layer on the Si particle surfaces. For instantaneous nucleation of Si_3N_4 and one-dimensional diffusion-controlled growth of the disc-shaped nuclei, the thickness has been shown to give $m = 0.5$ [10]. Also radial diffusion-controlled growth of a Si_3N_4 mat or surface layer on Si particles has been reported to obey Janders' relation [15] for $n = 0.5$ [7].

The diminishing kinetic rate ($n < 0.5$) in Figs. 1, 2 and 3 may be due to Si_3N_4 nuclei growth impingement [9]. The radial disc growths of Si_3N_4 nuclei (for $m = 1$) eventually impinge upon each other, "choking-off" the kinetics and reducing the rate law. Also, microcracks caused by the ~22% volume expansion during the phase transformation $Si \rightarrow Si_3N_4$ [6], can act as diffusion barriers to reduce the kinetics, yielding a logarithmic rate law [16].

At present, it is difficult to generalize about which mechanisms are rate-controlling during each stage of the nitriding kinetics. The difficulty arises due to investigators using different particle size distributions, green densities, Si powder purities, N_2 gas purities and sources of gas impurities (e.g. oxygen) in the furnace. Nevertheless, the initial nitriding kinetics can be consistently described by an approximately linear rate law, which subsequently is followed by multi-stage rate laws.

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Comments on "A model of fatigue crack growth in polymers"

Williams has proposed an interesting model to describe fatigue crack propagation (FCP) in polymeric solids and to account for a number of experimental observations [1]. The purpose of this communication is to (1) examine the basic assumptions underlying the model, (2) compare recent data with values predicted from the model, and (3) present alternative explanations for polymer fatigue behaviour.

The first assumption is that upon unloading and reloading a craze at the crack tip, some of the craze ligaments become damaged, thereby reducing the craze stress σ_c. From this a two-stage craze zone is envisioned in which the newly formed craze material at the craze tip experiences a stress σ_c while the remaining part of the craze sustains a lower stress, $\alpha\sigma_c$. Use of this assumption leads to values of σ_c and $\alpha\sigma_c$ for several polymers in the ranges 325 to 720 and 29 to 2016 MPa, respectively (see Table II in [1] and [2]). In contrast, use of the Dugdale plastic strip formulation leads to

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values typically in the range of 40 to 80 MPa [2]. Since experimental values for crazing stresses are comparable for each of a number of polymers, it seems unlikely that the two-stage model can be generally valid, at least as currently stated. Instead we suggest that the bulk of the craze experiences a uniform stress, σ_c [3], similar to that postulated in the Dugdale plastic strip model.

We certainly agree with Williams that cyclic-stress-induced weakening will take place in some of the fibrils that span the craze. However, we postulate that the load across the craze will be redistributed among the remaining unbroken craze fibrils [3]. These fibrils are then envisioned to stretch further, thereby leading to enhanced orientation hardening. With further cycling, additional fibrils are expected to break and the remaining ligaments would correspondingly become more highly oriented. We suggest further that a steady-state balance is struck between these two competitive processes – weakening through fibril fracture, and strengthening due to orientation hardening of the remaining fibrils – with consequent development of a constant stress, σ_c, across the craze. Quantitatively, this stress level should correspond to the product of load-bearing fibril strength σ_f and fibril volume fraction ν_f so that $\sigma_c \approx \sigma_f \nu_f$. By way of confirmation, we find that computations involving fracture band widths, based on the Dugdale model, permit one to infer uniform craze stresses in several polymeric solids that, as mentioned above, are in good agreement with values reported in the literature by others [2].

Proceeding further, we believe that the weight of evidence does not support Williams' explanation for the sensitivity of FCP rates to test frequency. He argues that polymer crack growth rates may be given by

$$\frac{da}{dN} = A\left(\frac{\Delta K}{K_c}\right)^n \qquad (1)$$

where da/dN is the fatigue crack growth rate, A, n are material properties, ΔK the stress intensity factor range, and K_c the fracture toughness. Indeed, relationships of this form have been proposed by Wnuk [4] and supported by extensive experimental findings by several groups [5-7]. Using Equation 1, Williams then proposes that the sensitivity of FCP rate to frequency is controlled by the strain-rate sensitivity of K_c, the latter being given by

$$K_c^2 = E \cdot \sigma_{ys} \cdot \text{COD} \qquad (2)$$

where E is the elastic modulus, σ_{ys} the yield strength, and COD the crack opening displacement.

Earlier, Williams [8] assumed that the yield strain ϵ_y could be estimated from Hooke's Law as

$$\epsilon_y = \frac{\sigma_{ys}}{E} \qquad (3)$$

so that $K_c = E\sqrt{(\text{COD} \cdot \epsilon_y)}$. The use of Equation 3 in this situation seems questionable, especially since the modulus values used were defined at a strain of $3\frac{1}{2}\%$.

In any case, using yield strength and secant modulus data, along with Hooke's Law, Williams concluded that the yield strain was insensitive to strain rate and that the frequency sensitivity of K_c was due only to strain rate-induced changes in E.

We disagree with this analysis in principle and on the basis of lack of correlation with both existing data and new test results reported below. First, by defining a *secant* modulus at a strain of $3\frac{1}{2}\%$ and assuming a true elastic limit at a much lower strain level, one would expect the *secant* modulus to be strongly sensitive to the yield strength (see Fig. 1). It would not be surprising then to find the strong frequency sensitivity of E that was reported by Williams [8]. On the other hand, moduli of typical glassy polymers are stated to be relatively insensitive to strain rate, [9] and even semi-crystalline polymers show relatively small time-dependent changes below T_g [10]. If da/dN is to be changed by an order of magnitude (as is the case with some polymers [11–13]) then E would have to change by a factor of 1.33 even if we assume the high value of 8 for the exponent n in Equation 1 and assume that the frequency sensitivity of K_c is due only to strain rate-induced changes in E.

Second, in order to examine directly the frequency dependence of E, we recently obtained compliance measurements from standard compact-tension samples, using the same geometry used to generate our FCP test results. These measurements were obtained under cyclic loading conditions at test frequencies ranging from 0.1 to 100 Hz. With the aid of data processing from an on-line

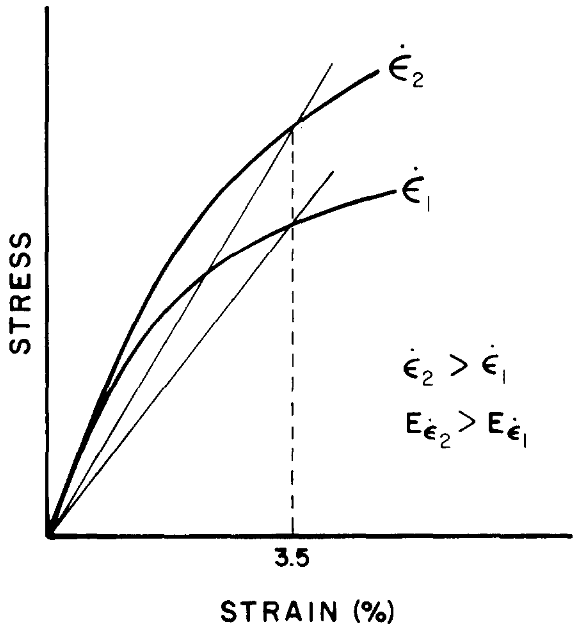

Figure 1 Secant modulus at 3.5% strain reflects strain rate induced changes in yield strength.

PDP-8e computer, 20 to 100 individual data points (depending on test frequency) corresponding to specimen load P and associated crack opening displacement ν were identified for each loading cycle. These values were used to establish a best-fit slope of the ΔP–$\Delta \nu$ line. Between 2 and 40 such slopes were then used to define a final average slope. For a given crack length to specimen width ratio a/W and specimen thickness B, the modulus of elasticity of each sample could then be computed from the known compliance calibration relationship for the test specimen. It is of particular note that for most of the materials tested, the computed value of elastic modulus did not change to any significant degree (Table I). Since the body of the compact tension sample is predominantly elastic and experiences very small strains, the results from these compliance measurements should reveal the material's *elastic* modulus rather than the *secant* modulus which Williams reported at a strain level of 3.5%. Because the FCP process and the associated crack-tip stress intensity conditions are controlled by the elastic volume surrounding the small crack-tip zone, the values of E reported here are considered to be more meaningful in assessing the FCP frequency dependence on $E(\dot{\epsilon})$. The reported E values are in some cases higher than those normally reported, based on conventional stress–strain data, but in general agreement with values reported based on dynamic mechanical data [14]. Higher values would not be surprising since the specimen strains are very low.

The results confirm the relative insensitivity to frequency anticipated for diverse polymers. Note in poly(vinyl chloride) (PVC), polystyrene (PS), and poly(phenylene oxide) (PPO), that the measured values of E changed by only about 1% for each of

TABLE I

Material	0.1 Hz	1 Hz	10 Hz	100 Hz	n	*$(E_{10\,\text{Hz}}/E_{1\,\text{Hz}})^n$	FSF [12]
Nylon 66 Dry	4160 MPa	4190 MPa	4190 MPa	4140 MPa	6.4	1	1
PVC ($\bar{M}_w = 1.4 \times 10^5$)	4590	4560	4600	4670	4.2	1.05	2.3
PVC ($\bar{M}_w = 2.3 \times 10^5$) + 6% DOP)	4290	4340	4410	4470	5.0	1.08	–
NORYL	3410	3490	3550	3580	4.9	1.09	2
ABS	3100	3170	3210	3210	3.7	1.05	1
PS	3930	3990	4120	4200	2.8	1.09	2.2
PMMA (laboratory cast $\bar{M}_w = 1.9 \times 10^5$)	5210	5740	6320	6980	9.3	2.44	1
PMMA (commercial $\bar{M}_w = 1.6 \times 10^6$)	3590	3960	4320		8.0	2.02	2.6
PC	3250	3270	3320		4.2	1.06	1

*Ratio of moduli at frequencies of 1 and 10 Hz.

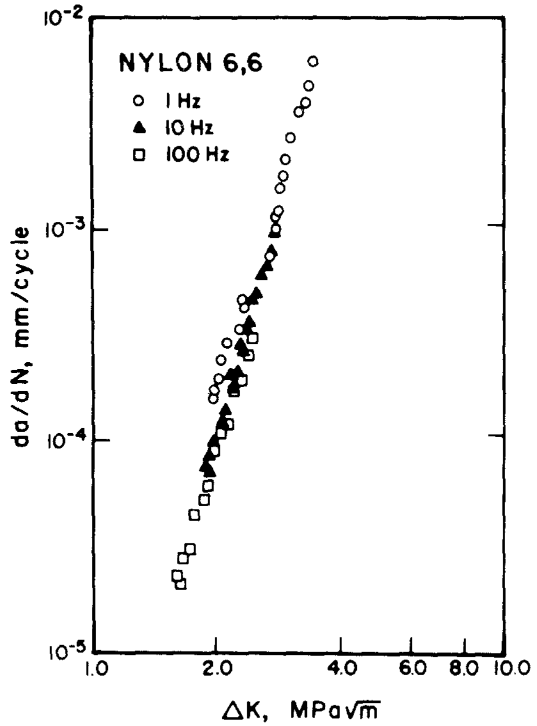

Figure 2 Fatigue crack propagation rates in nylon 66 at 1, 10 and 100 Hz. Note lack of frequency sensitivity on fatigue response.

several decade changes in cyclic test frequency. Compare this lack of modulus–frequency sensitivity with the previously documented strong FCP frequency sensitivity for these materials [11-13]. Clearly, frequency-induced changes in E cannot as a general rule account for the large frequency sensitivity factors (FSF) reported. Instead, we maintain our view that FCP frequency sensitivity is largely controlled by a resonance condition between test machine frequency and the frequency of molecular segmental motions associated with the β damping peak [11–13].

For the case of commercially prepared PMMA, we report an 8 to 10% change in E per decade change in test frequency which is considerably smaller than that reported by Williams, based on the 3.5% secant modulus [6]. This highlights the difference in E based upon different strain level reference points. When the $E(\dot{\epsilon})$ values are included in Equation 1 along with the material parameter n, the computed change in FCP rate per decade change in frequency is less than that actually measured. In fact, a similar $E(\dot{\epsilon})$ sensitivity was found in laboratory-cast PMMA and, yet no sensitivity of FCP to frequency was found in this material (Table I). Finally, tests were conducted on dry Nylon 66 to establish both the FSF and $E(\dot{\epsilon})$. We found no change in E as a function of test frequency and no sensitivity of FCP to frequency (see Fig. 2), as was also the case for nylon 66 containing an unknown amount of moisture [11]. The reason for the difference in frequency sensitivity of FCP rates between our results and those of El-Hakeem [15] (see [1], Fig. 9) for dry nylon 66 is not clear at this time.

We certainly agree that the value of E to be used is the value at the test frequency selected. However while the *secant* modulus may show a strong strain-rate sensitivity (presumably related to the strong strain-rate sensitivity of σ_{ys}), we conclude that the secant modulus is not the appropriate parameter for evaluating modulus effects on fatigue crack propagation behaviour. Rather, we conclude that the modulus defined at small elastic strains is a more meaningful parameter for this purpose. However the fact that $E(\dot{\epsilon})$ does not explain the FCP dependence on test frequency, supports our previously reported hypothesis that β-peak related segmental motions hold the key to the FCP frequency sensitivity in polymeric solids [11–13].

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Reply to 'Comments on "A model of fatigue crack growth in polymers"'

The comments cover two aspects of the paper; namely, the value of craze stresses predicted, and the frequency sensitivity. To consider first the very high values of craze stresses given, it must be pointed out that these arise from the very small crack growths per cycle which are measured and the necessity of maintaining equilibrium. These are observed in *steady-state* crack propagation which is what the model describes. The values quoted in the discussion, which are close to the static values, are deduced from *discontinuous* crack growth, where a craze was formed during cycling and the crack jumped through it. These crazes are much larger than the steady-state growth rate (i.e. $r_1 - r_0$ in the model) and hence the corresponding craze stresses are lower. It is suggested in the original paper that the G_c calculated in the steady-state growth may represent an elastic stress concentration which is broken down by fatigue to form a strong craze which sustains a stress of $\alpha\sigma_c$. Although the values of $\alpha\sigma_c$ are high for nylon 66, they are certainly not unreasonable for PMMA, PC and PS (unpublished data).

It is also worth noting that the model provides a possible explanation for steady-state and continuous crack growth. For steady state growth to occur, the new plastic zone, r_0, must be able to grow at least as fast as the crack moves in the craze so that equilibrium can be maintained, i.e.

$$\dot{r}_0 = \dot{a} = w\frac{\mathrm{d}a}{\mathrm{d}N}.$$

If a limiting plastic zone growth rate, $\dot{r}_{oc}$, were to exist, then the crack opening displacement would increase for $w\,\mathrm{d}a/\mathrm{d}N > \dot{r}_{oc}$ and the crack would grow through the whole craze, thus giving discontinuous growth. Those materials in which crazes form easily would, therefore, be expected to tend to give steady-state growth since they are more likely to have high $\dot{r}_{oc}$ values, while materials which craze with difficulty would be more likely to give discontinuous growth. It has been noted by Hertzberg (private communication) that steady-state growth is usually associated with multiple crazing at the crack tip which is frequently a sign of easy crazing and supports the basic contention here.

The second point discussed is that of frequency sensitivity and it is apparent that the paper is not clear in its main emphasis in that this has been construed as implying that the frequency sensitivity *must* be a reflection of modulus changes, whereas the text was meant to indicate that it *would* be. The basic physical argument in the paper is that the usual Paris law is of the form:

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$$\frac{da}{dN} \propto \left(\frac{K}{K_c}\right)^m$$

and that changes in da/dN with frequency are really reflections of changes in K_c. This is not a new concept and, indeed, it has been noted before that changes in K_c are reflected in da/dN. It is then proposed that the changes in K_c due to frequency are due to the visco-elasticity of the β transition in most cases (other transitions could be relevant) and that this can be represented approximately by:

$$K_c \propto w^{\tan \Delta}$$

where $\tan \Delta$ is the loss factor appropriate to the transition. This derivation is based on a constant crack opening displacement and assumes a modulus appropriate to the highly strained crack-tip region (hence, the use of a relatively high strain value). The high frequency sensitivity of da/dN is then seen to be the product $-m \tan \Delta$ and reflects the β transition through $\tan \Delta$. In their comments, the authors show that they can measure a small strain modulus which does not reflect the β transition, which is probably correct but the value is not relevant since the fatigue crack growth is influenced by the β transition. It is considered that the argument given here, while not complete, does provide a physical basis for the effect with some quantitative support. The author apologises for the lack of clarity on this point in the original presentation.

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The Larson–Miller C constant as applied to a cobalt-based directionally solidified eutectic alloy

The mechanical properties of the eutectic composite C73 [1] have attracted much interest over the past years with particular attention being given to the improvement of the ductility and creep strength of the alloy [2–6].

To carry out experiments within a reasonable time, a method has to be chosen which allows the extrapolation of long-time rupture data from short-time results. From the many methods available [7], the Larson–Miller parameter [8] is commonly used, with

$$(\log F_\sigma) = P_{\mathrm{LM}} = T(C + \log t_{\mathrm{B}})$$

where T is the absolute temperature, t_{B} is the rupture life and C is a constant widely assumed as being 20.

However, the use of this approach with data for directionally solidified high-temperature eutectic composites has been shown to be questionable. Buchanan and Tarshis [9], for example, found that the Larson–Miller parameter was dependent on stress level for the Co–15Cr–13TaC* eutectic alloy.

Recently, Woodford [10], working on the system Ni–13Ta found it necessary to vary the C constant in order to obtain a reliable correlation, the parameter becoming $P = T\,[(2000/\sigma) + \log t]$, where σ denotes the stress.

The purpose of this letter is to show that similar deviations are also to be found with a modified C73 eutectic alloy of composition 56.8% Co, 39% Cr, 2.2% C and 2% Al. A des-

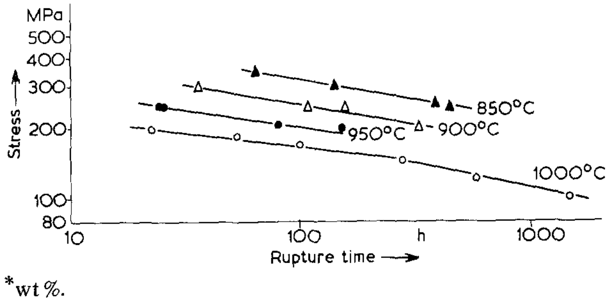

Figure 1 Logarithmic plot of stress versus rupture life for air data.

*wt %.

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