A statistical approach to slow crack propagation in craze-prone polymers

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The Paris law describing slow crack propagation behaviour in several materials is deduced for craze-prone polymers from schematic considerations matching the craze fibril breakdown statistics, first introduced by Yang and co-workers, with the Dugdale–Barenblatt model of the plastic zone at the crack tip. The exponent in the Paris law is shown to be simply equal to $2\rho_w$, where ρ_w is the Weibull modulus of the fibril breakdown statistics. A promising, if not definitive, agreement between the two parameters is found from literature data for several craze-prone polymers.

(Keywords: slow crack propagation; fatigue; Paris law; crazing; fibril breakdown statistics; Dugdale model)

Introduction

It is now generally agreed that the phenomenon of slow crack propagation during fatigue tests in notched specimens is reasonably well described for several polymers by the Paris law[1–3]:

$$\dot{a} = A\Delta K^n \tag{1}$$

where $\dot{a}$ is the crack tip velocity, ΔK the difference between the maximum and the minimum values, K_{max} and K_{min}, of the stress intensity factor at the crack tip, and the two parameters A and n are phenomenological constants that have to be extracted from experimental data.

For several homopolymers it has been shown that:

1. the value of n is, in quite a large range of experimental conditions[3–5], independent of the test frequency ν;
2. the value of n is approximately independent of the ratio R, defined as[6]:

$$R = \frac{K_{min}}{K_{max}} \tag{2}$$

3. the value of n is barely sensitive to the molecular weight M of the tested polymer, at least when M is above a critical value[7–9].

These observations suggest that n could be considered as an important, intrinsic parameter characterizing the slow crack propagation in a given material. However, as far as we know, no successful attempt has been made to derive the value of n from existing and well corroborated models on the mechanical and molecular characteristics of plastic deformation, at least of pure crazing, in homopolymers.

Discussion

It is now well established that fracture in many glassy polymers can be traced to the formation and subsequent breakdown of fibrils inside the crazes[10–14]. In a notched specimen the crack tip velocity can be reasonably assumed to be proportional to the fibril breakdown probability p_{bd} at the crack–craze interface:

$$\dot{a} \propto p_{bd} \tag{3}$$

Yang *et al.*[11], by means of an approach involving Weibull statistics, first introduced for the craze fibrils breakdown probability the following expression:

$$p_{bd}(\varepsilon_p) = 1 - \exp\left[-\frac{V_0}{V_b}\left(\frac{\varepsilon_p}{\varepsilon_w}\right)^{\rho_w}\right] \tag{4}$$

where ε_p is the so-called *plastic strain* defined as the difference between the actual strain and the strain for craze nucleation, V_0 is the initial volume considered in the statistics, V_b is a volume in which one fibril breakdown will be encountered at a reference stress of σ_b and the two coefficients ε_w and ρ_w are the Weibull scale parameter and Weibull modulus, respectively. The Weibull scale parameter and the Weibull modulus, which have to be derived from experimental data, have been demonstrated to be independent of the size of the samples considered[11].

Also because of the details inherent to their experiments, performed on thin polystyrene (PS) films bonded to annealed copper grids, Yang and co-workers did not try to relate the parameters involved in their approach with more macroscopic ones – nor did researchers who continued studies of the breakdown statistics following this first, original method[14,15]. Nonetheless, referring to *Figure 1** and assuming that the craze widens by surface drawing having a constant fibril volume fraction[10] ϕ, it is easy to demonstrate that the craze opening displacement at the crack tip, h, is approximately related to the plastic strain in the following way:

$$\varepsilon_p \sim \frac{h(1-\phi)}{L_0} \tag{5}$$

Equation (4) can be reformulated in terms of the craze opening displacement at the crack tip.

The next step would be to relate the craze opening displacement, which is a quasi-macroscopic parameter rarely measured during slow crack experiments, to a more macroscopic and more easily detectable one, namely the stress intensity factor. The easiest way of doing that is

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*The figure shows a single edge notched specimen, however the considerations presented in this paper are independent of the specimen geometry

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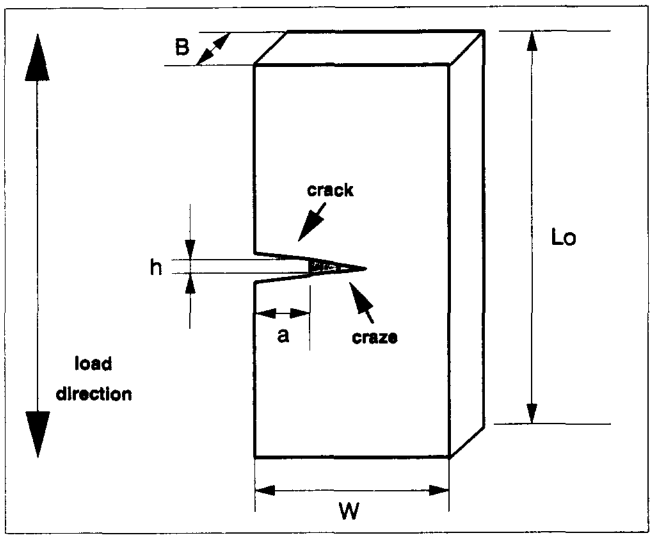

Figure 1 Sketch of a standard notched specimen used during fatigue experiments. The grey region at the crack tip represents a craze. L_0, W and B are the specimen's dimensions, a is the crack depth and h the craze opening displacement

to utilize the Dugdale–Barenblatt model which is now well documented to be a good description of the shape and size of the crazed zone at the crack tip[16–22]. Considering its purely geometric constraints it is possible to express h as:

$$h = \frac{K_{\mathrm{max}}^2}{\sigma_c E^*} \tag{6}$$

where K_{max} is the stress intensity factor at the crack tip, σ_c is the compressive stress that counterbalances the crazing stress in the plastic zone and E^* is the reduced Young's modulus. By combining equations (5) and (6) with equation (4), we obtain:

$$\dot{a} \propto 1 - \exp\left\{-\frac{V_0}{V_b}\left[\frac{K_{\mathrm{max}}^2(1-\phi)}{L_0 \sigma_c E^* \varepsilon_w}\right]^{\rho_w}\right\} \tag{7}$$

We stress here that the use made of the Dugdale model is free from the major criticism it encountered in the application to craze-prone polymers. The model, in fact, does not provide a criterion for crack advance and the critical crack opening displacement criterion is often introduced in the description, disregarding the fact that a true critical craze opening displacement can hardly exist for crazes which widen by surface drawing[23]. In our approach no critical displacement is assumed, the slow crack propagation being controlled by fibril breakdown statistics, and only the geometrical features of the model, which are largely accepted, are applied.

Considering that for slow crack propagation in bulk specimens of glassy polymers it is in general true that:

$$\frac{K_{\mathrm{max}}^2}{L_0 \sigma_c E^*} \ll 1 \tag{8}$$

we can arrest the Taylor series for equation (7) at the first order:

$$\dot{a} \propto \frac{V_0}{V_b}\left(\frac{1-\phi}{L_0 \sigma_c E^* \varepsilon_w}\right)^{\rho_w} K_{\mathrm{max}}^{2\rho_w} \tag{9}$$

Equation (9) can provide information on the fatigue behaviour of the craze-prone polymers if a sort of *separation principle* is introduced, stating that the fatigue behaviour of the craze-prone polymers is affected by two distinct sets of features which do not overlap: the first being described by equation (9) and relating to the intrinsic, probabilistic aspects of craze fibril breakdown, and the second concerning the peculiar fatigue features, i.e. features depending on the variables which control the test execution and which are not accounted for by equation (9), for example, the frequency ν and the ratio R. In mathematical terms, this is equivalent to:

$$\begin{aligned}\dot{a} &= f(\nu, R, \ldots)\left(\frac{1-\phi}{\sigma_c E^* \varepsilon_w}\right)^{\rho_w} K_{\mathrm{max}}^{2\rho_w} \\ &= f'(\nu, R, \ldots)\left(\frac{1-\phi}{\sigma_c E^* \varepsilon_w}\right)^{\rho_w} \Delta K^{2\rho_w}\end{aligned} \tag{10}$$

where f and f' are functions only of the test parameters and not of the material properties. The fact that the terms ΔK and K_{max} keep the same dependence on the Weibull modulus is due to their relationship:

$$K_{\mathrm{max}} = \frac{\Delta K}{1-R} \tag{11}$$

It is evident that the validity of equation (10) must be carefully restricted to experimental situations in which phenomena, like adiabatic heating or discontinuous crack propagation, which clearly demonstrate violations of any separation principle, are absent or controlled. In order to assess all our propositions, equation (10) should be accurately tested. At any rate, if the above assumption is correct, equation (10), which is derived in a way which is completely independent of the Paris law, expresses the same form of dependence of the crack tip velocity on the variation of the stress intensity factor, ΔK. Then, what is important to check at this point is that:

$$n \sim 2\rho_w \tag{12}$$

Encouraging evidence for relation (12) is that, as for n, ρ_w has been demonstrated to be approximately independent of the molecular weight for a number of craze-prone polymers, namely for PS[11], poly(methyl methacrylate) (PMMA), poly(α-methylstyrene) and a full set of compatible blends of PS and poly(2,6-dimethyl-1,4-phenylene oxide)[14]. Also from the numerical point of view relation (12) is quite well satisfied by a considerable set of experimental data. Berger[14] reports a value for $\rho_w = \sim 3.5$ for PMMA at a temperature of 75°C below the glass transition temperature (approximately room temperature), while Williams[6] gives an estimate of $n = \sim 6$ for the same material in a series of fatigue experiments with different values of R^*. Yang *et al.*[11] found a value for $\rho_w = \sim 3$ in PS, which corresponds to the value of $n = 5$ found by Michel *et al.*[8] in the already mentioned series of fatigue tests on PS with different molecular weight distribution. Also for values of ρ_w for poly(styrene-*r*-acrylonitrile) not reported in the literature, the value of $n(=6–7)$ from Bucknall and Faitrouni's[9] data is in quite reasonable agreement with our assumption.

We are aware, however, that relation (12) is far from confirmed by the data discussed, which come from very diverse sets of material. Conclusive proof would require

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*The correspondence between n and $2\rho_w$ for PMMA is not completely unambiguous: Kim *et al.*[7] obtained values of n well above those expected from our considerations

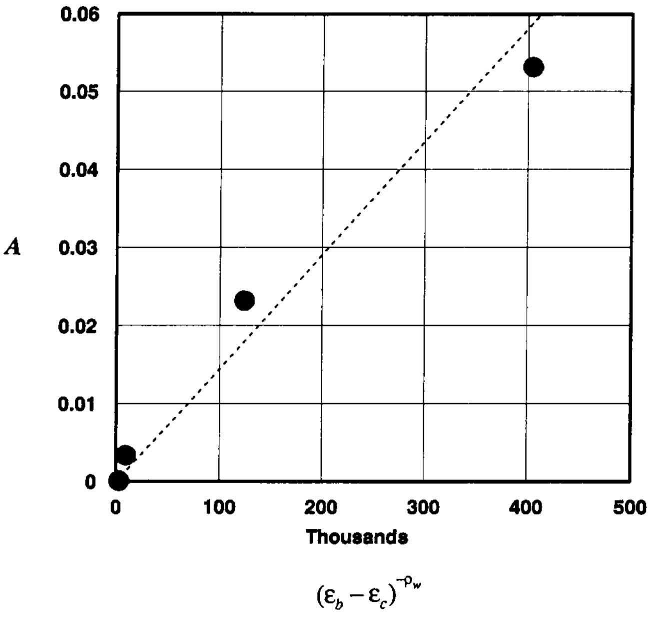

Figure 2 Plot of A *versus* $(\varepsilon_b - \varepsilon_c)^{-\rho_w}$ with data from references 7 and 14 (●). The broken line is a guide for the eye. The units of A depend on the value of n in equation (1)

appropriate, *ad hoc* experimentation which should be very carefully designed and performed to be unambiguous because the exponent in the Paris law is similar for all craze-prone polymers ($n = 5$–7). A further, conceptual problem is caused by the fact that some polymers, like polycarbonate, whose plastic deformation mechanism at room temperature is certainly not crazing, have an exponent in the Paris law which is similar to that of craze-prone materials. Also if this evidence is not in contrast with relation (12), it suggests that, underlying the slow crack propagation behaviour, a more basic aspect of deformation, common to crazing and shear yielding, could be involved.

From equation (10) some other consequences can be extracted, that are either in agreement with already reported experimental data or can be easily tested. Let us consider, for example, the dependence of the crack tip velocity on the molecular weight M: the molecular weight effects are mainly concentrated in the coefficient A of the Paris law, being less important or negligible compared with n. Considering that M only slightly affects ϕ (ref. 10), σ_c (ref. 24) or E^*, equation (10) suggests that, for a set of experiments performed in the same conditions:

$$A \propto (\varepsilon_w)^{-\rho_w} \qquad (13)$$

Yang *et al.*[11] and Berger[14] measured the fibril stability parameter defined as the difference between the average strain for fibril breakdown and the strain for craze nucleation, $\varepsilon_b - \varepsilon_c$, which was, in their experiments, equivalent to the Weibull scale parameter and they always found an incontestable molecular weight dependence: $\varepsilon_b - \varepsilon_c$ increasing with increasing M. *Figure 2* is a plot of A *versus* $(\varepsilon_b - \varepsilon_c)^{-\rho_w}$ for a series of PMMAs with different molecular weights: the values of A are derived from data shown in Figure 7 of reference 7, while the values of $(\varepsilon_b - \varepsilon_c)^{-\rho_w}$ are extrapolated for the corresponding M from the theoretical curve shown in Figure 2 of reference 14. The plot shows an approximate agreement with relation (13), but it has only a qualitative value, taking into account that at least two other different models have been proposed[25,26] in order to justify the dependence of the fatigue behaviour on M and both exhibit a similar agreement with the experimental data.

Another consequence of equation (10) concerns the effects of molecular orientation on slow crack propagation behaviour: it is well known that E^* and σ_c change with molecular anisotropy[27–31]. Maestrini and Kramer[15] showed that the degree of molecular orientation plays an important role also on the craze structure, and demonstrated that it influences ϕ and ε_w, while ρ_w is unchanged. In principle, then, slow crack propagation in a series of materials prepared with different degrees of orientation can be predicted using equation (10).

A final remark involves the physical meaning of ε_w and of ρ_w. Following Yang *et al.*[11]:

$$\Lambda = \left(\frac{\varepsilon_p}{\varepsilon_w}\right)^{\rho_w} \qquad (14)$$

where Λ is the *breakdown seed density*, i.e. it represents the concentration of impurities and local inhomogeneities that give rise to the fibril breakdown phenomenon. The state of cleanliness of the sample considered strongly modifies the values of the Weibull scale parameter and modulus with $\varepsilon_w = {\sim}0.05$–${\sim}0.15$ and $\rho_w = 3$–>6 for ultra-clean, high molecular weight PS samples[11]. According to our approach, fatigue behaviour should show the same, strong dependence on the concentration of impurities and dust particles in the tested specimens. Hence a very simple but effective method for obtaining better fatigue or creep performance would be to produce cleaner materials. In terms of cleanliness it could also be possible to explain the features of fatigue behaviour of the rubber toughened polymers with respect to their matrix if it is considered that the rubber particles can modify the breakdown seed density, as, for example, the phenomenon of trapping small particles inside the craze texture and the subsequent local fibril breakdown[32] suggest, the variation of the parameters in the Paris law from the matrix to the rubber toughened material could be estimated by our model.

Conclusions

Using a sort of separation principle, distinguishing the probabilistic aspects of fibril breakdown from genuine fatigue features, a way of deriving the Paris law for slow crack propagation in notched specimens of craze-prone polymers was proposed which matches the statistics ideas of Yang and co-workers for the phenomenon of craze fibril breakdown and the well established Dugdale–Barenblatt model. The qualitative, promising agreement between the literature data and our results was discussed. A consequence of this approach is the possibility of explaining the effects of molecular weight, degree of molecular anisotropy and presence of a dispersed phase on the fatigue behaviour of polymers.

We believe that, if our idea proves to be correct, it could be useful for stating clear connections between macroscopic mechanical performance and molecular and microscopic features of plastic deformation. This is a critical and urgent task from both practical and fundamental points of view.

References

1 Paris, P. C. in 'Proc. 10th Sagamore Conference', Syracuse University Press, Syracuse, 1964
2 Hertzberg, R. W. and Manson, J. A. in 'Fatigue of Engineering Plastics', Academic Press, London, 1980
3 Hertzberg, R. W. and Manson, J. A. in 'Encyclopedia of Polymer Science and Engineering', Vol. 10, John Wiley & Sons, New York, 1985, pp. 243–318
4 Hertzberg, R. W., Manson, J. A. and Skibo, M. D. *Polym. Eng. Sci.* 1975, **15**, 252
5 Hertzberg, R. W., Skibo, M. D. and Manson, J. A. ASTM STP 700, American Society for Testing and Materials, Philadelphia, 1980
6 Williams, J. G. in 'Fracture Mechanics of Polymers', Ellis Horwood, Chichester, 1984
7 Kim, S. L., Skibo, M. D., Manson, J. A. and Hertzberg, R. W. *Polym. Eng. Sci.* 1977, **17**, 194
8 Michel, J. C., Manson, J. A. and Hertzberg, R. W. *Am. Chem. Soc. Polym. Prepr.* 1985, **26**, 141
9 Bucknall, C. B. and Faitrouni, T. in 'Proc. 8th International Conference on Deformation, Yield and Fracture of Polymers', The Plastics and Rubber Institute, London, 1991
10 Kramer, E. J. *Adv. Polym. Sci.* 1983, **52/53**, 1
11 Yang, A. C. M., Kramer, E. J., Kuo, C. C. and Phoenix, S. L. *Macromolecules* 1986, **19**, 2010
12 Yang, A. C. M., Kramer, E. J., Kuo, C. C. and Phoenix, S. L. *Macromolecules* 1986, **19**, 2020
13 Kramer, E. J. and Berger, L. L. *Adv. Polym. Sci.* 1990, **91/92**, 1
14 Berger, L. L. *Macromolecules* 1990, **23**, 2926
15 Maestrini, C. and Kramer, E. J. *Polymer* 1991, **32**, 609
16 Dugdale, D. S. *J. Mech. Phys. Solids* 1960, **8**, 100
17 Barenblatt, G. I. *Adv. Appl. Mech.* 1962, **7**, 55
18 Brown, H. R. and Ward, I. M. *Polymer* 1973, **14**, 469
19 Weidmann, G. W. and Doell, W. *Colloid Polym. Sci.* 1976, **254**, 205
20 Mills, N. J. and Walker, N. *Polymer* 1976, **17**, 439
21 Morgan, G. P. and Ward, I. M. *Polymer* 1977, **18**, 1987
22 Fraser, R. A. and Ward, I. M. *Polymer* 1978, **19**, 220
23 Kramer, E. J. and Hart, E. W. *Polymer* 1984, **25**, 1667
24 Fellers, J. F. and Kee, B. F. *J. Appl. Polym. Sci.* 1974, **18**, 2355
25 Michel, J. C., Manson, J. A. and Hertzberg, R. W. *Polymer* 1984, **25**, 1657
26 Woll, R. P. *Am. Chem. Soc. Polym. Prepr.* 1982, **23(2)**, 62
27 Lindsay, S. M., Hartley, A. J. and Sheperd, I. W. *Polymer* 1976, **17**, 501
28 Hennig, J. *Kunststoffe* 1967, **57**, 385
29 Robertson, R. and Buenker, R. J. *J. Polym. Sci. A* 1964, **2**, 4889
30 Wright, H., Faraday, C. S. N., White, E. F. T. and Treloar, L. R. G. *J. Phys. D* 1971, **4**, 2002
31 Beardmore, P. and Rabinowitz, S. *J. Mater. Sci.* 1975, **10**, 1763
32 Maestrini, C., Castellani, L., Merlotti, M. and Vighi, M. *Polym. Commun.* 1992, **33**, 1556