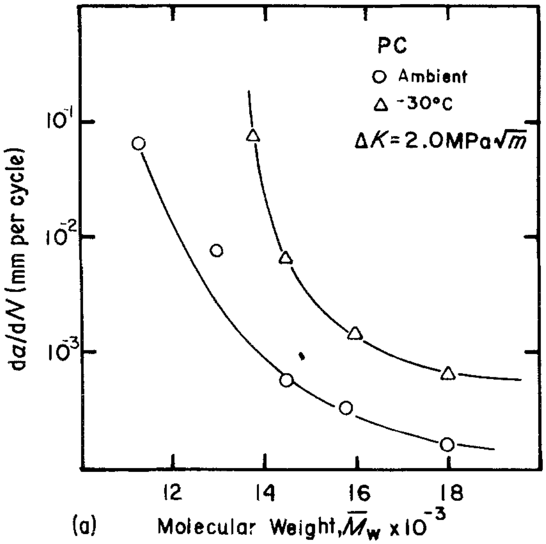
Discussion

Comments on "The molecular weight dependence of fatigue crack propagation in polycarbonate"

In a recent paper, Pitman and Ward [1] drew attention to the important influence of variations in molecular weight and thickness on fatigue crack propagation (FCP) resistance in polycarbonate (PC) at both ambient and −30° C test temperatures. The several-decade decrease in crack growth rates at a given ΔK level associated with a relatively small (about 38%) increase in weight-average molecular weight, $\bar{M}_w$, is, indeed, striking (Fig. 1a). [We have assumed that the two values of number-average molecular weight, $\bar{M}_n$, 5600 and 7150, cited for the −30° C tests were inadvertently mislabeled in the original paper. When the designations are transposed, the dependence of FCP on the molecular weight becomes consistent with the data for room temperature.] The increase in crack growth rate at 1 Hz in polycarbonate when the test temperature was reduced from ambient to −30° C is consistent with results reported by Martin and Gerberich [2] and Skibo *et al.* [3]. It is interesting to note that these results closely parallel similar observations reported for poly (vinyl chloride) (PVC) and poly (methyl methacrylate) (PMMA) (Fig. 1b and c) [4–6]. In all three materials, FCP rates are seen to decrease



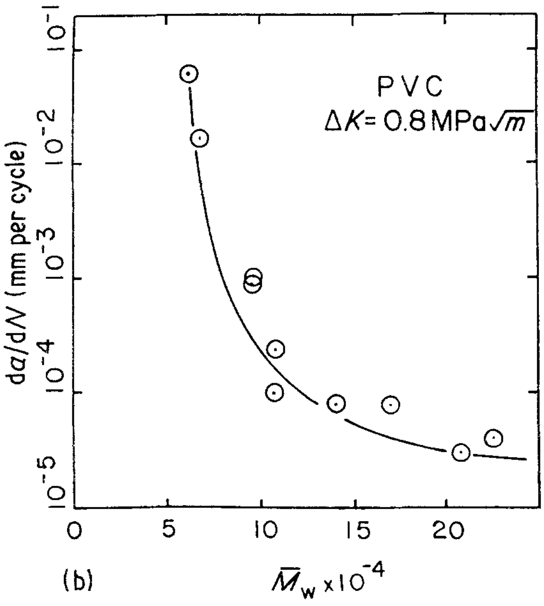
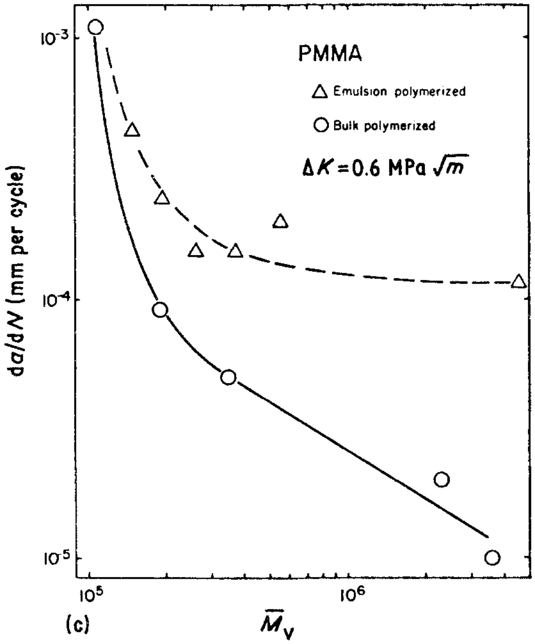


Figure 1 Effect of molecular weight, $\bar{M}_w$, on crack growth rate at constant ΔK for (a) PC [1], (b) PVC [4, 5], (c) PMMA [6].



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sharply at first with increasing molecular weight but then more slowly at relatively high values of $\bar{M}_w$; the latter observation suggests that further improvements in FCP resistance with increasing $\bar{M}_w$ would be far less dramatic and indicative of an approaching asymptote in the dependence of crack growth rate on molecular weight. In fact, to a good approximation the dependence may be expressed as $da/dN \propto e^{B/M}$, a relationship that can be derived from the dependence of network stability on the proportion of molecules that can entangle effectively with each other [6–8].

The manner by which sample thickness influences fatigue crack growth in polycarbonate requires further study, though a clear trend toward decreasing crack growth rates with decreasing specimen thickness in polycarbonate was established previously by Manson and Hertzberg [9] and supported by the recent findings by Pitman and Ward (Fig. 2). It has been suggested [1, 9] that FCP rates might decrease with an increasing tendency towards plane-stress test conditions, corresponding to large ratios of the crack tip plastic zone to specimen thickness and formation of shear lips. [Note that the plastic zone dimension should vary with the quantity $(K/\sigma_{ys})^2$.] It follows, therefore, that for a given material and test condition (i.e., K level) thin samples should experience a stress field more typical of plane stress than of plane strain conditions. The latter conditions are usually associated with flat fracture surfaces, and with a low ratio of plastic zone size to thickness.

Pitman and Ward [1] argued that the beneficial influence of decreasing specimen thickness and increasing molecular weight on fatigue crack propagation resistance was related to the increase in width of the shear lip on the fracture surface. For

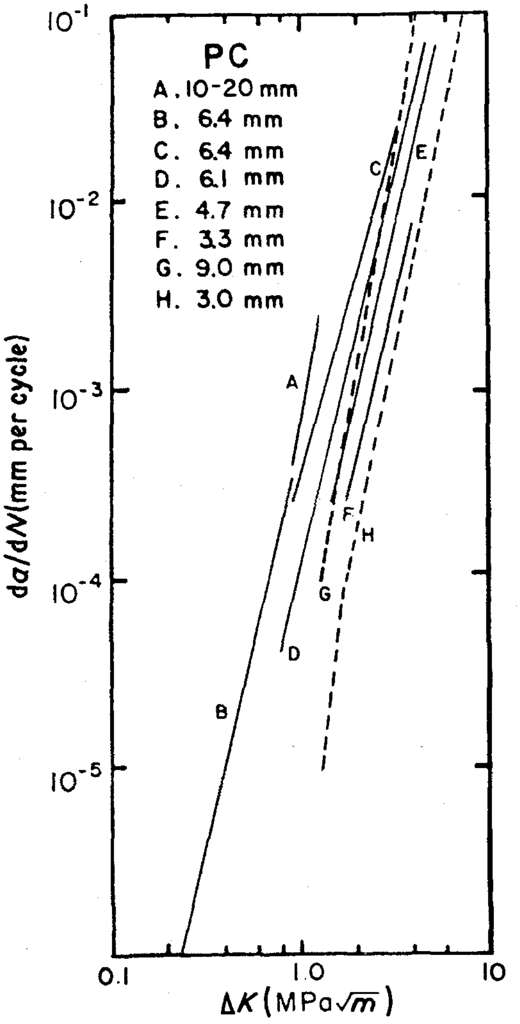

Figure 2 Effect of specimen thickness on fatigue crack propagation behaviour of PC [1, 9].

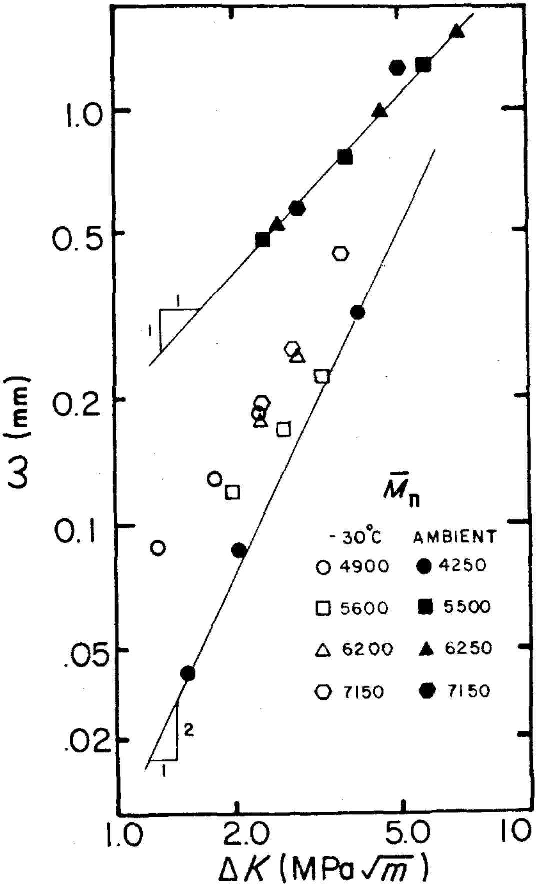

Figure 3 Dependence of ω, total width of shear lips evident on the fracture surface, on the stress intensity, ΔK.

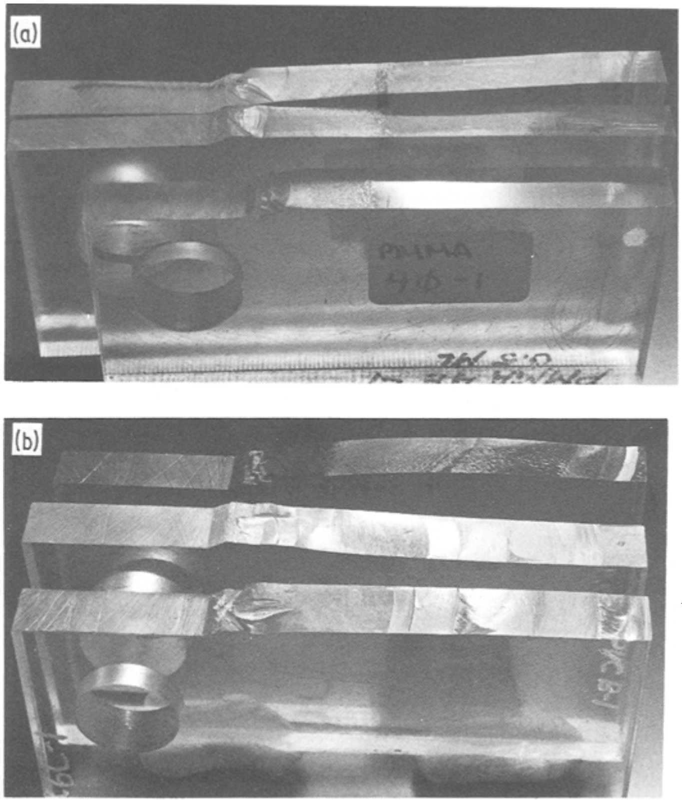

Figure 4 Fracture surfaces of PMMA and PVC samples which show a dependence of fatigue behaviour on molecular weight. Note the absence of shear lips. From top to bottom: (a) PMMA $\bar{M}_v = 48 \times 10^5$, $\bar{M}_v = 23 \times 10^5$, $\bar{M}_v = 1.9 \times 10^5$, (b) PVC $\bar{M}_v = 0.605 \times 10^5$, $\bar{M}_v = 0.965 \times 10^5$, $\bar{M}_v = 1.41 \times 10^5$.

example, they showed that shear lip sizes increased with increasing $\bar{M}_w$ when examined at constant crack growth rates (see Figs 6 and 9 of [1]). We propose an alternative explanation for the influence of $\bar{M}_w$ on FCP resistance and on the associated role of shear lips. We suggest that shear lip development is a consequence of improvements in FCP resistance due to an increase in molecular weight, rather than a cause of the observed improvement in crack growth resistance. In other words, we propose that the increase in FCP resistance that occurs with increasing molecular weight results in the development of larger shear lips for a given value of da/dN due to the larger ΔK necessary to drive the crack at that speed; Fig. 3 is a log–log plot of the Pitman and Ward data (taken from Figs 5, 6, 8 and 9 of [1]) for total shear-lip width on the fracture surface, ω_f, as a function of ΔK, for several molecular weights at both room temperature and $-30°$ C. Note that the line corresponding to the lowest $\bar{M}_w$ data at room temperature has a slope of 2, whereas the other lines have slopes ranging from 1.1 to 1.9. Since the shear-lip width should vary with the square of K, the reason why only one set of data fulfills this requirement is not clear at this time. Nevertheless, the increase in shear lip width with increasing molecular weight at constant crack growth rates (seen in Figs 6 and 9 of [1]) must surely reflect the fact that the ΔK levels necessary to drive a crack at a given velocity increase with increasing $\bar{M}_w$. Since the K level increases, the shear-lip width must increase accordingly.

Recall from Fig. 1 that the FCP resistance of PMMA and PVC exhibits a strong dependence on $\bar{M}_w$. Yet, when the respective fracture surfaces of both materials are examined at the several molecular weights investigated, no shear lips are found (Fig. 4)*. Therefore, large changes in crack velocity due to changes in molecular weight can occur in the absence of any change in shear-lip development. Consequently, we conclude that the shear-lip development observed by Pitman and Ward [1] in PC is a consequence of the larger stress intensity level required to drive a crack at a given growth rate as molecular weight is increased. As

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*This is consistent with the much smaller ΔK levels experienced during the fatigue tests of the PVC and PMMA samples.

noted previously [8], we maintain that the beneficial effect of increasing molecular weight on FCP resistance is primarily the result of an increase in the number of effective chain entanglements per molecule and hence in enhanced craze stability and associated slower cracking rates.

An additional point bears further comment. The absolute values of $\bar{M}_w$ (13 000 to 18 000) reported by Pitman and Ward appear to be surprisingly low. By contrast, Schnell [10] states that polycarbonate materials with values of $\bar{M}_w$ in the range 10 000 to 25 000 are low in strength and that the $\bar{M}_w$ of commercial PC is in the range from 32 000 to 35 000. Skibo *et al.* [11] reported a viscosity-average molecular weight, $\bar{M}_v = 49\,000$ (equivalent to $\bar{M}_w \gtrsim 49\,000$) for commercial PC used in their study. Moreover, the agreement between earlier data and the data by Pitman and Ward in Fig. 2 suggests that the molecular weights in the various material supplies are similar and in the range of 40 000 to 50000.

In summary, we concur with the experimental observations made by Pitman and Ward [1] that FCP rates in engineering plastics decrease markedly with increasing molecular weight (though to a more limited extent at higher values of $\bar{M}_w$) and that FCP rates in polycarbonate decrease with decreasing sample thickness. However, we conclude that shear lip development is a consequence and not the cause of molecular-weight-induced changes in fatigue crack propagation response in polymers.

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Author's reply to 'Comments on "The molecular weight dependence of fatigue crack propagation in polycarbonate"'

The thesis of our paper is that fatigue is similar to fracture in that *both* the plane strain craze contribution and the plane stress shear lip contribution are important. Our recent studies of fatigue and fracture [1, 2] suggest that both contributions are affected by molecular weight. The absolute magnitude of the plane strain craze contribution, per unit area of crack surface, increases markedly with increasing molecular weight due to increases in both craze stress and crack opening displacement. The absolute magnitude of the shear lip energy per unit volume also increases very slightly with increasing molecular weight. Because of the increase in the craze stress with increasing molecular weight the volume of the shear lips may also increase, since the latter relates to competition

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between crazing and yielding [2–4]. Tables II and III of [2] show that the shear lip contribution is between 16 and 32% of the total.

I am indebted to Professor Hertzberg and his colleagues for their kind acknowledgment of my comments on the first draft of their comments [5] on our fatigue paper [2]. I am pleased to confirm that we did not intend to convey the impression that shear lip development was the sole cause of the improved fatigue crack growth resistance with increasing molecular weight. I had hoped that we had made it clear that both the shear lip contribution and the plane strain craze contribution are important, as stated in the abstract to [2]. Finally, we are entirely in agreement with Professor Hertzberg and his colleagues with regard to the importance of a load bearing network, and the presence of molecular entanglements.

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Comments on "Fracture stress-reflecting spot relations in hot-pressed alumina"

Kirchner and Richard [1] recently reported that the reflecting spot boundaries observed on Al_2O_3 fracture surfaces occured at $>K_{IC}$, as have Kirchner and Gruver [2, 3]. Thus they note that these boundaries cannot be the end of subcritical crack growth in contrast to their earlier suggestions that these boundaries may occur at K_{IC} [4]. However, Kirchner and Richard claim that variations in K along the reflecting spot boundary are inconsistent with these features being the "inner mirror", i.e. the analogue of the mirror–mist boundary on glass fractures. The purpose of this note is to point out that both the variation and size of the "reflecting spot" area are not inconsistent with this area being the "inner mirror". Furthermore, arguments are presented to show that the average size of the reflecting spot area may also be consistent with its being an inner mirror.

Rice [5] has recently summarized R_m/C data (where R_m is the "inner mirror" (mirror-mist boundary) and C is the flaw size) from several investigators on several polycrystalline materials (including Al_2O_3). R_m/C ratios were typically in the range of 4 to 8, and more commonly 5 to 7 in contrast to $\gtrsim 10$ for dense glasses. Materials having substantial to total transgranular fracture in the mirror region had increased intergranular fracture at and beyond the edge of the mirror region. It was proposed that this increase in intergranular failure was consistent with the concept of mist formation by secondary crack nucleation at, or ahead of, the main crack tip, as in glasses. However, it was pointed out that in polycrystalline materials, individual grains and grain boundaries would frequently be sources of crack nucleation. Thus, the local fracture energy for secondary crack nucleation would be the single crystal (γ_c) or grain boundary fracture energy (γ_B) in constrast to the polycrystalline fracture energy (γ_{pc}) typically required for the main (primary) crack. This difference in secondary versus primary crack γ values in polycrystals in contrast to a single, uniform γ value for both types of cracks in glass quantatively agreed with the R_m/C ratio differences between polycrystals and glasses.

The general observations of Kirchner and co-workers are consistent with Rice's model, and some provide direct support for it. First, although there are a variety of complications in analysing Al_2O_3 data (discussed below), the data of Kirchner and co-workers does show increase in intergranular failure at distances of 4 to 9 times the apparent flaw size (i.e. at stress intensities of approximately 2 to 3 times those at the boundary they identify as the original flaw in their analysis),