The Effect of PEEK Fibres and Powder on Joints Made with a High Temperature Adhesive

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High temperature adhesives typically exhibit low levels of peel strength since they tend to be more brittle than typical toughened adhesives used for lower temperature applications. It was found that incorporating thermoplastic fibres or powder into the bondline of a joint made with a high temperature epoxy-based adhesive resulted in significant improvements in peel strength. Poly(ether ether ketone) (PEEK) fibres and powder were incorporated into the adhesive resin and used in aluminium joints. These were tested in peel and single lap shear using a range of fibre lengths, orientations and volume fractions. It was seen that large increases in peel strength could be achieved but that lap shear strength was degraded with most types of modification. However, some modifications resulted in significant increases in peel strength with limited decrease in lap shear strength. These improved properties have been achieved using physical modifications rather than chemical alteration of the resin.

Keywords: High temperature adhesives; aluminium; peel testing; fracture; physical modifications

INTRODUCTION

Structural adhesives have been used in the aerospace industry for half a century and a large body of experience has been built up, covering the formulation, processing and design of adhesive joints, particularly with reference to epoxy adhesives. A typical toughened epoxy adhesive will have a glass transition temperature of about 100°C when dry and a peel strength of 7–10 kN/m as measured in a floating roller test. If higher service temperatures are required there is a range of other

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adhesives available: modified epoxies can have glass transition temperatures around 180°C and bismaleimides and polyimides have greater thermal stabilities with glass transition temperatures beyond 250°C. There are even more exotic adhesives which exist with service temperatures beyond 350°C. Generally, however, it is the case that adhesives with a higher operating temperature require more complex processing and possess worse mechanical properties than those that operate at a lower temperature. In particular, the high temperature thermoset adhesives tend to be brittle with strains to failure of around 2% compared with 6% for an aerospace epoxy. Recent work [1–4] has shown that the peel strength of a commercially-available high temperature epoxy-based adhesive can be improved by the addition of PEEK (poly(ether ether ketone)) fibres. This earlier work used a variety of thermoplastic fibre cloths embedded within the adhesive resin and resulted in significant increases in peel strength, particularly when a carbon fibre-PEEK fibre fabric was used. The peel strengths were typically raised from about 1 kN/m to over 4.5 kN/m, measured at −55°C, 20°C, 130°C and 180°C. The corresponding lap shear strengths were slightly reduced. However, when this type of modification was used in a bonded stiffened laminate tested in four-point bending, there was a small increase in strength but a significant increase in damage tolerance whereby the modified test-pieces continued to carry load after first failure compared with a more catastrophic failure mode in the specimens made with standard adhesive. The work presented below was intended to investigate the strengthening effect of PEEK additions to a high temperature adhesive resin with the aim of optimising and understanding the important mechanisms. PEEK was incorporated into the adhesive resin in the form of continuous fibres (in three orientations: 0°, 90°, and +45/ −45°), as chopped fibres, as powder and as woven cloth (plain weave, 273 g m^{-2}). A range of volume fractions was investigated.

EXPERIMENTAL

Materials

The high temperature adhesive used in this work was FM 350NA, a modified epoxy adhesive containing aluminium filler particles and a glass transition temperature of around 180°C; it is manufactured by

Cytec Engineered Materials Inc. The adhesive is normally available with glass or nylon carrier cloths or as an unsupported film. This work used adhesive with a film weight of 300 grams per square metre. Curing is carried out with a typical epoxy cure cycle (177°C, 1hr, 200 kPa). The adherends used were 2024-T3 aluminium alloy, pre-treated using a chromic-sulphuric etch. The pretreatment consisted of a degreasing step (wipe and wash in butanone) followed by immersion for 25 minutes at 60°C in a solution of sulphuric acid (25g/l) and chromium trioxide, CrO_3 (50g/l). The etched coupons were then washed in running tap water for 20 minutes and dried in warm air for 20 minutes. Bonding took place within four hours. 1.6 mm thick adherends were used for the lap shear joints; the peel joints used 1.6 mm thick aluminium for the thick adherend and 0.5 mm thick flexible adherends.

PEEK fibre (approximately 25 µm diameter fibres) were incorporated into unsupported FM 350NA resin by sandwiching them between two layers of adhesive film. In a few cases, three layers of film were used; these are noted in the Tables. Layup, cutting and weaving were all done by hand. PET (Polyethylene terephthalate) cloth was also used in some tests to examine the use of another thermoplastic modifying fibre.

Procedures

Single lap shear joints were made using 25 mm wide specimens with a 12.5 mm overlap. These were tested at a crosshead speed of 2 mm/min. Floating roller peel specimens were made using 25 mm wide specimens with a 200 mm long bonded area; these were tested in a floating roller peel jig (Fig. 1) at a crosshead speed of 100 mm/min. Testing was carried out at room temperature using an Instron 4507 Universal testing machine. The results from three test specimens were used for each data point.

Small specimens were cut from the larger ones on a Struers Accutom saw to produce 2 mm wide peel specimens. The edges were polished using 4000 grit SiC paper and sputter-coated with Au-Pd to enable them to be observed while testing was carried out on a straining stage fitted inside the work chamber of a scanning electron microscope.

Small resin specimens, approximately 6 mm × 6 mm × 0.2 mm were made for water uptake measurements and immersed in de-ionised water at 35°C and 70°C. Water uptake was measured by weighing and the diffusion coefficients calculated.
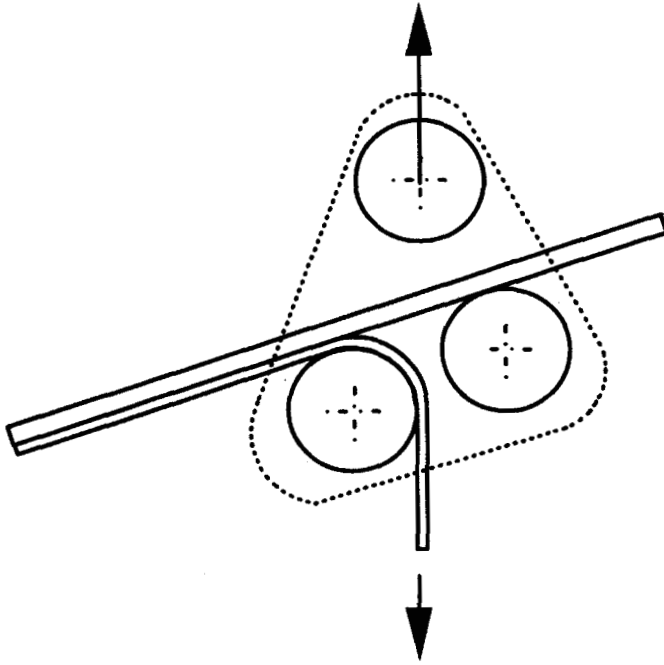
FIGURE 1   Floating roller peel strength test. Flexible adherend thickness ≈ 0.5 mm.

In order to examine the energy required to deform PEEK fibres when they are pulled from the adhesive resin, a zero gauge length specimen was made in which a tow of PEEK fibres was sandwiched between layers of the adhesive resin. After curing, the specimen was notched and cut with a razor blade then each half was bonded to aluminium plates and pulled in a universal testing machine. Before the test there were no free, uncoated PEEK fibres; after the test the length of deformed fibres was measured, allowing the energy per unit length of deformed fibre to be calculated. The extent of fibre pull-out (if any) was also noted.

RESULTS

Results of the mechanical tests are given in Tables I to IV and plotted in Figures 2 to 8. Table I gives the floating roller peel strength and

TABLE I Adhesive Joint Test Results for Modified FM 350NA Chopped Random PEEK fibres

Fibre length (mm)	PEEK Areal density (g m⁻²)	Peel Strength (kN/m)	Lap shear Strength (MPa)	Bondline thickness (peel specimens) (μm)	Notes
0 (CONTROL)		0.75	24.6	110	glass supported adhesive film
0		0.91		65	unsupported film
0		0.55			2 layers of
0		1.50		350	unsupported film 7 layers of
1	50	0.98		180	unsupported film
1	267	5.71			
1	50		22.4		
1	267		17.8		
3	50	1.50		220	
6	25	1.26		200	
6	50	2.44		140	
6	115	3.94		300	
6	141	125		500	
6	51		21.3		
15	50	2.84		200	
15	267	6.70		450	

average of three specimens.

single overlap shear strength values for specimens modified with chopped randomly-oriented PEEK fibres. This table also shows the peel strength of control specimens with single and multiple layers of unsupported adhesive and for single layers of glass-supported adhesive. The glass-supported adhesive is taken to be the control because this is likely to be the most commonly-used commercial form and hence exhibits the performance which any improved form should exceed. Four PEEK fibre lengths, ranging from 1 mm to 15 mm, were used at volume fractions up to about 50% at which point it begins to be practically difficult to incorporate more fibre into the bond using a sandwiching method. Since the PEEK fibres were not evenly distributed throughout the adhesive resin but concentrated towards the centre of the bondline, it is more appropriate to denote the amount of reinforcement by weight per unit area rather than volume fraction. The peel strength and lap shear strength of control specimens, made using commercially-supplied adhesive film with a woven glass carrier cloth, were 0.75 kN/m and 24.6 MPa, respectively.

Failure was cohesive in all cases. Peel strength increases as more fibre is added to the resin and for a given mass of fibre, the longer fibres generally produce a higher peel strength. Significant increases in peel strength were seen, raising the value of 6.7 kN/m in one case. However, the distribution of the chopped fibres was uneven, with a degree of "clumping" which led to oscillating peel values during the peel test; a conservative value for peel strength, at the lower limit of the oscillations, was taken in these cases. The peel results are plotted in Figure 2.

Table II shows the results of tests using continuous PEEK fibres. Most joints were made using the 0° orientation in which the fibres run along the joint in the testing direction. As the amount of PEEK fibre increases, the peel strength increases but the lap shear strength tends to decrease. Table III shows results for cloths woven from tows of continuous fibres, using PEEK and PET (polyethylene terephthalate). The combined results of Tables II and III are plotted in Figure 3. Peel strength is seen to increase as the amount of PEEK fibre is increased and continuous unidirectional fibres produce a greater increase than a woven cloth. When three orientations of continuous fibre are compared, the 0° orientation is stronger than the ±45° orientation which is in turn stronger than the 90° orientation.
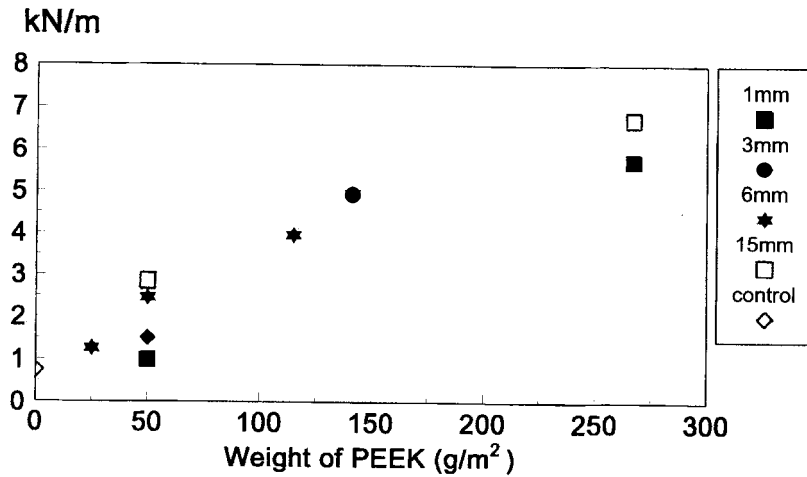
kN/m

FIGURE 2   Peel strength as a function of the amount of PEEK incorporated into the adhesive. Chopped PEEK fibre length 1 mm, 3 mm, 6 mm and 15 mm.

The adhesive was also modified by sandwiching PEEK powder between two films of resin. The results are given in Table IV and plotted in Figure 4. As with the fibre-modified adhesive, the peel strength increases with amount of PEEK but for a given mass of PEEK the measured peel strengths using powder are less than those observed using fibres. Table V shows results from the earlier work [1, 2] for comparison. The peel strengths of all types of modifications are plotted on a single graph in Figure 5. Figure 6 shows the effect of PEEK additions on bondline thickness and Figure 7 shows the effect of bondline thickness on peel strength. Increasing the amount of PEEK in the adhesive causes an increase in bondline thickness from about 100 μm when unsupported adhesive is used to about 350 μm at the highest loadings of PEEK; large amounts of chopped fibres pro-duced higher bondline thicknesses but this was probably due to un-even distributions of the fibres which tended to form "clumps" within the resin. The higher peel strengths were also associated with the thicker bondlines although the thickest bondlines did not result in the highest peel strengths.

The above results show that peel strength can be progressively and consistently increased by including PEEK fibres or powder in the

TABLE II   Adhesive Joint Test Results for Modified FM 350NA Continuous PEEK fibers

No. of Fibre tows per 25 mm	Fibre Orientation	PEEK Areal density (g m^{-2})	Peel Strength (kN/m)	Lap shear Strength (MPa)	Bondline thickness (peel specimens) (μm)	Notes
0 (CONTROL)				24.6		glass carrier cloth
0 (CONTROL)			0.75		140	glass carrier cloth
2	0°	9	0.91		170	
2	0°	9	2.09		170	3 layers of FM350 NA
4	0°	18	2.44		200	
4	0°	18	2.29		160	3 layers of FM350 NA
4	0°	18		23.6		
8	90°	36		22.6		
10	0°	45		24.1		
20	0°	90		18.2		
20	90°	90		19.7		
20	±45°	90		18.7		
6	0°	26	2.17		110	
10	0°	45	3.23		160	
20	0°	90	4.53		300	
20	90°	90	5.32		300	
20	±45°	90	4.93		250	
30	0°	130	5.12		300	
40	0°	180	5.52		340	
30	0°	130	4.45		350	3 layers of FM350 NA
40	0°	180	4.45		350	3 layers of FM350 NA

average of three specimens.

TABLE III Adhesive Joint Test Results for Modified FM 350NA PET and PEEK woven cloth

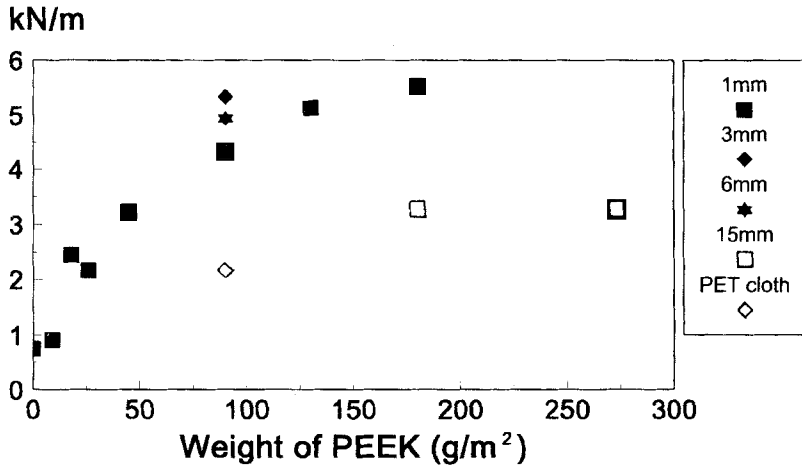| Material	Fibre Orientation	Areal density ($g\,m^{-2}$)	Peel Strength (kN/m)	Lap shear Strength (MPa)	Bondline thickness (peel specimens) (μm)	Notes
PEEK	0/90°	273	3.27		360	
PEEK	0/90°	273	3.47		350	3 layers FM350NA
PEEK	0/90°	180	3.27		200	ref 1, 2
PET	0/90°	92		15.8		
PEEK	0/90°	273		17.7		
PET	0/90°	92	2.17		150	

average of three specimens.

kN/m

FIGURE 3   Peel strength as a function of the amount of PEEK incorporated into the adhesive. Continuous PEEK fibres in three orientations and PEEK cloth.

adhesive bondline. The effect of these modifications on lap shear strength is given in the above Tables and plotted in Figure 8 where lap shear strength is shown as a function of the amount of PEEK in the bondline. The lap shear strength is reduced by the addition of PEEK

TABLE IV   Adhesive Joint Test Results for Modified FM 350NA PEEK powder

PEEK Areal density $(g\,m^{-2})$	Peel Strength (kN/m)	Lap shear Strength (MPa)	Bondline thickness (peel specimens) (μm)	Notes
5	1.30		200	
13	1.69		170	
26	1.97		150	
52	2.44		170	
93	2.84		270	
51		25.8		
160		17.9		
0	0.75			glass carrier cloth(CONTROL)
0		24.6		glass carrier cloth(CONTROL)

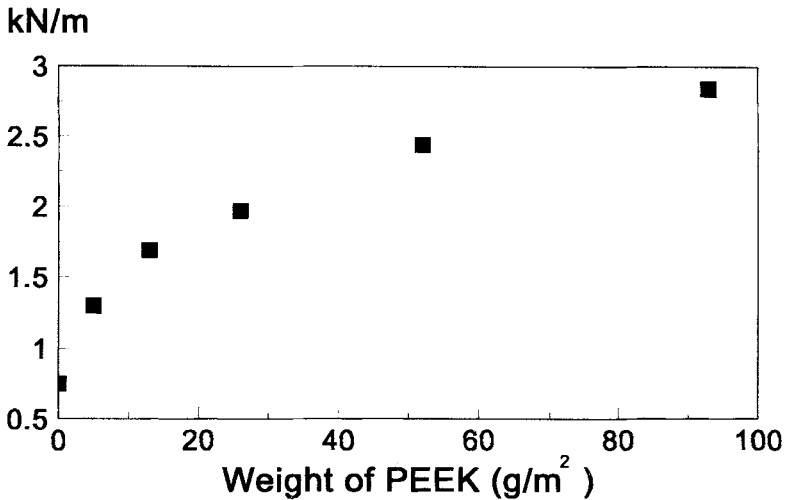average of three specimens.

kN/m

FIGURE 4   Peel strength as a function of the amount of PEEK incorporated into the adhesive. PEEK powder.

TABLE V   Adhesive Joint Test Results for Modified FM 350NA Results from references 1 and 2

Material	Areal density $(g\,m^{-2})$	Peel Strength (kN/m)	Bondline thickness (μm)
Carbon-PEEK fibres 0° u/d	250	5.20	350
glass-PPS cloth 0/90°	350	5.04	420
C-PEEK cloth 0/90°	250	3.31	800
C-PPS cloth 0/90°	250	5.12	800

but for values up to 50 g m^{-2} there is only a small reduction and in one case, when PEEK powder was used, there was a small increase.

The peel fracture process was monitored in the scanning electron microscope (SEM) by sectioning the full-sized peel joints to produce small peel specimens which were 2 mm wide. These were pulled apart in a straining stage situated within the work chamber of the SEM. The propagation of fracture could then be observed at the edges of the specimen and recorded on video. Figure 9 shows the peel failure of an aluminium alloy joint bonded with the unsupported adhesive. The fracture appears to run cleanly along the metal-adhesive interface but
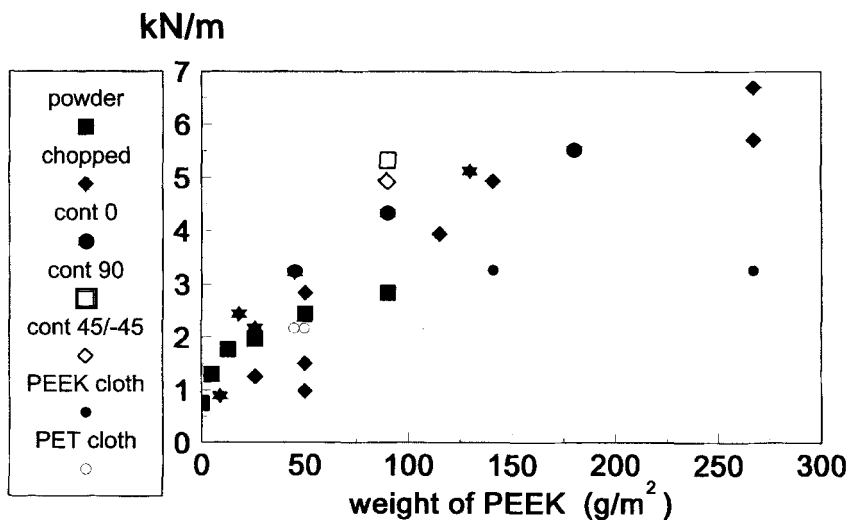
FIGURE 5   Peel strength as a function of the amount of PEEK incorporated into the adhesive. All forms of PEEK.
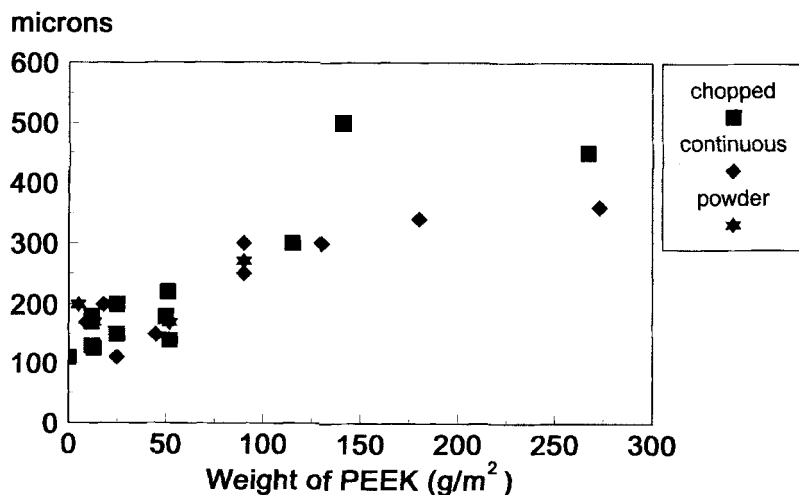

FIGURE 6   Adhesive bondline thickness as a function of PEEK incorporated into the adhesive.

subsequent analysis of the fracture surfaces reveals that failure was cohesive, albeit close to the metal. When the adhesive containing a glass carrier cloth was tested (Fig. 10) the failure ran close to the metal but
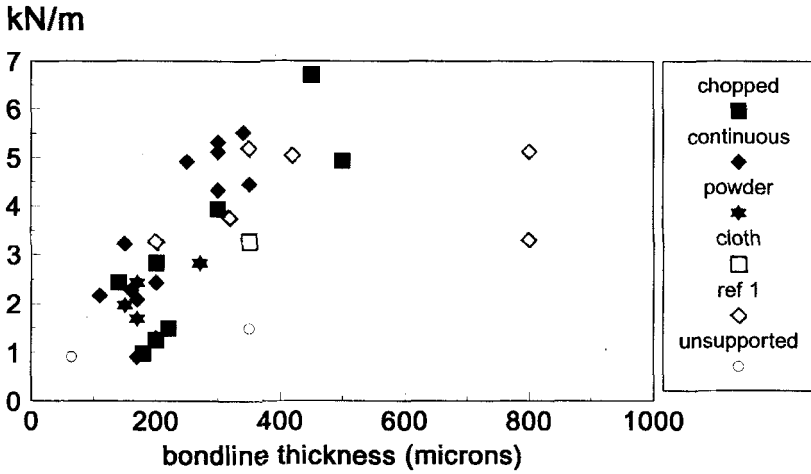
kN/m

FIGURE 7   Peel strength as a function of bondline thickness.
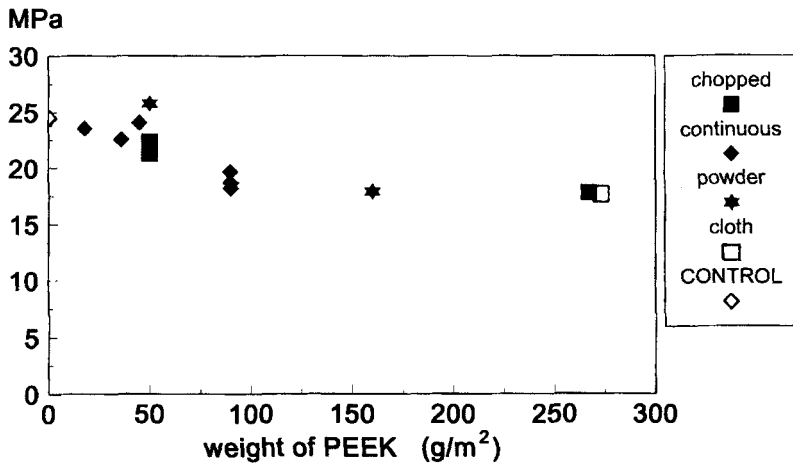
MPa

FIGURE 8   Lap shear strength as a function of the amount of PEEK incorporated into the adhesive.

cracking was also observed around the glass cloth fibres, often taking place ahead of the main crack tip. The fracture surfaces from these samples showed that the fibres were coated with adhesive resin. Figure 11 shows the peel failure of the adhesive containing a knitted

nylon carrier cloth. In this case there is more resin-fibre debonding ahead of the main crack tip and the fracture path is more convoluted than with the unsupported or glass-supported resin. The nylon fibres from these samples were cleanly disbonded from the resin (as determined by SEM observation). Scanning electron micrographs of peel failure in the PEEK-modified specimens are shown in Figures 12 to 16. The fracture of a joint reinforced with unidirectional PEEK fibres running along the length of the joint (0°) is shown in Figure 12. The PEEK loading in this example is 90 g m^{-2} and extensive fibre-resin debonding is visible ahead of the main crack tip. Fibre bridging is evident after complete resin failure. Similar effects are seen in Figure 13 which shows the peel failure of a joint with the same amount of PEEK but where the fibres are oriented across the length of the joint (90°). Figure 14 shows the fracture of a peel joint reinforced with woven PEEK cloth. In the peel failure of a joint reinforced with powder at a loading of 5 g m^{-2} (Fig. 15) the crack appears to run near the metal-adhesive interface but not so close as in the case of the unreinforced specimen. When the amount of powder is increased to 52 g m^{-2} the crack path is more tortuous and runs near the centre of the bondline (Fig. 16).
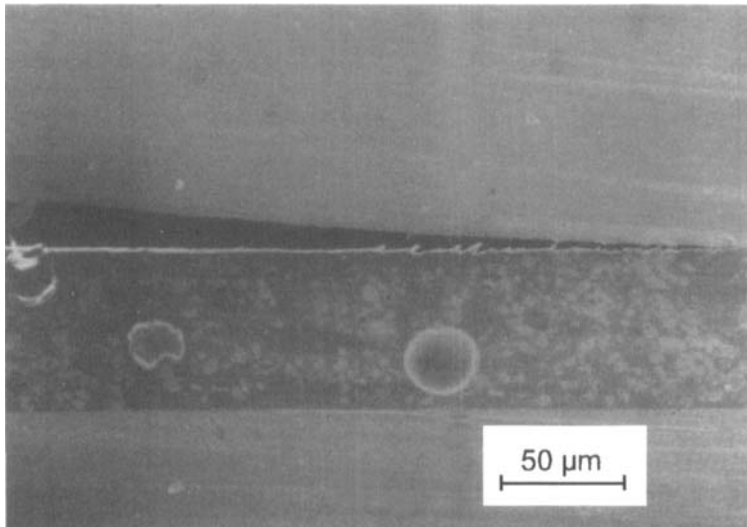

FIGURE 9   Scanning electron micrograph of *in-situ* peel test on small scale specimen. Unsupported adhesive.
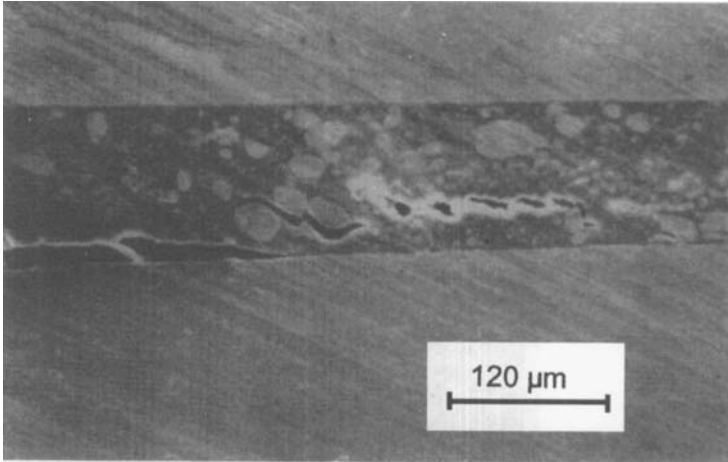
FIGURE 10 Scanning electron micrograph of *in-situ* peel test on small scale specimen. Adhesive resin containing glass carrier cloth.

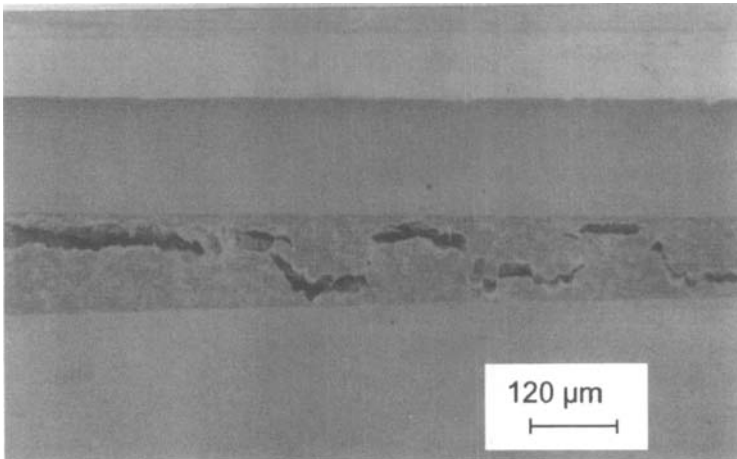FIGURE 11 Scanning electron micrograph of *in-situ* peel test on small scale specimen. Adhesive resin containing nylon carrier cloth.

Peel fracture surfaces were also examined in the scanning electron microscope. The fracture surfaces of the joint made with unsupported adhesive is shown at two magnifications in Figure 17. The fracture surface is relatively smooth, exhibiting limited amounts of

300 μm

FIGURE 12   Scanning electron micrograph of *in-situ* peel test on small scale specimen. Adhesive resin containing PEEK fibres, 90 g m^{-2}, 0° orientation.

FIGURE 13 Scannining electron micrograph of *in-situ* peel test on small scale specimen. Adhesive resin containing PEEK fibres, 90 g m^{-2}, 90° orientation.

FIGURE 14 Scanning electron micrograph of *in-situ* peel test on small scale specimen. Adhesive resin containing PEEK fibres, 273 g m^{-2}, woven cloth.

FIGURE 15   Scanning electron micrograph of *in-situ* peel test on small scale specimen. Adhesive resin containing PEEK powder, 5 g m^{-2}.
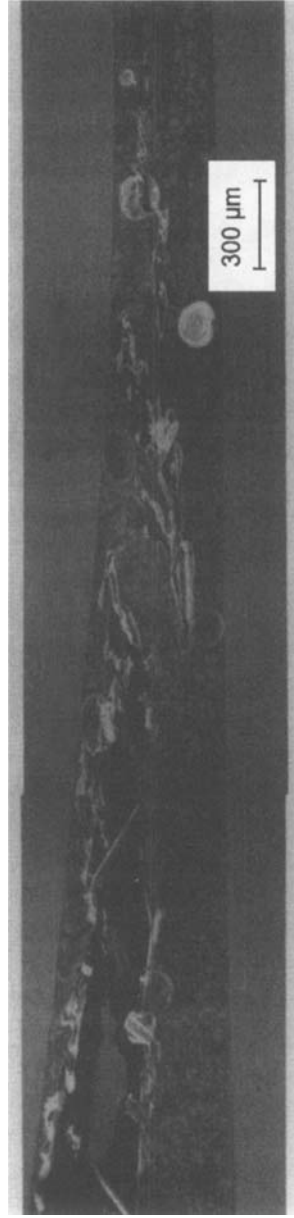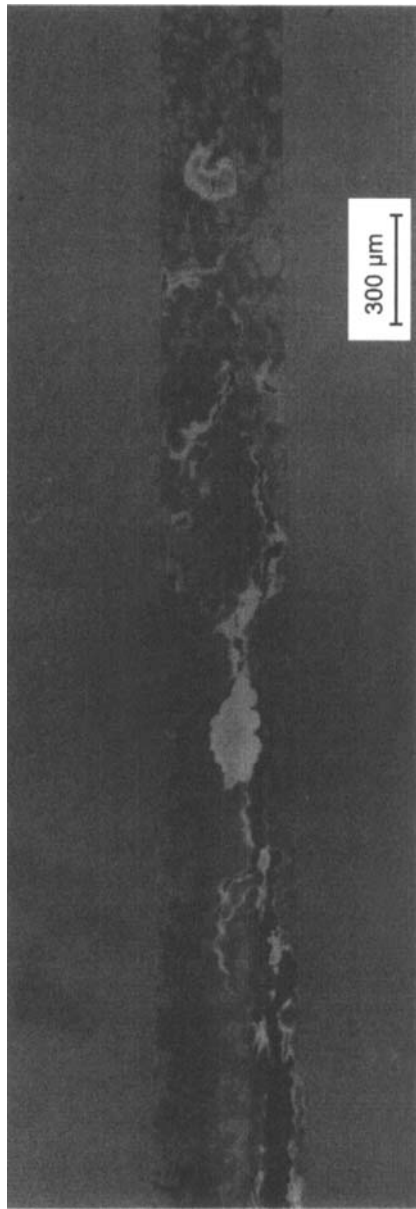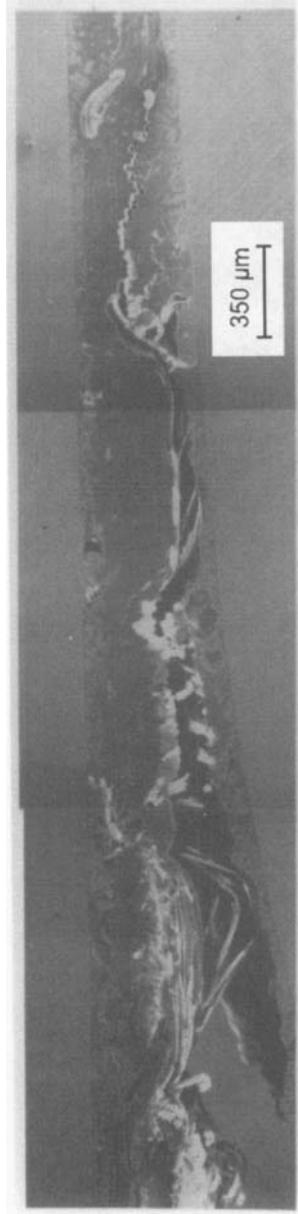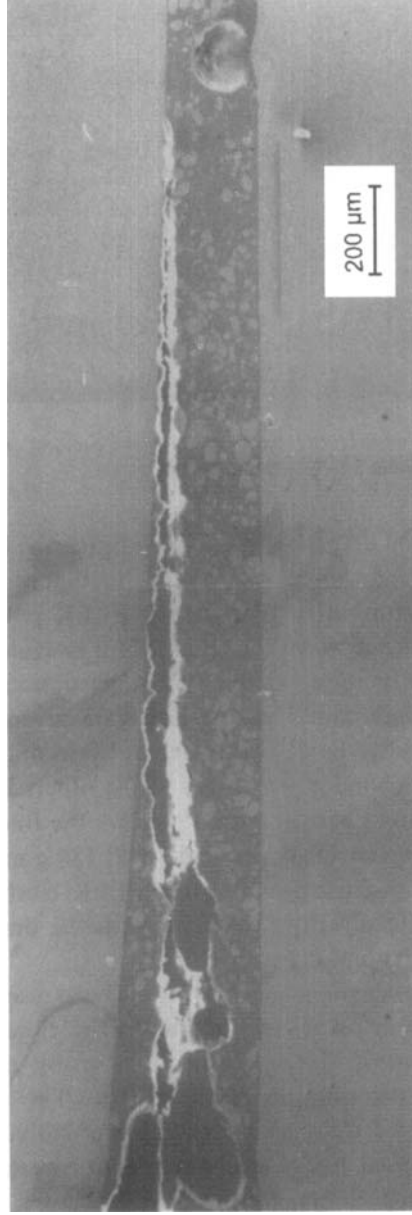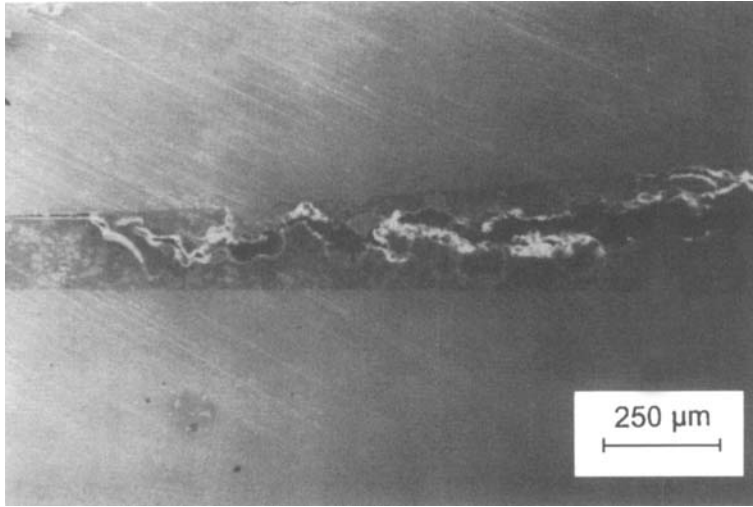
FIGURE 16   Scanning electron micrograph of *in-situ* peel test on small scale specimen. Adhesive resin containing PEEK powder, 52 g m^{-2}.

plastic deformation and roughness. In contrast, the fracture surface of a powder-reinforced sample (52 g m^{-2}) in Figure 18 is rough, with extensive resin deformation. Particles of PEEK powder are also visible and at higher magnification (Fig. 18b) it is evident that there has been surface deformation on the PEEK particles and resin-particle debonding. The fibre-reinforced specimens are covered in loose PEEK fibres which appear to have cleanly-debonded from the adhesive resin. Some fibres are debonded but intact whilst others have been broken and display distorted ends. Figure 19 shows the fracture surface of a PEEK fibre reinforced specimen made with 180 g m^{-2} of continuous fibre. When the specimens made using PEEK cloth were tested, the cloth debonded cleanly from the resin with the limited deformation and failure of individual fibres (Fig. 20).

The zero gauge length specimen (Fig. 21) was used to estimate the energy needed to deform and fracture PEEK fibres. Since no fibre pull-out was observed, the length of fibres visible after failure arises from the plastic deformation of the PEEK. The total energy was calculated to be 7×10^{-2} J per metre length of individual PEEK fibre. This quantity is used below (see discussion) to estimate the energy contributed to the peeling failure by fibre bridging.
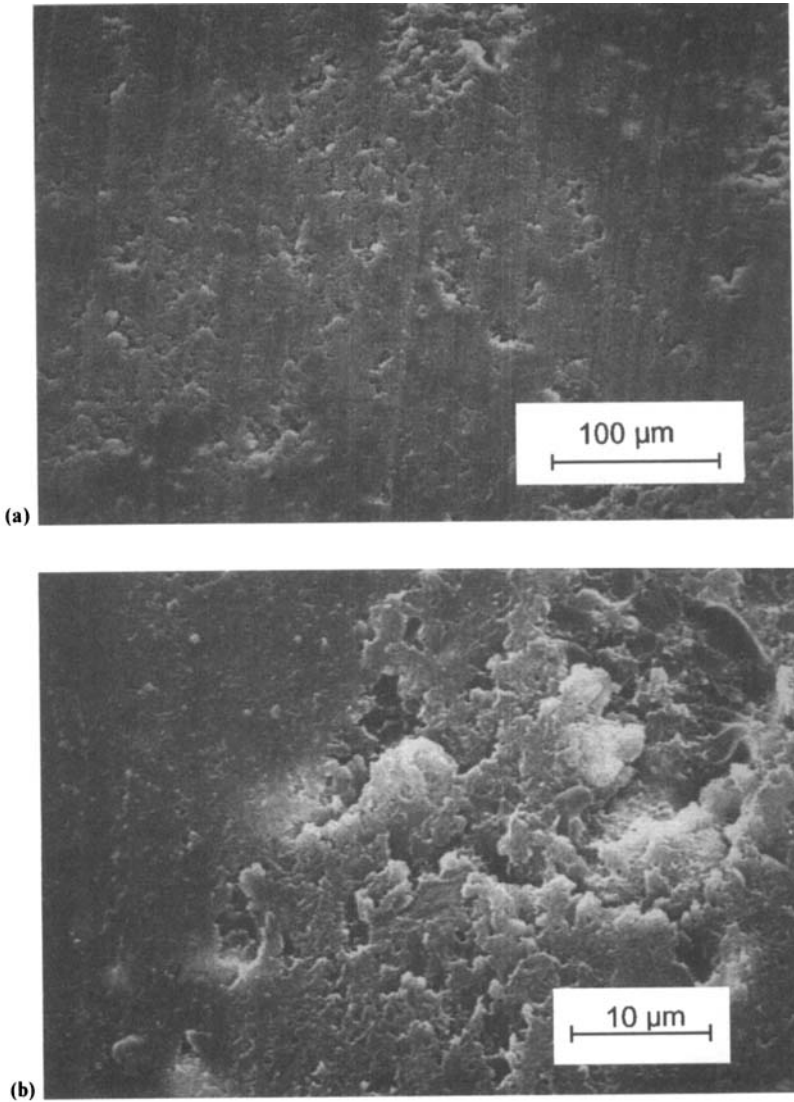
FIGURE 17   Scanning electron micrograph of a fracture surface from a peel specimen. Unsupported adhesive resin. a. Low magnification b. High magnification.

The adhesive bonding of aerospace structures requires not only high initial joint strength but also the ability to retain that strength over long periods of time. The incorporation of an extra physical

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(a)

(b)

FIGURE 18   Scanning electron micrograph of a fracture surface from a peel specimen. Adhesive resin containing PEEK powder. a. Low magnification showing debonded PEEK particles in the adhesive resin. b. High magnification showing resin-particle debond and plastic deformation on the surface of the PEEK particles.
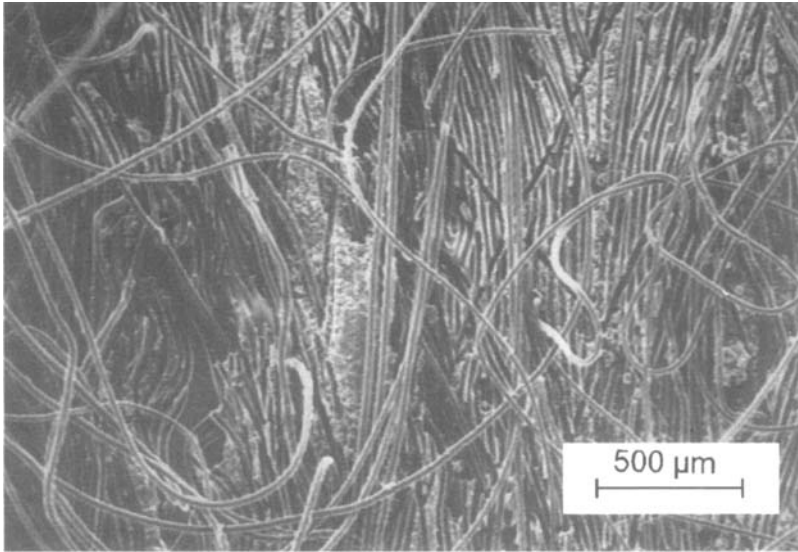
FIGURE 19   Scanning electron micrograph of a fracture surface from a peel specimen. Adhesive resin containing continuous PEEK fibres.
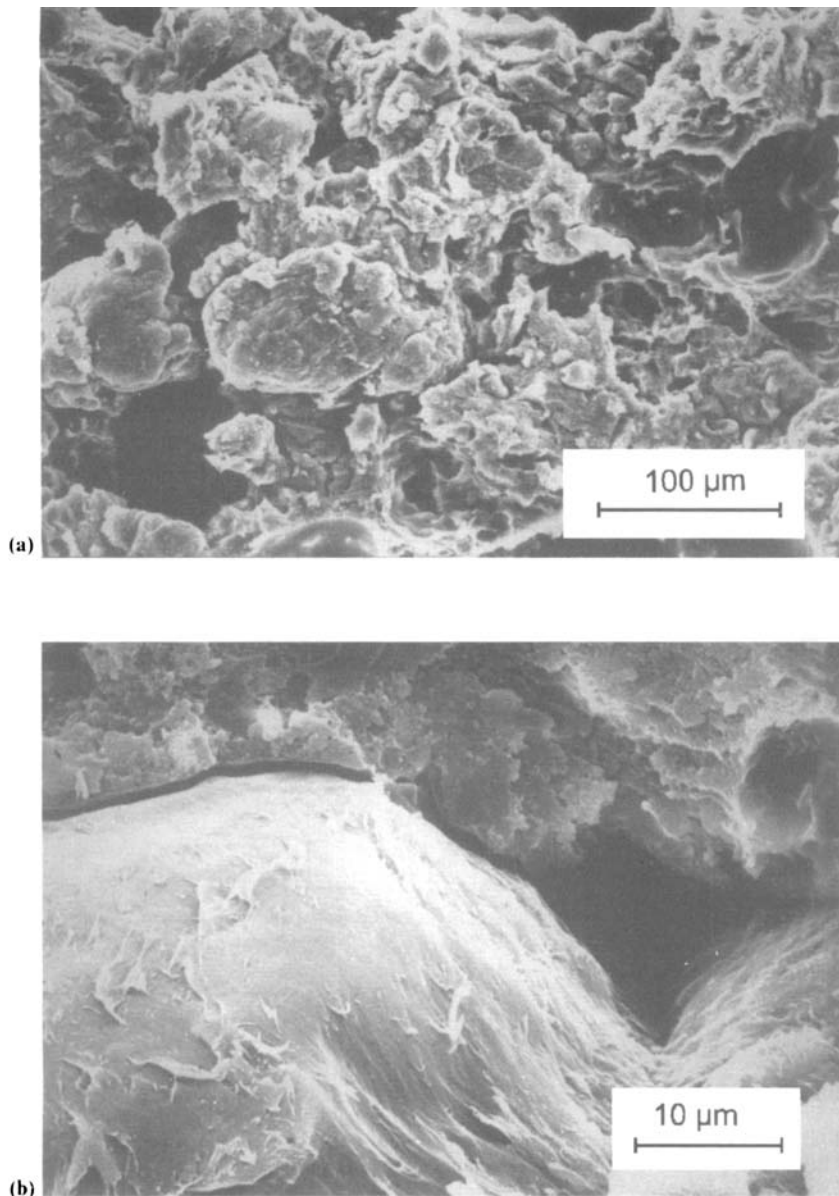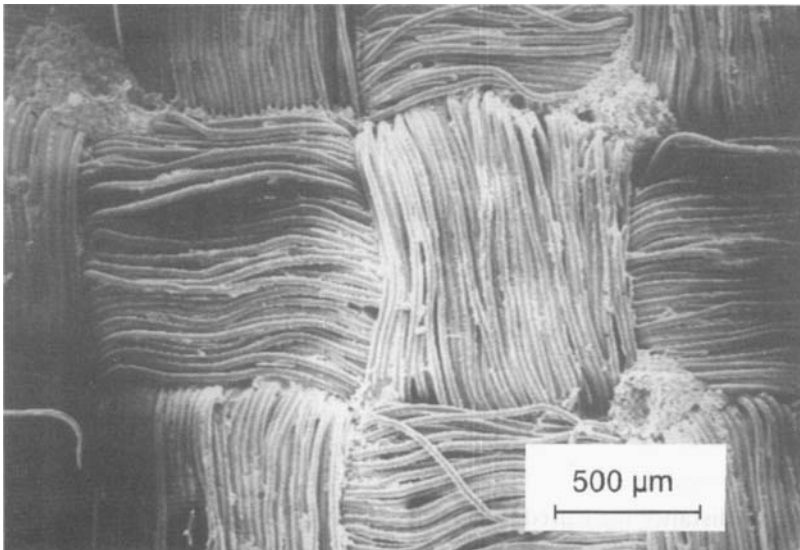

FIGURE 20   Scanning electron micrograph of a fracture surface from a peel specimen. Adhesive resin containing PEEK cloth.

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RESIN
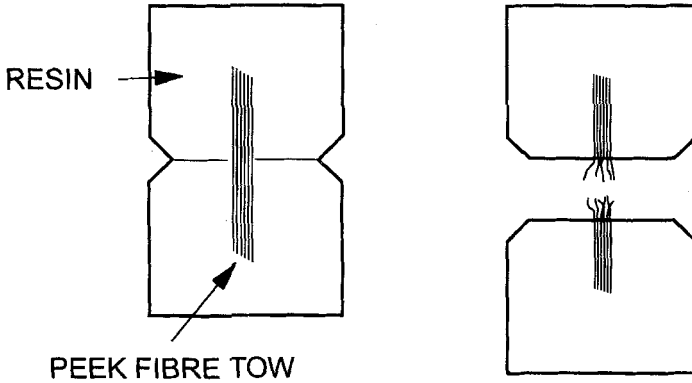
PEEK FIBRE TOW

FIGURE 21   The zero gauge length specimen. The PEEK fibre tow is embedded in the adhesive resin.

phase into the bondline may offer the opportunity for enhanced water diffusion along the extra interfaces, leading to bond deterioration and this might be expected to be worse when continuous fibres are introduced into the adhesive resin due to the introduction of continuous diffusion pathways. In order to test this, water diffusion tests were carried out by soaking plaques of cured adhesive in de-ionised water. The water uptake was measured gravimetrically and water diffusion coefficients were measured. Specimens of neat FM 350NA resin and specimens with PEEK fibres and carbon fibres incorporated into the adhesive were tested.

Diffusion coefficients were calculated by assuming Fickian diffusion, *i.e.*:

$$F = -D \, dC/dx$$

where

F = rate of transfer per unit area of section
C = concentration
x = distance measured normal to section
D = diffusion coefficient

Several analyses of the diffusion equation have been made [5, 6]. For the case of a thin sheet, as used in these experiments, it is possible

to assume that the water diffusion takes place through the plane faces of the specimen and that:

$$\frac{M_t}{M_I} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \frac{-D(2n+1)^2 \pi^2 t}{4l^2}$$

where

M_t = total amount of water which has entered the sheet at time t
M_I = amount of water after infinite time
l = half sheet thickness

For small times, this simplifies to

$$\frac{M_t}{M_I} = 2\left(\frac{Dt}{l^2}\right)^{1/2} \pi^{-1/2}$$

The diffusion coefficient, D, can be derived from a graph of M_t/M_I where the gradient is $(2/l)(D/\pi)^{1/2}$.

The adhesive specimens were prepared by curing the resin under pressure between films of release paper. After curing, the adhesive was approximately 600 μm thick and was cut into sheets approximately 6 mm square. The edges and faces were polished lightly with SiC paper to remove cutting damage and any residual release agent. They were then dried in an oven at 70°C and their weight loss was monitored until a stable value was achieved; this was taken to be the dry weight of the specimens. The measurements were made using a micro-balance with an error of less than 0.02%. The specimens were then immersed in de-ionised water at 35°C and 70°C, stable to $\pm$ 0.5 deg C. Their weight increase was then measured for periods up to 9000 hours and used to calculate the diffusion coefficients which are given in Table VI

TABLE VI   Water Diffusion Coefficients, D, (m^{-2} s^{-1})

Adhesive	carrier cloth/fibre	D at 35°C	D at 70°C	weight gain, % 35°C	70°C
FM 350NA	glass	4.3×10^{-13}	7.3×10^{-13}	4.36	4.46
FM 350NA	nylon	4.8×10^{-13}	4.4×10^{-13}	3.39	3.88
FM 350NA	C-PEEK	2.0×10^{-13}	8.0×10^{-13}	2.41	2.44

for specimens which contain a glass carrier cloth and a nylon carrier
cloth (both commercially-available products) and a specimen contain-
ing a mixture of PEEK fibres and carbon fibres at a volume loading of
approximately 40%. It can be seen that there is little difference in the
water diffusion coefficients between the adhesive containing PEEK
fibres and the adhesive containing glass or nylon fibres. When the
volume fraction of adhesive is taken into account there is no signifi-
cant difference in the water uptake.

DISCUSSION

The thermal stability of high temperature thermoset adhesives is invari-
ably gained at the expense of peel strength and usually lap shear
strength. It is common for the aerospace industry to use adhesives in
the form of one-part films; this form assists application, ensures even
coverage over large areas and enables large areas of adhesive to be
easily applied. Film adhesives often contain a carrier cloth which can
offer some control over bondline thickness and flow during cure as well
as improving the handling properties of the uncured adhesive. Typi-
cally, film adhesives contain a woven or knitted cloth and the adhesive
used in this work is commercially available with a woven glass cloth, a
knitted nylon cloth or in an unsupported version. Earlier *in-situ* SEM
straining studies [1–3] had demonstrated that the fracture process was
altered according to which type of carrier cloth was present and
prompted an investigation into the effect of separate physical phases
within the adhesive layer. It has been demonstrated that incorporating
PEEK into a high-temperature epoxy adhesive produces a significant
increase in peel strength. PEEK powder, fibre and cloth have been
sandwiched between two layers of unsupported adhesive resin and
cured, giving a range of PEEK weights up to about 275 g m^{-2}. Increas-
ing the PEEK content beyond this value presented practical difficulties
which could probably be overcome by an automated method in which
the resin and PEEK were combined during the film manufacturing
process. Values for weight per unit area have been given rather than
volume fractions since the PEEK was concentrated towards the centre
of the bondline; had the PEEK fibre reinforcement been evenly distrib-
uted a value of 50 g m^{-2} would have corresponded to a volume

fraction of about 20%. In general, the more PEEK fibre or powder was added, the greater was the peel strength but the increases appeared to be diminishing; no limit was found but it is certain that a maximum would have been observed it if were possible to increase the loading of PEEK in the resin. Peel strengths were increased from a value of about 0.75 kN/m for the commercially-available systems to over 2.75 kN/m when powder modifications were used; when fibres were added to the resin the peel strength was raised further, to values as high as 6.7 kN/m.

The general effect on lap shear strength was the opposite of that seen in peel testing with the strength diminishing with increasing amounts of PEEK. However, the reduction was small at PEEK values up to about 50 g m^{-2} with no reduction (in fact, a small increase) seen when powder reinforcement was used at this level. At PEEK levels above about 100 g m^{-2}, the lap shear strength was constant at about 18 MPa, reduced from the control value of 25 MPa, measured on joints made with the standard glass-supported adhesive.

The effect of orientation of continuous fibres was examined at one fibre weight. There was a small difference in peel strength in the order $90° > \pm 45° > 0°$ and there is some evidence to suggest that the longer fibres produce higher peel strengths and, for a given weight of PEEK, fibres were more effective than powder or cloth.

Three mechanisms are offered to explain the increase in peel strength seen in this work: (1) Increase in bondline thickness, leading to the availability of a larger plastic zone ahead of the advancing crack tip; (2) Microstructural effects within the bondline, ahead of and near the crack tip, allowing crack branching and increasing the distributed damage by resin-fibre debonding prior to failure; (3) Fibre bridging, whereby PEEK fibres remain attached to each side of the adherend after the joint has fractured; the peel strength would be apparently increased by the energy needed to deform and break the fibres. If the PEEK fibres were to pull out of the resin there would be a further energy-absorbing mechanism as noted for some fibre-reinforced composite materials [7].

The bondline thickness of peel specimens is given in Tables I to IV and plotted in Figure 7. From these and earlier [1,2] results it is seen that there is a general but not consistent correlation of bondline thickness with measured peel strength. A comparison of unsupported adhesive and PEEK-reinforced adhesive with similar bondline thick-

nesses should clarify the effect of bondline thickness but practical
difficulties were encountered when the manufacture of thick bondlines
using unsupported adhesive resin was attempted. However, single
layers of unsupported resin produced peel strengths of 0.9 kN/m with
a bondline thickness of 65 μm and the peel strength of double layers
was less (0.55 kN/m). A bondline thickness of 350 μm, achieved by
using seven layers of unsupported film, yielded an average peel
strength of 1.5 kN/m from three specimens. This is almost twice the
strength of the control specimens but significantly less than the
strength of PEEK-reinforced adhesives with similar thicknesses. Thus,
it is fair to say that whilst an increase in bondline thickness does result
in an increase in peel strength for this adhesive, the incorporation of
PEEK produces an apparent further increase.

Microstructural effects have been observed in the earlier work.
Scanning electron micrographs of the peel fracture and the fracture
surfaces show that when PEEK fibres or powder are included within
the bondline there is an increase in the amount of cracking ahead of the
main crack tip and that the crack path is complex, with crack branch-
ing and diversion. This is presumably due to resin-PEEK debonding
occurring ahead of the main crack, altering the stress distribution and
absorbing energy by the creation of new surfaces. These effects are less
obvious in the glass-supported adhesive where the glass is well-bonded
to the resin; in the nylon-supported adhesive there is more debonding
but the volume fraction of nylon is low. For strengthening to occur it is
evidently necessary to have a high volume fraction of PEEK which
allows a large area of resin-PEEK debonding to occur and which forces
the crack to propagate along a more tortuous path. The PEEK fibres
show no evidence of adhering resin after fracture and no evidence of
plastic deformation on their surfaces although the fibre ends are often
deformed. The PEEK powder particles, however, do exhibit signs of
plasticity on their surfaces but no large scale deformation or tearing.
This suggests that debonding occurs before the crack has opened, as
seen in the *in-situ* micrographs, and that fibre deformation has taken
place at high crack opening displacements. It may be that the
strengthening seen when PEEK powder and cloth are used is due to
these microstructural effects of crack branching/diversion and resin-
PEEK debonding because in these cases there is little or no opportun-
ity for fibre bridging to occur. These mechanisms are often cited as

strengthening mechanisms in composite materials. It is worth noting that the micrographs of the *in-situ* joint testing can only observe the edge of the joint and that the fracture propagation within the joint may be taking a different path. For example, the unsupported adhesive appears to fail interfacially in the SEM micrographs but the fracture surface images clearly show cohesive failure (but close to the interface). However, the general trends indicated by the SEM *in-situ* observations are in agreement with the conclusions gained from the observations of the fracture surface after testing and it is probably fair to use the *in-situ* SEM technique to infer the mechanisms of failure.

It may be that the powder results follow the same distribution of strengths as the cloth results. This could be explained if the extra strength exhibited by the fibre-reinforced specimens were due to fibre bridging effects which were essentially absent from the powder and cloth samples. Fibre bridging is a likely toughening mechanism in these specimens. When a double cantilever beam test was used [4] to measure G_{IC} of bonded composite specimens in which a carbon fibre/PEEK fibre cloth was used to reinforce FM 350NA the strain energy release rate was raised from 302 Jm^{-2} (for the standard glass-supported adhesive at 20°C) to 2708 Jm^{-2} for the C-PEEK modified adhesive. In these tests there was ample visible evidence of fibre bridging but this effect is likely to be somewhat reduced in a floating-roller peel test compared with a double cantilever beam test since the crack opening displacement is much greater in the former, thus reducing the area over which the fibre bridging can be effective. Figure 2 also shows that for a given amount of chopped PEEK the longer fibres produce the higher peel strength. There is no evidence that fibre pull-out is a strengthening mechanism in these specimens: separate tests conducted on zero gauge-length specimens of PEEK fibre tows embedded in the adhesive resin did not result in the fibres being pulled out of the resin but caused the PEEK fibres to neck and break. Thus, the energy-absorbing mechanism in fibre bridging is due to the deformation and fracture of PEEK fibres whose ends are buried in the resin on different sides of the crack. Micrographs of the fracture surface on fibre-reinforced specimens clearly show troughs where the fibres have been debonded (probably ahead of the main crack) and deformed fibre ends where the fibres have necked and broken. An estimate of the energy associated with fibre bridging, G_F, can be made by counting

the number of deformed fibres and their length on the fracture surface
of a peeled fibre-reinforced specimen. This was done by cutting the
peeled fracture surface into 2 mm wide strips and counting the fibres
which protruded from the resin surface; in this way, those fibres which
did not play a role in the fibre bridging (*i.e.*, those which were com-
pletely disbonded) would be lost and only those fibres which still had
one end embedded in the adhesive would remain. The total length of
deformed fibre per unit area, L, remaining on a peel fracture surface
was measured to be 2.11×10^3 m/m^2 for a continuous fibre reinforced
specimen with 45 g m^{-2} of PEEK and a peel strength of 3.23 kN/m. A
value for G_F can be calculated by measuring the energy needed to
deform and break PEEK fibres. This was done for a zero gauge-length
specimen consisting of a PEEK fibre tow embedded in the adhesive
resin. The energy, E_F, was measured to be 7×10^{-2} J per metre length
of deformed fibre remaining after fracture. The energy per unit area of
peel fracture surface due to fibre deformation, G_F, is therefore

$$G_F = L \ E_F \sim 150 \ \text{Jm}^{-2}$$

This figure, approximately half the fracture energy of the resin, shows
that fibre bridging is a significant toughening mechanism but it is
clear that there is a further major contribution to the improved peel
strength and it is assumed that this is due to both the microstructural
toughening effects and the deformation of the adherends.

Other workers have incorporated thermoplastics or rubbers into
brittle adhesive resins [8–11] but this has usually been done at the
resin blending stage so that the toughening phase is developed during
processing and is seen as a dispersion on the micrometre scale or
below. The larger-scale physical modifications described in this work
do not require alterations to the resin formulation and may be appli-
cable to a wide range of resin types. Initial work suggests that PEEK
may not be suitable for toughening bismaleimide resins but that it
shows promise for modifying cyanate esters. Other thermoplastic
fibres and powders might also be considered since there are several
alternatives which have economic advantages compared with PEEK.
This type of toughening, by incorporating a thermoplastic powder
phase into a more brittle resin, is used commercially in at least one
structural adhesive based on a phenolic resin, Redux 775 [12] but in

that case there is a degree of intermingling of the two phases during care. It used to be the case that the mixing of the two phases, resin and powder, was undertaken immediately prior to bonding but that adhesive is now made on an automated production line and demonstrates that the technology to incorporate powders into film adhesives is already mature. Whilst promising results have been shown in this work, there remains a need to examine the effect of these modifications on other mechanical and physical properties before the material could be used for safety-critical applications. Initial results from water diffusion measurements show that the water uptake of resin containing PEEK fibres is no worse than in resin containing glass or nylon fibres (which are commercially-available systems). The calculations of the diffusion coefficients assumed isotropic Fickian diffusion. In the case of fibre-reinforced samples this may not be the case because there may be enhanced diffusion along the fibre-resin boundaries; however, the initial results here are encuoraging in that there is no increase in water uptake which would be expected if enhanced diffusion were taking place. However, if the effect of moisture on PEEK-reinforced adhesive is to be demonstrated it will be necessary to carry out strength tests on water-exposed adhesive joints; these tests are currently underway.

If fibre-bridging is a major toughening mechanism it could be exploited in situations where energy absorption is needed over the maximum range of crack opening displacements such as the crashworthiness of structures bonded with brittle high-temperature adhesive resins.

Earlier results [3] tested similarly-modified joints and found that an increased peel strength was seen at temperature ranging from $-55°C$ to $180°C$. It is not unreasonable to expect, therefore, that the effects observed in this work would also be seen over a wide temperature range.

CONCLUSIONS

Physical modifications have been made to a commercial high-temperature epoxy-based adhesive, FM 350NA. Fibres and powder, mostly of PEEK, have been incorporated into the bondline with the result that peel strengths have been significantly raised. These modifications

produced a drop in lap shear strength at higher volume fractions. In general, PEEK fibres are more effective in raising the peel strength than powder or cloth; longer fibres are more effective than short fibres.

There appears to be an orientation effect when continuous PEEK fibres are used: in peel, the 90° orientation is stronger than the $\pm 45°$ orientation which is stronger than the 0° orientation.

The increase in peel strength may be due to a combination of bond-line thickening, fibre bridging and microstructural effects. Further work is needed to clarify this.

These effects are likely to occur if other thermoplastic fibres such as PET are used.

The incorporation of PEEK fibres into the resin does not affect water uptake at 35°C and 70°C when compared with the commercially-available adhesive resin which incorporates glass or nylon fibres. Further work is needed to determine the effect of water exposure on joint strength when these PEEK-modified adhesives are used.

Acknowledgements

References

[1] Dixon, D. G., unpublished results.
[2] Dixon, D. G., Unger, W., Naylor, M., Dublineau, P. and Figgures, C. C., to be presented at the Thirty-fifth Annual Conference on Adhesion and Adhesives, 9 April 1997, Oxford, UK.
[3] *Adhesive Bonding for High Temperature Applications (ABHTA)*, SRC Final Report JS 13504, May 1996. Brite-EuRam proposal BE-5104, Contract No. BRE2- 0149.
[4] Lemettais, T., ABHTA Progress Report DCR/M-61387-11/95 (Aerospatiale).
[5] Carslaw, H. S. and Jaeger, J. C., *Condition of Heat in Polymers* (Clarendon Press, Oxford, 1959).
[6] Crank, J., *Mathematics of Diffusion* (Clarendon Press, Oxford, 1975).
[7] Harris, B., Morley, J. and Phillips, D. C., *J. Mater. Sci.* **10**, 2050–2061 (1975).
[8] Kunz-Douglass, S., Beaumont, P. W. R. and Ashby, M. F., *J. Mater. Sci.* **15**, 1109–1123 (1980).
[9] Meyer, G. W., Pak, S. L., Lee, Y. J. and McGrath, J. E., *Polymer* **36**, 2303–2307 (1995)
[10] Bauer, R. S., Stenzenberger, H. D. and Römer, W., Proc 34th Int. SAMPE Symposium, May 8–11, 1989, pp. 899–909.
[11] Pascault, J.-P., Galy, J. and Méchin, F., "Additives and Modifiers for Cyanate Ester Resins," *Chemistry and Technology of Cyanate Ester Resins*, Hamerton, I., Ed. (Blackie, London, 1994).
[12] Ciba Composites, Duxford Cambridge CB2 4QD, UK.