in *Tables 1* and *2*. The methodology used for these measurements was reported previously[7].

TESTING

Preparation of fracture specimens

Test specimens were machined from large blocks of polymer. These blocks were produced with an extrusion moulding technique in conjunction with a temperature-programmable press. The polymer was annealed by holding it in a press at 130°C for 2 h and then cooling at 1 K min^{-1} to ambient temperature. These annealed blocks were machined to make specimens of the dimensions desired. Specimens 30 or 40 mm wide (W) and 10, 15, 25 and 54 mm deep (B) were used. The initial crack depth to width ratio (a_0/W) was 0.5. This crack was machined into the specimens with a 60° rotating cutter, which produced a blunt notch that was extended by impressing a sharp razor into its base to produce a sharp notch.

Mechanical testing

The mechanical properties were determined with dumb-bell specimens cut from sheets having an identical thermal history to the fracture specimens. The modulus (E) and the yield stress (σ_y) of the specimens were determined at strain rates from 10^{-6} to 10^{-1} s^{-1} and at 23 ± 2°C.

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Fracture testing

The multispecimen technique developed by Begley and Landes[9] was used. This technique has been applied by Chan and Williams[2] to measure crack initiation in samples that exhibit stable crack propagation. The method consists of loading several identical specimens to different degrees of deflection to produce cracks of different lengths, Δa. The specimen and its dimensions are shown in *Figure 1*. The specimens were subsequently broken, after immersion in liquid nitrogen, to reveal the extent of crack growth. The test specimens were fractured in a three-point bending test at 23 ± 2°C. In all tests the span to width ratio was four. In this series of tests the fracture resistance of the materials listed in *Table 1* was determined at strain rates from $2 \times 10^{-7}\ \mathrm{s}^{-1}$ to $0.1\ \mathrm{s}^{-1}$.

Fracture analysis

Crack initiation. Pipe-grade HDPE is a tough material. Analysis of the fracture behaviour of such materials requires that their plasticity should be considered. The J-integral is an energy-based fracture parameter that takes into account crack tip plasticity. Crack initiation occurs at a critical value of the J-integral, J_c. For deeply notched specimens in bending, the J-integral can be calculated by

$$J = \frac{2U}{B(W - a_0)} \qquad (1)$$

where U is the energy to initiate and propagate the crack Δa. The value of U is determined from the area under the load–deflection curve. B and W are the specimen dimensions and a_0 the initial depth of the crack (*Figure 1*). To determine J_c, the value of J is calculated for each value of Δa. The $J(\Delta a)$ data are then plotted as shown in *Figure 2*. The value of J at $\Delta a = 0$ is its critical value for crack initiation, J_c. In tough materials an initial pseudo-extension of the crack, due to blunting at the crack tip, often occurs[2]. To take this initial extension of the crack, prior to initiation, into account a crack blunting line is used. Crack blunting is accounted for in

$$J = 2\Delta a \sigma_y \qquad (2)$$

In this case the value of J_c is given by the intersection of the $J(\Delta a)$ data line and the blunting line of equation (2). The crack blunting line for material 2 at the strain rate of 2×10^{-4} is shown in *Figure 2*. As can be seen, the intersection of the crack blunting line and the $J(\Delta a)$ data results in a higher value for J_c. For the materials listed in *Table 1* this analysis has been made previously[8].

The relationship between the critical value of the J-integral, J_c, and the strain rate, $\dot{e}$, was found to fit a power-law equation. This power-law relationship is given by

$$J = a\dot{e}^b \qquad (3)$$

The values of a and b for the materials tested are given in *Table 3*. These parameters characterize the strain rate dependency of crack initiation. The value of J_c becomes dependent on the dimensions of the specimen when the region of plastic deformation at the tip of the crack becomes comparable in size to the dimensions of the specimen. All J_c values at fracture initiation, quoted in this investigation, are independent of the dimensions of the specimen.

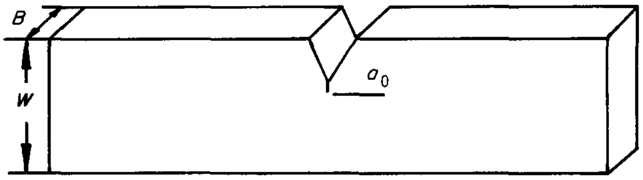

Figure 1 Specimen for three-point bending fracture test geometry

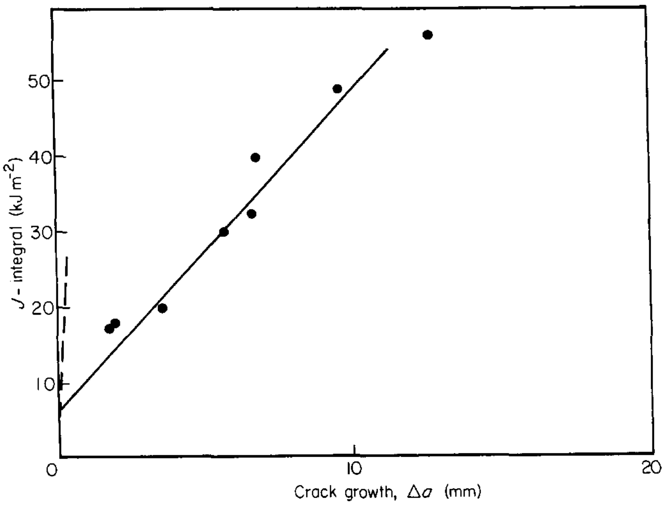

Figure 2 J-integral as a function of crack growth: the broken line is the crack blunting line given by equation (2)

Table 1 Materials tested

Material	Density (g cm^{-3})	Melting temp. (°C)	Crystallinity (%)
1	0.970	135	75
2	0.960	132	69
3	0.951	134	66
4	0.961	136	75
5	0.943	130	65
6	0.962	131	60

Table 2 Molecular structure and morphology

					Side chains (C/1000 C)						
Material	$\bar{M}_n$ ($\times 10^3$)	$\bar{M}_w$ ($\times 10^4$)	g (%)	l_c/l_a	Methyl	Ethyl	Propyl	Butyl	Hexyl	Short	Long
1	10.4	12.9	0.92	2.9	2.0	2.0					2.0
2	9.5	11.4	1.11	2.3		2.0				1.5	2.2
3	19.2	10.1	0.66	1.9	4.0		1.4				1.2
4	10.1	10.6	0.88	2.8		0.7					1.1
5	19.6	10.1	1.35	1.1				4.4			
6	15.3	14.0	1.42	1.5				3.0	0.5		

Table 3 Fracture parameters

Material	Crack initiation		Crack propagation
	a (kJ m^{-2})	b	Tearing modulus at 0.1 s^{-1}
1	13	0.14	0.85
2	25	0.13	1.20
3	103	0.28	0.78
4	14	0.22	0.54
5	20	0.18	0.33
6	8	0.10	0.31

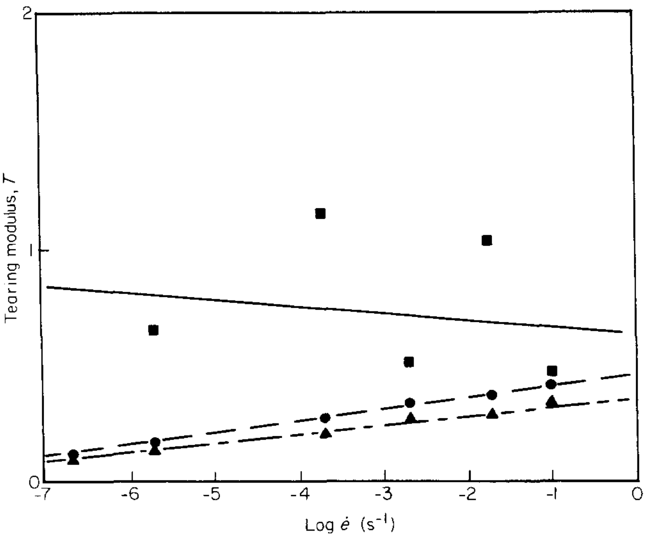

Figure 3 Tearing modulus as a function of strain rate, ė: (■) sample 3; (●) sample 5; (▲) sample 6

Crack propagation. The slope of the $J(\Delta a)$ line, $\mathrm{d}J/\mathrm{d}a$, represents the resistance of the polymer to the propagation of the crack. Narisawa[6] suggested that the resistance of materials to tear can be evaluated by determining a tearing modulus T. This concept can also be utilized to measure the resistance of crystalline polymers to crack propagation. The tearing modulus is calculated from

$$T = \frac{\mathrm{d}J}{\mathrm{d}a}\frac{E}{\sigma_y^2} \qquad (4)$$

The values of the tearing modulus are plotted in *Figures 3* and *4* as a function of strain rate. For samples 2, 4, 5 and 6 there is a clear increase in the tearing modulus as the strain rate increases. For samples 1 and 3 the scatter in the results precludes establishing a trend in the data. The values of T for all materials, at a strain rate of 0.1 s^{-1}, are given in *Table 3*.

DISCUSSION

Crack initiation

In HDPE crack initiation occurs by a process of void nucleation, growth and coalescence[5,10,11]. Distributed throughout the material are sites at which voids can nucleate. The material adjacent to these nucleation sites must be able to be deformed in order for the void to grow. The deformability of the material is governed by the degree of order and thickness of the crystalline regions, the number of tie molecules between the crystalline regions, side chains and physical entanglements within the non-crystalline regions. Lu and Brown[5] have proposed that it is the 'thinning' of the fibrils between the expanding voids that controls both the initiation of the crack and its subsequent propagation.

The voids nucleate and initially grow in the amorphous regions. Here the resistance to void growth is determined by the deformability of these regions, ties across the amorphous regions and physical entanglements within them. Eventually the growing voids reach the crystalline lamellae. Stress transfer to the lamellae and their deformability also influence the crack initiation process.

The thicker and better ordered the crystalline lamellae, the more rigid they are, and hence the greater their resistance to void growth. The fibrils between the voids control the final stages before crack initiation. The greater the amount of deformation and energy that fibrils absorb before rupturing, the higher the resistance to crack initiation.

Crystalline order is measured by the paracrystalline distortion factor g. The number of intercrystalline ties is proportional to the high molecular weight component of the polymers. Short and long side chain concentrations are measured directly by using ^{13}C n.m.r. The relative thickness of the lamellae is gauged by measuring the ratio of the thickness of the crystalline to amorphous regions, l_c/l_a. This ratio is a good measure of the average lamellar thickness, because the thickness of the amorphous regions was approximately constant in the polymers tested in this investigation.

The constant in the power-law equation for crack initiation, a, represents the energy per unit area of the cross section of the sample necessary to initiate a crack at a strain rate of 1 s^{-1}. The exponent, b, describes the dependency of crack initiation resistance on strain rate. An ideal fracture-resistance material has a high value of a and low value of b.

Morphological data (*Table 2*) and crack initiation resistance data (*Table 3*) show that material 3, with a high value of a, also has the lowest value of g. Similarly, material 6 with the highest value of g has the lowest resistance to crack initiation. It seems that, generally, the more ordered the crystalline regions in the material the greater their resistance to deformation. This analysis also shows that the relative thickness of the crystalline regions,

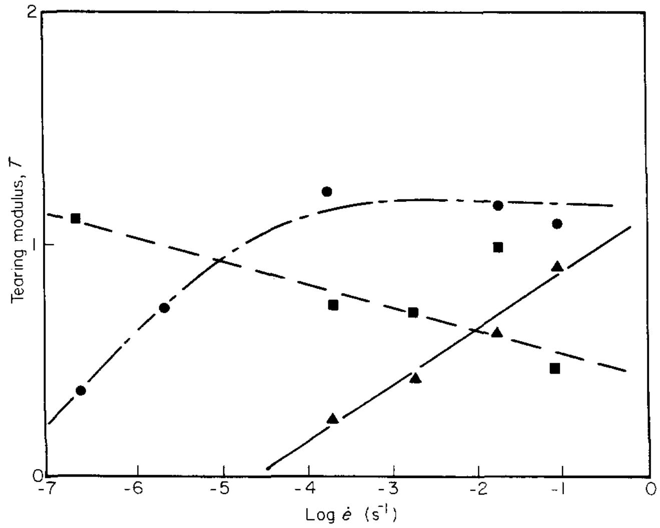

Figure 4 Tearing modulus as a function of strain rate, ė: (■) sample 1; (●) sample 2; (▲) sample 4

l_c/l_a, is less important in determining the resistance of the material to crack initiation.

The relationship between crack initiation and side chain concentration is complicated by the dependence of crystalline order on the incorporation of the side chains into the crystalline regions[12]. Material 3 with a high degree of crystalline order also has the advantage of having a large concentration of short side chains. These side chains increase the entanglements in the amorphous region where void nucleation and growth occurs and also increase strain hardening of the fibrillar material during the final stages of crack incubation, just before crack initiation. Conversely, material 4, with virtually no short side chains, has a low value of a, even though it has relatively well ordered crystalline regions, i.e. a low value of g.

Analysis of the fracture and morphological data for materials 5 and 6 indicates that just having a high concentration of short side chains is not sufficient to impart crack initiation resistance. The effect of having a high concentration of short side chains is overridden by the consequence of these materials having thin, imperfect crystalline regions.

The exponent b is, clearly, dependent on the ratio of the thicknesses of the crystalline and amorphous regions and the concentration of side chains. Consider materials 1 to 4, which were produced with the same type of catalyst, and hence could be expected to have a similar side chain distribution along the polymer backbone. Materials 1 and 2, with l_c/l_a ratios in excess of two and high concentrations of side chains, have values of b of 0.14 and 0.13, respectively. Whereas material 4, with a low concentration of side chains and a crystallite thickness comparable to that of materials 1 and 2, has a higher value of b of 0.22. Whilst material 3, with a low relative crystalline thickness, $l_c/l_a = 1.90$, and a high concentration of side chains has the highest value of b.

Materials 5 and 6, produced by a Phillips catalyst system, have a different molecular make-up to materials 1 to 4. Once again the polymer with the thickest crystalline regions has the lowest value of b. However, for these two materials the effect of side chain concentration is not clear.

Crack propagation

Crack propagation in tough HDPE occurs by a process of void coalescence, as the material between the voids ruptures. The polymeric chains between the growing voids are oriented. The degree of orientation of the polymeric tie chains increases as the voids expand. The mechanical properties of this oriented material are very different to those of the surrounding bulk material. The resistance to crack propagation is related to the strength of the oriented inter-void material and to the resistance of this material to further extension. If this inter-void material ruptures easily, without absorbing a lot of energy, its resistance to crack propagation is low. Conversely, if the polymer forms strong oriented fibrils between the expanding voids and these fibrils stabilize the propagating crack, then the material has a high resistance to crack propagation. Such material will have a high tearing modulus.

Crack propagation in tough grades of HDPE is an extension of the crack initiation process as the fibrils at the tip of the crack rupture. The same morphological factors that effect crack initiation also affect crack propagation. Examining the values of the tearing modulus in *Table 3* and the side chain analysis given in *Table 2*, there appears to be a correlation between the concentration of short, stiff side chains ($>$C2 and $<$C6) and the tearing modulus.

Consider the Ziegler–Natta polymers, materials 1 to 4. Material 2, with a concentration of 3.5 short side chains per 1000C of the backbone, has the highest tearing modulus. Conversely, material 4 with the lowest side chain concentration has the lowest tearing modulus. Materials 1 and 3 have intermediate values of the tearing modulus and of the concentration of side chains.

Comparison of materials 5 and 6 with materials 1 to 4 shows that there is a major difference in crack tearing resistance between the Ziegler–Natta and Phillips polymers. The two materials, produced by using the Phillips catalyst, have a very low resistance to crack propagation, even though they have a high concentration of side chains. The reason for this difference is not clear, but it could be due to the different distribution of side chains along the molecular backbone compared to the materials 1 to 4.

Figures 3 and *4* show that there is an increase in resistance to crack propagation and the value of the tearing modulus as the rate of testing is increased. At higher testing rates the time available for disentanglement of the chains in the fibrils is reduced. This increases the strain hardening of the fibrils, thus increasing the tearing resistance of the polymer. The dependence of fracture on the side chain concentration, outlined in this paper, is in agreement with the results of Lu *et al.*[11].

CONCLUSIONS

Investigations presented here have shown that the fracture behaviour of HDPE can be interpreted in terms of the morphology of the polymers. Correlation of the morphological data and the fracture parameters demonstrates that the resistance to crack initiation is influenced by the thickness of the crystallites, the side chain concentration and the degree of order in the crystallites. The thicker and the more ordered the crystalline regions the greater the resistance of the materials to crack initiation. The tearing modulus is a measure of the resistance of a polymer to crack propagation. The numerical value of this modulus is rate dependent. Generally, the higher the testing rate the greater the resistance of the polymer to crack propagation, for the strain rates tested. It was also found that the tearing resistance was related to the concentration of short side chains.

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NOMENCLATURE

a	Constant in the power-law equation for crack initiation
Δa	Length of crack (mm)
B	Depth of specimen (mm)
b	Exponent in the power-law equation for crack initiation
COD	Crack opening displacement (μm)
E	Modulus of elasticity (MPa)
e	Strain rate (s^{-1})
G	Strain energy release rate (kJ m^{-2})
g	Paracrystalline distortion factor (%)
J-integral	(kJ m^{-2})
J_c	Critical value of the J-integral (kJ m^{-2})
l_a	Thickness of the amorphous region (10^{-10} m)
l_c	Thickness of the crystalline region (10^{-10} m)
T	Tearing modulus
U	Energy to initiate and propagate the crack (kJ)
W	Width of specimen (mm)
σ_y	Yield stress (MPa)