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Stress-corrosion failure envelopes for E-glass fibre bundles

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Tests have been conducted on stressed and unstressed fibre bundles under attack by aqueous hydrochloric acid of various concentrations. Without an applied stress, fibre weakening occurs at long times by core-sheath development. With an applied stress, failure occurs more rapidly, following a fatigue law with an exponent that is a function of acid concentration. The value of this exponent and the time required for bundle failure are in agreement with data obtained from experiments on the stress corrosion of composites.

1. Introduction

The stress corrosion of fibre reinforced composites, such as E-glass reinforced polyester resins, occurs as a result of a combination of tensile loads and exposure to a corrosive medium such as an aqueous acid. Sharp cracks nucleate and propagate through the material as a direct consequence of the weakening of the glass fibres by the acid. Since the majority of the load is carried by the fibres, these cracks can propagate through the material provided that the local load on the weakened fibres exceeds their fracture strength. The presence of the corrosive medium causes the failure of fibres at loads much below their normal failure strength. The acid is believed to reach the fibres by flowing through microcracks, crazes or similar voids in the matrix, which occur as a consequence of the stress intensification ahead of the tip of a growing stress-corrosion crack [1]. Fibre weakening and failure is thus a process that occurs sequentially at the tip of a growing crack and evidence is available to show that the fibres fail in a stepwise manner, with a discrete waiting period between individual fibre breakages [2]. This waiting period is associated with the time required for the acid to reach the fibre surface and to promote the weakening that eventually causes the fibre to break under the action of the local load.

To relate the waiting period to physical mechanisms it is important to separate two contributory factors; firstly, the time taken for the acid to cross the resin web separating the fibres in the composite, and secondly, the time needed for the acid to weaken the fibres. In different circumstances either of these processes may be rate-determining. The first of these has been considered elsewhere [3]. This paper considers the latter. The weakening time will depend on both the acid concentration and the local stress at the fibre surface.

The weakening of both stressed and unstressed glass fibres exposed to a range of acid concentrations has been examined using bundle specimens made from E-glass roving. Bundle tests [4] were used to allow a much wider range of stress corrosion test conditions to be explored than would conveniently be possible with single fibre techniques. The main area of interest is that in which the mean fibre failure time is between 5–20 min, since this is the typical time between individual fibre fracture events during stress corrosion crack propagation at low stress intensities [2]. The principal aim of this work is to identify the conditions under which fibre failure will occur within this timescale.

2. Experimental procedure

Bundles containing 4000 E-glass fibres (Pilkington Equerove 2347 roving) were subjected to a range of tensile strains and acid concentrations. To ensure that the load is concentrated in the gauge length rather than in the grips and to avoid mechanical damage, the ends of the bundles were embedded in an epoxy resin. These ends are then somewhat stronger than the central glass strand and fibre fracture occurs within the gauge length. Card end-tabs were affixed to the specimen ends to facilitate gripping during the tensile tests.

Two types of test were conducted. Firstly, ageing tests in which bundles were subjected to acid corrosion in a stress-free condition [5], and secondly static fatigue tests [6, 7], where acid attack and stress were simultaneously applied. The protective size on the filaments was removed by immersing the gauge length successively in acetone, deionised water, and again in acetone. This was done to ensure that the environment had unrestricted access to the filament surface. The fibres were allowed to dry in air and were then immersed in the test solution for the prescribed exposure time. After exposure the specimens were

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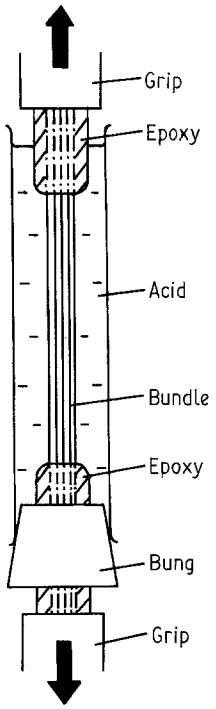

Figure 1 Schematic diagram of static fatigue test cell, with E-glass bundle surrounded by corrosive medium.

washed again with deionised water and acetone and then dried in air. All the tensile tests were performed using an Instron 1185 test machine. With care it was found possible to conduct the exposures and mount the specimens in the machine without mechanically damaging the fibre bundles.

The static fatigue tests were carried out in a creep rupture rig, which provided the means for loading the fibres to the required extent through a 10:1 lever arm. The rig had provision for automatically recording the time at which bundle fracture occurred. To enable stress and acid to be applied simultaneously a simple environmental cell was designed and is shown schematically in Fig. 1. In this case the region of composite material at the specimen ends was extended, such that a short length of roving outside the end tabs was treated with epoxy resin. A split rubber bung was used to form a seal around the bundle ends, the faces of the split bung being coated with silicone rubber sealant before assembly. A glass tube attached to the bung provided an enclosure within which the gauge length could be continuously exposed to an aqueous solution whilst under tensile load, as shown in Fig. 1.

3. Results of bundle tests

3.1. Aged bundles

Tests using the bundle ageing method were carried out to explore the effects of exposure time and acid concentration on the residual bundle strength. The gauge length of the specimens varied between 70 and 90 mm and did not appear to have a significant effect on the results. The tests were conducted at a constant crosshead speed of 0.5 mm min^{-1}, and the results obtained are shown in Fig. 2. The maximum load to failure is plotted for different acid concentrations after exposures of 2, 4 and 16 h. At short exposure times, in the range 0–20 min, the weakening produced by ageing was insignificant, even with molar hydrochloric acid.

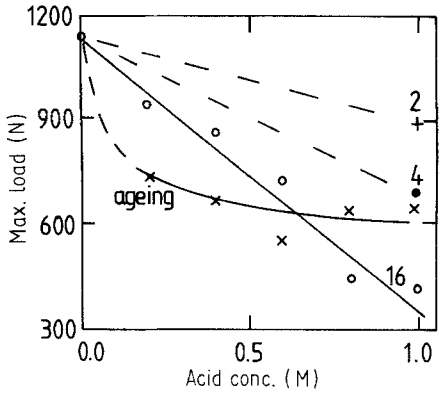

Figure 2 Plots of maximum load at failure against acid concentration for ageing tests of 2 (+), 4 (●) and 16 h. (○). Also, plot for 2 h ageing followed by Instron tensile test in corrosive environment (×).

Before proceeding to tests where the fibres were exposed to the acid under load, an intermediate experiment was carried out. In this series of tests the fibres were exposed to the molar acid solution in an unstressed condition. They were then tested in tension as before, except that the acid environment still surrounded the fibre bundle. The purpose of this test was to contrast the long-term fibre weakening, associated with fibre ageing, with the short-term static fatigue effects that can occur even during the relatively short duration of the tensile test (approximately 3 min). For the ageing part of these tests a 2 h exposure period was used. The results obtained in this way are also shown in Fig. 2.

3.2. Static fatigue tests

To evaluate the combined effects of applied stress and acid concentration on the failure times of the bundles, tests were carried out at a series of constant loads. The results from these tests are given in Fig. 3, which shows the time for bundle breakage as a function of acid concentration at various loads. Unexposed bundles withstood a load of 1200–1300 N for up to 1 min before the strand broke in the gauge length. At lower loads the unexposed fibres maintained their strength indefinitely until the acid environment was introduced. In Fig. 3, each curve is annotated with the applied load, expressed as a fraction of the dry failure load of the bundle, which is 1250 N. For an average fibre diameter of 17 μm this corresponds to a bundle

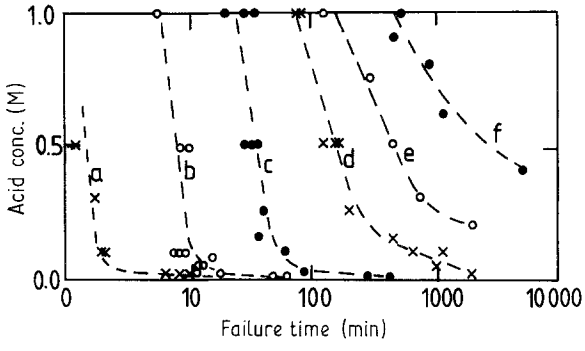

Figure 3 Plot of acid concentration against failure time for static fatigue tests of bundles at fractions of the dry fibre failure load of 1250 N. Load fractions: (a) 0.625, (b) 0.416, (c) 0.333, (d) 0.250, (e) 0.167, (f) 0.125.

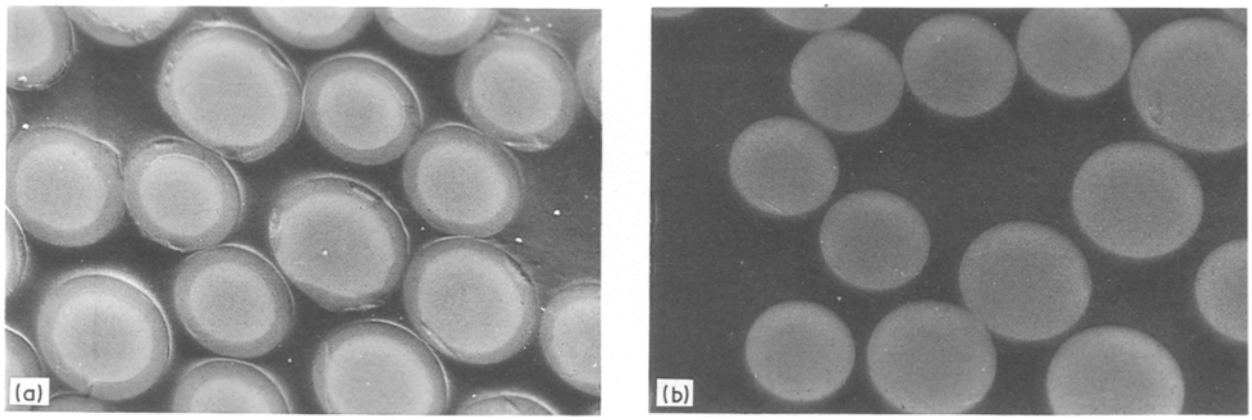

Figure 4 SEM photograph of (a) core-sheath morphology seen in fibres exposed to molar HCl for 16 h, (b) absence of core-sheath structure in fibres exposed to molar HCl for 20 min.

strength of 1.38 GPa. Accurate measurements of the fibre diameters for these bundles are given elsewhere [5].

In examining the effect of acid concentration on the failure time, the experimental data at low loads was confined to the higher concentrations because of the very long failure times observed at lower concentrations. At higher loads the tests were conducted over a very wide range of acid concentrations. At loads greater than 80% of the dry bundle strength exposure to pure water reduces the bundle failure time, as shown by the results listed in Table 1. In Fig. 3 the relative insensitivity to acid concentration at the higher loads and the existence of a lower limit to the acid concentration, below which significant weakening does not occur, leads to the occurrence of a characteristic "knee" in the plots.

4. Discussion

4.1. Core-sheath structures in aged fibres

The results in Fig. 2 show that, without applied stress, severe reductions in bundle strength only occur after prolonged exposure to molar hydrochloric acid. Thus, a reduction by a factor of two in bundle strength was observed at an exposure time of about 4 h. The weakening is also seen to be a strong function of concentration. At a concentration of 0.1 M and below very little weakening of the unstressed fibres occurred, even after an exposure time of 16 h. It should also be noted that only very slight reductions in bundle strength resulted from short exposures to the acid. Thus, exposure times of up to 20 min did not cause unstressed fibres to be weakened significantly.

It is well known that the long term exposure of unstressed E-glass fibres to mineral acids, at concentrations of around 1.0 M, results in the selective removal of calcium and aluminium from the surface of the glass [5, 9–12]. This demineralisation process has a very marked effect on the mechanical strength of the glass. E-glass fibres exposed to acid solutions for periods in excess of 8 h develop a characteristic core-sheath morphology. This is shown in Fig. 4, which is an SEM photograph of cross-sections of some of the fibres from a bundle that had been exposed in an unstressed condition to molar HCl for 16 h. Bledski *et al* [12] and Evans *et al* [5] have shown that the demineralised siliceous sheath is much weaker than the E-glass core and have made a detailed study of the strength reduction of fibres exhibiting the core-sheath structure. Their results show that the reduction in tensile strength is well correlated with the reduction in area of the load-bearing core of the acid treated fibre. This analysis provides a satisfactory explanation of the effects of long term exposure of unstressed fibres to acid solutions on filament strength. However, it does not explain how fibres can be weakened by this mechanism in much shorter times, in the range 1–20 min, by dilute acid solutions that do not produce the core-sheath structure even after prolonged exposure. The results of the present work, taken together with the other available data on the formation of the core-sheath structure, show that, even with acid concentrations in the region of 1.0 M, the timescale for core-sheath formation is relatively long at 25° C. The reduction in area associated with exposures of 1–20 min is extremely small, and cannot be seen at all in the scanning electron microscope (SEM) (see Fig 4b). It is therefore concluded that fibre area reduction is not the cause of fibre failure during stress corrosion crack propagation.

TABLE I Fibre weakening by pure water in static fatigue tests

Fractional applied load, relative to dry strength of bundle of 1250N	Failure time, minutes
> 0.95	< 5
0.90	100
0.85	200
0.80	> 2000

The data in Fig. 2, relating to fibres that had been aged and then tested whilst still in contact with the acid, provide further support for this view. These data highlight the importance of stress as a crucial factor in short term fibre weakening. During the relatively short duration of the tensile test, there is significant fibre weakening, even with the most dilute acid tested. The data do not show a strong dependence on acid concentration over the range studied, a similar strength reduction being observed for all the tests. This reduction was similar to that obtained in the simple ageing tests with molar hydrochloric acid at an exposure time of 4 h. Thus the additional weakening

seen in these bundles occurred during the tensile test itself. This suggests that a second, more severe, mechanism of fibre weakening exists, in which the combined effects of the environment and the stress lead to an enhanced rate of fibre failure.

4.2. Static fatigue

Static fatigue is known to be a much more severe test condition than fibre ageing [4, 7]. This is borne out by the results shown in Fig. 3, where it can be seen that the combination of high applied stress and high acid concentration leads to bundle failure in very short times. The level of the applied stress has a dominant effect on the bundle failure times. Provided that the acid concentration is above the threshold defined by the "knee" in the profile, the failure time is relatively insensitive to this concentration, especially at loads near to the breaking load of the untreated bundle. The results in Table 1 show that in very high load regimes pure water is capable of weakening the fibres. This is consistent with the results reported by Metcalfe and Schmitz [16] for static fatigue tests carried out on single fibres exposed to water vapour in a humidity cabinet. Aveston and Sillwood [8] have also found that in very long term tests exposure to water was capable of weakening E-glass fibres that had been exposed under load. The timescale for this weakening was, however, of the order of years. Again, this is in agreement with the results in Table 1, which show that at loads below 80% of the dry fracture load the failure time in pure water is extremely long.

The effect of acid concentration becomes more important at lower loads, as can be seen by the change in the slope of the profiles shown in Fig. 3. At these lower loads the time to failure is sufficiently large that the core-sheath effect has time to develop. The limiting case is when the load is zero, at which point the time to failure is effectively that for complete sheath formation, since the sheath has negligible strength [5]. Sheath formation is very dependent on acid concentration [4, 7, 11] and does not lead to significant fibre weakening in medium-term exposures at concentrations below 0.1 M.

Figure 3 shows that the range of fibre failure times observed in the static fatigue tests includes the critical timescale of 1–20 min associated with the crack propagation data of Kumosa *et al.* [2]. The present results suggest that, with aqueous hydrochloric acid concentrations in the range 0.5–1.0 M, fibre loading of the order of one third to half of the dry breaking load would lead to fibre failure within this timescale. In a composite system where a crack is propagating such loads can easily be reached locally, due to crack tip stress concentrations, for much lower applied loads. The results are thus in accord with the view that static fatigue, rather than fibre ageing, is the dominant fibre weakening process during stress-corrosion crack propagation in E-glass/polyester composites.

To describe the failure mechanism in static fatigue, a defect initiated fracture mechanism is considered, rather than a core-sheath weakening process. The results in Fig. 3 for three acid concentrations have been replotted in Fig. 5, where it can be seen that they

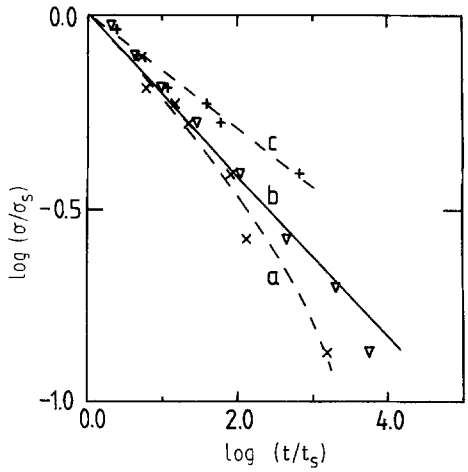

Figure 5 Log-log plot of failure stress against time to failure for (a) M HCl, (b) 0.5 M HCl and (c) 0.1 M HCl. The normalising constants t_s and σ_s are defined in the text.

conform with the standard fatigue equation [6]:

$$(\sigma/\sigma_s)^{-n} = t/t_s \quad (1)$$

In this equation t_s is the high stress failure time at a stress σ_s and t is the time required for the fibres to fracture when exposed to a lower stress, σ. In deriving this plot σ_s was arbitrarily chosen as 750 N and t_s is therefore the failure time at this load, i.e. 1 min. At this high load the failure time is essentially independent of the acid concentration.

This equation can easily be related to the usual expression for the crack propagation rate, $\dot{a}$ [8] given by:

$$\dot{a} = \alpha K_I^n \quad (2)$$

where K_I is the stress intensity factor and α is a constant. Let the crack propagation rate at the stress σ_s be $\dot{a}_s$ with intensity factor K_{Is}. For short times $K_{Is} \approx K_{IC}$, the critical stress intensity factor for dry fibres. Then:

$$\dot{a}_s = \alpha K_{Is}^n \quad (3)$$

Dividing Equation 2 by 3 gives:

$$(\dot{a}/\dot{a}_s) = (K_I/K_{Is})^n \quad (4)$$

If we assume a constant crack growth rate and that the stress intensity factor is linearly related to stress, then:

$$\dot{a}_s \propto 1/t$$
$$K_I \propto \sigma$$

Using these two assumptions in Equation 4 yields:

$$(t_s/t) = (\sigma/\sigma_s)^n \quad (5)$$

which is identical to Equation 1.

Equation 1 asserts that $\log(\sigma/\sigma_s)$ against $\log(t/t_s)$ will be linear with a slope of $-1/n$. In Fig. 5 the continuous line has been fitted to the data for the three acid concentrations. The line drawn through the data has a slope corresponding to an n value of 4.8. It is interesting to note that this value compares well with the value of approximately 4 obtained by Price and Hull [13] by the direct measurement of crack velocity in a range of E-glass polyester composites exposed to 0.6 M hydrochloric acid. This indicates that there are equivalent fracture processes both with fibre bundles and reinforced composites.

Figure 5 shows that all the points fit the linear relationship well for failure times up to about 10 h. At longer times the data for the 1.0 M and 0.5 M acid deviate to give failure at shorter times than predicted by the line. This attributed to the fact that core-sheath effects become significant by this time, with an appreciable loss of core area. The data for 0.1 M are seen to show a lower gradient. The dashed lines show separate fits for the 0.1 M and 1.0 M concentrations. The data for the 0.5 M concentration still gives an n value of 4.8, while the 0.1 M data gives an n of 6.8. This is in agreement with Equation 4 where a larger value of n will produce a slower crack propagation rate (since $K_I/K_{Is} < 1$). As expected, a lower acid concentration results in a slower crack propagation rate. It is noteworthy that the 1.0 M acid gives a non-linear response at longer exposure times, presumably due to the increasing importance of core-sheath formation in this situation.

Equation 1 has also been derived from a detailed model of bundle failure by Kelly and McCartney [14], using a full Weibull analysis [15] for bundle failure by stress-corrosion. It was shown that the stress/time behaviour of the bundle is relatively insensitive to the Weibull shape parameter m, provided that m is about 8 or larger. Such values for m have indeed been measured in these bundle samples [5]. Thus, stress-corrosion appears to generate or activate similar flaw distributions in all fibres, leading to a narrow fibre failure distribution (i.e. large m). This is consistent with the static fatigue data obtained by Aveston and Sillwood on fibre bundles [8], where it was found that 90% of the fibres in the bundle were intact up to the failure time, when the majority of the fibres failed together. It is also in agreement with the high measured value for m found previously [5] in tensile tests on bundles. Hence, the difference between the bundle fracture load and the mean single fibre fracture strength is not large because the distribution of strengths is not wide, i.e. the m value is high.

5. Conclusions

Results from ageing and static fatigue tests on E-glass fibre bundles exposed to aqueous hydrochloric acid have been used to map the stress–acid concentration–exposure time envelope within which fibre failure will occur. From these data the stress/acid concentration combinations required for failure within the times typical for composites undergoing stress-corrosion crack propagation can be specified. The results have been examined critically to see if the mechanism of fibre weakening during stress-corrosion crack propagation in composites can be attributed to either fibre ageing or static fatigue.

Fibre ageing, which occurs when unstressed fibres are exposed to the aqueous acid, is a relatively long-term fibre weakening process. it is not thought to be directly involved in the short-term weakening that is characteristic of fibre failure during stress-corrosion crack propagation in composites. The experimental results support the view that the development of a well-defined core-sheath morphology is not essential to the stress corrosion crack propagation mechanism.

In contrast to this, the static fatigue results strongly indicate that short-term fibre weakening is the principal cause of fibre failure during composite stress-corrosion. The dominant factor is the level of the applied stress at the crack tip, which, acting in concert with the acid concentration, is capable of bringing the fibre failure times into the range that accords with observed composite crack propagation rates.

References

1. P. J. HOGG and D. HULL, "Developments in GRP technology", (Edited by B. Harris, Applied Science Publishers, London). Vol. 1, 1983, pp. 37–90.
2. M. KUMOSA, D. HULL and J. N. PRICE, *J. Mater. Sci.* **22** (1987) 331.
3. B. D. CADDOCK, K. E. EVANS and D. HULL, *J. Mater. Sci* **22** (1987) 3368.
4. B. A. PROCTOR "Glass - Current Issues", Proceedings of NATO Advanced Study Institute Conference, 1984 (Dordrecht, Netherlands; Martinus Nijhoff, 1985) pp. 524–50.
5. K. E. EVANS, B. D. CADDOCK and K. L. AINSWORTH, *J. Mater. Sci.*, **23** (1988) 2926.
6. S. M. WIEDERHORN, *J. Non-Cryst. Solids* **19** (1975) 169.
7. G. SCRIMSHAW, "Paper 6 in PipeCon" in Proceedings of Conference on Large Diameter Plastic Pipes, (Fibreglass Ltd., and Amoco Chemicals S.A., London, 1980).
8. J. AVESTON and J. M. SILWOOD, *J. Mater. Sci.* **17** (1982) 3491.
9. H. A. BARKER, I. G. BAIRD-SMITH and F. R. JONES, Paper 12, Symposium on Reinforced Plastics in Anticorrosion Applications, National Engineering Laboratory, East Kilbride, September 1979 (NEL, East Kilbride, Glasgow).
10. A. G. METCALFE, M. E. GULDEN and G. K. SCHMITZ, *Glass Technol.* **12** (1971) 15.
11. D. R. COCKRAM, K. L. LITHERLAND, B. A. PROCTOR and B. YALE, "Assessing the durability of glass composites", 13th International Congress on Glass, Hamburg, 1983, pp. 644–649, (Deutsche Glastechnische Gesellschaft).
12. A. BLEDSKI, R. SPAUDE and G. W. EHRENSTEIN, *Compos. Sci. and Technol.* **23** (1985) 263.
13. J. N. PRICE and D. HULL, *J. Mater. Sci.* **18** (1983) 2798.
14. A. KELLY and L. N. McCARTNEY, Proceedings Royal Society London, **A374** (1981) 475.
15. W. WEIBULL, *J. Appl. Mech.* **18** (1951) 293.
16. G. SCHMITZ and A. G. METCALFE, *Am. Chem. Soc., Ind. and Eng. Chem., Prod. Res. and Dev.* **5** (1966) 1.

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