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Effect of impact modification on slow crack growth in poly(vinyl chloride)

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The effect of impact modification on slow crack growth in a poly(vinyl chloride) (PVC) compound was examined in order to test a methodology for predicting long-term creep fracture from short-term tension-tension fatigue tests. In all cases the crack propagated in a stepwise manner through a crack tip craze zone. Step length was analyzed in terms of the Dugdale model for a crack tip plastic zone. The overall crack growth rate in fatigue and creep followed the conventional Paris power law with the same power 2.7, $\mathrm{d}a/\mathrm{d}t = A_\mathrm{f}\Delta K_\mathrm{I}^{2.7}$ and $\mathrm{d}a/\mathrm{d}t = BK_\mathrm{I}^{2.7}$, respectively. The effects of frequency, temperature, and R-ratio (the ratio of the minimum to maximum stress intensity factor in the fatigue loading cycle) on the Paris prefactor were determined. Crack growth rate was modeled as the product of a creep contribution that depended only on the maximum stress intensity factor and a fatigue contribution that depended on strain rate $\mathrm{d}a/\mathrm{d}t = B_\mathrm{f}K_\mathrm{I,max}^{2.7}(1 + C\dot{\varepsilon})$, where C is a coefficient defining the strain rate sensitivity. A linear correlation allowed for extrapolation of the creep prefactor B_f from fatigue data. Impact modification decreased B_f but had no effect on C. © *2004 Kluwer Academic Publishers*

1. Introduction

Field failures of PVC-based structural materials generally occur by slow crack growth under static loads that are well below the yield stress. Typically, a part fails catastrophically after a long period of apparently satisfactory performance. Because the long failure times often make testing of candidate materials under exact field conditions impractical, predictive methods are required. Predictive tests must be highly accelerated while at the same time retaining the fracture mechanism of field failure. Elevating the test temperature is one method of accelerating fracture, as exemplified by the PENT creep test (ASTM F 1473-94) specifically designed for predicting long-term failure of polyethylene gas pipe resins [1]. Alternatively, dynamic fatigue testing can accelerate fracture by many orders of magnitude compared to creep, and has the additional advantage that elevated temperatures are not required.

Numerous studies address the nature of fatigue crack propagation in PVC compounds [2–12]. The relationship between crack growth rate ($\mathrm{d}a/\mathrm{d}t$) and stress intensity factor K_I is often described by the empirical Paris relationship:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = A_\mathrm{f}\Delta K_\mathrm{I}^\mathrm{n} \tag{1}$$

where A_f is the Paris prefactor and ΔK_I is the change in stress intensity factor during one fatigue cycle ($\Delta K_\mathrm{I} = K_\mathrm{I,max} - K_\mathrm{I,min}$). The power n appears to be a constant for PVC compounds. Values range from 2.6 to 3.0 in most reports [3, 8, 10], and $n = 2.7$ is reported for PVC compounds independent of molecular weight [11, 12]. The prefactor A_f measures the resistance to slow crack growth and strongly depends on molecular weight and formulation [2, 12–15]. Increasing PVC molecular weight from 40,000 to 80,000 decreases the prefactor by three orders of magnitude from 50 to 0.06 μm s^{-1} (MPa$\sqrt{\mathrm{m}}$)$^{-2.7}$ at 23°C [12]. Impact modifiers that enhance resistance to fast crack propagation also increase resistance to fatigue crack propagation [14]. The magnitude of the effect depends on the amount of impact modifier and the molecular weight of the PVC resin.

Formulation of slow crack growth rate as expressed in Equation 1 does not accommodate data obtained

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at different frequencies [2, 3, 10, 16]. Moreover, Equation 1 may not describe the effect of changing mean stress under conditions of constant ΔK_I [2, 17]. Finally, Equation 1 does not apply to creep where $\Delta K_I = 0$. Correlation of creep and fatigue requires alternative formulations of slow crack growth kinetics.

Following an approach developed for exceptionally creep-resistant polyethylene resins [18, 19], where even the PENT test was impractical, a testing protocol was demonstrated for correlating fatigue and creep in PVC extruded pipe [11]. Extrapolation of crack growth rate from fatigue to creep was achieved by systematically decreasing the dynamic component in tension-tension fatigue tests. The total crack growth rate was described by a creep contribution that depended on stress intensity factor parameters and a fatigue contribution that depended on strain rate:

$$\frac{da}{dt} = B_f K_{I,max}^{2.7}(1 + C\dot{\varepsilon}) \quad (2)$$

where the term $(1 + C\dot{\varepsilon})$ is a fatigue acceleration factor that is a linear function of strain rate $\dot{\varepsilon}$. The magnitude of the coefficient C defines the strain rate sensitivity and, hence, the fatigue acceleration. At zero strain rate, Equation 2 reduces to the Paris relationship for creep in PVC:

$$\frac{da}{dt} = BK_I^{2.7} \quad (3)$$

with $B_f = B$. The fatigue-to-creep correlation for PVC pipe as formulated in Equation 2 was verified over the temperature range from 23 to 70°C [11].

Any prediction of creep performance from fatigue tests requires preservation of the mechanism of slow crack growth. Correlation in mechanism is inferred from a common exponent in the Paris laws for fatigue and creep, and is confirmed by examination of fracture surfaces. Mechanistically, the resistance to slow crack growth of tough polymeric materials is a consequence of their ability to relieve the stress concentration by forming a quasi-stationary damage zone at the notch root [2, 20–23]. The craze damage zone temporarily arrests the crack until the craze fibrils deteriorate enough to rupture. This can occur by apparently continuous fracture of craze fibrils at the crack tip and simultaneous lengthening of the craze damage zone. Alternatively, the craze can temporarily arrest the crack until the craze fibrils deteriorate enough for the craze to rupture, whereupon the crack jumps forward within a relatively small number of cycles. This results in periodic features known as steps or striations on the fracture surface. Both continuous [5, 7, 11] and stepwise [2, 4, 5, 10, 12] modes of crack propagation have been reported in PVC compounds.

At the molecular level, deterioration of craze fibrils occurs by a combination of disentanglement and scission of highly oriented chains in the craze fibrils [24–27]. In creep, disentanglement by the processes of chain slippage and pullout dominates as the mechanism of fibril failure. When the temperature is well below T_g and the molecular weight is relatively high, disentanglement is very slow and the time to creep failure is very long. Fatigue is seen as accelerating deterioration of craze fibrils by enhancing the rate of chain scission. Fatigue dramatically increases crack growth rate when disentanglement is very slow, as reflected by a large value of the factor C of Equation 2. Increasing temperature dramatically enhances the rate of disentanglement. Under these conditions, fatigue does not accelerate failure as strongly. Indeed, the factor C for PVC pipe decreases by an order of magnitude upon an increase in temperature from 23 to 70°C [11].

The present study tests the generality of the fatigue-to-creep correlation developed for PVC pipe with a lower molecular weight PVC compound where disentanglement occurs more easily. The specific compound chosen for investigation exhibits stepwise crack growth, in contrast to continuous crack growth found in PVC pipe [11, 12]. To extend the fatigue-to-creep correlation further, the effect of impact modification on the kinetics and mechanism of slow crack growth is examined.

2. Experimental

A PVC pipe fitting compound was prepared by compounding 100 parts of a PVC resin of $M_w = 56$ kg mol^{-1} and $M_n = 28$ kg mol^{-1} (Oxyvinyl) with 1.2 parts dimethyl tin 2-ethylhexyl thioglycolate, 1.2 parts paraffin wax, 0.3 parts oxidized polyethylene, 0.8 parts calcium stearate, 1 part acrylic processing aid, 1.5 parts titanium dioxide and 0.001 parts carbon black. An additional 10 parts Paraloid BTA 751 MBS (Rohm & Haas) was added to obtain the impact modified compound. Impact modification decreased the glass transition temperature (T_g) slightly from 83° to 81°C. The compounds were roll milled into sheets at 170°C and compression molded at 200°C into square plaques approximately 9 mm thick. Compact tension specimens 6 mm thick with all other dimensions in accordance with ASTM D 5045-93 were machined from the plaques as described previously [12]. In order to minimize the contribution of plain stress conditions near the edges the specimens were side grooved to a depth of 0.5 mm. Specimens were notched with a fresh razor blade at 1 μm s^{-1} at a temperature 4°C below T_g. The notch length was kept constant at 1.8 mm.

Mechanical fatigue units capable of applying a very stable and accurate load (±0.2 N) were used to conduct creep and tension-tension fatigue tests. The loading cycle defined the maximum, minimum and mean stress intensity factors at the notch root ($K_{I,max}$, $K_{I,min}$, and $K_{I,mean}$, respectively). Frequency was varied from 0.01 to 1.0 fatigue cycles per second. The R-ratio, defined as $K_{I,min}/K_{I,max}$, was also varied. A manual zoom macrolens attached to a video camera was used to record the crack length.

Fracture surfaces were examined for features of stepwise crack propagation in the optical microscope using bright field and normal incidence illumination. Resolution of striations was enhanced by coating the fracture surface with 15 nm of gold. The gold-coated fracture surfaces were also examined in a Jeol JSM 840A scanning electron microscope (SEM). The accelerator

voltage was 10 kV and the probe current was 6×10^{-11} A to minimize radiation damage to the specimens.

In a few instances strain rate at the crack tip was measured as described previously for PVC pipe [11]. Good correlation with previous results indicated that strain rate was not affected significantly by PVC molecular weight, and therefore strain rate values for the various fatigue loading conditions were taken directly from the previous study [11].

3. Results and discussion

3.1. Kinetics of crack growth

Experiments were carried out using different $K_{\mathrm{I,max}}$ for given conditions of temperature, frequency, and R-ratio. The crack length was monitored with a video camera during the fatigue experiment. Typical results for PVC compound at 25°C, frequency 0.5 Hz, and R-ratio 0.1 are shown in Fig. 1a. The data were fit to an exponential growth function, the slope of which determined the crack growth rate ($\mathrm{d}a/\mathrm{d}t$).

Data in Fig. 1a are plotted according to the Paris relationship, Equation 1, in Fig. 1b. Each experiment appears as a series of points because ΔK_{I} increased as the crack propagated. An initial region with crack growth rate slower than the steady state propagation rate was observed as a tail on each set of data. The steady state region conformed to the Paris relationship.

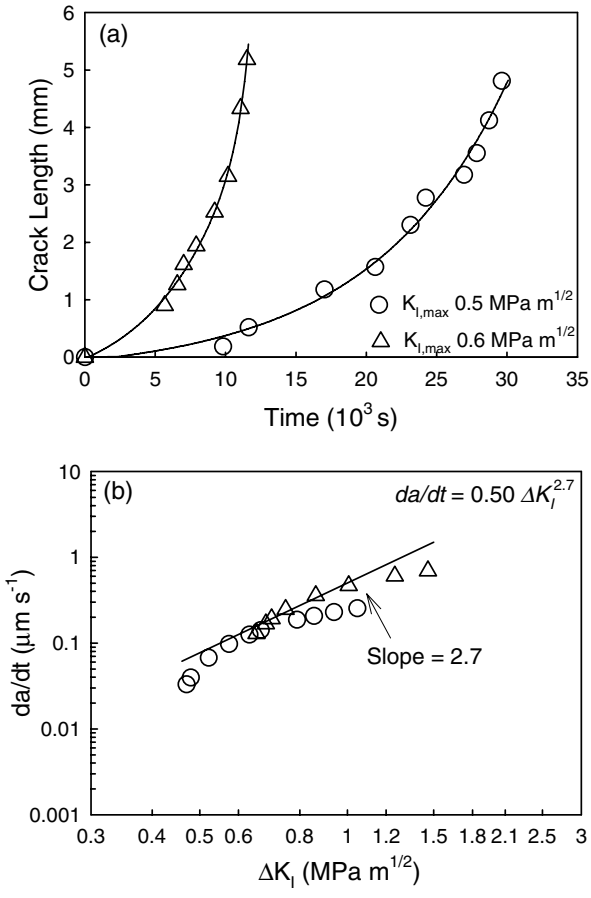

Figure 1 Fatigue crack propagation in PVC compound at 25°C, frequency 0.5 Hz and R-ratio 0.1: (a) Crack length as a function of fatigue time and (b) Paris plot of crack growth rate.

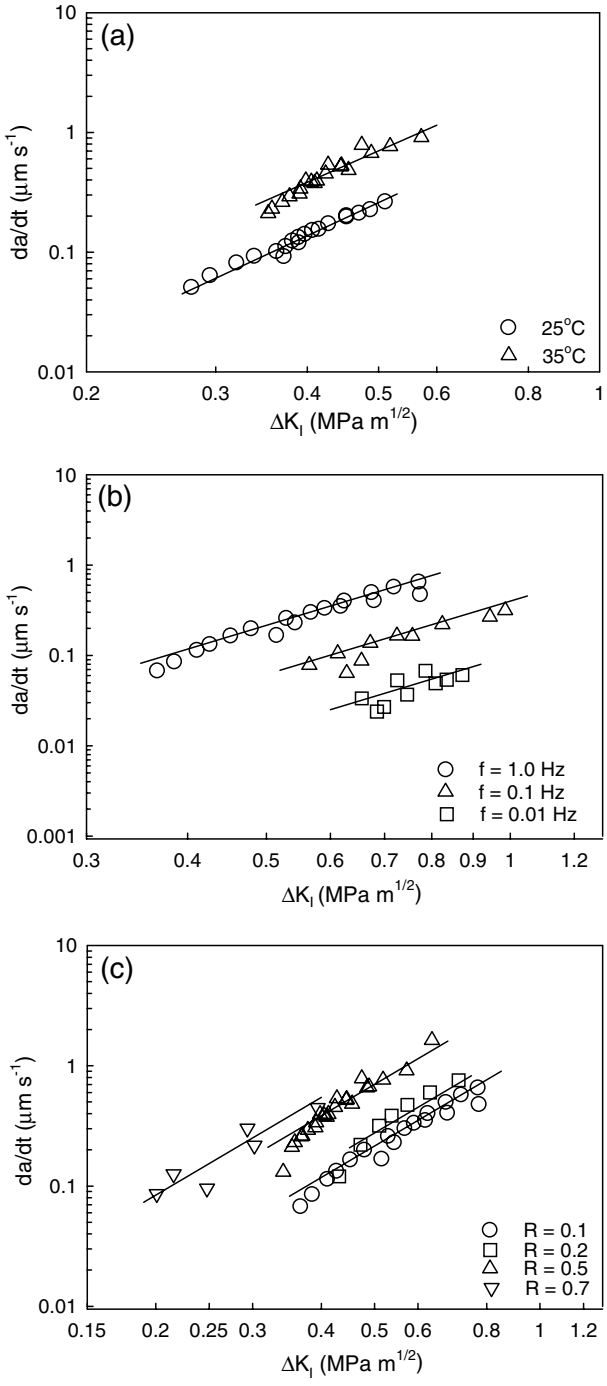

Figure 2 Paris plots for fatigue crack growth in PVC compound: (a) Effect of temperature at frequency 1.0 Hz and R-ratio 0.5, (b) effect of frequency at 35°C and R-ratio 0.1, and (c) effect of R-ratio at 35°C and frequency 1.0 Hz.

The slope provided the power n in Equation 1, and the crack growth rate at ΔK_{I} equal to unity defined the prefactor A_{f}. All the analyses utilized only data in the steady state region of crack propagation.

The effects of temperature, frequency and R-ratio on the kinetics of fatigue crack growth are shown in Fig. 2. In all cases, fatigue crack propagation followed the Paris relationship with the same power dependence on ΔK_{I}, $n = 2.7$. The power 2.7 was previously observed for PVC compounds of different molecular weight [12], for PVC pipe [11], and in other studies of PVC [3, 8, 10]. This feature is generally taken to indicate that the mechanism of fatigue crack propagation is the same

TABLE I Effect of loading conditions on the fatigue prefactors, A_f and A_{max}, for fatigue crack propagation in PVC compounds with M_w of 56,000

Loading condition	Strain rate [11] (s^{-1})	A_f $\mu m\ s^{-1}$ $(MPa\sqrt{m})^{-2.7}$	A_{max} $\mu m\ s^{-1}$ $(MPa\sqrt{m})^{-2.7}$
	PVC compound at 25°C		
R-ratio 0.1, $f = 1.0$ Hz	8.10	0.9 ± 0.1	0.7 ± 0.1
R-ratio 0.2, $f = 1.0$ Hz	6.00	1.3 ± 0.0	0.7 ± 0.0
R-ratio 0.1, $f = 0.5$ Hz	4.75	0.6	0.4
R-ratio 0.3, $f = 1.0$ Hz	4.00	1.2 ± 0.2	0.45 ± 0.07
R-ratio 0.5, $f = 1.0$ Hz	1.60	1.7 ± 0.0	0.26 ± 0.00
R-ratio 0.1, $f = 0.1$ Hz	0.95	0.18 ± 0.00	0.14 ± 0.00
R-ratio 0.7, $f = 1.0$ Hz	0.70	3.2 ± 1.4	0.13 ± 0.05
R-ratio 0.5, $f = 0.1$ Hz	0.25	0.7 ± 0.1	0.10 ± 0.02
R-ratio 0.1, $f = 0.01$ Hz	0.10	0.06 ± 0.00	0.04 ± 0.00
R-ratio 0.5, $f = 0.01$ Hz	0.04	0.23	0.04
	PVC compound at 35°C		
R-ratio 0.1, $f = 1.0$ Hz	5.30	1.5 ± 0.1	1.1 ± 0.05
R-ratio 0.2, $f = 1.0$ Hz	3.80	1.8	0.99
R-ratio 0.5, $f = 1.0$ Hz	1.76	4.6 ± 0.5	0.70 ± 0.07
R-ratio 0.5, $f = 0.5$ Hz	0.88	1.9 ± 0.2	0.28 ± 0.03
R-ratio 0.1, $f = 0.1$ Hz	0.60	0.36 ± 0.06	0.27 ± 0.04
R-ratio 0.7, $f = 1.0$ Hz	0.55	6.5 ± 0.1	0.25 ± 0.04
R-ratio 0.5, $f = 0.1$ Hz	0.20	0.8	0.12
R-ratio 0.1, $f = 0.01$ Hz	0.05	0.11 ± 0.04	0.08 ± 0.03
R-ratio 0.5, $f = 0.01$ Hz	0.02	0.26	0.04
	Impact modified PVC compound at 35°C		
R-ratio 0.1, $f = 1.0$ Hz	5.30	0.70	0.53
R-ratio 0.1, $f = 0.7$ Hz	3.90	0.55	0.41
R-ratio 0.2, $f = 1.0$ Hz	3.80	0.90	0.50
R-ratio 0.1, $f = 0.5$ Hz	2.80	0.50	0.38
R-ratio 0.3, $f = 1.0$ Hz	2.80	0.90	0.34
R-ratio 0.5, $f = 1.0$ Hz	1.76	1.20 ± 0.42	0.18 ± 0.065
R-ratio 0.1, $f = 0.1$ Hz	0.60	0.17	0.13
R-ratio 0.1, $f = 0.01$ Hz	0.05	0.04 ± 0.004	$0.03 \pm .003$

under different conditions of temperature and rate. On the other hand, PVC compounds were clearly differentiated by the prefactor A_f. Differences in A_f alone described the reduction in crack growth rate for PVC compounds of increasing molecular weight [12]. Effects of temperature and rate were also contained in A_f, Table I. The change in A_f with increasing temperature from 25° to 35°C represented approximately a doubling of the crack growth rate, Fig. 2a. Decreasing frequency or increasing R-ratio systematically reduced the dynamic component of fatigue loading and approached creep. The crack growth rate decreased significantly with decreasing frequency, Fig. 2b. At 35°C and R-ratio 0.1, the prefactor A_f at frequency 0.01 Hz was more than an order of magnitude lower than at frequency 1.0 Hz, Table I. Similar results were observed at 25°C. Varying R-ratio also affected crack growth rate, Fig. 2c. At 35°C and frequency 1.0 Hz, increasing R-ratio from 0.1 to 0.7 increased A_f by about a factor of 4, Table I.

The effect of impact modification on fatigue crack propagation rate of the PVC compound at two frequencies is shown in Fig. 3. Fatigue crack propagation followed the Paris relationship with the same power dependence on ΔK_I, $n = 2.7$, indicating that impact modification did not alter the mechanism of crack propagation. On the other hand, the effect of impact modification was clearly differentiated by the prefactor A_f. Impact modification retarded fatigue crack growth as indicated by a decrease in A_f from 1.5 to 0.7 $\mu m\ s^{-1}$ $(MPa\sqrt{m})^{-2.7}$ at 35°C, frequency 1.0 Hz,

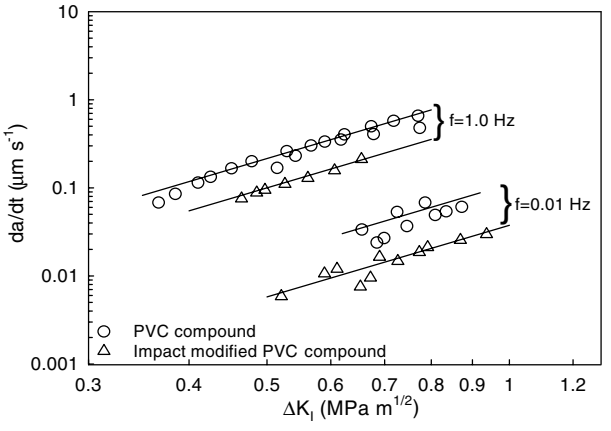

Figure 3 Effect of impact modification on fatigue crack propagation rate of PVC compounds at 35°C and R-ratio 0.1.

and R-ratio 0.1. Similar results were observed at frequency of 0.01 Hz and at other testing conditions. For most of the testing conditions, impact modification retarded the crack growth rate by 2 to 3 times as deduced from comparisons of A_f in Table I.

Creep crack propagation in PVC compound and impact modified PVC compound at 35°C conformed to Equation 3 with power 2.7 as observed previously for creep in PVC pipe [11]. Conservation of the power indicated that the mechanism of crack propagation was the same for fatigue and creep. Greater crack growth resistance of the impact modified compound was indicated by the decrease in creep prefactor B from 0.045 to 0.015 $\mu m\ s^{-1}$ $(MPa\sqrt{m})^{-2.7}$.

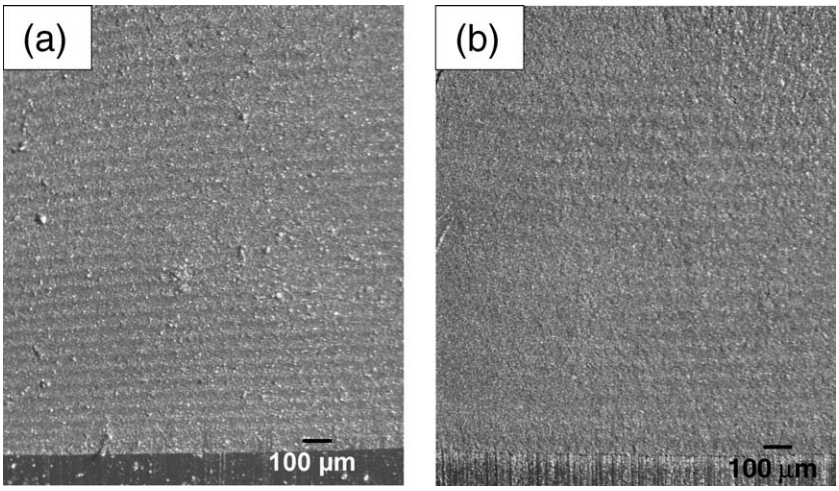

Figure 4 Fracture surface showing the steps at 35°C, frequency 0.01 Hz and R-ratio 0.1: (a) PVC compound at $K_{\mathrm{I,max}} = 0.6\ \mathrm{MPa}\sqrt{\mathrm{m}}$, and (b) impact modified PVC compound at $K_{\mathrm{I,max}} = 0.5\ \mathrm{MPa}\sqrt{\mathrm{m}}$.

3.2. Mechanism of crack growth

Periodic features known as steps or striations were observed on fatigue and creep fracture surfaces of PVC compounds used in this study, Fig. 4. Under similar loading conditions, the steps were about twice as long in the impact modified PVC compound. Consecutive periods of crack arrest and crack propagation create the striations. In the stepwise crack propagation mode, a craze forms ahead of the crack tip while the crack is arrested. The craze temporarily arrests the crack until the craze fibrils deteriorate enough for the craze to rupture, whereupon the crack jumps forward within a relatively small number of cycles.

A previous study of PVC compound determined that step jump length depended on $K^2_{\mathrm{I,max}}$ [12]. This was consistent with the Dugdale model prediction for the length of the plastic zone ℓ_{c} in a material of yield stress σ_{y} [28]:

$$\ell_{\mathrm{c}} = \frac{\pi}{8}\left(\frac{K_{\mathrm{I}}}{\sigma_{\mathrm{y}}}\right)^2 \tag{4}$$

provided that $K_{\mathrm{I}} = K_{\mathrm{I,max}}$ and also provided that the crack jumps through the entire craze zone (i.e., step length ℓ equals craze length ℓ_{c}). The dependence of step length on $K_{\mathrm{I,max}}$ at 35 and 25°C is plotted in Fig. 5 for different frequencies and R-ratios. Step length in impact modified PVC compound followed a $K^2_{\mathrm{I,max}}$ relationship for all $K_{\mathrm{I,max}}$ studied, as indicated by the solid line. Step length in PVC compound also followed a $K^2_{\mathrm{I,max}}$ dependency at lower $K_{\mathrm{I,max}}$. For higher $K_{\mathrm{I,max}}$, the step length fell below the line. Probably, the crack did not propagate through the entire length of the longer crazes formed under conditions of higher $K_{\mathrm{I,max}}$. A previous study, in which stepwise fatigue crack propagation through a PVC craze zone was observed directly, revealed that the fatigue crack jumped through only about two thirds of the craze [4]. According to Equation 4, the effect of impact modification on step length is embodied in the yield stress σ_{y}. Table II compares the yield stress extracted from the fits in Fig. 5 with the yield stress reported for similar PVC compounds [29]. Excellent agreement supports the mechanistic understanding of discontinuous crack growth in PVC.

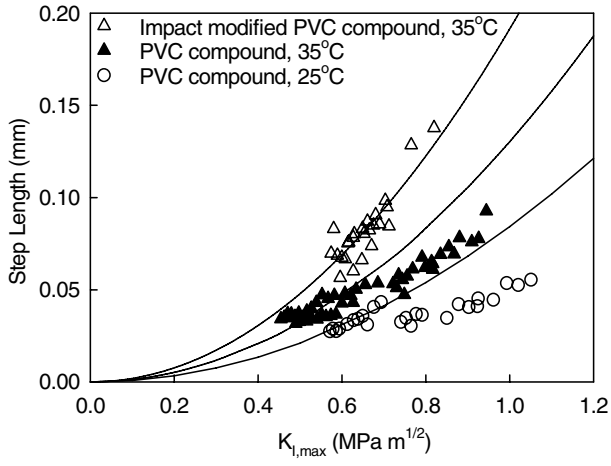

Figure 5 Correlation between step length and $K^2_{\mathrm{I,max}}$ (solid lines) for PVC compound at 25 and 35°C, and for impact modified PVC compound at 35°C.

3.3. Step lifetime

Crack growth rate in stepwise propagation is determined by both jump length, which depends on $K_{\mathrm{I,max}}$, and the time duration between crack jumps, which depends on the fracture resistance of highly drawn craze fibrils. The crack rate can be expressed in terms of the stepwise features as:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{\ell}{t} \tag{5}$$

TABLE II Comparison of the calculated yield stress using the Dugdale model to reported values

	σ_{y}, literature [29] (MPa)	σ_{y}, Equation 4 (MPa)
PVC compound (25°C)	61	68
PVC compound (35°C)	53	54
Impact modified PVC compound (35°C)	42	45

TABLE III Temperature and frequency dependence of step lifetime for PVC compounds with M_w of 56,000 at constant $K_{I,max}$ of 0.5 MPa$\sqrt{m}$ and R-ratio 0.1

Temperature (°C)	Frequency (Hz)	Step lifetime (10^3 s) PVC compound	Impact modified PVC compound
25	0.01	3.6	–
35	0.01	2.6	11.6
35	0.10	0.8	2.5
35	1.00	0.2	0.6

where ℓ is the step length and t is the step lifetime, which includes the time of crack arrest and the time of crack propagation. Rewriting the Paris relationship in terms of $K_{I,max}$ as:

$$\frac{da}{dt} = A_{max} K_{I,max}^{2.7} \tag{6}$$

where $A_{max} = A_f(1 - R)^{2.7}$ and R represents the R-ratio, and considering only the range of $K_{I,max}$ where Equation 4 applies, the step lifetime is given as:

$$t = \frac{\pi}{8\sigma_y^2} A_{max}^{-1} K_{I,max}^{-0.7} \tag{7}$$

Step lifetime under fatigue loading at various frequencies was calculated for $K_{I,max}$ of 0.5 MPa$\sqrt{m}$ and R-ratio 0.1, Table III. At 35°C, step lifetime increased by an order of magnitude as frequency decreased from 1.0 to 0.01 Hz. Because step length remained constant under different frequencies, slower crack growth rate at lower frequency (Fig. 2b) was due to the strong dependence of step lifetime on strain rate. The effect of temperature on step lifetime was not as significant, Table III. Indeed, step lifetime was considered independent of temperature within the experimental uncertainty. Slower crack growth at lower temperature (Fig. 2a) was due to shorter crazes and therefore shorter step jumps, not to longer craze lifetime. At all strain rates, impact modification increased the step lifetime, Table III. However, longer step lifetime, by 3–5 times, was partially offset by longer step jumps, by about 2 times, resulting in the overall decrease in crack growth rate achieved with impact modification of about 2 times.

Crack propagation through a pre-existing craze of highly drawn craze fibrils left remnants of fractured craze fibrils on the fracture surface. Fig. 6 shows a sequence of fracture surfaces that demonstrate the effect of decreasing frequency from 1.0 to 0.01 Hz to creep at 35°C. All the fracture surfaces exhibited features of cavitation and broken fibrils that are characteristic of craze fracture. The similarity confirmed the preservation of the craze fracture mechanism in fatigue and creep. The result of decreasing strain rate was an increase in the density of fractured fibrils. The complementary sequence of fracture surfaces of impact modified PVC compound is shown in Fig. 7. At each loading condition, the density of fractured fibrils was higher on the impact modified compound. Considering the combined results in Figs 6 and 7, higher density of craze fibrils on the fracture surface qualitatively correlated with longer step lifetime at the given temperature.

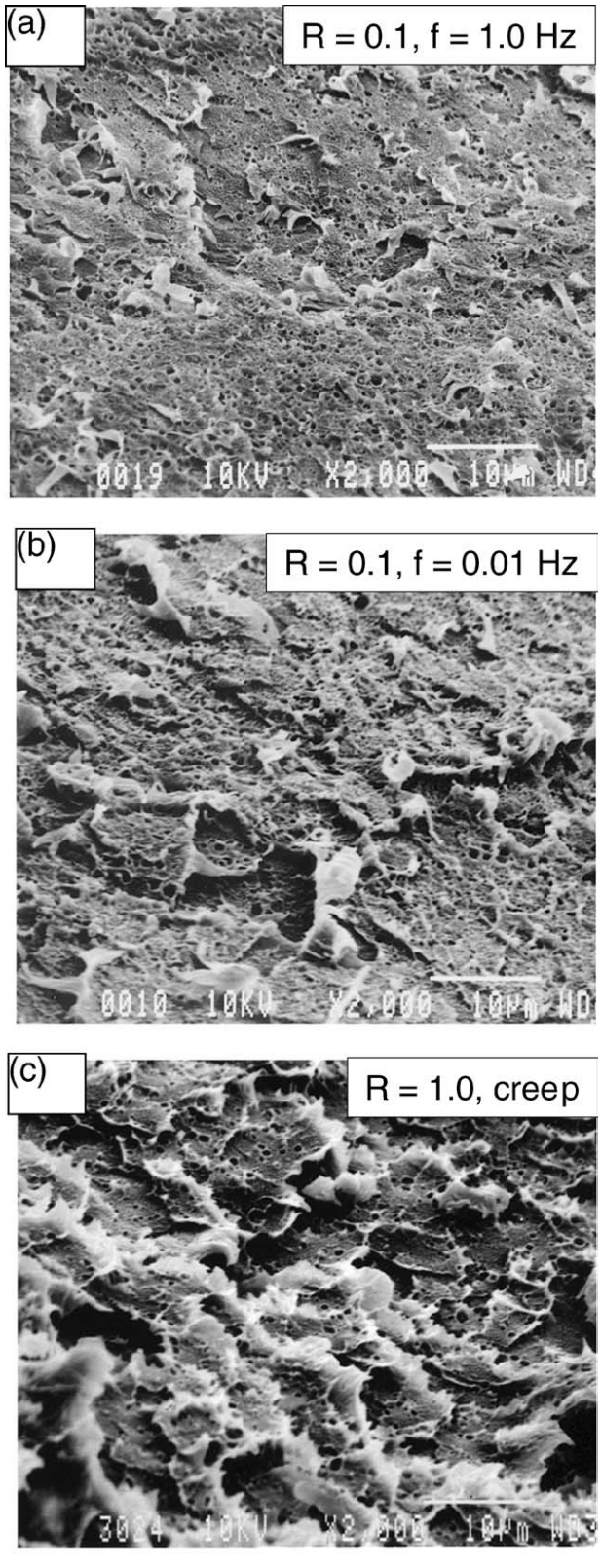

Figure 6 Effect of loading rate on the fracture surface of PVC compound at 35°C: (a) Fatigue at frequency 1.0 Hz and R-ratio 0.1, (b) fatigue at frequency 0.01 Hz and R-ratio 0.1, and (c) creep.

3.4. Fatigue acceleration of slow crack growth

The same power dependence of crack growth rate in the Paris relationship and the same crazing mechanism

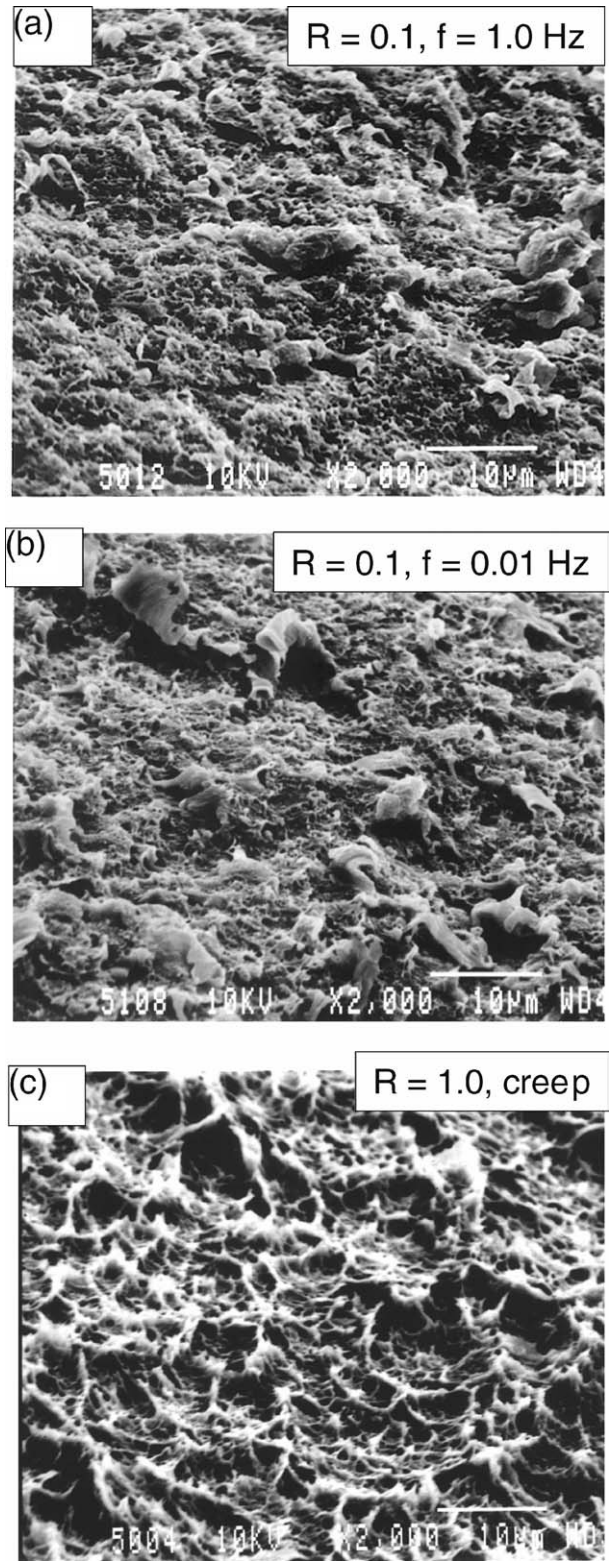

Figure 7 Effect of loading rate on the fracture surface of the impact modified PVC compound at 35°C: (a) Fatigue at frequency 1.0 Hz and R-ratio 0.1, (b) fatigue at frequency 0.01 Hz and R-ratio 0.1, and (c) creep.

in fatigue and creep previously allowed for correlations between fatigue and creep in polyethylene [13, 14, 30], and in PVC pipe [11]. Correlation was established by describing fatigue crack growth rate as a contribution from the creep process multiplied by a fatigue acceleration factor that is a linear function of strain rate only. Equation 2 can be rewritten in terms of known fatigue parameters A_f and R as:

$$\left(\frac{\mathrm{d}a/\mathrm{d}t}{K_{\mathrm{I,max}}^{2.7}}\right) = A_{\max} = B_f(1 + C\dot{\varepsilon}) \tag{8}$$

where $A_{\max} = A_f(1 - R)^{2.7}$. At zero strain rate, Equation 8 reduces to the Paris relationship for creep (Equation 3) with $B = B_f$. The prefactor for creep crack growth from fatigue B_f and the strain rate sensitivity factor C can be determined from the linear relationship between $A_{\max}$ and $\dot{\varepsilon}$.

The relationship between $A_{\max}$ and $\dot{\varepsilon}$ is plotted in Fig. 8 for PVC compound at 25° and 35°C, and impact modified PVC compound at 35°C. For $A_{\max}$ less than 0.8 μm s^{-1}(MPa$\sqrt{\mathrm{m}}$)$^{-2.7}$, a linear relationship described data for all frequencies and R-ratios. Deviation

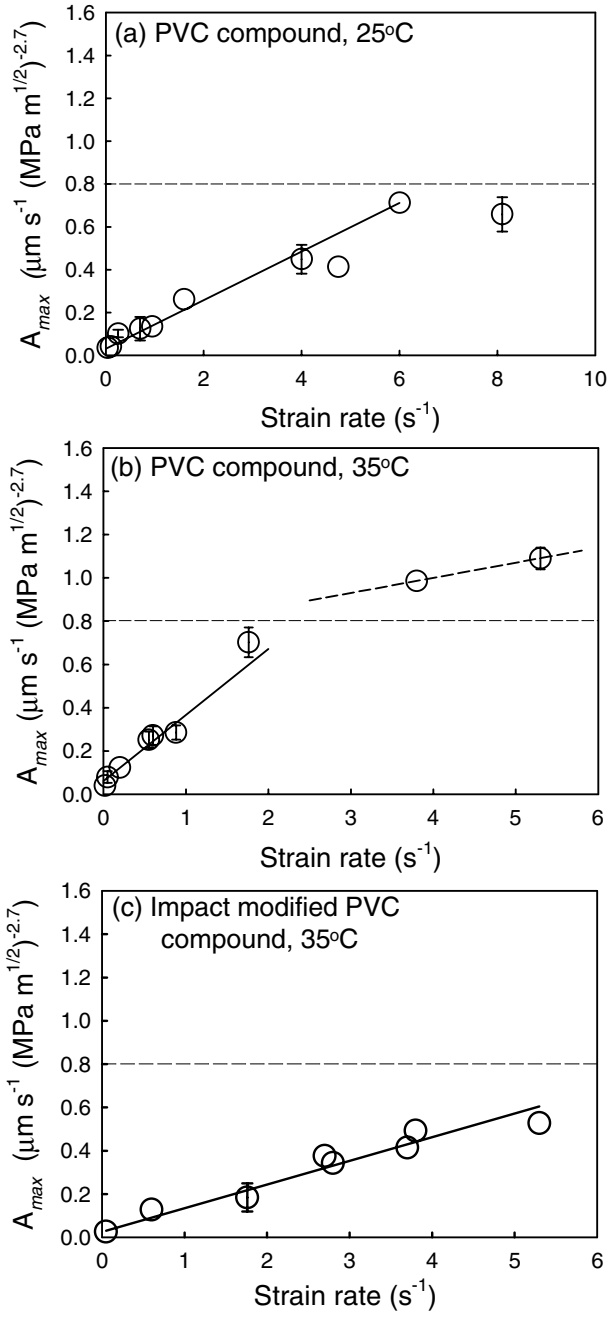

Figure 8 Relationship between strain rate and fatigue prefactor expressed as $A_{\max}$: (a) PVC compound at 25°C, (b) PVC compound at 35°C, and (c) impact modified PVC compound at 35°C.

from the linear relationship occurred at higher strain rates. This was understood by recognizing that craze lifetime includes contributions of craze formation and craze duration. Usually, craze lifetime is long enough that the time required for craze formation is negligible compared to craze duration. Accordingly, the processes of fibril deterioration that control craze duration also determine craze lifetime. However, under conditions of fast crack growth, such as encountered with less crack-resistant compounds loaded at high strain rate, the time for craze formation may not be negligible compared to the craze lifetime. This could produce transitional behavior in A_{max}.

It is anticipated that the craze formation processes of cavitation and fibril formation are less dependent on strain rate, temperature, and molecular weight than the craze deterioration processes of chain disentanglement and scission [31]. One indication that craze formation affects the kinetics of fatigue crack growth would be weakening in the strain rate dependence of A_{max}. This is indeed observed in PVC compound at higher strain rates. The fact that deviation from the linear relationship expressed by Equation 8 occurs at about the same value of A_{max} for both temperatures studied further indicates that craze formation starts to influence the kinetics of fatigue crack growth at A_{max} of 0.8 μm s^{-1} (MPa$\sqrt{\text{m}}$)$^{-2.7}$.

If A_{max} is less than 0.8 μm s^{-1} (MPa$\sqrt{\text{m}}$)$^{-2.7}$, for example in impact modified PVC compound at 35°C, no change in slope is observed and crack growth rate is determined by craze duration under all loading conditions studied. Because PVC pipe has higher molecular weight, A_{max} is generally lower than 0.8 μm s^{-1} (MPa$\sqrt{\text{m}}$)$^{-2.7}$ and the influence of craze formation on crack growth is not observed under typical fatigue loading conditions. However, at the time of the PVC pipe study [11], it was puzzling that A_{max} measured at the highest temperature and highest strain rate (70°C, frequency 1 Hz, R-ratio 0.1, and strain rate 2.4 s^{-1}) fell well below the linear correlation between A_{max} and strain rate as established at lower strain rates in accordance with Equation 8. The value of A_{max} was 0.83 μm s^{-1} (MPa$\sqrt{\text{m}}$)$^{-2.7}$. It is now possible to suggest that under this set of testing conditions, craze formation rather than craze deterioration controlled crack growth in PVC pipe. It appears general to PVC that Equation 8 applies only if A_{max} is less than 0.8 μm s^{-1} (MPa$\sqrt{\text{m}}$)$^{-2.7}$.

3.5. Correlation of slow crack growth in creep and fatigue

Good linearity between A_{max} and $\dot{\varepsilon}$ for PVC pipe allowed determination of the creep prefactor B_f and the strain rate sensitivity factor C in PVC pipe over the temperature range from 23 to 70°C [11]. Data comparing the creep prefactor from fatigue B_f and the prefactor measured directly from creep B in the temperature range 50 to 70°C are included in Fig. 9. The B values were systematically lower than the B_f values until they converged at 80°C, the T_g of PVC. The difference between B_f and B was attributed to damage of the craze fibrils during crack tip closure. The comparison, as published, did not extend to ambient temperature because of the extremely slow creep crack propagation rate. However B_f at 23°C was readily obtained from fatigue, and extended the Arrhenius temperature dependence of B_f accordingly. This justified the assumption that the Arrhenius temperature dependence of B also extended to 23°C and the failure time for creep at 23°C was estimated on that basis. From the creep failure time of 10 days at 50°C and the 2 orders of magnitude difference in B_f between 50 and 23°C, the failure time in creep at 23°C was estimated to be 1000 days for $K_{I,max}$ of 1.8 MPa$\sqrt{\text{m}}$.

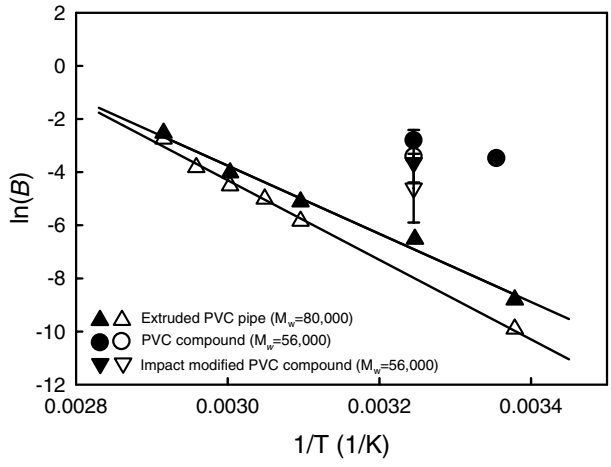

Figure 9 Comparison of the creep prefactor from fatigue B_f (solid symbols) with the prefactor obtained directly from creep B (open symbols). Data for PVC pipe from Ref. 11.

Since publication, a creep specimen of PVC extruded pipe failed after 765 days at 23°C. The fracture surface with many highly drawn and fractured craze fibrils closely resembled the fracture surface obtained in creep at 50°C, confirming conservation of the craze mechanism at 23°C, Fig. 10. The directly determined prefactor B for creep at 23°C is included in Fig. 9. It was slightly lower than B_f from fatigue in conformity with the systematic difference between

TABLE IV Comparison of the parameters obtained from the fatigue strain rate approach to creep for PVC of different molecular weights and formulation

T (°C)	PVC extruded pipe $M_w = 80{,}000$ [11]	PVC compounds $M_w = 56{,}000$ Unmodified[a]	Impact modified[a]
	(a) Creep resistance, B (μm s^{-1} (MPa$\sqrt{\text{m}}$)$^{-2.7}$)		
23	0.0002	0.031	–
35	0.0015	0.061	0.026
50	0.0060	–	–
60	0.0180	–	–
70	0.0800	–	–
	(b) Strain rate sensitivity, C (s)		
23	60	4	–
35	17	5	4
50	7	–	–
60	6	–	–
70	5	–	–

[a]Experiments were performed at 25°C.

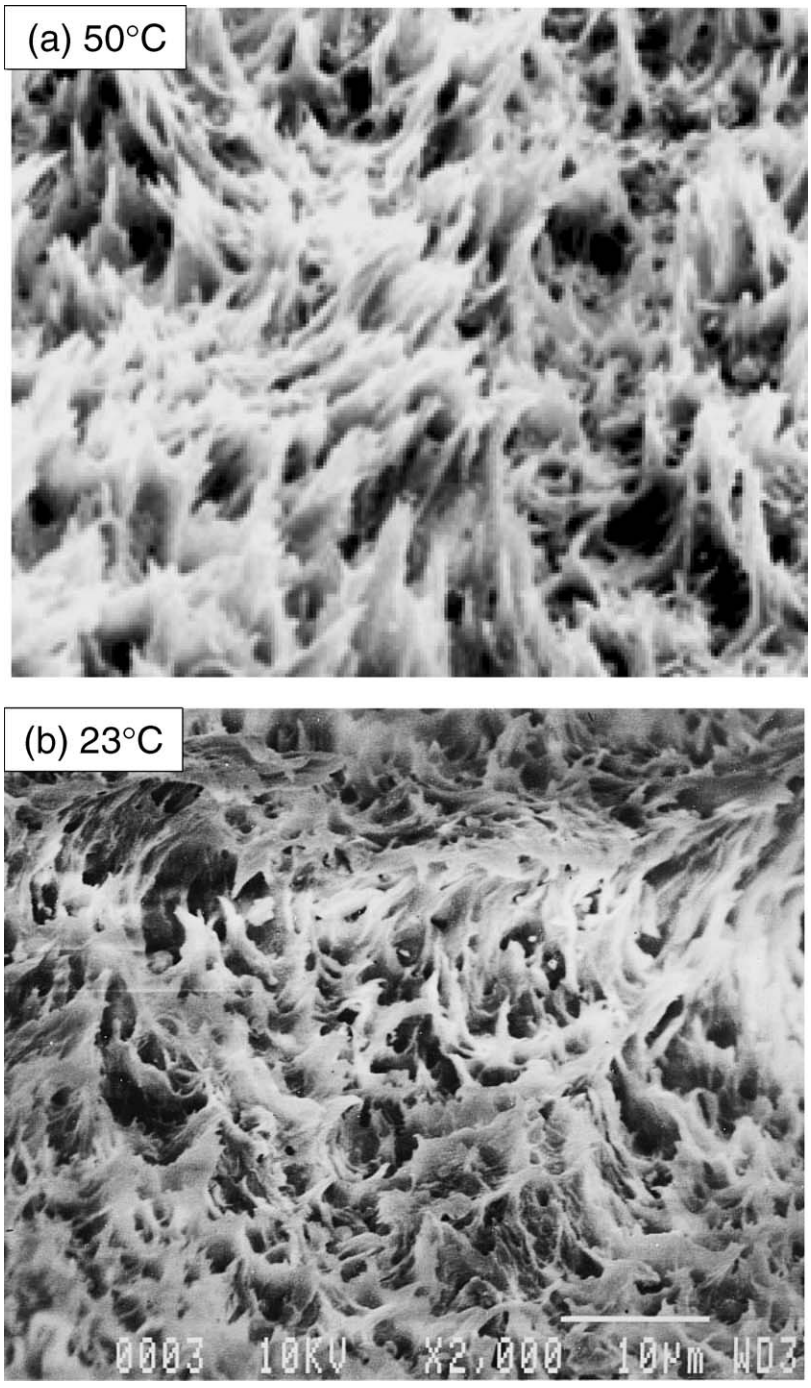

Figure 10 Creep fracture surfaces of PVC pipe: (a) At 50°C and (b) at 23°C.

B and B_f found at higher temperatures, and in accordance with the Arrhenius temperature dependence of B.

Lower molecular weight chains disentangle more easily and the creep crack growth rate increases correspondingly, as indicated by higher B values for PVC compound compared to PVC pipe, Table IV. Comparison of B (obtained from A_{max} less than 0.8 μm s^{-1} (MPa$\sqrt{\text{m}}$)$^{-2.7}$) with B_f from fatigue for PVC compound and impact modified PVC compound was made at 35°C. As was the case with PVC extruded pipe, B was consistently lower than B_f (Fig. 9). However creep crack growth rate in PVC compound and impact modified PVC compound exhibited considerable experimental scatter. In this case, B_f from fatigue provided a reliable method for comparing and ranking creep crack growth resistance of PVC materials.

Fatigue accelerates deterioration of craze fibrils by enhancing the rate of chain scission. Thus, the strain rate sensitivity parameter C is a measure of the relative contribution of chain scission and chain disentanglement. If disentanglement is very slow and the time for creep failure is very long, for example when the temperature is well below T_g and the molecular weight is relatively high, fatigue dramatically increases crack growth rate as reflected by the large value of C for PVC extruded pipe at 23°C. Because lower molecular weight chains disentangle more easily, fatigue enhancement as measured by the parameter C is almost an order of magnitude less for PVC compound compared to PVC pipe at a similar temperature.

Impact modification increases the resistance to creep crack growth as indicated by reduced values of B and B_f, but has no significant effect on the fatigue acceleration parameter C, Table IV. Fracture surfaces of impact modified PVC provide evidence that increased density of craze fibrils is responsible for increased resistance to creep crack growth. Apparently the impact modifier facilitates cavitation and shear processes involved in craze fibril formation. However, once the craze forms, it appears that impact modification does not affect the molecular processes of chain pullout and fracture that control deterioration of PVC craze fibrils and provide the basis for fatigue acceleration.

4. Conclusions

Fatigue and creep crack growth in PVC compound and impact modified PVC compound followed the Paris relationship with power $n = 2.7$. Conservation of the exponent suggested that the mechanism of crack propagation was the same for fatigue and creep. Stepwise propagation through a crack tip craze zone made it possible to analyze the roles of craze length and craze lifetime in the kinetics of crack growth. Step length followed the Dugdale model with a $K^2_{\mathrm{I,max}}$ dependence only at lower $K_{\mathrm{I,max}}$. Deviation at higher $K_{\mathrm{I,max}}$ was attributed to crack jumps that extended though only part of the craze zone. In contrast, the step length in impact modified PVC compound followed the Dugdale model for all $K_{\mathrm{I,max}}$ studied. In accordance with the model, the lower yield stress of impact modified PVC compound resulted in longer step lengths. Reduced fatigue crack growth rate in impact modified PVC compound was due to longer step lifetime, which offset the longer step length. Strain rate affected crack growth rate by changing step lifetime, whereas temperature affected step length. Examination of fracture surfaces confirmed that the craze mechanism was conserved in fatigue and creep and allowed for use of a previously developed strain rate approach for correlating fatigue and creep crack growth. The analysis was satisfactory for $A_{\max}$ less than $0.8\ \mu\mathrm{m\ s^{-1}}\ (\mathrm{MPa}\sqrt{\mathrm{m}})^{-2.7}$. At higher crack growth rates, the time for craze formation became comparable to craze lifetime. The predicted creep crack growth rate from fatigue B_f was found to decrease with increasing molecular weight and also decreased with the addition of impact modifier. For PVC compound of relatively low molecular weight, the experimental creep prefactor B exhibited significant scatter. In this case, B_f from fatigue provided a reliable method for comparing and ranking creep crack resistance of PVC materials.

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