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An acoustic emission study of failure by stress corrosion in bundles of E-glass fibres

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Fibre failures in bundles of parallel E-glass fibres loaded from their ends and immersed in aqueous HCl solutions or in water are detected using acoustic emission. In constant load and constant stress tests the times to failure of the fibres and the bundles are accounted for on the basis of a theory which assumes a Weibull distribution of initial strengths, and that the velocity (v) of subcritical stress-corrosion cracks in the fibres depends on the stress intensity (K_I) according to a power law ($v \propto K_I^n$). The crack growth parameter (n) is measured by three methods, and its variation with acid strength is correlated with other corrosion studies. The stress corrosion measurements also allow a determination of the Weibull modulus of the fibres.

1. Introduction

Individual fibre breaks in a bundle containing a large number of strong parallel fibres in tension can readily be detected using acoustic emission (AE): this has been shown for fibres of Kevlar [1], carbon [2] and glass [3].

Recently [3] we reported a technique which enables the parameters of single fibre strength distribution for nominally similar glass fibres to be determined from a bundle test using AE. The method is convenient and rapid in comparison with strength measurement tests on individual fibres, and avoids the problems of contamination and damage to single fibres caused by handling, since the material is tested in the form of a continuous tow, which is a conventional factory product.

An initial aim of the present work was to develop an AE bundle testing technique which would enable the rapid acquisition of statistical data on stress corrosion failures of glass fibres. We have chosen to study E-glass fibres in water and aqueous HCl because of the technical applications interest. In particular, mineral acid environments have an aggressive attack on these fibres [4, 5] and consequently can cause cracking in stressed E-glass–resin composites [6].

Although several studies [7–10] have been made of the mechanical effects and chemical corrosion processes which occur in E-glass fibres during simple immersion in mineral acids, the physical mechanisms leading to stress corrosion (static fatigue) failure of the fibres in these environments are unresolved.

One theory of stress corrosion failure which applies to some brittle materials is based on the experimental result that preferential corrosion will occur at a crack tip to produce a subcritical crack velocity given by

$$v = \frac{da}{dt} = \alpha K_I^n \tag{1}$$

where α and n are constants for the particular material and environment. K_I is the mode I stress intensity and is related to the crack length, a, by the relationship

$$K_I = y\sigma a^{1/2} \tag{2}$$

where σ is the applied gross stress and y is a constant which depends on geometry.

The crack growth theory has been developed [11, 12] to predict stress corrosion failure rates of similar brittle components which have a Weibull distribution of fracture stresses. For E-glass fibres in a bundle under constant load and exposed to water at 20 °C the theory has been found to account for times to failure of the bundles and for the rates of failure of the individual fibres [12, 13]. Thus a further aim of the present work was to determine whether the static fatigue crack growth model is applicable to the important case of acidic corrosion of E-glass fibres under either constant stress or constant load.

2. Theory of stress corrosion cracking

2.1. Constant applied stress

The E-glass fibres used in this work have, in their uncorroded state, a Weibull distribution of strengths [3], according to which the fraction of a large sample of N_0 fibres which will survive the application of a tensile stress σ is given by

$$\frac{N}{N_0} = P = \exp\left(-\frac{\sigma}{\sigma_0}\right)^m \tag{3}$$

where σ_0 is a scale parameter and m is the Weibull modulus. It is assumed that catastrophically rapid fracture will occur in a fibre when the stress intensity at a crack exceeds a critical value K_{Ic}. Thus an uncorroded fibre which breaks at stress σ does so by

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fast fracture of a pre-existing crack of length a_i, given from Equations 2 and 3 by

$$a_i = \left(\frac{K_{IC}}{y\sigma_0}\right)^2 \left(\ln\frac{1}{P}\right)^{-2/m} \qquad (4)$$

In stress corrosion, a fibre under constant gross stress σ fails at time t_f due to growth of a crack from an initial length a_i to critical length a_c.

From Equations 1 and 2

$$\int_{a_i}^{a_c} a^{-n/2}\,\mathrm{d}a = \alpha\sigma^n y^n \int_0^{t_f} \mathrm{d}t \qquad (5)$$

or

$$\frac{2}{2-n} a_i^{(2-n)/2} \left[\left(\frac{a_c}{a_i}\right)^{(2-n)/2} - 1\right] = \alpha\sigma^n y^n t_f \qquad (6)$$

Provided that $\left(\frac{a_c}{a_i}\right)^{(2-n)/2} \ll 1$ the time to failure is

$$t_f = \frac{2}{\alpha y^n \sigma^n (n-2)} a_i^{(2-n)/2} \qquad (7)$$

Substitution of a_i from Equation 4 into Equation 7 yields the time $t(P)$ for a large sample of fibres to reach survival fraction $P(t)$ under conditions of constant environment and constant stress

$$t(P) = \frac{2\sigma_0^{n-2}}{\alpha(n-2)y^2 K_{\text{Ic}}^{n-2}} \left(\ln\frac{1}{P}\right)^{(n-2)/m} \sigma^{-n} \qquad (8)$$

AE data are continuously monitored in the bundle corrosion tests and can easily be extracted in the form of t and $P(t)$. It is convenient to determine the time for (say) 50% of the fibres to fail ($P(t) = 0.5$) and this so-called median lifetime is given, from Equation 8 by

$$t_{f.5} = C_1 \sigma^{-n} \qquad (9)$$

where C_1 is a constant. A plot of $\log t_{f.5}$ against $\log \sigma$ should then be linear and the slope will yield a value for n, the crack growth parameter.

From Equation 8 the fraction $P(t)$ of fibres which survive at time t in a corrosion test at constant stress is given by

$$\frac{1}{P(t)} = \exp(C_2 t^{m/(n-2)}) \qquad (10)$$

where C_2 is a constant. A plot of $\log[\ln 1/P(t)]$ against $\log t$ will be linear, if the theory is appropriate, and the slope will yield a value for $m/(n-2)$.

2.2. Constant load

On the basis of the crack growth model outlined in Section 2.1, Kelly and McCartney [12] have shown that in bundles of parallel glass fibres whose strengths follow a Weibull distribution, the fibre survival probability $P(t)$ in stress corrosion with constant applied bundle load F is given by

$$\left[C_3 P - \frac{1}{m} P^{n-1} \left(\ln\frac{1}{P}\right)^{C_4}\right] \frac{\mathrm{d}P}{\mathrm{d}t} = C_5 \qquad (11)$$

where

$$C_3 = \left(\frac{F}{N_0 \sigma_0 A}\right)^{n-2}$$

$$C_4 = \frac{n-2}{m} - 1$$

$$C_5 = \frac{1}{2}\alpha K_{\text{Ic}}^{n-2} y^2 \sigma_0^2 \left(\frac{F}{N_0 \sigma_0 A}\right)^n$$

Kelly and McCartney also show that the time to failure of a bundle is given by

$$\log t_f = -n \log F + \log\left(\frac{m^{2/m} \mathrm{e}^{n/m}}{n} F_{\max}^n \frac{1}{C_6}\right) \qquad (12)$$

where

$$C_6 = \frac{1}{2}\alpha K_{\text{Ic}}^{n-2} y^2 \sigma_0^2 = C_5 \bigg/ \left(\frac{F}{N_0 \sigma_0 A}\right)^n$$

and $F_{\max}$ is the maximum load which can be sustained by the uncorroded bundle. Equation 12 predicts a linear plot of $\log t_f$ against $\log F$ for stress corrosion of an E-glass fibre bundle under constant load in a given environment. Such a plot should yield an n value for the given conditions.

2.3. Incubation periods

In all corrosion tests on bundles of fibres described in this paper the acid or water environment was introduced at $t = 0$ and the stress on the fibres was constant during the incubation period $0 < t < t_i$ where t_i is the time of the first fibre fracture. Since the number of fibres (normally 200) in the bundles was large, the length $a_i(\max)$ of the largest pre-existing crack (and thus the minimum fibre strength) was approximately the same for each bundle tested. According to the theory, the value of $a_i(\max)$ determines t_i. Putting $a_i = a_i\,(\max)$ into Equation 7 we obtain

$$t_i = C_7 \sigma^{-n} \qquad (13)$$

where C_7 is a constant. For a given environment Equation 13 predicts a linear plot of $\log t_i$ against $\log \sigma$ and the slope should yield a value for n.

3. Materials and methods

E-glass fibres of nominal diameter 10 to 12 μm were supplied by Owens Corning Fibreglas (GB) Ltd in the form of continuous parallel tow. The number of fibres (about 200) in samples taken for stress-corrosion testing were determined from scanning electron micrographs. Each bundle specimen was fixed at its ends to aluminium plates using epoxy resin. The free (uncoupled) length of the fibres was 20 ± 2 mm. The end plates were mounted in the grips of an Instron machine, and the bundle was surrounded by a sealed polyethylene capsule to contain the liquid corrodant.

As described previously [3], each fibre break in a bundle under tension produced a single AE burst of large amplitude which was detected using AET type 140 B sensors. The electrical signals were amplified by 40 dB and processed using an AET 5000A real time processor which output amplitude, rise time, duration, energy and ringdown counts for each event. The overall amplification was 58 dB and the system dead time some 60 μsec. Dead time losses of AE signals were negligible.

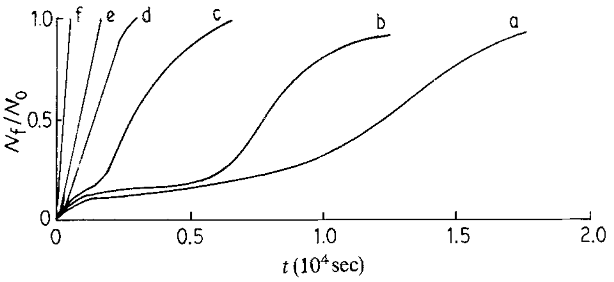

Figure 1 Failure fraction $N_f(t)/N_0$ plotted against time t for corrosion of E-glass fibres under constant applied stress in aqueous 2M HCl at 20 °C. The stress levels are (in GPa): curve a = 0.40; b = 0.43; c = 0.46; d = 0.57; e = 0.70; f = 0.97.

Loading of the bundles was done at 0.05 mm min^{-1}. There were normally zero fibre breaks due to application of the pre-load. The corrosive environment was introduced from a hypodermic syringe at $t = 0$. All tests were at room temperature, 20 ± 3 °C. Constant stress tests were done by maintaining the load to surviving fibre ratio, F/N constant. This gave constant stress on the fibres, provided that the mean fibre cross-sectional area was invariant during stress corrosion. In practice it was found that constant bundle strain effectively provided the constant stress condition.

In a separate corrosion test (without stress applied) 0.5 g samples of the E-glass fibres were immersed in 100 ml of aqueous HCl at 20 °C in polyethylene containers. This was done for HCl molarities in the range 0 to 6M. After immersion for 170 h the fibres were removed. The concentration of calcium in the surface layers of the fibres was measured by energy dispersive X-ray analysis (EDXRA), the calcium concentration in each case being referred to that of silicon. As a complementary test the calcium content of the acid solution was measured using atomic absorption spectroscopy (AA); the overall fractional loss of calcium from the fibres could then be deduced.

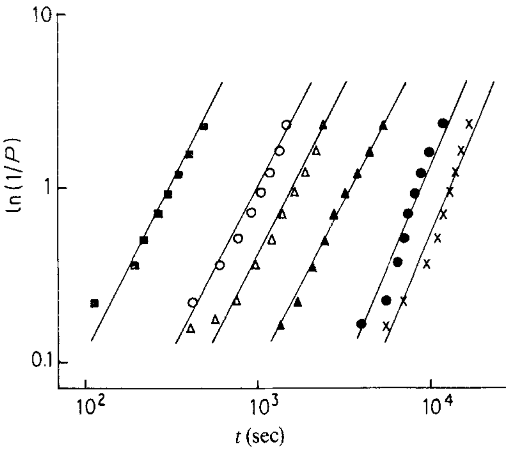

Figure 2 Log–log plot of ln 1/P against time t for corrosion of E-glass fibres under constant applied stress in aqueous 2M HCl at 20 °C. The stress levels are (in GPa): × 0.40; ● 0.43; ▲ 0.46; △ 0.57; ○ 0.70; ■ 0.97.

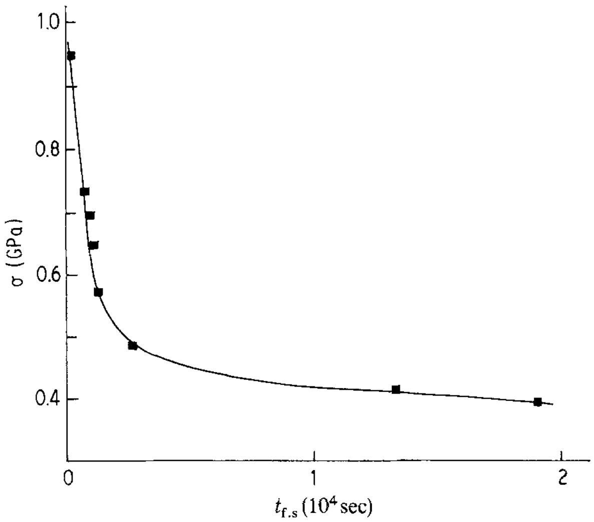

Figure 3 Median failure time $t_{f.5}$ plotted against applied stress for corrosion of E-glass fibres under constant applied stress in 2M HCl at 20 °C.

3. Results

3.1. Corrosion tests at constant stress

The results for constant stress were obtained using 2M aqueous HCl. Fig. 1 shows the failure fraction $N_f(t)/N_0$ plotted against time for bundles of E-glass fibres in this environment at several constant stress levels in the range 0.40 to 0.97 GPa. The curves in Fig. 1 are almost linear for stresses above ~ 0.5 GPa.

In Fig. 2 the failure data for the family of stress corrosion curves at constant stress is plotted in the form $\log(\ln 1/\rho)$ against $\log t$. The approximately parallel straight lines obtained are supportive of Equation 10, and their slopes yield a mean value $m/(n-2) = 1.8$.

Fig. 3 shows the variation of median failure time $t_{f.5}$ with applied stress in corrosion tests at constant stress in aqueous 2M HCl. A notable feature of Fig. 3 is that $t_{f.5}$ decreases with increasing applied stress much more rapidly at stresses between 0.4 and 0.5 GPa than is the case in the range 0.5 to 1.0 GPa.

Fig. 4 shows a plot on log–log axes of $t_{f.5}$ against applied stress. The graph is linear (correlation coefficient = 0.96) and the slope, from Equation 9, yields $n = 5.7$.

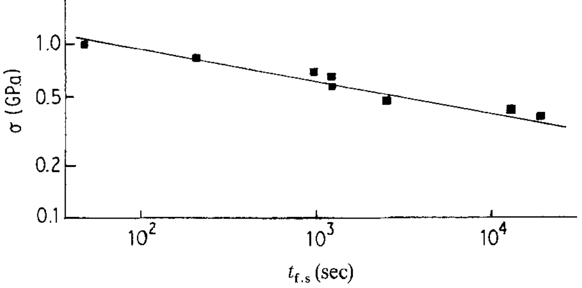

Figure 4 Log–log plot of median failure time $t_{f.5}$ plotted against stress for corrosion of E-glass fibres under constant applied stress in 2M HCl at 20 °C.

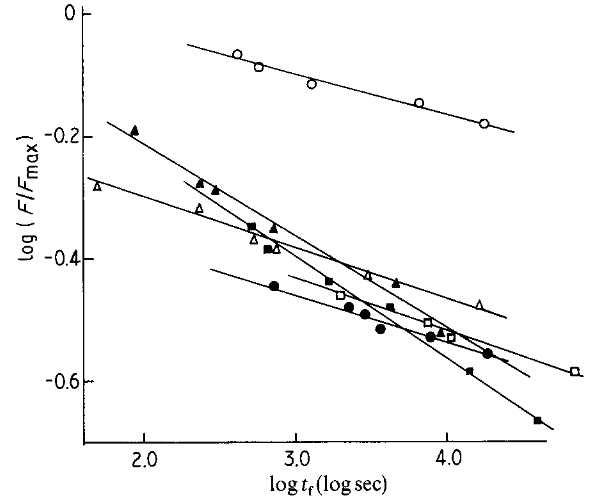

Figure 5 Log$(F/F_{\max})$ plotted against log t_f for corrosion of E-glass fibre bundles under constant load F at 20 °C. The corrodants were deionized water (○) and aqueous HCl of molarity 0.2M (●); 1M (▲); 2M (■); 4M (□) and 6M (△).

3.2. Corrosion tests at constant load

In the constant load tests times t_f to complete bundle failure were measured, and Fig. 5 shows, in accordance with Equation 12, linear plots of log t_f against log$(F/F_{\max})$ for aqueous HCl environments of molarity 6M, 4M, 2M, 1M and 0.2M and also for deionized water. In Fig. 6 the n values obtained from the slopes of the lines in Fig. 5 are plotted against acid strength. Fig. 6 shows that n is about 16 for deionized water and decreases with increasing acid strength until a minimum ($n = 5.7$) occurs at acid molarity $\simeq$ 2M. In the acid strength range 2M to 6M the n value increases with increasing acid molarity.

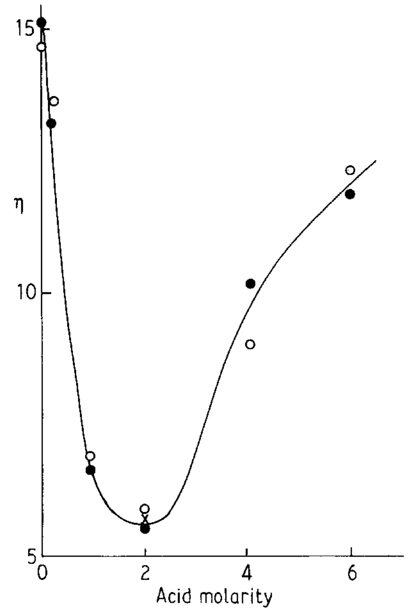

Figure 6 Crack growth parameter n plotted against acid molarity for stress corrosion of E-glass fibres in water and aqueous HCl at 20 °C. The n values were derived as follows (×) from $t_{f.5}$ data at constant stress (Fig. 4); (●) from t_f data at constant load (Fig. 5); (○) from t_i data (Fig. 8).

Fig. 7 shows the fraction of fibre breaks $N_f(t)/N_0$ plotted against t/t_f for bundle corrosion tests under constant load values $F/F_{\max} = 0$ and 0.38 (2M HCl acid, Fig. 7a); $F/F_{\max} = 0.67$ and 0.80 (deionized water, Fig. 7b). Fig. 7 also shows curves predicted by Equation 11 for several values of $F/F_{\max}$ with $m = 6.0$, taking $n = 5.7$ for 2M HCl acid (Fig. 7a) and $n = 16.0$ for deionized water (Fig. 7b). The solutions of Equation 11 are discussed in Section 4.

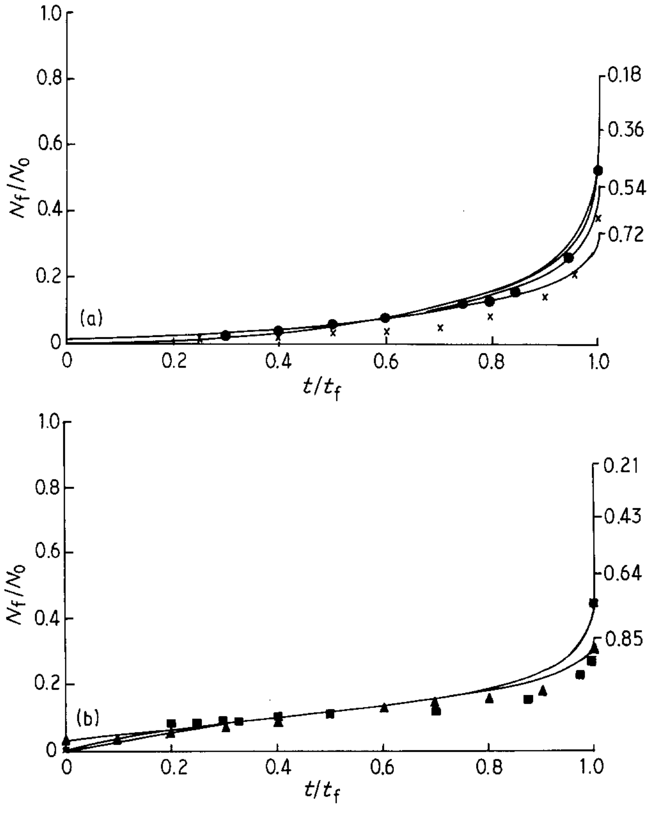

Figure 7 Fibre failure fraction $N_f(t)/N_0$ plotted against t/t_f for corrosion of E-glass fibres under constant applied load F at 20 °C. In aqueous HCl acid of molarity 2M (Fig. 7a) the applied loads $F/F_{\max}$ are 0.29 (●) and 0.38 (×); in deionized water (Fig. 7b) the applied loads $F/F_{\max}$ are 0.67 (■) and 0.80 (▲). The curves were generated using Equation 11 with $m = 6.0$ and $n = 5.7$ (Fig. 7a) or $n = 16.0$ (Fig. 7b); $F/F_{\max}$ values are indicated on the right-hand side.

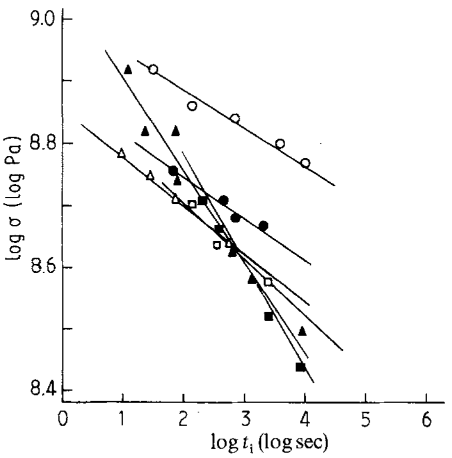

Figure 8 Log t plotted against log σ for corrosion of E-glass fibres at 20 °C. The corrodants are deionized water (○) and aqueous HCl of strength 0.2M (●); 1M (▲); 2M (■); 4M (□); and 6M (△).

3.3. Incubation times

The incubation time data in Fig. 8 indicate a linear variation of log t_i with log σ, in accordance with Equation 13. Values of n, the static fatigue parameter, derived from the slopes in Fig. 8 are plotted in Fig. 6 and show good agreement with the n values obtained by other methods.

3.4. Corrosion studies using AA and EDXRA

The AA and EDXRA results are shown in Fig. 9. Both sets of data indicate that loss of calcium from the E-glass fibres was zero at zero acid molarity and increased with increasing molarity in the range 0 to 1M. The peak loss of some 59% of the initial calcium content of the fibres occurred at acid strength ≃ 2M, while in the range 2M to 6M the loss of calcium decreased slowly with increasing acid molarity.

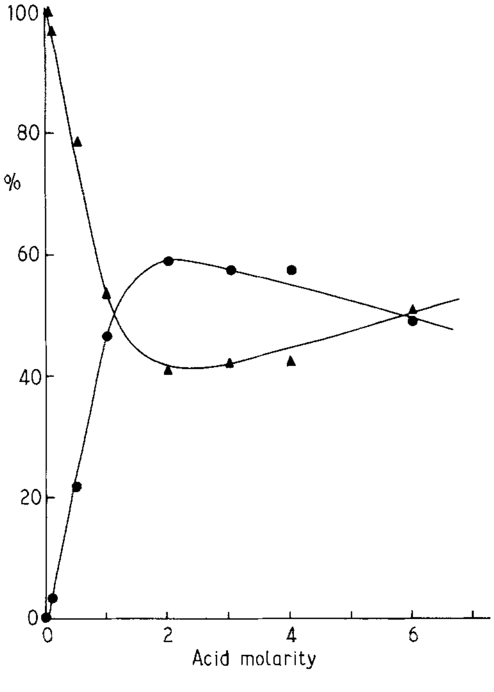

Figure 9 Percentage loss (●, from AA spectroscopy) and retention (▲, from EDXRA) of calcium in E-glass fibres following immersion for 170 h at 20 °C in aqueous HCl of various molarities in the range 0 to 6M.

4. Discussion

The results we have obtained for stress corrosion fractures in E-glass fibres and fibre bundles in aqueous HCl and water offer phenomenological support for the model of failure by static fatigue crack growth. It is surprising that this theory holds for a mineral acid environment, since there may be changes in structure [9] and tensile surface stresses are believed to arise in the fibres [6] principally by exchange of Ca^{++}, Al^{++} and Na^+ ions with H^+ ions from the acid.

With crack growth to critical size as the failure mechanism, determinations of the crack growth parameter, n (which depends on the particular material and environment) are of practical interest because n is an important quantity in determining stress corrosion failure times for either individual fibres or bundles. The present bundle tests show (Fig. 6) consistency among the direct determination of n by three methods, namely (i) variation of t_f with load in constant load tests; (ii) variation of $t_{f.5}$ with stress in constant stress tests; (iii) variation of t_i with stress. The t_i method for n has not previously been reported in the literature, perhaps because it requires large numbers of nominally similar components to be tested in the same conditions of stress and environment. In the bundle tests incubation times are readily measured by AE monitoring, and the number of fibres simultaneously under test can be so large that the incubation period observed approaches that of the total population.

There is an obvious correspondence between the minimum n value in Fig. 6 and the maximum loss of calcium ions from the fibres shown in Fig. 9: these turning points both occur at an acid molarity ≃ 2M.

Although the data of Figs 6 and 9 relate to different phenomena (Fig. 6 is indicative of the intensity of the HCl acid attack at crack tips in the stressed fibres, while Fig. 9 is concerned with a more general bulk or surface loss of calcium ions from the unstressed fibres) the results clearly imply that the more aggressive the acid attack, the lower is the n value. The fact that concentrated acids are less aggressive than diluted acids is believed [14] to be due to the larger dissociation constant of diluted acids.

The locations of the turning points in Figs 6 and 9 show a marked correlation with the results of Scrimshaw [10] who immersed unstressed E-glass fibres in aqueous HCl of various strengths at 22 °C for 96 h and then measured the tensile strengths of the dry fibres in air; the strength loss was maximum for acid molarity ≃ 2M.

For stress corrosion of E-glass fibres in 2M HCl acid we have obtained $n = 5.7$ and $m/(n-2) = 1.8$ from Figs 6 and 2, respectively, thus $m = 6.6$ from present data. This value for the Weibull modulus is similar to that obtained ($m = 6.5$) in our earlier tensile bundle tests [3] on the same material in inert conditions.

Fig. 2 shows that the variation of $N_f(t)$ with time is in accordance with Equation 10 for most of the duration of the constant stress tests, but there is a small excess number of fibre breaks at short test times. This effect may be due to the presence, already noted [3] in this material of a small proportion of fibres which have lower fracture stresses than predicted by the Weibull distribution of the majority population.

The predictions of theory [12] shown in Fig. 7 for fibre failures at constant load were obtained by numerical integration of Equation 11 using the Runge–Kutta–Merson method [15] assuming $m = 6.0$, $\sigma_0 = 1.95$ GPa and with $n = 5.7$ (2M acid, Fig. 7a) or $n = 16.0$ (deionized water, Fig. 16). The initial condition used was that at $t = 0$ in the inert environment, the P value was that predicted by the Weibull distribution for an applied load F.

The final boundary condition used was that the rate of fibre failure is very large at the end of the test, i.e. $d(1 - \rho)/dt \rightarrow \infty$ at $t = t_f$. The experimental points in Fig. 7a and b lie below the curves predicted by theory, yet clearly follow curves of similar shape. A further point of agreement between experiment and theory in Fig. 7 is that for each environment at the time of failure (and also at intermediate times where the theory curves are distinct, as in Fig. 7a) the value of $N_f(t)/N_0$ increases with decreasing $F/F_{\max}$.

5. Conclusions

This work has shown that the technique of acoustic emission monitoring of fibre breaks in bundles of parallel glass fibres in tension, which we have previously developed to determine fibre strength distributions, can further be exploited as a rapid and convenient means of studying stress corrosion failures. For many applications of glass fibres the study represents a more realistic test of the useful durability of these components than can be obtained by measuring environmental changes which occur during immersion under zero applied stress.

The results, concerning stress corrosion in water and aqueous HCl at room temperature, are consistent with the occurrence of a subcritical crack velocity $V \propto K_I^n$, together with a Weibull distribution of initial strengths.

The bundle test has enabled rapid determinations of the crack growth parameter, n, by three direct methods, including the novel one of incubation times. The n value is minimum for HCl acid molarity $\simeq$ 2M, and this acid strength also gives the highest loss rate of calcium ions. The result indicates that for mineral acids the more aggressive the acid attack on the glass the lower is the n value. The present stress corrosion measurements have also enabled a determination of the Weibull modulus for the fibres, $m = 6.6$, a result which is in good agreement with our earlier data obtained from tensile bundle tests on the same batch of material.

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