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Physical modifications for improved peel strength in a high-temperature epoxy adhesive*

D.G. Dixon[a], W. Unger[b], M. Naylor[c], P. Dublineau[d], C.C. Figgures[a]

[a] *British Aerospace (Operations) Ltd, Sowerby Research Centre, FPC 267, PO Box 5, Filton, Bristol BS12 7QW, UK*
[b] *Daimler Benz Aerospace, LME 29, D-81663 München, Germany*
[c] *British Aerospace Airbus Limited, New Filton House, Bristol, UK*
[d] *Aerospatiale, Centre Commun de Recherches Louis Blériot, 4 rue du Val d'Or, 92512 Suresnes, France*

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Abstract

The thermal performance of high-temperature thermoset adhesives is invariably gained at the expense of mechanical properties, particularly peel strength. A microscopic study of failure propagation in adhesive joints revealed that fibres within the bondline can affect the fracture path during peel failure in a commercially available modified epoxy adhesive, developed for high-temperature use. This adhesive has been further modified by the incorporation of polymer fibres and the resultant adhesive joints have shown significant increases in peel strength combined with both increases and decreases in lap-shear strength, depending on the fibre orientation. These effects were measured from −55°C to +180°C. Improvements were also seen when larger joints, more typical of aerospace structures, were tested. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Adhesive bonding has been successfully used for half a century by aircraft manufacturers to bond wood, metal and, latterly, composites. Epoxy adhesives are often used since they are well-developed materials with convenient processing conditions and good mechanical properties. Most aerospace structural adhesives for civil use are not expected to operate above about 100°C, so their thermal performances and curing methods reflect this. However, if adhesives are needed to operate at high temperatures, for example at 130°C and above, then other materials must be considered. Epoxy adhesives can be modified chemically to increase their glass transition temperature and thermal stability, and a number of formulations are currently available as commercial systems. Other types of polymers that are used as high-temperature adhesives include bismaleimides [1,2] and cyanate esters [3–5], which are generally capable of higher-temperature performance than modified epoxies. Further classes of adhesives [6–8] claim even higher operating temperatures but increased thermal performance requires high-temperature processing conditions, which often have economic or practical disadvantages compared with epoxies.

This work considers the use of FM 350 NA, a modified epoxy aluminium-filled adhesive manufactured by Cytec Engineered Materials Inc., for adhesive bonding over a range of temperatures. We describe the effect of physical modifications made to the adhesive by incorporating fibres into the bondline. Film adhesives are widely used in aerospace manufacture and these products are often supplied with woven or knitted carrier cloths embedded into the adhesive resin. These cloths assist in handling of the adhesive film during manufacture and may modify the resin flow during cure, but little attention has been given to their role in joint fracture. When the peel failure of adhesive joints was observed in the scanning electron microscope it was noted that Nylon carrier cloths produced markedly different fracture modes from glass carrier cloths. Both types of cloth are supplied commercially and can result in slightly different peel strengths [9].

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Table 1
Dimensions and materials used for metal and composite adhesive joint specimens

Adherend	Test method	Thickness (mm)	Width (mm)	Overlap (mm)
Metal (*aluminium*)				
2024-T3 Alclad	Single-lap shear	1.6	25	12.5
	Peel (rigid adherend)	1.6	25	200
	Peel (flexible adherend)	0.5	25	
Composite (*bismaleimide*)				
Plain-weave T650 carbon-fibre reinforcement F655-2 (Hexcel)	Double-cantilever beam	2 (10 plies)	20	165

Several different types of polymer fibres were embedded in adhesive resin and used as film adhesive to investigate further the effect of carrier cloths on fracture propagation. This was done by sandwiching the cloths between two films of unsupported FM 350 NA adhesive and curing the joint according to the manufacturer's instructions: 1 h at 177°C, 200 kPa pressure. Adhesion tests were then carried out at temperatures ranging from − 55°C to 180°C.

2. Results

The mechanical properties of adhesive joints were assessed by using single-lap shear tests, double-cantilever beam tests and floating roller peel tests with aluminium and bismaleimide composite adherends. These are typical test methods used in the aerospace industry and provide a convenient way of comparing adhesives. The aluminium adherends were prepared by degreasing in butanone followed by an FPL etch [10]; the composite adherends were prepared using a peel ply followed by light abrasion and butanone wipe. The single-lap shear specimen dimensions are given in Table 1. Further tests were made on small-scale specimens which were loaded to failure in a straining stage fitted inside the work chamber of a scanning electron microscope (SEM). This enabled the fracture propagation to be observed at the bondline. The small-scale peel specimens were made with the same materials as the full-size testpieces; adherends were cut into 2 mm widths and bonded with approximately 20 mm overlaps. After curing the edges were polished with 1000 grit SiC paper and coated with gold before insertion into the SEM straining stage.

Scanning electron micrographs of small-scale specimens bonded with commercially available versions of FM 350 NA are given in Figs. 1–3 showing unsupported adhesive, adhesive supported with knitted Nylon cloth and adhesive supported with knitted woven glass, respectively. Aluminium particles and the ends of the cloth fibres are visible on the polished surface of the adhesive.

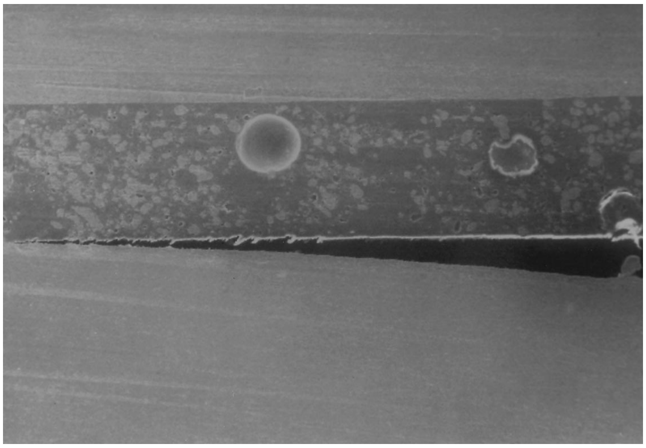

Fig. 1. Scanning electron micrograph of *in situ* peel test on unsupported FM 350 NA adhesive with aluminium adherends. Bondline thickness = 65 μm.

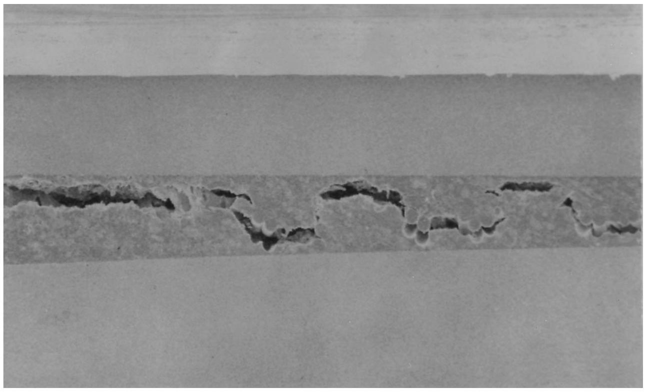

Fig. 2. Scanning electron micrograph of *in situ* peel test on FM 350 NA adhesive with a Nylon carrier cloth. Aluminium adherends. Bondline thickness = 100 μm.

The visibility of cracks in the adhesive, which is enhanced when the material which is not coated with gold, is revealed by the fracture and charges under the electron beam. It can be seen that the fracture paths are different

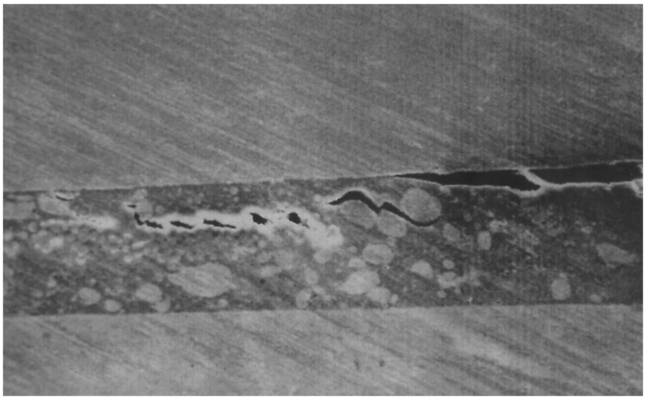

Fig. 3. Scanning electron micrograph of *in situ* peel test on FM 350 NA adhesive with a glass carrier cloth. Aluminium adherends. Bondline thickness = 100 μm.

in each case with little or no crack diversion of what is apparently a single near-interfacial crack in the unsupported adhesive; examination of the fracture surface after the test revealed that failure was cohesive but close to the metal adherend. There is extensive crack jumping and distributed debonding in the Nylon-supported adhesive and limited crack branching and diversion in the glass-supported adhesive. In both adhesives containing carrier cloths the fracture path is modified by the presence of the cloth fibres and debonding occurs ahead of the main crack tip. It should be noted that these are necessarily observations of the specimen surface and that care must be taken when interpreting these images since the stress states in the centre of a joint will be different to those at the joint edge. The Nylon fibres were pulled out of the adhesive resin and appeared to have no residual resin sticking to them. The glass fibres, however, were always coated with adhesive resin when they were observed on the fracture surface. The aluminium filler particles were only rarely disbonded and this did not appear to affect the crack propagation path significantly.

A set of full-size floating roller peel specimens, each 25 mm wide, was made with a range of embedded fibres to investigate the effect of different fibre types. The results from these tests are given in Table 2, where the standard glass-supported adhesive is compared with adhesive containing several types of high-temperature polymer fibres. Significant improvements in peel strength were achieved, raising the 20°C test value from 26 N/25 mm to over 100 N/25 mm in some cases. Only the joints made with totally unsupported adhesive gave a lower peel strength. The best variant from the 20°C tests used a unidirectional (UD) fabric of commingled carbon fibres and PEEK [poly(ether ether ketone)] fibres. This fabric was used in the 0° orientation (fibres aligned parallel to the testing direction) and in the 90° orientation (fibres running across the testing direction). This type of modification was then tested at four different temperatures on aluminium adherends in peel and single-lap shear tests and on bismaleimide composite adherends in single-lap shear and double-cantilever beam (DCB) tests. The results are given in Tables 3 and 4. The lap-shear tests with aluminium adherends were made with two orientations of carbon and PEEK fibres. The results show that when the fibres run along the test direction (i.e. 0° orientation) there is a decrease in lap-shear strength compared with the standard product but if the fibres are aligned parallel to the test direction (90° orientation) there is a small overall increase in joint strength. The strength increases that were measured in the DCB tests are considerably higher than recorded for the peel tests and this was probably due, at least in part, to extensive fibre bridging. Indeed, all the fracture surfaces displayed disbonded PEEK fibres which had been pulled from the resin and had failed in an apparently interfacial manner (as observed in the SEM). A scanning electron micrograph of a small-scale peel specimen tested at 20°C is shown in Fig. 4. This specimen was not coated with gold and it is clear that there is extensive crack diversion and bridging which runs at or very close to the PEEK

Table 2
Floating roller peel test results (N/25 mm) for aluminium adherends (average of three specimens)

Carrier cloth	Test temperature (°C)				Bondline thickness (μm)	Fibre orientation
	− 55	20	130	180		
Unsupported		23			65	
Glass	32	26	33	43	100	Woven 0°,90°
C and PEEK	100	132	105	117	350	UD 0°
C and PEEK		118	115		350	UD 90°
C mat		17			350	Random
Glass and PPS		128			420	Woven 0°,90°
C and PEEK		84			800	Woven 0°,90°
PEEK		83			200	Woven 0°,90°
PEEK × 2		95			320	Woven 0°,90°

Table 3
DCB test results (J m^{-2}) for composite adherends (average of three specimens)

Carrier cloth	Test temperature (°C)				Fibre orientation
	− 55	20	130	180	
Glass	244	302	544	443	
C and PEEK	2811	2708	2112	2387	0°

fibre/epoxy resin interfaces. When crack propagation was monitored in the SEM it was seen that the crack was forced to follow a more tortuous route through the bondline than was the case with adhesive containing glass or Nylon fibres.

The physically modified FM 350 NA adhesive was then tested in a configuration which is more typical of an aerospace structure than many adhesive tests. The stringer bonding test (SBT) specimen is shown schematically in Fig. 5. This test was developed during the ABHTA (Adhesive Bonding for High Temperature Applications) collaborative programme and is described elsewhere [11]. It consisted of a cured carbon fibre/bismaleimide (BMI) composite ‘A’ section stringer bonded onto a cured BMI laminate. Starter cracks were made in the ends of the bonded area and the assembly was loaded in four-point bending. Load was applied by using rubber pads inserted between the specimen and the loading rollers. Results are shown in Table 5 for tests in two orientations: standard, as shown in Fig. 5, and upside down. Unsupported FM 350 NA adhesive, standard glass-supported adhesive, double layers of glass-supported adhesive and physically modified adhesive containing carbon and PEEK fibres were tested. The SBT specimens with unsupported adhesive failed at the lowest load and were not able to sustain load after first failure; these all failed cohesively in the adhesive. The glass-supported specimens also failed catastrophically in the adhesive when tested in the standard configuration and increasing the adhesive thickness by using double layers of glass-supported adhesive did not significantly increase the strength. The upside down test configuration always produced non-catastrophic failures in which the specimen could continue to take load following first failure. Incorporating the carbon and PEEK layer into the adhesive both increased the strength and resulted in non-catastrophic failures in both test orientations.

3. Discussion

It is important to note that high-temperature adhesives generally have lower lap-shear strengths and particularly lower peel strengths than their lower-operating-temperature counterparts. For example, a 121°C cure toughened epoxy adhesive may have a single-lap shear strength of over 35 MPa and a peel strength of over 300 N/25 mm. The high-temperature adhesive FM 350 NA, however, is capable of operating at higher temperatures and possesses a glass transition temperature of approximately 180°C compared with 110°C for a lower-temperature epoxy. These special properties must be considered when high-temperature structures are designed. When an adhesive is being developed it is usual to make chemical modifications to the resins to manipulate their mechanical and thermal behaviour. However, the work described above has briefly examined the effect of physical modifications to the adhesive system and has shown that it is possible to significantly alter the peel strength without seriously degrading the lap-shear strength, at least with one particular orientation of fibres. Clearly, further work is needed to elucidate the mechanisms involved and to produce a material with more isotropic properties but some initial conclusions can be drawn.

From the SEM observations of fracture propagation and of the fracture surfaces it is apparent that it is the PEEK fibres which are instrumental in modifiying the fracture path; the carbon fibres play little role in this. There are at least three potential toughening mechanisms available to the modified joints. These are increased bondline thickness, fibre bridging and microstructural effects whereby the propagating crack is forced to branch and divert, possibly affected by an increased amount of distributed microcracking some distance ahead of the

Table 4
Single-lap shear test results (MPa) (average of three specimens)

Adherends	Carrier cloth	Test temperature (°C)				Fibre orientation
		− 55	20	130	180	
Al–Al	Glass	21.2	18.5	18.2	19.9	0°,90°
	C and PEEK	15.3	14.8	16.2	12.7	0°
	C and PEEK	20.6	20.6	21.4	21	90°
Composite–composite	Glass	18	16.4	10	8	0°,90°
	C and PEEK	13.4	10.5	10.2	15.4	0°

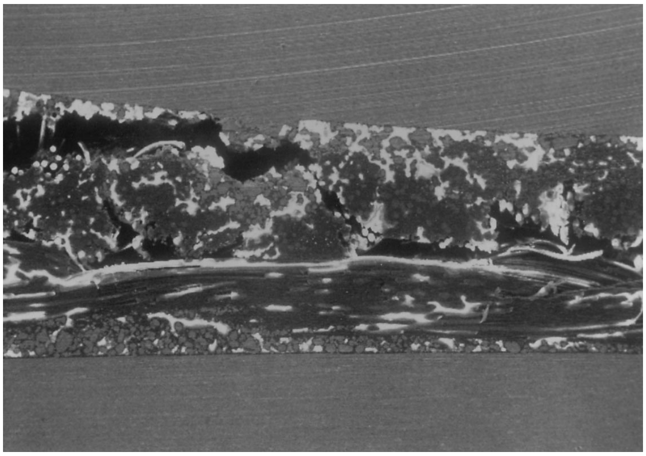

Fig. 4. Scanning electron micrograph of *in situ* peel test on FM 350 NA adhesive with carbon and PEEK fibres embedded in the resin. Aluminium adherends. Bondline thickness = 350 μm. Not coated with gold.

main crack tip. All these effects have been observed. Table 2 shows bondline thicknesses for several of the variants tested where the highest strengths are associated with thick layers, but there is no clear dependence of peel strength on bondline thickness. The toughening effect of increasing bondline thickness is minimal for some brittle adhesives [12] and the FM 350 NA is a relatively brittle material with strains to failure of less than 2%. Extensive fibre bridging can be seen in DCB tests and there is evidence for it on all fracture surfaces where cleanly disbonded, broken PEEK fibres have been pulled from the resin. This is a well-documented mechanism for increasing the apparent toughness in composites and can be a significant component to the measured toughness values when it operates over a relatively large fractured zone, as seen in the DCB tests. The adhesive resin containing a high proportion of fibres can be compared with a fibre composite microstrucure and some of the

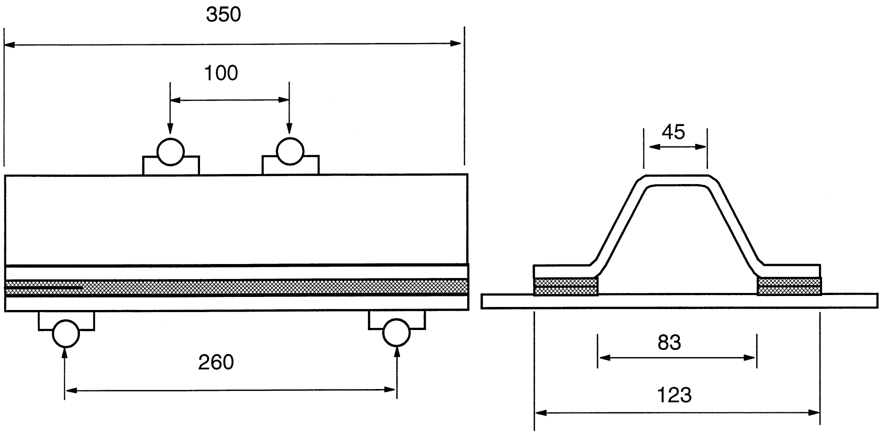

Fig. 5. Stringer bonding test specimen (schematic).

Table 5
Stringer bonding test results. Tests carried out at 20°C

Adhesive carrier cloth	Testpiece orientation	Maximum load (kN)	Load at first failure (kN)	Remarks
Unsupported	Standard	13.8	13.8	Cohesive in adhesive
	Standard	13.1	13.1	Cohesive in adhesive
	Upside down	22	22	Cohesive in adhesive
Glass	Standard	17.5	17.5	Cohesive in adhesive
	Standard	17.2	17.2	Cohesive in adhesive
	Upside down	27.5	24	Cohesive in adhesive
	Upside down	27.1	24	Cohesive in adhesive
Glass (double layer)	Standard	18.8	17	Cohesive in adhesive
	Standard	17.6	17.6	Cohesive in adhesive
	Standard	22.2	19	Stringer failure
	Standard	16	14	Stringer failure
Carbon and PEEK	Standard	20.4	18	Cohesive in adhesive
	Standard	21.8	20	Cohesive in adhesive
	Upside down	28.2	22	Stringer failure
	Upside down	34.5	24	Stringer + adhesive

microstructural toughening mechanisms that have been described in composites [13–15] are likely to be active in the adhesive layer.

The SEM observations show that the adhesive versions with the highest peel strength are those which exhibit complex crack propagation modes involving crack branching, crack diversion and fibre/resin debonding ahead of the main crack tip. Care must be taken when interpreting the *in situ* SEM fracture information because it is only possible to view the surface of the joint and different stress conditions exist at the surface compared with the bulk. Thus, the position of the crack within the joint may be different to the crack location as seen at the edge. For example, a single crack can be seen in the joint made with unsupported adhesive and it appears to be running at the resin/adherend interface. This is clearly not the case in the bulk of the joint, which fails cohesively in the adhesive. However, this technique is probably valid for the interpretation of the microstructural interaction of small cracks with different phases within the bondline as observations of the fracture surfaces after the test correspond with the inferences made from the *in situ* studies. It has proved useful in suggesting physical modifications which have improved the measured peel strength.

The modifications with carbon and PEEK fibres have been shown to increase peel strength significantly and, in one orientation, to produce a minor improvement in lap shear strength. Further work is underway [16] to investigate the mechanisms and to optimise a system that has more uniform properties in all test directions. The SBT specimen has a complex stress state and, while tests using the carbon and PEEK modification showed some improvement in strength and damage tolerance, it may be that a system with isotropic properties would perform better in this application.

4. Conclusions

Physical modifications have been made to FM 350 NA, a high-temperature modified epoxy adhesive, by embedding thermoplastic fibres in the adhesive resin. These have resulted in improved peel strengths, increasing the floating roller peel strength on aluminium from 26 N/25 mm to 132 N/25 mm at room temperature. Similar increases have been measured at temperatures ranging from − 55°C to + 180°C. The single-lap shear strengths, measured on aluminium and composite adherends, were reduced when the worst orientation was used but lap-shear strengths were improved slightly with another orientation of the fibres. When these modifications were tested in a stringer bonding test specimen there were some improvements in strength and damage tolerance.

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