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The damage zone ahead of the arrested crack in polyethylene resins

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Formation and growth of the crack tip damage zone during slow stepwise crack propagation in polyethylene resins was studied experimentally. The study focused on the differences between the damage zone in high density polyethylene (HDPE), that represented traditional single-craze morphology, and the damage zone in more fracture resistant ethylene copolymers (MDPE) under plain strain conditions. It was shown that improved fracture resistance correlated with development of an epsilon-shaped damage zone that consisted of the central craze and an accompanying pair of hinge shear zones of comparable length. The shear zones emanated from the crack tip immediately above and below the central craze where highly stretched material formed a membrane that separated the crack tip from the cavitated material in the craze. The remarkable observation that the shear zones underwent crazing despite the presumably unfavorable stress-strain conditions was attributed to a dilatational stress component resulting from partial re-distribution of the load as the main craze opened. Microscopic analysis revealed differences in the crazed material between the single-craze (HDPE) and the epsilon-shaped (MDPE) morphology. An array of cellular cavities separated by walls of biaxially oriented material in the MDPE craze contrasted with the traditional structure of uniaxially stretched fibrils in the HDPE craze. The stepwise development and fracture of the damage zone was monitored in time, and the differences in kinetics of these processes between the two types of morphologies were characterized.

1. Introduction

Recently, a fatigue technique was developed for the specific purpose of evaluating the resistance of polyethylene pipe resins to slow crack propagation [1–6]. Previously, this property was evaluated in the laboratory by testing creep failure at elevated temperature, 80°C (PENT test: ASTM F 1473-94). However, the proximity of the test temperature to the polyethylene pre-melting range caused uncertainty concerning the relationship to fracture at ambient temperature. In addition, creep testing of modern medium density polyethylene (MDPE) pipe resins took unacceptably long times even at such a high temperature [7]. An extensive study of the alternative fatigue approach demonstrated that correlation in kinetics and mechanism of crack propagation between creep and fatigue in the tensile-tensile mode could be achieved by systematically increasing the fatigue minimum-to-maximum load ratio (R-ratio) to approach creep ($R = 1$) [4–6]. Tests at temperatures up to 80°C confirmed the generality of this correlation [6]. This made it possible to evaluate the creep slow crack growth rate at any temperature, at or above ambient, in a reasonable time of days or weeks using fatigue. Thus, the resistance to slow creep fracture can be reliably quantified in fatigue.

The correlation is thought to arise from similarity in the stepwise mechanism of slow crack propagation in fatigue and creep fracture [1–6, 8]. Upon loading, the crack is arrested by the craze damage zone where the stress concentration at the crack tip is relieved by toughening of the drawn polymer material. The damage zone has a finite lifetime because of gradual deterioration of the load bearing elements, i.e. the craze fibrils, in the stress field [3]. The deterioration eventually leads to craze fracture, which occurs over a much shorter time than the arrest time. Upon complete fracture of the craze damage zone, the crack "jumps" the length of the broken craze to the region of intact material. The newly developed damage zone arrests the crack again, and the sequence of events repeats itself. It is important that the size and morphology of the damage zone are not affected by whether the loading is in fatigue or creep; the zone size is mainly determined by the mean stress [4–6]. Thus, resistance to slow, stepwise crack growth can be defined by the lifetime of the damage zone. The lifetime decreases in the oscillating stress field in inverse proportionality to the strain rate of deformation in the craze [5, 6]. Thus, the factor of strain rate accelerates crack propagation in fatigue while conserving all the mechanistic features of creep fracture.

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With the correlation between the fatigue and creep fracture firmly established, the fatigue test can be used to study the mechanism of slow stepwise crack propagation and to identify the material properties responsible for resistance to slow fracture with the knowledge that the results will be directly applicable to creep. Previous work [2, 3] revealed that polyethylenes with comparatively small differences in density and tensile stress-strain behavior exhibited dramatic disparities in resistance to slow fracture. Testing various linear ethylene copolymers showed the effect of molecular weight, short chain branch content, and short chain branch distribution, and elucidated the role of the molecular mechanism of chain disentanglement in deterioration of the material in the damage zone [3]. All the ethylene copolymers exhibited essentially the same damage zone morphology, the differences arose from the stability of the load bearing craze fibrils. However, another important feature differentiated ethylene copolymers from the linear, high density ethylene homopolymer (HDPE). This was a distinction in damage zone morphology between the more crack growth resistant MDPE and the less crack growth resistant HDPE [4, 6].

The traditional wedge-shaped craze morphology was typical of the HDPE damage zone. In contrast, the main craze in tougher MDPEs was always accompanied by an additional pair of crazes that extended from the crack tip at an angle above and below the main craze in the manner of hinge shear bands [6]. The "shear crazes", comparable in length to the central craze, formed the so-called epsilon-shaped damage zone. A similar complex morphology, with the craze coexisting with a pair of hinge shear bands, was observed during stepwise fracture of polycarbonate; coexistence of the two basic modes of plastic deformation was referred to as "schizophrenic" [9]. However, the cavitational transformation of the shear bands to crazes seen in tough polyethylenes has no precedents in other polymers. The shear crazes appear to be a general feature in the response of ethylene copolymers at a tensile stress concentration. Evidence of "shear crazes" in the damage zone appeared in studies of elevated temperature [8] and environmental [10] creep fracture of polyethylene pipe resins.

It can be thought that "shear crazes" play an important role in improving the fracture properties of the material by redistributing the crack tip stress concentration over a larger volume. The distinctly different morphologies of the damage zones in HDPE and MDPE resins calls for a detailed characterization. This is the subject of the present article, where the damage zones were investigated in terms of the dynamics of their formation and growth. A fatigue testing protocol that ensured correlation to slow creep fracture was employed for the study. In addition to HDPE and regular MDPE pipe resins, the damage zone in a modern polyethylene with superior fracture performance was explored.

2. Experimental

The materials used in the study were the same as described previously [4]. Specimens made from the material referred to as pipe resin were cut directly from an MDPE pipe extruded from category II PE-2406 DuPont Aldyl A resin in the manner defined previously [1–3]. Other polyethylenes were provided by BP Chemicals as pellets. The pellets were compression molded into plaques by the fast-cooling procedure developed to simulate properties of an extruded pipe [2, 3]. The materials were a linear ethylene homopolymer (HP1) ($M_w = 360{,}000$; a crystallinity of 72%), an ethylene-hexene copolymer (CP3) with 4.5 butyl branches per 1000 carbon atoms ($M_w = 180{,}000$; a crystallinity of 62%), and an ethylene-hexene copolymer (CP4) with 2.6 butyl branches per 1000 carbon atoms ($M_w = 300{,}000$; a crystallinity of 69%). The CP4 material was prepared by a cascade polymerization process that preferentially places branches on the higher molecular weight chains. This resin has superior fracture performance. The resistance to slow fracture of all the resins was quantified previously [3].

Test specimens were machined from compression-molded plaques. The specimens were of the compact-tension geometry with standard dimensions defined previously [1, 2]. The fatigue testing technique with simultaneous monitoring of the fracture parameters was described in previous publications [1–6]. Most of the experiments were performed at room temperature on specimens loaded under the maximum stress intensity factor in the fatigue cycle $K_{I,max} = 1.30$ MPa(m)$^{1/2}$ and the minimum-to-maximum load ratio $R = 0.1$. Selected specimens were loaded to a specific number of cycles, removed from the fatigue unit, and sectioned to obtain a side view of the damage zone ahead of the crack tip. Sections were placed on a special sample holder that held the crack open to the same crack tip opening experienced by the specimen during the fatigue test.

Cross-sections of the damage zone and fracture surfaces were viewed directly in the optical microscope. Features were best resolved in bright field using normal incidence illumination. Some of the specimens were coated with 9 nm gold and examined in a JEOL JSM 840A scanning electron microscope. The accelerator voltage was set at 5 kV and the probe current at 60 pA in order to minimize radiation damage to the specimens.

3. Results and discussion

Typical plots of change in crosshead displacement, defined as the difference in maximum and minimum crosshead positions in the fatigue loading cycle, are shown in Fig. 1 for the specimens loaded under $K_{max} = 1.3$ MPa(m)$^{1/2}$ and $R = 0.1$. As described previously [1–6], the stepwise crack growth mechanism, resulting from sequential formation and breakdown of a craze damage zone, was observed in each material. The plateau regions in Fig. 1 corresponded to periods of crack arrest, where a damage zone formed ahead of the crack tip. The sharp increases in crosshead displacement corresponded to step jumps, where the craze damage zone fractured and a new one formed.

In order to characterize the stepwise crack growth mechanism, the formation and fracture of the damage zone ahead of the crack tip was examined. To view the damage zone, specimens were loaded to a prescribed number of cycles, removed from the fatigue unit, and

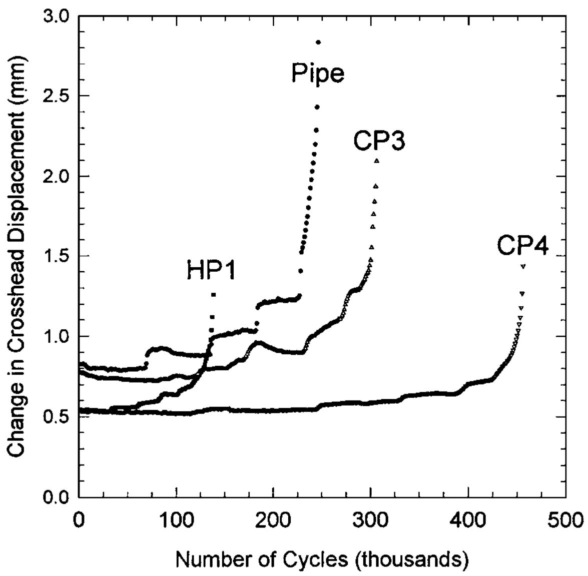

Figure 1 Change in the crosshead displacement during fatigue tests of various polyethylene resins. Specimens were loaded under $K_{I,max} = 1.3$ MPa m$^{1/2}$ and $R = 0.1$.

sectioned so that a side view of the zone was obtained. The growth and fracture of the first craze zone for loading under $K_{I,max} = 1.3$ MPa(m)$^{1/2}$ and $R = 0.1$, is shown in Fig. 2. Immediately after loading (10 fatigue cycles), a substantial craze zone about 0.2 mm long had formed. At 18,000 cycles, which was 25% of the damage zone lifetime, the craze length reached 90% of its final length. Subsidiary shear crazes emerged from the membrane region at an angle of about 30° with respect to the primary craze zone, and curved slightly with increasing length. In some instances the shear craze zones consisted of a pair rather than a single shear craze. Morphologically, these zones were connected to the thick membrane that developed at the crack tip and separated the crack from the main craze.

At 62,500 cycles craze breakdown began. Craze breakdown started about 0.25 mm ahead of the tough membrane at the crack tip, and fracture propagated through the craze. By 69,000 cycles the main craze had completely fractured, leaving only a remnant of the membrane still attached at the former crack tip, and

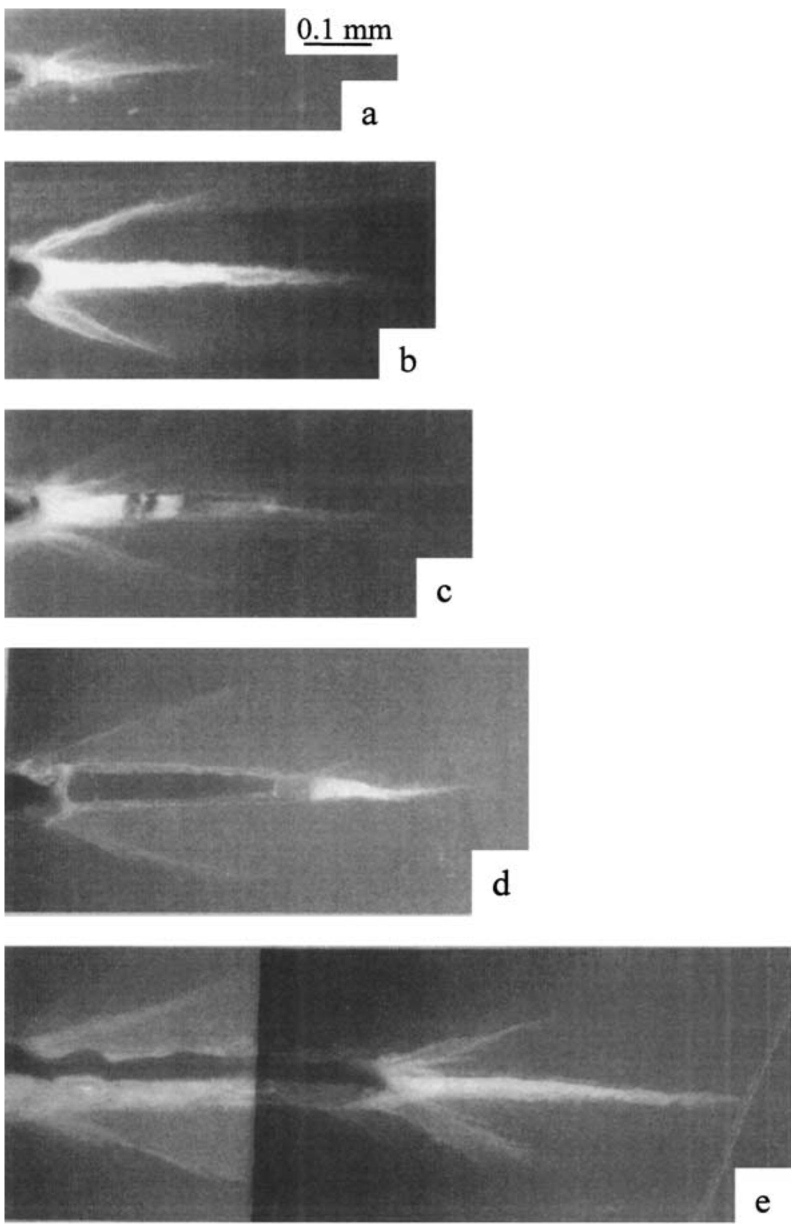

Figure 2 Optical micrographs of cross-sections of the crack tip damage zone showing periodical formation and fracture of the craze during stepwise crack propagation. Micrographs were taken after terminating the test at (a) 10 fatigue cycles, (b) 18,000 cycles, (c) 62,500 cycles, (d) 69,000 cycles and (e) 85,000 cycles. Pipe resin specimens were loaded under $K_{I,max} = 1.3$ MPa m$^{1/2}$ and $R = 0.1$.

a new zone had started to form. At this point, the front view into the crack showed voids in the membrane. Breakdown of the main craze, followed by rupture of the membrane, was consistent with previous observations of stepwise crack growth in polyethylene pipe materials [1–3, 6]. At 85,000 cycles, the second craze zone was well developed and a new set of shear crazes emerged from the crack tip.

Comparison was made with the damage zone in other polyethylenes, Fig. 3. In CP3 and CP4, the zones included the shear crazes that were observed in the MDPE pipe material. There were no significant differences in the damage zone morphology of CP3 and CP4 compared to the pipe material. In contrast, HDPE exhibited only a wedge-shaped main craze. Further comparisons were made between the damage zones of MDPE pipe

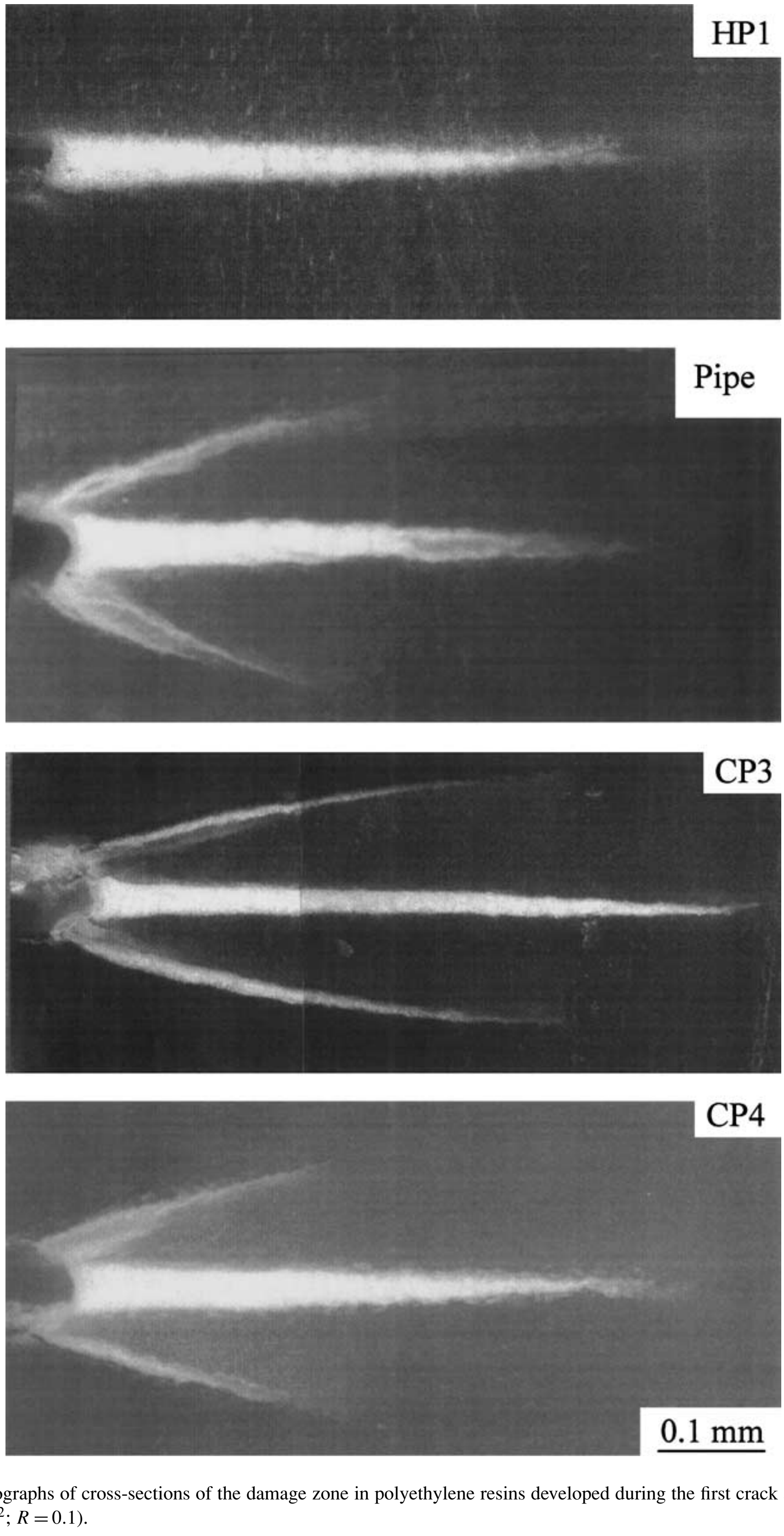

Figure 3 Optical micrographs of cross-sections of the damage zone in polyethylene resins developed during the first crack arrest in the fatigue test ($K_{I,max} = 1.3$ MPa m$^{1/2}$; $R = 0.1$).

resin and HP1, which represented the two cases with and without shear crazes, respectively.

Comparison of the damage zones of MDPE pipe material and HP1 is presented in Fig. 4, in the right and left columns, respectively. Specimens of the same geometry were tested under the same notching and loading conditions. Both materials exhibited prominent striations on the fracture surfaces, Fig. 4b. The striations were characteristic of stepwise crack propagation, and indicated the crack arrest lines. However, at higher magnification, the morphology of the damage zone was quite different. The fracture surface of the HDPE craze consisted of remnants of highly drawn fibrils whereas the surface of MDPE contained biaxially oriented sheets (Fig. 4c). The side-view of the main craze revealed a similar picture: stretched fibrils in the HDPE craze, and a cellular structure of the craze in MDPE. The drawn fibrils of HDPE were less than 1 μm thick.

To confirm the craze-like texture of material in the MDPE shear craze, a specimen was loaded so that fracture proceeded through the shear craze, rather than through the main craze, using fatigue loading parameters for this mode of fracture found previously [6]. The texture of highly drawn fibrillated material in Fig. 5 represents a typical craze surface.

The existence of "shear crazes" appears to be contradictory. Current theories consider crazes to form in zones of maximum negative hydrostatic stress component [11]; this component vanishes in pure shear. It can be proposed that co-existence of shear and craze

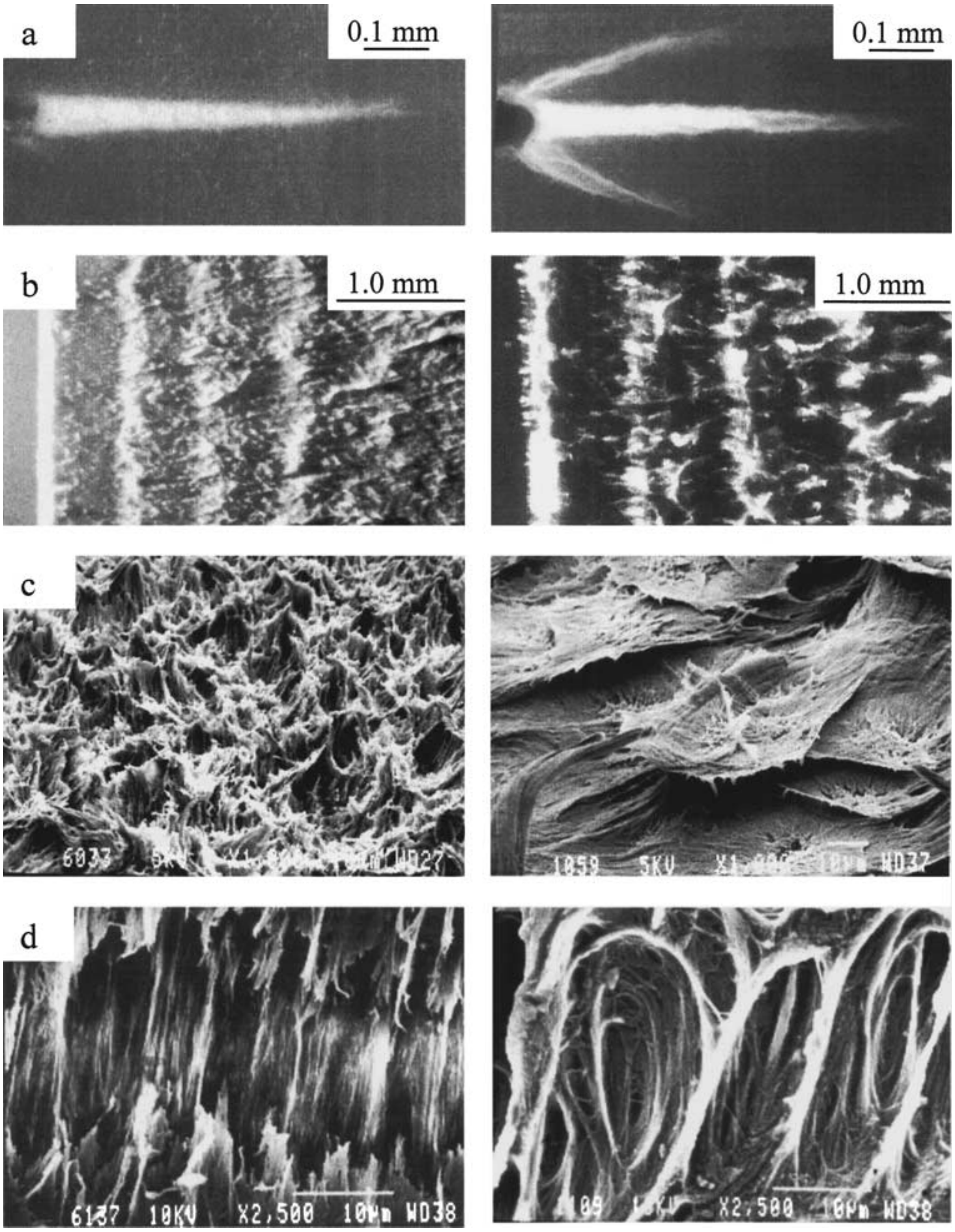

Figure 4 Comparison of the basic features of single-craze and epsilon-shaped damage zone morphologies developed in HDPE resin HP1 (left column) and MDPE pipe resin (right column): (a) optical micrographs of cross-sections of the damage zones, and (b) fracture surfaces; (c) high magnification SEM of the fracture surfaces between the periodic striations, and (d) the damage zone cross-sections. Specimens were loaded under $K_{I,max} = 1.3$ MPa m$^{1/2}$ and $R = 0.1$.

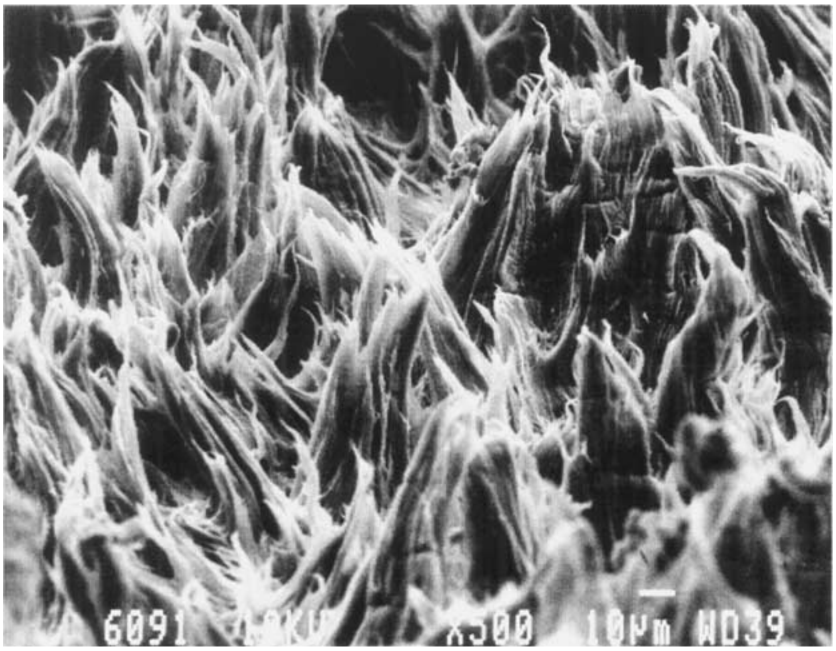

Figure 5 SEM of the fracture surface in a pipe specimen where fracture proceeded through a shear craze ($K_{\mathrm{I,max}} = 1.3$ MPa m$^{1/2}$ and $R = 0.6$).

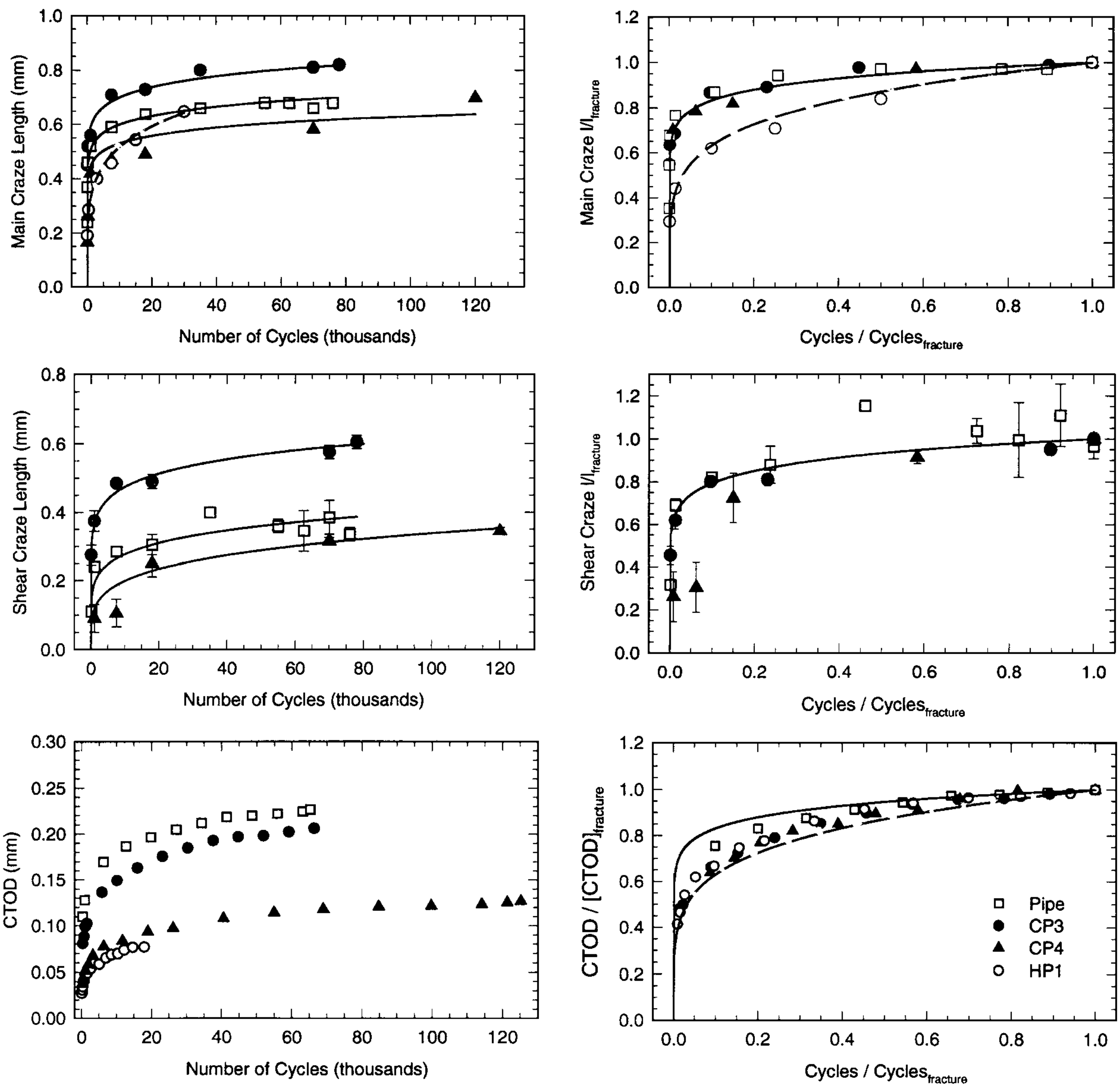

Figure 6 Kinetics of damage zone growth as characterized by increases in the main craze length, the shear craze length and the crack tip opening displacement (CTOD) during the period of the crack arrest in the fatigue test ($K_{\mathrm{I,max}} = 1.3$ MPa m$^{1/2}$ and $R = 0.1$). The right column represents scaling of these parameters for different resins with time when they are reduced to their maximum values at fracture. The lines are the fits to the power law dependence with exponents 0.08 (solid line) and 0.2 (dashed line).

modes of deformation is associated with strain hardening upon chain orientation, which is intrinsic to the mechanical constitutive behavior of polyethylene. The following scenario of the damage zone formation is suggested. Initially, upon loading, the crack is arrested by hinge shear bands. The hinge shear bands develop in the through thickness by shear plastic yielding until the magnitude of shear deformation at the crack tip (where it is maximum) increases up to the level of strain hardening. This re-concentrates the stress back to the center of the crack tip and causes tensile plastic yielding. Yielding promotes the formation of the main craze by the usual mechanism of cavitation in the extensional strain field with further strain hardening of the stretched material between cavities. Probably, the transformation of shear bands to crazes occurs upon opening of the main craze with partial re-distribution of the load. The resulting dilatational component of the stress field causes growth of cavities in the highly deformed material associated with the shear bands.

Formation of the central and shear crazes during damage zone development was examined. The length of the main craze, the length of shear crazes, and the crack tip opening displacement (CTOD) were measured in a series of tests terminated at different times before the fracture of the first damage zone. The time dependence of these parameters for the resins under investigation is presented in Fig. 6. For each material, craze length initially increased steeply with number of cycles and then gradually leveled off until breakdown of the main craze. The final craze length was between 0.65 and 0.82 mm for all materials.

The relative growth of the morphological features was compared by constructing a plot of the craze length normalized to the craze length at fracture vs. the number of fatigue cycles normalized to the number of cycles at fracture, Fig. 6. The time of fracture was defined by the appearance of voids in the membrane. The normalized parameters overlapped for all the MDPE resins that formed the epsilon-shaped damage zone. The kinetics

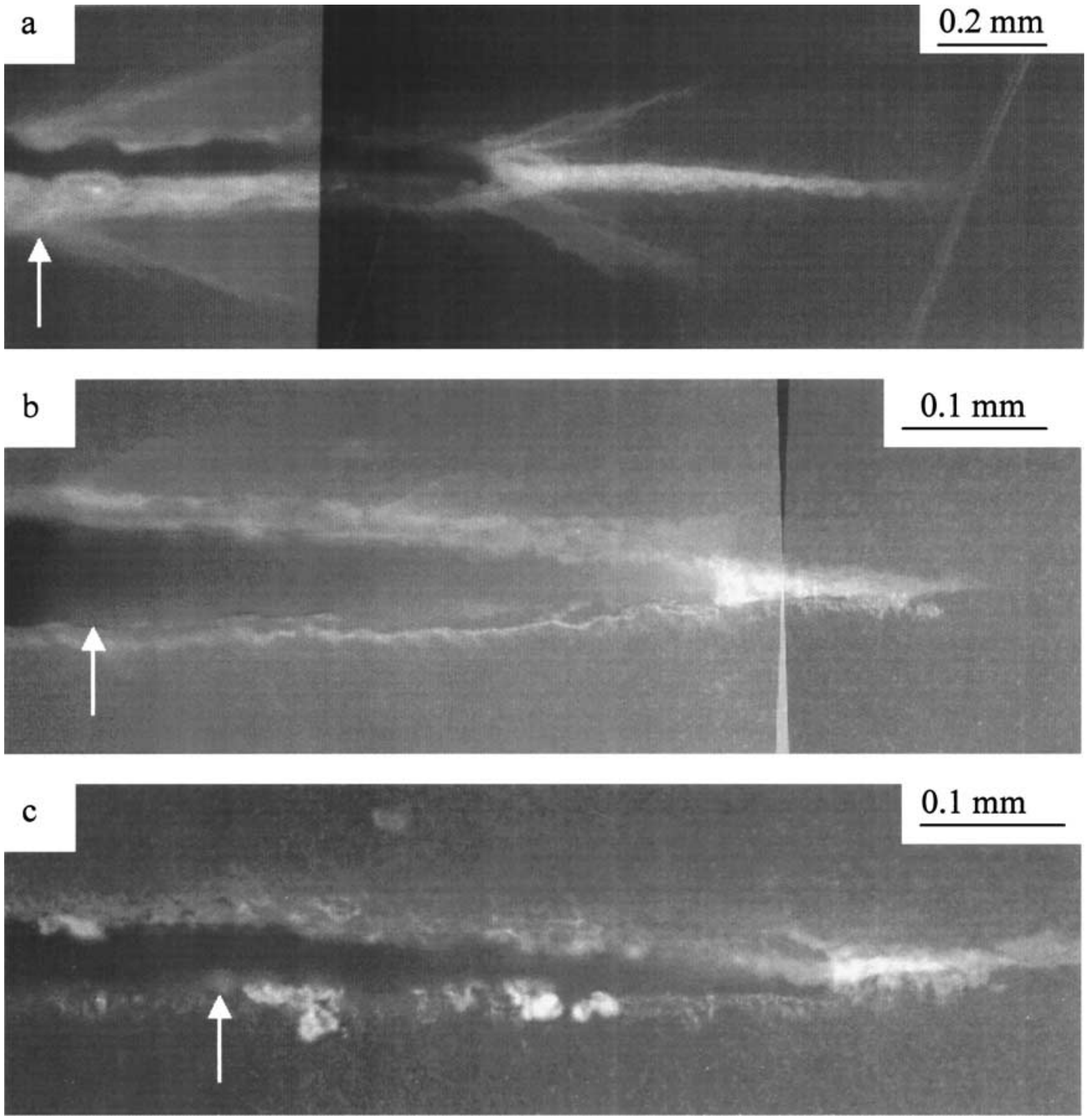

Figure 7 Disappearance of shear crazes with decreasing stress intensity factor in a pipe resin: (a) $K_{I,max} = 1.3$ MPa m$^{1/2}$, (b) $K_{I,max} = 0.78$ MPa m$^{1/2}$, (c) $K_{I,max} = 0.72$ MPa m$^{1/2}$; $R = 0.1$. An arrow indicates the position of the notch root.

for growth of the single-craze zone in HDPE was different. The craze grew more rapidly in the copolymers than in HDPE. This was demonstrated by fitting normalized craze growth to a power law relationship between length and cycles, $\ell/\ell_f = (N/N_f)^n$. The exponent n was 0.08 for the copolymers, and 0.2 for HDPE.

The growth of the shear crazes in MDPE resins is also shown in Fig. 6. For the shear crazes, two data points corresponding to the upper and lower shear crazes were measured. If instead of a single shear craze there was a pair of shear crazes, the length of the longer shear craze was measured. Like the main craze zone growth, shear craze length initially increased steeply with number of cycles and then leveled off until the main craze zone fractured. The power law dependence of the normalized shear craze length with the same exponent as main craze growth showed that the two components of the damage zone developed at the same rate.

The crack tip opening displacement (CTOD) was measured at the maximum opening at the peak of the loading cycle. The time dependence of this parameter, normalized to its value at fracture, was approximately the same for all resins, falling in between the time dependencies of the damage zone lengths for HDPE and MDPE. For the HDPE, this indicated that the angle of the main craze opening increased faster than the craze length. The opposite trend in MDPE was explained by opening of the shear crazes, which partially took the deformation and thereby reduced progressive stretching of the main craze fibrils.

It is suggested that shear crazing occurs due to the development of the dilatational component of stress near the hinge shear bands upon opening of the main craze. Because both the stress and the opening decrease with the load, the magnitude of the dilatational component should drop significantly within a comparatively narrow load range in the vicinity of the cavitation threshold value. In this case, transformation of shear bands to shear crazes should not occur. Provided this interpretation is correct, an abrupt disappearance of shear crazing upon decreasing stress intensity factor below a certain value is expected.

This expectation was confirmed. Specimens of MDPE pipe were fatigue loaded at $R = 0.1$ until the second step jump and then sectioned to reveal the damage zone structure, Fig. 7. When $K_{\mathrm{I,max}}$ was reduced from 1.3 to 0.78 MPa(m)$^{1/2}$, shear crazes were shorter and less easily discernable in the micrographs. When $K_{\mathrm{I,max}}$ was lowered further to 0.72 MPa(m)$^{1/2}$, shear crazes no longer formed. The transition occurred between $K_{\mathrm{I,max}}$ of 0.78 and 0.72 MPa(m)$^{1/2}$ for this material.

The effect of stress intensity factor on main craze length (measured as the first step jump length on the fracture surface) and on $[\mathrm{CTOD}]_{\mathrm{f}}$ is shown in Fig. 8. No discontinuity or change in functionality was seen where the shear crazes disappeared. This was an indication that the basic damage zone morphology did not change, and although no shear crazes formed at lower stress intensity factors, hinge shear bands nevertheless accompanied the main craze. Pure shear bands would not have been seen without special experimental techniques [12]. Thus, the epsilon-shaped damage zone morphology remained.

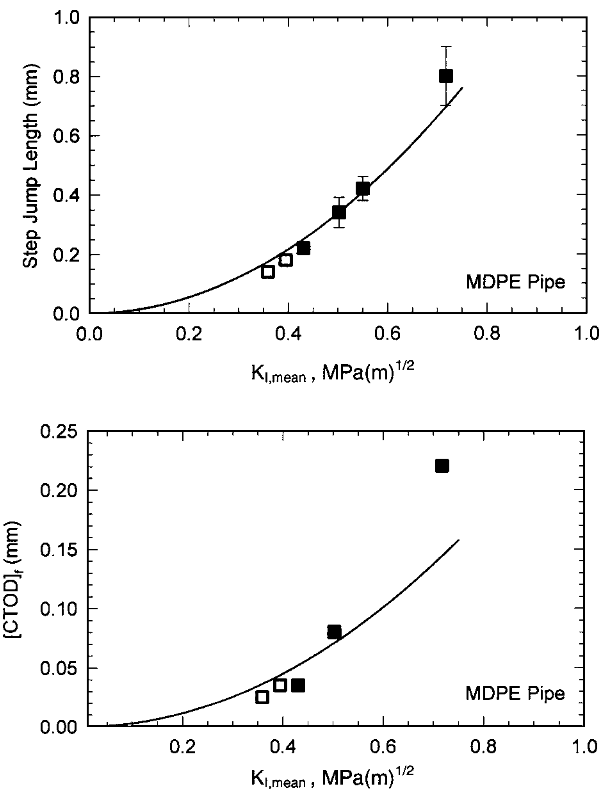

Figure 8 Dependence of the step jump length and crack tip opening displacement at fracture on the mean value of stress intensity factor in the fatigue cycle. The filled symbols indicate presence of the shear crazes in the damage zone, and the open symbols indicate the single-craze damage zone. The fit lines follow a $K^2_{\mathrm{I,mean}}$ dependence.

Whether the damage zone is epsilon-shaped (MDPE) or single-craze (HDPE) is probably determined by the constitutive material behavior, and cannot be changed by loading conditions. The particular feature of the constitutive behavior that determines the morphology has not yet been identified. It can be speculated that the strain hardening parameter controls how far hinge shear bands develop upon loading before cavitation in the central region and formation of the main craze occur. Stronger strain hardening suppresses propagation of the shear bands into the depth of the material and redistributes the load for formation of the main craze. This situation would apply to HDPE. In contrast, weaker strain hardening of MDPE would permit extensive shear yielding before the hydrostatic stress in the central area reaches the cavitation threshold. A recent computer model of the deformation near the crack tip demonstrates that the spatial pattern of plastic flow is highly sensitive to, and can change dramatically with, comparatively small variations in the parameters of the constitutive equation [13].

The most important kinetic parameter that characterizes the resistance to slow fracture, the lifetime of the damage zone, was strongly affected by the disappearance of shear crazes (Fig. 9). Typically, increasing $K_{\mathrm{I,mean}}$ decreased damage zone lifetime. However, an increase in $K_{\mathrm{I,mean}}$ from 0.39 to 0.43 MPa(m)$^{1/2}$, where shear crazes were first observed, actually increased the damage zone lifetime. As stress intensity increased further, the damage zone lifetime again decreased, but the dependence was much steeper than below the transition. This dependence, if extrapolated to the range of

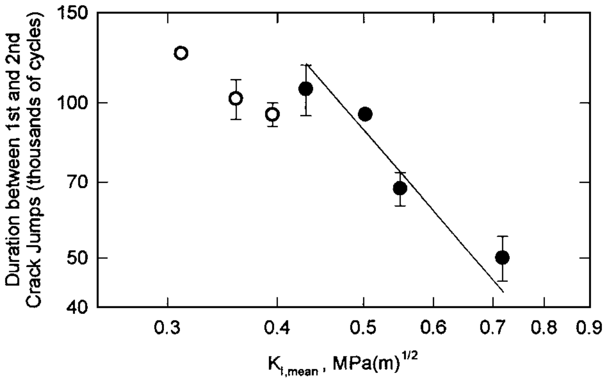

Figure 9 Effect of disappearance of shear crazes with decreasing stress on damage zone lifetime. The filled symbols indicate presence of shear crazes in the damage zone and the open symbols indicate the single-craze damage zone.

stress intensity factors below the transition, would predict slower fracture than was actually observed. This is consistent with the shielding effect of the shear crazes for the load-bearing entities in the main craze.

In summary, polyethylene resins presented two different notch root damage zones, the single-craze and epsilon-shaped zone. Comparisons of the two morphologies revealed considerable differences in the organization of the highly drawn material. The single HDPE craze contained uniaxially drawn fibrils, whereas the central craze in the epsilon-shaped zone of MDPE consisted of cellular cavities separated by biaxially deformed sheets. The kinetics of development of the two types of damage zone ahead of the arrested crack was also different. The single HDPE craze grew continuously, but with a decreasing rate, until fracture. Growth of the epsilon-shaped zone was essentially complete within the first 10% of its lifetime. In this case, accumulation of damage that led to fracture occurred in an almost stationary configuration. Decreasing the load suppressed the appearance of shear crazes. This resulted in accelerated fracture.

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