Effects of Mean Stress and Frequency on Fatigue Crack Propagation in Rubber-Toughened Polycarbonate/Copolyester Blends

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SYNOPSIS

The effects of an impact modifier, mean stress level, and test frequency on the fatigue crack propagation rate in a miscible amorphous blend of polycarbonate and a copolyester were investigated. Experiments were performed on a servohydraulic testing machine, in load control, using a sinusoidal waveform. The addition of a small amount of impact modifier improved the fatigue resistance of the blend. Fatigue crack propagation rate, da/dN, at any value of crack tip stress intensity factor range, ΔK, in the impact modified blend, was more than a factor of 20 lower than that in the untoughened blend. Significantly more plastic deformation occurred on the fracture surface of the toughened blend than on that of the untoughened blend. The effect of mean stress level on da/dN was determined by varying the minimum-to-maximum stress ration, R, from 0.1 to 0.5. Plots of $\log(da/dN)$ vs. ΔK showed that the fatigue crack propagation rate was unaffected by R and, consequently, the mean stress level. The effect of frequency on da/dN was determined by varying the frequency from 0.25 to 25 Hz. The fatigue resistance of the untoughened blend was not affected by test frequency, whereas the fatigue resistance of the toughened blend increased with increasing frequency. Hysteretic heating at the crack tip was minimal at the highest frequency. The frequency sensitivity of the toughened blend was explained in terms of creep-assisted crack growth. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The performance of glassy thermoplastics in notched impact tests can be improved dramatically by the addition of a rubbery phase.[1] These toughened thermoplastics are often more resistant to fatigue crack propagation (FCP) than their unmodified forms.[2–5] It is well known that FCP rates in engineering plastics may be affected by material variables, such as composition, molecular weight, crystallinity, cross-linking, and thermal history.[2] However, FCP rates may also be affected by experimental parameters, such as mean stress level, test frequency, waveform, and temperature.[2,5–10] The objective of this work was to determine the effects of an impact modifier, mean stress level, and frequency on FCP rates in a miscible amorphous blend of polycarbonate with an aromatic copolyester.

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A fracture mechanics approach is commonly used to describe fatigue crack propagation in engineering plastics. FCP rate per cycle, da/dN, is often related to the applied crack tip stress intensity factor range ΔK ($= K_{max} - K_{min}$) through the well-known Paris equation

$$da/dN = A(\Delta K)^m \tag{1}$$

where A and m are constants. In general, the stress intensity factor is given by

$$K = \sigma\sqrt{\pi a}\,Y(a)$$

where σ is the applied stress, a is crack length, and $Y(a)$ is a geometry factor. The mean stress intensity level, K_m, is related to ΔK through the following relationship

$$K_m = 0.5\,\Delta K\,\frac{(1+R)}{(1-R)}$$

Table I Molecular Weights of Polymers Used in This Work

Blend	Component	M_n ($\times 10^{-4}$ g/mol)	M_w ($\times 10^{-4}$ g/mol)
Neat	COP	2.36	4.34
	PC	0.70	2.00
Toughened	COP	2.18	4.01
	PC	0.67	2.02

where R is the minimum-to-maximum stress ratio ($= \sigma_{min}/\sigma_{max}$). The effect of mean stress on da/dN can be easily determined by comparing da/dN at the same ΔK, but varying values of R. Arad et al.[11] have suggested that FCP rates, recorded at varying mean stress (or stress ratio) values, can be normalized using the relationship

$$da/dN = B\lambda^n \tag{2}$$

where

$$\lambda = K_{max}^2 - K_{min}^2$$

Table II Compliance Coefficients[17]

c_0	1.0010
c_1	−4.6695
c_2	18.460
c_3	−236.82
c_4	1214.9
c_5	−2143.6

and B and n are constants. Since $\lambda = 2\,\Delta K \times K_m$, eq. (2) can be rewritten as

$$da/dN = B'(\Delta K \times K_m)^n$$

The parameter λ is related to the cycle potential energy release rate, ΔG, by

$$\Delta G = \lambda / E$$

where E is the Young's modulus. Thus, eq. (2) may also be rewritten as

$$da/dN = BE^n(\Delta G)^n \tag{3}$$

A modified form of eq. (3), proposed by Chow and Lu,[12,13] is claimed to be capable of unifying all FCP

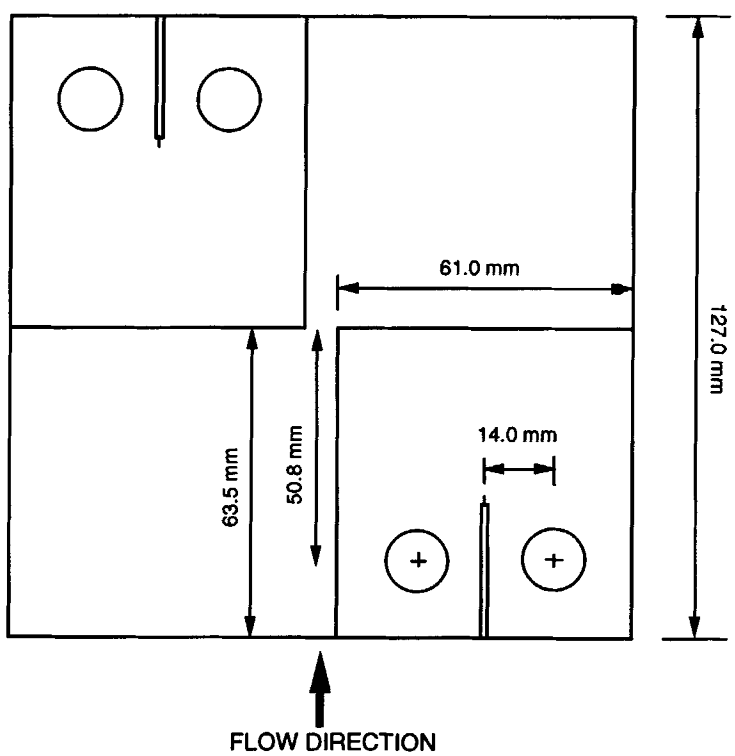

Figure 1 Diagram showing positions from which compact tensions were machined from injection-molded plaques.

data, regardless of material or mean stress level. This relationship is given by

$$da/dN = \frac{C(\Delta G)^D}{(G_c - G_{\max})} \quad (4)$$

where G_c is the critical strain energy release rate. Chow and Lu[12] have shown that FCP data from such diverse materials as poly(methyl methacrylate), poly(vinyl chloride), polystyrene, mild steel, and aluminium alloys can be normalized with eq. (4). The applicability of equations (1), (2), and (4) to fatigue crack propagation in rubber-toughened blends will be investigated in this work.

Fatigue crack propagation may also be affected by test frequency. Several investigators[2,8-10] have shown that for some polymers da/dN is insensitive to frequency, whereas in others it decreases with increasing frequency. Two possible explanations have been proposed for the latter behavior: (1) creep-assisted crack growth is minimized at the higher frequencies, and (2) hysteretic heating at the crack tip causes a localized temperature increase, which leads to crack tip blunting. Hertzberg and coworkers[2,8,9] also have shown that for many polymers, the degree of frequency sensitivity can be correlated with the dynamic mechanical losses associated with a secondary transition; the strongest frequency sensitivity occurs when the test temperature is near the secondary transition. The general application of this observation will be explored in this work.

EXPERIMENTAL

Sample Preparation

The polycarbonate (PC) used in this study was Makrolon 2608 from Mobay Corporation. A copolyester (COP) of dimethyl terephthalate, with ethylene glycol and 1,4-cyclohexanedimethanol, was supplied by Eastman Chemical Company. The toughener was a commercially available core-shell impact modifier with a glassy shell, a rubbery core, and an average particle diameter of approximately 0.30 μm. Blends, with and without the impact-modifier, were compounded and then injection-molded into 6.3-mm thick plaques. Molecular weights of the PC and COP components of the blends were determined from the molded plaques, using a size exclusion chromatography technique developed by Miller et al.,[14] the molecular weights are listed in Table I.

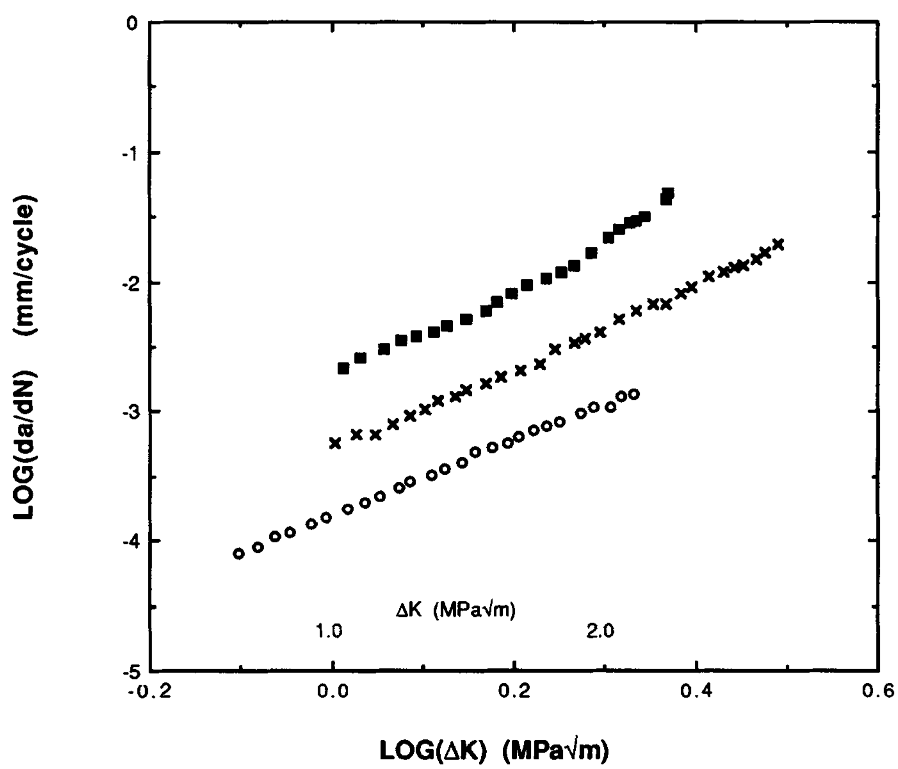

Figure 2 Log–log plot of da/dN vs. ΔK for the neat, (■), and toughened, (○), polycarbonate/copolyester blends, and polycarbonate, (×), at $R = 0.1$.

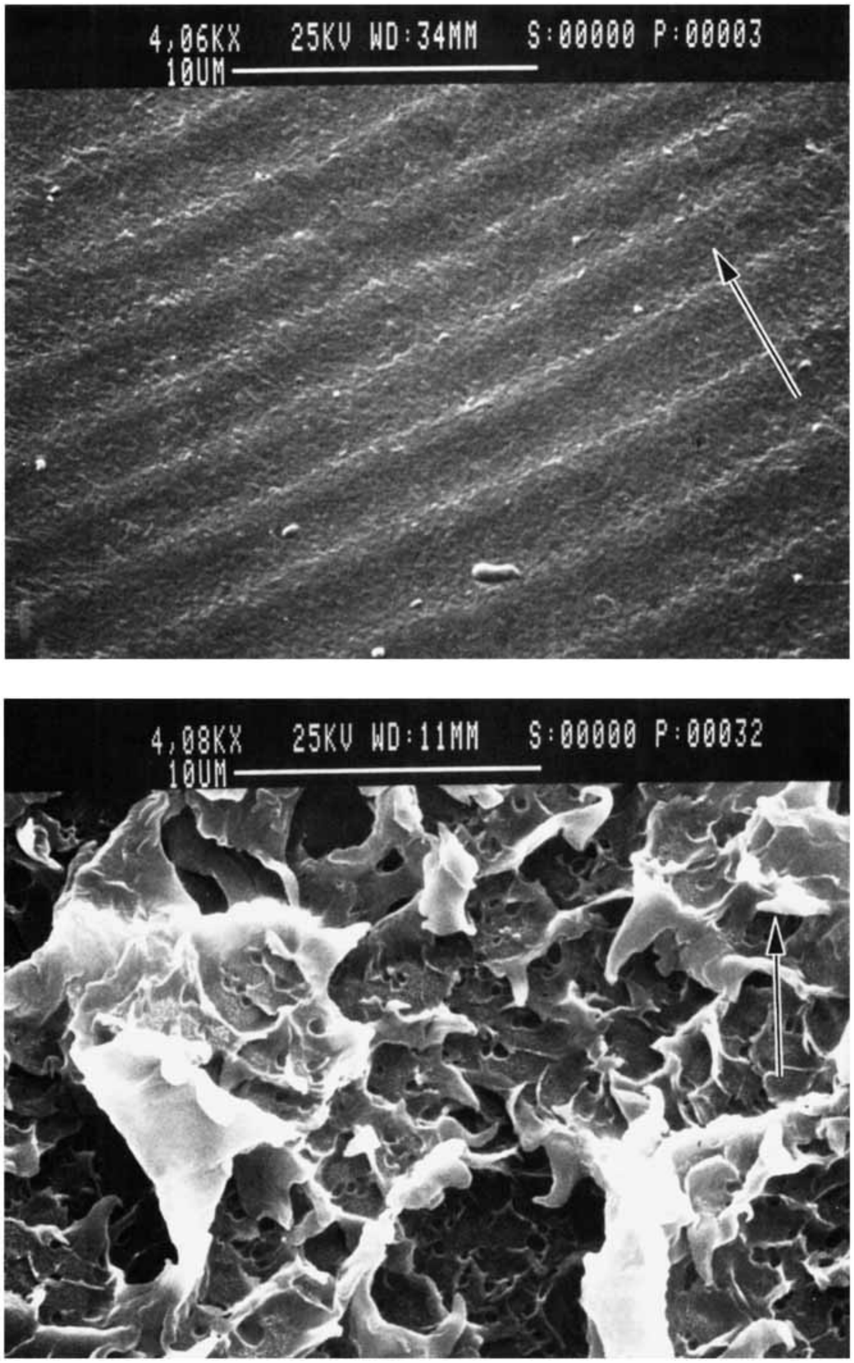

Figure 3 Scanning electron micrographs of fracture surfaces of (a) the neat blend, (b) the toughened blend, and (c) the toughened blend at higher magnification. Arrows indicate direction of crack growth.

Two compact tension (CT) specimens were machined from each plaque, as shown in Figure 1. The specimen width, W, was defined as the distance from the center of the loading pin holes to the back face of the specimen and was equal to 50.8 mm for all specimens used in this work. Specimens were notched with a band saw. The notch root was subsequently sharpened by controlled insertion of a razor blade. The notch length, a, was defined as the distance from the center of the loading pin holes to the tip of the notch. All specimens were notched along the mold-flow direction.

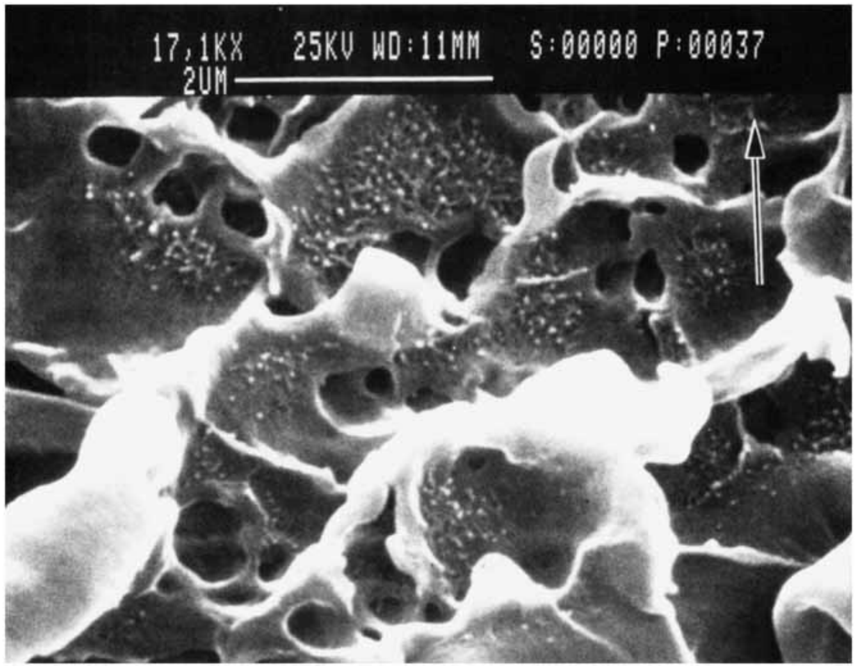

Figure 3 (*Continued from the previous page*)

Fatigue Crack Propagation

Fatigue tests were performed at room temperature on a MTS closed-loop servohydraulic testing machine, in load-control, using a sinusoidal waveform. Experiments on the effect of mean stress were performed at a frequency of 10 Hz, using stress ratios ranging from 0.1 to 0.5. Experiments on the effect of frequency were performed at a stress ratio of 0.1, using frequencies ranging from 0.25 to 25 Hz. Crack length was measured using an elastic compliance technique. Crack length is related to compliance of the CT specimen by the following relationship

$$a/W = c_0 + c_1 u_x + c_2 u_x^2 + c_3 u_x^3 + c_4 u_x^4 + c_5 u_x^5$$

where c_0, c_1, c_2, c_3, c_4, and c_5 are compliance coefficients and u_x is given by

$$u_x = \left[\sqrt{\frac{BEV}{P}} + 1 \right]^{-1}$$

where B is specimen thickness, E is elastic modulus, and V/P is the slope of the load-displacement data recorded during the experiment. Displacement data were recorded using a clip gage, which was mounted to the front face of the compact tension specimen. Compliance coefficients for this mounting geometry are given in Table II. An Aegma Model 470 Thermovision Camera was used to monitor temperature changes during the fatigue crack propagation experiments.

Fatigue crack propagation rate, da/dN, was computed using an incremental polynomial method that fits a second-order polynomial to sets of seven successive data points. Details of this method can be found in ASTM Standard E647-88a.[15] The stress intensity factor range for Mode I loading of a CT specimen is given by

$$\Delta K = \frac{\Delta P(2 + \alpha)}{(B\sqrt{W})(1 - \alpha)^{3/2}} (0.886 + 4.64\,\alpha - 13.32\,\alpha^2 + 14.72\,\alpha^3 - 5.6\,\alpha^4)$$

where P is load and α equals a/W. Each set of FCP data shown in this work was recorded from one specimen only. Repeat experiments yielded values of da/dN, at any value of ΔK, that agreed to within ±20%. All experiments on the neat (untoughened) blend were terminated at unstable crack propagation and all experiments on the toughened blend were terminated before instability, when the clip gage reached saturation.

Dynamic Mechanical Analysis

Dynamic mechanical spectra were recorded at 10 Hz on a Polymer Laboratories Thermal Analyzer.

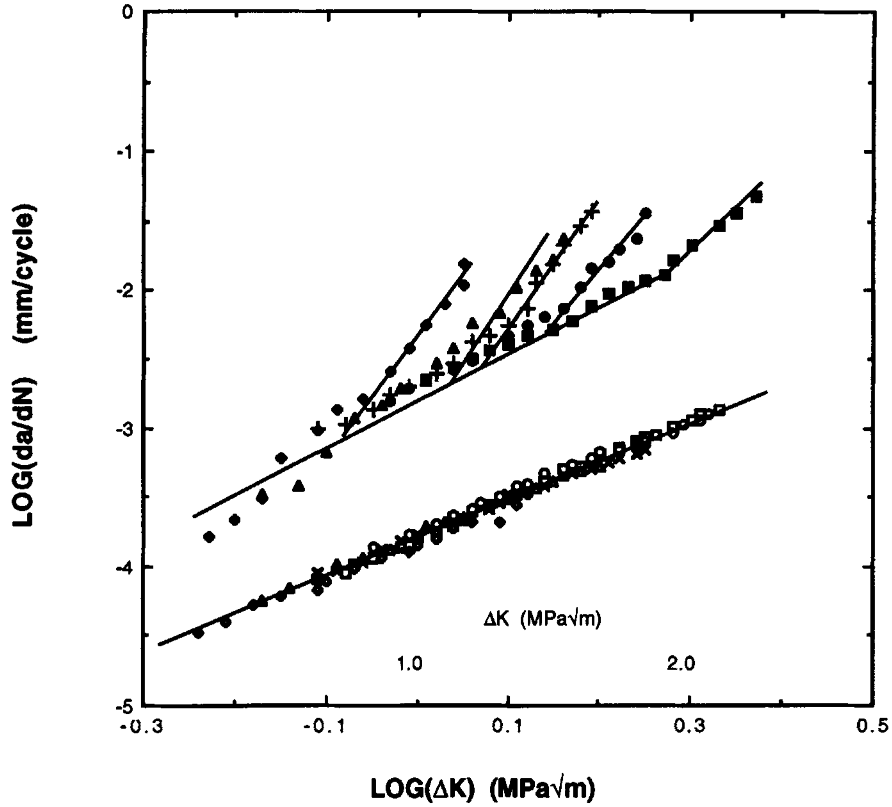

Figure 4 Log–log plot of da/dN vs. ΔK for the neat and toughened blends as a function of R-ratio. Neat blend: (■) 0.1, (●) 0.2, (+) 0.3, (▲) 0.4, (♦) 0.5. Toughened blend: (□) 0.1, (○) 0.2, (×) 0.3, (△) 0.4, (◇) 0.5.

Fractography

Scanning electron micrographs were obtained on a Cambridge Instruments Stereoscan 200 scanning electron microscope. The fracture surfaces were coated with a thin layer of gold in a sputtering chamber before the SEM observations.

RESULTS AND DISCUSSION

Effect of Impact Modifier

Fatigue crack propagation rates for the neat and toughened blends, recorded at a stress ratio of 0.1, are shown in Figure 2. FCP rates for polycarbonate are also shown for reference. At any particular value of ΔK, da/dN in the toughened blend is approximately a factor of 20 lower than that in the neat blend. Since the molecular weights of the polycarbonate and copolyester components of the neat and toughened blends are nearly identical (see Table I), the difference in FCP rates can be attributed solely to the impact modifier. Scanning electron micrographs of fracture surfaces of the neat and toughened blends are shown in Figures 3(a) and 3(b), respectively. In Figure 3(a), the fracture surface is relatively smooth and equally spaced striations are clearly evident. In Figure 3(b), however, the fracture surface shows a high degree of ductility and numerous holes approximately the size of the impact modifier. These observations suggest that the rubber particles have cavitated or debonded from the matrix. This would relieve the unfavorable triaxial stress field in the center of the material and would

Table III Onset of Rapid Crack Propagation in Neat Blend

Stress Ratio	ΔK (MPa$\sqrt{m}$)	K_{max}[a] (MPa$\sqrt{m}$)
0.1	1.85	2.05
0.2	1.48	1.85
0.3	1.19	1.70
0.4	1.10	1.83
0.5	0.87	1.74

[a] $K_{max} = \Delta K/(1 - R)$.

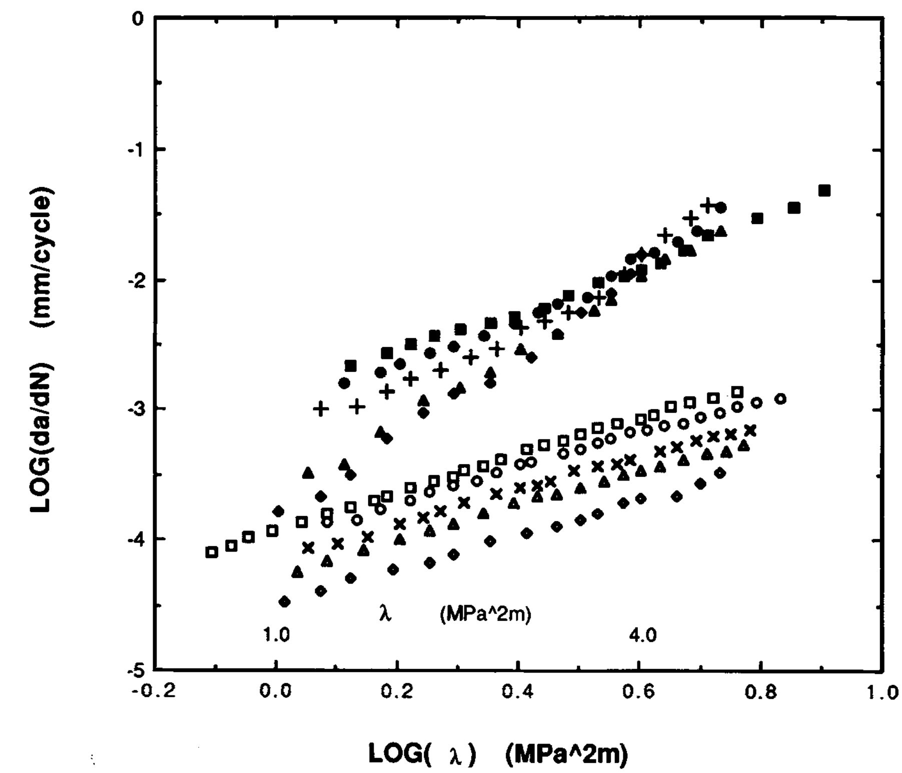

Figure 5 Log–log plot of da/dN vs. λ for the neat and toughened blends as a function of R-ratio. Symbols are the same as in Figure 4.

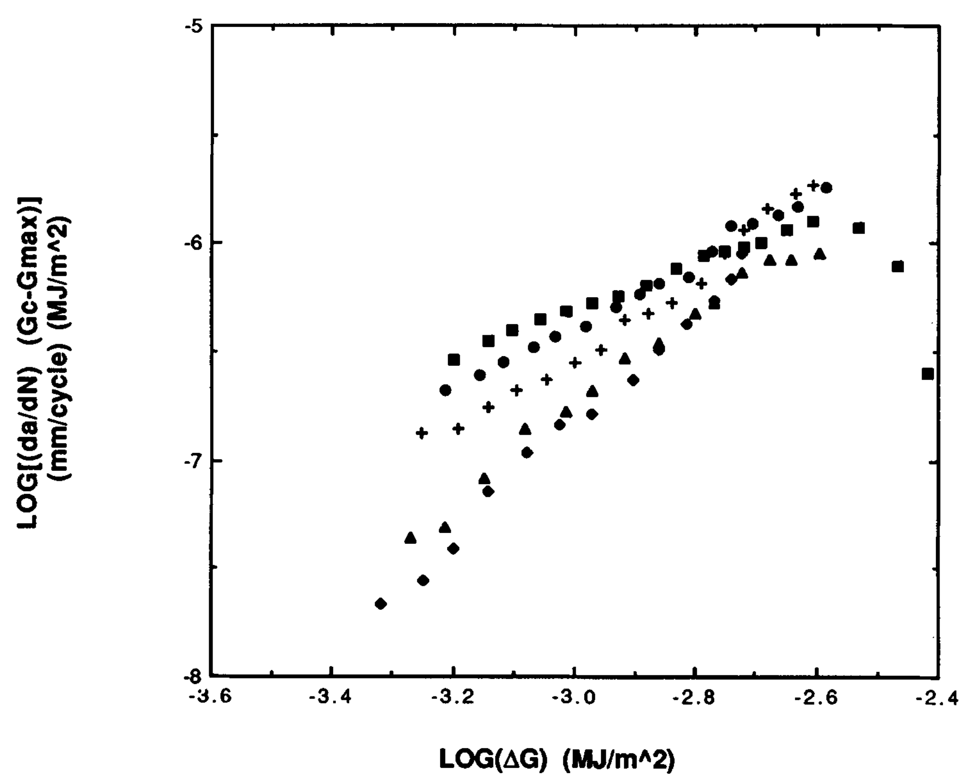

Figure 6 Log–log plot of $(da/dN)(G_c–G_{max})$ vs. ΔG for the neat blend. Symbols are the same as in Figure 4.

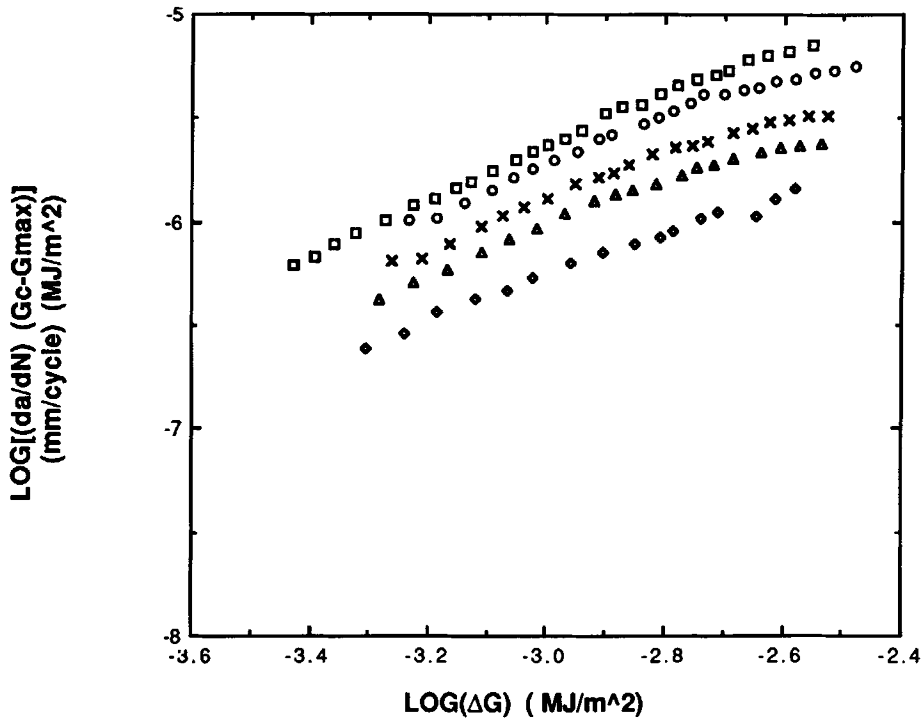

Figure 7 Log-log plot of $(da/dN)(G_c\text{-}G_{max})$ vs. ΔG for the toughened blend. Symbols are the same as in Figure 4.

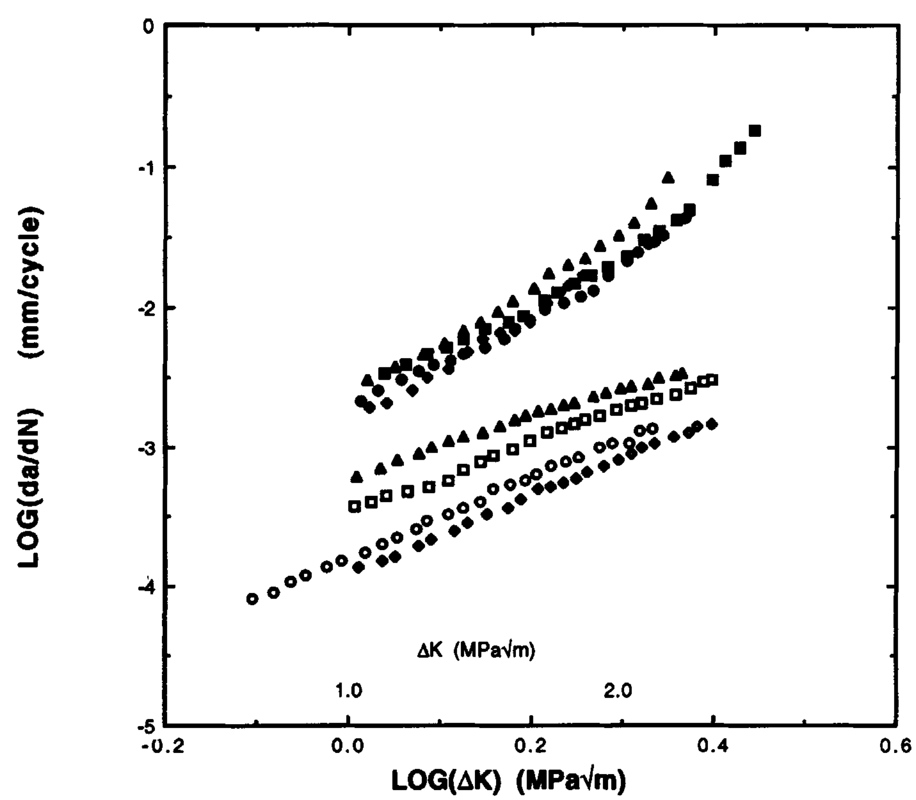

Figure 8 Effect of frequency on FCP behavior of neat and toughened blends: Neat (▲) 0.25 Hz, (■) 1 Hz, (●) 10 Hz, (♦) 25 Hz; toughened (△) 0.25 Hz, (□) 1 Hz, (○) 10 Hz, (◇) 25 Hz.

allow the matrix to yield more easily. Thus the lower FCP rates in the toughened blend, relative to the neat blend, arise from the enhanced deformation, which occurs during fatigue crack propagation. A micrograph of the fracture surface of the toughened blend at a higher magnification is shown in Figure 3(c). In this micrograph, the remnants of what appear to be craze fibrils are seen around the voids left by the rubber particles. Evidently, crazes are initiated at the rubber/matrix interface and act as precursors to shear yielding of the matrix.

Effect of Mean Stress

Figure 4 shows data for the neat and toughened blends, recorded as a function of R, and plotted according to eq. (1). The effect of mean stress on da/dN can be determined by comparing FCP rates at the same ΔK, but varying values of R. For the toughened blend, the effect of mean stress is negligible. The behavior of the neat blend is somewhat more complicated. For each value of R, two regions of crack propagation are observed: a region of stable crack growth, which is described by eq. (1), and a region of rapid crack propagation at the higher values of ΔK. The regions of stable crack propagation from each set of data fall on the same straight line, indicating that mean stress does not affect fatigue crack propagation in the region described by eq. (1). However, the onset of rapid crack propagation occurs at progressively lower values of ΔK as the value of R is increased. It is interesting to note that the onset of rapid crack growth occurs at approximately the same value of K_{max}, regardless of the value of R, as shown in Table III.

In Figure 5, the data from Figure 4 are reanalyzed and plotted according to eq. (2). Clearly, parameter λ fails to normalize the fatigue data independent of

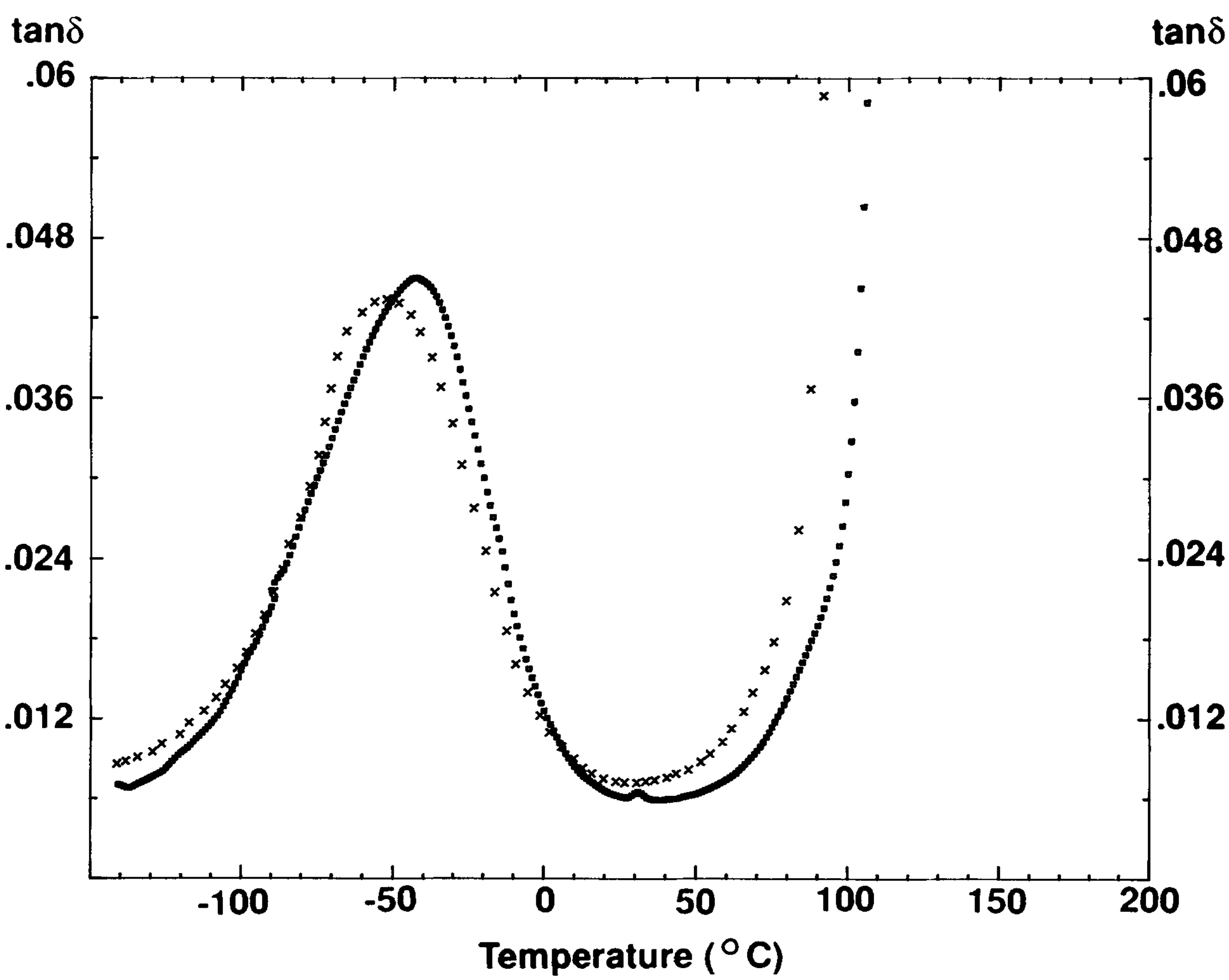

Figure 9 Dynamic mechanical spectra of the neat, (□), and toughened, (X), blends, recorded at 10 Hz.

mean stress. Analysis of the FCP data, according to eq. (4), is shown in Figures 6 and 7 for the neat and toughened blends, respectively. The value of G_c for the neat resin was 4.0 kJ/m^2 and the value of J_c ($= G_c$) for the toughened blend was 10.8 kJ/m^2.[16] The downturn in da/dN at large values of ΔG in Figure 6 is due to the fact that the rate at which $G_c - G_{max}$ is decreasing is higher than the rate at which da/dN is increasing. Contrary to the claims of Chow and Lu,[12,13] eq. (4) is not capable of providing a unique master curve for all materials independent of mean stress.

Effect of Frequency

Figure 8 shows the effect of frequency on da/dN in the neat and toughened blends. The fatigue resistance of the neat blend is not affected by changes in frequency, whereas the fatigue resistance of the toughened blend increases with increasing frequency. Hertzberg and coworkers[2,8,9] have suggested that frequency sensitivity can be attributed to the existence of a secondary relaxation at or near the temperature and frequency of the FCP test. Dynamic mechanical spectra of the two blends are shown in Figure 9. The neat blend has a secondary transition at approximately −50°C, which is well below the temperature of the fatigue tests. Furthermore, tan δ is at a minimum at the test temperature. Thus, hysteretic heating at the crack tip should be minimal, and the fatigue behavior of the neat blend should be insensitive to frequency. On the other hand, the dynamic mechanical spectrum of the toughened blend is practically identical to that of the neat blend (the slight deviations arise from underlying relaxations of the impact-modifier), and

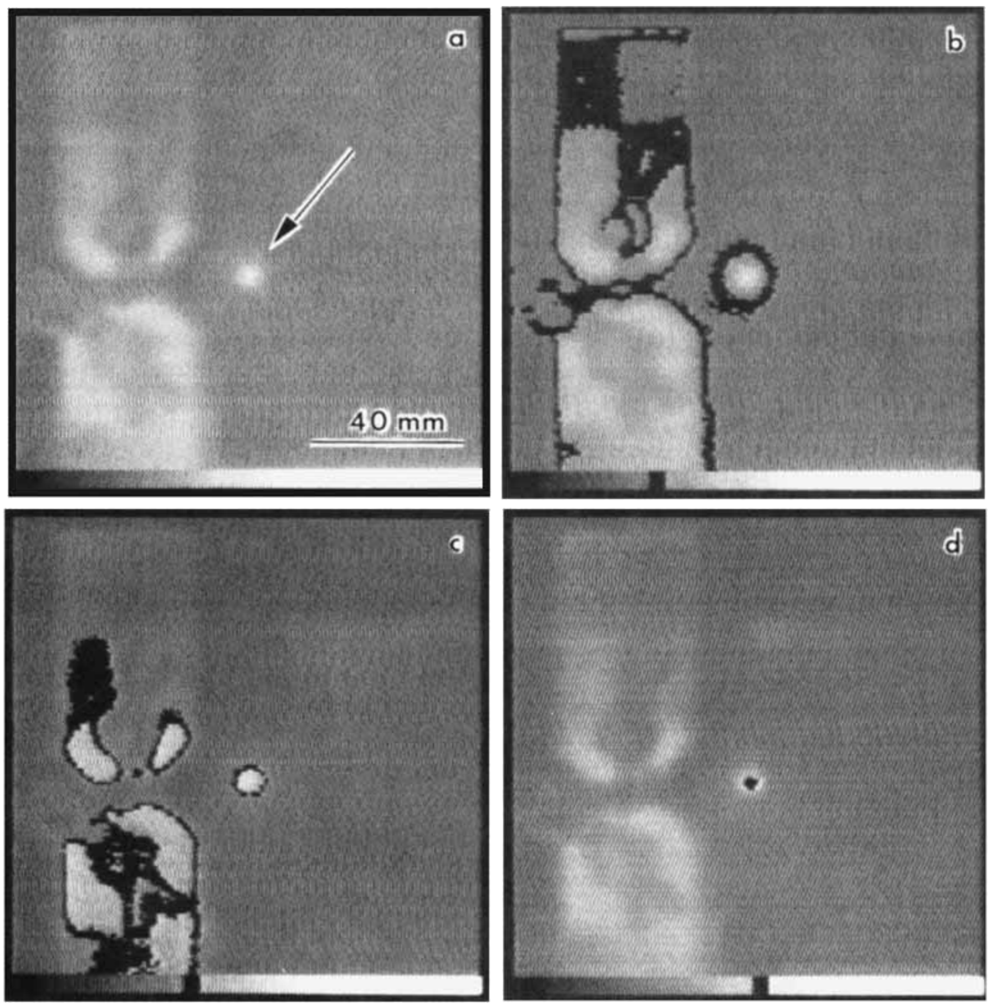

Figure 10 Thermogram of the toughened blend, recorded at a ΔK value of 1.5 MP$\sqrt{m}$, using a frequency of 25 Hz: (a) as recorded (arrow indicates crack tip), and digitally enhanced to show regions at (b) 25.6°C, (c) 27.8°C, and (d) 31.3°C.

yet the fatigue behavior of the toughened blend is significantly affected by frequency. To determine if hysteretic heating actually occurs, a thermography camera was used to monitor crack tip temperature during a fatigue experiment. A fatigue test was performed at a frequency of 25 Hz, the highest frequency used in this study, and a thermogram of the specimen was recorded at $\Delta K = 1.5$ MPa$\sqrt{m}$ [see Fig. 10(a)]. The various shades of gray in Figure 10(a) represent different temperatures. The grips and the crack tip region appear as light areas in the thermogram. The thermogram was digitally enhanced to show regions of constant temperature. In Figures 10(b), 10(c), and 10(d), the black pixels represent regions at temperatures of 25.6°C, 27.8°C, and 31.3°C, respectively. The ambient temperature was 23.3°C. These figures clearly show that the crack tip is the warmest region of the specimen. However, the increase in temperature was a modest 8°C. The temperature rise would be even lower at lower test frequencies. Thus, creep-assisted crack growth, and not hysteretic heating, would appear to be responsible for the frequency sensitivity of the toughened blend.

The overall fatigue crack propagation process can be described as a combination of creep-induced and cyclic-induced (or true fatigue) crack growth by[2,9,10]

$$\left(\frac{da}{dN}\right)_{\text{total}} = \left(\frac{da}{dN}\right)_{\text{fatigue}} + \left(\frac{da}{dt}\right)_{\text{creep}} \left(\frac{dt}{dN}\right)$$

where da/dt is the time period of oscillation (the inverse of the frequency in radians). Figure 11 shows a plot of the data for the toughened blend at a ΔK value of 1.5 MPa$\sqrt{m}$. The slope and the intercept of this plot represent contributions from creep damage (1.70 μm/s) and cyclic damage (0.46 μm/cycle), respectively. The contribution to crack growth from creep is the dominating factor at the lower frequencies. It should be noted that this approach does not take into account the effect of ΔK value on the fatigue process.

CONCLUSIONS

1. The fatigue resistance of a miscible amorphous polycarbonate/copolyester blend was enhanced by the addition of an impact modifier. Scanning electron micrographs showed that significantly more plastic deformation

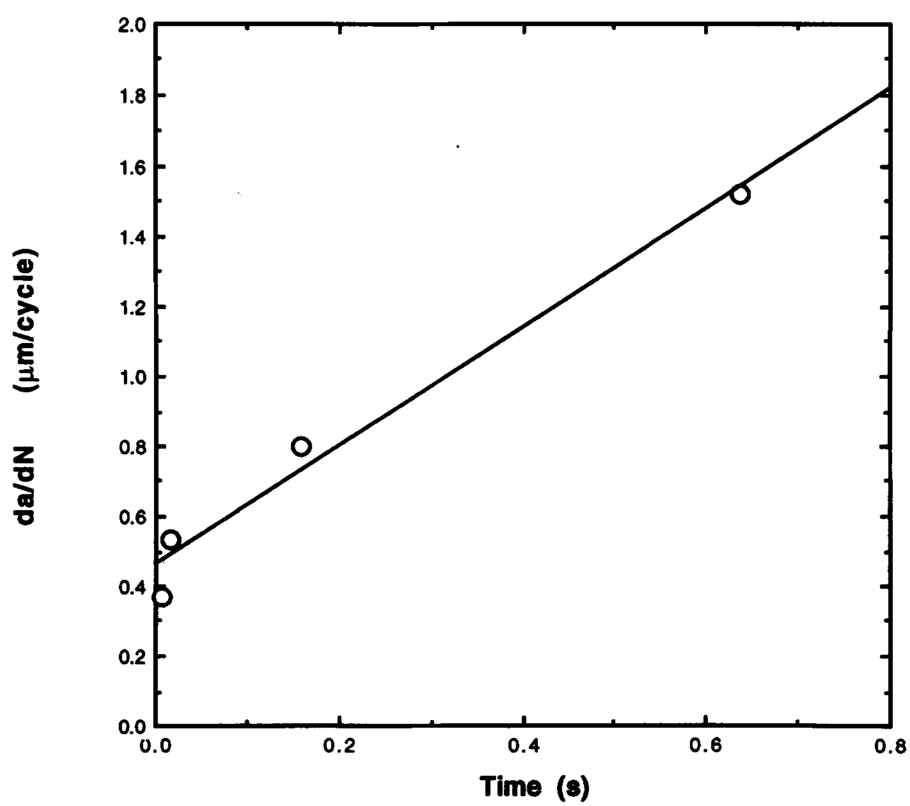

Figure 11 FCP rates for the toughened blend plotted vs. time period of oscillation.

occurred on the fracture surface of the toughened blend than on that of the neat bend.

2. Fatigue crack propagation data that was plotted vs. ΔK, according to the Paris equation, was not affected by varying stress ratio, and consequently mean stress. The relationships proposed by Arad et al.[11] and Chow and Lu,[12,13] however, failed to normalize da/dN data for mean stress.
3. The fatigue resistance of the neat blend was not affected by test frequency, whereas that of the toughened blend increased with increasing frequency. It was shown that hysteretic heating at the crack tip was minimal and that creep-induced crack growth could account for the enhanced fatigue resistance at the low frequencies.

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