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Study of the stress corrosion cracking of GFRP: effect of the toughness of the matrix resin on the fatigue damage and stress corrosion cracking of GFRP

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The stress corrosion cracking of glass fibre-reinforced plastic (GFRP) accompanies a phenomenon of catastrophic failure as a result of the rapid fall in strength owing to corrosion breaking of the glass fibres. This produces a flat surface without pulling fibres out of the plane. Attack on the glass fibres can only occur by contact with an acid which must first diffuse into the matrix resin. It is confirmed, however, that no diffusion occurs or that it is too slow to be detected. The relationship between fatigue damage and stress corrosion in an acidic environment, has been investigated, focusing on the effect of matrix toughness on the resistance to stress corrosion failure of GFRP. Three types of GFRP, made from matrices with different toughness, were studied after subjecting them to fatigue damage at different levels.

1. Introduction

Glass fibre-reinforced plastic (GFRP), made from glass/polyester, is a material with excellent chemical resistance. Today, GFRP equipment, such as pipes, tanks, chemical processing units, etc., is widely used.

It is a well-known fact that GFRP products can be easily fractured in an acidic environment at a relatively low load. This is due to stress corrosion, and the fracture surfaces have a special area with a glossy plane [1, 2]. Although the fundamental fracture mechanisms have almost been clarified by effective studies during the last decade [3–14], establishment of lifetime criteria and the standardization for GFRP structure designs, are only now in progress.

The stress corrosion cracking [15, 16] accompanies a phenomenon of catastrophic failure as a result of the rapid fall in the strength of GFRP caused by corrosion breaking of the glass fibres. This produces a flat surface with no fibre pull-out from the plane. Before attacking the glass fibres, however, an acid must diffuse into the matrix resin and contact them. It has been confirmed that no diffusion occurs or that it is too slow to be detected [17]. The phenomenon, which apparently seems to be contradictory, may be simply explained by acid permeation through damage existing as very small cracks in the matrix resin or on the glass/matrix interfaces. The development of cracks in the matrix is governed by the types and forms of glass fibres and the toughness of the matrix resins. With the fixed glass fibres, the resistance to stress corrosion failure for GFRP may, consequently, be evaluated by the fracture toughness of the matrix resin [7, 10].

The above-mentioned phenomenon in GFRP does not take place in any acidic conditions without being subjected to a load or beneath a certain load limit. This indirectly but clearly shows the acid transportation in the matrix resin through damage under load.

The present work is primarily concerned with the relationship between fatigue damage and stress corrosion in an acidic environment, focusing on the effect of matrix toughness on the resistance to the stress corrosion failure of GFRP. Three types of GFRP made from matrices with different toughness were studied after subjecting them to fatigue damage of different levels.

2. Experimental procedure

2.1. Materials

2.1.1. Matrix resins

The properties of the four types of matrix resin (all unsaturated polyesters), such as glass transition temperature, T_g, dynamic modulus, G, and fracture toughness, K_{IC}, are shown in Table I.

TABLE I Mechanical properties of the resins

Resin	Glass transition temperature, T_{g1} (°C)	Dynamic modulus, G (at 25 °C) (10^{10} dyn cm^{-2})	Fracture toughness, K_{1c} (MN $m^{-3/2}$)
A	129	1.49	0.465
B	104	1.43	0.670
C	100	1.21	0.830
D	60	1.10	1.838

2.1.2. Glass fibres

A plain woven cloth from E-glass fibre was used for reinforcement. Its characteristics are weight/unit area, 208 g m^{-2}, woven density 19/25 mm.

2.1.3. Moulding and cure conditions of GFRP

GFRP samples for test were moulded at room temperature by a hand-lay-up method, using a spacer for a constant thickness, and post-cured at 100 °C for 3 h. In these specimens, no anticorrosive layer, such as gel coating, was formed on the sample surface.

2.2. Tensile tests

2.2.1. Tensile fatigue test

Fatigue life-time curves up to 10^7 cycles in the atmosphere were first determined for GFRP with each matrix resin, using a hydraulic-servo-controlled fatigue testing machine under load control at a frequency of 10 Hz and an R ratio of + 0.1. From the curves obtained, a fixed fatigue damage at different levels was given to the specimens prior to the next tensile test in an acidic environment.

The damage procedure was as follows: from the fatigue limit, i.e. the critical point where the strength is no longer decreased, shown at 10^7 cycles in the curves, two levels of load were applied to the specimens, above and below the fatigue limit, e.g. 0.4 and 0.3 in the ratio of fatigue stress to the original tensile strength; under these levels of load, the specimens were subjected to a fixed fatigue damage at four different repeating stress cycles, such as 10^3, 10^4, 10^5, and 10^6 cycles.

2.2.2. Tensile tests in acidic environment

Using the testing machine shown in Fig. 1, the tensile strengths for the undamaged and pre-damaged specimens mentioned above were checked at a very low strain rate (10^{-3} mm min^{-1} crosshead speed) under immersion in an acidic environment (5 wt % HNO_3, 25 ± 1 °C).

3. Results

3.1. Static properties of matrix resins

Table I summarizes the characteristics of four types of polyester resins, as a matrix resin for GFRP, with different fracture toughnesses, K_{IC}, and glass transition temperatures, T_g.

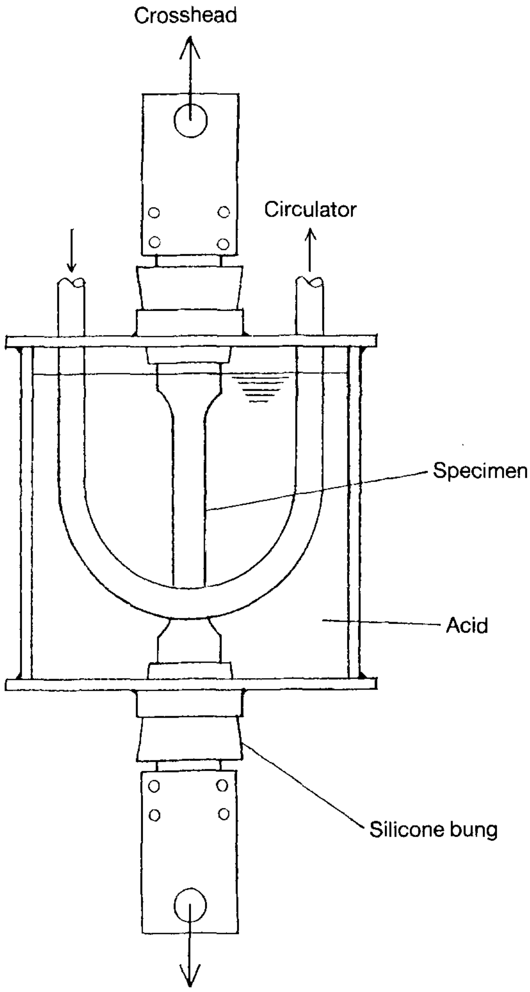


Figure 1 Slow strain-rate testing equipment in an acid environment.

3.2. Static properties of composites in air and in acidic environments

The effect of resin toughness on the results of a low strain-rate tensile test for cloth–GFRP in air and acidic conditions is shown in Fig. 2. Under the acidic environment, a remarkable decrease was shown in the tensile strength at the specified test conditions at a very low strain rate, compared with the results under an atmospheric environment.

3.3. Fatigue behaviour in an atmospheric environment

Fig. 3 shows fatigue curves based on the fracture failure of GFRP in an atmospheric environment. It is clearly indicated that all the GFRP tested had almost the same fatigue behaviour, such as fatigue strength, independent of the matrix resins with the different fracture toughnesses, except for the most toughened resin, D. From the figure, about 35% of the original tensile strength was obtained at the fatigue limit strength of 10^7 cycles.

3.4. SEM observation of damage

The fatigue tests were performed under two loading levels, 40% and 30% of the original tensile strength, as mentioned in Section 2.2.1. From the SEM observation, we confirmed the fact that the damage in GFRP

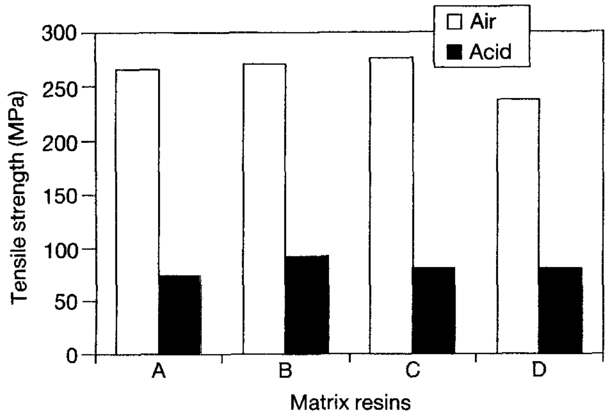


Figure 2 Tensile strength of the composite in air and acid environments.

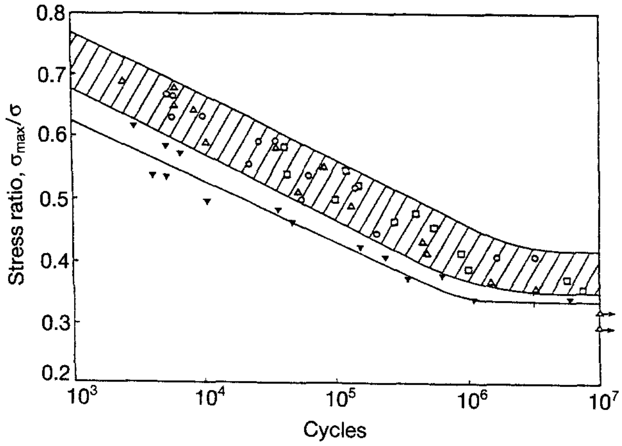
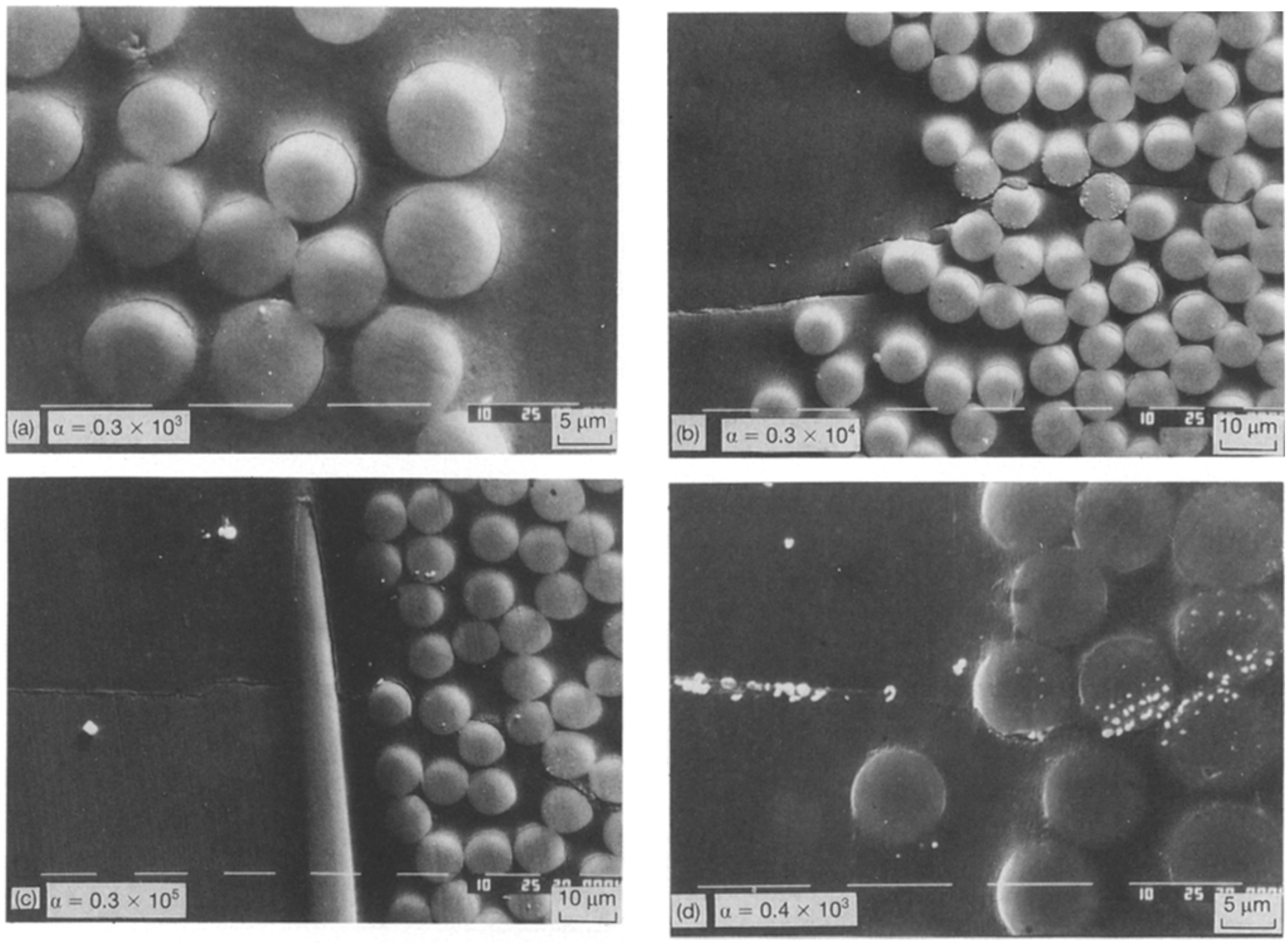


Figure 3 Fatigue curves of GFRP with matrix resins (○) A, (△) B, (□) C and (▼) D.



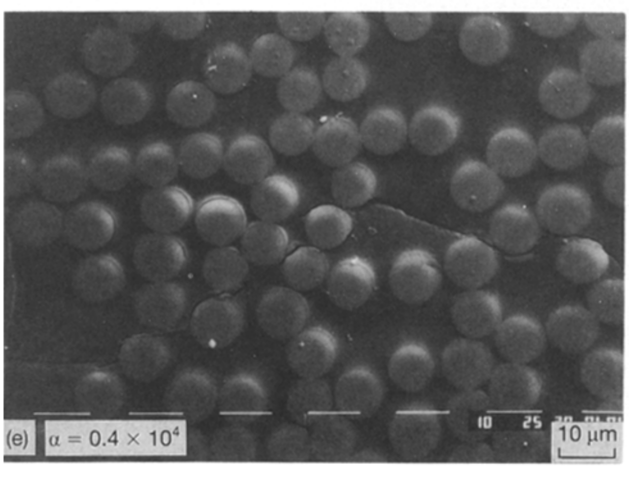


Figure 4 Scanning electron micrographs of fatigue-induced cracks in GFRP (Resin A).

was produced mainly in the transverse direction during the fatigue cycles, as shown in Figs 4–6.

Resin A (Fig. 4). In GFRP with a brittle matrix, Resin A, "debondings" could be seen along the transverse fibre bundles (tows) at 10^3 cycles under the 30% stress (Fig. 4a). At 10^4 cycles, cracks were formed in the fibre bundles as a result of these debondings becoming connected (Fig. 4b) and at 10^5 and 10^6 cycles the cracks in the transverse bundles propagated to the adjacent cross-bundles (Fig. 4c). Under 40%

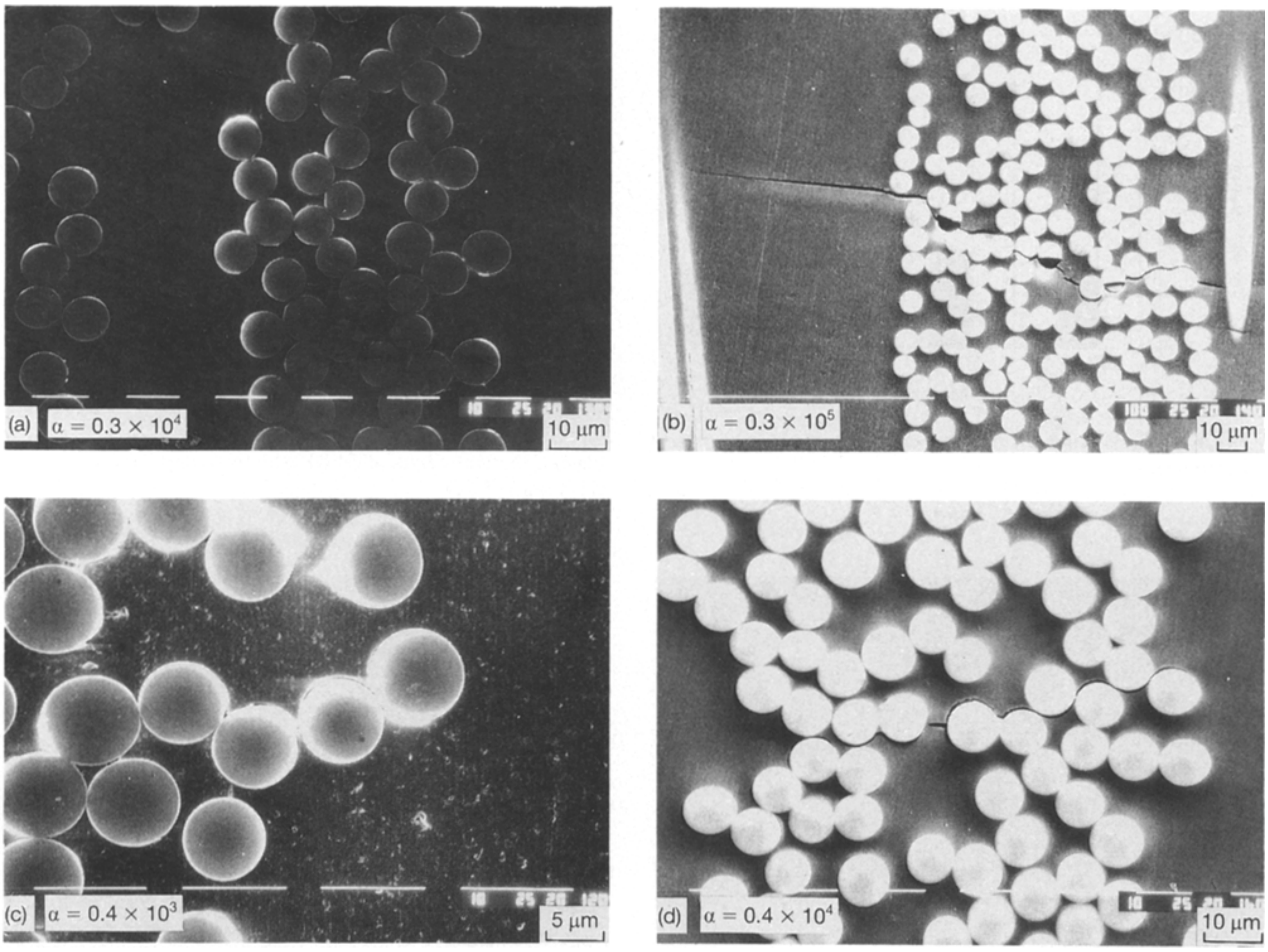


Figure 5 Scanning electron micrographs of fatigue-induced cracks in GFRP (Resin B).

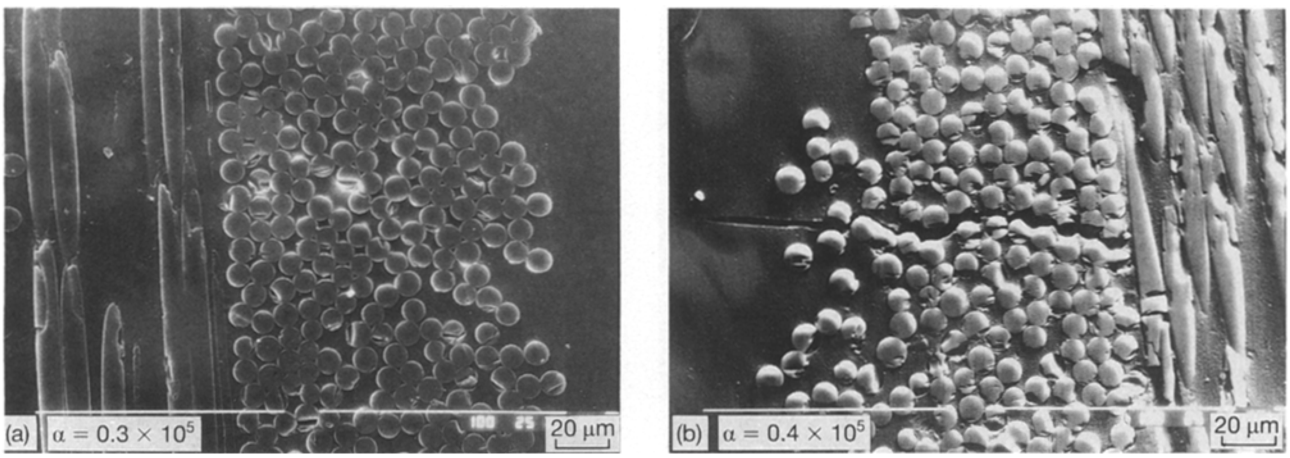


Figure 6 Scanning electron micrographs of fatigue-induced cracks in GFRP (Resin D).

stress, the cracks were already formed at 10^3 cycles (Fig. 4d), then extended to the next cross-bundles over 10^4 cycles (Fig. 4e).

Resin B (Fig. 5). In GFRP with a tough matrix, Resin B, debondings were recognized at 10^3 and 10^4 cycles under 30% stress (Fig. 5a), followed by crack propagation over 10^5 cycles (Fig. 5b). Under 40% stress, the development of debondings (Fig. 5c) and cracks (Fig. 5d), and propagation occurred at 10^3, 10^4, and 10^5 cycles, respectively.

Resin D (Fig. 6). In GFRP with the most toughened matrix, Resin D, damage occurred in the same manner as mentioned above. The cracks were not recognized at 10^5 cycles under 30% stress (Fig. 6a), but under 40% stress, the cracks were already formed at 10^5 cycles (Fig. 6b).

3.5. Influence of fatigue damage on the stress corrosion of GFRP

3.5.1. *The mechanism of stress corrosion coupled with fatigue damage*

The influence of fatigue damage is shown in Fig. 7 on the strength of GFRP with different matrix resins in

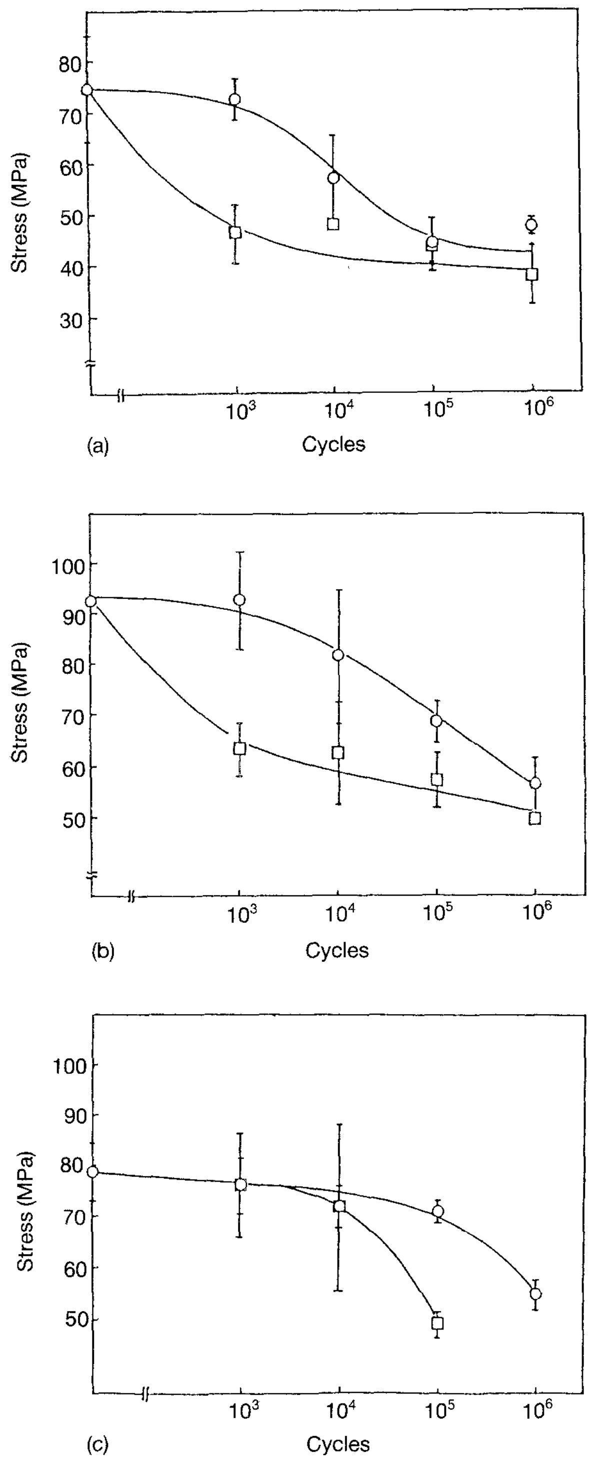


Figure 7 Dependence of the number of cycles on the tensile strength in the slow strain-rate test in 5 wt % HNO_3 at 25 °C in (a) Resin A, (b) Resin B, and (c) Resin D. (○) $\alpha = 0.3$, (□) $\alpha = 0.4$.

an acid environment. This is based on the results of the low strain-rate tensile tests under acidic conditions, using the test specimens with different levels of fatigue damage under an air atmosphere.

In GFRP with the low toughness matrix, Resin A, perfect retention of strength was obtained under mild fatigue conditions at low load (30% stress) and small cycle numbers ($< 10^4$), in spite of recognizing the development of interfacial debonding by SEM observation.

At 10^4 cycles, however, such cracks could be seen in the transverse fibre bundles, and at 10^5 cycles the existence of cracks which reach the fibre bundles parallel to the load direction was confirmed. These events were closely correlated with the decrease in strength.

In the specimen fatigued under 40% stress, even at 10^3 cycles, the strength rapidly decreased to about half of the original strength of the unfatigued specimen, at which level the strength stabilized over a wide range up to 10^7 cycles. This behaviour was almost the same as that of specimens fatigued under a large number of cycles under a lower load.

3.5.2. Effect of resin toughness on the stress corrosion of fatigued and unfatigued GFRP

The fatigued GFRP with the tougher matrix resins, B and D, also showed a decrease in the low strain-rate strength under the acid environment. Thus, a similar behaviour to that of the less-tough resin A can be observed in Fig. 7. On detailed observation, however, a difference was seen in the resistance to failure, which showed a shift of fatigue life to the longer side, in accordance with the increase in resin toughness. The strength reduction behaviour corresponds to the ease of crack formation in the glass fibre bundles, which was thought to be closely related to the toughness of the matrix resins, based on SEM observation (Section 3.4).

In the results of the influence of resin toughness on the resistance to stress corrosion failure of unfatigued cloth–GFRP, it was shown that the resistance was not necessarily governed by the factor of toughness, because there seems to exist an optimum value in toughness which gave the maximum resistance, as shown in Fig. 8.

4. Discussion

The drastic strength reduction in cloth–GFRP was considered to be caused directly by the fibre damage suffered due to acid attack, because none of the matrix resins would normally be corroded in such a short time even under acidic conditions. It was thought that the rate of strength reduction was governed by the

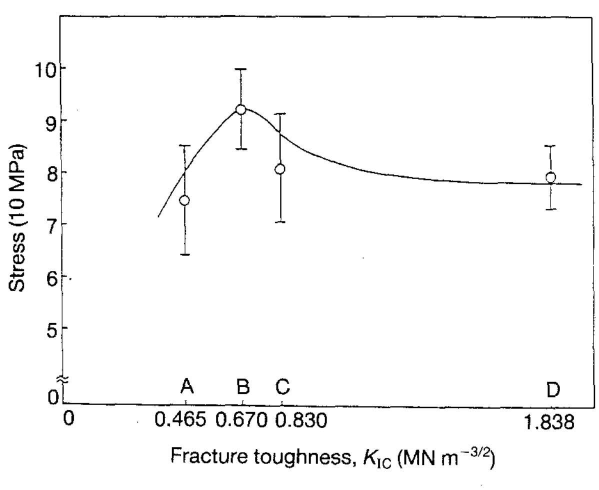


Figure 8 Dependence of fracture toughness of the matrix resin on tensile strength in the slow strain-rate test in 5% HNO_3 at 25 °C.

acid concentration and largely by the fracture toughness of the matrix resin through which the permeation of acid to the surface of glass fibres could occur. That is, easy penetration of acid under load resulted in small cracks in the matrix resin or debondings at the fibre/matrix interfaces. This development was markedly influenced by the fracture toughness.

Based on SEM observation, Fig. 9 schematically illustrates the propagation process of damage in cloth–GFRP, in the cross-section of fibre bundles perpendicular to the load direction. Under low stress conditions and small repeating cycle numbers, debonding occurs on the resin/fibre interfaces (Fig. 9a). Under more severe conditions, debonding proceeds forming cracks which may interconnect the fibres (Fig. 9b), followed by the cracks spreading beyond the fibre bundles (Fig. 9c) and by further propagation leading to interface damage in the bundles parallel to the load direction (Fig. 9d).

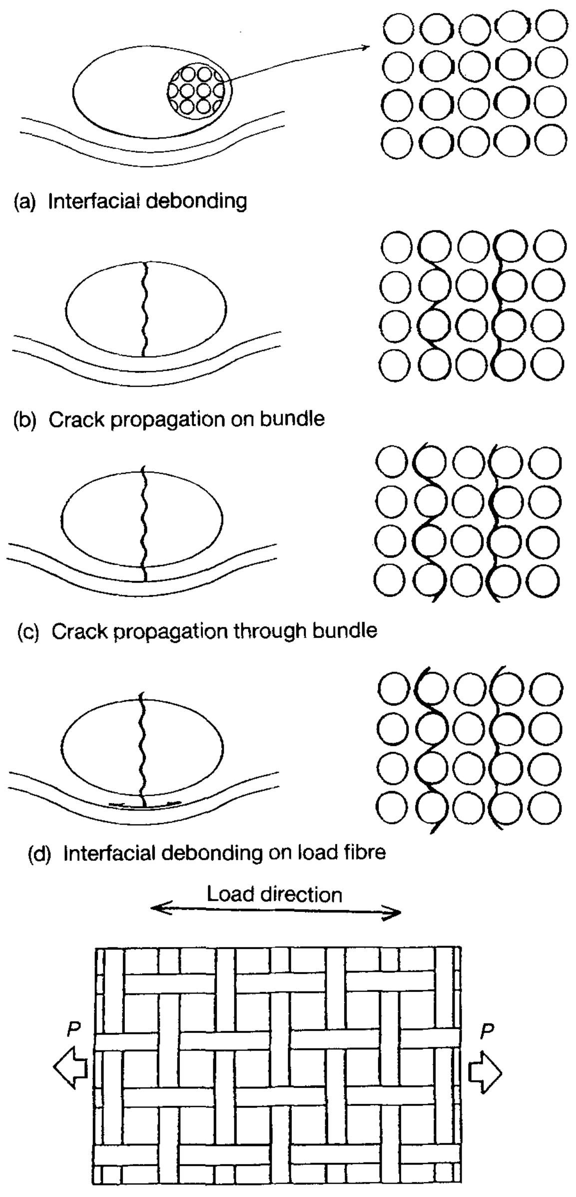


Figure 9 Mechanism of fatigue-induced crack propagation.

Caddock *et al.* [17] confirmed that the diffusion of acid through a matrix resin does not occur under zero load or at a load below the minimum value, above which environmental stress failure can take place due to acid transport through cracks or "microcavitation" [7].

Taking these facts into consideration, our results may be explained as follows. The test specimens predamaged under the milder fatigue conditions (30% stress, up to 10^3 cycles) may have a low level of damage such as "independent debondings". However, these defects do not interconnect, nor do they develop into cracks which allow a rapid penetration of acid through the matrix resin, unless the load reaches a considerably high level almost comparable to the original strength, during the tensile tests under an acidic environment. However, specimens with cracks caused by higher fatigue-predamage (30% stress, 10^5–10^6 cycles; or 40% stress, over all the range of cycles) can undergo crack opening to the extent of allowing a rapid acid penetration, at a fairly low load such as half of their tensile strength, during the test. This is thought to be the mechanism for the failure of predamaged GFRP under load in an acidic environment.

In addition, in an acidic environment, as shown in Fig. 7 (Resins A and B), the strength of the specimen fatigued at 10^3 cycles under 40% stress decreased to half the value, compared with that of a specimen under 30% stress. In this case, the influence of predamage level on the strength under an acidic environment is clearly shown. On the other hand, there was no difference in the strength and modulus of samples tested in air. This is shown in Table II, using the same predamaged specimens with 30% and 40% stress levels. Thus, it is considered that the mechanical properties will be strongly governed by fibre breakage due to acid penetration through the fatigue damage.

Hogg [12] reported that, in a unidirectional GFRP, the resin toughness reduced the crack propagation rate under acidic conditions, except for the extremely tough and somewhat flexible resin (the explanation for which was given as the increased rate of acid diffusion). Later, these phenomena have been re-examined, considering the relationship between the crack propaga-

TABLE II Residual strength and modulus of cloth–GFRP after fatigue testing

Matrix resin	Fatigue load ratio, σ_{max}/σ_c	Cycles	Tensile strength (MPa)		Residual strength ratio (%)	Tensile modulus (GPa)		Residual modulus ratio (%)
			After test	Virgin		After test	Virgin	
A	0.3	10^3	250	265	94	15.1	15.9	95
	0.4		256		97	14.4		91
B	0.3	10^3	270	271	100	15.7	16.3	96
	0.4		267		99	16.1		99

tion rate and the fibre stress which can decrease in the tougher resin, by limited yielding in a constrained layer parallel to the fibres at a crack tip [13]. This concept is in agreement with our results.

In the GFRP with a less-tough resin, cracks which allow an acid penetration are easily produced. The higher the toughness, the more difficult is the crack formation, and this leads to the maximum strength in the low strain-rate tensile test at the optimum toughness range. Above this range, limited yielding becomes noticeable, which restricts the growth of cracks, on the one hand, resulting in retention of original strength at the extent of the high fatigue cycles but, on the other hand, lessens the strength value itself, reflecting the resin strength (Resin D, in Figs 7 and 8).

In the case of cloth–GFRP, the cracks are first developed in the transverse fibre bundles, and are then propagated to the adjacent load-bearing fibre bundles parallel to the tensile direction. This results in catastrophic failure under acidic environments, as mentioned above.

Thus, an explanation can be given qualitatively for the environmental stress cracking of prefatigued cloth–GFRP specimens, by modifying the Hogg' proposal [13].

5. Conclusions

1. The tensile strength of cloth–GFRP in an acidic environment is remarkably low, compared with that in the atmosphere.

2. Tensile strength under acidic conditions reflects the levels of damage for fatigued specimens, corresponding to the existence of debonding in the fibre bundles and the spread of cracks beyond the bundles.

3. The rate of acid transport through the matrix resin differs according to the level of damage. This governs the resistance to environmental stress cracking.

4. The toughness of matrix resins is reflected in the development of fatigue damage.

5. There is an optimum value of toughness giving the maximum resistance to the reduction of strength under an acidic environment.

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