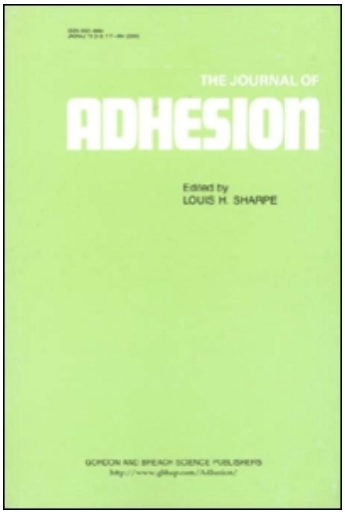

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Dodiuk, H. , Buchman, A. , Liran, I. and Kenig, S.(1993) 'Epoxy Adhesives for Repair of Composite Structures. Part V', The Journal of Adhesion, 40: 2, 127 — 138
To link to this Article: DOI: 10.1080/00218469308031279
URL: http://dx.doi.org/10.1080/00218469308031279

J. Adhesion, 1993, Vol. 40, pp. 127–138
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Printed in the United States of America.

Epoxy Adhesives for Repair of Composite Structures. Part V

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(Received May 19, 1992; in final form October 20, 1992)

A reduced temperature epoxy formulation for repair of epoxy-graphite composite laminates was characterized.

The epoxy formulation comprised selected high functionality aromatic epoxy resins and a multi-component polyamine curing system containing an elastomeric toughener.

Experimental results for bonding graphite-epoxy specimens have shown that, compared with a 175°C commercial film adhesive, the proposed formulation has better low temperature shear strength, comparable ambient properties and lower elevated temperature (120°) shear properties.

The epoxy formulation exhibits the same in-plane shear modulus as the commercial material and a plastic behavior at high shear strains. Consequently, the fatigue endurance of the epoxy formulation has been found to be superior to that of the 175°C commercial film adhesive.

KEY WORDS composite repair; epoxy adhesives; low temperature curing; epoxy-graphite; shear strength; shear modulus; shear fatigue.

INTRODUCTION

Polymer composites are used in a wide variety of aerospace structural applications which demand low-cost, short-time maintainability during their service life. Consequently, the composites industry is placing emphasis on repairability as part of the incorporation of composites into structures. To overcome moisture-related debonding and delamination due to high temperature curing, research and development programs are being conducted which are aimed at developing repair systems using low temperature curing resins.

Field repair of composites is carried out under constraints when compared with depot facility capabilities. Proper equipment such as autoclaves and freezers are normally not available in the field. Most field repairs are accomplished with the aid of heating blankets and vacuum bag processing.[1,2] The development of a low temperature curing (94°C) prepreg system with vacuum bag processing was reported by Hexcel Corporation, the resulting composite having thermal and laminate properties similar to those of a typical, 175°C cured, epoxy prepreg system.[3] Armstrong[4] reviewed major parameters, products, case histories and methods currently used for repairing aircraft composites. He has postulated that when choosing a low tem-

perature setting adhesive, it is important that repair resins should be of the same strength, stiffness and elongation to failure as the original resin. However, only a few low temperature curing resins have glass transition temperatures (T_gs) as high as 120°C. Subrahmanian[5] claimed that composites comprising resins cured at elevated temperatures cannot be repaired by wet lay-up of a low temperature curing system, since these systems are unlikely to give the required hot/wet performance. The use of lower temperature curing prepregs means that the repair material will typically be between 15% and 25% weaker than the original prepreg. New epoxy resins for fibre-reinforced composites and adhesives have been developed which can be cured in 5 min. at 149°C or at temperatures less than 100°C in 2 hrs.[5] Acceptable mechanical properties were obtained utilizing a vacuum bag only. Baker *et al.*[6] reviewed a wide variety of repair techniques for metallic as well as composite components. He has concluded that there are still considerable problems associated with metal and composites repair. Consequently, the basic requirement of composites repair is a material having a low curing temperature, in addition to elevated temperature service and endurance, under aggressive environmental conditions (heat/humidity).

As a first step to resolving some of these problems, a few novel epoxy formulations have been developed and characterized for repair of aluminum.[7-10] The structural epoxy formulation comprised selected high functionality aromatic epoxy resins and a multi-component polyamine curing system containing a rubber toughening agent. Experimental results showed that a few selected formulations developed good high temperature (120°C) properties while curing at ambient or moderate temperatures (50–60°C). Both shear and peel strengths of the proposed adhesives were found to be competitive with elevated temperature curing film adhesives. Consequently, the present work is a continuation of the authors' previous work[7-10] and is aimed at evaluating one moderate curing epoxy formulation[10] as an adhesive for repair of carbon composites.

METHODOLOGY

The objective of the present work was to study and characterize the mechanical properties of a room temperature curing epoxy adhesive[7-10] to be used as a repair material for epoxy-graphite composite structures.

All properties were compared with the high temperature curing structural adhesive FM-300K (product of American Cyanamid) which is currently used for this purpose.

The basic formulation comprised high functionality aromatic epoxy resins (tetraglycidyl-4-4′-diaminodiphenyl methane (TGDDM) and the monoglycidyl ether of *p*-aminophenol) combined with a two-component amine curing system (triethylenetetraamine (TETA) and amino-terminated butadiene-acrylonitrile (ATBN)).

Both adhesives were compared for their elastic shear and adhesion properties using lap shear specimens, over a wide range of test temperatures and after exposure to hot/wet environment. Various curing cycles and the effectiveness of pre-adhesion treatment with a primer were also tested for the epoxy formulation. Fatigue testing of the bonded joint was performed to evaluate the durability under dynamic shear

cycles. Fractured surfaces were analyzed by scanning electron microscopy (SEM) to study the morphology and mode of failure.

EXPERIMENTAL

Materials

The adhesive used in this work is a blend of two epoxy resins: A tetrafunctional epoxy resin (MY-721) and a trifunctional epoxy resin (ERL-510) both products of Ciba-Geigy (USA) and an amine curing agent (TETA) a product of Miller Stephenson (USA) and an amine-terminated reactive liquid rubber toughener ATBN (1300×35) a product of B. F. Goodrich (USA).

The mixing weight ratios were:

$$MY\text{-}721 : ERL\text{-}510 : TETA : ATBN = 50 : 40 : 18.6 : 36$$

The adhesive was supported on a polyester felt Fibermat IC-650, 0.1 mm thick, product of 3M (USA). The reference adhesive was FM-300K, a 0.98 psf epoxy adhesive with a polyester carrier 0.1 mm thick, product of American Cyanamid.

The composite adherend is a prepreg composed of an epoxy matrix (Narmco 5208) reinforced with continuous graphite fibers (AS-4) stacked in a quasi-isotropic arrangement ($0, \pm 45, 90$). The laminates were composed of 16 plies, 3.2 mm thick. One face of the composite plates was made rough using a special peel-ply (for adhesion), the other side was smooth (for ultrasonic C scanning).

Sample Preparation

The adhesives were first characterized by determining their lap shear properties using composite adherends. Test specimens were prepared from epoxy-graphite composite laminates. The release agent used for the molds was a non-silicone spray (Freecoat B 15, product of HYSOL). No mechanical surface treatment was needed due to the rough surface of the samples but they were wiped clean with acetone. Before application of the adhesive and the felt carrier, a silane primer (2% A-187 in 80/20 ethanol/water by volume) was applied on the composite adherend surface and allowed to dry for 30 min. at room temperature (RT) and 1 h at 100°C. The adhesive was applied by impregnation of the carrier with the adhesive, evacuation for 5 min. at 4 mm/Hg (absolute pressure) and squeezing out the excess of the resins. The test specimens were allowed to cure at the following cure cycles: at ambient temperature for 1 or 7 days, or at 60°C for 1 hour (in a press under a pressure of 0.5 atm.). The 1-day cure cycle at RT was carried out to evaluate the possibility of handling the repaired structure after a short duration.

Samples with FM-300K were cured at 177°C at 35 psi for 1 hour.

The −50°C and 120°C test data are reported after a 10-minute soak at the testing temperature. The effect of soaking was previously evaluated[7] and found to be of secondary importance.

Tensile lap shear specimens were prepared according to ASTM-D-1002 to characterize shear adhesive strength.

Single lap shear (SLS) specimens were prepared with a micro-measurement biaxial strain gage type KFC-2-D16-11L10, product of Kyowa, Japan, embedded between two layers of adhesive to determine the in-plane axial shear properties of the adhesive. The samples were prepared according to a procedure developed by Tuttle *et al.*,[11] as shown in Figure 1.

Double lap shear (DLS) specimens were prepared for tensile fatigue testing according to ASTM D-3166-73.

Five specimens for each adhesive were fabricated for each test by compression using a special mold for single specimens. Bond-line thickness for all SLS specimens was 0.15 $\pm$0.03 mm and for DLS 0.25 $\pm$0.03 mm. Part of the lap shear specimens were exposed for a 10-day duration to hygrothermal conditions, 60°C and 95% relative humidity (RH), in a humidity chamber.

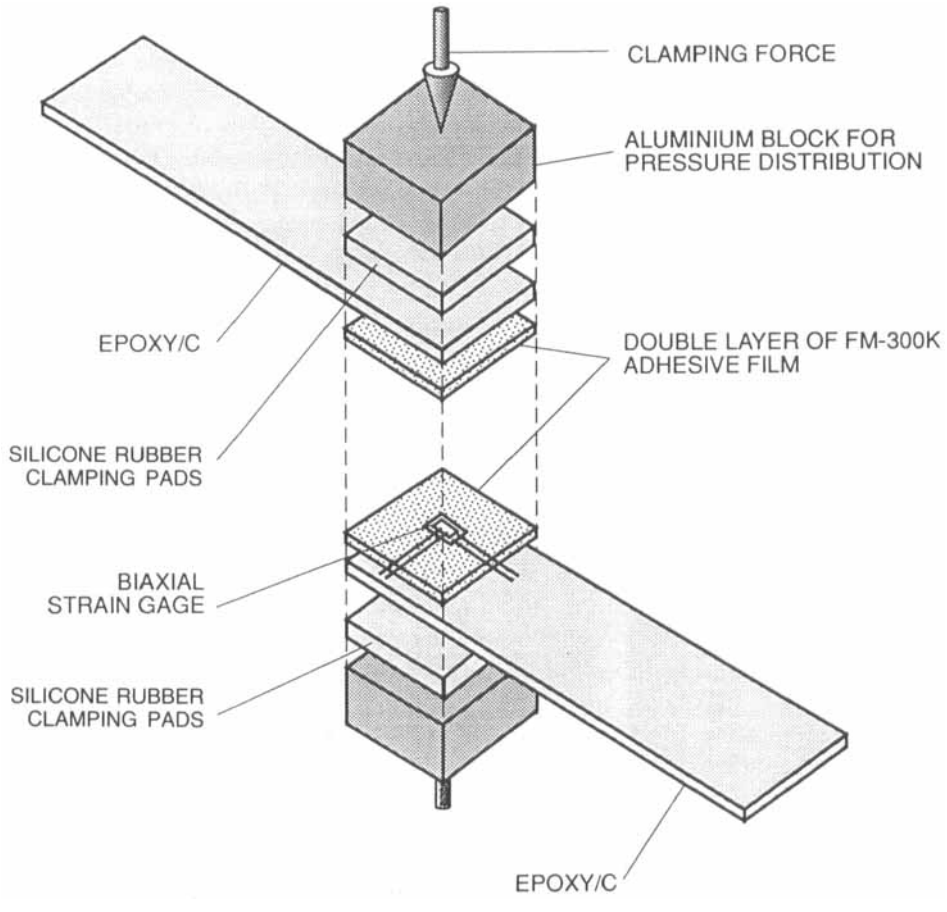


FIGURE 1 Schematic representation of an SLS sample with embedded strain gage.[11]

Mechanical Testing

Adhesive shear properties were determined at various temperatures using a 10-ton Instron machine at a cross head speed of 2 mm/min. according to ASTM D-1002.

In-plane shear properties were determined at the same above mentioned conditions. The samples were attached during testing to a double strain gage meter equipped with an X-Y recorder.

Fatigue tests were conducted on an MTS machine model 880 (USA) applying a sinusoidal cyclic axial (zero to maximal tensile) load at 1800 cycles/min. The number of cycles to failure were recorded at five different loads. The results were plotted on an S-N curve (stress-log cycle coordinates) according to ASTM D-3166.

Analysis of Fracture Surfaces

SEM and SEM/EDAX analysis of fracture surfaces was carried out using a Jeol SEM, Model JSM-840. Prior to observation, the specimens were coated with a thin layer (~20 nm) of Pd-Au to obtain a conductive surface and prevent surface charging.

RESULTS AND DISCUSSION

Adhesive Shear Strength

The shear strength of the epoxy formulation, with and without primer (A187) applied on the adherend, exposed to different test and environmental conditions, are summarized in Table I, and compared with the structural adhesive FM-300K. The aim of these tests was to determine whether the primer improved the adhesion. The results clearly show its high efficiency.

TABLE I
Lap shear strength (MPa) of epoxy formulation with and without primer at various exposure conditions

Adhesive cure		Epoxy formulation (Cured 1 hr 60°C)	
Test conditions	FM-300K (No primer)	With primer	Without primer
−50°C	(A)* 13.8±2 (−41%)**	(A) 18.1±3 (+2%)	(A) 16.8±3 (+1%)
RT (reference)	(A) 23.8±2 (−)	(M) 17.8±1 (−)	(M) 16.7±1 (−)
+120°C	(C) 14.3±1 (−38%)	(M) 8.8±2 (−51%)	(A) 5.9±1 (−65%)
RT, after exposure to 10 days 95% RH/60°C	(M) 27.7±9 (+19%)	(M) 24.3±2 (+37%)	(A) 20.3±3 (+20%)

*A − Adhesive (visual), C − Cohesive, M − Mixed mode of failure.
**Percent change relative to reference.

TABLE II
Lap shear strength (MPa) of epoxy adhesives at different curing conditions

Adhesive cure			Epoxy formulation with primer					
Test conditions	FM-300K (No primer)		RT 1 day		RT 7 days		60°C, 1 hour	
−50°C	(A)*	13.8 ± 2 (−41%)**	(A)	11.5 ± 2 (+49%)	(A)	11.9 ± 1 (−36%)	(M)	18.1 ± 3 (+2%)
RT (reference)	(A)	23.2 ± 2 (−)	(M)	7.7 ± 1 (−)	(M)	18.6 ± 2 (−)	(A)	17.8 ± 1 (−)
+120°C	(C)	14.3 ± 1 (−38%)	(M)	6.9 ± 2 (−1%)	(M)	4.8 ± 1 (−74%)	(A)	8.8 ± 2 (−51%)
RT, after exposure to 10 days 95% RH/60°C	(M)	27.7 ± 9 (+19%)	(A)	18.6 ± 3 (+142%)	(A)	25.3 ± 5 (+36%)	(M)	24.3 ± 2 (+37%)

*A – Adhesive (visual), C – Cohesive, M – Mixed mode of failure.
**Percent change relative to reference.

The shear strength of the epoxy formulation at various cure cycles exposed to different test and environmental conditions are summarized in Table II and compared with the structural adhesive FM-300K. According to these tests the preferred cure cycle was chosen (60°C, 1 h) but it can be seen that also at RT cure for 7 days the results are similar; therefore this schedule can be used when no heating conditions are available. The reference for all experiments was the testing of unexposed specimens at RT.

As is evident from Tables I and II, both adhesives reveal different behavior at below freezing temperature and similar behavior at other temperatures. The highest shear strength is obtained at low temperature (−50°C) for the epoxy formulation. At elevated temperatures (120°C) both adhesives exhibit lower shear strength. The epoxy formulation has lower shear strength than FM-300K due to partial interfacial failure (M) compared with the cohesive failure (C) of FM-300K. Improved surface treatment should yield higher 120°C shear strength. As shown in Reference 10 the reduction in shear strength is accompanied by increase in peel strength, which is a beneficial effect.

Table I shows that primer application on the composite surface results in better adhesion and higher lap shear strength at all conditions tested.

Table II indicates that curing at 60°C for 1 hour results in slightly better lap shear strength of the joint compared with curing at ambient conditions for 7 days. Curing for 1 day at RT yields 60% of the strength obtained at full cure (after 7 days). This result indicates that handling of the structure is possible after a relatively short period of cure. FM-300K displays the highest elevated temperature shear strength.

As displayed in Tables I and II, hot/wet environment enhances the shear strength of the adhesive, probably due to the temperature effect. The fact that the highest increase in lap shear strength was attained for the cure cycle of 1 day at RT (+142%) proves that the cure of these samples was not completed.

In-Plane Shear Properties

A comparison of the in-plane axial shear properties of both adhesives are summarized in Table III.

Figures 2 and 3 represent the in-plane axial shear stress-strain curves of both adhesives tested. It can be observed that FM-300K demonstrates almost a complete

TABLE III
In-plane shear properties of modified epoxy and FM-300K

Property	Shear stress (Ultimate)	Shear strain		Shear modulus	Poisson ratio
Adhesive	τ (MPa)	$\gamma\|\|$ (%)	$\gamma=$ (%)	G|| (MPa)	ν
Epoxy formulation	13.9 ±0.8	2.35 ±0.68	0.65 ±0.06	1278 ±32	0.28 ±0.01
FM-300K	18.3 ±3.1	1.37 ±0.19	0.38 ±0.04	1330 ±100	0.29 ±0.02

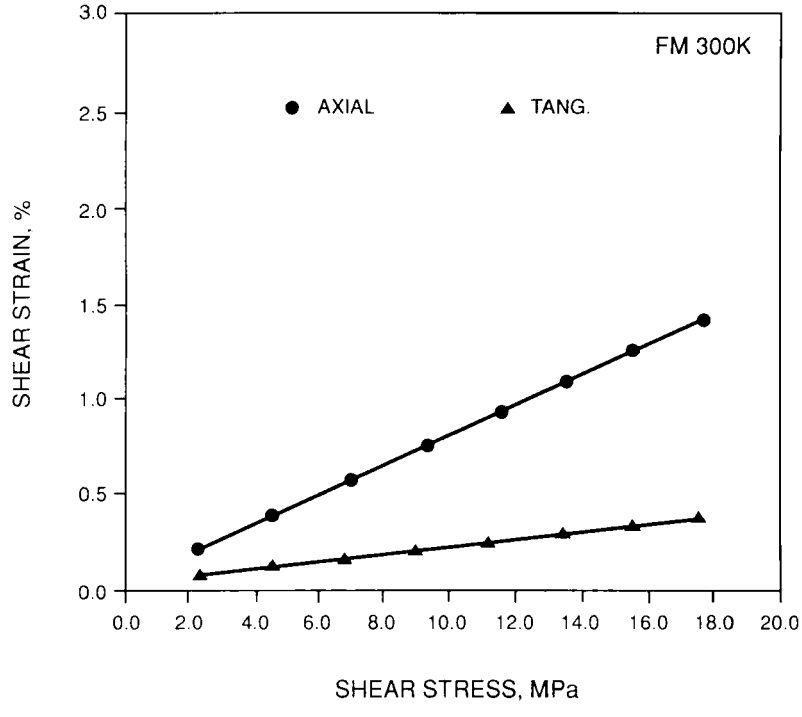


FIGURE 2 In-plane shear stress-strain diagram of FM-300K.

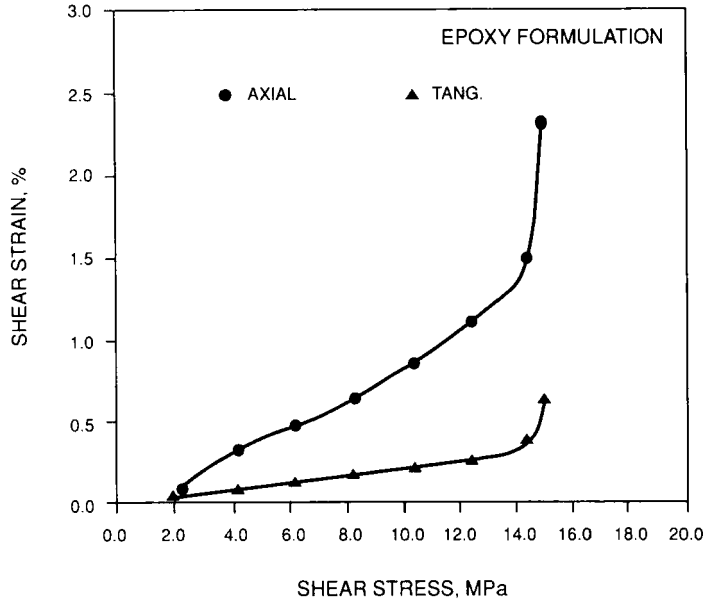


FIGURE 3 In-plane shear stress-strain diagram of modified epoxy formulation.

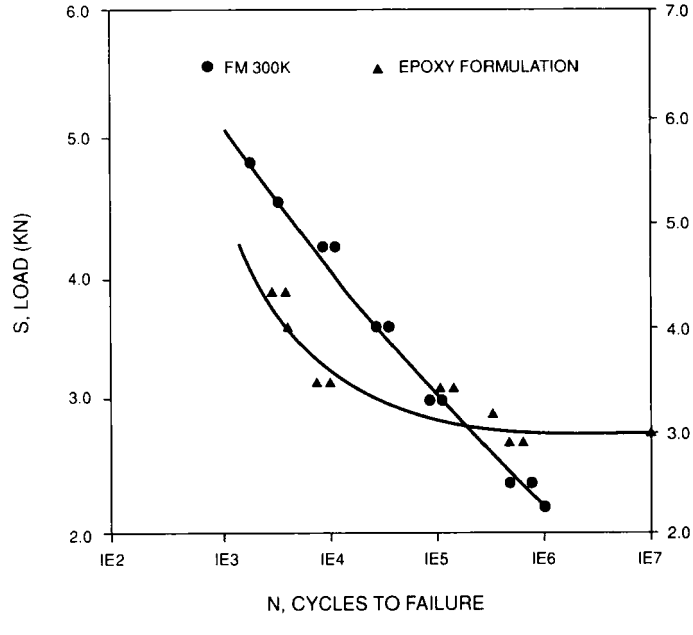


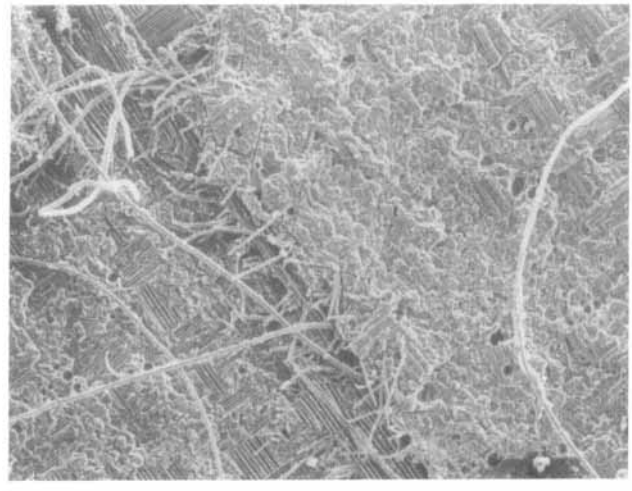
FIGURE 4 S-N fatigue curves of FM-300K and modified epoxy adhesives.

elastic response until failure, while the modified epoxy displays an elastic response up to 8–10 MPa and a plastic behavior at higher loads.

Both adhesives have a similar shear modulus while the modified epoxy shows higher strain to failure and lower Poisson ratio.

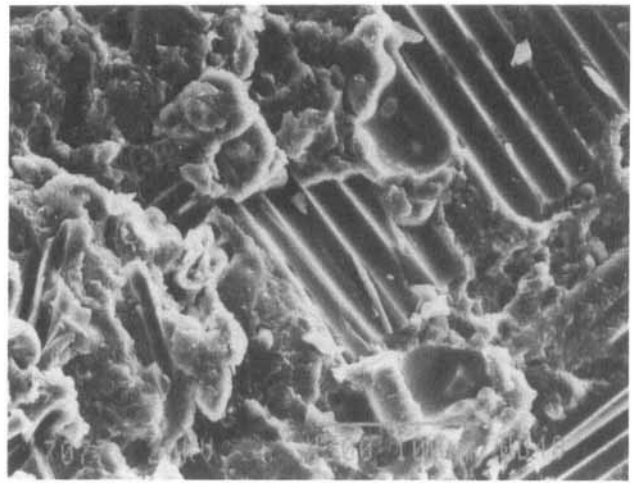
Fatigue Tests

Figure 4 shows the S-N curve of both adhesives. It is obvious that the epoxy formulation is much more durable to fatigue than the FM-300K, especially at low stress/long



x 40

a



x 300

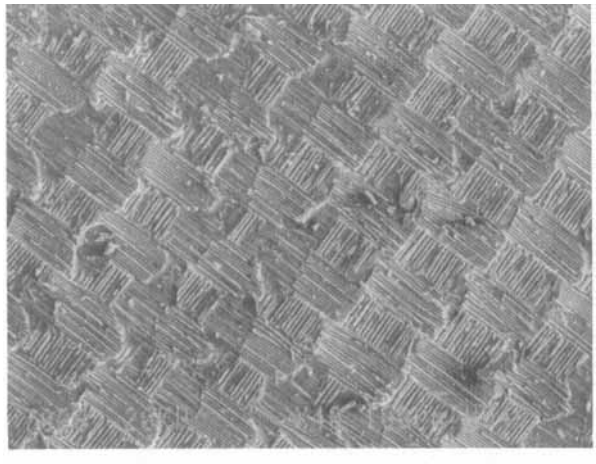
b

FIGURE 5 SEM micrograph of lap shear failure of carbon/epoxy joined with modified epoxy adhesive tested at RT.

term vibrations, as the epoxy formulation exhibits an endurance limit behavior that does not exist at the FM-300K fatigue test results. This result is probably due to the toughening of the modified epoxy by rubbery particles which are dispersed in the epoxy matrix as separate spherical phases. These particles create a yielding tendency in the material and tend to prevent small cracks from advancing in the matrix and causing premature failure. Consequently, the fatigue failure mechanism of the two adhesives is different, the modified epoxy formulations showing an advantage.

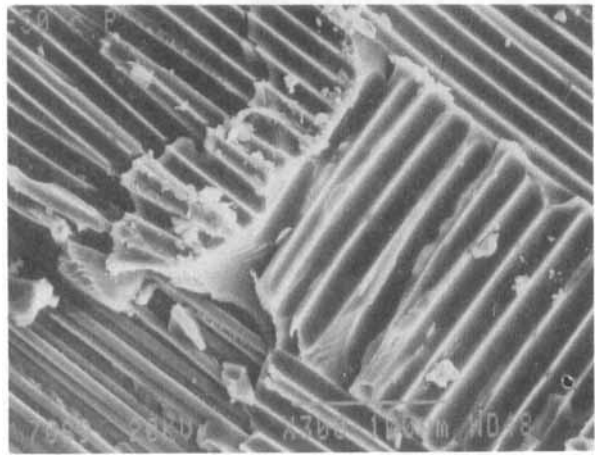
Microstructures

Figures 5–7 depict the mode of failure of the composite joint with the toughened epoxy adhesive at various temperatures. The fracture varies from mostly cohesive



x 40

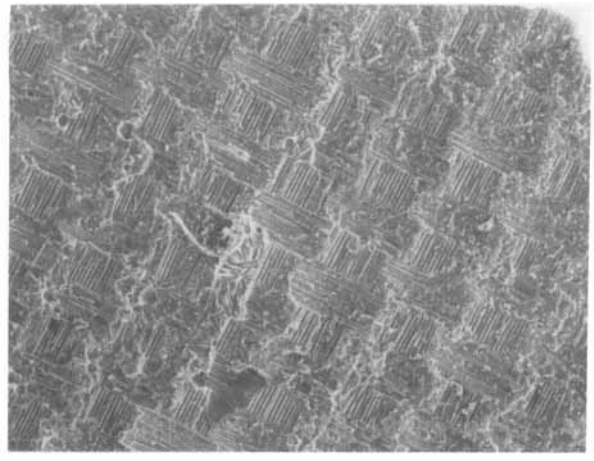
a



x 300

b

FIGURE 6 SEM micrograph of lap shear failure of carbon/epoxy joined with modified epoxy adhesive tested at −50°C.



x 40

a

x 300

b

FIGURE 7 SEM micrograph of lap shear failure of carbon/epoxy joined with modified epoxy adhesive tested at 120°C.

failure at 120°C and RT (7a, 5a) to total adhesive failure at −50°C (6a). The adhesive itself turns from brittle at −50°C (6b) to more flexible at RT and at 120°C (5b, 7b).

CONCLUSIONS

The epoxy formulation containing amino terminated elastomer cured at low temperatures displays comparable adhesive static properties and better dynamic properties compared to the structural commercial 175°C curing adhesive.

S-N curves, as well as in-plane shear properties measured by embedded strain gages, showed that the epoxy formulation is more flexible and can endure higher strains and fatigue compared to the commercial FM-300K. The modified epoxy formulation can thus be used for field repairs with the advantage of curing at low

temperature exhibiting better durability but sacrificing some properties at elevated temperatures.

Acknowledgements

The authors wish to thank Mr. Y. Cohen for performing the fatigue tests and the Israeli Air Force for supplying the composite adherends.

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