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Fatigue mechanisms in poly (methyl methacrylate) at threshold: effects of molecular weight and mean stress

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Fatigue tests were conducted on three linear poly (methyl methacrylate) (PMMA) resins having weight average molecular weights (M_w) of 82 000, 205 000 and 390 000 and on a fourth, cross-linked sample ($M_c = 3337$ g mol^{-1}). Fatigue threshold test conditions included a constant load ratio ($R^c = 0.1$) and a constant maximum stress intensity level ($K^c_{max} = 0.52$ MPa m$^{1/2}$). The $R^c = 0.1$ test results demonstrated that fatigue resistance increased with increasing M_w, and that the cross-linked sample possessed a higher fatigue threshold than the linear low-M_w material. However, the K^c_{max} test results revealed the opposite trend, with fatigue resistance decreasing with increasing M_w and chemical cross-linking. The marked change in relative fatigue resistance of the PMMA resins investigated under high mean stress conditions is believed to be a consequence of the competition between two molecular deformation mechanisms: chain scission and chain slippage. The presumed shift in operative mechanism as a function of the R level is reflected in differences noted on the fracture surfaces of the PMMA resins studied. Discontinuous growth band formation, which is indicative of large amounts of chain slippage, is favoured by low M_w and low R ratios, but disappears in association with high-M_w and high R-ratio test conditions.

1. Introduction

With the increased use of polymers in load-bearing components, a corresponding increase of awareness concerning their mechanical properties is indicated. Although such obvious properties as tensile strength and impact strength play an important role in the materials selection process, the more insidious accumulation of fatigue damage is often the controlling factor in the final failure of the component. Therefore, the need for a better understanding of the complex fatigue behaviour of polymers is required to prevent these often unnecessary failures.

In order to examine the propagation state of fatigue alone, a pre-existing flaw is assumed. Using fracture mechanics concepts, the stress state at the tip of the crack is defined by the stress intensity factor (K). For the case of fatigue, it was shown by Paris [1] that a log–linear relationship exists between the fatigue crack growth rate and the applied stress intensity range (ΔK)

$$\frac{da}{dN} = A\Delta K^m \qquad (1)$$

where da/dN is the fatigue crack growth rate, ΔK is the stress intensity factor range ($\Delta K = K_{max} - K_{min}$), and A and m are functions of the material variables, environment, frequency, temperature and stress ratio.

It can be seen from Fig. 1 that although the Paris equation is valid for intermediate ΔK levels (stage II), the relationship becomes non-linear at extreme ΔK values. At low ΔK values (stage I) the growth rate becomes vanishingly small until, for all intents and purposes, the crack can be considered to have stopped growing. Furthermore, it can be inferred that pre-existing cracks would not be expected to propagate under these conditions. Therefore, this ΔK level defines a design criterion referred to as the fatigue threshold (ΔK_{Th}). That is analogous to the fatigue limit, determined from traditional S–N curves.

To define the ΔK_{Th} value of a material, a precracked specimen is cyclically loaded under decreasing ΔK conditions until the growth rate falls below 10^{-7} mm cycle^{-1} [2]. The prevailing ΔK level at that da/dN is then defined as the fatigue threshold of the material, ΔK_{Th}. Although the threshold test procedure necessitates that ΔK be reduced, the specific method by which this decrease is brought about can vary. From Fig. 2, three different test procedures, involving constant R ratio, constant K_{mean} and constant K_{max} values, can effect the desired reduction in ΔK levels with continuing crack extension.

The constant R ratio (R^c) procedure shown in Fig. 2a lowers the stress intensity range while maintaining a constant R, where R is defined by the ratio

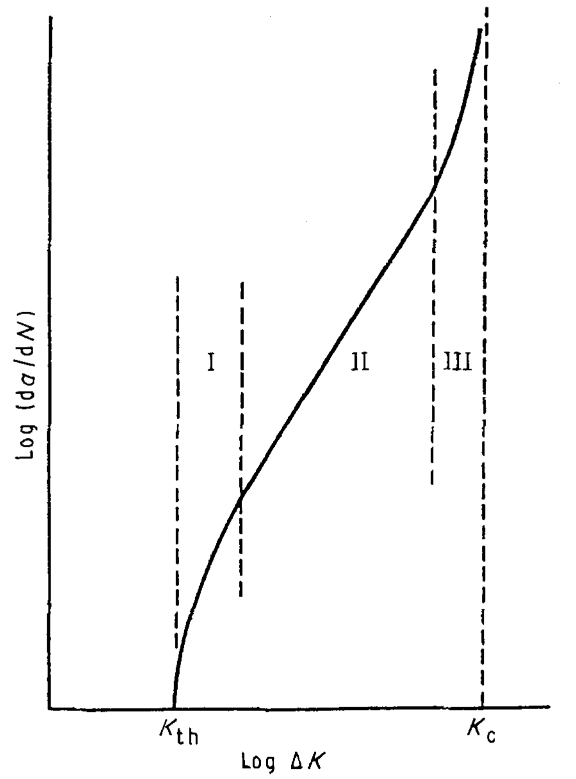

Figure 1 Schematic ΔK versus da/dN diagram showing the three regimes of fatigue crack growth.

K_{min}/K_{max}. The constant K_{mean} (K^c_{mean}) test method maintains a constant mean stress intensity factor as the maximum K value is lowered, and while the minimum value is raised (Fig. 2b). This results in a higher mean stress [mean stress $= \frac{1}{2}$ (maximum stress + minimum stress)] value at threshold as compared with the R^c method. The constant K_{max} (K^c_{max}) test procedure results in an even higher final mean stress than the previous two procedures, as shown in Fig. 2c. In this case the maximum stress intensity is maintained constant while the minimum K level is raised as the test proceeds.

Historically, the R ratio chosen by the vast majority of researchers has been $R^c = 0.1$, due to its similarity to a loading cycle between zero and the maximum load, but without the added difficulty of causing the test apparatus actually to pass through a zero-load condition. Realistically, however, many structural components experience a mean stress superimposed on their cyclic loads. This mean stress may arise from internal residual stresses or from externally applied static loads. A slightly detrimental mean stress effect on the growth rate of metals (up to a factor of 2 in the growth rate) during stage II has been seen by a number of researchers, and ΔK_{Th} has been shown to be very sensitive to R [1, 3–8]. Therefore, ΔK_{Th} is not strictly a material constant, but is to some extent a function of the stress level and test environment. As a result of the viscoelastic behaviour of polymeric solids, the influence of mean stress on the response of these materials is often more evident than that seen for metal systems. Previous work done by our group [9] clearly reveals this influence (see Fig. 3).

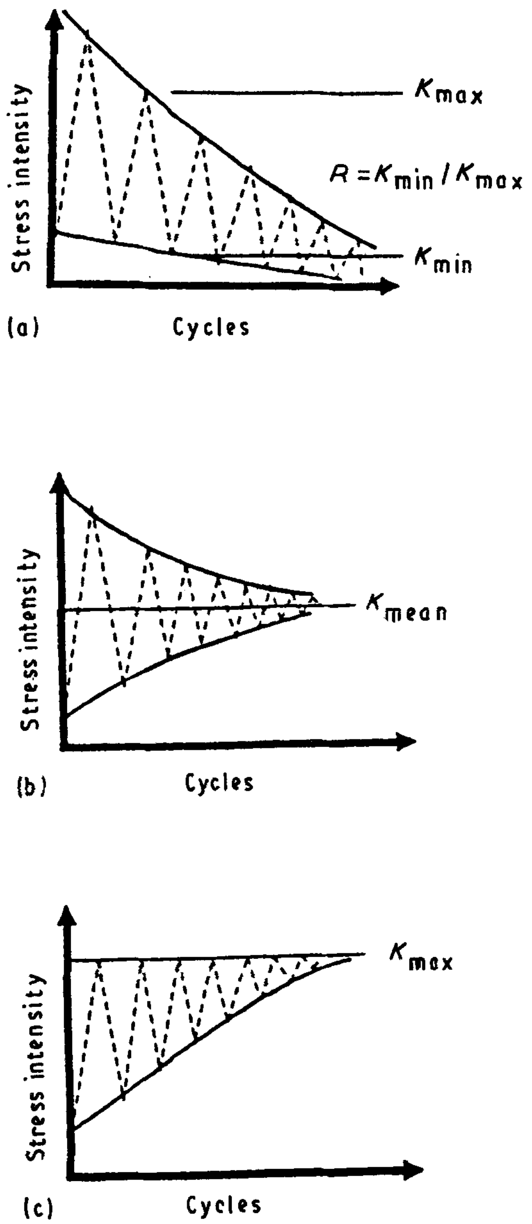

Figure 2 Schematic diagrams showing the three possible fatigue threshold procedures: (a) constant R-ratio method, R^c, (b) constant K_{mean} method, K^c_{mean}; and (c) constant K_{max} method, K^c_{max}.

Useful insight concerning fatigue and fracture processes in polymers can be gained by examining the behaviour of the material at the molecular level [10, 11]; at this scale, failure can be described as a competition between disentanglement and chain scission. Under stress, secondary bonding between polymer chains can be broken, allowing the chains to slip past one another and become disentangled. However, if this viscous flow process is restricted and the associated flow rate is too slow, portions of the chains become extended to their ultimate elongation. As a result, fracture of primary bonds in the main chain (scission) will occur [12, 13]. Although the actual fracture stress for unoriented polymers is much less than their theoretical fracture stress, the measured value of absorbed energy is greater than that required solely to break a single plane of primary bonds. This indicates that entanglements and subsequent slippage play a large role in energy absorption.

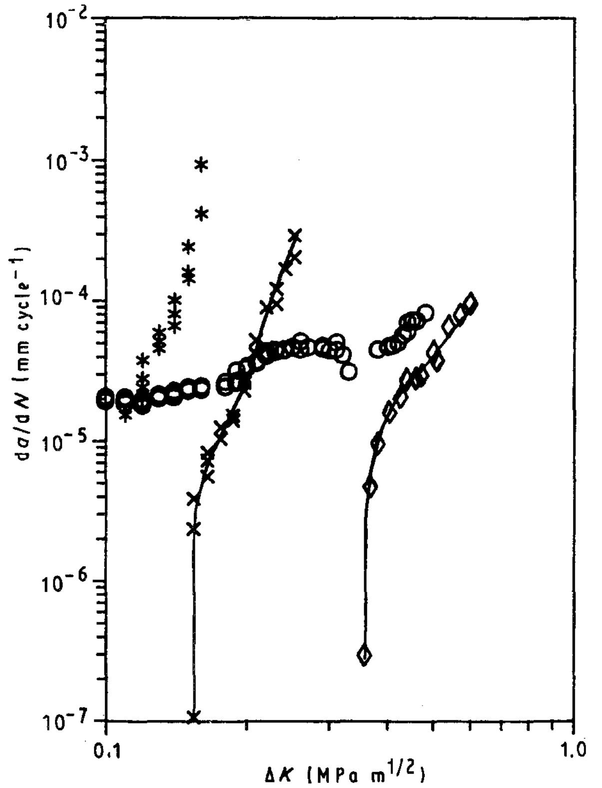

Figure 3 Detrimental effect of mean stress on FCP resistance in PMMA [9]: (◇) $R^c = 0.1$, (×) $R^c = 0.65$, (✱) $R^c = 0.8$ and (○) $K^c_{max} = 0.52$ MPa $m^{1/2}$.

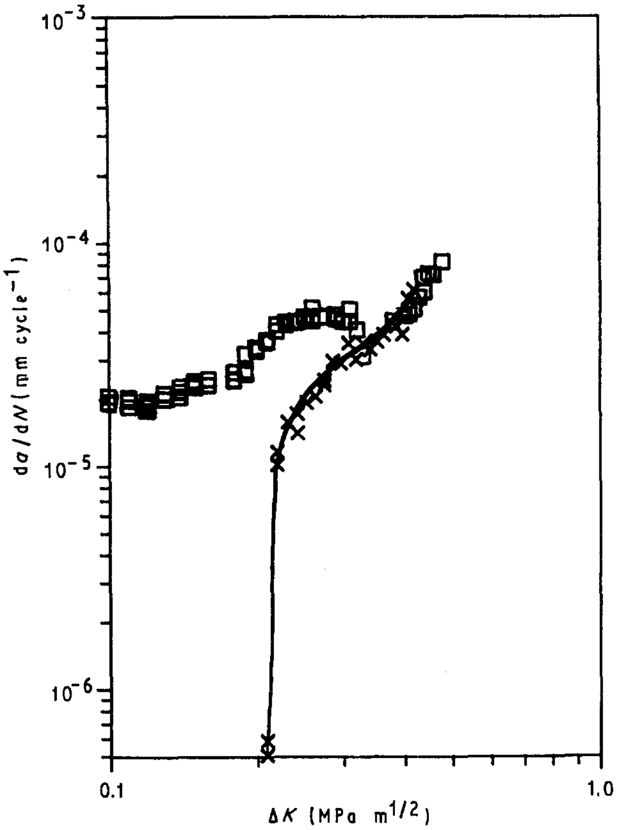

Figure 4 K^c_{max} test results showing the M_w/R-ratio effect, such that a low-M_w material is shown to be superior to a high-M_w material under high mean stress ($K^c_{max} = 0.52$ MPa $m^{1/2}$) [29]: (□) commercial PMMA and (×) low-M_w PMMA (10^5).

It has long been recognized that the physical properties of a polymer are strongly dependent on the M_w of the material [14]. For example, both the tensile strength and the toughness of a polymer increase initially with M_w to a critical M_w, beyond which properties change little [15–17]. By sharp contrast, fatigue resistance increases strongly with M_w where $M_w > M_{critical}$. Sauer and co-workers [18–21] demonstrated a definite increase in fatigue life with M_w in unnotched samples under conditions of zero mean stress (i.e. $R = -1$). In addition, a series of fatigue studies by Manson and co-workers [22–28] revealed increased fatigue resistance with M_w (above $M_{critical}$) in a number of polymeric materials under $R^c = 0.1$ conditions. This behaviour has been attributed to increased craze stability, increased orientation strengthening and reduced molecular stress concentrations associated with chain ends.

Previous threshold experiments ($R^c = 0.1$) conducted on a low-M_w injection-moulded PMMA resin revealed inferior fatigue resistance to that of three high-M_w cast PMMA resins [29]. This result is consistant with previously reported findings [18–28]. However, additional tests conducted by us indicate that under conditions of high mean stress (e.g. those conditions present at the end of a K^c_{max} threshold test procedure) a low-M_w material may exhibit superior fatigue resistance to a high-M_w material (Fig. 4).

2. Fractography

An examination of the polymer fracture surface may yield both interesting and useful information concerning the deformation mechanisms of fatigue in the material. An extensive review of these micromechanisms and their accompanying surface features was presented by Hertzberg and Manson [30]. A microscopic examination of a fatigue fracture surface often reveals a series of parallel lines known as striations. Other fatigue markings, referred to as discontinuous growth bands (DGB), have also been found in polymers under certain test conditions, and correspond to the sudden advance of a crack through a pre-existing craze.

Whereas striations are indicative of a single loading cycle, the DGB may be the cumulative result of anything from two cycles to several thousand cycles. The final length of these crazes has been successfully predicted by the Dugdale plastic zone model

$$r_y \approx \frac{\pi}{8} \frac{K^2_{max}}{\sigma^2_{ys}} \qquad (2)$$

where r_y is the plastic zone size, K_{max} is the maximum stress intensity and σ_{ys} is the yield stress. Conversely, if the length of the DGB is known and equated to r_y, one may infer an apparent yield strength corresponding to crazing in the material. DGBs are more likely to occur under conditions of high ductility (i.e. low-M_w, high plasticizer content, low cross-linking, etc.)

The object of this study was to examine the combined effects of M_w and mean stress on the fatigue behaviour of PMMA. In contrast to most studies, which relied solely on $R^c = 0.1$ conditions, an investigation into the M_w influence on the fatigue resistance of PMMA was carried out using both $R^c = 0.1$ and the K^c_{max} threshold test procedures. The concurrent investigation of the fracture surfaces should yield insight into the operative fracture mechanisms in the materials under study.

3. Experimental

3.1. Polymerization

PMMA sheets were prepared by ultraviolet polymerization between glass plates based on the compositions shown in Table I. The methyl methacrylate monomer (Polysciences, Inc.) was purified by removing the inhibitor through a neutral alumina-packed column. The photo-initiator (benzoin; Polysciences, Inc.), chain transfer agent (1-dodecanethiol; Kodak Co.) and cross-linking agent (tetraethylene glycol dimethacrylate; Polysciences, Inc.) were used as-received.

3.2. Characterization

Determination of the molecular weight of the linear samples (Table II) was accomplished by gel-permeation chromatography (Waters). The molecular weight (M_c) between cross-linking points of the cross-linked sample was determined by the following procedure.

First, the cross-linked sample was swollen in a high boiling point solvent (xylene) at 120 °C, which is above the glass transition point of the polymer. Therefore, solvent stress cracking of the sample was avoided. In this step the weight of the sample increased 200% as a result of solvent absorption. However, xylene is not a good solvent for PMMA [$\delta_{xylene} = 8.8\ (\mathrm{cal\,cm^{-3}})^{1/2}$; $\delta_{PMMA} = 9.45\ (\mathrm{cal\,cm^{-3}})^{1/2}$], so the extent of swelling is limited [31]. Nevertheless, the amount of absorbed solvent was sufficient to change the PMMA to a rubbery state. Secondly, the swollen sample was cooled to room temperature and left overnight in chlorobenzene, which is a good solvent [$\delta_{chlorobenzene} = 9.5\ (\mathrm{cal\,cm^{-3}})^{1/2}$] for PMMA. Finally, the sample was then transferred to fresh chlorobenzene. This step was repeated several times to ensure that all of the xylene was replaced by chlorobenzene. The initial and final weights of the sample were then used in the Flory–Rhener equation to calculate the cross-linking density.

TABLE I Polymerization recipes of PMMA cast sheets

Ingredient	Parts by weight (g)
MMA	100
1-Dodecanethiol (n-DDM) (chain transfer agent)	0,0.073, 0.22[a]
Ethylene glycol dimethacrylate	1.98[b]

[a]The amount of chain transfer agent that was used for 400 000, 200 000 and 80 000 (g mol^{-1}) samples, respectively.

[b]Cross-linked sample.

TABLE II Molecular weight and cross-linking information

Material	M_W (g/mol^{-1})	M_c (g/mol)
Low-M_W	82000	
Medium-M_W	205000	
High-M_W	390000	
Cross-linked	(82000)	3337

3.3. Sample preparation and testing

The PMMA cast sheets were dried under vacuum at 50 °C for 24 h to remove the unreacted monomer and relieve residual stress. Test specimens were then machined into the form of either wedge-opening-load (WOL) or compact tension (CT) geometry.

All fatigue experiments conducted in this study were performed at a cyclic frequency of 20 Hz on an MTS elecrohydraulic closed-loop testing machine utilizing Instron electronics. Crack lengths were monitored via a compliance technique, a clip gauge being attached to the mouth of the notch; the gauge was secured with knife-edges mounted on the front face of the samples. Visual verification of these readings was made at appropriate times with the aid of a Gaertner travelling microscope.

All samples were precracked under constant-load conditions, such that the final K_{max} of precracking was less than the initial K_{max} of the ΔK-decreasing portion of the test, in order to preclude any significant load interaction. The ΔK-decreasing portion of the test was controlled with a fatigue testing system designed by Fracture Technology Associates, Inc. This system constantly monitored the load and crack length, and automatically corrected the resulting stress intensity factor range, according to [32]

$$\Delta K_i = \Delta K_o \exp[c\ (a_i - a_o)] \qquad (3)$$

where ΔK_i is the instantaneous ΔK level, ΔK_o is the original ΔK level, c is the normalized K-gradient, defined as $(\mathrm{d}K/\mathrm{d}a)/K$, a_i is the instantaneous crack length and a_o is the original crack length.

A previous study [9] demonstrated that threshold tests in PMMA may be conducted with a gradient as steep as $-0.2\,\mathrm{mm^{-1}}$ as opposed to the maximum American Society for Testing and Materials recommended value of $-0.06\ \mathrm{mm^{-1}}$. Both R^c and K^c_{max} threshold test procedures were utilized in this study. All K^c_{max} tests were conducted with a value of $0.52\ \mathrm{MPa\,m^{1/2}}$.

Fracture surfaces were examined using an ETEC scanning electron microscope (SEM) at 3–20 kV. SEM samples were mounted with carbon paste and coated with gold.

4. Results and discussion

Fig. 5 demonstrates that the fatigue resistance in PMMA at low mean stress levels (i.e. $R^c = 0.1$) does, indeed, decrease with decreasing M_w. The low-M_w sample revealed a ΔK_{Th} of $0.2\ \mathrm{MPa\,m^{1/2}}$, compared with the high-M_w sample which had a ΔK_{Th} of $0.33\ \mathrm{MPa\,m^{1/2}}$. The cross-linked sample, which had $M_w = 82\,000$ before cross-linking, was inferior at high

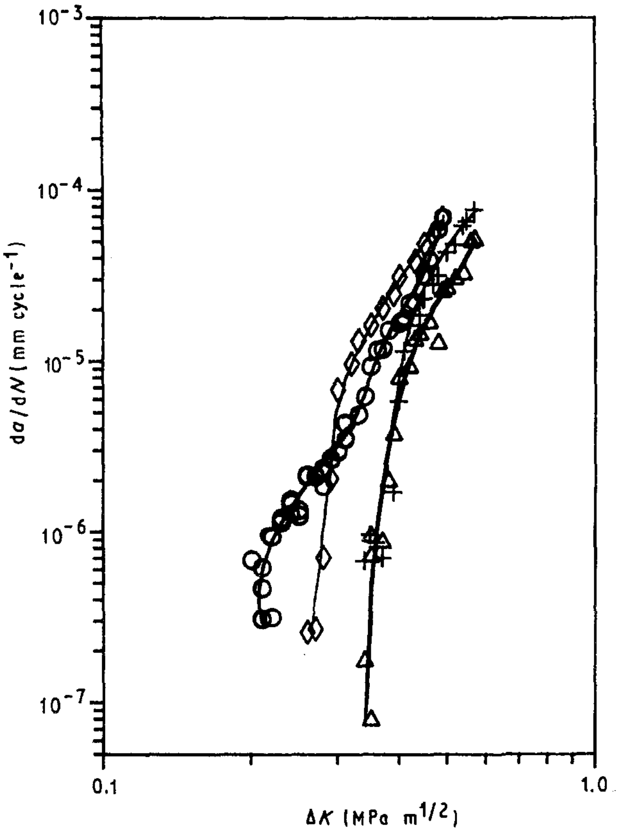

Figure 5 $R^c = 0.1$ test results. Note the expected improvement in fatigue response with increasing M_w: (○) low-M_w (8×10^4), (+) medium-M_w (2×10^5), (△) high-M_w (4×10^5) and (◇) cross-linked.

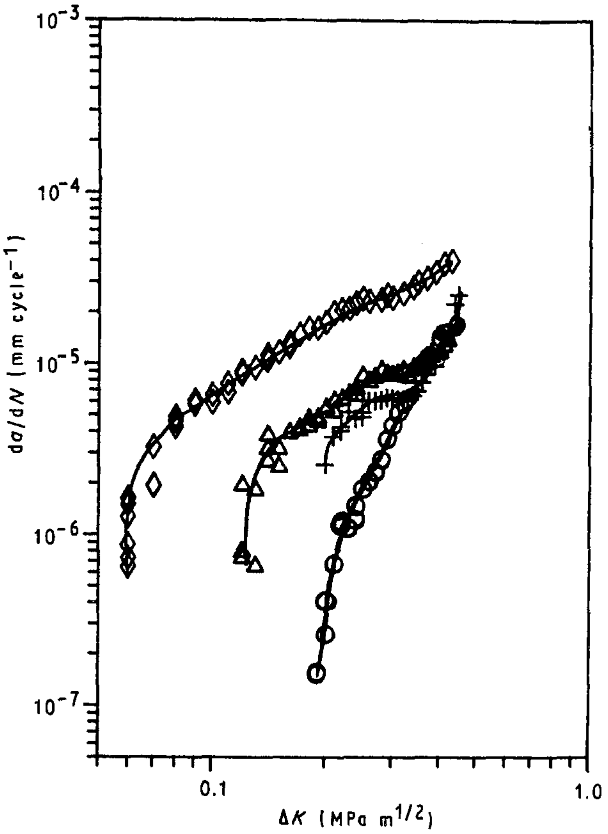

Figure 6 $K^c_{max} = 0.52$ MPa m$^{1/2}$ test results. Note the definite improvement in fatigue resistance with decreasing M_w under K^c_{max} conditions: ○ low-M_w (8×10^4), (+) medium-M_w (2×10^5), (△) high-M_w (4×10^5) and (◇) cross-linked.

growth rates, but had a greater ΔK_{Th} than the original low-M_w material.

The ranking of fatigue resistance of the four materials differed dramatically when the samples were tested under K^c_{max} threshold test conditions (Fig. 6). In this instance the low-M_w sample exhibited the most fatigue resistant behaviour over the entire range of ΔK examined, whereas the high-M_w material exhibited the worst response for the case of the linear resins tested. The cross-linked sample clearly exhibited the lowest level of fatigue resistance of all of the materials tested, with $\Delta K_{Th} = 0.06$ MPa m$^{1/2}$.

These results indicate that a low-molecular weight, linear PMMA resin exhibits superior fatigue behaviour to that of a higher-molecular weight material in association with high R ratio test conditions. This surprising trend was also reported earlier by Clark *et al.* [29, 33] for a different PMMA resin. Furthermore, some preliminary research performed by Skibo [34] and work reported by Kubo *et al.* [35] tend to confirm these observations. The explanation for the surprising low-M_w/high-R effect has proved to be elusive. In fact, all of the factors mentioned previously could be used to predict the opposite result.

It is therefore necessary to re-examine the fracture of polymers at their molecular level to attempt to give a suitable explanation for their macroscopic fatigue response under high mean stress conditions. As fatigue involves the accumulation of damage over a period of time, the kinetics of the specific deformation mechanism at the molecular level should influence the fracture process. Kinloch and Young argued that chain scission is the rate-determining step in the failure process [10]. They supported this conclusion with studies by other researchers who utilized such experimental procedures as activation energy investigations, electron–spin resonance and infrared spectroscopy. Recent work by Plummer and Donald [36] demonstrates that craze damage initiated by disentanglements can be recovered, whereas scission dominated craze damage results in substantial and permanent damage to the chains.

In the polymer structure there will always exist some chains that are more highly stressed than others as a result of their morphology, orientation and degree of constraint. Consequently, these highly stressed chains will probably be the first to fracture. Once a primary bond is broken, the stress will be transferred to surrounding chains and a stress concentration will be formed at that site. Thus, chain scission will not be truly random, but will accumulate preferentially at the stress concentrator. Therefore, to improve the fatigue resistance of a material, the irreversible nucleation of molecular defects should be avoided in favour of the more preferred, high energy-dissipative process of chain slippage.

Clearly, the large number of entanglements found along each chain in the high-M_w materials will suppress viscous flow, thereby causing these chains to experience higher stresses than would arise in the low-M_w material. Hence, chain scission should be more likely to occur in a high-M_w material as opposed to a low-M_w material. Termonia and Smith [13] established a kinetic model for the tensile behaviour of polymers which predicted longer extension ratios for a medium-M_w material as opposed to a higher-M_w counterpart once these entanglements were taken into account. The precedents for the present experimental results can be seen from the opposing examples of cross-linking [37] and plasticization [23]. Lowering M_w can be compared with the addition of plasticizers, in that both aid in increasing viscous flow, and each would tend to increase potential energy absorption while acting to blunt the crack tip [22, 23, 38] Westbrook and Feller [39] developed a β-parameter which can be related to short-term versus long-time relaxation behaviour. Using this parameter, they observed that energy absorption due to viscous relaxations increased with decreasing M_w. Alternatively, physical cross-links of a high-M_w, linear material are analogous to chemical cross-links, in that they restrict viscous flow, thereby reducing both the toughness and the fatigue resistance under high mean stress conditions.

Therefore, it is our contention that, at the high-stress conditions that are present during high R-ratio and K^c_{max} test procedures, the mechanism of slippage plays a beneficial role in the overall fracture process (Fig. 7). At high mean stress levels, even chains that are in normally relaxed orientations may experience a stress sufficiently high to result in fracture. The added effect of the increased constraint found in the high-M_w material creates a local stress environment more suitable for chain scission (Fig. 7d). This detrimental constraint at the molecular level is also found in the cross-linked sample. However, a linear, low-M_w material, having fewer constraints, is more able to compensate for this high stress by chain slippage (Fig. 7b).

This scenario is in contrast to what may occur for the case of $R^c = 0.1$ test conditions. In this low-stress situation there are fewer chains experiencing the critical fracture stress as a result of unfavourable orientation. Therefore, the increased constraint found in the high-M_w material is no longer a liability, but rather a distinct asset in that excessive chain slippage is suppressed (Fig. 7c).

The importance of M_w and mean stress, as well as their respective influence on prevailing deformation mechanisms during fatigue cycling, may be viewed by considering the schema shown in Fig. 8. Here the relative fatigue resistance of a polymer is shown as an inverse function of M_w. (Note: ΔK^* represents the ΔK level to drive the crack at some given velocity, 5×10^{-6} mm cycle^{-1} in this instance.) Considering first the case of low R-ratio test conditions (curve a), the FCP resistance of linear resins increases continually with increasing M_w. Although no maximum in FCP resistance was reported in this or earlier studies, one is assumed to exist. This assumption is based on the lower FCP resistance of the cross-linked form of the PMMA resins. As such, we contend that chain slippage becomes increasingly more difficult to achieve at some undefined higher M_w with the result that these extensive amounts of physical entanglements essentially simulates the restrictive role of cross-linking sites on chain slippage. The vertical broken line then represents the boundary about which either chain scission or chain entanglement dominates. With increasing mean stress (higher R-ratios), the ΔK^*–$1/M_w$ curve is seen to shift to the right (curve b), along with the aforementioned mechanism transition boundary. In this study the intersection of curves A and B corresponds to the similar FCP response of the lowest M_w

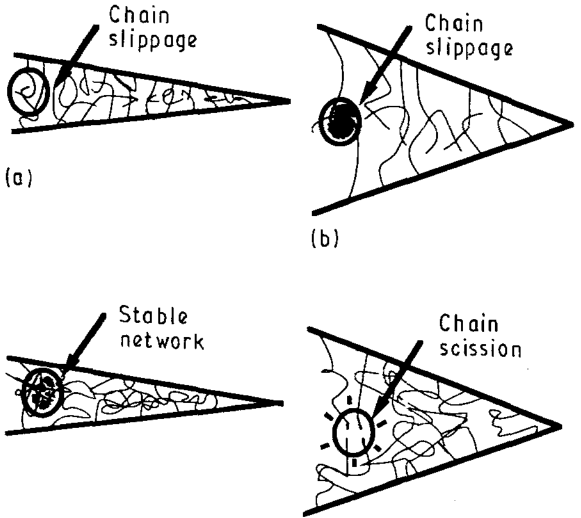

Figure 7 Schematic diagram showing the fatigue processes in each M_w/R-ratio condition: (a) low-M_w/low-R, (b) low-M_w/low-K_{max}, (c) high-M_w/low-R and (d) high-M_w/high-K_{max}.

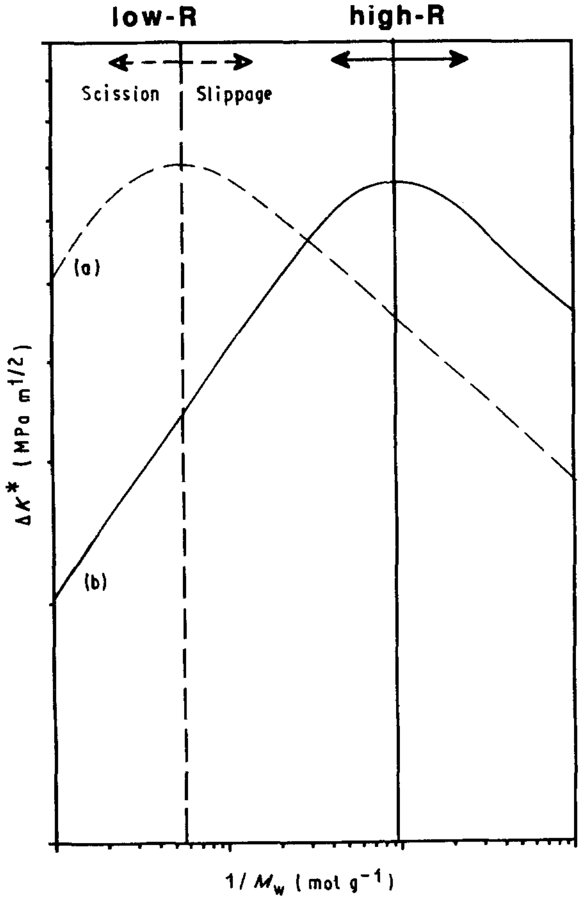

Figure 8 Schematic diagram of ΔK^* versus $1/M_w$. Note the expected shift of the curve to the right with increasing R-ratio: (– – –) low R and (——) high R.

(82 000 g mol^{-1}) resin under both R^c = 0.1 and K^c_{max} = 0.52 MPa m$^{1/2}$ test conditions (Fig. 9). One may speculate that curve B would shift back to the left at higher test temperatures, at lower cyclic test frequencies and/or with increased plasticizer content, in association with enhanced levels of chain disentanglement.

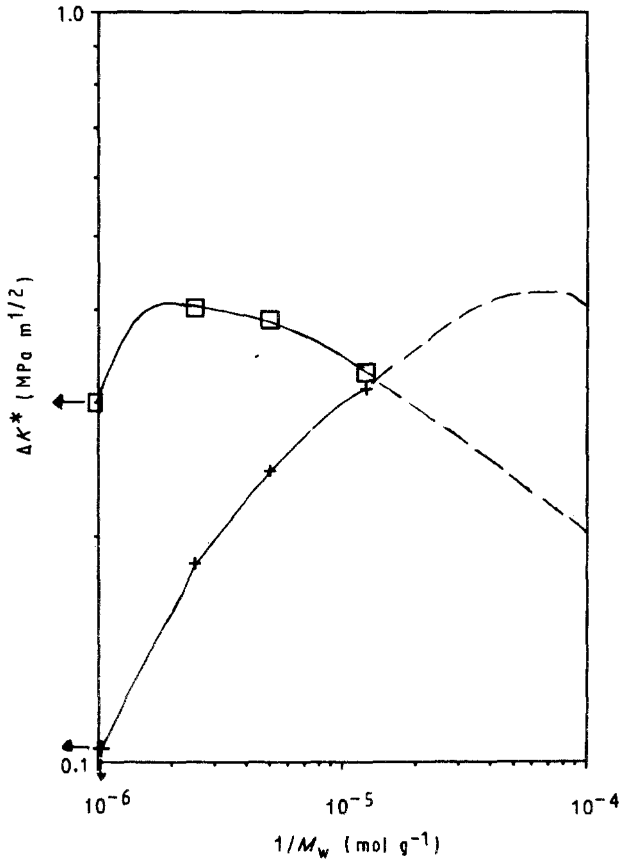

Figure 9 Plot of ΔK^* versus $1/M_w$ for both the R^c and K^c_{max} data. Note how the peak has shifted to the right with increasing mean stress: (□) R = 0.1 and (+) K_{max} = 0.52 MPa m$^{1/2}$.

5. Fractography

The explanations presented are further supported by an investigation of the fracture surface. Under R^c = 0.1 test conditions DGBs are present in the low-, medium- and high-M_w samples (Fig. 10e–g); however there are no DGBs observed in the cross-linked sample (Fig. 10h). This is not surprising since DGBs are not expected to occur in cross-linked materials due to the large amount of constraint induced by the cross-links. The same samples tested under K^c_{max} test conditions are less likely to exhibit DGBs (Fig. 10a–d). While DGBs are still present on the low-M_w sample (Fig. 10a), none of the other samples demonstrate this particular fatigue mechanism. This result follows the reasoning discussed previously. When a chain that has many entanglement points (physical or chemical) is exposed to a high stress (as is present in a K^c_{max} threshold test) there is a much greater likelihood that chain scission will occur before slippage, and result in a stress concentrator on the molecular level, while absorbing little energy in the process. Chain slippage-dominated DGB formation would, therefore, be suppressed.

6. Conclusion

The viscoelastic response of polymers is complex and is a direct result of the competition between two deformation micromechanisms; namely, chain slippage and chain scission. Changes in M_w and mean stress are shown to affect this competition for conditions of cyclic loading. Although R^c = 0.1 test results

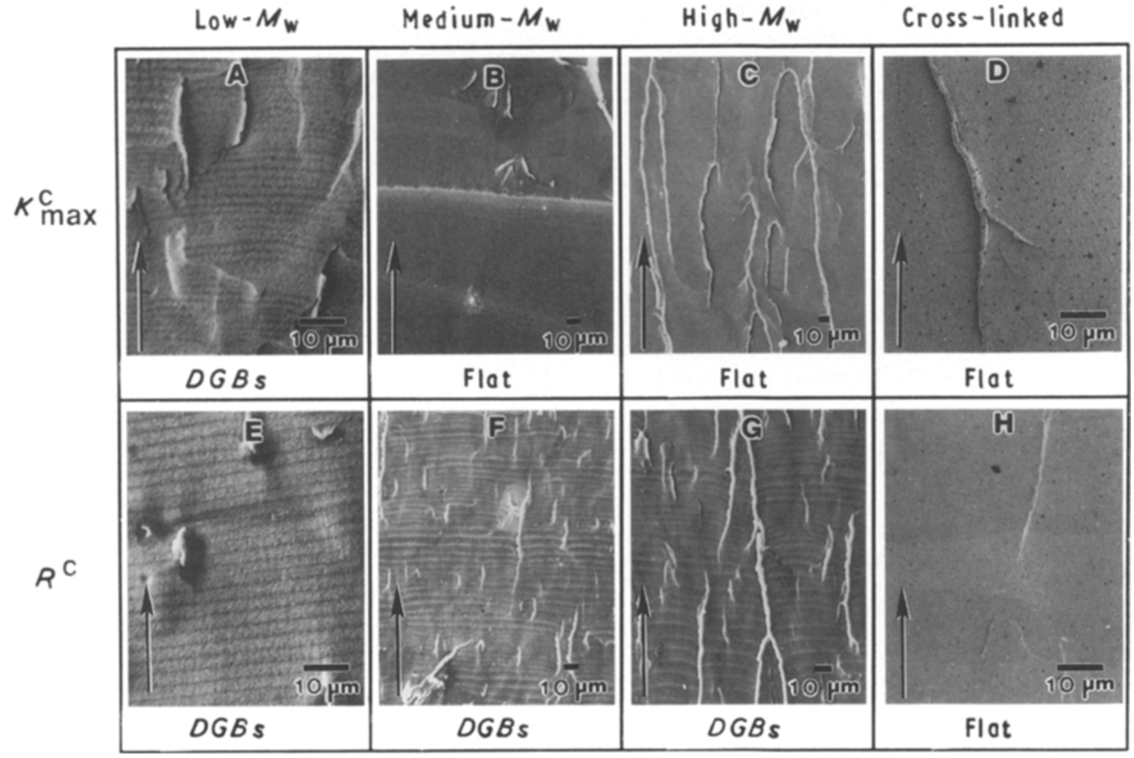

Figure 10 Influence of M_w and R-ratio on the fracture surface of PMMA. Note that DGBs disappear as M_w and cross-linking increase and as the mean stress increases.

confirmed the increasing fatigue resistance of PMMA resins with increasing M_w, K^c_{max} results demonstrated that the fatigue resistance actually increases with decreasing M_w at high mean stress levels. This unexpected result is explained by an examination of the competition between chain scission and chain slippage at the crack tip. At low mean stress levels, the large amount of entanglements associated with long molecular chains act to suppress slippage, thereby increasing craze stability and improving fatigue crack resistance.

In contrast, it is believed that these entanglements become detrimental at the high mean stress levels found during K^c_{max} testing. In this instance large numbers of entanglements encourage high chain stress and hinder beneficial energy absorption associated with molecular slippage. This point was further demonstrated by the poor FCP resistance exhibited by the cross-linked form of the low-M_w material.

Fractographic results are consistent with our explanation of this M_w/R effect. Enough chain mobility under $R^c = 0.1$ threshold test conditions was apparent in all but the cross-linked sample to allow for the formation of DGBs. However, under K^c_{max} threshold test conditions, DGBs were observed only in the low-M_w sample. This reflects the shift in dominating deformation mechanism from chain slippage (in the case for low entanglement density and low mean stress conditions) to chain scission (for high chain entanglement density and high mean stress conditions.)

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