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# Craze development and breakdown in PVC during cyclic loading

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The nature of the development and breakdown of crazes during cyclic loading has been examined in poly(vinyl chloride) (PVC). The results show that the relative kinetics of craze development and breakdown are the same, regardless of molecular weight, plasticizer content or stress intensity level. Through optical and fractographic observations, it is found that the full equilibrium length is established early in the cyclic lifetime of the craze. Finally, the fracture path through the craze depends on the amount of cyclically induced damage experienced by the craze prior to the passage of the crack.

## 1. Introduction

It is well established that crazing is often a precursor to fracture in glassy polymers. For this reason, much attention has been given to examining the nature of craze development under statically applied loads as well as the mode of ultimate crack propagation through the craze [1–4]. With regard to craze development, it has been shown that a region develops along the midplane or midrib of the craze which has a lower fibril density than the craze matter surrounding it [5]. Once the craze attains a characteristic thickness, craze breakdown continues by the development of large voids at the craze–matrix interfaces due to the fracture of cross-tie fibrils between major fibril bundles [3]. Thus, two regions of low fibril density are created in the craze: along the midplane and at the craze–matrix interfaces; crack propagation through a pre-existent craze usually follows one of those low-fibril-density paths. When the crack growth is slow, the fracture path is observed to follow the midplane or midrib; however, under rapid crack-growth conditions, the crack is seen to jump alternately from one craze–matrix interface to the other [3].

Crazing has also been shown to be a precursor to fracture under cyclic loading conditions, with the process of craze formation and breakdown at the crack tip resulting in discontinuous crack growth [6]. Examination of the fatigue-fracture surface reveals bands lying perpendicular to the direction of crack growth. The length of these discontinuous growth (DG) bands corresponds well to the length of the plastic zone at the crack tip, as computed by the Dugdale model [7], and is thus a function of the prevailing stress intensity, $K$. Furthermore, the number of loading cycles $N^*$ associated with the development of the craze and its gradual breakdown prior to final rupture can be determined by dividing the band length by the corresponding crack growth rate $\mathrm{d}a/\mathrm{d}N$:

$$N^* = \text{band length}/(\mathrm{d}a/\mathrm{d}N). \qquad (1)$$

Through cinematographic studies, Hertzberg *et al.* [8] observed that the final craze length $l_\mathrm{d}$ did not immediately develop, but instead grew continuously throughout its lifetime.

The morphology of discontinuous growth bands has been examined in several amorphous polymers, including poly(vinyl chloride) (PVC), as a function of select material and test variables [9–11]. While there can be some deviations, the DG band morphology is typically found to be composed of an array of microvoids which decrease in size in the direction of crack growth; a stretch zone follows each band owing to the blunting of the crack tip as it encounters initially uncrazed polymer. This morphology is believed to arise from crack propagation through the midrib of the craze.

Though the structure of discontinuous growth bands has been extensively examined in their

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final state, little is known about the nature of craze development and subsequent breakdown corresponding to cyclic lives less than $N^*$. A preliminary report on the nature of craze development and breakdown during fatigue has already been presented [12]. The objective of this report is to examine more thoroughly the effect of cyclic loading on craze development and breakdown and to compare these results with the behaviour of crazes generated under static loading conditions.

## 2. Experimental procedure
### 2.1. Materials
Three blends of poly(vinyl chloride) (PVC) were employed in this study, referred to as PVC 13B, PVC 6D and CPPVC. PVC 13B and PVC 6D were supplied by the B. F. Goodrich Co. and CPPVC is a commercial blend of PVC supplied by Cadillac Plastics. Table I gives the designation, molecular weight, plasticizer content and plaque thickness for each PVC blend. Plasticized PVC was used in this investigation because of the known ease of DG band formation in such materials and the relatively large band lengths that form at a given $K$-value [9].

### 2.2. Fatigue crack propagation (FCP) testing
Fatigue specimens were prepared in the form of compact tension coupons with a height-to-width ratio ($H/W$) of 0.6, in accordance with the ASTM Standard E647-81T [13]. FCP tests were conducted on a closed-loop electro-hydraulic testing apparatus using Instron electronics. All tests were performed in laboratory air and at ambient temperature, with a sinusoidal waveform and a stress ratio, $\sigma_{min}/\sigma_{max}$, of 0.1. The stress intensity factor range $\Delta K$ was determined from the relationship

$$\Delta K = [\Delta P/(BW^{0.5})] \times [(2 + a/W)/(1 - a/W)^{1.5}] f(a/W) \quad (2)$$

TABLE I Materials

| Sample designation | Plasticizer content | Plaque thickness (mm) | $\bar{M}_w \times 10^{-5}$ |
|---|---|---|---|
| 13B | 13* | 6.3 | ~ 0.55 |
| 6D | 6* | 6.3 | ~ 1.00 |
| CP | ?† | 3.2 | ~ 0.60 |

*Parts per hundred (phr) of dioctyl phthalate (DOP), an external plasticizer.
†Believed to be plasticized [10].

where

$$\begin{aligned} \Delta P &= \text{applied stress range} \\ B &= \text{specimen thickness} \\ W &= \text{specimen width} \\ a &= \text{crack length} \\ f(a/W) &= 0.886 + 4.64(a/W) - 13.32(a/W)^2 \\ &\quad + 14.72(a/W)^3 - 5.6(a/W)^4 \end{aligned}$$

Fatigue crack propagation tests were conducted at constant $\Delta K$ so as to maintain a constant nominal crack growth rate throughout the test. In order to maintain the desired $\Delta K$ level, the loads were shed every 1.0 mm, following a calculated schedule. The test frequency was 1 Hz so that cyclic stability and visible band length could be accurately monitored. Fluorescent back-lighting was employed to allow for constant observation of band development at the crack tip without specimen heating. The point of failure for a given DG band was detected by the observation of a flash of light (and sometimes an audible acoustic emission) accompanying the jump of the crack through the craze. Certain bands were deliberately ruptured after being cycled for 5%, 10%, 25%, 50% and 75%, respectively, of $N^*$, with the latter being calculated from the stable life of preceding bands subjected to the same $\Delta K$ level.

### 2.3. Microscopy
Band growth and development at the crack tip was observed using two methods of optical microscopy. During cyclic loading, band extension as a function of $N$ was followed with the aid of a travelling microscope. Fig. 1 is a schematic representation of the craze ahead of a crack tip; the arrow at A indicates the direction along which the growth of the craze was observed. The bands were also examined using the interference fringe method described by Kambour [14]. When a crack tip is viewed with

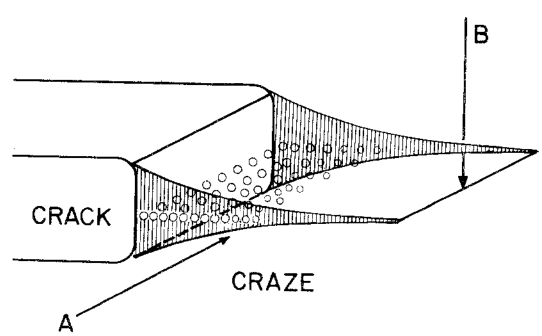



*Figure 1* Two methods of viewing craze at crack tip: A, laterally; B, vertically [12].

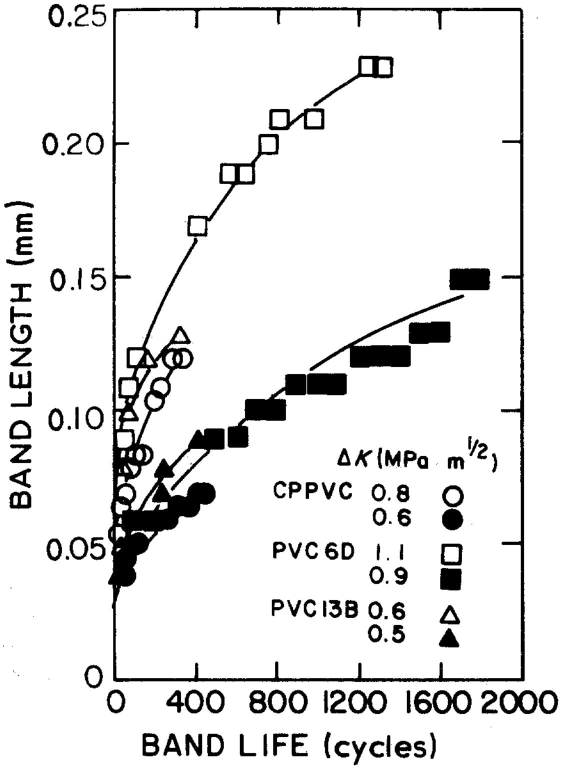



*Figure 2* Band length against band life for PVC13B, PVC6D and CPPVC.

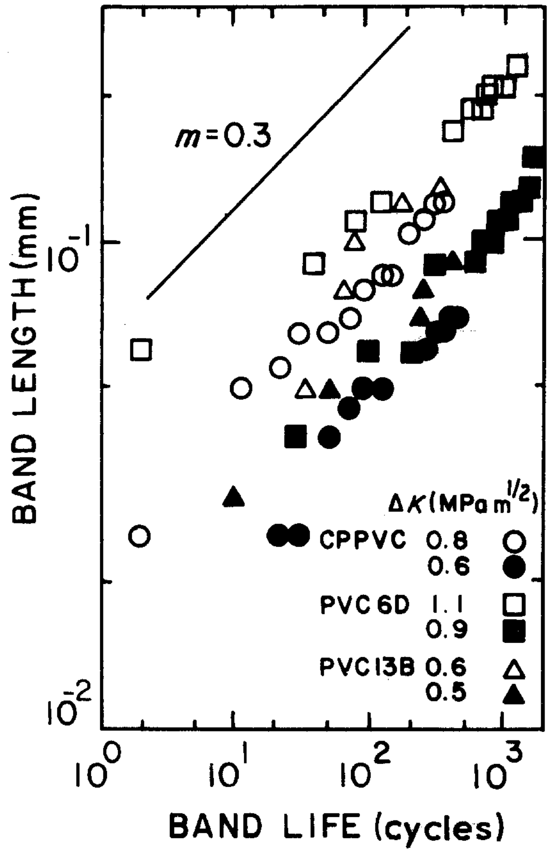



*Figure 3* log (band length) against log (band life) for PVC13B, PVC6D and CPPVC.

reflected light along a direction perpendicular to the crack plane (line of sight B in Fig. 1), the interference fringe patterns arising from the crack and craze can be examined. Determination of the crack–craze boundary was aided by the comparison of transmitted and reflected images. In transmitted light, the stretch zones of the preceding DG bands are clearly observed, including the stretch zone between the last uninterrupted DG band and the intermediate-life DG band. This last stretch zone was considered to be the crack–craze boundary. After the specimens were fractured, the fatigue-fracture surfaces were examined in the light microscope and then sputter-coated for examination in an ETEC scanning electron microscope (SEM) at an accelerating voltage of 20 kV.

## 3. Experimental results and discussion

### 3.1. Kinetics of DG band growth

It was of interest to examine more closely the kinetics of DG band extension as a function of loading cycles $N$, as in the cinematographic study mentioned earlier. Plots of band length against cycles (each at two different stress-intensity levels) for the three PVC blends examined are shown in Fig. 2. As expected, the higher the $K$ level, the larger is the final length of the DG band and the smaller is its cyclic stability $N^*$. Also, note that in every case the band growth rate is initially rapid, but then quickly decelerates to much lower levels. Following the initial nearly instantaneous extension of band length, it is found that the kinetics of additional band growth may be described by a relationship of the following form:

$$l = AN^m \tag{3}$$

where $l$ is the band length, $N$ is the number of loading cycles, $A$ is a constant dependent on material and test variables, and $m$ is the slope of the line described by log ($l$) against log ($N$). Plots of log ($l$) against log ($N$) for each PVC blend at the various $\Delta K$ levels are shown in Fig. 3. It is interesting that despite the fact that these data cover several different molecular weights, plasticizer contents and stress intensity levels, the slope of each data set is similar and approximately 0.3. In fact, when the data are normalized, they are

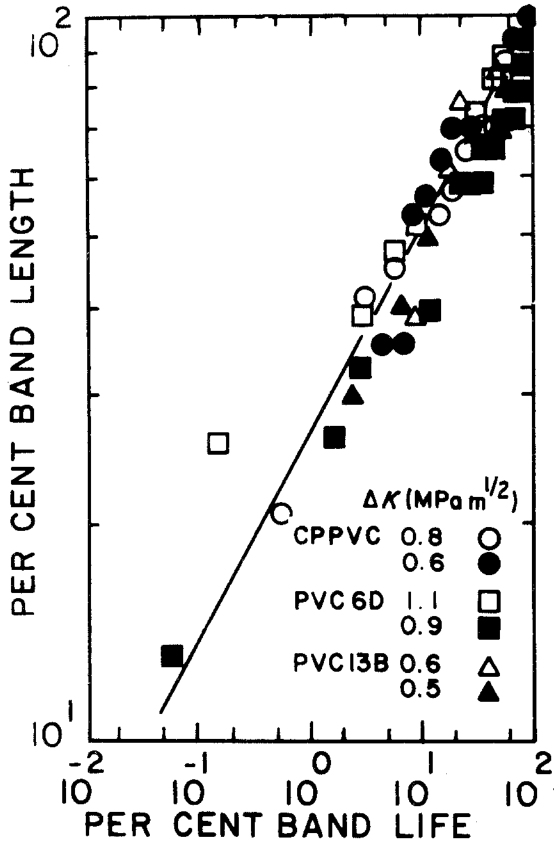



*Figure 4* Per cent band length against per cent band life for PVC13B, PVC6D and CPPVC.

seen to fit a single line as shown in Fig. 4 and described by Equation 4:

$$(l/l_d) = B(N/N^*)^{0.3} \tag{4}$$

where $l$ is the band length at a specific number of cycles $N$, $l_d$ is the final band length, and $N^*$ is the cyclic stability. This result suggests that, regardless of material or stress intensity levels, the kinetics of craze development and breakdown during fatigue are the same for all three blends of PVC.

If Equation 3 is differentiated, we can describe the band growth rate, $dl/dN$, as a function of loading cycles $N$:

$$dl/dN = C/(N^{0.7}). \tag{5}$$

Bucknall has observed this same power law relationship between craze strain and time during monotonic loading of impact-modified PVC [15]. Several investigators, including Regel [16], Spurr and Niegisch [17] and Wales [18] have observed a relationship between craze growth rate and time under static loading conditions of the form

$$dl/dt = D/t \tag{6}$$

where $dl/dt$ is the craze creep rate, $t$ is time and $D$ is a constant dependent on material and test variables.

Equations 5 (modified for time rather than number of cycles) and 6 have both been found to describe the transient or primary stage response of classical creep curves for metals [19]. This is the first stage of creep in metals in which the strain rate $d\epsilon/dt$ is observed to decrease continually with time. In early creep studies by Cottrell [20], it was found that slow creep rates and low strains favoured logarithmic creep in the primary stage, that is, creep behaviour of the type described by Equation 6. However, at faster creep rates and higher strains, the exponent of time is less than one and, in fact, is often observed to be 2/3. In such cases, this transient creep behaviour is often referred to as Andrade creep [21]. In the present study, the exponent of Equation 5 is close to that for Andrade creep (0.7 against 0.667). This result is not surprising in that the strain rates associated with fatigue loading of a notched specimen are likely to be much greater than those imposed in a static creep test of an unnotched test bar. Therefore, it is reasonable that the creep behaviour of crazes under static loading conditions would frequently follow logarithmic creep (as has been observed), while under fatigue loading conditions the behaviour would be expected to tend towards an Andrade-type creep relationship. Both relationships describe a decreasing strain rate with time. In the case of metals, this continued decrease in strain rate with time is attributed to substructure changes resulting in greater resistance to dislocation movement. For the case of DG band development and breakdown, it is suggested that this relationship reflects continued strain hardening of the remaining unfractured fibrils up to the point of total breakdown. This idea is consistent with the mechanism of fatigue craze breakdown proposed by Hertzberg and Manson [11].

## 3.2. Intermediate-life micromorphologies

### *3.2.1. Unfractured DG band appearance*

Let us now consider the appearance of the intermediate-life DG bands when viewed along a direction perpendicular to the crack plane (line of sight B in Fig. 1). Kambour and others have shown that the interference fringes arising from the

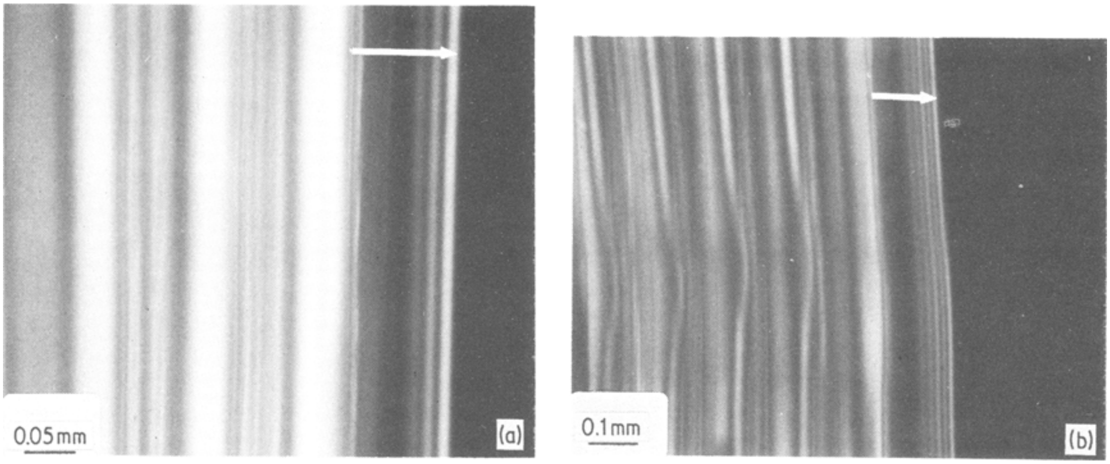



*Figure 5* Interference fringe pattern for DG bands interrupted after (a) 25% life [12] and (b) 50% life.

presence of a craze are finely spaced and increase in width in the direction of crack growth. In contrast to this pattern, an air wedge, resulting from the separation of the fatigue-fracture surfaces, yields a more widely spaced fringe pattern which decreases in width in the direction of crack growth. Figs. 5a and b show the fringe patterns arising from DG bands interrupted after 25% and 50% life, respectively. While the visible band length at the crack tip (line of sight A in Fig. 1) was only 65% of $l_d$ after load cycling for 25% of $N^*$, the fringe pattern extended the full length (0.1 mm) of the DG band (arrow). Similarly, the 50% life band was observed to be 0.115 mm long at interruption, whereas the interference fringe pattern was 100% of the expected $l_d$ dimension (0.125 mm).

The fringe pattern of a DG band interrupted after 90% life was also examined. In this case, the band, when observed laterally, attained virtually 100% of its expected final length (0.105 mm against $l_d = 0.11$ mm). Again, the length of the fringe pattern corresponded well to $l_d$ for this band (Fig. 6). Finally, consider the fringe pattern of a DG band interrupted only after 5% of $N^*$ (Fig. 7). In this case, the length of the fringe pattern was only 80% of $l_d$ (0.09 mm against 0.11 mm). However, note that it too was still longer than the 43% of $l_d$ predicted by the data in Fig. 4.

Thus, in all but the 90% life case, the length of the craze as viewed along the line of sight A in Fig. 1 was significantly less than that viewed along the line of sight B. The smaller-than-equilibrium width of the packet of interference fringes associ-

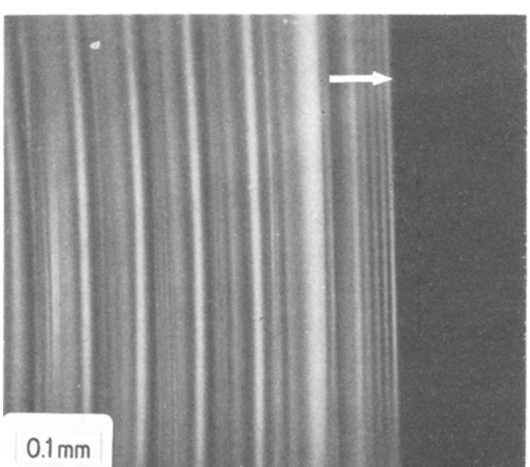



*Figure 6* Interference fringe pattern for DG band interrupted after 90% life.

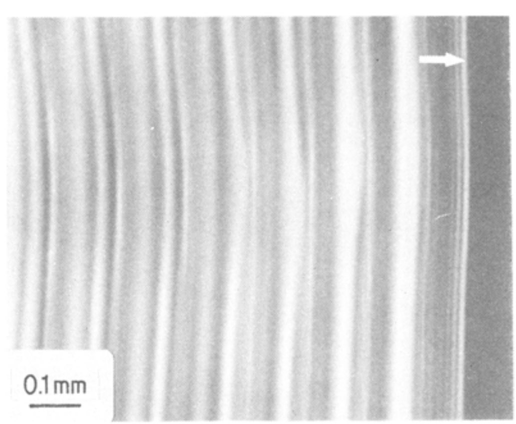



*Figure 7* Interference fringe pattern for DG band interrupted after 5% life.

ated with the 5% life band suggests that a finite period of time during cycling is required to develop the entire length of the DG band. However, the observation of a packet of interference fringes equal in size to the final band width at 25%, 50% and 90% life is evidence that the entire craze in the damage zone is established prior to 25% life and is, as yet, unbroken. Therefore, we conclude that the data in Fig. 2 do not represent a measure of craze length, as was originally believed [8]; instead, we suggest this measurement describes some level of damage within the craze. Thus, most of the cyclic lifetime involves the breakdown of the initial craze structure after the craze has attained its equilibrium length.

It is of interest to note that Döll *et al.* [22] observed recently that discontinuous crack growth during the cyclic fatigue of PVC occurred by the crack jumping only part of the way (approximately 2/3) through the craze at the crack tip. Takemori and Matsumoto [23], in their examination of "$\epsilon$-DG" bands in polycarbonate (PC), also noted crack propagation only 2/3 of the way through the craze structure ahead of the crack tip. In our case, however, recall that the fringe pattern at 90% life did not extend beyond the final expected $l_d$ for the DG band. From our observations of band growth and development, we consider it unlikely that the craze at the crack tip could develop an additional 50% in length in the remaining 10% of its life when little growth occurred during the cyclic period from 50% to 90% of total craze life. Therefore, we suggest that at final instability, the crack jumps through *all* of the craze matter present at the crack tip. It is not clear why the present results differ from those reported by Döll *et al.* and Takemori and Matsumoto; additional studies are indicated. In the next section, we will examine the fatigue-fracture surface micromorphologies of the intermediate-life crazes in order to characterize more completely the nature of the craze breakdown process during fatigue.

### 3.2.2. Fractured DG band appearance

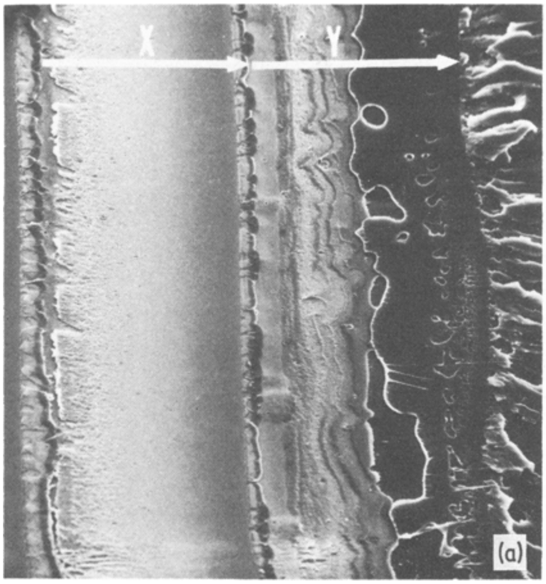
DG bands interrupted after 25%, 50% and 75% life are shown in Figs. 8a to c, respectively. Preceding the intermediate-life bands are DG bands which correspond to the anticipated cyclic life $N^*$ (region X). The cyclic lives of these preceding bands were used to compute the number of loading cycles corresponding to the 25%, 50% and 75% fractional lives noted above. In each case, the length of the interrupted band (region Y) in Fig. 8 is equal to the length of the preceding band (region X). This observation is in good agreement with the band length measurements obtained from the interference fringe patterns discussed earlier.

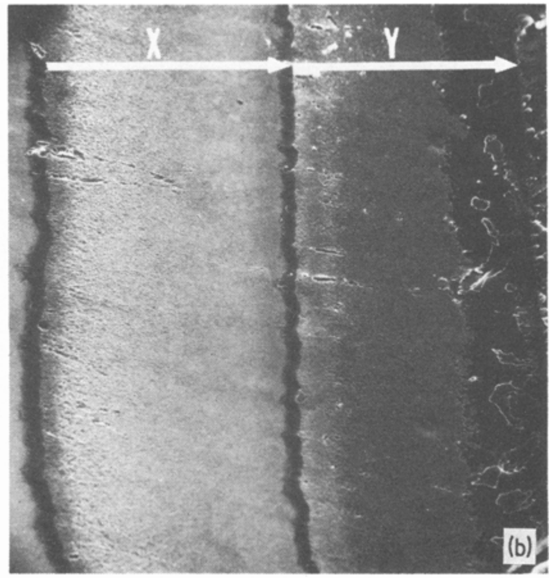
While the interrupted bands have the same length as the preceding DG bands formed without interruption, their morphologies exhibit distinct differences. For example, the interrupted band in Fig. 8a exhibits a voided structure for the first 25% to 65% of its length. This morphology, similar to that of an uninterrupted DG band, suggests that crack propagation occurred along the midrib of the craze in this region. However, the remainder of the interrupted band shows a patch morphology. A patch structure has been identified by Beahan *et al.* [3] and Doyle *et al.* [2] as reflecting rapid crack propagation along the craze–matrix interfaces of a pre-existent craze. Therefore, the intermediate-life band initially experiences failure along its craze midrib, but at some point the fracture path jumps alternately from one craze–matrix interface to another. Note that this latter portion of the craze was not observed by lateral viewing.

In Figs. 8b and c, the 50% and 75% bands again exhibit a transition from midrib to interfacial failure; however, in each case the transition occurs at a progressively larger fraction of the final band length. It is significant to note that the amount of midrib failure in all three cases compares well with the visible craze length as observed laterally prior to specimen fracture.

Finally, Figs. 9a and b show the micromorphologies of DG bands interrupted after 5% and 10% life, respectively. Unlike the bands of 25% life or more, these bands attain lengths of only 80% of $l_d$, the full equilibrium length of the preceding uninterrupted bands. These results are in good agreement with the fringe measurements discussed earlier for a 5% life band which also showed a band length of $0.8 l_d$. The fact that the band is still short of its full equilibrium length after $0.1N^*$ allows us to narrow further the cyclic loading range during which the craze becomes fully developed. That is, we conclude that the craze establishes its full equilibrium length between 10% and 25% of its total cyclic lifetime.

Examination of the micromorphologies of these intermediate-life bands (corresponding to lives less than $0.1N^*$) reveals some interesting differ-



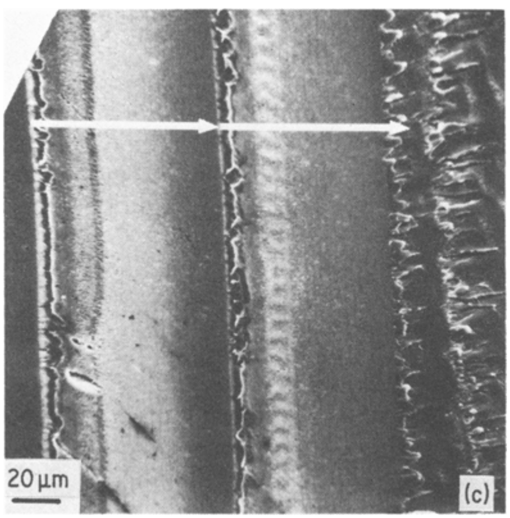




*Figure 8* Morphology of interrupted DG bands after (a) 25%, (b) 50% [12] and (c) 75% life.

ences from those bands that experienced more than 25% of their anticipated life. First, note that the fatigue-fracture surfaces of the bands appear to be fairly flat. We interpret this observation as meaning that little craze thickening has occurred at 10% or less of cyclic lifetime. Supporting this interpretation is the fact that the stretch zone preceding these bands is not yet developed to its full length (compare, on the one hand, the stretch zones associated with the intermediate-life bands (Y) with, on the other, the stretch zones of the preceding uninterrupted bands (X) in Figs. 9a and b). As the craze thickens with load cycling, the length of the preceding stretch zone should increase, since it varies directly with the craze opening displacement. The early stages of void formation can be seen clearly in Fig. 10a, though little void coalescence is in evidence (compare Figs. 10a and b). Since the breakdown of discontinuous growth bands surely involves void coalescence in the midrib region of the craze, the lack of large voids clusters in the beginning of the 5% intermediate-life band is strong evidence for limited craze breakdown, even though the craze length is as much as $0.8\,l_{\mathrm{d}}$. Finally, note that there is no transition from midrib to interfacial failure in these bands. This result may be explained by the fact that the craze–matrix interfaces have not yet begun to break down, and therefore, are not sufficiently weakened to be a viable fracture path. Recall that Beahan *et al.* [3] observed that midrib development occurred first, followed by void formation at the craze–matrix interfaces only after the craze had attained its characteristic thickness. Thus, we believe that during the early stages of DG band development, when the band has not yet attained its full thickness (as witnessed by the narrow stretch zone), the only fracture path available to the crack lies along the midplane.

## 4. Conclusions

From our observations of discontinuous crack growth during cyclic loading, we conclude that regardless of molecular weight, plasticizer content,

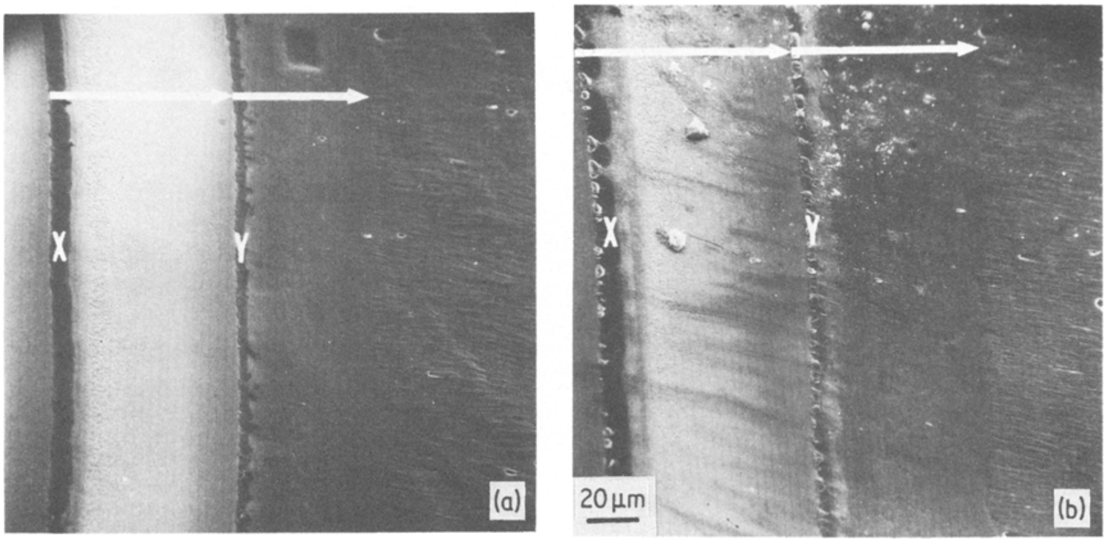



*Figure 9* (a) Morphology of DG band interrupted after 5% life. (b) Morphology of DG band interrupted after 10% life.

or stress intensity level, the relative kinetics of craze development and breakdown in PVC are the same and may be described by a power law relationship between per cent visible band length and per cent cyclic life. Through the correlation of interference fringe microscopy and fractographic observations, it is found that the entire craze length is established in the first 10% to 25% of cyclic life. Finally, whether the fracture path through a discontinuous growth band follows the midrib or the craze–matrix interface depends upon the amount of cyclic damage to the craze prior to the passage of the crack.

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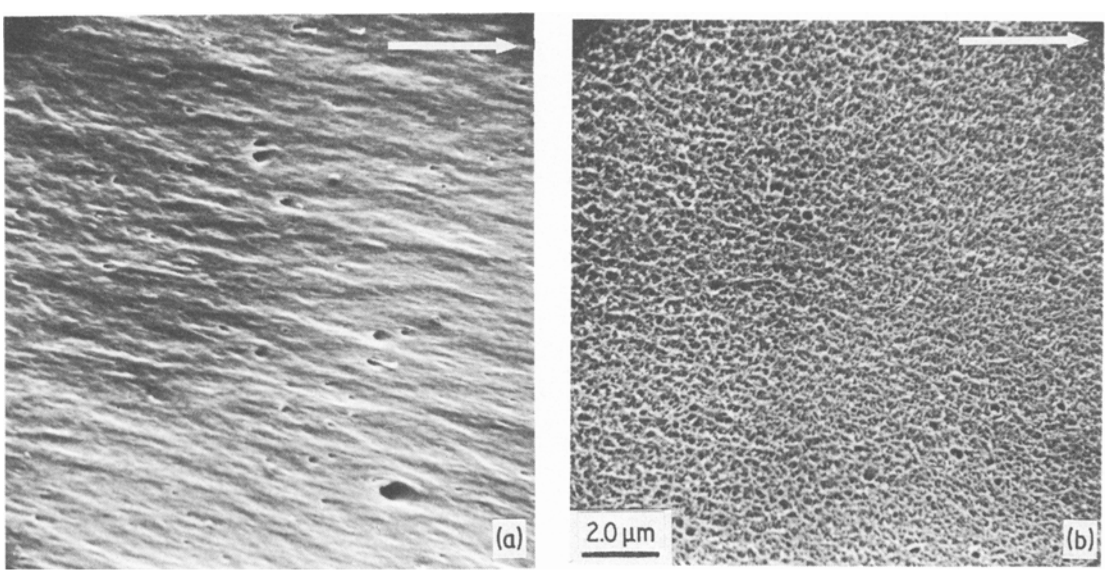


*Figure 10* (a) Higher-magnification view of DG band interrupted after 5% life showing little void coalescence. (b) Void coalescence in an uninterrupted DG band.

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