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Statistical changes during the corrosion of glass fibre bundles

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The mechanical properties of E-glass fibre bundles have been measured after corrosive attack by hydrochloric acid of various concentrations for various times. The effective stiffness of the fibre bundles is seen to be proportional to the effective cross-sectional area of the fibres as identified with the characteristic core–sheath geometry found in fibres exposed to long-term acid attack. However, the strength of the fibre bundles is not simply related to the effective area of the fibres and the statistics of fibre strength vary considerably with time. In particular the Weibull shape parameter is seen to increase rapidly at short times, before core–sheath formation is observed, and then fall slowly with core–sheath formation. Hence we have a short-term narrowing of the strength distribution followed by a long-term broadening.

1. Introduction

The statistical variation of the tensile strength of glass fibres has been the subject of considerable research over many years, both experimentally and theoretically. Two main areas of research have been considered: the mechanical behaviour of collections of dry fibres [1, 2] and the behaviour of fibres in corrosive environments [3]. These areas have been of interest in more recent research, in the first case [4, 5] because of new developments in the theoretical understanding of fibre statistics and in the second case [6, 7] because of the problems of stress corrosion effects in composites. An understanding of the corrosion of glass-reinforced plastic (GRP) composites requires information about the migration of the corrosive medium and about the failure process initiated by the medium. Both these areas are currently under study [8–10] and it is the latter that this paper considers.

The principal cause of failure in the stress corrosion of GRP composites is the loss of strength caused by the corrosive degradation of the glass fibres. In the particular case of E-glass fibres under attack by strong acids the mechanism for failure is believed to be due to decalcification of the fibres by the acid [9, 10]. The exact mechanism for failure in composite systems is still not fully understood, as the characteristic core–sheath phenomenon to be seen in glass fibres suffering from long-term acid corrosion is not present in fibres that have failed in composites [7]. As will be shown later, this paper will identify short-term phenomena present in unprotected glass fibres that are of relevance to the failure of glass-reinforced composites.

The majority of work on the stress corrosion of glass fibres has used one of two methods. Either statistical data have been collected by the sequential testing of many single fibres [3] or average properties have been obtained from the testing of fibre bundles [9, 10]. The former technique involves very large numbers of difficult tests to obtain adequate statistics of failure, given the variation in failure strength from fibre to fibre. The latter method only provides information on the average performance of large numbers of fibres which, as we shall see below, is an inadequate description of their behaviour.

However, it has been shown [11, 12] that the statistical variation in mechanical properties, as well as the average strength, can be obtained from the testing of fibre bundles. The statistical data obtained are then comparable to those from many single-fibre tests and are much more conveniently obtained. The statistical analysis of fibre strength is normally described using a two-parameter Weibull distribution. This technique will be used here since this distribution provides an adequate description of the properties of the fibres. Essentially, we require a distribution containing a measure of the average strength, $\bar{\sigma}$, of a single fibre, the scatter in this strength provided by the Weibull shape parameter m, and some measure of the maximum strength of a single fibre provided by the Weibull scale parameter σ_0. It should be noted, however, that although the Weibull distribution has been shown to provide an accurate description of the behaviour of glass fibres there is no *ab initio* calculation available, based on any physically reasonable description of fibre failure, that has obtained this distribution directly.

2. Experimental methods

All the tests involved the exposure of bundles of E-glass fibres (Pilkington Equerove 2347, 4000 fibres per bundle with a nominal mean fibre diameter of 17 μm) to hydrochloric acid of concentration between 0.0 and 1.0 M. The times of exposure varied between 0 and 72 h.

The specimens were prepared using a variant of the standard card method for single-fibre tensile tests [13, 14] by carefully coating the ends of the fibre

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TABLE I Fraction of fibre area in core region, as a function of time, during attack by 1 M HCl (fibre diameter = 16.7 μm)

Time (h)	0	1.0	2.0	3.0	4.0	5.0	7.0	12.0	16.0	21.0	48.0	72.0
Area fraction	1.0	1.0	1.0	0.93	0.92	0.91	0.87	0.78	0.75	0.71	0.57	0.50

bundles in epoxy resin and sandwiching them between cards. The gauge length of the specimens throughout the tests was 90 mm. Before exposure to acid the majority of samples were desized by repeated washing in acetone, followed by drying in air. After exposure to acid for the appropriate time the specimens were washed with water, dried with acetone and mechanically tested using an Instron 1185 tensile testing machine. To ensure good bonding and transfer of strain from the Instron to the specimens, comparison was made between the strain measured by the rate of crosshead movement and the strain measured directly, using an optical extensometer, from the change in gauge length. The difference in data obtained by the two methods was not found to be significant within the experimental error of the measurements. By testing between 5 and 10 samples for each acid concentration and time period it was found that the results were very consistent, and hence that variations due to problems of fibre bonding within the grips from specimen to specimen were negligible. The bundles were also seen to fail at random positions from fibre to fibre, producing a characteristic cotton-wool appearance and hence indicating that there was no stress intensification at the grips.

A selection of samples were polished and examined using an SEM to measure the extent of corrosive attack by the acid. The characteristic core-sheath phenomenon [6, 10, 15, 16] was observed and image analysis techniques were used to obtain the fractional area of the core relative to the initial fibre area; these data, for 1 M HCl, are presented in Table I. The average fibre diameter was 16.7 μm.

Over 150 tensile tests were performed. The results obtained, for differing times of exposure and acid concentration, using the analysis described in the next section, are summarized in Tables II to V below.

3. Analysis of results

The method used to determine the Weibull parameters for the fibre bundles follows that described by Chi *et al.* [12]. This utilizes the tensile load–strain curve to obtain the fibre modulus, bundle strength and Weibull parameters. The method is fully described elsewhere [12] but, for convenience, this is summarized below.

We assume that fibre strength statistics can be described by a two-parameter Weibull distribution

$$F(\sigma) = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right] \quad (1)$$

where $F(\sigma)$ is the probability of failure of a fibre subjected to a load no greater than σ, and m and σ_0 are the Weibull shape and scale parameters, respectively. It is well known [17] that m is inversely proportional to the coefficient of variation (width) of the distribution and σ_0 may be thought of as an approximation to the strength of a perfect fibre at a particular gauge length. Since a constant gauge length is used throughout it is not necessary to include this explicitly in our description.

This expression may then be used to determine the load P on a fibre bundle, as a function of bundle strain, ε, as

$$P = AN_0E\varepsilon \exp\left[-\left(\frac{\varepsilon}{\varepsilon_0}\right)^m\right] \quad (2)$$

where A is the average area of a single fibre and N_0 the initial number of fibres; E is the fibre modulus and $\varepsilon_0 = \sigma_0/E$. From this equation we may determine the following:

(a) The fibre modulus E is determined by measuring the initial gradient of the P/ε curve (Fig. 1):

$$S_0 = \left(\frac{dP}{d\varepsilon}\right)_{\varepsilon=0} \quad (3)$$

Hence

$$E = \frac{S_0}{AN_0} \quad (4)$$

(b) The Weibull shape parameter is obtained from

$$m = \left[\ln\left(\frac{\varepsilon_m S_0}{P_m}\right)\right]^{-1} \quad (5)$$

where P_m is the maximum attainable load.

TABLE II Young's modulus, bundle strength and Weibull shape parameter for glass-fibre bundles under various initial conditions

Conditions	E (GPa)	σ_b (GPa)	m
Dry, desized	69.0 ± 4.0	1.14 ± 0.05	9.1 ± 0.3
Dry, sized	58.0 ± 5.0	1.32 ± 0.07	14.0 ± 3.0
Water, desized	60.0 ± 4.0	1.38 ± 0.01	9.6 ± 0.3
Water, sized	53.0 ± 1.0	1.30 ± 0.07	12.7 ± 3.0

TABLE III Young's modulus, bundle strength and Weibull shape parameter for fibre bundles exposed to 1 M HCl for various times

Time (h)	E (GPa)	σ_b (GPa)	m
1	57.0 ± 9.0	0.83 ± 0.03	9.0 ± 1.0
2	60.0 ± 3.0	0.90 ± 0.01	25.0 ± 4.0
3	63.0 ± 2.0	0.93 ± 0.04	19.0 ± 3.0
4	56.0 ± 5.0	0.78 ± 0.02	12.3 ± 0.1
5	60.0 ± 2.0	0.78 ± 0.05	15.0 ± 5.0
7	63.0 ± 3.0	0.77 ± 0.02	12.0 ± 3.0
12	56.0 ± 8.0	0.45 ± 0.02	5.0 ± 2.0
16	44.0 ± 1.0	0.42 ± 0.06	4.3 ± 0.7
21	48.0 ± 2.0	0.57 ± 0.02	11.0 ± 1.0
48	30.0 ± 10.0	0.27 ± 0.06	6.0 ± 2.0
72	25.0 ± 5.0	0.17 ± 0.06	4.0 ± 2.0

TABLE IV E, σ_b and m for different acid concentrations after 2 h

Concentration (M)	E (GPa)	σ_b (GPa)	m
0.2	68.0 ± 1.0	0.96 ± 0.08	10.0 ± 1.0
0.4	69.0 ± 3.0	1.00 ± 0.04	14.0 ± 1.0
0.6	62.0 ± 2.0	1.02 ± 0.02	8.0 ± 1.0
0.8	49.0 ± 1.0	0.7 ± 0.1	6.0 ± 1.0
1.0	60.0 ± 2.0	0.90 ± 0.01	25.0 ± 4.0

(c) The bundle strength is simply defined as

$$\sigma_b = \frac{P_m}{AN_0} \quad (6)$$

The Weibull scale parameter is also obtainable from

$$\varepsilon_0 = E\varepsilon_m(m)^{1/m} \quad (7)$$

and also the average strength of a single fibre can be obtained [14] from

$$\sigma = \sigma_0 \Gamma\left(\frac{m+1}{m}\right) \quad (8)$$

where Γ is the standard gamma function, and hence

$$\sigma_b < \bar{\sigma} < \sigma_0 \quad (9)$$

However, only three parameters, S_0, P_m and ε_m, are obtained from the tensile tests. A and N_0 are obtained from direct microscopic examination. Hence only E, m and σ_b can be expected to be obtained with any confidence since only they are directly dependent on the measured variables. Although it is of interest to quote obtained values of σ_0 and $\bar{\sigma}$ as well, they are much less confidently known, due to the compounding of errors in the appropriate formulae. Indeed, even m could be subject to significant errors, due to the logarithmic variation of Equation 5. However, the results obtained proved to give a reasonably accurate prediction.

In Tables II to V we summarize the results obtained, with standard deviations, for E, m and σ_b for differing acid concentrations and times of exposure.

4. Discussion of Results

In Table II we tabulate the starting parameters for the uncorroded fibres in the sized and desized conditions. As can be seen, exposure to distilled water for 24 h is not significantly different to exposure to air. However, the effect of desizing is significant. Desizing the fibres leads to a modulus and shape parameter value equivalent to values obtained from single-fibre tests. Sized fibres, in contrast, are bound together. This may be interpreted using the i-plet concept for failure in the composite case [18] since sized fibres are equivalent to a weak composite. The i-plet increases in the sized system so the shape parameter m also increases. In other words scatter is reduced by cooperative behaviour. In practice the differences between these cases are not significant compared to the changes found on exposure to acid, and lie within the values expected for glass. In fact, it has been shown [10] that the presence of size does not inhibit corrosion in strong acids. However, for the purposes of comparison the reference values taken are those for the dry, desized fibres. These values also agree with the nominally expected values for the fibres.

TABLE V E, σ_b and m for different acid concentrations after 16 h

Concentration (M)	E (GPa)	σ_b (GPa)	m
0.2	50.0 ± 3.0	1.10 ± 0.01	13.0 ± 1.0
0.4	53.0 ± 3.0	0.98 ± 0.01	23.0 ± 1.0
0.6	50.0 ± 1.0	1.04 ± 0.01	15.0 ± 5.0
0.8	42.0 ± 1.0	0.63 ± 0.03	6.7 ± 0.1
1.0	44.0 ± 1.0	0.42 ± 0.06	4.3 ± 0.7

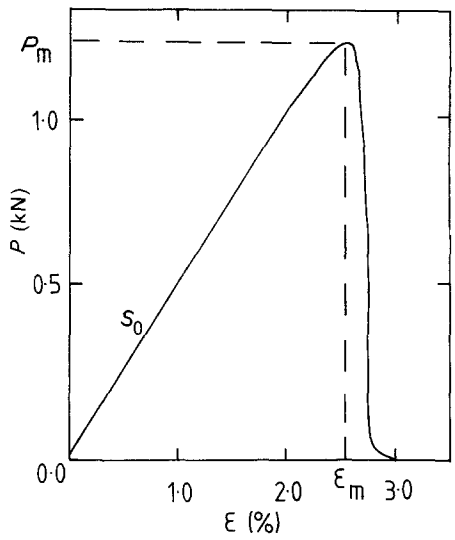

Figure 1 Schematic diagram of load against strain for a fibre bundle after acid attack, showing P_m, ε_m and S_0.

In Fig. 2 the change of modulus is plotted as a function of time for 1 M HCl. If one assumes that the sheath material of the fibres is so weakened by decalcification that all the mechanical strength and stiffness is provided by the core region, then one may correct the modulus to allow for changes in the effective area of the fibre by using Table I. This is also shown in Fig. 2, and as can be seen the corrected values are

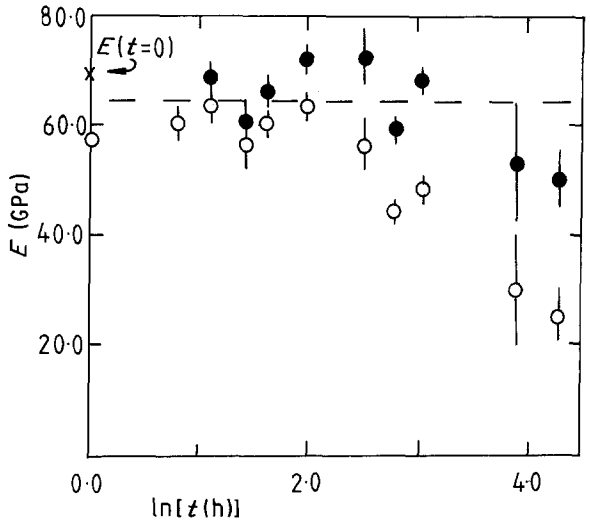

Figure 2 Variation of Young's modulus with time for 1 M HCl, (○) measured and (●) corrected for area change of core.

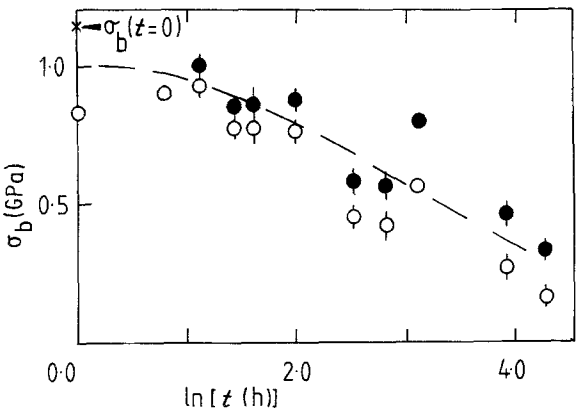

Figure 3 Variation of bundle strength with time for 1 M HCl, (○) measured and (●) corrected for area change of core.

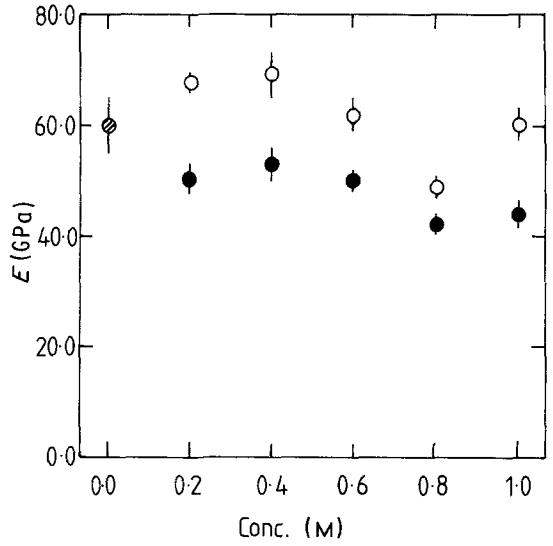

Figure 5 Variation of modulus with acid concentration after (○) 2 h and (●) 16 h exposure.

essentially constant throughout the exposure. This is in agreement with previous results [10].

This is not true, however, for the bundle strength (Fig. 3). This is seen to diminish even when the area correction is taken into consideration. This is perhaps not entirely surprising as the modulus is not a statistically dependent quantity, subject to corrosive attack, provided the core material is essentially undamaged. However, the strength may well be strongly dependent on corrosive attack if this attack leads to significant variations in surface defects. This hypothesis is strongly borne out by the remarkable variations in the Weibull shape parameter (Fig. 4). This quantity is independent of the area correction, as one would expect since it is a measure of the statistical fluctuations of strength which are critically dependent on the surface condition of the fibres. As can be seen, during the first 2 h there is a very significant rise in the value of m (far above the values typically quoted for glass of 5 to 15), indicating a considerable narrowing of the distribution of fibre strength. Close examination of the value of σ_b also indicates a small rise during this period but not approaching the initial fibre strength. So it is not simply a case of all the fibres having their surface defects eliminated. Alternatively, during this time the core–sheath phenomenon is not yet measurable so one does not expect it to have caused any significant number of fibres to have failed because of core area reduction. This leaves the possibility that acid attack activates defects of some typical size in all fibres, allowing them to fail at some "average" strength, less than that of a perfect fibre. As time proceeds this effect diminishes, and the distribution again broadens. By this stage significant variations in strength from fibre to fibre may be explainable in terms of variations of the core-sheath effect or the enlargement or activation of internal rather than surface defects. These now reside at the core–sheath interface, which is the effective surface that determines the fibres' mechanical properties. It is also known that internal stresses within the fibres may contribute to fibre failure [10] and would become more significant for smaller core sizes.

In Figs 5 to 7 the effects of acid concentration at two times, 2 and 16 h, are shown. From Fig. 5 it can be seen that the modulus is not significantly affected by acid concentration. Systematic variations in the bundle strength (Fig. 6) are seen at 16 h due to core-sheath effects, but are not noticeable at 2 h. The peak in m values at 2 h (Fig. 7) for 1 M HCl is not present at lower acid concentrations. However, at 16 h a peak in

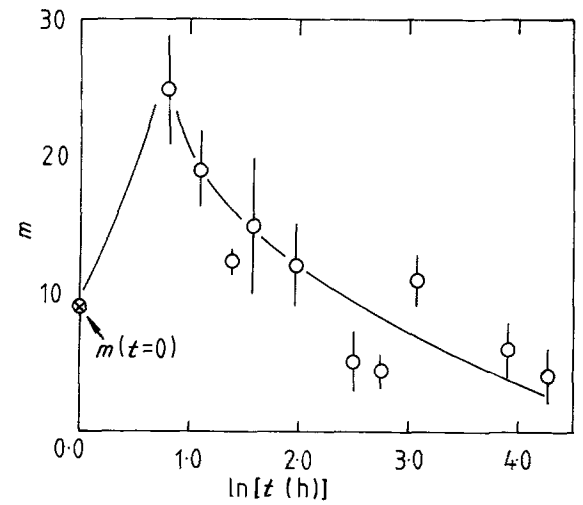

Figure 4 Variation of Weibull shape parameter, m, with time for 1 M HCl.

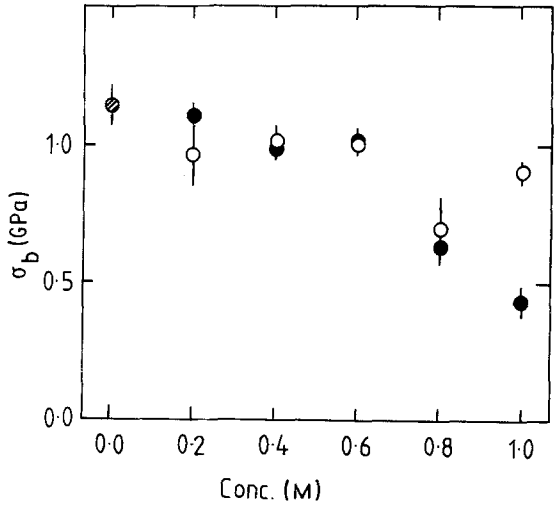

Figure 6 Variation of bundle strength with acid concentration after (○) 2 h and (●) 16 h exposure.

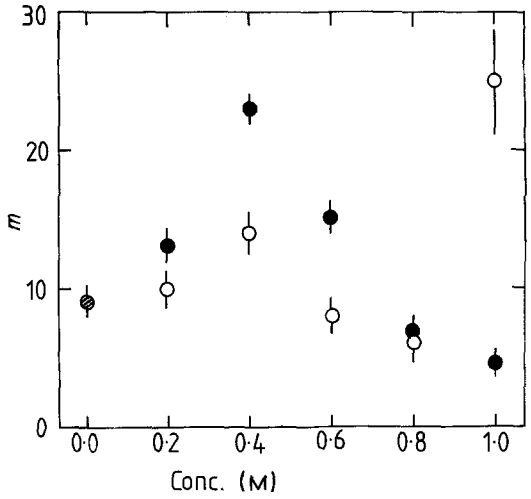

Figure 7 Variation of Weibull shape parameter with acid concentration after (○) 2 h and (●) 16 h exposure.

m value is again seen at around 0.4 M HCl. So the narrowing of the distribution is seen to occur at longer times for weaker acids. The core–sheath phenomenon is also correspondingly slower in developing for lower acid concentrations.

5. Conclusion

These results indicate that the change in mechanical properties of glass fibre bundles under the effects of concentrated acid is due to a combination of two factors. Firstly, there is a systematic corrosive effect which causes a slow reduction in surface area leading to an effective stiffness that can be satisfactorily explained in terms of reduction in core area. Secondly, a shorter-time statistical fluctuation is observed to occur before any significant reduction in surface area has occurred. This causes a very significant narrowing of the fibre strength distribution without a significant change in strength. It is possible that there has been failure of a number of weak fibres that have little significant effect on the average strength of the distribution but that significantly alter the distribution tail. An i-plet explanation of the strength distribution only applies to bundles where the cooperative failure of a critical number of fibres occurs. This may be the case with sized bundles but it does not apply to desized bundles where there is no direct transfer of stress between the fibres. This is shown by the random position of the breaks in the fibres which gives the fractured bundle a characteristic cotton-wool appearance. However, the reason for the observed variation in m is not satisfactorily explained and requires further quantitative examination.

These initial variations in m suggest that the fibre strength is strongly dependent on surface rather than internal defects. However, it is not clear whether the long-time distribution broadening is due to the activation of internal volume defects, fluctuations in the core–sheath thickness distribution or to the presence of internal stresses.

It is, however, tempting to propose that "short-time" acid treatments might improve the statistical variability of glass fibre strengths and hence produce an even higher value of m when used in composite systems. The practical consequence of this would be significant improvements in composite strength.

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