

A fundamental theory for slow crack growth in polyethylene

N. Brown* and X. Lu

Department of Materials Science and Engineering, University of Pennsylvania,
Philadelphia, PA 19104-6272, USA

(Received 12 April 1994; revised 4 August 1994)

The following theoretical equation has been obtained for measuring the rate of slow crack growth in polyethylene in terms of the crack opening displacement rate $\dot{\delta}$:

$$\dot{\delta} = \frac{\sigma_y(1-\gamma^2)^2}{\eta d_0 E^2 \sigma_c^2} K^4$$

Here σ_y is the yield point, K is the stress intensity, η is the intrinsic viscosity of the fibrils in the craze, E is Young's modulus, σ_c is the stress to produce a craze, d_0 is the primordial thickness from which the craze originates and γ is Poisson's ratio. The theoretical equation agrees with the experimental observation:

$$\dot{\delta} = CK^4 e^{-Q/RT}$$

Thus, for the first time, the dependence of $\dot{\delta}$ on stress and notch depth have been derived in fundamental terms and the physical parameters that constitute the factor C have been identified. The intrinsic viscosity η can be calculated from the theory using specific experimental data. For example at 42°C, the fibrils in a craze in a homopolymer have an intrinsic viscosity of 3×10^{11} Pa s. This is much larger than the melt viscosity of the amorphous region, which is about 10^5 – 10^6 Pa s. Thus, the resistance of polyethylene to slow crack growth is governed by the crystals and not by the amorphous region.

(Keywords: slow crack growth; polyethylene; modelling)

INTRODUCTION

Time-dependent fracture occurs in many materials when exposed to a constant load and without the concurrence of an environmental effect. Polymers are especially prone to this long-time failure mode because their mechanical properties are generally time-dependent. Fracture often occurs in the craze that forms at the crack tip. A theory for the 'relaxation-controlled growth' of a craze has been presented by Williams and Marshall¹ where the time to failure is determined by the decrease with time of the elastic modulus and/or the stress to produce the craze. Their theory predicts that the time t_B to initiate fracture is related to the stress intensity by:

$$t_B \sim K^{-2/n} \quad (1)$$

when $J = J_c$ is the fracture criterion; or by

$$t_B \sim K^{-2/(m+n)} \quad (2)$$

when a critical crack opening δ_c is the condition for fracture. Here n and m are the exponents when a power-law relation exists between the time and the modulus or the stress to produce the craze. Williams² presents data for K versus t_B for several amorphous polymers where the exponent in the theoretical relations has values ranging from about 10 to 40 depending on the particular polymer. Kinlock³ has also presented data that agree with this theory.

Extensive data by Chan and Williams⁴ and Brown *et al.*⁵ on slow crack growth (SCG) in polyethylenes (PE) show:

$$\text{SCG rate} \sim K^n \quad (3)$$

where n varies from about 2.6 to 4.8 depending on the PE and only slightly on temperature. These values of n are much less than the values predicted by the 'relaxation-controlled growth' theory, which is based on the experimental values of the relaxation behaviour of the elastic modulus and the stress to produce yielding. The only theory to explain why n is only about 4 for PE has been presented by Chan and Williams⁴. Their theory assumes that spacing of defects in the PE are responsible for the phenomenon and that the diffusion of these defects accounts for the time dependence. This *ad hoc* theory has never been substantiated by experiments. If the concentration of defects determines n , it would be expected that the pigments that are often used in PE would cause n to vary widely. All PE, whether pigmented or not pigmented, have n values that vary over a narrow range of $2.6 < n < 4.8$.

In this paper a theory is presented which explains the experimental result for $n \approx 4$. Equation (4) represents results based on more than a thousand observations of SCG in an extremely wide range of polyethylene resins over a very wide range of stresses, notch depths and temperatures. The SCG rates have ranged from 10^{-1} to 10^{-6} and always the relationship between the rate of

* To whom correspondence should be addressed

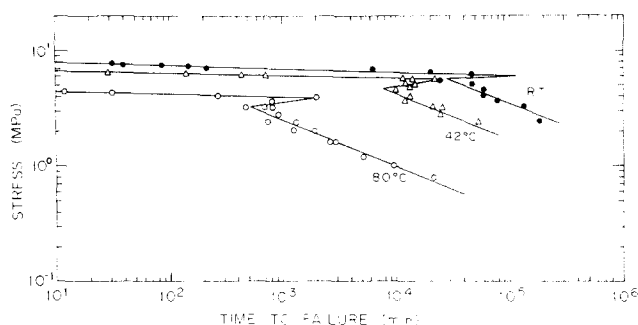


Figure 1 Stress versus time to failure at different temperatures; notch depth 3.50 mm

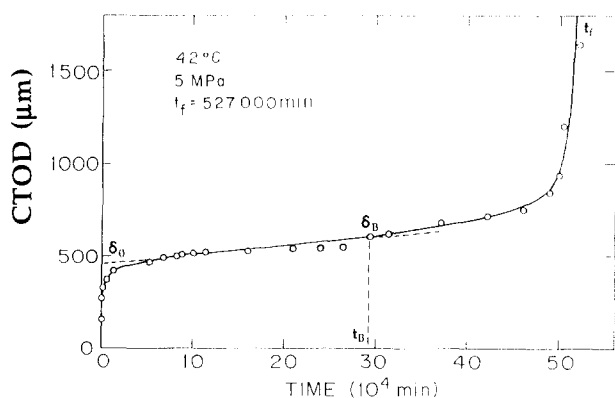


Figure 2 Crack tip opening displacement versus time; 5 MPa, 42 °C, 3.50 mm notch depth

failure and the stress σ and notch depth a is given by:

$$\text{SCG rate} = C\sigma^n a^m \quad (4)$$

where $2.6 < n \leq 5$ and $1.3 < m < 2$. Even though the data show that n is often slightly larger than $2m$, K correlates well with SCG. Bassani, Brown and Lu⁶ have used J instead of K as the correlating parameter to take into account the non-linear stress-strain behaviour of PE, but the general picture as represented by equation (4) is not altered. In this paper, a theory is presented that explains the dependence of SCG rate on K and gives the physical parameters that constitute the factor C . The theory is based on three components: (1) phenomenological data, (2) microscopic observations and (3) fracture mechanics.

PHENOMENOLOGY

The phenomenology of SCG is based on the following types of measurement: failure time t_f versus σ ; (2) t_f versus a ; (3) t_f versus T ; and (4) crack-tip opening displacement (CTOD) versus time. Figure 1 shows $\log \sigma$ vs. $\log t_f$. In the high-stress region, $t_f \sim \sigma^{-n}$, where $n = 20-40$ and the failure is ductile. This failure mechanism is a creep-type failure that is caused by the relaxation of the yield point with time. Failure occurs when the creep strain reaches a critical strain to produce macroscopic shear yielding. In the low-stress region, brittle failure occurs at a craze and $n \approx 4$. Generally, the brittle-type failure occurs at stresses less than about $0.5\sigma_y$, the yield point. This paper is concerned with the low-stress brittle failure. Both mechanisms of failure, i.e. creep and craze growth, occur simultaneously as described by Brown *et al.*⁷; it is essentially a question of which mechanism is the first to

produce fracture. It is important to know that brittle fracture requires a craze and the craze can only be generated under plane-strain conditions.

Figure 2 shows the general behaviour of crack-tip opening displacement (CTOD) δ versus time. As the notched specimen is loaded, a craze forms at the tip of the notch and quickly grows to a thickness δ_0 , as measured at its base. The CTOD increases with time at a rate $\dot{\delta}$ until fracture is initiated as evidenced by broken fibrils at the base of the craze. The time for crack initiation is called t_B and the corresponding CTOD is δ_B . Thus:

$$\dot{\delta} = \frac{\delta_B - \delta_0}{t_B} \quad (5)$$

and $\delta_B - \delta_0$ varies slightly with respect to σ , a and T . The large differences in δ are mainly produced by the value of t_B . The time for complete fracture is t_f . For a given resin, the ratio of t_B/t_f is rather insensitive to σ , a and T . The ratio of t_B/t_f varies from about 0.2 to 0.8 depending on the resin. For $t > t_B$, $\dot{\delta}$ begins to accelerate because the stress intensity increases as the crack grows. Thus, for a given resin, the three quantities $\dot{\delta}$, t_B and t_f are related and each has the same dependence on K and T . In this paper $\dot{\delta}$ will be used as the measure for SCG. Physically, $\dot{\delta}$ is related to the rate of disentanglement of the molecules in the fibril of the craze and specifically is related to those fibrils at the base of the craze where fracture initiates.

SCG in all polyethylenes obeys the following behaviour:

$$\dot{\delta} = C\sigma^n a^m e^{-Q/RT} \quad (6)$$

where $n = 5$ and $m = 2$ for homopolymers and $n = 3.2-2.6$ and $m = 1.3$ for ethylene copolymers. For a given resin, n varies slightly with temperature. The activation energy, $Q \approx 100 \text{ kJ mol}^{-1}$ for all polyethylenes, which is the same as the activation energy of α relaxation of the crystals. This result signifies that the same fundamental molecular motion occurs in all PE during SCG. The constant C is a material parameter that is very sensitive to the molecular and morphological structure and may vary by a factor of 10^6 . It is important to understand the physical parameters that constitute C and to know the origin of the dependence of the SCG rate on K .

MICROSCOPY

Figure 3 (ref. 8) is a curve of CTOD versus time and the letters correspond to the micrographs shown in Figure 4 (ref. 8). Figure 4c shows the craze just before t_B when fracture initiated. Figure 4a shows the size of the craze immediately after loading. The growth rate of the craze between states b and c is represented by $\dot{\delta}$. During this period the fibrils at the base of the craze are slowly weakening.

It should also be noted that the original notch, which was produced by a razor blade, was extremely sharp with a radius of $1 \mu\text{m}$. After loading the specimen, the notch is greatly blunted, so that during the time prior to t_B its radius of curvature becomes on the order of $50 \mu\text{m}$.

In addition to the blunting of the original notch, the stress field surrounding the notch tip is relaxed. Figure 5b (ref. 9) is an SEM micrograph that shows a craze with its fibrillated structure, which is essentially confined to the plane of the initial notch. Figure 5a is an optical

transmission micrograph that shows that the damage zone extends completely along the edge of the blunted notch. It is important to note that the stress field on the boundary of the fibrils at the base of the craze, where fracture initiates, is located within a region of highly deformed material.

Experimental determinations of the stress on the boundary of crazes in PE (Figure 6) by Wang, Brown and Fager^{10,11} show that the boundary stress is essentially constant and approximately equal to the yield point. These observations strongly indicate that the stress on the boundary of the fibrillated material is equal to the yield point:

$$\sigma_B = \sigma_y \quad (7)$$

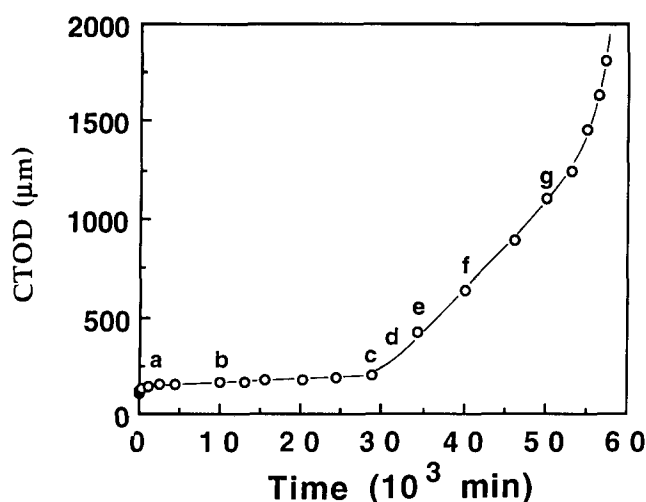


Figure 3 CTOD versus time (see Figure 4 also)

The CTOD δ_0 soon after loading was measured as a function of K , the initial stress intensity, by Bassani *et al.*⁶ as shown in Figure 7. These data show that δ_0 is proportional to K^2 in accordance with the Dugdale theory.

Microscopic examinations of the fractured surface by Lee and Epstein¹², Chan and Williams⁴ and Lu and Brown¹³ showed that the surface consists of broken fibrils and that the coarseness of the structure increases with the applied stress. Figure 5b shows that the thickness of the craze increases from its tip to its base. The fibrils are more extended at the base. Figure 8 shows how the structure of the fibrils changes from the tip to the base. At the tip the fibrils are very coarse and slightly extended. From the tip to the base the coarse fibrils become more extended and more fibrillated to form microfibrils. The microscopic data indicate that the porosity of the craze increases with its thickness.

THEORY

The theory is based on the phenomenological and microscopic observations of the fracture process. Figure 9a shows the model for the theory. There, σ_B is the stress along the boundary of the craze as given in equation (7). The most important stress is the local stress on the fibrils at the base of the craze where fracture initiates, called σ_f . Figure 9b shows the local stress situation at the base of the craze where for equilibrium:

$$\sigma_B A_0 = \sigma_f A \quad (8)$$

where A_0 is a unit area on the boundary of the craze and A is the cross-sectional area of the microfibrils that are associated with the boundary area A_0 ; A is related to the porosity of the craze. If it is assumed that the craze

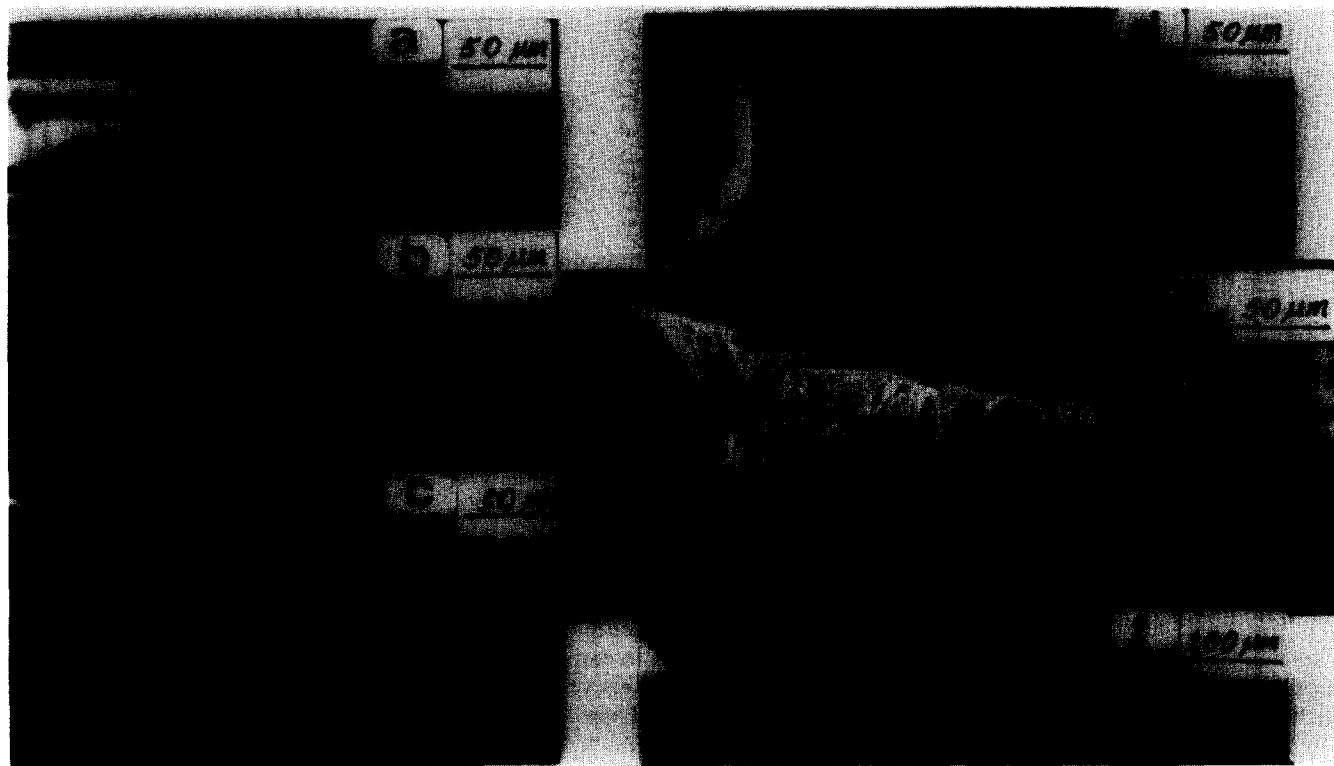


Figure 4 Development of a craze with time and fracture initiation; letters correspond to the letters in Figure 3

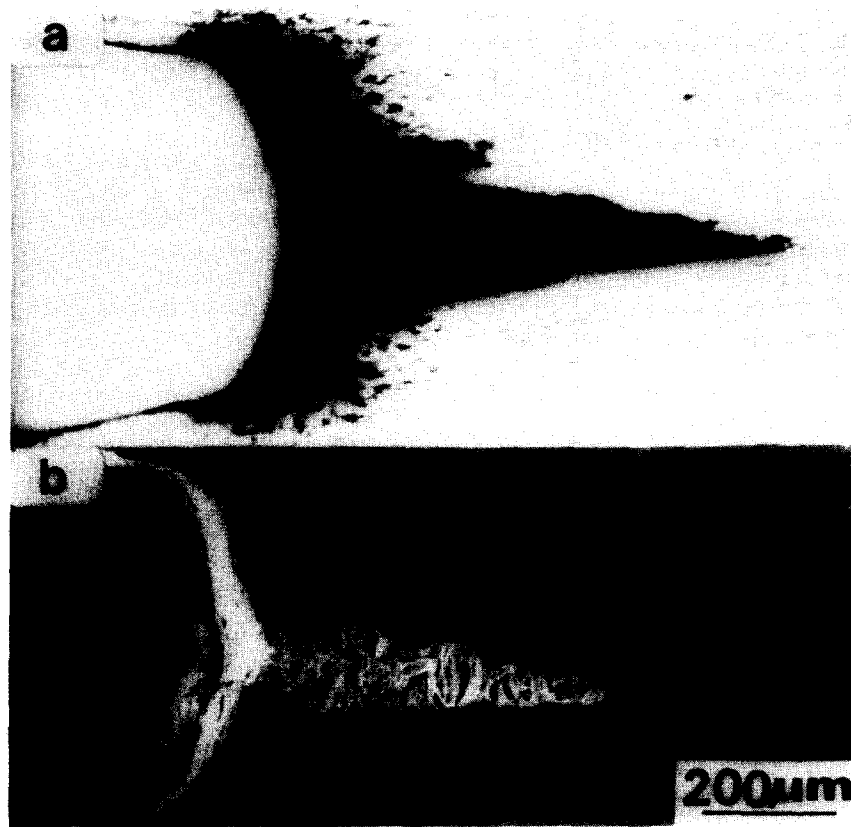


Figure 5 (a) Optical transmission micrograph of a craze. Dark area shows regions of non-elastic deformation. (b) SEM of craze in Figure 5a

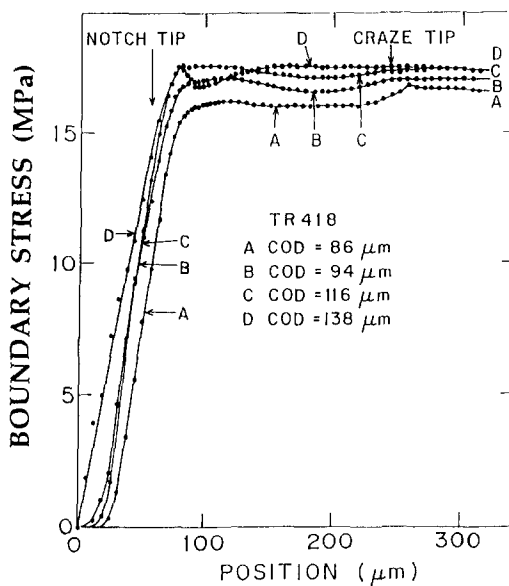


Figure 6 Stress distribution along the boundary of a craze for various notch opening displacements

originates from a primordial volume $A_0 d_0$ then:

$$A \delta_0 = A_0 d_0 \quad (9)$$

where δ_0 is the initial CTOD when the load is fully applied. Thus, the average stress on the fibril at the base of the craze is:

$$\sigma_f = \frac{\sigma_y \delta_0}{d_0} \quad (10)$$

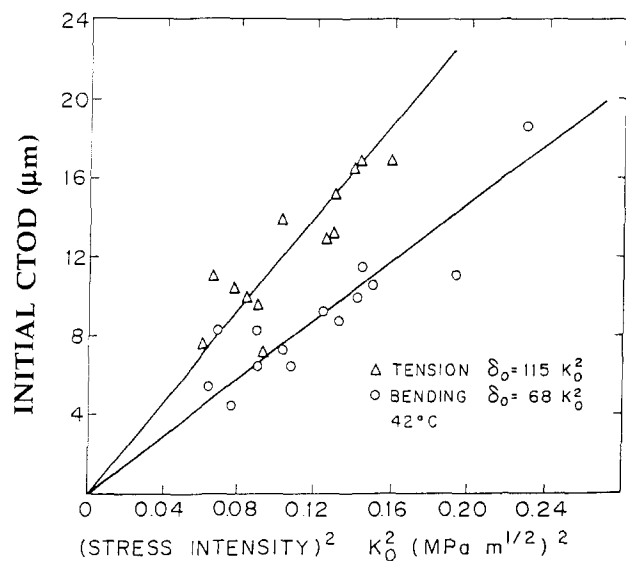


Figure 7 Initial CTOD versus K^2 for notched bend and notched tensile specimens under plane-strain conditions

σ_f can be greater than σ_y because the fibrils are strengthened by being oriented. The rate of disentanglement as exhibited by the stretching of the fibrils is $\dot{\delta}$. Since $\dot{\delta}$ is a very slow process, it is assumed that $\dot{\delta}$ is a linear function of the local stress σ_f . It is assumed that this very slow viscous process involves Newtonian flow. Thus:

$$\dot{\epsilon} = \frac{\dot{\delta}}{\delta_0} = \frac{\sigma_f}{\eta} \quad (11)$$



Figure 8 Structure of fibrils in the craze shown in Figure 5b. Porosity decreases in going from the base (a) to the tip (d)

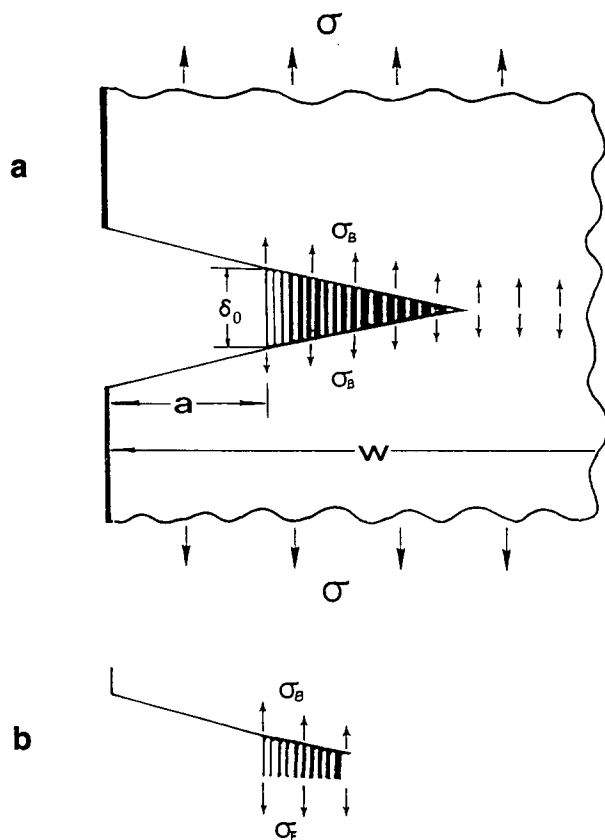


Figure 9 Model of the craze; σ_B = stress on boundary, σ_F = stress on fibrils, σ = applied stress

where $\dot{\epsilon}$ is the strain rate and η is the intrinsic viscosity of the fibrils.

Combining equations (7), (10) and (11):

$$\dot{\delta} = \frac{\sigma_y \delta_0^2}{\eta d_0} \quad (12)$$

According to the Dugdale theory and for plane-strain conditions:

$$\delta_0 = \frac{K^2}{E \sigma_c} (1 - \gamma^2) \quad (13)$$

where γ is Poisson's ratio, E is Young's modulus and σ_c is the stress to produce the craze:

$$K = Y \sigma a^{1/2} \quad (14)$$

where Y is the usual geometric term, being a function of a/w .

Combining equations (12), (13) and (14):

$$\dot{\delta} = \frac{\sigma_y Y^4 (1 - \gamma^2)^2}{\eta d_0 E^2 \sigma_c^2} \sigma^4 a^2 \quad (15)$$

When the theoretical equation (15) is compared with the general phenomenological equation (6) the physical quantities that determine C can be displayed:

$$C = \frac{\sigma_y Y^4 e^{2/RT}}{\eta d_0 E^2 \sigma_c^2} (1 - \gamma^2)^2 \quad (16)$$

The experimental values of n and m in equation (6) are sometimes less than 4 and 2, respectively, and vary with

the material; n and m tend to be higher in homopolymers than in copolymers. The theory does not explain the small variations in n and m , for several reasons. Probably, d_0 , the primordial element from which the craze originates, is not constant for all polyethylenes. Possibly, d_0 increases with K depending on the polymer. The Dugdale equation (13) should vary with the degree of non-linearity of the stress-strain curve.

The value of the intrinsic viscosity η can be determined from equation (12) in terms of experimentally observed quantities:

$$\eta = \frac{\sigma_y \delta_0^2}{d_0 \dot{\delta}} \quad (17)$$

For example, a homopolymer was tested at 42°C: $\delta_0 = 15 \mu\text{m}$, $\sigma_y = 20 \text{ MPa}$ and $\dot{\delta} = 2.1 \times 10^{-3} \mu\text{m s}^{-1}$. $(1 - d_0/\delta_0)$ is equal to the porosity of the craze, which is about 0.5 based on microscopic observations; thus, $d_0 = 7.5 \mu\text{m}$. From equation (17), $\eta = 3 \times 10^{11} \text{ Pa s}$.

It is interesting to compare this value of η with the melt viscosity of the amorphous region. Data presented by Carley¹⁴ indicate that at 42°C the melt viscosity of linear polyethylene is $10^5 - 10^6 \text{ Pa s}$, which is many orders of magnitude less than the observed value of $3 \times 10^{11} \text{ Pa s}$ calculated above. These results have the following physical significance with respect to the fundamental mechanism that determines the resistance to SCG. A fundamental theory concerning SCG in terms of the molecular and morphological structure has been given by Huang and Brown¹⁵. The model involves the lamella crystals with tie molecules joining the crystals. The model assumes that the resistance to slow crack growth is determined by the number of tie molecules and by the strength of the crystals that anchor them. It is also assumed that the amorphous region offers no resistance to the motion of the tie molecules as they disengage from the crystal. The current results shown that the viscosity of the amorphous region is on the order of 10^5 less than the intrinsic viscosity of the fibrils. Thus, the view that the amorphous region offers no resistance during the disentangling process that occurs during SCG in PE appears to be correct.

SUMMARY

The time to initiate fracture by slow crack growth is determined by the rate of extension of the fibrils at the

base of a craze, $\dot{\delta}$. The following theoretical equation was obtained:

$$\dot{\delta} = \frac{\sigma_y(1-\gamma^2)^2}{\eta d_0 E^2 \sigma_c^2} K^4$$

where η is the intrinsic viscosity of the fibrils, d_0 is the primordial craze thickness, σ_y is the yield point, E is Young's modulus, σ_c is the stress to produce the craze and γ is Poisson's ratio. This theoretical equation, for the first time, exhibits the fundamental physical quantities that determine the experimental observation that:

$$\dot{\delta} = CK^n$$

where $n=4$. Also, the theoretical equation enables the value of η , the intrinsic viscosity of the fibrils, to be calculated. The value of η is shown to be many orders of magnitude greater than the viscosity of the amorphous region, so that it can be concluded that the amorphous region offers no resistance to the disentanglement process that governs the rate of slow crack growth.

ACKNOWLEDGEMENTS

The research was supported by the Gas Research Institute. The Central Facilities of the Materials Research Laboratory as supported by the National Science Foundation under Grant No. DMR91-20668 were most helpful.

REFERENCES

- 1 Williams, J. G. and Marshall, G. P. *Proc. R. Soc. (A)* 1975, **342**, 55
- 2 Williams, J. G. 'Fracture Mechanics of Polymers', Wiley, New York, 1984, Ch. 7
- 3 Kinlock, A. J. *J. Mater. Sci.* 1980, **14**, 305
- 4 Chan, M. K. and Williams, J. G. *Polymer* 1983, **24**, 234
- 5 Brown, N., Lu, X., Huang, Y. and Qian, R. *Makromol. Chem., Macromol. Symp.* 1991, **41**, 55
- 6 Bassani, J. L., Brown, N. and Lu, X. *Int. J. Fract.* 1988, **38**, 43
- 7 Brown, N., Donofrio, J. L. and Lu, X. *Polymer* 1987, **28**, 1326
- 8 Lu, X. and Brown, N. *J. Mater. Sci.* 1990, **25**, 29
- 9 Lu, X. and Brown, N. *J. Mater. Sci.* 1991, **26**, 612
- 10 Wang, X., Brown, N. and Fager, L. *Polymer* 1989, **30**, 453
- 11 Wang, X. and Brown, N. *Polymer* 1989, **30**, 1457
- 12 Lee, C. S. and Epstein, M. M. *Polym. Eng. Sci.* 1982, **22**, 549
- 13 Lu, X., Qian, R. and Brown, N. *J. Mater. Sci.* 1991, **26**, 917
- 14 Carley, J. F. 'Introduction to Science and Technology: An SPE Textbook' (Eds. H. S. Kaufman and J. J. Falcetta), Wiley, New York, 1977, Table 2, p. 436
- 15 Huang, Y. and Brown, N. *J. Polym. Sci., Polym. Phys. Edn.* 1991, **29**, 129