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The effect of molecular weight on slow crack growth in linear polyethylene homopolymers

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The rate of initiation and growth of cracks in linear high-density polyethylene with different molecular weights was observed in single-edge-notched tensile specimens under plane strain condition as a function of applied stress, notch depth and temperature. The initial rates of crack initiation all have the form of $C\sigma^m a_0^n \exp(-Q/RT)$ or $AK^P \exp(-Q/RT)$ where σ = stress, a_0 = notch depth and K = stress intensity factor. For the different molecular weights, m,. n, P and Q are almost the same where $m = 5$, $n = 2$, $P = 4.7$ and $Q = 115\,\text{kJ}\,\text{mol}^{-1}$, but the constants C and A varied as $(\bar{M}_w - \bar{M}_c)^{-1}$ where $\bar{M}_c$ is a limiting molecular weight for sudden fracture. A molecular model based on tie-molecules has been used to explain the dependence on $\bar{M}_w$. The effect of $\bar{M}_w$ on the fast-fracture strength at low temperature and the relationship to tie-molecules have also been investigated. Quantitative relationships between the concentration of tie-molecules and the fracture behaviour have been obtained.

1. Introduction

Polyethylene (PE) fails in the neighbourhood of room temperature under low stresses in a brittle mode after a period of time. The failure mode is called "long time brittle failure". There is little macroscopic deformation throughout the material; however, microscopic observations of the fracture process show a state of large deformation. Lu and Brown [1, 2] and Bhattacharya and Brown [3] found that the crack initiation stage plays an important role in determining the lifetime. The fracture process of PE under plane strain condition consists of the following sequences of micro-events: (a) generation of micro-craze; (b) increase in size of the micro-crazes to form coarse fibrils; (c) fibrillar extension to fracture. For a homopolymer with $\bar{M}_w = 106\,000$, the kinetics of fracture has been determined as a function of stress, notch depth and temperature [1, 2].

In this investigation the effects of stress, notch depth and temperature on the kinetics of fracture were found to be independent of molecular weight. The rate of crack initiation and growth varies as $(\bar{M}_w - \bar{M}_c)^{-1}$ where $\bar{M}_c$ is a limiting molecular weight for sudden fracture. These results have been compared with the effect of molecular weight on the fracture strength at a very low temperature. It is emphasized that the effects of molecular weight are based on the number of tie-molecules. An estimate of the concentration of tie molecules for a given molecular weight has been made.

2. Experimental procedure

The linear PE resins supplied by the Phillips Chemical Company (Bartlesville, Oklahoma) were homopolymers. The material parameters are shown in Table I. The molecular weight distributions were determined by the DuPont Company.

The following method of compression moulding minimizes the scatter in the data. The compression die is a square chamber 16 cm × 16 cm and 1.8 cm deep with a close-fitting piston. When the polymer was heated to about 160° C, a pressure of 6.6 MPa was alternately exerted and released for about 3 cycles; at 180° C, the same process was repeated. Finally the melt was solidified under a pressure of 1.7 MPa and very slowly cooled to room temperature.

The compression-moulded plaques were 4.5 to 5 mm thick. The dimensions of the single-edge-notched specimens are shown in Fig. 1. Specimens were notched with a razor blade to depths of 0.15 to 0.35 mm. The notching was carefully controlled by using a fresh razor blade per notch and using a slow notching speed of $0.05\,\text{mm}\,\text{min}^{-1}$.

TABLE I Characteristics of the materials

Material	Density ($\text{g}\,\text{cm}^{-3}$)	$\bar{M}_n$ ($\times 10^3$)	$\bar{M}_w$ ($\times 10^3$)	$\bar{M}_z$ ($\times 10^3$)	Yield stress (MPa) ($T = 42°\text{C}$, $\dot{\varepsilon} = 0.4\,\text{min}^{-1}$)
Marlex 6060	0.970	19.9	66.8	174	24.2
Marlex 6006	0.964	20.3	106	539	24.0
Marlex 6003	0.961	20.9	137	786	23.6
Marlex 6001	0.958	19.8	158	1001	23.1

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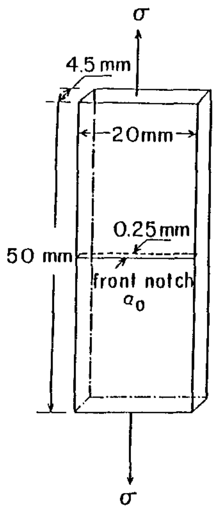

Figure 1 Single-edge-notched tensile specimen.

Specimens were exposed to a constant stress over a temperature range of 30 to 42° C. The applied stress was kept below half the yield stress to avoid large scale yielding. The opening of the notch at the surface of the specimen and at the root of the original notch (COD) were measured as a function of time with a microscope with a filar eyepiece. SEM was used to observe the structure of the damaged zone (Fig. 2).

3. Results

3.1. General shape of damage zone and notch angle

For all molecular weights, the damaged zone is nearly triangular in shape during the initial stage (Fig. 3). By measuring both the notch opening at the surface and at its root, the apex angle α of the damaged zone was calculated to be about 8°. This result is consistent with direct observation of the damaged zone as viewed by SEM and as reported by Lu and Brown [1, 2].

3.2. Typical COD against time curves

Fig. 4 shows representative curves of COD against time with $\sigma = 10\,\mathrm{MPa}$, $a_0 = 0.25\,\mathrm{mm}$ and $T = 42°\mathrm{C}$ for different molecular weights. All curves give the same general behaviour. Several features can be seen: (a) there exists an instantaneous COD at the root of the notch at $t = 0$; (b) the initial COD rate $\dot{\delta}_0$ is constant, which is followed by an acceleration to ultimate failure. $\dot{\delta}_0$ decreases with increasing molecular weight, whereas time to failure increases. The entire course of the kinetics is essentially determined by $\dot{\delta}_0$.

3.3. Effect of stress σ and notch depth a_0

The dependence of $\dot{\delta}_0$ on σ and a_0 at $T = 42°\mathrm{C}$ for different molecular weights is shown in Figs 5 and 6. The data are represented by the following equation:

$$\dot{\delta}_0 = C_1\,\sigma^{5.0}\,a_0^{2.0} \qquad (1)$$

where only C_1 is a function of molecular weight.

3.4. $\dot{\delta}_0$ dependence on K

Using the same data that were used to determine Equation 1, $\dot{\delta}_0$ was plotted against the stress intensity K. For the single-edge-notched tension specimen

$$K = Y\,\sigma\,a_0^{1/2}$$

where for such specimens $Y = 1.12\pi^{1/2}$ [4]. From Fig. 7,

$$\dot{\delta}_0 = A_1\,K^{4.7} \qquad (2)$$

with a correlation coefficient of 0.98. However, Equations 1 and 2 are not completely compatible since the exponent of a_0 is not equal to one-half the exponent σ. This is an example of how log–log plots tend to obscure fine details of a phenomenon. A_1 depends on the molecular weight.

3.5. Dependence of $\dot{\delta}_0$ on the temperature

Fig. 8 gives $\log\dot{\delta}_0$ against $1/T$ plots for the various molecular weights. The activation energy does not depend on molecular weight and has the value of $115\,\mathrm{kJ\,mol^{-1}}$. Chan and William [5] and Lu and Brown [2] obtained about the same result. All the data

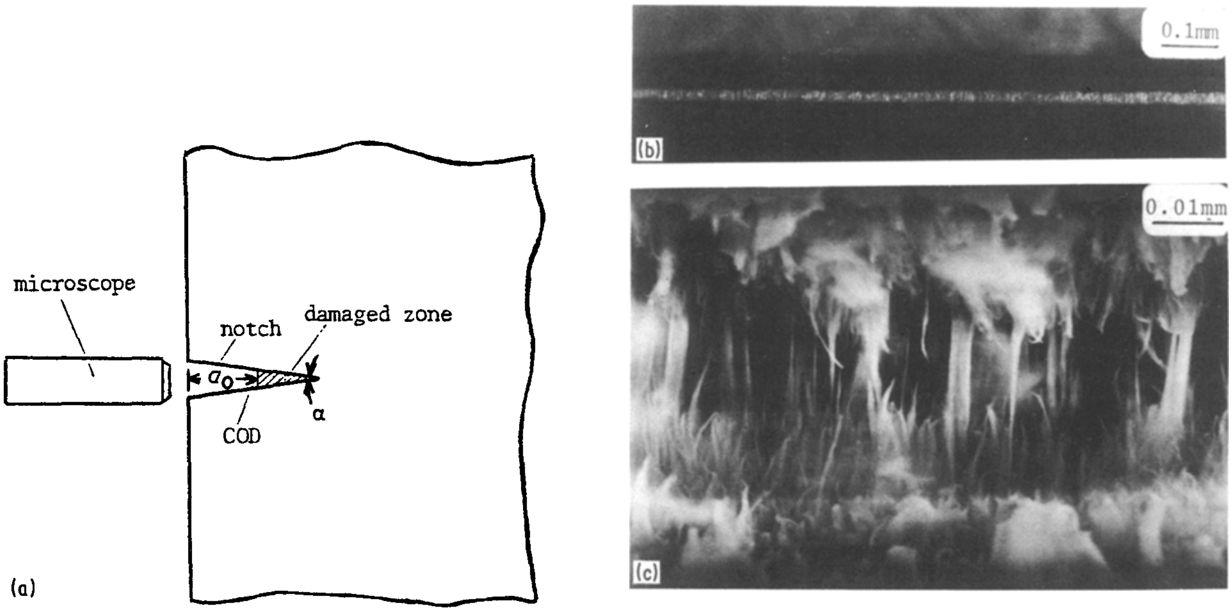

Figure 2 (a) Experimental set-up; (b) optical view of notch; (c) SEM view of notch.

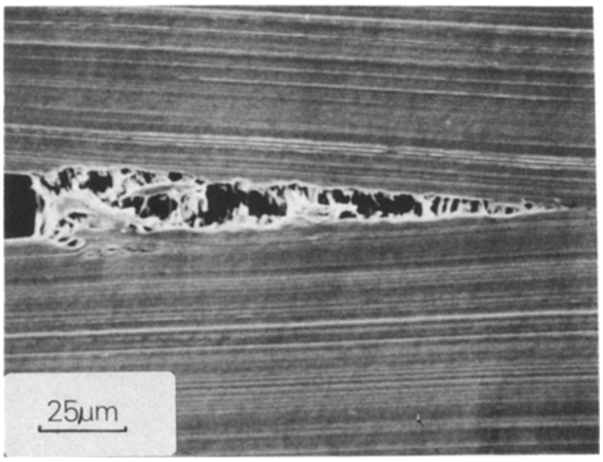

Figure 3 Shape of damaged zone by SEM.

can be represented by the equation

$$\dot{\delta}_0 = C\sigma^{5.0} a_0^{2.0} \exp(-115\,000/RT) \qquad (3)$$

where C varies inversely with $\bar{M}_w$ (Fig. 9).

3.6. Relationship between $\dot{\delta}_0$ and $\bar{M}_w$

Fig. 10, a plot of $1/C$ against $\bar{M}_w$, shows that

$$C \propto (\bar{M}_w - \bar{M}_c)^{-1} \qquad (4)$$

where $\bar{M}_c = 18\,000$.

3.7. SEM observations

Fig. 11 shows the fracture surfaces for different molecular weights. All the structures are fibrillar. The higher the molecular weight the longer the fractured fibrils. In addition, the length of the fractured fibrils increases with crack growth rate for a given molecular weight as was also observed by Chan and Williams [5].

3.8. Fracture stress in liquid nitrogen

Brown and Kamei [6] showed that the low-temperature brittle fracture stress can be measured in liquid nitrogen by measuring the time to failure as a function of stress. The time to failure, t_f, against stress (Fig. 12) is described by the equation

$$t_f = A \exp(b\sigma) \qquad (5)$$

where the molecular weight dependence resides in A. The fracture stress σ_f, for short-time failure is plotted against $\bar{M}_w$ in Fig. 13 with the result

$$\sigma_f = 84 + 1.4 \times 10^{-4}\,\bar{M}_w \quad \text{(MPa)} \qquad (6)$$

Equation 6 states that for $\bar{M}_w = 0$ the fracture stress is 84 MPa. This value should correspond to the fracture stress of an aggregate of small molecules that are bonded only by Van der Waals forces.

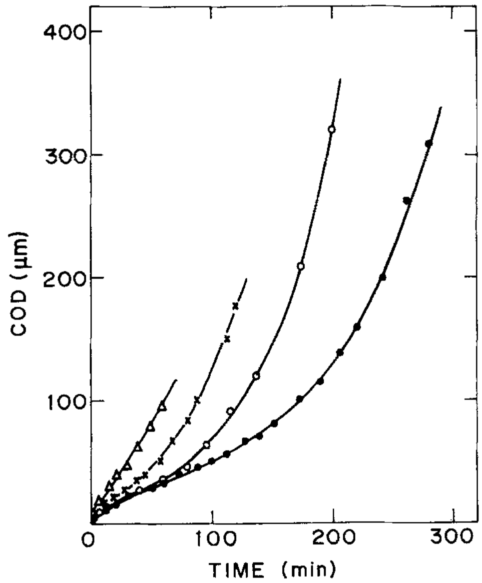

Figure 4 Opening of initial notch at the root (COD) against time for different molecular weights where σ = 10 MPa, a_0 = 0.25 mm and T = 42° C. $\bar{M}_w$ = (△) 67 000, (x) 106 000, (○) 137 000, (●) 158 000.

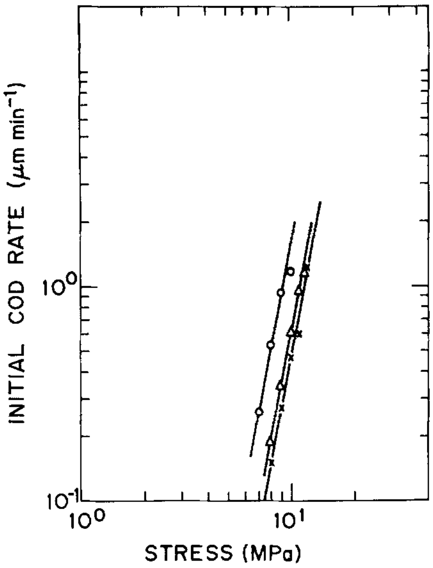

Figure 5 Initial rates of notch opening at the root, $\dot{\delta}_0$, against stress σ for different molecular weights where a_0 = 0.25 mm and T = 42° C. $\dot{\delta}_0 = A\sigma^{5.0}$. $\bar{M}_w$ = (○) 67 000, (△) 106 000, (x) 137 000.

4. Discussion

The phenomenon of crack initiation and slow crack growth in linear PE is exhibited by the curves in Fig. 4. Starting at $t = 0$ there is an initial damaged zone at the root of the notch whose size is that predicted by the Dugdale theory. The fibrillated damage zone grows at an initial rate called $\dot{\delta}_0$. When the COD reaches a critical value, δ_c, true crack growth starts and the curve begins to accelerate. As shown by Lu

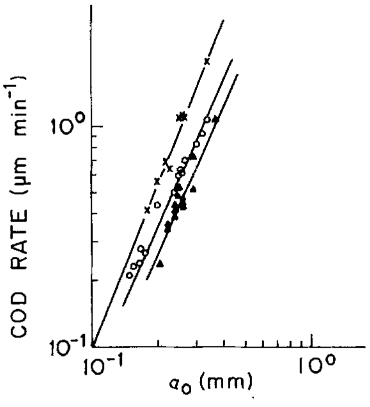

Figure 6 Initial rates of notch opening at the root, $\dot{\delta}_0$, against notch depth a_0 for different weights where σ = 10 MPa and T = 40° C. $\bar{M}_w$ = (x) 67 000, (○) 106 000, (▲) 137 000. Slope = 2.0.

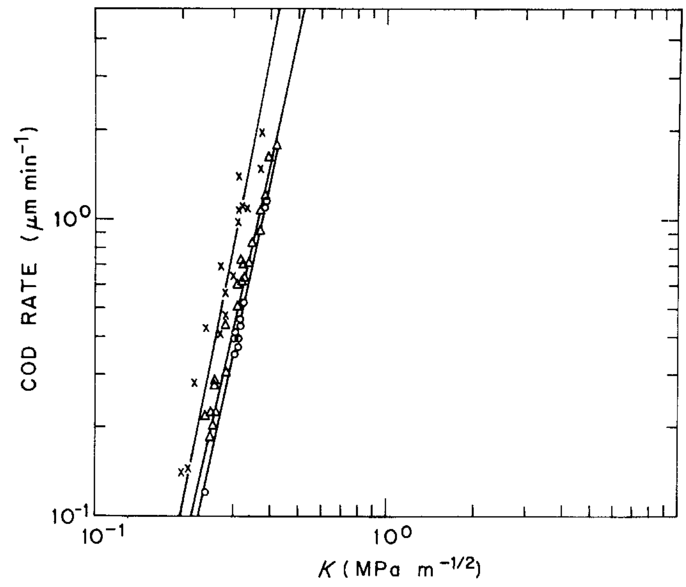

Figure 7 Initial rates of notch opening at the root, $\dot{\delta}_0$, against stress intensity K at $T = 42°$C for various molecular weights. $\bar{M}_w$ = (x) 67 000, (Δ) 106 000, (o) 137 000. Slope = 4.7.

and Brown [1, 2], the subsequent damage zone which includes the fibrillated and the fractured regions grows at a rate $\dot{\delta}$ which depends on $\dot{\delta}_0$ as follows:

$$\frac{\dot{\delta}}{\dot{\delta}_0} = \left(\frac{\alpha a_0 + \delta}{\alpha a_0 + \delta_c}\right)^2 \qquad (7)$$

where δ is the COD at time t and δ_c is the critical COD where true fracture begins. Thus, the kinetics for the initiation of crack growth and the subsequent crack growth rate stems from $\dot{\delta}_0$, the initial COD rate.

Equation 3 shows that the effects of stress, notch depth and temperature on $\dot{\delta}_0$ are independent of molecular weight. This suggests that the fracture mechanism is the same for all molecular weights. Since the activation energy is also the same for all different molecular weights, it indicates that the micro-molecular process of thermal activation is independent of molecular weight. In a previous paper Lu and Brown [7] showed that $\dot{\delta}_0$ is based on two processes: (i) the nucleation rate for the damaged zone and (ii) the rate of disentanglement of the fibrils. The nucleation rate was shown to increase as the yield point decreased. However, in this investigation, the yield point decreases slightly as the molecular weight increases whereas $\dot{\delta}_0$ decreases. We are led to the conclusion that it is the effect of $\bar{M}_w$ on the rate of disentanglement that is important.

In order to understand the disentanglement process, Fig. 14 is introduced. This is a model of oriented PE by Gibson *et al.* [8] which is probably applicable to the oriented fibrillar structure that constitutes the damaged zone (Fig. 2). The light regions correspond to the amorphous regions. Since our investigation is well above T_g, the amorphous regions are in the liquid-like state where the Van der Waals bonding is essentially zero. The key to understanding the effect of molecular weight is the tie-molecules which join the crystalline blocks together. As shown by Keith *et al.* [9] the number of tie-molecules increases markedly with molecular weight. Below a critical molecular weight no tie-molecules could be observed. This observation is in complete accord with our observation that sudden fracture occurs when $\bar{M}_w < 18\,000$. This result is in agreement with the general observation in polymers that crazes do not form below a critical molecular weight. In the case of amorphous polymers, the concept of random entanglement is invoked and the critical molecular weight is that required to form random entanglements as pointed out by Kramer [10]. In the case of a semi-crystalline polymer above T_g, the

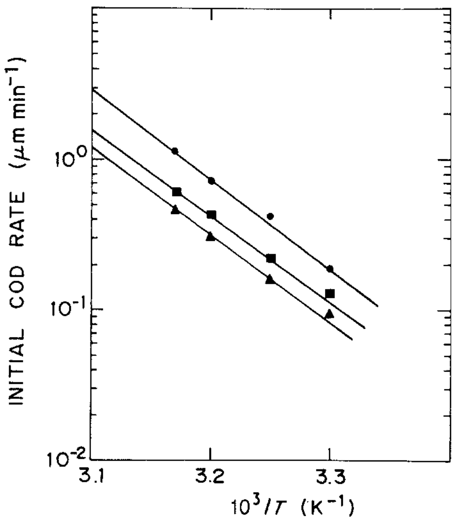

Figure 8 log $\dot{\delta}_0$ against $1/T$ for different molecular weights. $\bar{M}_w$ = (●) 67 000, (■) 106 000, (▲) 137 000. ΔH = 115 kJ mol^{-1}.

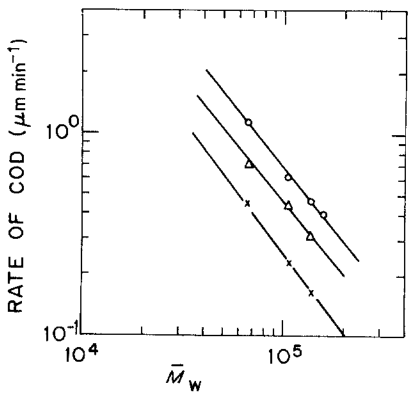

Figure 9 log $\dot{\delta}_0$ against log $\bar{M}_w$ at different temperatures: (x) 35° C, (Δ) 39° C, (o) 42° C.

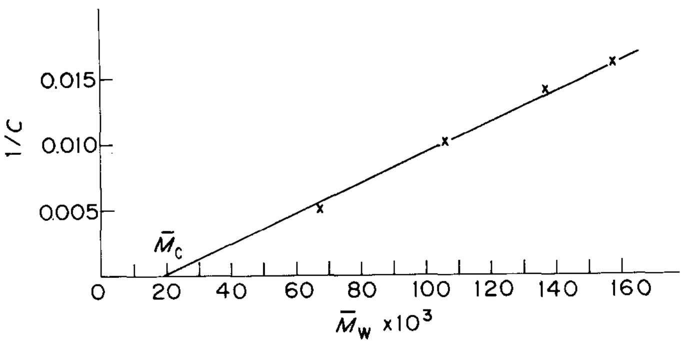

Figure 10 $1/C$ against $\bar{M}_w$. C is from Equation 3. Slope = 1.14×10^{-7}; $\bar{M}_c = 18000$.

crystalline blocks take the place of the entanglement in that they join the fibrils together by means of the tie-molecules. Thus, the tie-molecules form a network that is tied together by the crystalline blocks.

The experimental data indicate that for $\bar{M}_w < 18000$ fibrils do not form. This observation can be explained quantitatively in terms of the morphology. As measured by Capaccio and Ward [11], for a molecular weight of about 100 000 in slow-cooled PE, the thickness of the crystalline block is about 21 nm and the thickness of the amorphous region is 6 nm so that the long period is 27 nm. In the liquid state the root mean square value of the end-to-end distance of a random coil, $\bar{r}$, is given by

$$\bar{r} = (D\,n' l^2)^{1/2} \tag{8}$$

For PE, $D = 6.8$ and the link length $l = 0.153$ nm [12]. For $\bar{M}_w = 18000$, the number of links $n' = 1300$ so that $\bar{r} = 14$ nm. Thus, when a random coil in the liquid has an end-to-end distance r that is less than twice the long period, it is not likely that a molecule will crystallize simultaneously within adjacent crystal blocks. The probability of a given end-to-end distance r is given by

$$p(r) = a\,r^2 \exp\,(-b^2 r^2) \tag{9}$$

where a is a constant; $b^2 = 3/2\bar{r}^2$.

If it is assumed that in the melt the end-to-end distance of a random coil, r, must be greater than twice the long period in order to form a tie-molecule, then the probability for forming a tie-molecule is given by

$$P = \frac{1}{3}\,\frac{\int_{2L}^{\infty} r^2 \exp\,(-b^2 r^2)\,\mathrm{d}r}{\int_0^{\infty} r^2 \exp\,(-b^2 r^2)\,\mathrm{d}r} \tag{10}$$

where L is the long period. The factor 1/3 was introduced because two dimensions of the lamellar structure are much larger than the long period. In Fig. 15, P is plotted against molecular weight for $L = 27$ nm. We note that for the molecular weight less than 60 000 the number of tie-molecules rapidly approaches zero and $\bar{r}$ is much less than $2L$. The probability that a molecule will be a tie-molecule from Equation 10 is based on a monodisperse system. In order to calculate the actual number of tie-molecules, the distribution of molecular weights for each material must be taken into account (Fig. 16). Thus, the probability that a molecule will be a tie-molecule for a given molecular weight distribution is given by

$$\bar{P} = \frac{\int_0^{\infty} nP\mathrm{d}M}{\int_0^{\infty} n\mathrm{d}M} \tag{11}$$

where $n\mathrm{d}M$ is the number of molecules with molecular weight between M and $(M + \mathrm{d}M)$. Since the molecular distribution in Fig. 15 is based on the weight fraction w, n is obtained from w/(mol wt). $\bar{P}$ (Equation 11) was evaluated for the various materials as shown in Table II. It is to be noted that $\bar{P}$, which is the same

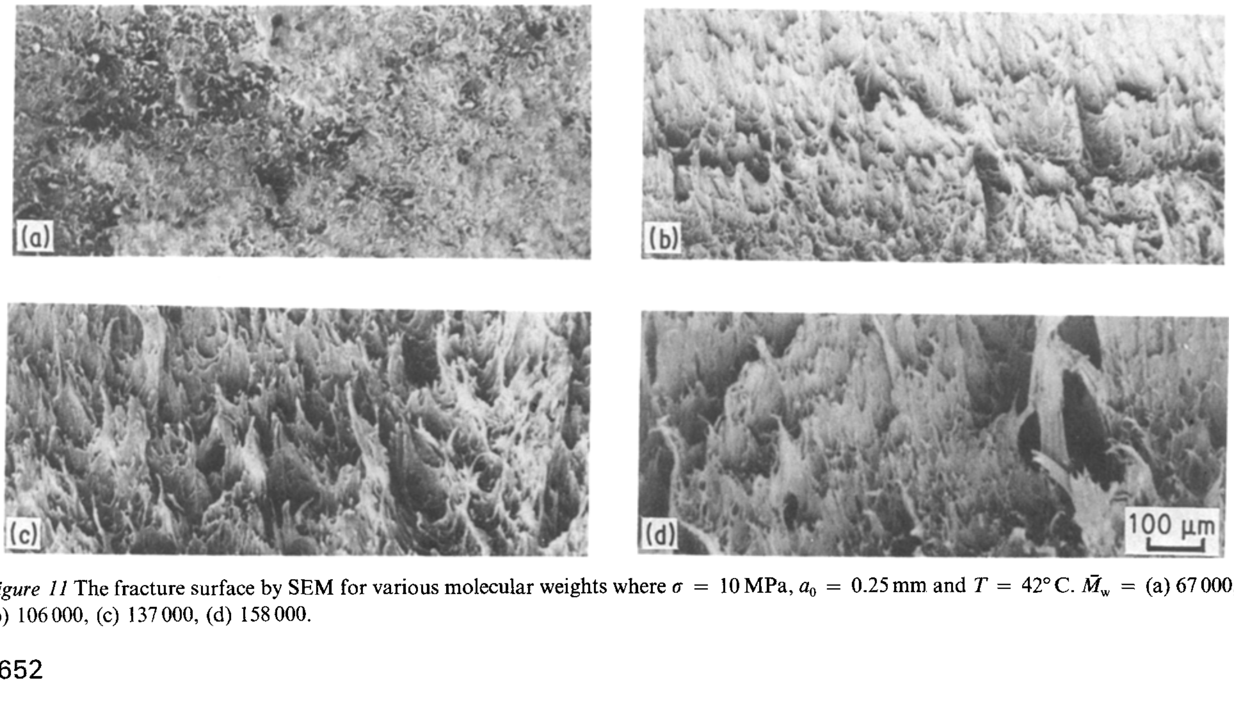

Figure 11 The fracture surface by SEM for various molecular weights where $\sigma = 10$ MPa, $a_0 = 0.25$ mm and $T = 42°$C. $\bar{M}_w$ = (a) 67 000, (b) 106 000, (c) 137 000, (d) 158 000.

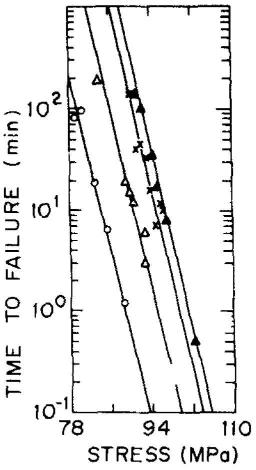

Figure 12 Time to failure against stress in liquid nitrogen for different molecular weights. $\bar{M}_w$ = (○) 67 000, (△) 106 000, (×) 137 000, (▲) 158 000.

as the fraction of all molecules that are tie-molecules, is only about 1%. Thus, although the tie-molecules are relatively few in number, their effect is very significant.

The actual number of tie-molecules is probably somewhat less than that calculated from Equation 11. There is a kinetic factor which also should be considered. If one end of a molecule begins to crystallize before the other end, the probability that the other end will crystallize in an adjacent lamella is somewhat reduced. In order to make a more complete calculation, it is necessary to know the probability in time that one end begins to crystallize before the other, and also the rate at which the molecule is incorporated within a crystal. This more complex calculation has not been done.

Table I shows $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$. $\bar{M}_n$ is about the same for all the resins, and therefore does not appear to provide a good correlation with the number of tie-molecules. $\bar{M}_w$ and $\bar{M}_z$ both increase uniformly with $1/C$. However, when $1/C$ goes to zero $\bar{M}_w$ goes to a critical value of 18 000. This value is reasonable in that no tie-molecules are expected for this value of $\bar{M}_w$. If $1/C$ is plotted against $\bar{M}_z$, a linear curve is obtained, but as $1/C$ goes to zero $\bar{M}_z$ approaches a negative value, which is not a reasonable result. It was also observed that whereas σ_f is a linear function of $\bar{M}_w$ (Fig. 13), it is a non-linear function of $\bar{M}_z$. Thus, for the molecular weight distributions in these resins, $\bar{M}_w$ appears to be the best parameter for describing the effect of molecular weight on slow crack growth and on the low-temperature fracture stress.

TABLE II Fraction of molecules that are tie-molecules in each material

Material	$\bar{M}_w$ ($\times 10^3$)	$\bar{P}$ (Equation 11)	f (Equation 25)
Marlex 6060	67	12×10^{-3}	2×10^{-3}
Marlex 6006	106	25×10^{-3}	4×10^{-3}
Marlex 6003	137	28×10^{-3}	5×10^{-3}
Marlex 6001	158	31×10^{-3}	6×10^{-3}

A model suggested by Prentice [13] will be presented to describe the relationship between the tie-molecules and $\dot{\delta}_0$. The basis of the model is the structure of an oriented fibril as shown in Fig. 14. Let σ be the local stress on a fibril and let N be the number of tie-molecules per unit area of the fibril. Then the force F on each tie-molecule is given by

$$\sigma = FN \tag{12}$$

This equation is based on the assumption that the force F is required to pull a tie-molecule through the crystal. If the velocity V of the tie-molecule is small then it may be described by

$$F = \mu V \tag{13}$$

where μ is a viscosity.

Combining Equations 12 and 13,

$$V = \sigma/N\mu \tag{14}$$

V is expected to be proportional to the rate of fibril lengthening as measured by $\dot{\delta}_0$:

$$V = B_1\dot{\delta}_0 \tag{15}$$

Assume that the local stress σ depends on the stress intensity in the following way:

$$\sigma = B_2K^s \tag{16}$$

μ is expected to be related to the micromechanism by which the tie-molecule slides through the crystal and probably has the same activation energy as measured for $\dot{\delta}_0$, so that

$$\mu = B_3\,e^{Q/RT} \tag{17}$$

If Equations 14 to 17 are combined,

$$\dot{\delta}_0 = \frac{B_2K^s}{B_1\,B_3\,N\,e^{Q/RT}} \tag{18}$$

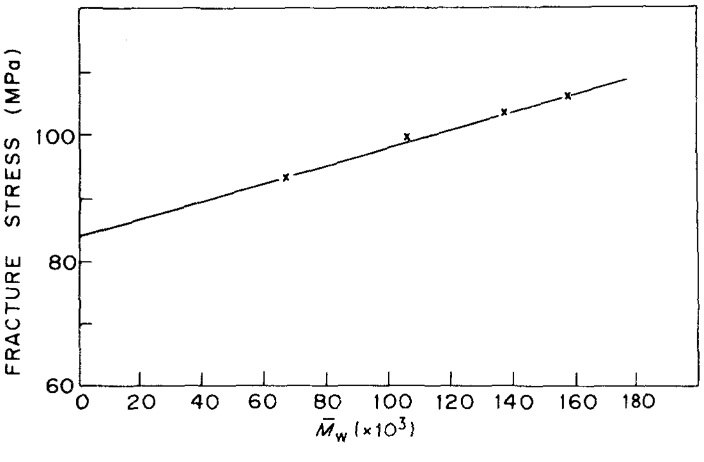

Figure 13 Fracture stress against $\bar{M}_w$ for fast fracture in liquid nitrogen.

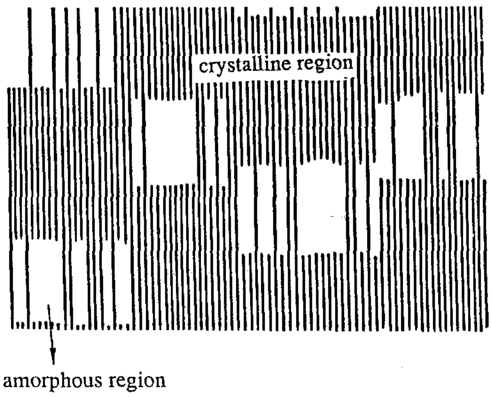

Figure 14 Model of oriented PE [8].

If Equation 18 is compared with the experimental observation that

$$\dot{\delta}_0 = A\,K^{4.7}\,e^{-Q/RT} \qquad (19)$$

and if s is expected to be = 4.7, then

$$NA = \text{constant} \qquad (20)$$

Since N is approximately proportional to $(\bar{M}_w - \bar{M}_c)$ and A is proportional to $(\bar{M}_w - \bar{M}_c)^{-1}$, Equation 20 is satisfied. The theory is consistent with the experimental results that the effect of stress, notch depth, and temperature on $\dot{\delta}_0$ are independent of molecular weight. Consequently the effect of these variables should also be independent of the concentration of tie-molecules.

The number of tie-molecules will now be calculated from the low-temperature brittle fracture stress. Using the model in Fig. 14, it is assumed that the low-temperature fast fracture runs through the amorphous region. The fracture stress depends on the fracture strength of the amorphous region and is enhanced by the number of tie-molecules. Thus, the measured brittle fracture stress σ_f is related to the number of tie-molecules as proposed by Brown and Ward [14]:

$$\sigma_f = \frac{1}{q}\,[f\sigma_t + (1 - f)\,\sigma_a] \qquad (21)$$

where q is a stress concentration factor which must be considered whenever a brittle fracture is produced; f is the fraction of the area occupied by tie-molecules, σ_t is the ideal strength of tie-molecules and σ_a the ideal strength of the amorphous region. Smook *et al.* [15] measured the strength of highly oriented PE and found that the strength of flawless PE fibres was 26 GPa. This value agrees with the theoretical prediction that $\sigma_t = (1/10 \text{ to } 1/20)E_t$ [16] since Young's modulus of the tie-molecules $E_t = 300$ GPa. σ_a/q is the value of σ_f when $f = 0$; this value of 86.5 MPa is obtained directly from Fig. 10 by extrapolating σ_f to $\bar{M}_w = 18\,000$. Thus, Equation 21 becomes

$$\sigma_f - 86.5 = 26\,000\,(f/q) \qquad (22)$$

q is expected to be the order of 10, but its value can be estimated more directly. The predicted value of σ_a is $(1/10 \text{ to } 1/20)E_a$. Since Young's modulus, E_a, of the amorphous region is 8 GPa at 77 K, $\sigma_a \approx 600$ MPa. If the experimental value of the fracture stress at zero molecular weight is σ_a(exp), then from Fig. 11 $\sigma_a(\text{exp}) = 84$ MPa. Therefore $q = \sigma_a/\sigma_a(\text{exp}) = 600/84 = 7$.

Thus Equation 22 becomes

$$\sigma_f - 86.5 = 4 \times 10^3 f \qquad (23)$$

From Fig. 12

$$\sigma_f - 86.5 = 1.4 \times 10^{-4}\,(\bar{M}_w - 18\,000) \qquad (24)$$

Therefore

$$f = 4 \times 10^{-8}\,(\bar{M}_w - 18\,000) \qquad (25)$$

where f is the fraction of the area of the amorphous region that is occupied by tie-molecules. The actual number of tie-molecules is small, e.g. when $\bar{M}_w = 10^5$, $f = 3 \times 10^{-3}$. However, their effect on low-temperature brittle fracture and slow crack growth at room temperature is very significant. The values of f for each resin are shown in Table II. The concentrations of tie-molecules as determined from the low-temperature fracture stress agree very well with the concentrations from the statistical calculation, $\bar{P}$, considering the uncertainties in the theories.

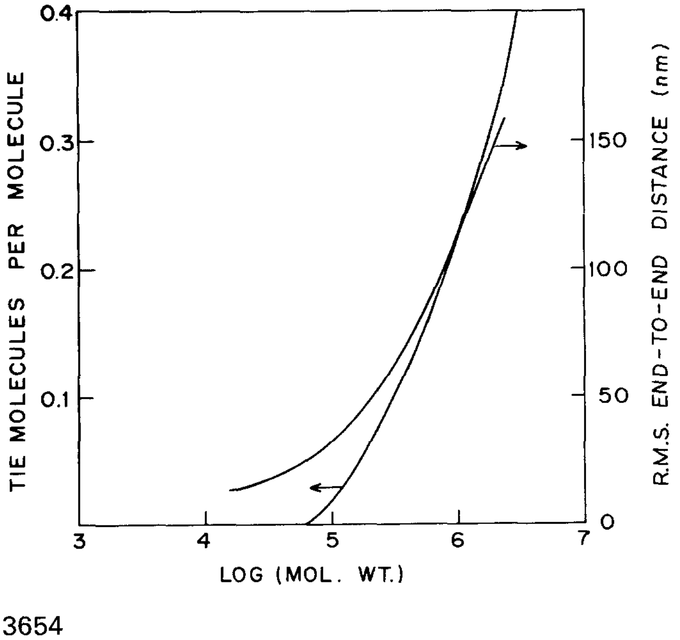

Figure 15 Probability that a molecule will form a tie-molecule against molecular weight for a monodisperse polymer if the long period is 27 nm (r.m.s. end-to-end distance of molecule) against molecular weight.

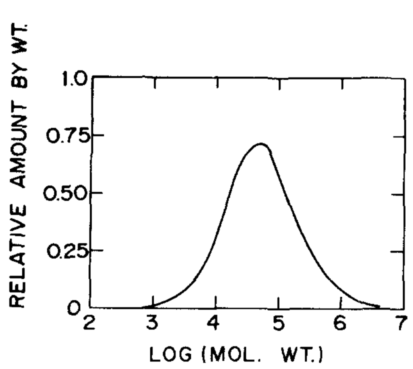

Figure 16 Molecular weight distribution of Marlex 6003.

5. Summary and conclusions

1. The rate of slow crack growth is described by

$$\dot{\delta}_0 = 9.9 \times 10^{13} (\bar{M}_w - 18\,000)^{-1} \sigma^5 a_0^2 \times \exp(-115\,000/RT)$$

in μm min^{-1}; σ is in MPa, a_0 in μm and R in J mol^{-1} K^{-1}.

2. The molecular weight affects the rate of disentanglement of the fibrils that occur in the damage zone.

3. The rate of disentanglement depends on the number of tie-molecules.

4. The number of tie-molecules is directly determined by the size of the domain of the random coil in the melt relative to twice the size of the long period.

5. The low-temperature brittle fracture stress is directly related to the number of tie-molecules.

6. From the dependence of low-temperature fracture stress on molecular weight, it was found that f, the fraction of area in the amorphous region that contains tie-molecules, is given by

$$f = 4 \times 10^{-8} (\bar{M}_w - 18\,000)$$

7. $\bar{M}_w = 18\,000$ is the critical molecular weight below which no tie-molecules are formed.

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References

1. X. LU and N. BROWN, *J. Mater. Sci.* **21** (1986) 2423.
2. *Idem, ibid.* **21** (1986) 4081.
3. S. K. BHATTACHARYA and N. BROWN, *ibid.* **19** (1984) 2519.
4. J. G. WILLIAM, “Fracture Mechanics of Polymers” (Wiley, New York, 1986) p. 64.
5. M. K. V. CHAN and J. G. WILLIAM, *Polymer* **24** (1983) 234.
6. E. KAMEI and N. BROWN, *J. Polym. Sci., Polym. Phys. Edn* **22** (1984) 543.
7. X. LU and N. BROWN, *Polymer* **28** (1987) 1505.
8. A. G. GIBSON, S. A. JAWARD, G. R. DAVIES and I. M. WARD, *ibid.* **23** (1982) 349.
9. H. D. KEITH, F. J. PADDEN Jr and R. G. VADIMSKY, *J. Polym. Sci., Part A-2* **4** (1966) 267.
10. E. J. KRAMER, in “Advances in Polymer Science”, Vol. 52/53, edited by H. H. Kausch (Springer, New York, 1983) p. 33.
11. G. CAPPACCIO and I. M. WARD, *J. Mater. Sci.* **15** (1980) 2897.
12. L. MANDELKERN, “Introduction to Macromolecules”, 2nd Edn (Springer Verlag, New York, 1982) p. 39.
13. P. PRENTICE, *J. Mater. Sci.* **20** (1985) 1445.
14. N. BROWN and I. M. WARD, *ibid.* **18** (1983) 1405.
15. J. SMOOK, W. HAMERSMA and A. J. PENNINGS, *ibid.* **19** (1984) 1359.
16. A. KELLY, “Strong Solids”, 2nd Edn (Clarendon, Oxford, 1973) p. 10.

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