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Stress corrosion cracking of GRP pultruded rods in acid environments

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Stress corrosion cracking of GRP pultruded rods has been investigated in 0.0001 to 5.0 N hydrochloric acid environments under bending and tensile loading modes. Crack initiation takes place at exposed glass fibres in the surface of the rod, and crack propagation is planar and at right angles to the rod axis. Leaching of calcium and aluminium from the fibres takes place during the cracking process, and time-to-failure is dependent on the acid concentration, the stress level and the ease of access of the acid to the glass fibre surface. Possible mechanisms of crack propagation through the glass fibres and resin are discussed.

1. Introduction

Pultruded rods are manufactured by passing glass fibres through a liquid resin bath and pulling the wetted fibres through a heated steel die. This results in a uniaxially aligned fibre-reinforced composite with a very high strength and which, in normal environments, will not fracture in a direction perpendicular to the axis of the rod. Such material has found application in radio antennae, electrical insulators, ladders and similar products. Under certain conditions some of these components may be susceptible to stress corrosion in acid environments, failure taking place at stresses as low as 20% of those typical of glass-reinforced plastic (GRP) rods tested in air. Even extremely dilute acid solutions can be a problem since under service conditions the acid can concentrate in local areas, e.g. in crevices and surface irregularities on the GRP product.

Very little previous work has been carried out on the stress corrosion properties of the pultruded rod, but results have been reported in the literature for other GRP products, particularly the stress and strain corrosion of GRP pipes and pressure vessels for use in the chemical industry [1–3]. Recently, Hogg and Hull [3] have studied the nucleation and propagation of cracks in glass fibre-reinforced polyester rings in the presence of hydrochloric acid. They have shown the cracking to be planar with very little fibre pull-out.

The present paper describes the work carried out on the stress corrosion behaviour of pultruded GRP rods, under bending and tensile loading conditions. Such materials contain a very high volume fraction of glass fibre with a thin coating of resin over the rod surface. Detailed examination of the fracture surfaces has been made and related to the mode of failure.

2. Experimental details

A 22 mm diameter GRP rod was prepared by pultruding E-glass fibre with an epoxy resin (type MY740/HY917/K61B). The glass fibres had been coated with a suitable coupling agent. The glass content of the composite was 80% by weight and this meant that many of the glass fibres were in close contact with each other (Fig. 1a). However, in spite of this high fibre content, resin-rich areas were still present in the microstructure (Fig. 1b).

Samples of the pultruded rod have been mechanically tested under bending and tension loading conditions, and with acid and air environments. The acid environments have been principally 0.0001 to 5.0 N hydrochloric acid, but some tests have also been carried out in nitric acid solutions.

The bend tests were carried out under three-point loading using 400 mm long specimens. Acid was applied to the rod at the mid-length position by means of a reservoir prepared from glass slides and silicone rubber sealant. The area exposed to

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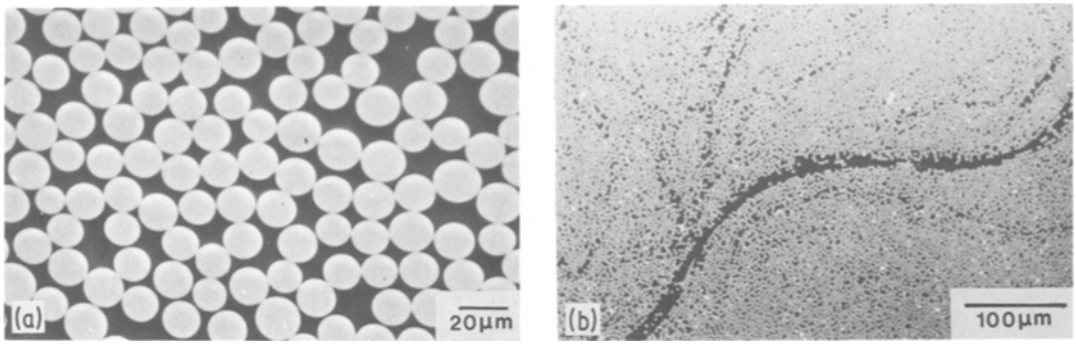


Figure 1 (a) Microstructure of the pultruded rod showing high volume fraction of glass fibre, and (b) resin-rich areas in the pultruded rod.

acid attack was approximately 100 mm long × 25 mm wide.

Tension tests necessitated end fittings being potted to the pultruded rod and acid was again applied by a reservoir technique. Tests were also carried out on samples where the acid was allowed to contact only one localized spot on the surface of the rod. This was achieved by encapsulating a short length of the rod with cycloaliphatic resin filled with crushed silica. A bolt was cast into the cycloaliphatic resin such that when it was subsequently removed it left a 3 mm diameter hole giving direct access to the surface of the rod. The hole was filled with acid and closed with a screw; the sample was then subjected to tensile loading.

3. Results

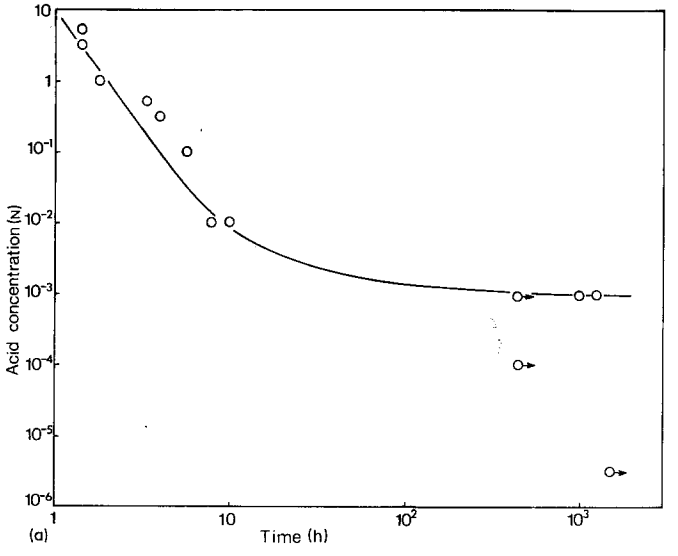
3.1. Bend tests

Stress corrosion tests were carried out at 20° C under a variety of concentrations of hydrochloric acid and applied stresses. For the purpose of these tests failure was taken as the time at which fine cracks could be detected on the surface of the rod. Fig. 2a shows that at constant stress, decreasing the acid concentration increases the time-to-failure. For a stress of 260 MN m^{-2} the curve is tending to become asymptotic at an acid concentration of 0.001 to 0.0001 N (pH 3–4). Fig. 2b shows that for a constant acid concentration of 5 N the time-to-failure increases as the applied stress is lowered, the curve becoming asymptotic at a stress of around 50 MN m^{-2}. It should be noted that tests were carried out for 1000 h only, and that longer test times may well produce lower threshold values.

In order to study the nature of crack initiation, a series of samples were subjected to a stress of 207 MN m^{-2} in an environment of 0.01 N hydrochloric acid for times of 2, 4, 8, 16, 32 and 64 h. Transverse cracks were initiated at several points and these could be observed visually on the surfaces of the 32 and 64 h specimens (Fig. 3). Incipient cracks could also be found on the 16 h specimen by scanning electron microscopy. The 16 and 64 h specimens were subjected to a detailed microscopic examination. Fig. 4a shows after 16 h the characteristic appearance of the surface of the rods with prominent fibres and incipient cracks extending across 3 or 4 fibres. Axial sectioning (Fig. 4b) confirmed that these cracks did not extend to subsurface fibres or into the adjacent resin. Transverse sections showed the absence of axial splitting at this stage of the tests.

In the case of the 64 h specimen the transverse cracks are well developed. On the surface their apparent length is similar to the diameter of individual rovings and at this stage of testing cracking can now be observed in the resin as well as the glass fibres (Fig. 5). Axial sections of the rod reveal crack penetration for distances up to 150 fibre diameters (3 mm), as shown in Fig. 6a. It was noted that where misalignment occurred between adjacent rovings, the crack was sometimes deflected from its planar path (e.g. at a depth of 10 fibres in Fig. 6a). Where fibres were well aligned or in close proximity to one another the crack propagated in a very planar manner (Fig. 6b). Examination of the crack-tip region showed the crack opening to be small and that cracks had only partially propagated through fibres (Fig. 6c). There was also evidence that fibres may have cracked before failure of the resin occurred.

One specimen was tested to complete failure in bending and the fracture produced was brittle but multi-faceted (Fig. 7). Crack initiation



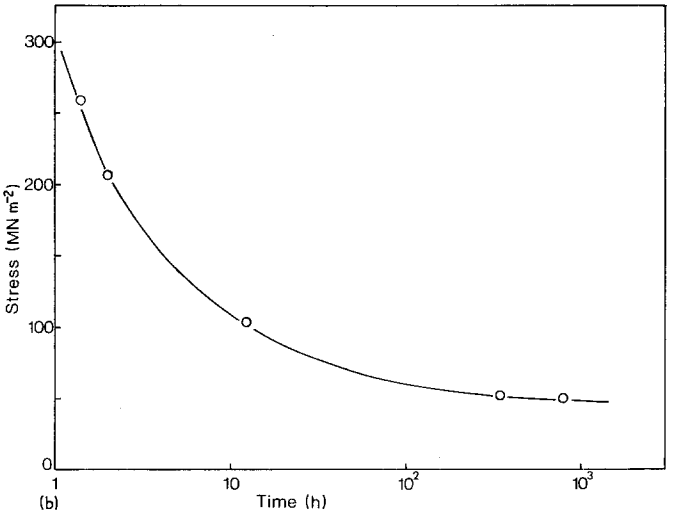


Figure 2 (a) Effect of acid concentration on the time required to produce surface cracking in three-point bend test. Stress constant at 260 MN m^{-2}. Temperature 20° C. (b) Effect of stress level on the time required to produce surface cracking in three-point bend test. Acid concentration constant at 5 N hydrochloric acid. Temperature 20° C.

and propagation has obviously taken place at several points producing a characteristic stepped fracture.

A further specimen was tested in 1.0 N nitric acid at a stress of 207 MN m^{-2} and cracking observed to commence after a test time of 2.6 h. The result is consistent with those obtained in hydrochloric acid environments and indicates that it is the hydrogen ion concentration that is controlling the stress corrosion cracking and not the nature of the anions.

3.2. Tension tests

Stress corrosion tests in tension produced multiple transverse cracking at the surface of the rod similar to that observed for bend testing, but the final fracture surface tended to be much rougher and irregular due to extensive longitudinal splitting having taken place.

Samples that were encapsulated to produce acid attack at a localized region resulted in a fracture face that was very flat, the crack having propagated in a plane perpendicular to the rod axis. River markings are present on the fracture surface and these run towards the origin of fracture (Fig. 8).

3.3. Fractography of the failure surfaces

On a microscopic scale the fracture surfaces were similar irrespective to whether the specimens were tested in bending or tension. Both types of specimen had river markings on the fracture surface that ran towards the apparent origin of failure. At higher magnification the river markings

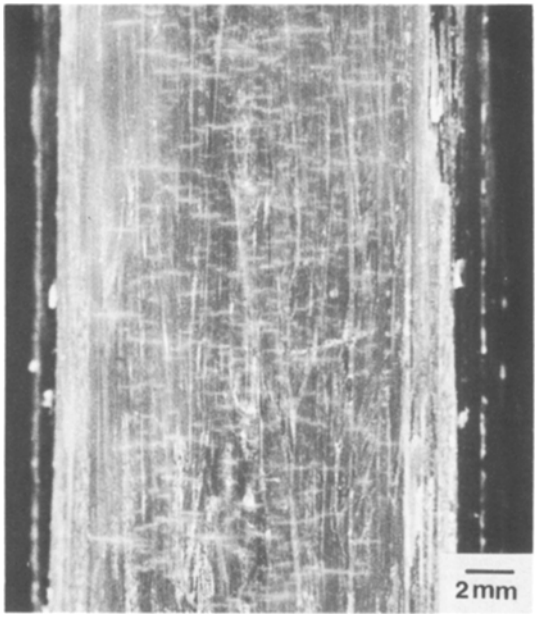
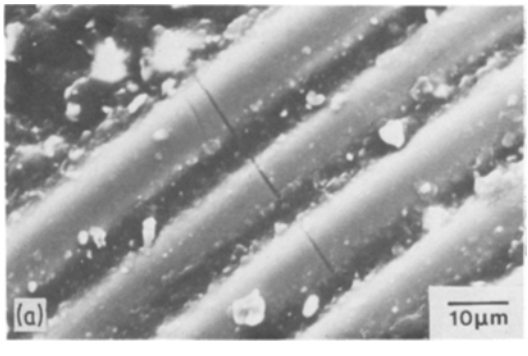


Figure 3 Transverse cracking on the surface of a GRP pultruded rod subjected to a stress of 207 MN m^{-2} in an environment of 0.01 N hydrochloric acid for a time of 64 h. Magnification × 3.

are seen to be steps (cliffs) on the fracture surface caused by the crack propagating on different levels (Fig. 9). Undercutting of the glass fibres occurs at the base of many of these steps (Fig. 10).



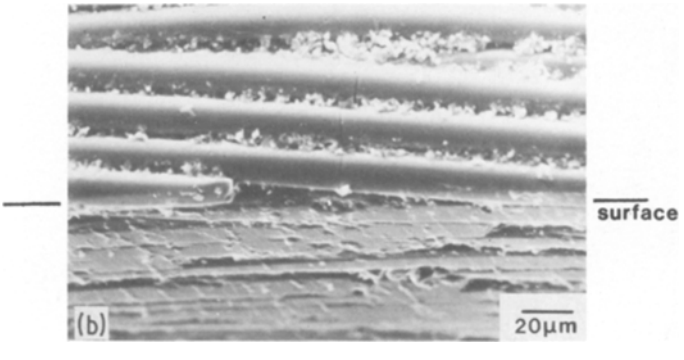


Figure 4 (a) Cracking of surface fibres after bend testing at a stress of 207 MN m^{-2} in 0.01 N hydrochloric acid for 16 h, and (b) axial section of specimen shown in (a) showing that surface cracks are restricted to a single fibre depth.

The individual fractured fibres have characteristic fracture faces, smooth in the crack initiation regions and becoming progressively rougher as the crack propagates through the fibre. The smooth region is approximately perpendicular to the fibre length but as the failure progresses through the fibre the crack bifurcates and this leaves a small wedge of glass on many of the fractured fibres (Fig. 11). X-ray analysis on both the smooth regions and the wedges showed them to be lower in aluminium and calcium than glass fibre away from the fracture face (Table I). This indicates that aluminium and calcium have been preferentially leached out from the fibres during or subsequent to the fracture process. The analysis results also indicated a reduction in the sodium and potassium concentrations, but the analysis technique used was not sufficiently sensitive to measure these changes with any degree of accuracy, since both Na_2O and K_2O are present at concentrations $< 1\%$.

Parts of the fracture face of the rod near the point of crack initiation were frequently covered by a surface film that almost obscured the individual fibres (Fig. 12). X-ray analysis of the film showed it to consist mainly of aluminium, calcium and chlorine (probably $AlCl_3$ and $CaCl_2$) thus confirming the preferential leaching of aluminium and calcium from the fibres.

Longitudinal debonding between fibres and resin was apparent in many of the fracture faces, and transverse sections of the rod some 50 mm away from the fracture face showed that debonding occurred over considerable distances (Fig. 13).

An interesting feature was noted on the fracture of the tension sample that had been encapsulated with the silica-filled cycloaliphatic resin. Examination at low magnification (Fig. 14) shows a variation in the texture of the fracture

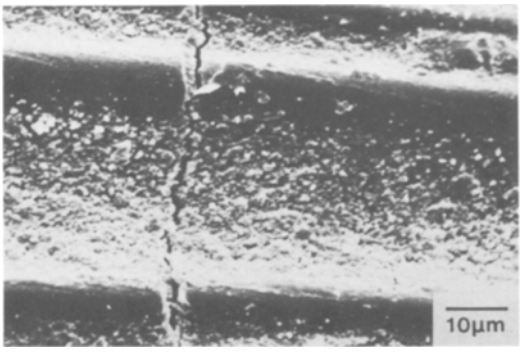


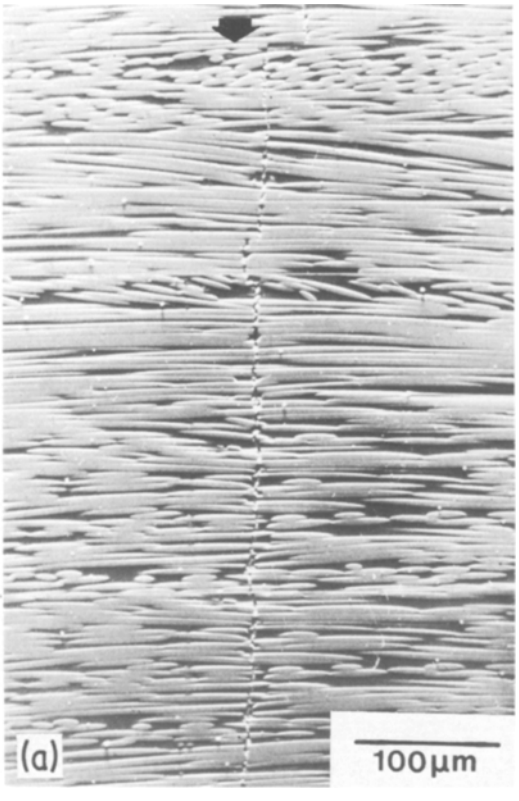
Figure 5 Transverse crack running through fibre and resin in a rod bend-tested for 64 h at a stress of 207 MN m^{-2} in 0.01 N hydrochloric acid.

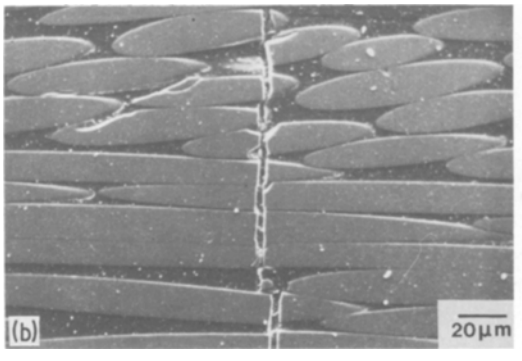
surface of the encapsulating resin. Near the origin of the fracture in the GRP rod a slow crack propagated in the encapsulating resin and examination at high magnification shows the crack to have followed the SiO_2 filler/resin boundaries, i.e. an intergranular type of fracture (Fig. 15). Away from the origin of fracture in the GRP rod the fracture has been more rapid in the encapsulating resin, and in this case the fracture path is through the SiO_2 particles, i.e. a transgranular type of fracture (Fig. 16).

3.4. Effect of surface finish on rod

Bend tests on bars of epoxy resin without reinforcing glass fibres and using stresses and acid concentrations similar to those used for the GRP rod did not produce any damage or cracking. It therefore seems likely that the stress corrosion of the GRP rod is governed primarily by attack of the glass fibres.

For certain applications, the pultruded rod is ground down to its final dimensions. Figs. 17 and 18 show the rod before and after the grinding operation. The grinding marks can be clearly seen on the cylindrical surface of the sample and some of the fibres have been ground down almost to their centre-line. There is no evidence of fibres being torn out the surface by the grinding process and this implies a strong fibre–resin bond in the rod. Acid stress–corrosion bend tests on these ground





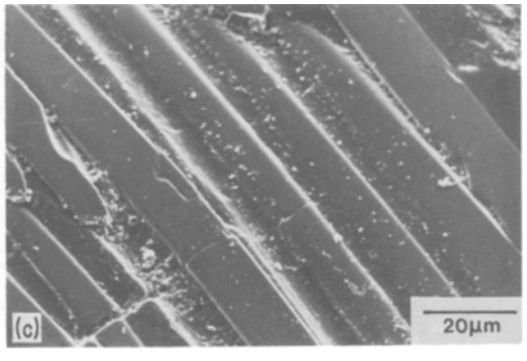


Figure 6 (a) Axial section of a rod bend-tested for 64 h at a stress of 207 MN m^{-2} in 0.01 N hydrochloric acid. The transverse cracks extend up to 150 fibre diameters into the rod. (b) High magnification micrograph of axial section of a rod bend-tested in 0.01 N hydrochloric acid, showing the very planar nature of the fracture as the crack propagates from fibre to fibre. (c) Crack tip of the fracture shown in (b) showing cracking of fibres ahead of resin failure.

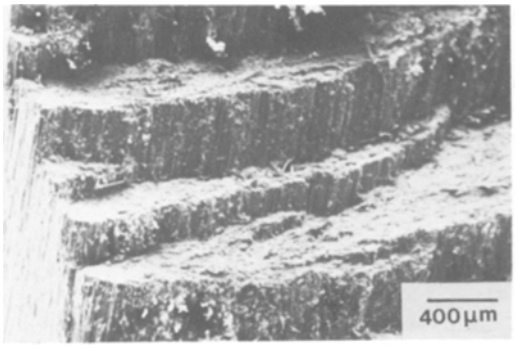


Figure 7 Fracture surface of rod that has been bend-tested to complete failure (5 N HCl).

rods showed them to fail in a shorter time than similar pultruded rods in the "as-manufactured" condition. This is principally due to a shortening of the crack initiation stage in the abraded glass fibres.

4. Discussion

4.1. General observations on the failure processes

Under the combined action of stress and an acid environment, transverse cracks are initiated in the pultruded rod by fracture of the surface fibres. An incubation period precedes crack initiation and the length of this period appears to be more sensitive to stress level than acid concentration, e.g. compare Figs. 2a and b. For a bending stress of 207 MN m^{-2} in 0.01 N hydrochloric acid the incubation period is approximately 12 h. Similar incubation periods have also been observed by Metcalfe and Schmitz [4] for the stress corrosion of single fibres of E-glass.

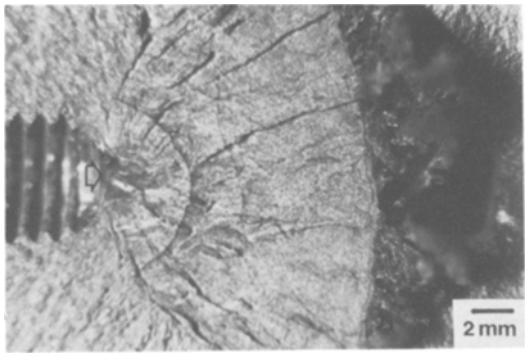


Figure 8 Fracture surface of rod that has been tension-tested to complete failure (5 N HCl). The sample has been encapsulated with cycloaliphatic resin to restrict acid contact to one localized area (arrowed). Magnification X 2.5.

Figure 9 Detail of river markings on the fracture surfaces.

Initially the transverse cracks in the pultruded rod are restricted to a single fibre depth and are of a width of 1 to 4 fibres. With increasing exposure time the crack lengthens by propagating in a very planar manner, particularly if the acid is restricted to a very localized area on the rod surface. The presence of resin-rich regions in the composite does not deflect the crack significantly from its planar path. Some longitudinal debonding accompanies the planar crack growth, particularly at changes in fibre alignment (see Fig. 6a), but again this does not appear to blunt or deflect the crack.

4.2. Fracture of individual glass fibres

Evidence from the fracture surface of the pultruded rod indicates that the fracture of individual glass fibres is a two stage process. The initial propagation of the crack through the fibre is slow and this produces the mirror regions shown in Fig. 11. The mirror regions tend to be more pronounced in fibres close to the crack initiating point at the rod surface. After about 25% of the fibre has fractured the crack growth rate increases

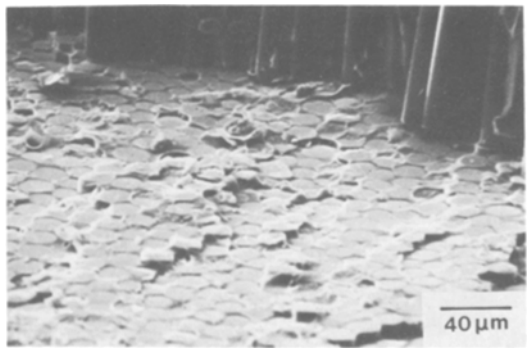


Figure 10 Undercutting of the glass fibres at the base of the river steps.

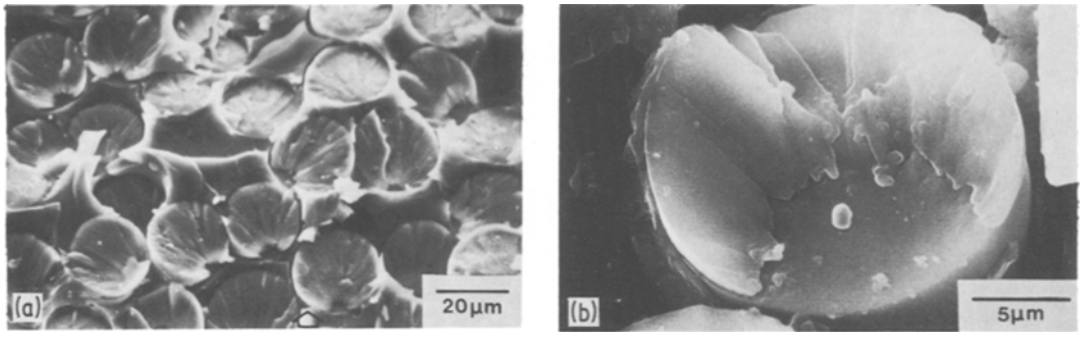


Figure 11 (a) Characteristic glass wedges that are present on many of the fractured fibres. Direction of crack propagation arrowed. (b) High magnification micrograph of the glass wedge on a fractured glass fibre.

and as the crack becomes unstable it bifurcates to form the characteristic wedges.

The actual mechanism of stress corrosion in single glass filaments has been studied by Metcalfe and Schmitz [4] who conclude that it operated by an ion exchange mechanism. Small hydrogen ions from the acid environment replace larger ions in the surface of the glass fibre, leading to the generation of tensile stresses. These stresses in combination with the applied stress are sufficient to fracture the fibre. The X-ray analysis data in Table I show that calcium and aluminium are certainly removed from the fractured region of the fibres either during or subsequent to the fracture process, thus supporting the possibility of an ion exchange reaction. The removal of calcium and aluminium from the glass fibre is in agreement with the work of Barker *et al.* [2] who showed that a similar effect occurred in GRP pipes subjected to stress corrosion in dilute sulphuric acid. As pointed out by these workers the removal of calcium and aluminium is far more serious than the leaching of sodium or potassium since it will significantly reduce the strength of the alumino–silicate network.

It has been demonstrated by Evans [5] that the velocity, $\dot{a}$, of crack propagation in a glass fibre is dependent on the stress intensity, K_I, at the crack tip, through the relationship:

$$\dot{a} = \alpha K_I^n$$

where α and n are material constants. For conditions of small crack size and low crack velocity a plot of log $\dot{a}$ against K_I is linear and remains linear with a constant slope when the fibre is tested in a variety of atmospheres in the range 0 to 100% relative humidity [6]. However, as the concentration of water in the atmosphere increases the linear plot is displaced to lower stress intensities. A similar situation can be expected to apply for the acidic environments used in the present work, i.e. the higher the acid concentration at the crack tip then the lower the stress intensity required to maintain a given crack propagation rate.

The data given in Fig. 2b may be used to generate approximate log $\dot{a}$ against K_I plots if note is taken of the experimental observation that crack initiation in the first row of fibres takes place at approximately half the time required for the propagation of a "visible" crack of 50 μm depth. Assuming that the major proportion of this time is taken up by the propagation of the slow crack in the mirror region, which is of depth 2.5 μm, the mean crack velocity varies between 10^{-9} and 10^{-12} m sec^{-1} for the stress

TABLE I Composition of glass fibres on fracture surface

	Composition (wt %)*					
	SiO_2	CaO	Al_2O_3	MgO	K_2O	Na_2O
Polished fibre (reference)	55.0	22.0	15.0	0.6	0.5	0.3
Fractured fibre	56.9	20.6	13.8	0.3	0.2	0.1
Fractured fibre	58.1	19.1	13.3	0.4	0.2	0.1
Fractured fibre	57.5	20.2	13.4	0.3	0.3	0.2

*Balance of composition is principally B_2O_3 which could not be detected by the X-ray technique used for the analysis. Note that the volume of fibre analysed will approximate to a layer 1 μm deep on the surface of each fibre.

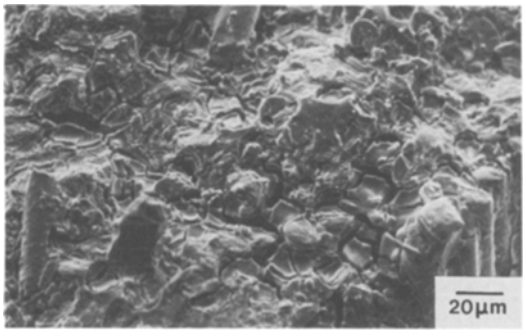


Figure 12 Surface film on fracture surface of sample that has been tension-tested to complete failure. Film is probably a mixture of $AlCl_3$ and $CaCl_2$.

levels used in 5 N HCl. For the same crack length the stress intensity values are in the range 0.14 to 0.73 MN m$^{-3/2}$. Fig. 19 shows the resulting plot of log (average crack velocity) against stress intensity. The feature controlling the form of the curve will be the slow growth of the crack through the initial part of each glass fibre that has fractured at this stage of the test. Reducing the acid concentration from 5 to 0.5 to 0.001 N will displace the plot to higher stress intensity values as shown schematically in Fig. 19.

This semi-quantitative description of the crack initiation process predicts an incubation period for cracking, the extent of which depends on the magnitude of the applied stress and on the concentration of acid in the environment. In this respect it is of interest to note the acoustic emission work of Harris [7] undertaken at the University of Bath on identical pultruded rods at similar stresses and acid concentrations. An incubation period existed before acoustic emission events started to be appreciable thus indicating that fibres do not start to break immediately the

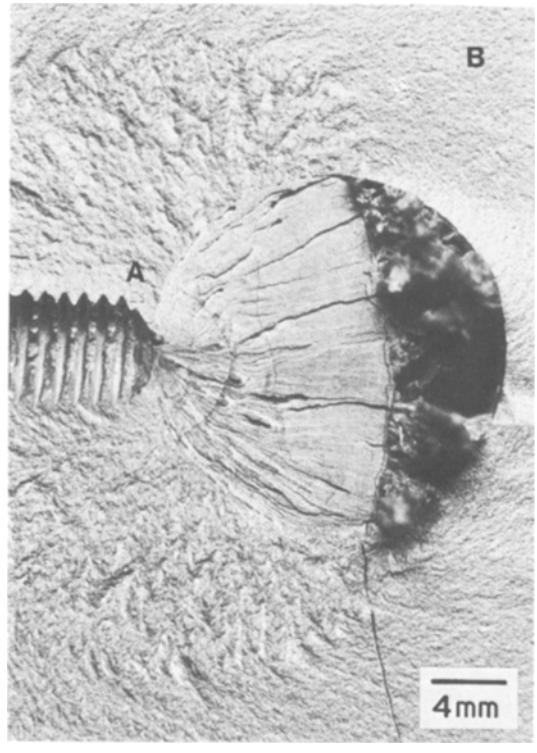


Figure 14 Detail of the fractured cycloaliphatic resin showing rough and smooth textured areas.

stress is applied. Furthermore, the subsequent energy output of the acoustic emission events are smaller than would be expected from glass fibres breaking in a composite which is not being influenced by an acid environment. This is consistent with the observations in the present work since the slow chemical-assisted formation of the mirror fracture region would not be expected to produce a very high acoustic energy release. Also the subsequent fast failure of the fibre takes place on a reduced fibre cross-section and there-

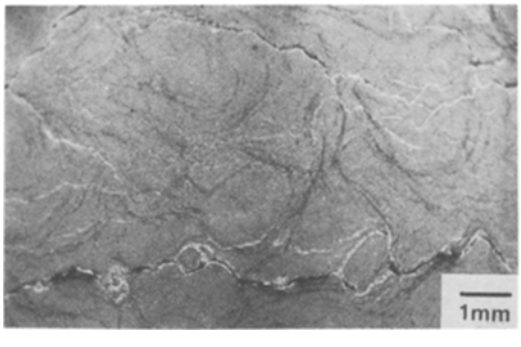


Figure 13 Transverse section from sample shown in Fig. 8 that has been taken 50 mm from the fracture surface. Appreciable longitudinal splitting present.

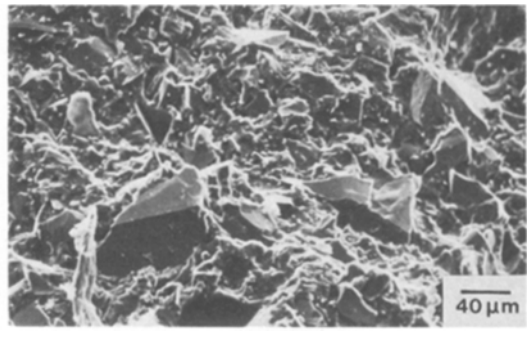


Figure 15 High magnification micrograph of cycloaliphatic resin taken from near the fracture origin (Mark A in Fig. 14).

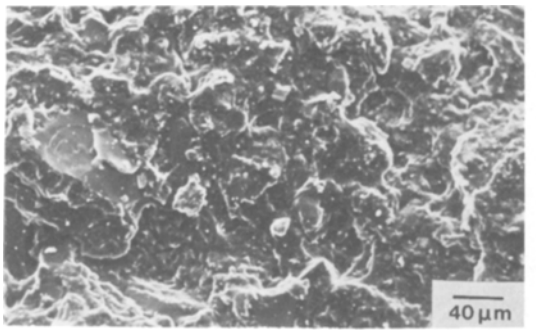


Figure 16 High magnification micrograph of cycloaliphatic resin taken from region B away from the fracture origin.

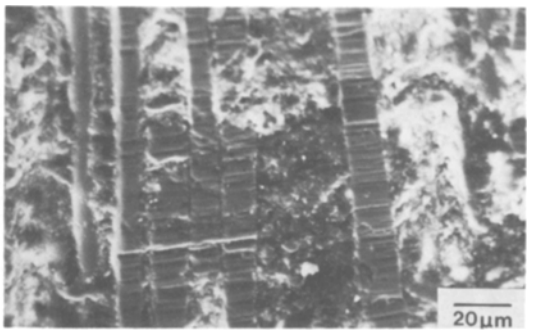


Figure 18 Abraded glass fibres at the surface of a pultruded rod that has a ground finish.

fore the energy emission from these events will be at a lower level than those from the sudden fracture of a whole fibre.

4.3. The effect of resin on the fracture initiation process

The pultruded rod used in the present study had a thin film of resin over its outer surface, the thickness being of the order of a few microns. This film may influence the crack initiation processes and therefore it is important to estimate the possible magnitude of this effect.

Work by Marshall *et al.* [8] using radioactive tracer techniques on a variety of resins indicated that diffusion readily takes place through resin systems: the diffusion coefficient being around 10^{-8} cm^2 sec^{-1}. Application of Ficks law, and assuming that the acid does not react chemically with the resin, suggests that diffusion through a resin coat of thickness 10 μm will take place in a few seconds. The resin film on the surface of the pultruded rod will therefore not add significantly to the fracture initiation period which is of the order of several hours.

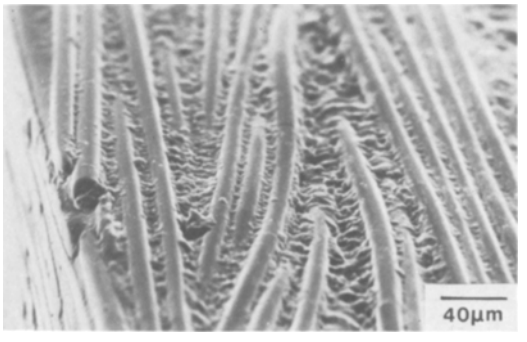


Figure 17 Glass fibres at the surface of the as-pultruded rod.

Cracking of the surface resin film is unlikely during the early stages of testing, even under the combined actions of stress and acid environment. In many instances [9] the presence of aqueous acid solutions can tend to plasticize the resin. It would therefore appear that transport of the acid to the glass fibre takes place by diffusion through the resin film on the rod surface and any surface treatment of the glass fibres. Once at the glass surface the ion exchange reaction can take place and cracking of the fibre commences. It follows that any resin layer or gel-coat that is applied to the rod to provide protection from the acid environment would have to be of appreciable thickness, i.e. of the order of several millimetres.

A number of tests were carried out on the pultruded rod which had been surface ground prior to testing in the acid environment. Such treatment will obviously remove the resin surface layer and introduce severe damage to the surface fibres (Fig. 18). The resulting stress concentrations in combination with the acid environment will promote very rapid cracking leading to early failure.

4.4. Propagation of cracks through the pultruded rod

After the first few fibres have cracked, other adjacent fibres on the surface will begin to fail. The cracks will initiate and spread around the outside surface of the rod more quickly than they will penetrate the section of the rod. Before an individual crack has a chance to propagate deeply into the rod, crack initiation occurs at numerous sites along the length of the rod (as in Fig. 3). The spacing of these surface cracks will be governed by the fibre transfer length and fibre–matrix bond strength.

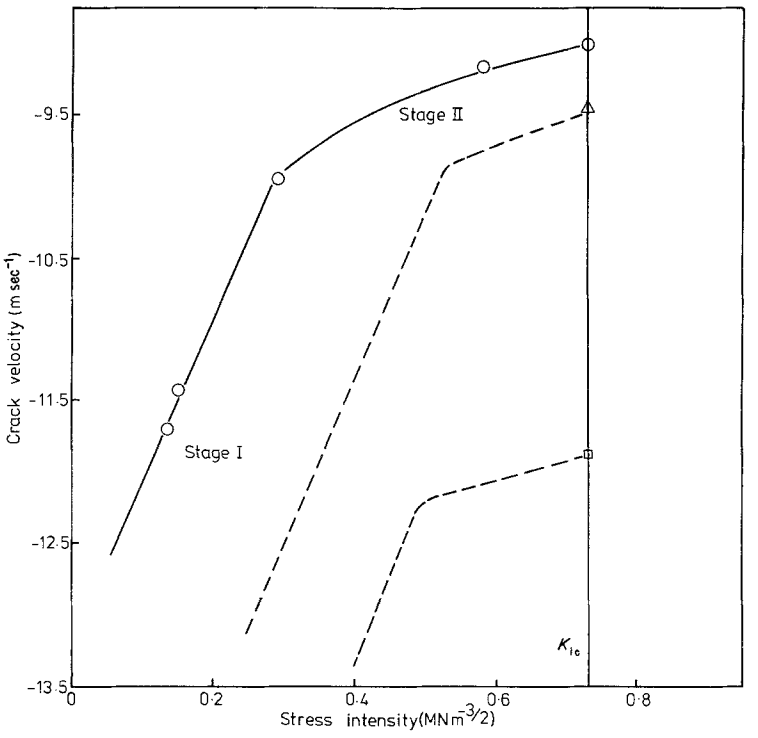


Figure 19 Plot of crack velocity against stress intensity in various acid environments: ○ 5 N HCl; △ 0.55 N HCl; □ 0.001 N HCl. ———— represents the experimental plot and – – – – – – – – represents the schematic plot.

As the crack moves into the section of the rod it will either propagate from fibre to resin to fibre or, because of the high fibre volume fraction in the rod, it may propagate directly from fibre to fibre. In the present experimental conditions where the applied stress is significantly below the normal failure stress in air it is likely that the former process occurs. As the crack passes through the glass fibre and meets the resin, one of two processes may occur.

1. The resin may remain intact and the acid environment will reach the next fibre by diffusion through the resin. This will result in the formation of resin "bridges" behind the crack front. The resin bridges will eventually fail as the crack opening displacement increases.

2. The resin may crack immediately the crack front has passed through a glass fibre.

Microscopic observations made on the failed rod suggest that process 1 takes place during the early stages of crack propagation, and that process 2 becomes increasingly important as the stress intensity at the crack tip increases.

The topography of the fracture face of the rod shows a relatively smooth semi-circular region near the point of crack initiation (Figs. 8 and 14). River marking features cover most of the fracture surface, all radiating from the crack initiation site. The river markings are vertical walls or steps on the fracture surface and represent regions where the crack has grown at slightly different levels in the rod. Many of the vertical walls are associated with resin-rich regions in the rod and with local differences in the alignment of the fibre tows that have occurred during manufacture by the pultrusion process.

Once the microscopic crack has propagated over approximately two thirds of the section of the rod, the stress intensity rises to the point where total fracture of the rod no longer requires chemical assistance. Normal fast failure processes then dominate, resulting in a very uneven fracture surface with extensive fibre pull-out.

5. Summary and conclusions

Brittle fracture of GRP pultruded rods can take place in acid environments at stresses well below those typical of GRP tested in air. The brittle fracture process is dependent on the stress intensity at the crack tip and this is governed by (a) the applied load, (b) the concentration of acid in the environment, and (c) the ease of access of acid to the glass fibre. The rate controlling process is the slow growth of the crack through the glass

fibres. This involves an ion exchange mechanism and results in the formation of mirror regions on the surfaces of individual glass fibres.

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