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The environmental fatigue behaviour of carbon fibre reinforced polyether ether ketone

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The fatigue behaviour of carbon fibre/PEEK composite is compared with that of carbon/epoxy material of similar construction, particularly in respect of the effect of hygrothermal conditioning treatments. Laminates of both materials were of 0/90 lay-up, and they were tested in repeated tension at 0° and at 45° to the major fibre axis. The superior toughness of the polyether ether ketone and its better adhesion to the carbon fibres results in composites of substantially greater toughness than that of the carbon/epoxy material, and this is reflected in the fatigue behaviour of the carbon fibre/PEEK. The tougher PEEK matrix inhibits the development of local fibre damage and fatigue crack growth, permitting a 0/90 composite with compliant XAS fibres to perform as well in fatigue as an epoxy laminate with stiffer HTS fibres. Hygrothermal treatments have no effect on the fatigue response of either material in the 0/90 orientation. The fatigue response of a cross-plied carbon/PEEK laminate in the ± 45° orientation is much better than that of equivalent carbon/epoxy composites, again because the superior properties of the thermoplastic matrix.

1. Introduction

High performance composites based on thermoplastic materials have recently been introduced by ICI. Aerospace applications for carbon fibre composites have hitherto been satisfied by epoxide-resin-based composites (CFRP), particularly where mechanical performance at low density is required. The introduction of a carbon fibre composite based on a thermoplastic matrix allows the advantages currently derived from CFRP systems to be met, but with the addition of new and hitherto unavailable benefits; namely significantly easier fabrication, repairability and an improved property profile [1].

The thermoplastic composite system, which is known as Aromatic Polymer Composite (APC), has been developed around a continuous process for the production of carbon fibre reinforced polyether ether ketone (an aromatic polymer) where the individual carbon fibres are fully wetted. The product, typically, is made as a uniaxial tape, about 0.1 mm thick, which can be processed into sheet and moulded items.

The matrix material is thermoplastic polyether ether ketone (PEEK), which has excellent high temperature properties, having a "glass" transition temperature at about 150° C. In addition, PEEK is a semi-crystalline polymer which affords it good environmental and chemical resistance. In order to produce thick sheet mouldings, the pre-impregnated strips of APC are pressed together using compression moulding technology in the usual laid-up laminates. Moulding temperatures are about 380° C and heating times depend on the laminate thickness (e.g. 1 min per ply of pre-impregnated strip is usually sufficient). Post-consolidation cooling was critical to development versions of APC, and particularly the first commercial grade, APC1. In order

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to ensure optimum crystallization it was necessary to cool from 380 to 200° C in less than 5 min. Optimum crystallization, in turn, achieves balance of mechanical properties. Subsequent technical developments have resulted in a material which has a much broader processing window and this is known as APC2. A development version of APC, however, was used in the work reported here (see Materials section), being very similar to APCl. The only difference between the APC used in this work and APC2 was that there was a cooling period longer than 5 min between the consolidation temperature and 200° C. Consequently, slightly lower strength and toughness values can be expected compared with both APCl and APC2.

An accepted problem with the familiar epoxide-resin-based composites (CFRP) currently favoured by aerospace engineers is their sensitivity to hygrothermal exposure, especially in respect of its effects on such properties as shear resistance and toughness which are dominated by matrix and interface characteristics. Since PEEK is a crystalline resin with excellent environmental resistance, it would be expected therefore that PEEK-based composites would have advantages over conventional CFRP in applications where the reinforcing fibres are not dominating composite behaviour. Some initial environmental testing of carbon fibre/PEEK composites has been described elsewhere [2].

In the set of experiments described here we have investigated the effects of hygrothermal conditioning on the tensile fatigue behaviour of some carbon fibre/PEEK laminates (APC). We have attempted to match the characteristics of the test material as closely as possible with those of a carbon/epoxy laminate for which we had already reported results of similar experiments [3] in order that direct comparisons could be drawn, and effects attributable to differences between the two matrix resins identified.

2. Materials

The carbon fibre/PEEK composites were prepared by ICI, being laid up so as to reproduce the laminate structure of the carbon/epoxy composites described in [3]. They were 0/90 laminates with 11 plies, six in the 0° direction and five in the transverse direction. They were laid up with double layers of tape so as to produce a laminated thickness of about 3 mm, similar to that of the carbon/epoxy samples. The finished laminates contained 54% by volume of Courtaulds XAS carbon fibre. The laminated plates were slightly twisted, indicating the presence of residual stress from lamination, but this distortion was insignificant after the moulded plates had been cut into fatigue and tensile test samples. All samples tested in fatigue were cut well away from the plate edges so as to avoid the effects of imperfect bonding at the edges. The surfaces of the moulded plates showed extensive evidence of buckling of the reinforcing fibres in the skin of the plate. This would normally be expected to provide sites for initiation of premature failure, but it will be apparent from the results that this was not a serious problem.

The carbon/epoxy laminates used for comparison were autoclaved at the Royal Aircraft Establishment, Farnborough, from pre-preg manufactured by Rotorway Composites, Clevedon, Somerset. They were laid up as described above, and contained 58% of Courtaulds HTS fibre in Code-69 epoxy resin.

Fatigue tests were carried out in repeated tension ($R \approx 0.1$) on straight-sided samples 200 mm long x 10 mm wide. Samples were end-tabbed for testing by bonding on soft aluminium tabs with Ciba–Geigy Redux 318A adhesive. Slight surface roughening of the moulded carbon/epoxy material was all that was needed to produce a strong bond, but it was necessary to shot-blast the carbon/PEEK samples in the end regions where the tabs were fixed.

3. Preconditioning treatments

Samples for testing were preconditioned in three standard ways:

1. Oven drying at 60° C.
2. Holding at 23° C and 65% RH.
3. Immersion in boiling water.

The weight changes under these conditions are shown in Figs. 1 and 2. In boiling water an equilibrium uptake of about 0.45% in carbon/PEEK is reached after about 3 weeks, whereas at 65% RH equilibrium has not been attained after 1000 h, by which time the weight gain is only 0.08%. Drying the as-received PEEK composite resulted in a small loss of about 0.02%, and it is effectively in this condition that all of the preconditioning treatments began after the end-tabbing operation. It can be seen from Fig. 1 that shot-blasting the surface of a carbon/PEEK laminate does not affect water penetration. Comparable water uptake

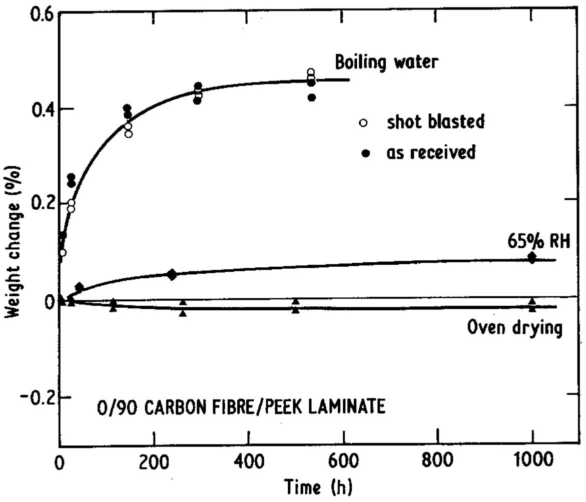

Figure 1 Weight changes of 0/90 carbon fibre/PEEK laminates on oven drying at 60° C, boiling in water, and storage at room temperature and 65% RH.

results for the carbon/epoxy laminate are given in Fig. 2. It can be seen that this material loses more water on oven-drying, and therefore the net gain after 3 weeks at 65% RH is 7 times greater than that of the carbon fibre/PEEK, and after 3 weeks in boiling water it is roughly 4 times that for the PEEK composite. The moisture diffusivity in the carbon fibre/PEEK is clearly much lower than that in carbon/epoxy.

4. Mechanical properties

Tensile properties of the two types of composite in the as-received condition are given in Table I. The tensile strengths and moduli of both sets of composites are roughly what would be estimated from a mixture-rule model predicting that 6/11 of the total fibre volume fraction (in the 0° plies) determines the composite properties. The tensile failure strains of the two materials are roughly equal. When tested at ± 45°, however, the carbon/PEEK composite shows properties superior to those of the carbon/epoxy in two respects, its strength being 60% greater and its average failure strain, 0.043, being over 3 times that of the carbon/epoxy. These features reflect the greater strength and ductility of the polyether ether ketone by comparison with the Code-69 epoxy resin, and may also indicate improved fibre–matrix bond strength. This observation, moreover, does not even reflect the performance of CF/PEEK in an optimistic light. The particular laminate structure of 6 x 0° plies and 5 x 90° plies naturally results in an unbalanced system when conducting tests on ± 45° specimens. This feature, together with the relatively slow cooling after consolidation for the carbon fibre/PEEK sheet, results

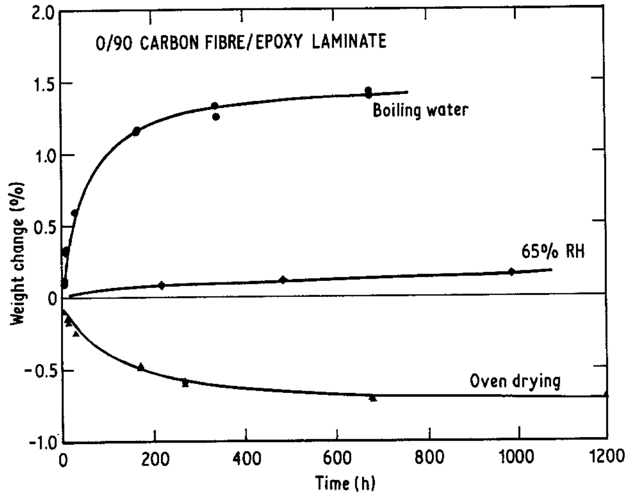

Figure 2 Weight changes of 0/90 carbon/epoxy laminates on oven drying at 60° C, boiling in water, and storage at room temperature and 65% RH.

TABLE I Mechanical properties of CF/PEEK and CF/epoxy (data obtained on $[0_2, \overline{90}_2]_{3S}$ sheet for CF/PEEK and $[0, \overline{90}]_{3S}$ sheet for CE/epoxy)

Material	Orientation	No. of specimens	Tensile strength (MPa)	Tensile modulus (at 0.5% strain) (GPa)	Tensile fracture strain (%)
CF/PEEK	0/90	3	740	61	1.1
CF/epoxy	0/90	10	932	83	1.1
CF/PEEK	± 45	5	194	14	4.3
CF/epoxy	± 45	4	126	–	1.3

(Tensile test cross-head speed 0.5 mm min^{-1})

in a pessimistic value for tensile strength. For example, Table I quotes a value of tensile strength of 194 MPa, whilst a value of 340 MPa has been recorded on a balanced 0/90 fast cooled sheet in ± 45° direction. Interestingly, tensile modulus is unaffected.

The fracture toughness of the carbon/PEEK laminate, as measured by K_{Ic} measurements on centre-notched tensile samples 30 mm wide, with the notch-length/specimen-width ratio ($2a/w$) about 0.45, was 69 MPa $\text{m}^{1/2}$, about 40% greater than that for the equivalent carbon/epoxy composite, for which $K_{\text{Ic}} \approx 50$ MPa $\text{m}^{1/2}$. (The appropriate finite width correction was made in each case.)

Some of the tensile tests, for which results are given in Table I were monitored with acoustic emission equipment in order to study the failure mechanisms of the composites. The equipment, an AETC amplitude analysis system, has been described elsewhere [4]. It is informative to present the results of these tests as curves of acoustic emission (AE) events as a function of stress, showing at the same time the frequency of events falling in given bands of amplitude above threshold. Fig. 3 shows typical results from a tensile test on a

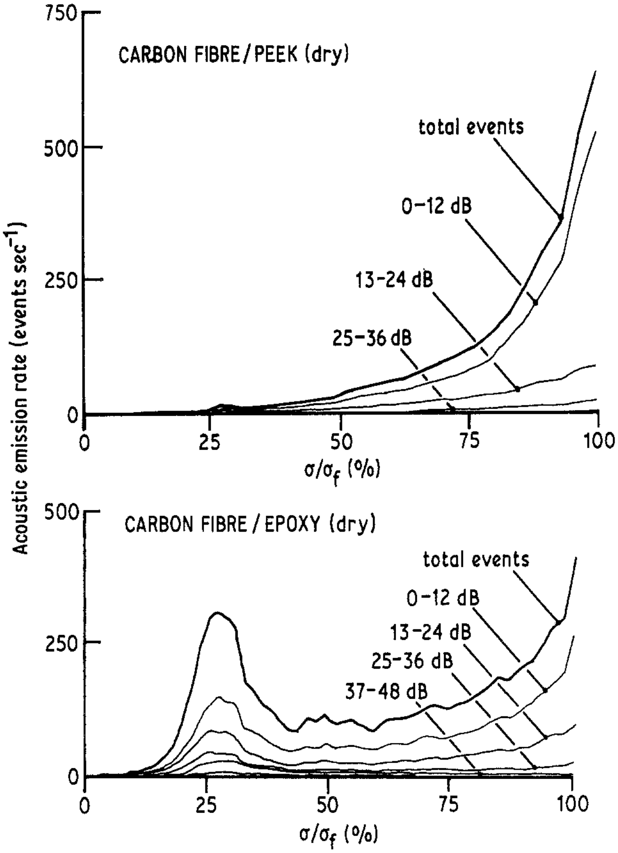

Figure 3 Acoustic emissions during tensile tests on 0/90 carbon/PEEK and carbon/epoxy composites. The curves show rate of acoustic emission events as functions of stress level, given here as a fraction of the final failure stress, σ_f. The top curve in each case is the total event count rate, and the lower curves represent the emissions falling in the amplitude ranges indicated (above threshold).

0/90 carbon/epoxy composite, together with a comparable curve for carbon/PEEK material: each curve is typical of the behaviour of the type of material it represents. The AE curve for the carbon/epoxy laminate is also typical of most carbon or glass fibre reinforced resins of brittle character, such as Code-69 resin, having a 0/90 laminating sequence [4]. The peak in rate of emission at low stress levels for the carbon/epoxy composite represents the cracking of the transverse plies which may occur at stresses as low as 10 to 20% of the overall fracture stress of the composite. The stress level at which the onset of transverse ply cracking occurs is sensitive to the brittleness of the matrix and to the presence of residual thermal stresses, and we have shown, for example, that the AE peak is shifted to higher stress levels and is itself reduced in height as the resin is plasticized by the absorption of water [4]. It can be seen, however, that the carbon fibre/PEEK shows almost no evidence of an AE peak at low stress levels although transverse ply cracking does occur in this material, as discussed later. No stress waves were therefore being generated by transverse ply cracking in the PEEK resin, by contrast with that in epoxy composites. As we shall see later, the high degree of ductility of the PEEK resin and the strong fibre/matrix bond probably substantially alter the mechanism of transverse ply cracking in these carbon fibre/PEEK composites.

5. Fatigue behaviour and the effect of moisture

When discussing the fatigue behaviour of materials which exhibit viscoelastic characteristics, confusion sometimes arises when comparing tensile strength values obtained at normal test machine speeds with fatigue properties obtained at higher frequencies. Not only is there an inherent difference in properties under the different test conditions, but in constant frequency fatigue tests over different load ranges the effective strain rate must vary widely. We therefore adopt the principle of Sims and Gladman [5] of carrying out fatigue tests at constant rate of stress application (RSA) instead of constant frequency, and making comparisons with tensile properties measured at the same loading rate. Fig. 4 shows results of tensile tests carried out over five orders of magnitude of loading rate, from which it can be seen that the materials show relatively little rate-dependence of tensile strength. There is, nonetheless, a suggestion of a slightly greater rate-dependence of tensile strength for the carbon/PEEK composites than for the carbon/epoxy (which can be seen from Fig. 4 to be zero over this range of testing speeds).

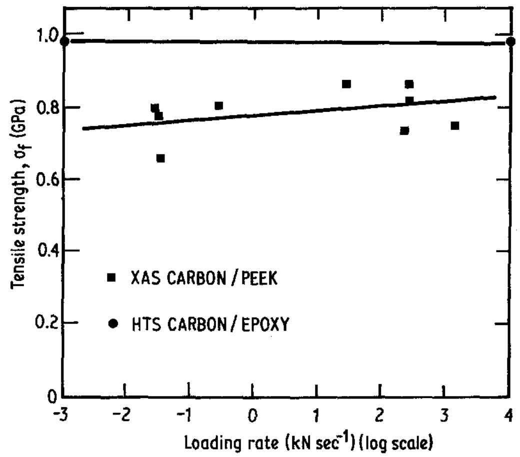

Figure 4 Loading rate dependence of the tensile strength of 0/90 carbon/PEEK and carbon/epoxy composites.

All of the fatigue tests reported here were carried out in repeated tension, maintaining a small positive load at the bottom of the cycle ($R \approx 0.1$) so as to prevent inadvertent buckling of the sample on unloading, in an Instron 1332 servo-hydraulic fatigue machine. Immediately after pre-conditioning, and prior to inserting in the testing machine, each sample was wrapped in plastic film in order to avoid changes in the moisture content of the sample during the test.

Tests were carried out on the laminates in both the 0/90 and ± 45° orientations in order to study the extent to which the thermoset and thermoplastic matrices influence fatigue behaviour under conditions in which first the fibres and then the matrix dominate. The 0/90 tests were carried out at an RSA of 200 kN sec^{-1}, and the ± 45° tests at 25 kN sec^{-1}. These rates had previously been found to cause no significant hysteretic heating of carbon/epoxy composites tested in these two orientations [3]. A small number of fatigue tests were also carried out, for comparison purposes, on some samples of unidirectionally reinforced carbon/PEEK material.

Stress–log life or S–$\log N$ curves for the carbon fibre/PEEK composites are presented in Fig. 5. The different hygrothermal conditioning treatments are distinguished by the plotting symbols, and it can be seen that the scatter bands for the three conditions are almost completely overlapping. It would seem, therefore, that neither the

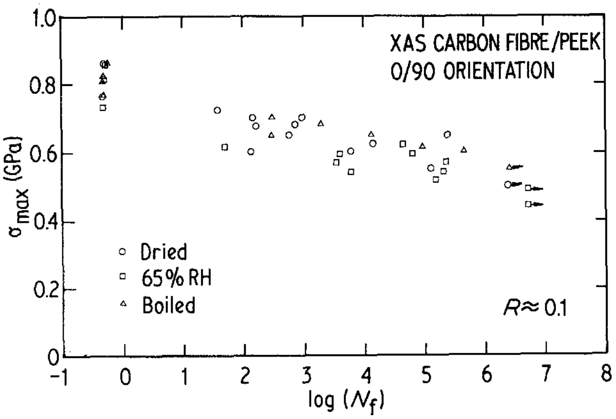

Figure 5 Effect of conditioning treatments on the S–log N curves for tensile fatigue of 0/90 XAS carbon fibre/PEEK laminates tested in the 0° (6 plies) direction.

hygrothermal treatments used for conditioning nor the different moisture levels present in the composites after conditioning have any significant effect on the fatigue response of a 0/90 carbon/PEEK laminate, as would have been expected. If the data are separated, and best fit lines of the form

$$\sigma = \sigma_0 - B \log N_f$$

and fitted by eye through the points, the slopes, B, are slightly different, being 23 MPa per decade of life for the dried composite, 29 for the boiled material and 34 for samples conditioned at 65% RH, revealing, perhaps, a slight effect of water on the resistance to crack propagation in the plastic matrix.

The points representing the "life" at a half cycle are in fact tensile strength results obtained at testing speeds equivalent to those used in the fatigue tests. These results are 728 MPa for the oven-dried laminate, 768 MPa for the boiled and 753 MPa for the composite conditioned at 65% RH. These results are not significantly different, and indicate negligible effects of conditioning on short-term tensile strength.

Comparable results for the 0/90 carbon/epoxy laminates are reproduced from [3] in Fig. 6. The scatterbands are again fully overlapped, but in this case we are unable to distinguish any effects of conditioning on the S–log N curve. The dynamic tensile strengths for the laminates are 955 MPa in the dried state, 956 MPa in the boiled and 932 MPa in the composite conditioned at 65% RH. With a coefficient of variation of about 7%, these differences are again insignificant. The overall slope of the carbon/epoxy S–log N curves is about 35 MPa per decade, compared with an average slope for the carbon/PEEK composites of about 30 MPa per decade.

Fatigue tests at ± 45° were carried out on both types of composite in the 65% RH condition. The results are shown in Fig. 7. Under conditions where there are substantial shear forces in the matrix, the epoxy-based laminate is initially considerably weaker, the dynamic strength being only 140 MPa, compared with a value of 195 MPa for

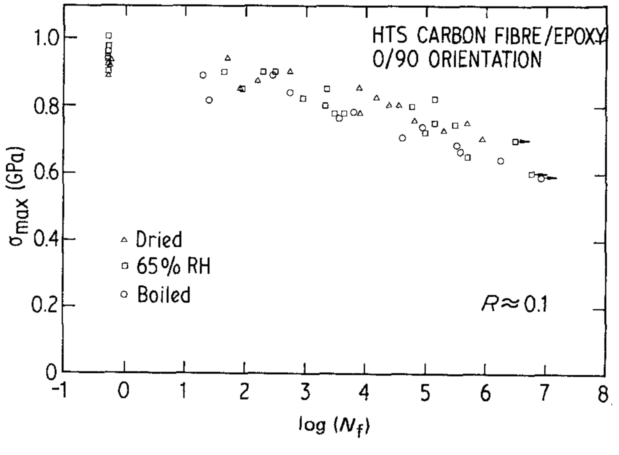

Figure 6 Effect of conditioning treatments on the S–log N curves for tensile fatigue of 0/90 HTS carbon/epoxy laminates tested in the 0° direction.

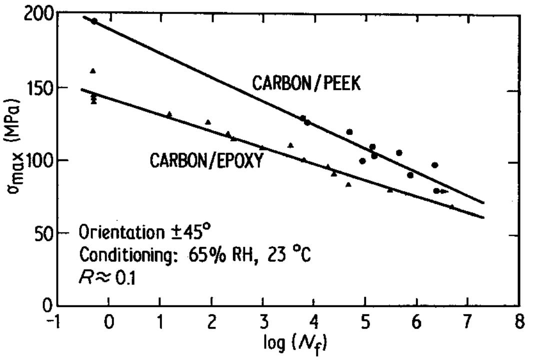

Figure 7 S–log N curves for 0/90 carbon/PEEK and carbon/epoxy composites tested in the ± 45° orientation (65% RH).

the carbon/PEEK. The S–log N curve for the carbon/PEEK has a slope of about 16 MPa per decade, by comparison with 11 for the carbon/epoxy, and the two curves appear to be drawing to an intersection at about 10^8 cycles, implying a poorer long term fatigue resistance in the thermoplastic laminate. This picture is misleading, however, for not only will the PEEK composite withstand some 10^3 cycles at a stress equal to the dynamic failure stress of the carbon/epoxy material, but its life at 80 MPa is nearly 9 million cycles greater.

6. Discussion

There is only slight evidence, as we have indicated, that the fatigue response of the carbon fibre/PEEK is in any way affected by moisture, and certainly, as Fig. 4 suggests, there could be no statistical justification for supposing that there is any effect. We note, however, that the slope of the S–log N curve is lowest for the dried composite and highest for the material conditioned at 65% RH. We have previously found [3] that combinations of heating and wetting are able in epoxy-based composites to bring about relaxation of the residual thermal stresses in cured laminates, with consequent improvement of mechanical properties. In the case of thermoplastic PEEK-based material, it seems possible that relaxation could also occur during heating, either while drying or in the boiling water. Since the effect of moisture on the crystalline polymer is much less significant than on an epoxy resin, mere exposure in a humid atmosphere should perhaps permit little relaxation, by contrast with its beneficial effect in carbon/epoxy laminates, and during boiling the small effect of the water may also be almost completely offset by the stronger effect of temperature.

Since the PEEK composites contain XAS fibres and the epoxy laminates contain HTS fibres, a direct comparison between the results in Fig. 5 and 6 cannot be made without some attempt at normalization. This can be done by plotting fatigue stresses in the S–log N curves as a percentage of the composite tensile strength which effectively removes variations in both fibre volume fraction and fibre strength. This is done in Fig. 8, where all results are plotted for the two types of material, and, given the very slight effects of water, without regard to conditioning treatment. It can readily be seen that the two sets of data are overlapped to a very considerable extent, although it is also clear that the bottom of the scatter band for the carbon/PEEK composites is slightly below that of the carbon/epoxy. Indications are, however, that a carbon/PEEK laminate is no less fatigue resistant than a comparable carbon/epoxy material, notwithstanding the fact that the composites we tested, as we have indicated, were far from optimized in terms of laminate quality.

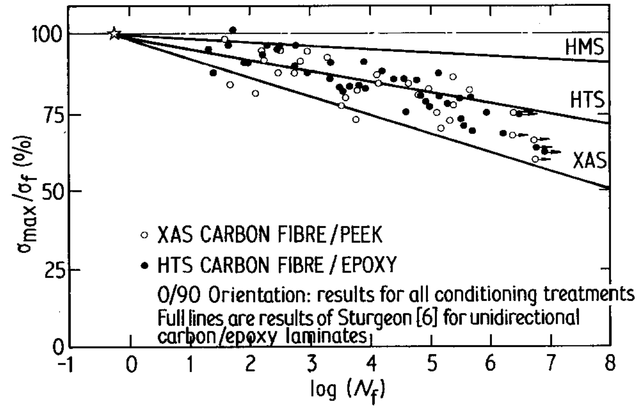

Figure 8 All 0/90 fatigue test results for carbon/PEEK and carbon/epoxy composites normalized to the composite failure stress, σ_f. Also on this graph are lines representing results of Sturgeon [6] for unidirectional carbon/epoxy composites reinforced with HMS, HTS and XAS fibres.

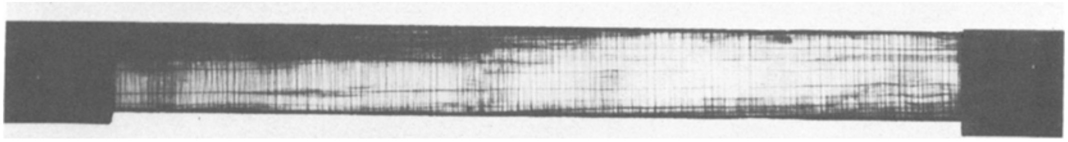

Figure 9 X-radiograph of carbon fibre/PEEK composite sample after 2 million cycles of tensile fatigue at 550 MPa.

Further useful information may be obtained by comparing these two sets of results, on the same normalized basis, with the established behaviour of unidirectional carbon/epoxy laminates reinforced with different varieties of carbon fibre. Such a comparison also presents the possibility of assessing the effect of transverse plies on the composite fatigue resistance. Sturgeon [6] has shown that S–$\log N$ curves for unidirectional carbon/epoxy laminates containing the three common types of carbon fibre, HMS, HTS and XAS, are linear over a wide range of lives, and that the slopes of these curves are characteristic of the fibre type. Normalized curves taken from Sturgeon's paper are also plotted in Fig. 8, and it can be seen that the fatigue resistance of the composites, in terms of the slopes of the S–$\log N$ curves, is greater the stiffer the reinforcing fibres. Clearly, then, the fatigue process in unidirectional composites is determined by the extent to which the compliance of the fibres permits the development of significant levels of strain in the resin matrix. Although our results for the two types of 0/90 composites show slight signs of downward curvature towards the longer lives, it is evident that the points are mostly clustered about the line for unidirectional HTS carbon/epoxy composites. It is logical to conclude, therefore, that the fatigue response of the 0/90 carbon/epoxy laminate is controlled by exactly the same mechanism as that of a unidirectional HTS composite. Furthermore, this mechanism, which must presumably be gradual accumulation of a critical level of damage in the longitudinal plies, is apparently unaffected by the familiar multiple cracking in the transverse plies of which clear evidence is given both by the acoustic emission results of Fig. 3 and by microscopic and X-radiographic studies. This conclusion contradicts the opinion, based on extensive careful studies of fatigued CFRP laminates, of Reifsnider and his co-workers [7, 8] that the transverse ply cracks act as stress concentrators which, in time, accelerate the rate of accumulation of damage in the longitudinal plies of a 0/90 laminate. The slight downward trend of the S–$\log N$ curves in Figs. 5 and 6 does suggest, however, that at lower stresses the rate of accumulation of fibre damage in the longitudinal plies may be accelerated by the developing array of cracks in the transverse plies.

In principle, the normalized S–$\log N$ data for the carbon fibre/PEEK should be distributed about the line for unidirectional XAS composites in Fig. 8. That they fall largely above this line is, by the arguments just put forward, a clear indication that the material is actually *more* fatigue resistant than would have been expected, taking carbon/epoxy performance as a base. Its superiority can be judged from the fact that it performs as though reinforced by fibres one "grade" stiffer than is actually the case. The improvement must therefore be due to the greater toughness, or crack growth resistance, of the thermoplastic matrix which has already been found for carbon fibre/PEEK compared to CFRP [9]. It does not derive from an absence of transverse ply cracking for, as Fig. 9 shows, fatigued carbon/PEEK laminates exhibit a fully developed network of both transverse and longitudinal ply cracks, precisely as do carbon/epoxy composites. The tougher PEEK matrix must therefore act to retard localized build-up of the critical accumulations of 0° fibre breaks that ultimately form the crack nuclei responsible for final failure.

A further useful comparison may be made here with the fatigue behaviour of unidirectional carbon/PEEK material on which a small number of tests were made in the as-received condition. These results are shown in Fig. 10, and to put them into perspective the broken line also shown in this figure refers to a unidirectional carbon/epoxy composite. This is, in fact, the line from Fig. 8, representing Sturgeon's results for HTS carbon/epoxy, again drawn on a normalized basis so as to coincide with the mean dynamic tensile strength of the carbon/PEEK on the extreme left of the graph. The implication is again obvious – the unidirectional XAS carbon/PEEK shows fatigue

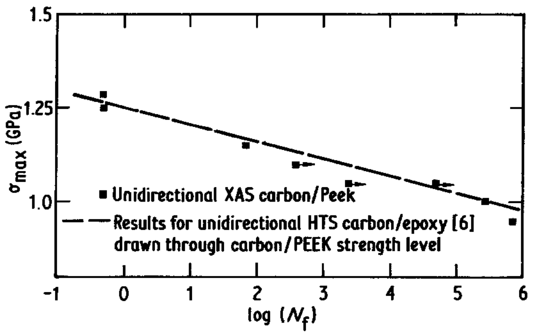

Figure 10 S–log N curve for unidirectional carbon/PEEK composite tested in the as-received state. The broken curve represents the Sturgeon results from Fig. 8 for unidirectional HTS carbon/epoxy composites, normalized to coincide with the carbon/PEEK tensile strength.

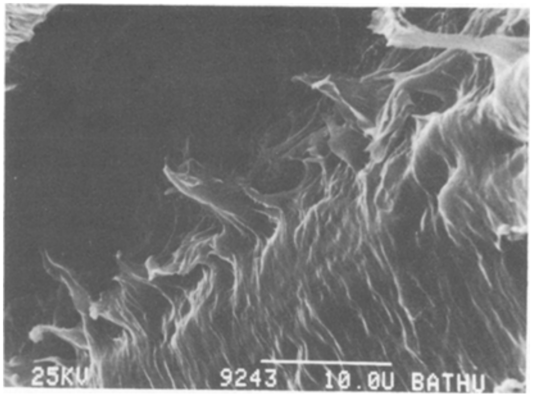

Figure 11 Scanning electron micrograph of fracture surface of 0/90 carbon/PEEK sample fatigue tested at ± 45° to failure, showing extremely tough appearance of the deformed matrix.

resistance comparable with that of the stiffer HTS carbon/epoxy. It is easily ascertained that if the points in Fig. 10 are plotted on the normalized graph in Fig. 8 they fall in the centre of the scatterband for all of the 0/90 results. This corroborates our view that the thermoplastic composite is inherently more fatigue resistant than comparable carbon/epoxy laminates, and that the transverse ply cracks have no effect on the composite behaviour. These features are undoubtedly a reflexion of the higher toughness of the PEEK matrix, which also manifests itself in the higher composite K_{IC}. A similar indication of superior fatigue behaviour of carbon fibre/PEEK over a carbon fibre/epoxy system is reported by Hartness and Kim [10] for 0/90 and quasi-isotropic laminates. Their laminate sheets were quite different from the mouldings prepared from pre-impregnated strips, however, since PEEK film (0.5 μm thick) was stacked in alternate layers with carbon cloth. Consequently, the mechanisms of fracture would be quite different.

In a normal, high quality laminate the transverse ply cracks would be regularly spaced throughout the stressed region, but Fig. 9 also shows that there is a greater incidence of transverse ply cracking and intensified longitudinal splitting in the neighbourhood of regions where buckled fibres occur. There is also some suggestion that delamination damage (the black shaded areas) is associated with this fibre buckling effect. We have not observed this phenomenon in 0/90 epoxy laminates, although we have reason to believe that similar fibre buckling occurs in unidirectional hybrid carbon/glass laminates as a result of differential thermal contraction.

The S–log N curves for laminates tested in the ± 45° orientation again show the superiority of PEEK as a carbon fibre composite matrix in terms of conferring fatigue resistance. Here it is unnecessary to perform any normalization to make the effect clear, for the extent of the superiority is shown directly by the two curves in Fig. 7. For fatigue tests in this orientation, the differences between the fibre types will not affect the results. In our earlier paper, for example, we show that ± 45° S–log N curves for the same epoxy resin reinforced with E-glass and with HTS carbon fibre are to all intents and purposes identical, despite the very large difference in stiffness of the fibres. The tough behaviour of the PEEK matrix is clearly shown in Fig. 11, taken from the fracture surface of a sample tested at ± 45°. Scanning electron micrographs of these fracture surfaces also clearly reveal a much greater degree of bonding of the fibres to the PEEK matrix (Fig. 12a) than is common with carbon/epoxy composites (Fig. 12b). This would of course be highly advantageous under conditions in which stress transfer by shear is a critical factor in determining the behaviour of the composite.

The implication of these results for composite materials development is of some significance. It is normally accepted that attempts to toughen a basic epoxy resin, by the addition of flexibilizing agents for example, seldom result in significant improvements in the toughness of a composite containing that resin as matrix, for the case when crack propagation is occurring perpendicular to the fibres [11]. It is also well known that improv-

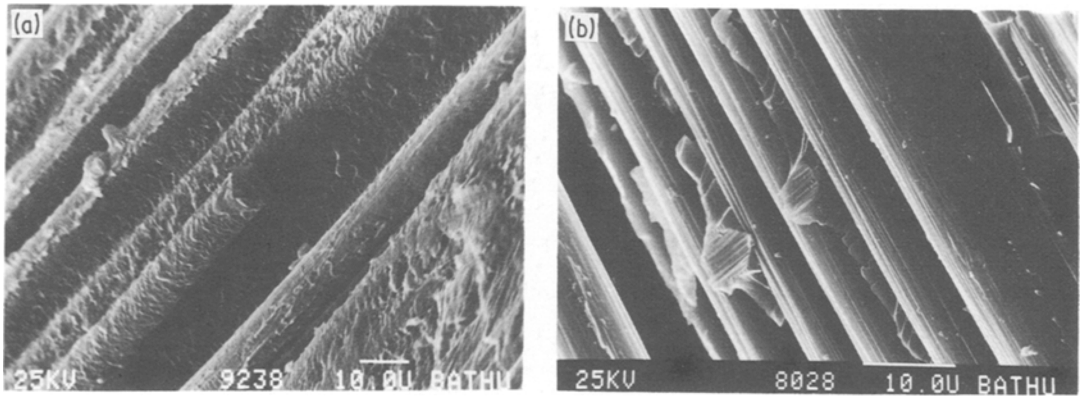

Figure 12 High degree of bonding between XAS fibre and PEEK matrix (a) by comparison with conventional appearance of carbon/epoxy composites (b).

ing the fibre–matrix bond strength in a glass or carbon/epoxy composite results in a *reduction* in composite toughness [12]. Both of these effects, regarded separately, are explained reasonably well in terms of conventional models of fracture toughness of fibre composites [13], but are seldom considered as part of the same problem. In the case of carbon/PEEK composites, we have a matrix of apparently high intrinsic toughness that is also well-bonded to the fibres, as shown by Fig. 12, and the composite is about 40% tougher than a carbon/epoxy laminate of similar construction, despite the fact that fibre/matrix debonding, which normally contributes substantially to the toughness of carbon/epoxy composites, does not occur in the carbon/PEEK. The improved toughness clearly results from the *combination* of tough matrix plus good bonding. Since epoxy resins are all more or less brittle, even when flexibilized, and never show such good bonding as that indicated in Fig. 12, it follows that carbon/epoxy composites are unlikely to be able to compete with carbon/PEEK in providing such an extraordinary combination of strength, toughness and fatigue resistance.

7. Conclusions

1. The tensile fatigue response of 0/90 (cross-plied) carbon fibre reinforced polyether ether ketone tested parallel with a fibre direction (0°) is comparable with that of similar composites based on epoxide resins.

2. In terms of the efficacy of the fibre reinforcement in conferring fatigue resistance, it appears that the tougher PEEK matrix inhibits the development of local fibre damage and fatigue crack growth, permitting a composite with compliant fibres like XAS to perform as well as an epoxy laminate with stiffer HTS fibres. The improved fatigue resistance is clearly related to the better crack resistance, or ductility of the PEEK.

3. The fatigue process in both epoxy and PEEK 0/90 composites is similar, and is the same as that which controls fatigue in unidirectional laminates of comparable combinations. The transverse ply cracks do not appear to affect the fatigue resistance of the longitudinal fibres to any great extent.

4. Tensile fatigue of 0/90 PEEK laminates is almost entirely unaffected by hygrothermal ageing treatments.

5. The fatigue response of cross-plied carbon fibre/PEEK in the ± 45° orientation is much better than that of carbon/epoxy composites because of the inherently superior properties of the thermoplastic matrix.

6. From the results, we infer that more complex laminates of carbon fibre PEEK, such as $(0,\pm 45,90)_s$ combinations could prove to have substantially better fatigue resistance than equivalent carbon/epoxy composites.

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