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Effect of temperature on fatigue crack growth in unplasticized polyvinyl chloride

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The effect of temperature on the fatigue crack growth in a 150 mm class 12 unplasticized polyvinyl chloride (uPVC) pipe-grade material over a temperature range −30 – 60 °C was studied. The Arrhenius relationship between fatigue crack growth rate, da/dN, and absolute temperature, T, was found to describe the experimental data very well independent of the applied stress intensity factor range, ΔK. In the temperature range −30 – 10 °C the activation energy was 8.8 kJ mol^{-1} and between 26 and 60 °C this was 30 kJ mol^{-1}. The two activation energies were found to be associated with two distinctly different crack growth mechanisms. In the low-temperature range there was a predominant shear mechanism, but in the high-temperature range multiple crazing was the major fatigue mechanism. Finally, a "stress intensity factor"—biased Arrhenius equation for fatigue crack growth was suggested and found to predict rather accurately the data of uPVC, as well as those of other polymeric materials at different temperatures.

1. Introduction

It is well known that the fatigue properties of many polymers, especially thermoplastics, are sensitive to temperature changes [1]. Generally, the fatigue crack growth rates, da/dN, increase with increasing temperature, T. For example, da/dN in PS (polystyrene) [2], ABS (acrylonitrile butadiene styrene) [3], PVC (polyvinyl chloride) [4], PMMA (polymethyl methacrylate) [5], and PSF (polysulphone) [5], all increase monotonically with increasing temperature at a given stress intensity factor range, ΔK. However, some polymers show a somewhat different response in that da/dN has a maximum value at a certain temperature but it decreases on either side of this temperature. PC is a good example of this type of behaviour. Martin and Gerberich [6] attempted to rationalize this behaviour for PC in terms of the temperature-dependent fracture toughness, K_c, and viscoelastic response. Recently, Engdahl [7] also reported that da/dN in a CTBN rubber-toughened epoxy resin was not sensitive to temperature changes at any given stress ratios. This paper is mainly concerned with those polymers and, in particular, uPVC that show a monotonic increase in da/dN with T. Fatigue crack growth data are often plotted in accordance with the Paris power law equation, i.e.

$$\frac{\mathrm{d}a}{\mathrm{d}N} = A(\Delta K)^m \qquad (1)$$

where A and m are constants which depend on test temperature and environment. Whilst this equation is useful to describe fatigue crack growth data, it does not explain the temperature effect and does not provide any physical understanding of the crack growth mechanisms that occur in the crack tip process zone. There has been an attempt to rationalize fatigue crack growth data at different temperatures based on a modified WLF (Williams–Landel–Ferry) equation [3] in conjunction with Equation 1, i.e.

$$\log_{10} Q = \alpha\left[\left(\frac{T_c - T_0}{\beta + T_c - T_0}\right) - \left(\frac{T - T_0}{\beta + T - T_0}\right)\right] \qquad (2)$$

where Q is an empirical shift factor to move a set of data at a temperature, T, to a reference temperature T_c, T_0 is approximately equal to the glass transition temperature, T_g, plus 50 °C, and α, β are constants of the polymeric material. Although the empirical shift factor, Q, can be used to obtain a master da/dN versus ΔK curve, the applicability of the WLF equation below T_g is physically unacceptable because it is derived based on the free volume theory [8] and is valid only above T_g.

Arrhenius [9] proposed an equation to account for the influence of temperature on the rate of inversion of sucrose so that the variation of the specific rate of the reaction with temperature is expressed as

$$k = A_1 \exp\left(\frac{-\Delta H}{RT}\right) \qquad (3)$$

where ΔH is activation energy, R the universal gas constant, T the absolute temperature, and A_1 a quantity that is independent of or varies relatively little with temperature. Equation 3 describes the exponential increase in the rate of chemical and physical reactions as the temperature is increased, because the fraction of particles in the excited state, and consequently the number of particles able to react, increases in the same way [10, 11]. Recently, Krausz and Krausz [12, 13] have related the rate constant, k, to a crack velocity, $\mathrm{d}a/\mathrm{d}t$, based on an atomistic model as

$$\frac{\mathrm{d}a}{\mathrm{d}t} = A_2 k \tag{4a}$$

Thus, Equation 4a becomes

$$\frac{\mathrm{d}a}{\mathrm{d}t} = A_2 \exp\left(\frac{-\Delta H}{RT}\right) \tag{4b}$$

and

$$\begin{aligned}\frac{\mathrm{d}a}{\mathrm{d}N} &= \frac{\mathrm{d}a}{\mathrm{d}t}\frac{\mathrm{d}t}{\mathrm{d}N} \\ &= \frac{\mathrm{d}a}{\mathrm{d}t}\frac{1}{f}\end{aligned} \tag{4c}$$

where f is cyclic frequency. Therefore, $\mathrm{d}a/\mathrm{d}N$ can be related to the Arrhenius equation as

$$\frac{\mathrm{d}a}{\mathrm{d}N} = B \exp\left(\frac{-\Delta H}{RT}\right) \tag{5}$$

where B is a constant. For a given temperature and testing conditions, i.e. stress ratio and frequency, ΔH represents the apparent activation energy for that predominant fracture or deformation mechanism actually taking place at the crack tip. To apply to fatigue crack growth, Equation 5 needs to be expressed in terms of fracture testing parameter, ΔK. The apparent activation energy, ΔH, is rewritten as

$$\Delta H = \Delta H_{\mathrm{th}} - \gamma \log \Delta K \tag{6}$$

Therefore, Equation 5 becomes

$$\frac{\mathrm{d}a}{\mathrm{d}N} = B \exp\left[\frac{-(\Delta H_{\mathrm{th}} - \gamma \log \Delta K)}{RT}\right] \tag{7}$$

Note that ΔH_{th} in Equation 6 is the thermal activation energy independent of mechanical work and $\gamma \log \Delta K$ is a "stress intensity factor"-biased term.

The main purposes of this paper are to identify the fatigue crack growth mechanisms in uPVC as may be affected by temperature variations using the activation energy analysis; and to demonstrate the applicability of Equation 7 to uPVC and other polymers in describing the temperature effect on fatigue crack growth rate.

2. Experimental procedure

The uPVC pipes were taken from normal production 150 mm class 12 (wall thickness ~ 9 mm) and they were made from unmodified, lead-stabilized PVC resin with a K value of 67 corresponding to an approximate molecular weight average of 170 000. The pipes showed no attack on immersion in methylene chloride for 15 min at 20 °C and were thus considered well processed. The methylene chloride temperature (MCT) for 20 min [14] was found to be 24 °C. The pipes were slit and warmed in an oven at 100–105 °C for 15 min before being opened up and pressed between metal plates to produce a flat sheet. Single-edge notched (SEN) samples $70 \times 210\ \mathrm{mm}^2$ were cut from the flattened sheets so that the crack would propagate in the pipe extrusion direction.

Crack growth was monitored by a computerized data acquisition system developed by Mai and Kerr [15–17] using a conductive surface grid interfaced to a microcomputer which also controlled a Shimadzu Servopulser with a load range of ± 10 t. Details and accuracy of this computer-based data acquisition method have already been described [15–17]. Additional tests were conducted to confirm the accuracy of the crack length measurements at high temperatures. Fig. 1 shows a comparison of the present automated technique with manual measurements made with a low-power microscope at 60 °C. A temperature chamber controlled to ± 1 °C was used in the experiments and the cycling frequency was 5 Hz with a sinusoidal load waveform and a stress ratio, r, equal to 0.2 (Fig. 2).

3. Results and discussion

The fatigue crack growth data of uPVC over a temperature range from −30 – 60 °C are represented by the least squares lines given. The Paris power law constants A and m are given in Table I.

To determine the apparent activation energy ΔH, $\Delta K = 1.0\ \mathrm{MPa\,m^{1/2}}$ was chosen and $\ln a_{\mathrm{T}}$ was thus plotted versus $1/T$. Data for other ΔK values could also be used, but the effect on ΔH was insignificant. Because (see Equation 5)

$$\ln a_{\mathrm{T}} = \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{r}}}\right) \tag{8}$$

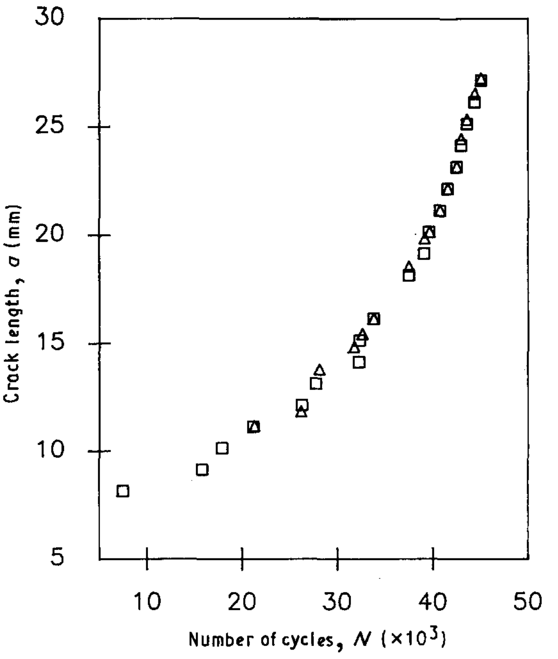


Figure 1 Comparison of (□) screen printing and (△) optical techniques at 60 °C.

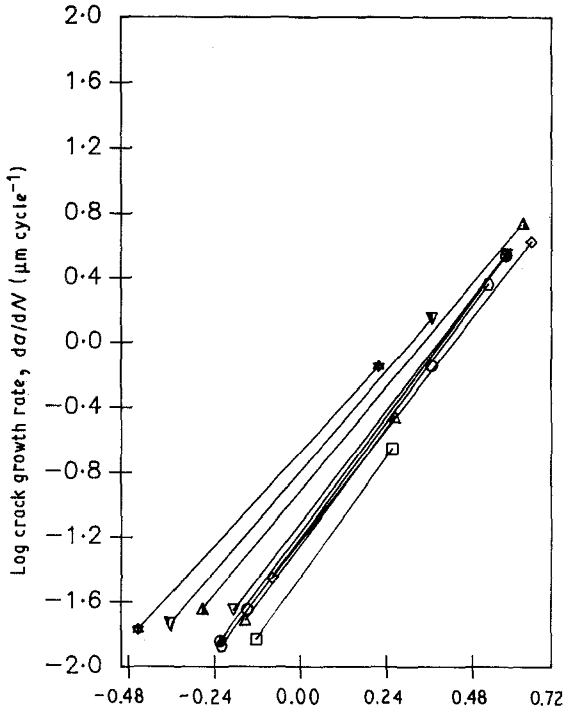


Figure 2 Fatigue crack growth rates at 5 Hz and $r = 0.2$ at different temperatures (°C): (□) − 30, (△) − 10, (◇) 0, (○) 10, (⬡) 23, (◑) 32, (▽) 36, (▲) 40, (▼) 50, (✡) 60.

TABLE I Constants A and m in the Paris equation from experimental results in uPVC (da/dN in μm cycle^{-1}, ΔK in MPa m$^{1/2}$)

Temperature (°C)	A	m
− 30	0.036	3.10
− 10	0.056	3.01
0	0.059	2.88
10	0.063	2.98
23	0.062	3.00
32	0.068	2.97
36	0.078	2.88
40	0.123	2.66
50	0.160	2.58
60	0.211	2.42

and

$$\frac{\partial(\ln a_{\mathrm{T}})}{\partial(1/T)} = \frac{\Delta H}{R} \tag{9}$$

where $a_{\mathrm{T}} = (da/dN)_r/(da/dN)$ and the subscript r denotes the reference condition. In Fig. 3, the fatigue crack growth data for uPVC are plotted in accordance with Equation 8 with $T_r = 23\,°\mathrm{C}$. Clearly, there are two straight lines obtained with a transition around 23 °C. From Equation 9 the different slopes of these lines indicate two ΔH values for two separate cyclic fatigue mechanisms. To confirm this prediction, fracture surfaces and sections perpendicular to the fracture surface at $\Delta K = 1.0$ MPa m$^{1/2}$ were examined. In the high-temperature range (23–60 °C) multiple crazing was found to be the predominant mechanism, but in the low-temperature range (−30 – 10 °C) shear yielding becomes the predominant mechanism. Fig. 4 shows typical features of these two separate mechanisms at $\Delta K = 1.0$ MPa m$^{1/2}$. Also, the disappearance of multiple crazing at low temperatures was independent of the magnitude of the applied ΔK. The finding that multiple crazing occurred at high rather than low temperatures is in agreement with that of Cornes and Haward [18] who observed that crazes first appeared at normal temperature but the maximum size and frequency of crazes happened at around 40 °C in their monotonic tensile tests. Further evidence is provided in Fig. 5a and b taken from specimens fatigued at 0 and 40 °C with $\Delta K = 1.0$ MPa m$^{1/2}$, respectively. Fig. 5a is a microtomed section of a 0 °C specimen and it clearly reveals that localized shear bands exist on and off along the crack path instead of multiple crazing. On the other hand, Fig. 5b shows a section of a 40 °C specimen with distinct multiple crazes in the crack tip region. Crack growth is, therefore, by coalescence of crazes and this makes the fracture surfaces much rougher than are produced by the shear yielding dominant mechanism (see Fig. 4). Fig. 6 shows the roughness measurements of the fracture surfaces at various temperatures and these results support the contention given above.

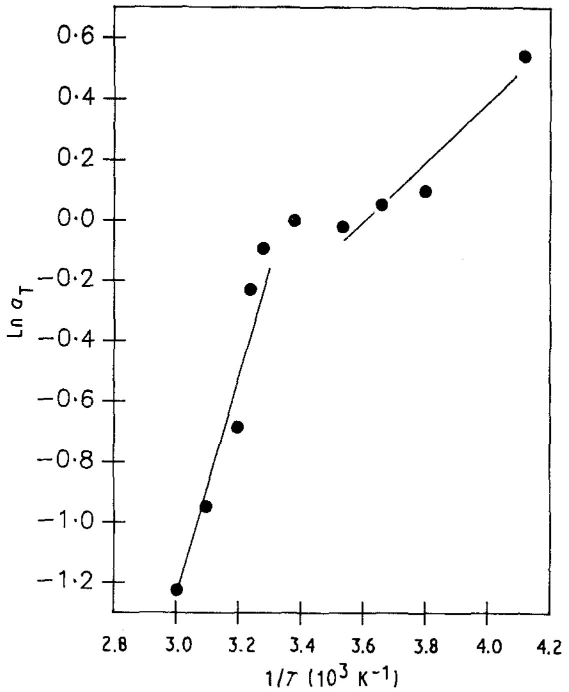
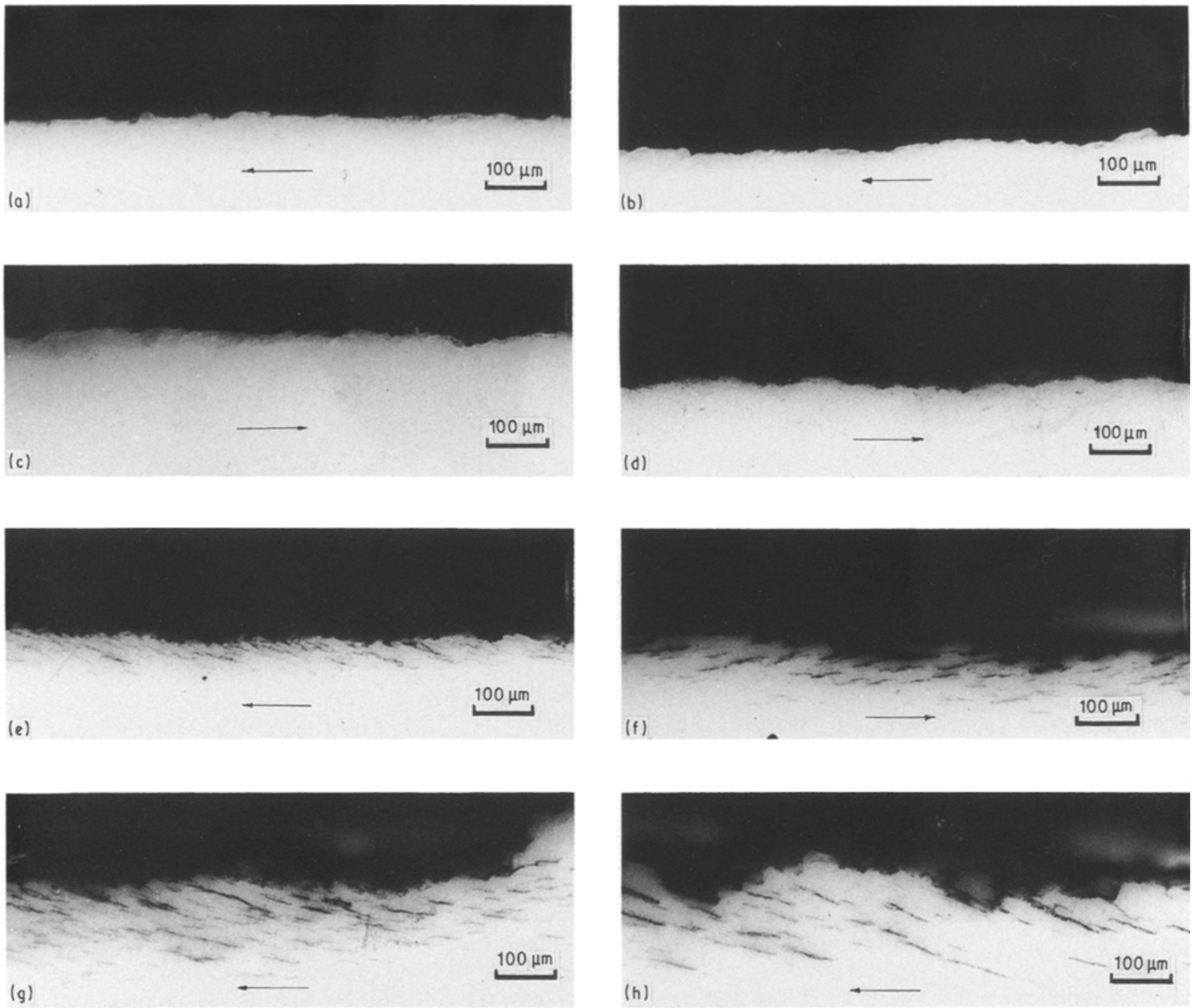


Figure 3 A plot of $\ln a_{\mathrm{T}}$ against $1/T$ at $\Delta K = 1.0$ MPa m$^{1/2}$ for uPVC ($T_r = 23\,°\mathrm{C}$).

The two fatigue mechanisms identified above allow the data to be treated separately depending on the temperature range. There are three unknowns, ΔH_{th}, B and γ in Equation 7 for each temperature range. Using an optimization programme, values of ΔH_{th}, B and γ were found to be 8.8 kJ mol^{-1}, 2.81 and 15.15, respectively, in the low-temperature range and 30 kJ mol^{-1}, 10737 and 16.48, in the high-temperature range. When Equation 7 is used in conjunction with these parameters to predict da/dN versus ΔK curves for all the temperatures studied and are fitted to the Paris equation (Equation 1), we obtain A and m values shown in Table II. Comparisons of these values with



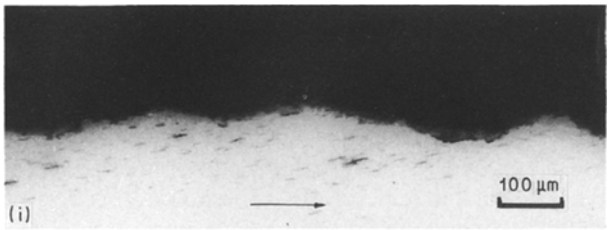


Figure 4 Sections normal to fracture surface: (a) − 30 °C, (b) − 10 °C, (c) 0 °C, (d) 10 °C, (e) 23 °C, (f) 32 °C, (g) 40 °C, (h) 50 °C and (i) 60 °C. Arrows indicate crack growth direction. The disappearance of multiple crazing occurs below 23 °C.

TABLE II The Paris power law constants A and m values predicted from Equation 7 for uPVC (da/dN in μm cycle^{-1}, ΔK in MPa m$^{1/2}$)

Temperature (°C)	A	m
− 30	0.034	3.17
− 10	0.047	2.93
0	0.065	2.82
10	0.074	2.72
23	0.058	2.91
32	0.083	2.82
36	0.096	2.79
40	0.112	2.75
50	0.160	2.66
60	0.223	2.58

those given in Table I show excellent agreement with each other. This means that Equation 7 is very useful in predicting da/dN at any given temperature and ΔK provided the fatigue mechanism is identified precisely with associated values of ΔH_{th}, B and γ.

Finally, based on Equation 7, $RT\ln[(da/dN)/B]$ versus $\log \Delta K$ are plotted for uPVC which shows that master curves for the two temperature ranges corresponding to shear yielding and multiple crazing mechanisms can be obtained with good correlations (Fig. 7). The correlation coefficients for uPVC and other polymers (see Section 4) are listed in Table III.

4. Analysis of fatigue crack growth data for other polymers

Whilst the Arrhenius equation and the activation energy analysis are useful to identify the fatigue mechanisms and to predict the fatigue crack growth rates at different temperatures for uPVC, their extension and applicability to analyse fatigue data of other polymers ought to be investigated because many such data are available in the published literature. This is carried out below for PVC, ABS and PS.

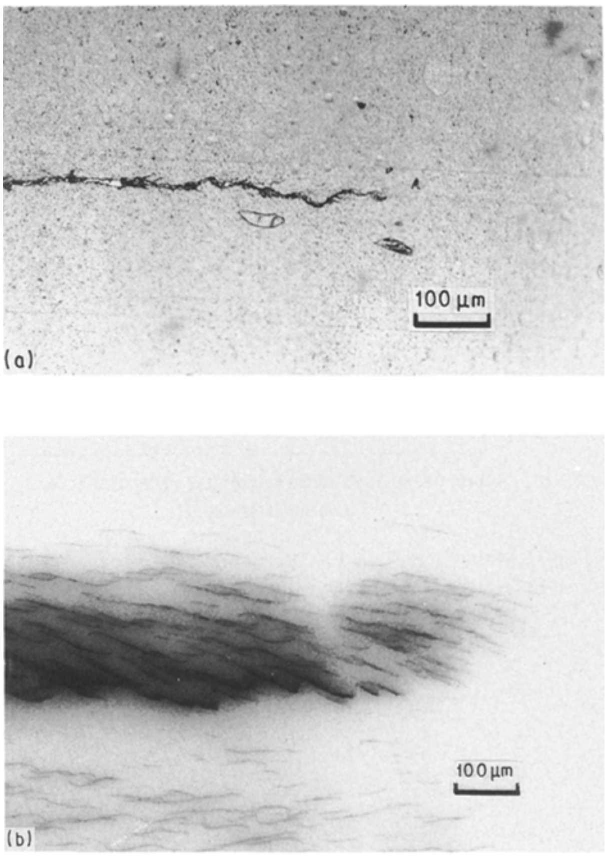


Figure 5(a) Microtomed section for the sample tested at 0 °C, $\Delta K = 1$ MPa m$^{1/2}$ and $r = 0.2$. (b) Section normal to fracture surface for sample tested at 40 °C.

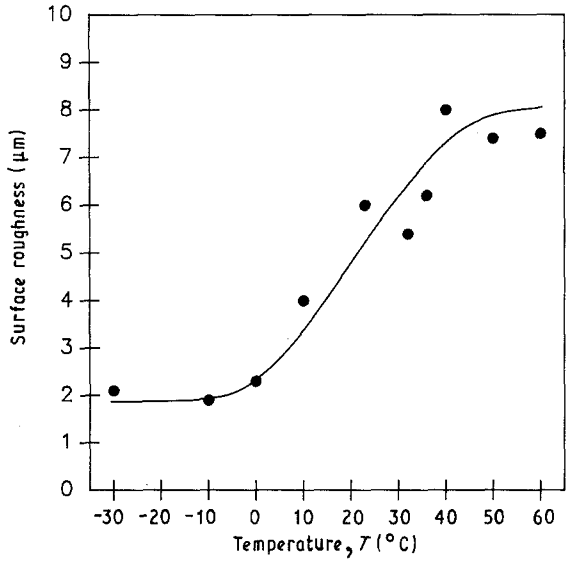


Figure 6 Roughness measurements of fracture surfaces at $\Delta K = 1.0$ MPa m$^{1/2}$ in uPVC at different temperatures.

To determine any change of fatigue mechanisms, $\ln a_T$ are plotted against $1/T$ in accordance with Equation 8. To avoid having to extrapolate for da/dN the ΔK value chosen is one that intersects the data for all temperatures. Fig. 8 shows a plot of $\ln a_T$ versus $1/T$ for PVC [4] without a transition, indicating that there is only one fatigue mechanism for the whole temperature range (50 to −30 °C) studied. The values of ΔH_{th}, B and γ in Equation 7 are computed

TABLE III Correlation coefficients obtained from Figs 7 and 11–13

Material	Temperature range (°C)	Correlation coefficient, r^2
uPVC	−30 – 10	0.993
	23 – 60	0.995
PVC	−30 – 55	0.975
ABS	−10 – 10	0.999
	30 – 70	0.998
PS	−60 – 0	0.957
	20 – 60	0.992

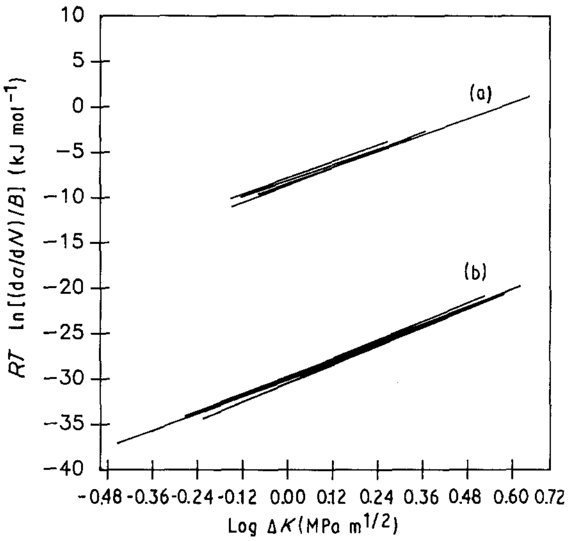


Figure 7 Master curves according to Equation 7 for uPVC. Temperature range: (a) −30 – 10 °C and (b) 23–60 °C.

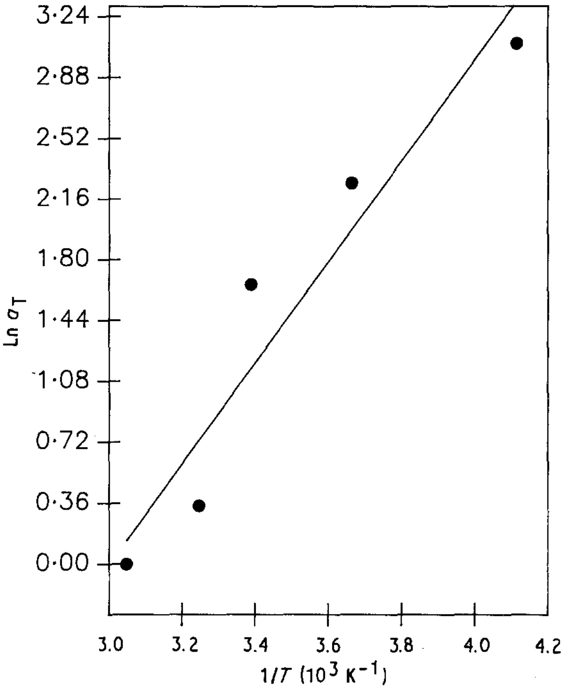


Figure 8 A plot of $\ln a_T$ versus $1/T$ at $\log \Delta K = -0.15$ MPa m$^{1/2}$ for PVC [4].

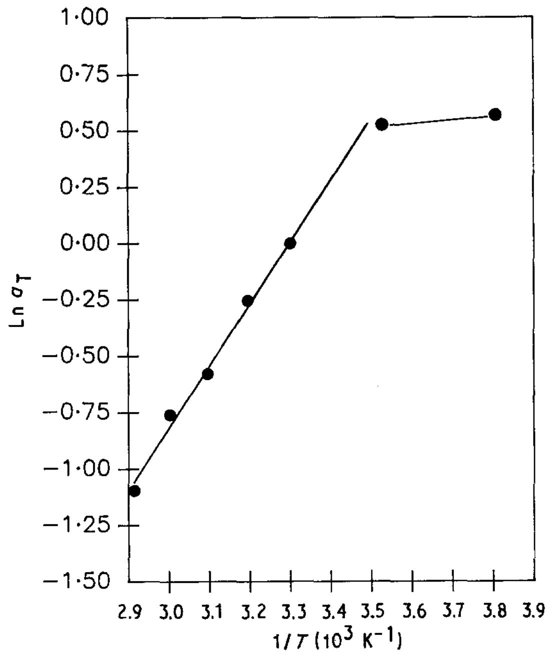


Figure 9 A plot of $\ln a_T$ versus $1/T$ at $\log\Delta K = -0.26$ MPa m$^{1/2}$ for ABS [3].

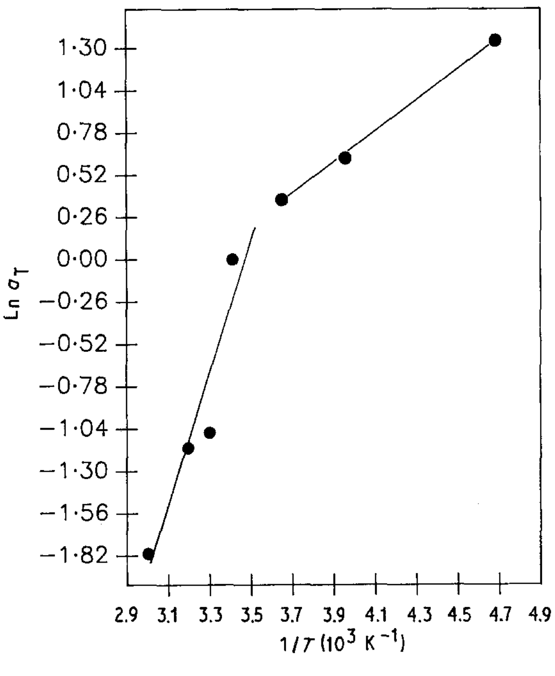


Figure 10 A plot of $\ln a_T$ versus $1/T$ at $\log\Delta K = -0.22$ MPa m$^{1/2}$ for PS [2].

to be 23 kJ mol^{-1}, 1567 and 15 at $\log\Delta K = -0.15$ MPa m$^{1/2}$. It would appear that the fatigue mechanism is one of crazing.

A plot of $\ln a_T$ versus $1/T$ for ABS [3] is given in Fig. 9 showing a distinct transition at around 10 °C. Consequently, there are two least squares lines. The values of ΔH_{th}, B and γ at $\log\Delta K = 0.26$ MPa m$^{1/2}$ are computed to be 9.5 kJ mol^{-1}, 4.98 and 19.61 in the low-temperature range (−10 – 10 °C), and 28 kJ mol^{-1}, 10330 and 20.41 in the high-temperature range (30–70 °C), respectively. Unfortunately, the fatigue mechanisms in these two temperature ranges were not studied in any detail.

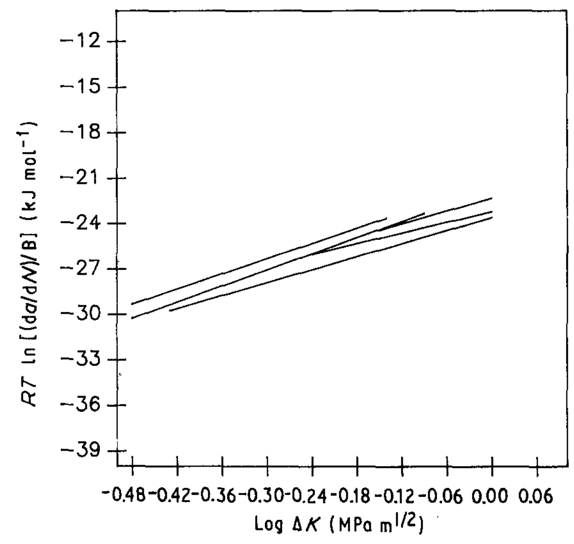


Figure 11 Master curves for PVC according to Equation 7 in the temperature range −30 – 55 °C.

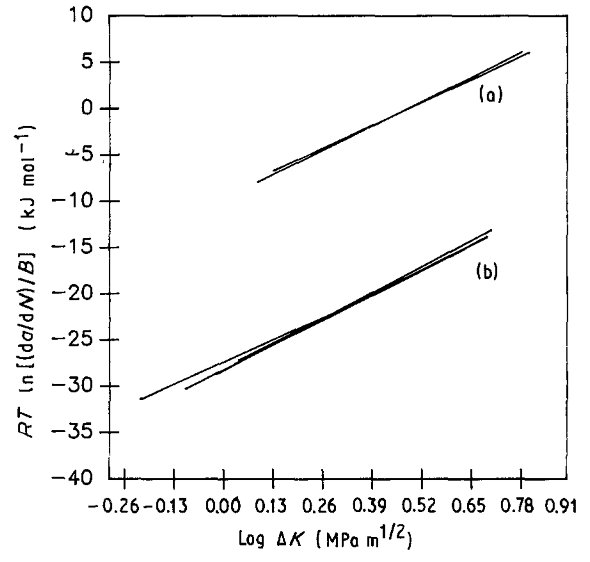


Figure 12 Master curves for ABS according to Equation 7 in the temperature range (a) −10 – 10 °C and (b) 30–70 °C.

To check any fatigue mechanism change with temperature range in PS [2], $\ln a_T$ is plotted against $1/T$ at $\log\Delta K = 0.22$ MPa m$^{1/2}$ in Fig. 10. There is a slope change somewhere between 20 and 0 °C. This transition is in agreement with the occurrence of the β transition around 20 °C [2]. The values of ΔH_{th}, B and γ are computed to be 17.40 kJ mol^{-1}, 4233 and 21.45, respectively, in the temperature range 20–60 °C, and 6.36 kJ mol^{-1}, 15.76 and 16.71 in the temperature range −60 – 0 °C. Again, no detailed study of the fatigue crack growth mechanisms was made although crazing was identified throughout the whole temperature range investigated.

Finally, based on Equation 7, $RT\ln[(\mathrm{d}a/\mathrm{d}N)/B]$ versus $\log\Delta K$ are plotted for PVC, ABS and PS to show that master curves can indeed be obtained with good correlations (Figs 11–13). These results show that the Arrhenius equation is useful to describe fatigue crack growth in a range of polymers including

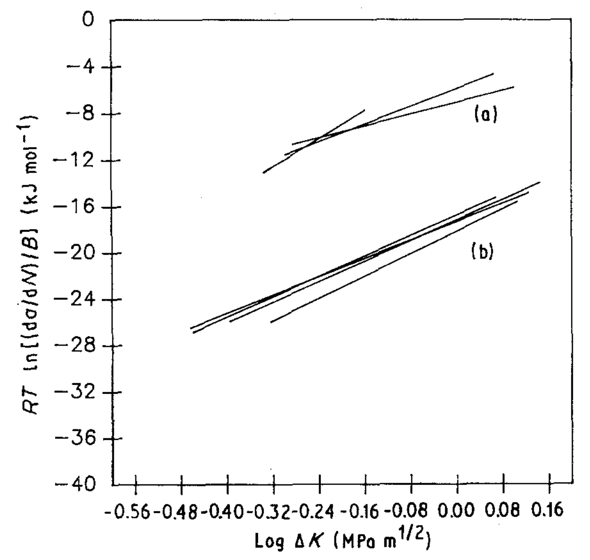


Figure 13 Master curves for PS according to Equation 7 in the temperature range (a) −60 – 0 °C and (b) 20–60 °C, respectively.

PVC, PS, ABS and uPVC with respect to effects of temperature.

5. Conclusions

The Arrhenius relationship between fatigue crack growth rate and absolute temperature was found to describe the uPVC data well and it also allows ΔH of the fatigue mechanisms to be distinctly determined. At high temperatures (23–60 °C) multiple crazing was predominant, but at low temperatures (−30 – 10 °C) shear yielding/bands was dominant. Also, a ΔK-biased Arrhenius equation for fatigue crack growth was successfully shown to give predictions in good agreement with the experimental data of uPVC as well as other polymers in the Paris regime at different temperatures.

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