

Slow Crack Growth in Polyethylene: A Novel Predictive Model Based on the Creep of Craze Fibrils

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SYNOPSIS

An extensive series of homopolymers and copolymers has been investigated to test earlier indications of a possible link between resistance to slow crack growth and creep of macroscopic oriented samples. It was found that in the majority of cases a good correlation exists between a single creep parameter and slow crack growth. The existence of such a correlation supports the model presented, in which crack growth is primarily controlled by the creep of fibrils spanning the craze zone. The limit of improvement achievable by increasing molecular weight and the greater effectiveness of short-chain branching to improve fibril creep have been highlighted. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Slow crack growth is an important failure mechanism in polyethylene, relating to phenomena such as environmental stress cracking (ESC). Over the past decade this phenomenon has been studied extensively by Brown and co-workers,¹⁻⁹ and by Barry and Delatycki.^{10,11} It has been shown that in notched samples under static tensile stress and in three-point bending a damage zone is formed at the notch tip, which consists of highly voided material with a fibrillar structure. Several processes contribute to and determine crack initiation and growth: yield, yield propagation, and drawing are associated with the conversion of isotropic material into highly oriented fibrils; the fibrils in turn undergo creep deformation and eventually rupture.

While the phenomenology of the failure process has been satisfactorily elucidated over the years, a quantitative knowledge of the mechanisms involved is still lacking.

Preliminary results reported by Cawood et al.¹² indicated the possibility of a new approach to the problem. These authors argued that the time to initiate a crack may well be controlled by the creep rupture of the fibrils which develop in the crazed

zone. This remarkable statement would imply a completely new perspective on the study of the failure phenomenon, i.e., the prediction of fracture performance by means of a nonfracture parameter. The experimental evidence, however, was limited to three materials, corroboration calling for a more extensive study.

Reported here is an appraisal of the link between crack growth and creep for a comprehensive series of materials, both homopolymers and copolymers.

CRAZING AND CRACK INITIATION IN POLYETHYLENE

In many important respects crazing in polyethylene (PE) differs in kind from that of amorphous glassy polymers. Appreciation of these differences is key to the rationale of the present work. Such an appreciation also places into context the limited extent to which it is feasible to transfer information from one class of polymers to the other.

Upon loading a sharply notched specimen of PE, a wedge-shaped damage zone, or craze, develops at the notch tip. Unlike in the case of glassy polymers, its length is time-dependent; moreover the rate of growth depends upon the polymer molecular weight and presence of branching.^{4,11} The time scale may be very long, i.e., of the order of hundreds of hours, and dimensions of hundreds of microns may be

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reached. The typical features of a craze are present in these damage zones: voided material at the tip of the wedge and, further out, well-developed fibrils (Fig. 1).

Craze growth is conveniently followed by monitoring crack opening displacement (COD) as a function of time.⁴ Two regimes are clearly detectable. In the initial slow regime, several processes contribute to the growth of the craze, i.e., yield and drawing of isotropic material into fibrils and creep of the fibrils.

The point at which a sharp upsweep is observed in the COD vs. time curves marks the beginning of rapid crack growth. At this point rupture of the first fibril(s) occurs and the failure process intervenes and becomes self-accelerating. Thus it is the slow regime, i.e., the formation of fibrils and their subsequent creep prior to fracture, which controls the time scale in a slow crack growth experiment.

ORIGINALITY OF THE PRESENT APPROACH AND MODEL

Suggestions and evidence of a link between craze growth rate and "ease of molecular disentangling" have been reported in the literature.⁴ In the current program we set out to establish whether in fact a single fundamental creep parameter could be defined to predict craze growth and hence stress crack performance.

The originality of approach adopted lies in the assumption that the structure and behavior of craze fibrils are identical to those of macroscopic-oriented tensile specimens. Such an assumption can be readily justified. First, crazing in PE occurs well above the glass transition temperature and tensile drawing is carried out in comparable conditions. Second, the lateral dimensions of the craze fibrils, of the order of microns, are much larger than those of the structural units (crystalline and amorphous regions) which are of the order of nanometers in size. Finally, there is ample experimental evidence

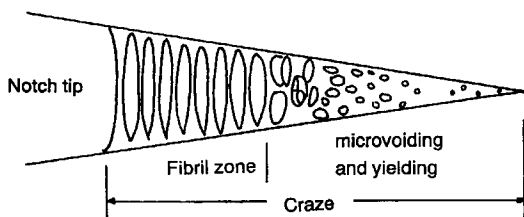


Figure 1 Schematic diagram of the craze structure in polyethylene.

of a unique structure/property correlation for oriented samples over a very wide range of dimensions, from very thin fibers to thick rods.¹³ An important corollary is that the well-established body of knowledge on how molecular factors control yield and creep of both isotropic and oriented PE on a macroscopic basis¹⁴ becomes translatable to the case of craze fibrils and hence stress cracking.

Implicit in the above considerations is the special nature of the PE case, in comparison with amorphous glassy polymers. Crazing in glassy polymers is confined to temperatures below T_g . Orientation of macroscopic samples, on the other hand, requires temperatures above T_g , i.e., in conditions most unlikely to produce the same structural changes. Therefore, the good understanding of the molecular factors controlling crazing in glassy polymers¹⁵ cannot easily be applied to slow crack growth in PE.

One of the critical aspects of our approach is the definition of the draw ratio of the fibrils and of the stress to which they are subjected. It is assumed that the fibrils are drawn to the "natural draw ratio" of the material (see experimental section) and that they experience the same load as a tensile specimen when drawn to the same natural draw ratio. The associated stresses do not differ significantly from those estimated by Wang and Brown³ at the interface between fibril and isotropic material.

EXPERIMENTAL

The characteristics of the materials used are given in Table I. They consist of a series of homopolymers (HP series) of systematically increasing molecular weight and a range of ethylene/butene-1 and ethylene/hexene-1 copolymers (CP series).

Sheets were pressed at 200°C with a preheat time of 5 min at zero load and 5 min at full pressure (17 MPa). The standard cooling rate of $\sim 125^\circ\text{C}/\text{min}$ was achieved by water cooling of the press. Density measurements were obtained on samples taken from pressed sheet using density columns.

Dumbell samples, with gauge dimensions 20×5 mm, were cut from 200- μm -thick sheets and drawn at 10 mm/min (strain rate 0.25 min^{-1}) and 23°C. The draw ratio was defined by the separation of dots marked at 2-mm intervals prior to drawing. Drawing was halted once the full gauge length had undergone plastic deformation. The specimens at this stage had reached what we define as their natural draw ratio (λ_n).

Creep specimens of length ~ 90 mm for creep testing were cut from the drawn portion of the dum-

Table I Density, Molecular Weight, and Short-Chain Branch Concentration (SCB)

Sample	Density (kg m ⁻³)	\bar{M}_w ($\times 1000$)	\bar{M}_n ($\times 1000$)	SCB/1000C ^a
HP1	960	134	18	—
HP2	955	134	24	—
HP3	954	211	30	—
HP4	954	385	48	—
HP5	932	1,557	269	—
CP1	960	226	11	0.5 (E)
CP2	955	150	17	0.5 (B)
CP3	955	210	9	1.1 (E)
CP4	952	393	19	1.3 (E)
CP5	950	241	10	1.7 (B)
CP6	944	204	22	1.6 (B)
CP7	943	272	22	2.0 (B)
CP8	942	232	21	1.8 (B)
CP9	937	190	11	4.9 (B)

^a (E), ethyl branches; (B), butyl branches.

bell. Cross-sectional areas were measured and the actual draw ratio checked immediately prior to the creep tests. In previous work,¹² the stress applied was taken as the material draw ratio multiplied by the yield stress. This approach was subsequently revised. It was considered that a more appropriate choice was the final draw load, i.e., the load to which the sample had actually been subjected when it reached its natural draw ratio. The tests were carried out at $23 \pm 1^\circ\text{C}$. Values of yield stress, natural draw ratio, and applied creep stress are shown in Table II.

Stress crack performance was assessed by the bottle stress crack (BSC) test.¹⁶ In this test blow-molded bottles are held under constant internal pressure in a thermostatically controlled water bath (80°C) and an electrical resistance method is used for crack detection. A key feature of the test is that the crack grows under constant stress conditions.

RESULTS AND DISCUSSION

Applicability of the Creep Rate Approach

At the outset of this series of experiments, it was considered appropriate to refine the presentation of the creep data to better reflect the differences between materials. In the earlier work,¹² creep data were plotted as creep rate vs. strain (Sherby-Dorn plots). Different materials, however, have different natural draw ratios and the creep response is best

represented with plots of creep rate vs. draw ratio rather than strain.

Typical plots are shown in Figure 2. Data of this kind were obtained for all the materials in Table I, but for clarity, only a selection is shown here. The curves exhibit a horizontal spread that reflects the difference in natural draw ratio between materials. In the majority of cases, the differentiation between short-term and long-term response is clearly visible as a division of the curves into two regimes of high and low creep rate, respectively. The pattern is consistent with the general observations on the creep of oriented samples,¹⁴ the long-term element being significant in the present context. The absolute value of the gradient of the long-term component in the curves in Figure 2 will be referred to as the creep rate deceleration factor (CRDF).

Figure 3 shows a plot of BSC performance vs. CRDF for most of the materials in Table I (in a few cases BSC data were not available). The correlation is astonishingly good. The results for a wide range of materials of very different molecular weight distribution, as well as type and concentration of branching, fall within a very narrow band. Thus the indications of the earlier work are confirmed.¹² That said, it should be emphasized that the current results are not sufficient to prove conclusively that in general creep is the only mechanism controlling slow crack growth. The other contributors, yielding, yield propagation, and fibril fracture must all play a role. However, it is clear that sufficient quantitative data

Table II Yield Stress (σ_y), Natural Draw Ratio (λ_n), and Actual Applied Stress (σ_a) in the Creep Test

Sample	σ_y (MPa)	λ_n	σ_a (MPa)
HP1	26	9	193
HP2	24	7	148
HP3	24	5	148
HP4	20	5	127
HP5	18	3	79
CP1	26	9	157
CP2	24	9	164
CP3	24	8	138
CP4	22	6	112
CP5	22	6	102
CP6	21	6	126 ^a
CP7	22	6	132 ^a
CP8	21	6	126 ^a
CP9	16	5	80 ^a

^a Sample loaded at $\sigma_y \times \lambda_n$.

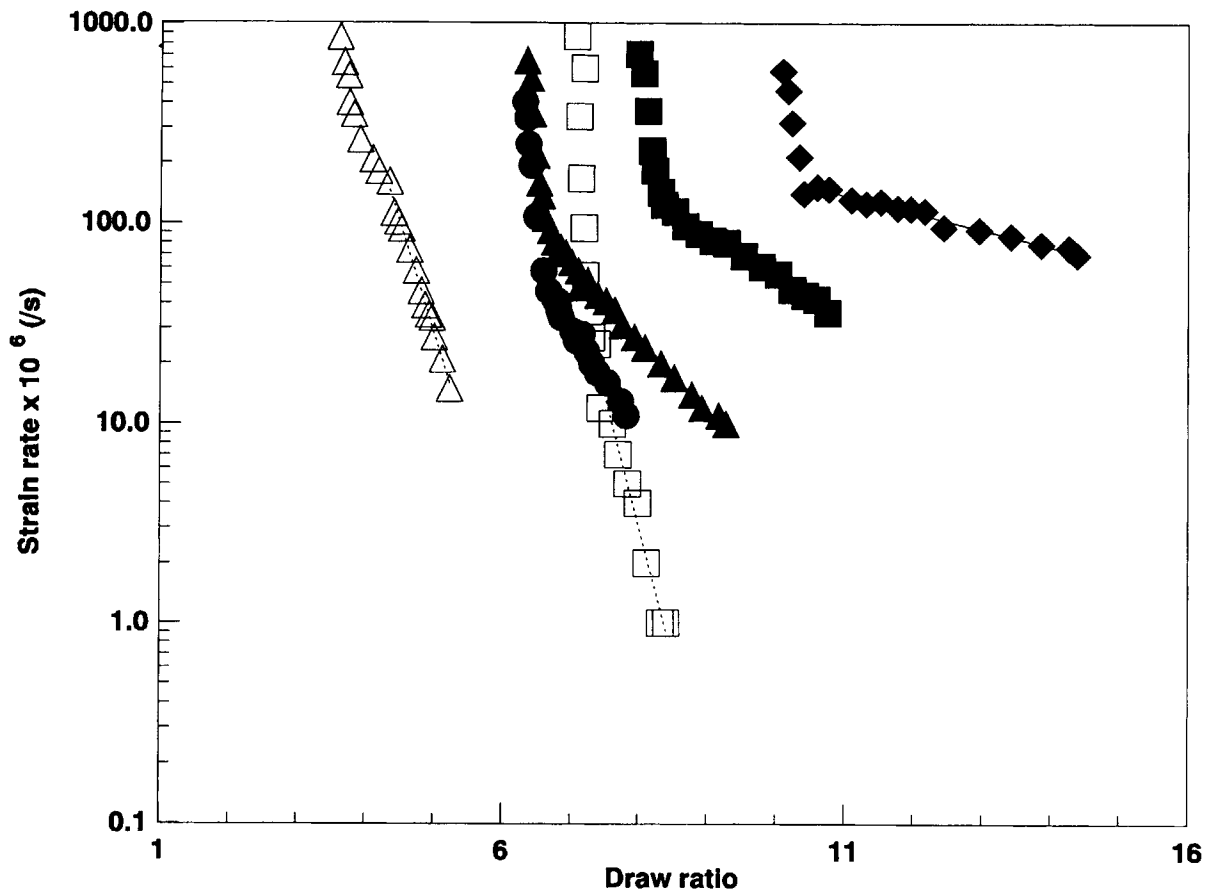


Figure 2 Strain rate vs. draw ratio plots for selected samples: (◆) HP1, (■) HP2, (▲) HP3, (●) HP4, (△) HP5, (□) CP4.

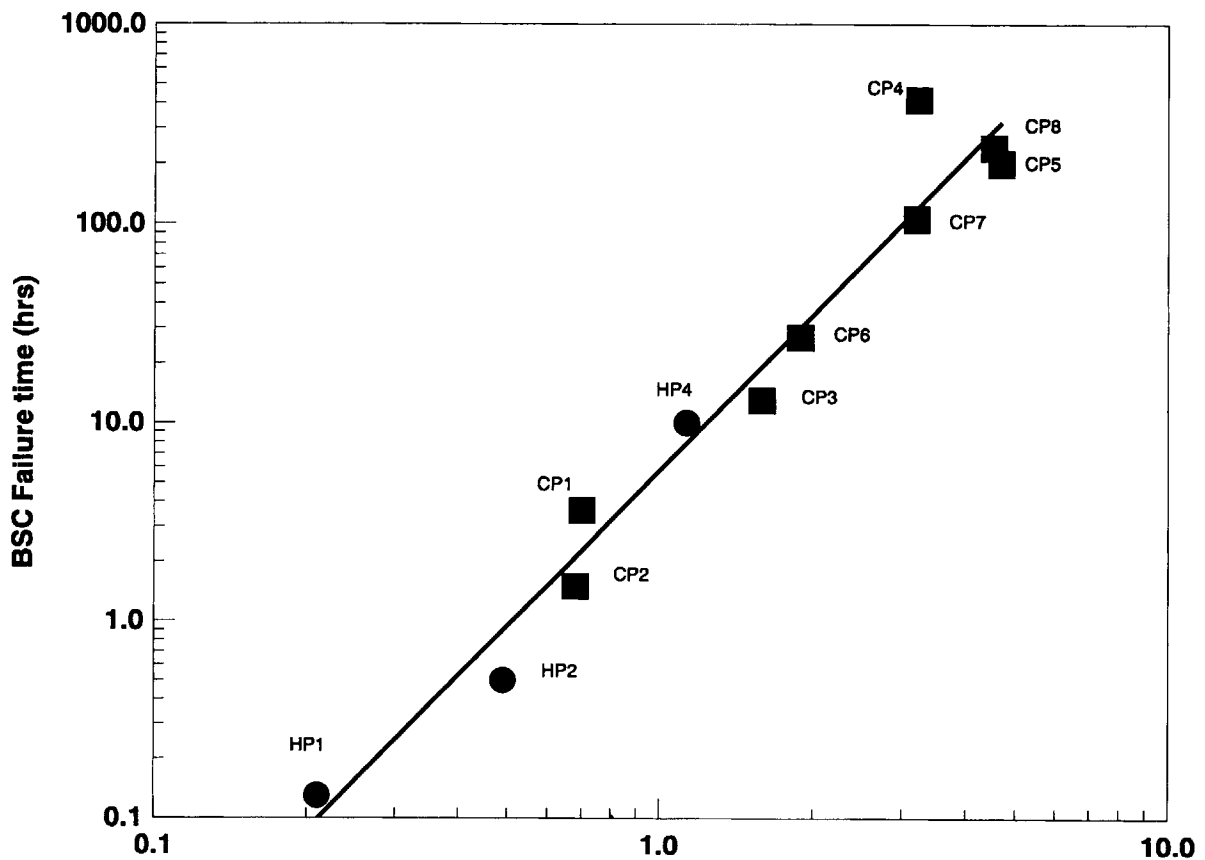


Figure 3 Correlation between the bottle stress crack (BSC) failure time at 80°C and the creep rate deceleration factor (CRDF): (●) homopolymers, (■) copolymers.

exist, or are readily obtainable, for slow crack growth to be simulated by a mathematical model combining quantitatively the contribution of each process. Work to develop such a model is in hand and will be the subject of separate reports.

It is instructive to plot CRDF as a function of weight-average molecular weight, \bar{M}_w and results for a range of homopolymers and copolymers are shown in Figure 4.

CRDF increases by an order of magnitude by increasing \bar{M}_w . It is apparent, however, that other considerations such as processability become an overriding factor, because melt viscosity increases rapidly with \bar{M}_w . There is therefore limited scope to enhance stress crack performance merely by increasing \bar{M}_w . High levels of crack resistance, corresponding to CRDF values of 4 and higher, may be achieved by the introduction of SCB as is evident from Figure 4, clearly demonstrating the advantage of copolymerization.

The effects of both molecular weight and copolymerization are consistent with the extensive literature on creep of oriented samples.¹³ Two processes are operative: the pulling of molecules through

the crystalline lamellae and molecular disentanglement in the amorphous regions. The extent of entanglement is governed by the length of the molecules and hence by molecular weight. Copolymerization, on the other hand, introduces short-chain branches that greatly inhibit the movement of molecules through crystalline regions, thereby providing effective anchor points for the molecular network.⁹

CONCLUSIONS

It has been shown for a wide range of homopolymers and copolymers that the creep rate of drawn specimens correlates with their behavior in ESC tests. Such a correlation suggests that fibril creep makes an important contribution to governing crack initiation and growth.

The improvement in ESC performance of homopolymers with increased molecular weight relates directly to improved fibril creep resistance. A practical limit to the improvement achievable by increasing molecular weight has been highlighted. A more effective means of enhancing stress crack per-

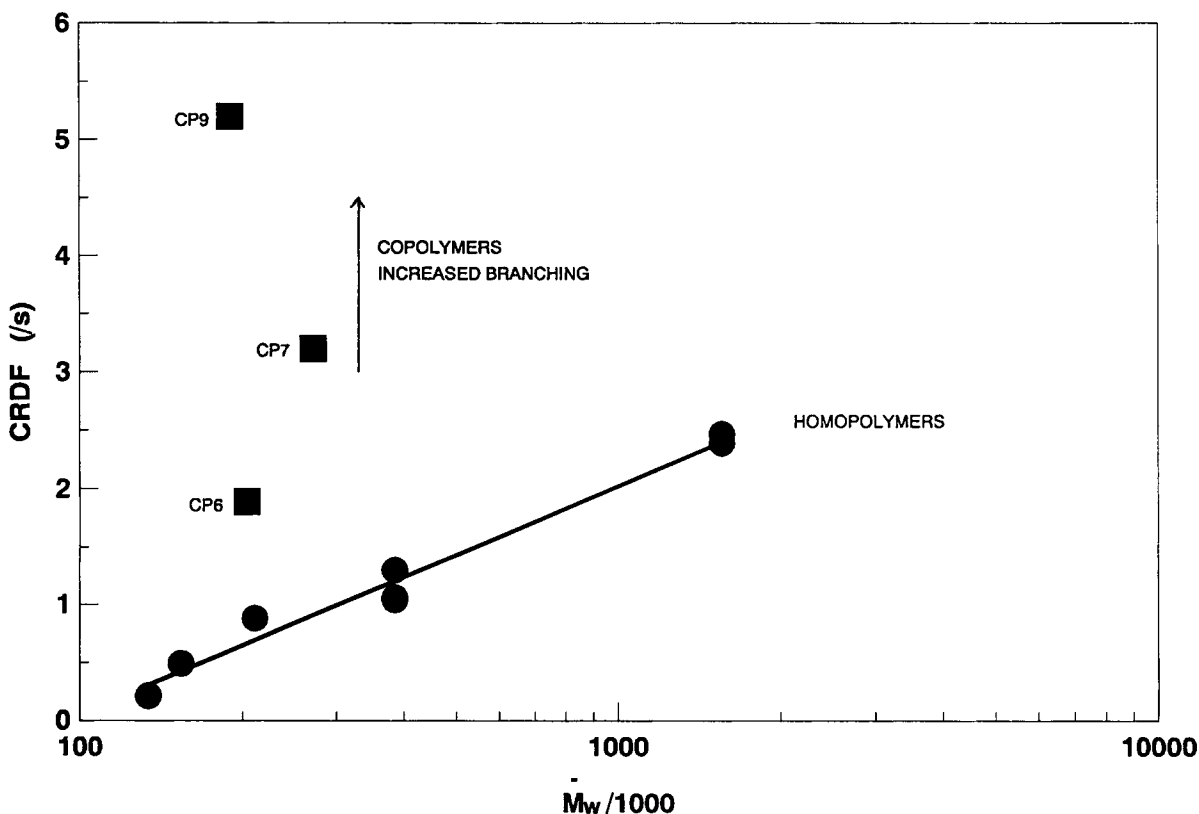


Figure 4 Dependence of the creep rate deceleration factor (CRDF) on weight-average molecular weight (\bar{M}_w) and branching: (●) homopolymers, (■) copolymers.

formance is the introduction of short-chain branches, which reduces fibril creep to a much greater extent than changes in homopolymer molecular weight or density.

The results presented lay a foundation for a new experimental approach to the understanding of slow crack growth in PE, and the associated phenomenon of environmental stress cracking. The partitioning of the complex fracture phenomenon into a number of fundamental physical processes, yielding, yield propagation, creep of fibrils, and their ultimate fracture should provide a deeper understanding of the failure process and enable the influence of molecular structure to be more readily accessed.

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