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Long-term strength of glass-reinforced plastics in dilute sulphuric acid

J. AVESTON, J. M. SILLWOOD
Division of Materials Applications, National Physical Laboratory, Teddington, Middlesex, UK

Data are presented on the long-term strength of unidirectional and cross-ply glass-reinforced polyester resin in dilute sulphuric acid, under both static and cyclic loading. Two reinforcements were used – conventional E-glass, and Cemfil which is an alkali-resistant glass developed for reinforcement of cement. It is shown that E-glass GRP rapidly falls in strength and fails by brittle crack propagation. Direct observation of crack-growth rates have been used to predict failure times under both static and fatigue loading. Cemfil GRP, on the other hand, is inert to dilute acid and appears to have an almost indefinite life.

1. Introduction

Although the use of glass-reinforced plastics (GRP) in corrosive applications is becoming widespread, there is increasing evidence that its long-term strength may be suspect. This is particularly so in dilute mineral acids, which are not only one of the more common environments in chemical plant but are frequently encountered in other applications, for example, large-diameter industrial effluent and sewage pipes [1]. It is also becoming clear that failures arise from a stress-corrosion mechanism, and therefore conventional environmental immersion followed by short-term strength testing and an arbitrary safety factor provides no proper basis for design.

It has long been known [2], that E-glass fibres without any protective resin are subject to spontaneous cracking in dilute acid, and it has been assumed that this arises from ion exchange of the sodium ions in the fibre surface for the protons in the mineral acid. As these have a smaller volume, the surface layer undergoes restrained shrinkage and multiple (or helical) cracking results. However, Barker *et al.* [1] have recently shown that it is the calcium and aluminium ions, whose oxides account for about 30% by weight, which are the predominant species removed from the fibre surface. The obvious implication is that a glass free from calcium and aluminium may be immune from such attack. Such a glass is Cemfil which, paradoxically, was developed to provide alkali resistance.

The purpose of the work described below was therefore to make a start on predicting a design stress for E-glass-based GRP, or at least a method of extrapolating medium-term data, and also to evaluate Cemfil-based GRP as an alternative material.

2. Experimental detail

Unidirectional specimens were made by winding single strands of glass on to square sheets of perspex, previously coated with PVA release agent, using a coil winder. The same method was used to make the 0°–90°–0° balanced ply specimens, but in this case the perspex former was rotated through 90° for each ply. The E-glass strands contained more fibres than the Cemfil (total cross-sectional areas of glass 12.0×10^{-4} cm^2 and 2.83×10^{-4} cm^2, respectively) and so the pitch of the coil winder was adjusted to give the same glass volume content per layer. Unidirectional specimens contained 14 layers and cross-ply 7–14–7 layers. The chemical compositions of the glasses, which were supplied by Pilkington Bros and coated with a polyester compatible size, are shown in Table I. Scott Bader Crystic 189 LV (orthophthalic) polyester resin with 2% catalyst M

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TABLE I Chemical composition of E-glass and Cemfil (wt %)

	E-glass	Cemfil
SiO_2	52.4	71
K_2O	0.8	11
Na_2O		
B_2O_3	10.4	–
Al_2O_3	14.4	1
MgO	5.2	–
CaO	16.6	–
ZrO_2	–	16
Li_2O	–	1

and 0.05% accelerator E was used for impregnation.

After completion of the winding operation, two sheets of PVA-coated perspex were placed on the surfaces on the uncured composite and the assembly was squeezed between the platens of a hydraulic press down to stops, such that a nominal volume fraction of 50% would be achieved. After hardening overnight the composite sheets were removed from the former and post-cured for 3 h at 80° C.

Tensile specimens were cut from the sheets and the unidirectional specimens waisted in the thickness direction to reduce the likelihood of interlaminar failure. Aluminium tabs were glued to the ends of the specimen to reduce the possibility of damage from the grips which may have led to premature failures outside the waisted region. Specimen design and dimensions are shown in Figs. 1 and 2.

During testing, the environment of 1 N H_2SO_4 was contained in a glass tube sealed at one end with a split rubber bung. To compare the performance of E-glass and Cemfil composites in acid, a static load was applied and time-to-failure recorded. The effect of a square-wave loading cycle on the E-glass composite in acid conditions was investigated using a 0.1 Hz waveform in tension between maximum and 0.1 maximum load. A number of E-glass specimens were immersed in acid for a period of 1.8×10^6 sec prior to testing.

Most of the tests were conducted in a standard Instron 1272 servo hydraulic machine but a mechanical lever-arm machine incorporating a variable cam, designed and built at NPL, was used for the long-term fatigue tests.

Double-cantilever-beam specimens prepared from the cross-ply material (but with 8–16–8 layers) as shown in Fig. 3, were used to measure slow crack growth normal to the fibres in a 1 N sulphuric acid environment. The crack tip was observed with a travelling microscope and the load applied either through the Instron cross-head or by means of a cantilever and dead-weight system for longer times. Time intervals were chosen so that changes of K_1 resulting from load change (with the Instron) or crack length (both loading systems) were small and mean values over the time interval were used.

3. Results

3.1. Crack-growth measurements

The results are shown in Fig 4. The stress intensity, K_I, was calculated from the equation given by Wiederhorn and Bolz [3]:

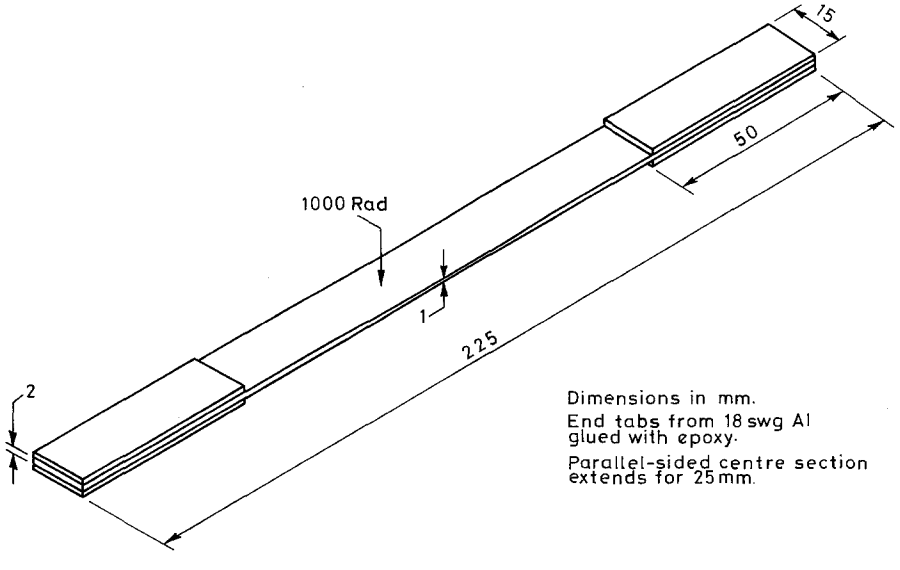

Figure 1 Shape and dimensions of unidirectional specimens.

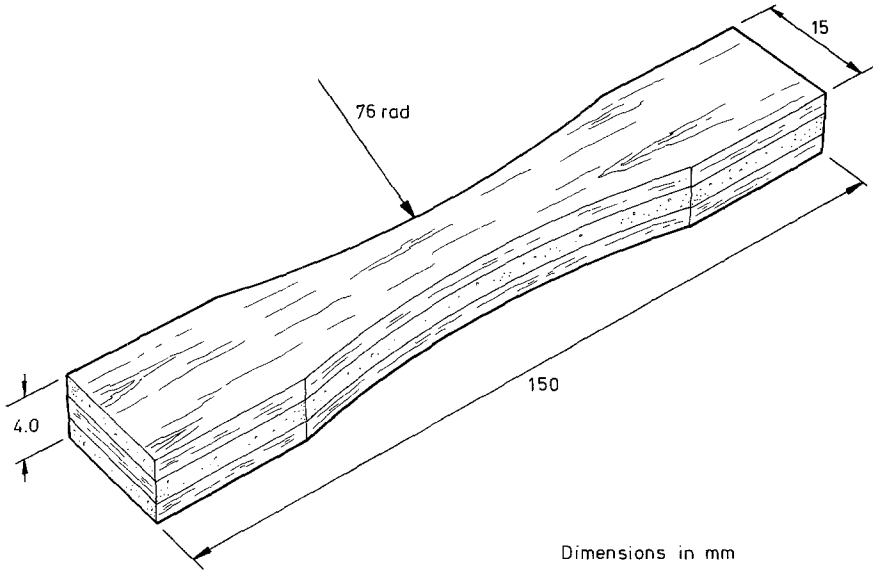

Figure 2 Shape and dimensions of cross-ply specimens.

$$K_I = \left(\frac{PL}{(wb)^{\frac{1}{2}}t^{\frac{3}{2}}}\right)\left(3.47 + 2.32\,\frac{t}{L}\right), \quad (1)$$

where the dimensions are defined in Fig. 3. Although Equation 1 was originally derived for an isotropic material it can be shown that it is a good approximation for the situation considered here, and is exact for small t/L where only bending moments need be considered. A linear least-squares fit to the points above $\log V = -7.9$ gives a slope 3.1. To simplify the following discussion we approximate this to 3, indicated by the broken line in Fig. 4, and well within experimental error. The intercept $\log A$ then becomes -10.02, and

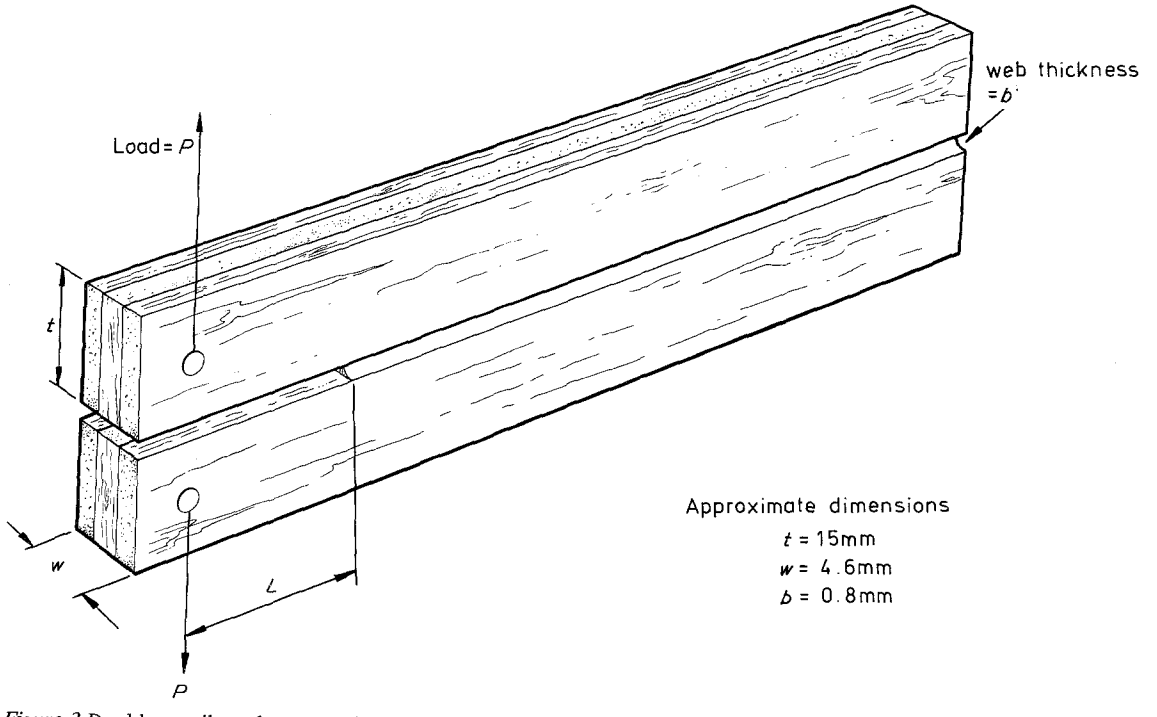

Figure 3 Double-cantilever-beam specimen.

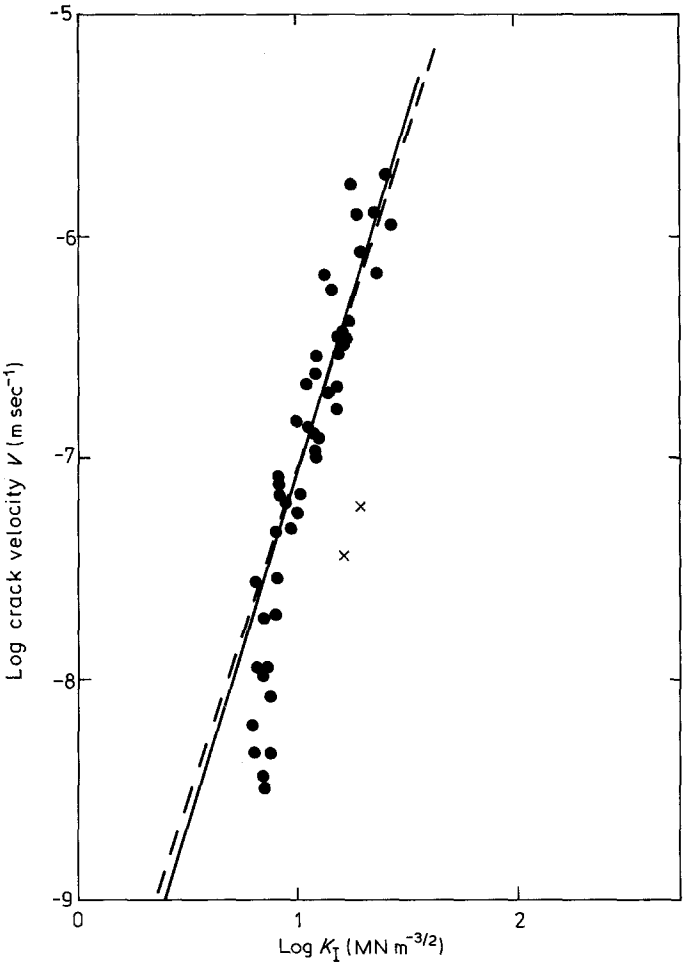

Figure 4 Crack-growth data for unidirectional E-glass polyester composite in 1 N H_2SO_4. Line is least-squares fit to points above log $V = -7.9$, gradient $n = 3.1$, intercept log $A = -10.1$. Broken line drawn with gradient $n = 3.0$ and intercept log $A = -10.02$. Crosses are fatigue loading.

we have

$$V = AK_I^n = 9.55 \times 10^{-11} K_I^3. \quad (2)$$

At low K_I, where crack velocities are less than about 10^{-8} m sec^{-1} (ca. 1 mm day^{-1}), the points begin to depart significantly from this line and there is some evidence of a stress-corrosion limit. At low crack velocities the fracture surface is observed to be essentially planar (Fig. 5a) but fibre pull-out increases with velocity (Fig. 5b)

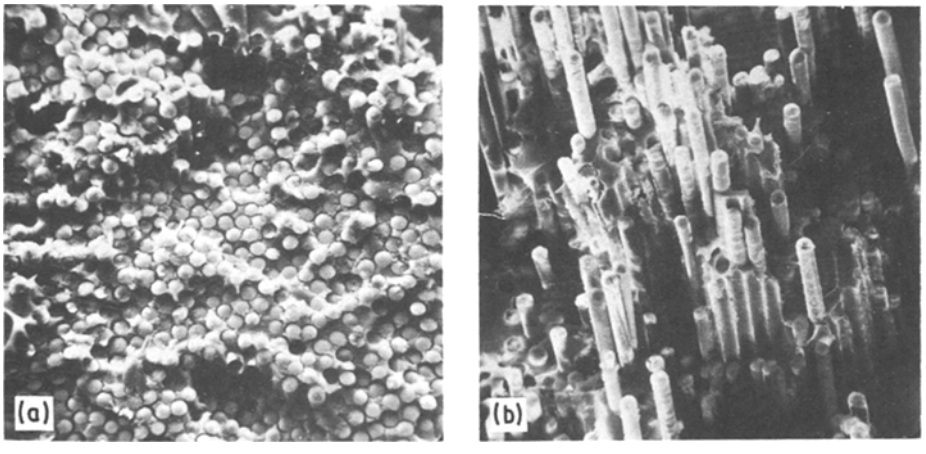

Figure 5 Fracture surfaces from double-cantilever crack-growth measurements on unidirectional E-glass polyester composite in 1 N H_2SO_4: (a) $V \sim 10^{-8}$ m sec^{-1}; (b) $V \sim 10^{-6}$ m sec^{-1}.

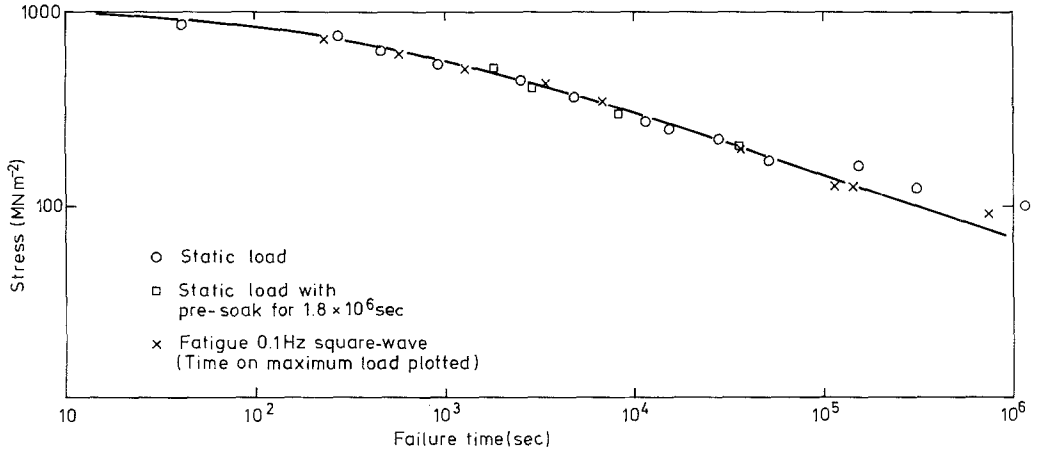

Figure 6 Static and fatigue loading of unidirectional E-glass polyester in 1 N H_2SO_4.

until a point is reached at about 10^{-5} m sec^{-1} where there is no well-defined crack front but just a damage zone around the tip of the starter crack. In two experiments where a sine-wave alternating load (between zero and that corresponding to K_I) was applied, the crack velocities were almost a factor of ten lower. Crack-growth measurements were not possible with Cemfil–GRP specimens as a damage zone formed at the tip of the starter crack and this simply increased with size as the load was increased.

3.2. Long-term strength

Times-to-failure of unidirectional E-glass GRP as a function of tensile stress, under both static and 0.1 Hz square-wave fatigue loading (maximum to 0.1 maximum) are shown in Fig. 6. The time plotted for the fatigue specimens is the time actually under maximum load, i.e. one half the elapsed time. Also shown are the failure times of specimens which had been conditioned in acid (for 1.8×10^6 sec) before loading. Failure surfaces (Fig. 7b and c) were analogous to those observed in the crack-growth experiments; long-term failures showed a comparatively flat fracture surface (b), whereas short-term failures (c) tended towards the brush-like appearance normally associated with failure of GRP in air (Fig. 7a).

In contrast, Cemfil GRP specimens were hardly affected at all by acid (Fig. 8) and invariably failed in a brush-like manner (Fig. 7d) irrespective of loading time.

A few results were obtained for unidirectional E-glass GRP in air. Rather surprisingly the rate of

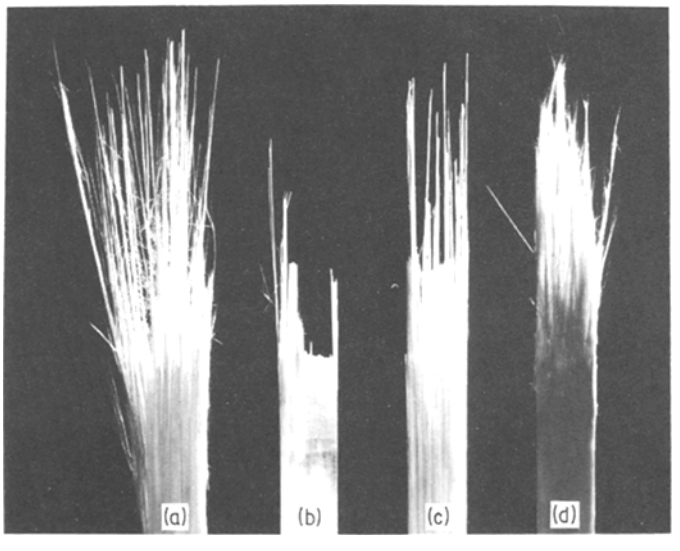

Figure 7 Failed glass polyester composites: (a) short-term E-glass failure (1.7×10^3 sec) in air; (b) long-term E-glass failure (1.0×10^5 sec) in 1 N H_2SO_4; (c) short-term E-glass failure (4.5×10^2 sec) in 1 N H_2SO_4; (d) long-term Cemfil failure (3.6×10^5 sec) in 1 N H_2SO_4.

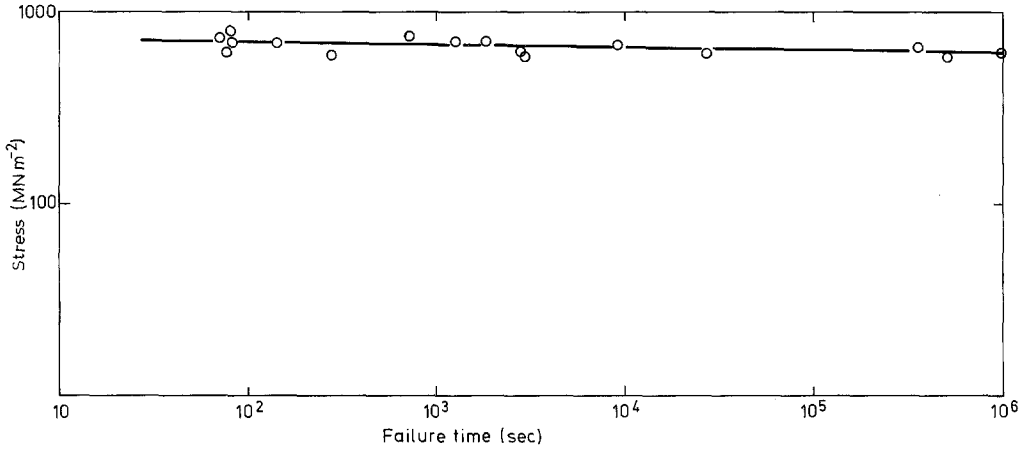

Figure 8 Static loading of unidirectional Cemfil polyester composite in 1 N H_2SO_4.

reduction of strength with time, at about 5% decade^{-1} is actually rather greater than that of Cemfil GRP in acid, again demonstrating the superior performance of the Cemfil material. It is, however, consistent with previous work [4] on polyester-impregnated E-glass strands in air, and indicates again that some stress corrosion is present even in ambient conditions.

Failure of cross-ply E-glass GRP was similar (Fig. 9) except that the centre ply underwent multiple cracking, as described by Aveston and Kelly [5], and of course the short-term UTS was only about one-half that of the unidirectional material as the cracked transverse ply carries very little load.

4. Discussion

The essential experimental points are:

1. composites containing E-glass suffer a rapid reduction in strength to a tenth or less of their initial value;
2. it makes no difference whether the loading is static or fatigue;
3. pre-soaking in acid in the unstressed state has very little effect on subsequent strength;
4. Cemfil-based GRP composites are insensitive to dilute acids, falling in strength by only something of the order of 1% decade^{-1} of time.

The photographs (Figs 5 and 7) clearly suggest that long-term failure of E-glass GRP in an environment of 1 N sulphuric acid is by brittle crack propagation, and the question is whether fracture mechanics may be used to quantitatively interpret the results, perhaps providing a basis for extrapolation of relatively short-term tests to predict service life.

In the following we assume that the specimen either already contains flaws or cracks of length a_i,

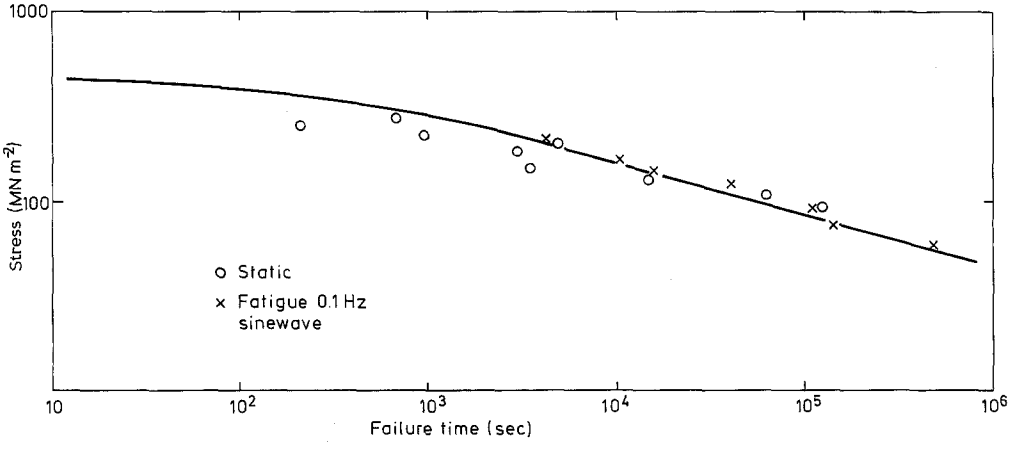

Figure 9 Static and fatigue loading of cross-ply E-glass polyester composite in 1 N H_2SO_4.

or that cracks of this length may be easily formed at low stress – for example by multiple cracking. We further assume that subsequent growth obeys Equation 2, according to the results in Section 3.1, i.e.

$$V = \frac{da}{dt} = AK_I^n, \quad (2)$$

where

$$K_I = \sigma_a Y a^{\frac{1}{2}}. \quad (3)$$

σ_a is the applied stress, a the crack length at time t, and Y a geometrical factor equal to $\pi^{1/2}$ for a centre crack. K_I increases as a result of increasing crack length to a value K_{IC} at which catastrophic failure occurs. The time to failure, t_C, is given by

$$t_C = \int_{a_I}^{a_{IC}} \frac{da}{V} = \int_{K_{Ii}}^{K_{IC}} \frac{2}{\sigma_a^2 Y^2} \frac{K_I}{V} dK_I$$

$$= \frac{2}{\sigma_a^2 Y^2 A(n-2)} [K_{Ii}^{2-n} - K_{IC}^{2-n}], \quad (4)$$

using Equations 2 and 3. If the initial flaw size, a_i, is sufficiently small, $K_{Ii} \ll K_{IC}$ and substituting $K_{Ii} = \sigma_a Y a_i^{1/2}$ reduces Equation 4 to

$$t_C = \frac{2K_{Ii}^{(2-n)}}{(n-2)A\sigma_a^2 Y^2} = \frac{2a_i^{(1-n/2)}}{(n-2)A\sigma_a^n Y^n}. \quad (5)$$

Hence the time-to-failure is inversely proportional to σ_a^n and a plot of log stress against log time-to-failure should be linear with slope $-1/n$ at long times. For $n = 3$, and putting $K_{IC} = \sigma_{max} Y a_i^{1/2}$ where σ_{max} is the short-term UTS, Equation 4 reduces to

$$t_C = \frac{2}{A\sigma_a^2 Y^2} \left(\frac{1}{K_{Ii}} - \frac{1}{K_{IC}} \right)$$

$$= \frac{2}{A\sigma_a^3 Y^3 a_i^{\frac{1}{2}}} \left(1 - \frac{\sigma_a}{\sigma_{max}} \right). \quad (6)$$

The initial crack length, a_i, is unknown and so to test the equation we first fit it at one point and then establish, firstly whether the remaining points fit the predicted curve, and secondly whether the resulting value of a_i is plausible. The line in Fig. 6 was obtained by fitting at $\sigma_a = 460\,MN\,m^{-2}$, $t = 2000$ sec and $\sigma_{max} = 1000\,MN\,m^{-2}$. The fit is quite good over 5 decades of time but there is some deviation at the longest times corresponding to an initial strain of about 0.3% and similar deviations in the crack-growth experiment (Fig. 4). This suggests the possible existence of a stress-corrosion limit and is consistent with the observation of Collins [6] that strain-corrosion cracking did not occur at strains less than 0.3%.

The computed value of the initial flaw size, a_i, is 0.14 mm, which is of the same order as the equivalent strand diameter of 0.3 mm, although in fact the strands are actually elliptical with a minor axis of ca. 0.1 mm.

It is thus tempting to speculate that a crack starts at an exposed fibre under the combined influence of environment and stress, passes easily through a single strand to give an initial crack of the order of the strand size which then propagates more slowly through the composite, being retarded at the resin-rich regions between the strands.

When the same value of a_i is used in an attempt to fit the cross-ply results, the experimental points are found to lie below the computed curve, and the fit shown in Fig. 9 could only be obtained by increasing the assumed value of a_i to 2.4 mm. However, this is very close to the length of cracks (ca. 2 mm) that are known to exist in the multiply cracked centre ply.

It is known from our own results (not reported here) and others that the presence of a thick gel coat retards but does not entirely prevent acid attack. This implies that there must be sufficient diffusion of acid through the gel coat to allow eventual crack propagation through a strained specimen, although, judging from the small effect that pre-soaking has in the present experiments, not sufficient to cause spontaneous cracking of the fibres.

Stereoscan pictures of E-glass fibres after acid immersion are shown in Fig. 10a. Similar effects have been reported previously [2]. It is assumed that multiple cracking results from restrained shrinkage of a surface layer which has undergone ion exchange of calcium and aluminium ions for (smaller) protons. Because glass-fibre surfaces are relatively free from flaws, stress relief is achieved more easily by propagation of a single helical crack than multiple initiation of separate cracks which is the norm in composites. Cemfil fibres were unmarked under the same exposure conditions (Fig. 10b).

5. Conclusions

It has been shown that E-glass GRP fails by stress corrosion in dilute acid solutions. Although not entirely unexpected, since it is known that the fibres themselves are subject to spontaneous cracking under these conditions, it is somewhat

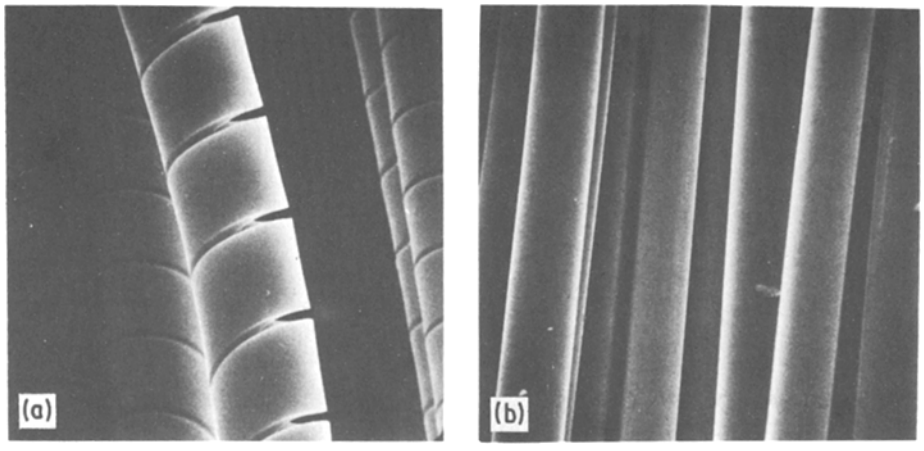

Figure 10 Comparison between E-glass fibres (a), and Cemfil fibres (b), after immersion in 1 N H_2SO_4 for 6×10^5 sec.

surprising that the resin does not provide better protection. It is perhaps even more surprising that an alkali-resistant glass should remain completely unaffected by acid.

It is also shown that fatigue failure of unidirectional material in acid is simply a special case of stress corrosion, and that there is no additional degradation as a result of load cycling. Finally, long-term strengths can be safely predicted by extrapolation of medium-term tests plotted in the form of log strength against log time, any deviation from the line due to a stress corrosion limit being positive and increasing the margin of safety.

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