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IMPROVED FATIGUE STRENGTH ADHESIVE

THE DEXTER CORPORATION
HYSOL DIVISION

TECHNICAL REPORT AFML–TR–74–169

NOVEMBER 1974

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
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In spite of their high static strengths over the temperature range of -67°F to 350°F, adhesives presently used by the aircraft industry limit structural design loadings to as little as 20% of static properties if fatigue lives on the order of 10^7 cycles are needed. Recent work with composites has shown that an increase in fiber modulus greatly increases fatigue loading limits. Related increases in fatigue resistance on inclusion of high modulus fibers in adhesives bondlines have also been observed in work of the Air Force Materials Laboratory. Continued development of this concept with examination of bond

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20. Abstract

line parameters such as resin and fiber type, fiber/resin volume ratio, fiber-fabric construction and fabric orientation, has confirmed and defined such fatigue improvement in high-modulus fiber reinforced adhesives. A fifty-fold increase in fatigue life at equivalent stress levels was achieved when a woven high modulus graphite fabric was substituted for the conventional nylon knit support in a 350°F service adhesive. Using a graphite/epoxy composite to titanium test specimen, the stress level which could survive 10^7 fatigue cycles was increased from approximately 30 percent of the ultimate shear strength with nylon knit supports to as much as fifty percent with the high modulus fiber bond line reinforcement. The stress level which could withstand 10^7 fatigue cycles was thus increased from 1400 psi to 2000 psi by this reinforcement substitution. Slightly lower fatigue strengths were shown using titanium to boron/epoxy composite adherends.

The highest level of fatigue life improvement was found using a woven PWA graphite fabric as the adhesive support. No fabric orientation sensitivity was observed. Good results were also obtained with a style 120 KEVLAR®-49 fabric and with unidirectional type AS graphite tow supports. Reinforcement with monofilament boron and with a radom AS graphite fiber mat gave poor fatigue results.

Further definition of bond line parameters leading to optimum fatigue performance are under study in continuing work.

FOREWORD

This report was prepared under contract F33615-73-C-5133, by the Adhesives Department, Hysol Division, The Dexter Corporation, Pittsburg, California as prime contractor and the McDonnell Aircraft Company, St. Louis, Missouri, as sub-contractor. This contract was administered under Project Number 7340, "Non-Metallic and Composite Materials," Task Number 7340002, "Structural Adhesives." The Air Force Materials Laboratory contract monitor was T. J. Aponyi (AFML/MBC) of the Plastics and Composites Branch, of the Nonmetallic Materials Division. The project effort was conducted during the period of June 1973 to June 1974.

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This technical report has been reviewed and is approved for publication.

T. J. Aponyi
T. J. APONYI
Project Engineer

T. J. Reinhart Jr.
T. J. REINHART, JR., Chief
Composite and Fibrous Materials Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

In spite of their high static strengths over the temperature range of -67°F to 350°F, adhesives presently used by the aircraft industry limit structural design loadings to as little as 20% of static properties if fatigue lives on the order of 10^7 cycles are needed. Recent work with composites has shown that an increase in fiber modulus greatly increases fatigue loading limits. Related increases in fatigue resistance on inclusion of high modulus fibers in adhesives bondlines have also been observed in work of the Air Force Materials Laboratory. Continued development of this concept with examination of bond line parameters such as resin and fiber type, fiber/resin volume ratio, fiber-fabric construction and fabric orientation, has confirmed and defined such fatigue improvement in high-modulus fiber reinforced adhesives. A fifty-fold increase in fatigue life at equivalent stress levels was achieved when a woven high modulus graphite fabric was substituted for the conventional nylon knit support in a 350°F service adhesive. Using a graphite/epoxy composite to titanium test specimen, the stress level which could survive 10^7 fatigue cycles was increased from approximately 30 percent of the ultimate shear strength with nylon knit supports to as much as fifty percent with the high modulus fiber bond line reinforcement. The stress level which could withstand 10^7 fatigue cycles was thus increased from 1400 psi to 2000 psi by this reinforcement substitution. Slightly lower fatigue strengths were shown using titanium to boron/epoxy composite adherends.

The highest level of fatigue life improvement was found using a woven PWA^R graphite fabric as the adhesive support. No fabric orientation sensitivity was observed. Good results were also obtained with a style 120 Kevlar^R-49 fabric and with unidirectional type AS graphite tow supports. Reinforcement with monofilament boron and with a random AS graphite fiber mat gave poor fatigue results.

Further definition of bond line parameters leading to optimum fatigue performance are under study in continuing work.

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IMPROVED FATIGUE STRENGTH ADHESIVE

1.0) OBJECTIVES OF THE PROJECT

The objective of the project has been the development of a 350°F adhesive system with higher usable strength in fatigue than state-of-the-art structural adhesive systems thorugh reinforcement by high strength, high modulus fibers. This improvement should be demonstrated as an increase in the percent of static ultimate strength at which the system will survive 10^7 cycles when used in metal to composite bonds.

2.0 SUMMARY AND CONCLUSIONS

Structural adhesives, in general, can be stressed at only about 20% of their static strength in fatigue if lives of 10^7 cycles or greater are to be expected[1]). The same appears to be true concerning epoxy/glass composites[2]). However, recent work with composites of epoxy and high modulus, high strength fibers such as graphite [3,5]) and Kevlar-49[4]) has increased this useable fatigue strength to 80-90% of the static strength.

Recent experimental work, by AFML (in RFP F 33615-73-Q-5133), has also shown that the fatigue life of an adhesive bond using aluminum adherends can be improved significantly by reinforcement with a high modulus high strength fiber. Therefore, further definition of this finding is needed and the optimized system must be demonstrated in metal-to-metal, as well as metal to boron or graphite composite bonding. In such work to define the important bondline parameters, the 10^7 cycle fatigue life of ADX-653; a tough, 350°F service adhesive, was increased to 2150 psi from 1400 psi by replacement of the nylon knit support fabric with style PWA woven graphite reinforcement. Compared on the basis of the percent of ultimate strength surviving 10^7 cycle fatigue tests this represented an increase from 30% with a nylon support to as much as 50% with the high modulus fiber support. A 50-fold increase in fatigue life at equal stress levels was also obtained on substituting the high modulus fiber for the nylon support. The maximum improvement was obtained using a graphite/epoxy to titanium test specimen. Some reduction in fatigue life improvement was noticed when boron/epoxy composite adherends were used. The fatigue improvement due to reinforcement with style PWA appears to be essentially isotropic with respect to the fabric orientation.

The results are summarized as follows:

Reinforcement	Adherend	Fabric Orientation	Ultimate Shear Strength	10^7 cycle Fatigue Strength	
				(psi)	% Ult.
Nylon Knit	boron-epoxy/Ti	0°	4675	1400	30
Nylon Knit	graphite/epoxy	0°	4890	1420	28.5
PWA Graphite	boron-epoxy/Ti	0°	4645	1900	41
PWA Graphite	boron-epoxy/Ti	45°	4915	2000	40
PWA Graphite	graphite-epoxy/Ti	0°	4320	2150	49.5
PWA Graphite	graphite-epoxy/Ti	45°	4505	2020	45

The effect of the resin system on fatigue life improvement was investigated using ADX-653, ADX-655 and ADX-523, two modifications of an improved toughness adhesive and a representative of state of the art adhesives respectively. The ADX-523 system did not develop significant strength in combination with graphite fiber. Although both ADX-653 and ADX-655 had equivalent fatigue life improvement, the former was selected as optimum because of superior ultimate shear strength. The effect of fiber type and form on fatigue resistance was investigated by examining

ADX-653 reinforced with two woven forms each of Kevlar-49 and graphite, unidirectional fabrics of graphite and boron, and a random direction graphite mat. Except for the boron filament and random graphite mat, such variables influenced the fatigue performance only by affecting the ultimate shear strength of the system. Effects due to modulus or weave on fatigue were not observed. Poor results were obtained with the boron filament, presumably because of the very low total area of fiber resin interface area. The poor results with the mat may well be due to a very low fiber volume in the total adhesive bond line.

Determination of the effect of fiber/resin volume ratio on the fatigue life improvement was not possible due to the inability to separate it from variations in bondline thickness. The results with the random mat suggest that a fairly high fiber volume might be needed to get good fatigue performance. Further examination of these bond line parameters directed toward development of an optimized, practical improved fatigue adhesive system is the goal of continuing work.

3.0 PHASE I, TASK 1 RESIN SELECTION

3.1) BACKGROUND

The ability of high modulus, high strength fibers to improve the fatigue life of an epoxy adhesive bond line was first demonstrated at the Air Force Materials Laboratory using HTS graphite tow and ADX-516. ADX-516 is the result of two AFML contracts let to Hysol (F33615-69-C-1451 and F33615-71-C-1419) and is a combination of epoxy resin and a highly polar sulfone polymer which yields a very tough, high temperature resistant adhesive. It, however, requires a curing temperature of 450°F. The boron and graphite epoxy prepreg materials in current use on advanced aircraft cure at 350°F. Appreciable exposure of these materials to temperatures in excess of 420°F results in significant property loss especially in the case of the boron/epoxy composite. Additionally, cure temperatures in excess of 400°F have been found to lead to special bonding difficulties on complex production hardware, requiring special processing precautions. Combined with other potential problem areas on actual structures, such as aluminum honeycomb temperature capabilities, these factors preclude the use of 450°F curing adhesive systems with the presently available composite materials and fabrication techniques. For the above reasons, the following three adhesive systems were used in this effort:

1. ADX-653 An improved state of the art, 350°F service adhesive resistant to high temperature (420°F) air aging, with improved durability under stress in conditions of high humidity.
2. ADX-655 Similar performance to ADX-653 but increased cure rate and improved handling properties.
3. ADX-523 An unfilled version of a state of the art, 350°F service adhesive. Good initial adhesive properties but deficient in high temperature air aging and durability under stress.

The adhesive properties of these systems are summarized in Table 1.

Most current 350°F-service adhesive tapes contain a metallic filler which generally improves performance properties as well as handling in the uncured state. However, such fillers would interfere with inclusion of a high modulus fiber. For this reason, all metallic fillers have been removed from the previously listed adhesives to be used in this effort. This quite conceivably could result in lower high temperature properties for every system. The removal of the aluminum filler from ADX-523 gives an extremely tacky and essentially unhandlable adhesive, even when used at dry ice temperatures. The handling properties were improved by adducting 7% of the available epoxy with an aromatic diamine. A comparison of the adhesive properties shows little difference due to this modification (Table 2) of the filler-free film.

3.2) PERFORMANCE TEST RESULTS

Adhesive films were manufactured from the above resin systems and Hercules' HTS Carbon tow at a density of 3 tow/in.width and a fiber weight content of 35-40%. Preparation details are summarized in the Appendix. (Section A.1.1)

3.2.1) Initial Fatigue Test Screening

Fatigue tests using titanium double overlap tensile specimens (Figure 1) resulted in a very significant improvement in fatigue life with the inclusion of high modulus carbon fibers in the adhesive bond (Table 3). As a control, ADX-653 containing a knitted nylon fabric survived an average of 2900 cycles before failure when stressed at 50% of its ultimate shear strength. In contrast, when stressed at the same percentage of ultimate ADX-653 reinforced with the HTS tow survived an average of 118,000 cycles. When tested at the same actual stress level (1800 psi), carbon reinforcement gave a two fold increase in fatigue life over the nylon supported system. ADX-655, with a nylon support, gave an average of 2700 cycles before failure when reinforced with HTS tow, the average cycles to failure increased to 425,000.

ADX-523 was eliminated from testing because of its relatively low 75°F ultimate shear strength (1980 psi). This strength did not compare well with the 3620 psi exhibited by the ADX-653 system and 3000 psi exhibited by the ADX-655. It was felt that even if this system gave the best fatigue life at 50% of its ultimate shear strength, it would not be usable in practical applications because of its low ultimate strength.

In this initial work there was an extremely large variation of the results in fatigue life tests. For example, the ADX-655/HTS system had a minimum of 64,000 and a maximum of 786,000 cycles to failure. One reason for this extreme data scatter was the sample preparation technique. Initially, test specimens were prepared as finger panels using a titanium center shim and spacers between the fingers. These spacers, during cure, became bonded to the panels and had to be cut out before testing. Later spacer removal could result in the formation of edge defects in the test specimens. A new panel assembly technique, involving use of much softer spacing material, such as teflon, resulted in both increased initial shear strength and a much tighter distribution of fatigue screening data (Table 3, specimen preparation technique 2).

3.3) CONCLUSIONS

A 40 to 50 fold increase in the adhesive fatigue life (stressed at 50% of the ultimate shear strength) resulted when the resin was reinforced with a type HTS unidirectional tow fabric. The selection of resin systems could not be made only on the basis of this initial fatigue screening since the ADX-653 and ADX-655 systems appear to give similar fatigue lives at 50% of the ultimate shear strength when tested with either the nylon or the HTS reinforcements. ADX-653 was selected as resin system with which to continue the program. This was done mainly on the basis of its better static properties.

4.0 PHASE 1, TASK 2 FIBER DISTRIBUTION STUDY - FABRIC EVALUATION

4.1) BACKGROUND

Analysis of an overlap bond in tension reveals that the stress in the bondline is not uniformly distributed but is concentrated at the edges of the bond. When the above situation is viewed from a fatigue standpoint, it appears that the areas that fail in fatigue are the same that initiate failure in a static test. While the applied fatigue stress may be low as a percentage of static strength, it is concentrated at the bond edges. Inclusion of high modulus fibers in the bondline reduces the stress concentration gradient across the bond area by distributing the loading over a larger area of the bond. This bond edge plane is subjected to shear stress and consequently a reinforcement which is planar and lying parallel to the adherends is not optimally distributed to transmit the stress from one adherend to the other. A reinforcement with fibers oriented at 45° to the plane of the adherend should more effectively transfer these stresses. However, no practical means of so ordering individual fibers of short length is known. Even if this was possible, adhesive flow during bond formation would destroy this orientation. More practically, applied stresses are rarely uniaxial, and an adhesive in which the fiber distribution was optimized for one type of applied stress would not be widely useful.

Because of these considerations, the optimum approach to effective fiber orientation would be via use of a fabric. Because the fibers are tied into the construction, a fabric would be expected to withstand the distortions caused by bond formation, accomodate multi-axial stresses, and ensure fiber orientation in the desired direction.

To achieve fiber paths at angles to the adherends, one naturally first considers plain weave fabrics. The warp direction of the weave follows a sinusoidal path, giving the desired distribution. However, the fill direction fibers are very nearly parallel to the adherends. This could cause variation of fatigue improvement with fiber direction, depending on the importance of fiber path. A fine suspension of high aspect ratio fibers would be expected to distribute themselves randomly through the bondline, thus giving significant numbers of fibers at angles to the surface with no dependence on direction.

4.2) FABRICS

In order to determine the affect of fiber distribution, four fabrics, two woven of carbon and two of Kevlar^{R}-49, were purchased. The characteristics of these, as well as a mat made of 1/8" AS carbon fibers are shown in Table 4.

WCG and PWA are square weave carbonaceous fabrics. The WCG fabric is woven from a rayon precursor and subsequently carbonized.

Physical properties have not been measured on the fibers making up this fabric because weaving as rayon causes the subsequent carbon fibers to be kinked. However, it is the manufacturer's belief that these fibers have a modulus of 6 million. This is primarily due to the lack of orienting of the fiber during carbonization. The PWA fabric, in contrast, is made of staple fibers with a 30 million modulus.

Styles 120 and 220 are square weave fabrics made up of Kevlar[R]-49. This fiber has a modulus of 19 million and the fabrics were measured at their advertized thickness of 5 mils. A 2.4 oz/yd^2 mat was manufactured from Hercules' AS fiber by paper handsheet manufacturing techniques. The 1/8" long fibers were dispersed in a water medium using a Waring Blender and the mat formed in a deckle box. The water was removed by air drying overnight at 200°F. Because of the high modulus of the carbon fibers, the mat did not compact well, resulting in an 18 mil thickness and 90% void content (interstitial). However, as will be shown later, the resulting adhesive film compacts to approximately ten mils when cured. Details of the mat manufacturing technique can be found in the Appendix (Section A.1.3).

All the aforementioned fabrics and the mat were purchased with the finish the manufacturer prescribed for use with epoxies. In all cases, the fibers were unfinished with no special sizing.

4.3) INITIAL TEST RESULTS

4.3.1) Kevlar-49 Fabrics

Two square woven fabrics constructed of Kevlar-49 fibers, styles 120 and 220 X, were manufactured into adhesive tapes using ADX-653 as the matrix resin. These adhesive tapes were prepared by solvent impregnation. The tapes contained the amount of resin which would fill the interstitial voids of the fabric, plus a constant excess to allow for flow during bond formation. (Details in Appendix, Section A.1.2)

Initial screening test results, using an aluminum single overlap shear specimen (per MMM-A-132) showed that the single overlap shear bonds had strengths comparable to the unidirectional carbon tow tapes previously tested (Table 5). However, examination of the failure surfaces revealed a lack of adhesion between the matrix resin and the Kevlar-49 fiber (Figures 3a&3b). The macrophotographs (1.7X) show that there was complete adhesive failure from the fabric surface. The photomicrographs (Figure 4a & 4b) reveal that there was complete adhesive failure, even to the point of leaving a replica of the individual fibers in the resin.

This same type of failure was also found in tensile shear tests with two commercial resin systems using a 120 style Kevlar-49 fabric as support (Table 5). These systems yielded strengths (ca. 2500 psi) similar to those found with the ADX-653 containing system and also showed the same adhesive failure of the resin to the Kevlar-49 fiber. Since this type of fabric-matrix adhesion failure appears to be common and fiber surface modification was beyond the scope of the contract, the ADX-653/Kevlar-49 fabric systems were submitted for fatigue testing.

4.3.2) Carbon Fabrics

Supported tapes were manufactured from the two carbon fabrics using the resin contents and manufacturing techniques mentioned in connection with the Kevlar-49 tapes. Initial aluminum single overlap shear strengths were comparable to both the Kevlar-49 and HTS unidirectional tape adhesives. In contrast to the Kevlar-49 supported adhesives, the WCG appeared to fail along a plane near the center of the fabric (Figure 5b). Photomicrographs of this surface (Figure 6) indicated that this fabric behaved as if it were two layers. Woven carbon, apparently undamaged by failure, was seen on both surfaces and no adhesive was seen. This adhesive film had to be manufactured by solvent impregnation techniques using a low viscosity resin solution. Past experience has indicated complete wet-out of the fabric using this technique. The film weights were designed to have the majority of the resin filling the interstitial voids with only a thin film left on the surface of the uncured film. Visually, this appears to be what was manufactured. Since some compaction of the bond occurred during cure, with the significant resin flow, it appears that complete wetting should have occurred. However, no effort was expended to determine whether or not the fabric was completely wetted out and the reason for the phenomena remains unexplained.

The adhesion between the PWA fabric and the ADX-653 resin system appeared to be the best of all systems examined. The initial screening results, Table 5, revealed strengths equivalent to the nylon supported control. Examination of the failed bond revealed that the failure occurred in the resin near the resin/fiber interface (Figure 5a). This finding was reinforced by microscopic examination (Figure 4), which showed a failure in the resin, but near the fabric surface. The fabric remained intact with only a small amount of fibers being removed with the resin.

4.3.3) Boron Filament Reinforced Adhesives

Boron filament reinforced unidirectional adhesive tapes have been manufactured using 4 mil Type HS Boron filaments with the ADX-653 resin system. These tapes were manufactured by winding the filament around a 4 inch diameter drum and impregnating with 3 mil unsupported ADX-653 under vacuum. The tape was then cut off the drum and an additional adhesive layer was applied to the drum side. Initial screening tests using aluminum single overlap shear specimens, indicated the system has strength equivalent to the nylon supported control. Visual and microscopic examination of the failed bondlines showed an apparent lack of adhesion between the resin and boron filament.

4.3.4) Randomly Oriented Carbon Fiber Tapes

Type A carbon fiber, chopped to 1/8" lengths, has been used to manufacture randomly oriented carbon fiber tapes. "AS" fiber was used because of its availability. Its fiber modulus is very similar to HT fiber (32 vs. 35 X 10^6 psi respectively). This 1/8" length gives an aspect ratio of approximately 500. Although this fiber length precludes completely random orientation in the bondline it is the shortest fiber available.

Adhesive tapes were manufactured from these mats by vacuum impregnation using unsupported plies of ADX-653. The resultant tapes had a weight of approximately 0.080 lb./ft.^{2} and a fiber wt.% of 17%. This was comparable to the HTS unidirectional tapes used in Task 1. Aluminum single lap shear screening tests with these adhesives gave strengths comparable to the nylon control system. Examination of the broken bonds showed the failure occuring in the resin and near the resin/metal interface.

4.4) FATIGUE SCREENING RESULTS

4.4.1) Ultimate Shear Strength

The ultimate shear strengths as determined using the double lap shear specimen (Table 7) are 50 to 100% higher than those determined using the aluminum single lap shear specimen. Some of this difference can be explained by the higher modulus of the titanium but the significantly lower peeling stresses which are innate in this specimen should also account for some of the difference.

In contrast to results reported in Task 1, results using titanium test specimens along with the high modulus fiber reinforced systems, approached the ultimate shear strength of the nylon control. High strengths were found with a 3 tow per inch unidirectional HTS carbon tow tape, the boron unidirectional tape, and the PWA carbon fabric reinforced system.

4.4.2) Fatigue Results

4.4.2.1) Carbon Fabrics: Exceptionally high resistance to fatigue at 50% of ultimate shear strength was seen with the ADX-653/WCG carbon combination. Of the three specimens tested in fatigue, one failed at 1.7 million cycles which the other two were removed, intact, at 2.0 and 2.5 million cycles (Table 7). However, this system had the lowest ultimate shear strength tested, 3545 psi, and consequently the fatigue loading was only 1775 psi.

Examination of the fracture surface at 2.5X revealed the same type of failure as was seen with the aluminum single lap shear testing mentioned earlier. The failure occurred along the plane of the fabric and near its center point.

The PWA supported ADX-653 gave significantly greater ultimate shear strengths and failed at an average of 128,000 cycles when fatigued at 50% of this strength. Examination of the broken bond also showed that the failure was the same type as seen with the single overlap shear specimens. The failure occurred in the resin near the resin-fabric interface.

4.4.2.2) Kevlar-49 Fabrics: ADX-653 supported with style 120 Kevlar-49 gave 4285 psi ultimate shear strength and was consequently loaded at 2140 psi in fatigue. The three specimens failed at an average of 976,000 cycles, the highest combination of ultimate and fatigue strengths obtained. The broken bond showed what appears to be a complete lack of adhesion of the resin system to the fabric.

The style 220 Kevlar-49 supported ADX-653 failed at an average of 177,000 cycles when fatigued at 2160 psi. The broken bond revealed the same lack of adhesion between the resin and fabric as was seen with the style 120.

4.4.2.3) AS Fiber Mat: When the ADX-653 system reinforced with randomly oriented Type AS mat was fatigued at 2265 psi (50% of its ultimate shear strength) it failed in an average 445,000 cycles.

Examination of the failed bondline revealed that the fiber/resin combination was unaffected by fracture, the failure occurred at the metal/resin interface. In some instances, the failure surface transferred from one metal interface to the other. It did this by shearing through the fiber composite and no evidence of fiber debonding from the matrix was seen.

4.4.2.4) 4 mil Boron filament: The ADX-653 film using the 4 mil boron filament as reinforcement gave the highest ultimate shear strength of any high modulus fiber (5670 psi). However, it behaved extremely poorly when tested in fatigue at 50% of its ultimate strength, failing in an average of 2300 cycles. This was the only system with lower fatigue resistance than the knitted nylon control.

There appears to be a severe lack of adhesion between the resin and the filament. A replica of each filament was seen in the resin. The filaments were used as received and were assumed to have an epoxy compatible finish. This lack of adhesion on failure is of the same degree, visually, as was noticed with the Kevlar-49 fabrics. However, it must be assumed that the actual physical level of adhesion was greater to the Kevlar-49. No further work is planned with the boron filaments as modification of the adhesion to the reinforcement is beyond the scope of this work.

4.4.2.5) Knitted Nylon: This system was used as a control and produced the highest level of ultimate shear strength of any system (Table 7/5810 psi). It failed at an average of 4900 cycles when fatigued at 2905 psi. The system failed by fracture of the resin near the metal interface. The volume around the support was left relatively undisturbed.

4.5) DISCUSSION

The fatigue screening results of Table 7 add very strong support to the concept of fatigue life improvement by bond reinforcement with high modulus fibers. Several attempts have been made to find a correlation of fatigue resistance with important adhesive bond parameters.

4.5.1) Fiber Modulus

Recent literature 3,4,5) has shown correltation of fatigue resistance of composites with reinforcing fiber modulus. This could be interpreted as a reduction in composite deflection at the same applied stress level. However, correlation with fiber modulus was not apparent in the present work (Figure 8). Poor fatigue resistance was obtained with both the nylon knit ($E=4 \times 10^5$ psi) and 4 mil boron filament ($E=5.8 \times 10^6$ psi). The data from the remaining high modulus fibers clustered together with a downward trend of fatigue resistance with fiber modulus. However, large bondline thickness variations, different fiber arrangements, and different types of fracture upon failure makes any correlation difficult.

4.5.2) Bond Line Thickness

Several investigators have shown the importance of the bondline thickness on adhesive properties. Frazier[6] has shown in thick adherend tests that bond line thickness has a large effect on the quasi-elastic stiffness. Also, it has often been shown that the nature of the failure surface and the strength in peel tests vary considerably with bondline thickness.

No correlation of fatigue life and bondline thickness was apparent in the work so far completed (Figure 9). Variation in the type of fabric, its construction and the type of fiber occurred in most tested systems,so additional effort is needed to isolate these parameters and define the effect of bondline thickness.

4.5.3) Fatigue Stress Level

From a plot of fatigue stress level versus fatigue life (Figure 12) it appeared that, with the exception of the boron unidirectional fabric and the nylon tricot, the fatigue data was inversely proportional to the applied stress level. From the present data, no correlation can be made between the level of fatigue improvement and fiber modulus or fabric construction. In addition, it appears that the level of ultimate shear strength is not system dependent. An unknown parameter, perhaps fiber surface area or level of adhesion, may be influencing the results.

Also plotted in Figure 10 is one data point of the nylon control which when fatigued at 1800 psi (30% of ultimate) failed at 72,000 cycles. Connecting the two nylon data points forms a line parallel to that which can be drawn through the carbon and Kevlar-49 data. The second curve lies about 1.5 logarithmic units below that of the high modulus data. It thus appears that the use of high modulus reinforcements results in an increase in fatigue resistance of about 50 fold. The improvement in fatigue resistance is real and reproducible. However, the nature of the "necessary and sufficient" parameter which controls the level of improvement is not yet well defined.

4.5.4) Fracture Type

The apparent fact that the type of fiber is not the controlling factor in fatigue is emphasized by the attempted correlation of fatigue resistance and fracture type (Table 8). Three types of fracture were seen; 1) in the resin, 2) at the resin/fiber interface, and 3) in the fabric. The third type was descriptive of the WCG failure, and this produced the highest fatigue resistance numbers of all. The nylon (5000 cycles), PWA carbon (128,000 cycles) and the AS fiber (445,000 cycles) exhibited failure in the resin, while the boron (2000 cycles) and the style 120 Kevlar-49 (976,000 cycles) failed at the fiber/resin interface. There was obviously no correlation with failure type.

The lack of correlation implies that the gross mode of failure was not representative of the mechanism which initiated fatigue failure. Only a small number of the fatigue specimens were critically examined microscopically (the nylon and the HTS tow reinforced systems). No reproducible difference has been seen between the two.

4.6 CONCLUSIONS

The 10^5 cycle fatigue life of an adhesive system reinforced with woven high modulus fibers was similar to that of the system containing unidirectional fibers of the same type. This conclusion appears to hold because of the apparent correlation of fatigue life at 50% of the ultimate shear strength with the maximum applied fatigue stress. Although the HTS unidirectional tow system produced the shortest fatigue life at the highest fatigue stress of any experimental system, its fatigue resistance should equal the other reinforcements if it were stressed at an equivalent fatigue stress.

The most promising woven systems were chosen for continued work since their response to stresses applied at other than 0° to the major fiber axis should be more consistant.

5.0 PHASE I, TASK 3 FIBER VOLUME VARIABLE

5.1 BACKGROUND

The composite properties which can be expected from a resin/high modulus fiber combination are a function of the bulk properties of the components and the volume percent of each in the composite. This concept should also be operative within an adhesive. In past experimental work, improvement of fatigue strength on inclusion of reinforcing fibers was accompanied by an increase in joint stiffness. This joint stiffness or modulus is influenced by the fiber volume content. Therefore, the effect of fiber volume content on the fatigue strength of the adhesive was investigated.

The possible fiber/volume contents of a fabric/resin adhesive system are limited by fabric thickness and construction. Any decrease in fiber volume content below a level characteristic of the fabric would result in a bond line in which the fiber was inhomogeneously distributed. More ready variation of fiber/resin ratio can be obtained using fibers in less ordered structures than present in woven fabrics. Therefore, the influence of fiber volume content was measured using unidirectional graphite tow.

5.2) MANUFACTURE OF VARIABLE FIBER VOLUME SYSTEMS

Use of shims is often the easiest technique to use in controlling the fiber/resin volume ratio in a bondline. This technique, however, has two drawbacks: first, it is not readily adapted to the manufacture of complex double lap shear specimens such as are required for fatigue screening tests; second, if the overall fiber/resin volume ratio is so controlled, the fiber is not necessarily homogeneously distributed throughout the bondline.

Because of these drawbacks, initial attempts at controlling the fiber/resin ratio involved manipulation of three parameters which can influence adhesive bondline thickness. These were: 1) Variation of the wet adhesive fiber/volume content and film thickness, 2) variation in the cure pressure, and 3) variation in the cure heat-up rate. Variation of the amount the fiber is compressed and the amount of resin available for flow during cure could conceivably result in a variation in fiber/resin ratios of the final bondline.

None of these techniques gave reproducible or readily controllable variations in the bondline fiber/resin ratio (Table 9). Variation in the fiber volume in the uncured adhesive from 14.3% to 50% gave no appreciable variation in the cured bondline fiber/resin volume ratio. Variation of the cure pressure from 15 psi to 75 psi using an adhesive containing 30.8% fiber by volume gave fiber volumes from 42.9% for the 15 psi cure to 46.6% for the 50 psi cure. The 44% fiber volume level found with the 75 psi cure indicates that there is no significant variation in this property with variations in cure pressure.

The amount of resin flow can sometimes be varied by partially staging the adhesive at a temperature lower than the final cure temperature. Use of a high resin content adhesive (14.3% fiber volume) and prestaging at 250°F from 15 to 60 minutes did not result in any significant variation in the fiber volume content in the bond line. In this work the cured shear strength at 75°F did not vary significantly, suggesting that the resin systems all had flow sufficient that the final fiber volume content was not affected by the variation of cure conditions. Since bondline thickness, fiber resin ratio and the amount of fiber in the bondline could not thus be independently varied, no estimate of their individual influence on adhesive performance was obtained.

Some variation in fiber volume of the cured bondline might be possible, at the sacrifice of control of bondline thickness, by variation in the amount of tow used per inch of width of adhesive tape. Such adhesive tapes were manufactured using from 3 to 6 tows of high modulus fiber per inch of width. Variation of the fiber volume in the cured bondline in single overlap shear panels was found only when the assemblies were shimmed to a 10.5 mil thickness (Table 10). When shims were not used control over fiber volume content was absent. There were no significant variation in shear strength.

5.3) FATIGUE SCREENING RESULTS

Titanium double overlap specimens containing the varying number of tow per inch width tapes, for use in fatigue screening tests, were cured without shims(Table 11). In contrast to the shimmed tensile specimens described previously, the bond lines varied from 8 mils with a 3 tow per inch specimen to 20 mils with the 6. Ultimate shear strengths varied from 3600 psi in the case of the 3 tow per inch tape to 4700 psi for the 4 tow per inch tape.

The fatigue life appears to be adversely affected by too thick a bond line (Table 11). In the case of the 3 and 4 tow per inch tapes the 50% ultimate shear strength fatigue life were 118,000 cycles and 257,000 respectively. However, when the bond line was 20 mils (the 6 tow per inch tape) a fatigue life of 26,000 cycles was observed. The low value of the fatigue life of the 3 tow/in. sample may not be real since a repeat run gave an equivalent fatigue life but at a 1000 psi higher fatigue stress (Table 7, Figure 10). This data and that from the 4 tow/in. system both fall in the curve correlating fatigue resistance and fatigue stress (Figure 10) perhaps indicating that differences in fatigue resistance were due to differences in ultimate shear strength. The 6 tow per inch tape was definitely inferior to the others with a 10 fold difference in fatigue life observed between the 4 and 6 tow per inch tape. Cured bond line fiber volume contents were not measured. However, it can be hypothesised that there is probably no significant variation in this parameter between any of the three tapes used in this experiment. This conclusion is supported by the earlier single lap shear adhesive experiments (Table 10) in which the unshimmed adhesive showed no significant variations in cured fiber volume percent between the 3, 4 and 6 tow per inch adhesive films.

5.4) CONCLUSIONS

The effect of variable fiber/resin volume ratios at constant bond line thickness on the fatigue life of an adhesive bond line has not been demonstrated. However, at fairly constant fiber volume ratios, there is some indication that the fatigue life improvement decreases above some bond line thickness. Below that level (ca 12 mils) performance appears constant. This data, however, does show almost a 100 fold improvement in fatigue life over the nylon control by bond line reinforcement with a high modulus fiber.

6.0 PHASE II, TASK I <u>DETERMINATION OF THE EFFECT OF SUPPORT ORIENTATION</u>

6.1) BACKGROUND

Evaluation of the degree to which the fatigue improvements realized with the different high modulus reinforcements and fiber distributions are isotropic is essential in view of the multidirectional nature of loading of composite structures. Loading cannot be unidirectional in a complex assembly. Property improvements along a single axis will have little impact on component design if the properties in other directions remain near the base line level. In the composite laminate itself, unidirectional plies are laid up at angles to one another to develop multidirectional properties. This approach is not practical for structural adhesives within the thickness constraints of a bond line. Phase I efforts evaluated three approaches more suitable for use in an adhesive bond line: unidirectional high modulus fibers, woven fabrics and a high aspect ratio chopped fiber mat. In all cases, the extent of any non-isotropic property must be determined.

Testing at more than one angle to a fabric type support is especially important in view of the proposed mechanism for the improvement of fatigue properties due to the inclusion of high modulus materials in the bond line. The improvement in fatigue resistance could result from a decrease in the stress concentrations at the edges of a bond (Figure 2) by transfer of part of this stress to the interior of the bond by the high modulus fibers. This would best be accomplished by fibers running at an angle of 45° to the adherend surface. However, no fabric can distribute its fibers at this angle in both weave directions. In a plain weave fabric the fill direction will generally consist of relatively straight fibers while in the warp direction the fibers are woven over and under the fill fibers following a sinusoidal path. Tensile strength in these directions will vary with the number of fibers per inch but the fill direction will be the stronger for a fabric with equal numbers of fibers in each direction. By testing woven fabrics in both the fill and warp direction the importance of fiber path to fatigue improvement can be determined. Composites made of woven fabrics generally exhibit minimum properties when tested at 45° to the warp. Fatigue testing will allow a realistic appraisal of the usable improvements offered by each system.

6.2) SYSTEM SELECTION

Three high modulus fiber supports were selected for examination in Phase II, Task 1: 1) style PWA carbon fabric, 2) style 120 Kevlar-49 and 3) a chopped AS fiber random mat. These supports were selected on the basis of their maximum combination of ultimate shear strength and fatigue resistance. For practical design reasons, high ultimate shear strengths are important and should be greater than 5000 psi. Adhesive systems having less than 4000 psi shear strengths are not generally suitable for use in composite aircraft manufacture.

6.3) SPECIMEN DESIGN

The adhesive films using the aforementioned three reinforcements were prepared and assembled into titanium to titanium double lap shear test specimens. These test specimens were different than those used in Phase I and reflect the following design philosophy and acceptance criteria:

a. The adherend material and thicknesses were typical of aircraft applications.
b. The thicknesses of the inner and outer adherends (T_i & T_o were selected so the joints would be stiffness balanced).
$E_i T_i = 2E_o T_o$
c. The lap length was selected to insure that neither adherend would fail. This selection was made by use of $E_i T_i$ <u>versus</u> joint strength curves for various lap lengths. This data was

developed in the design of a current advanced fighter aircraft using a different adhesive system. However, the specimens designed using these curves meet the 3 selection criteria as long as the area under the stress strain curves is not significantly greater than that of the adhesive used in developing the curves. In addition a safety factor of 50% was included in the design.

6.4) RESULTS

6.4.1) Style 120 Kevlar-49

Titanium double lap shear specimens (Figure 11) were manufactured with the warp direction of style 120 Kevlar-49 fabric lying 0°, 45° and 90° to the direction of the applied stress. Variation of this parameter had no effect on the 75°F ultimate shear strength (Table 12). In addition, these strength levels were equivalent to those observed in the Phase I work. The failure mode of these specimens in shear tests occurred at the fabric resin interface in the same manner as noticed in Phase I testing.

The applied fatigue stress level used (2050 psi) was 50% of the average of static shear strengths of all three fabric orientation direction. This was similar to the 2140 psi applied stress used in Phase I work.

Fatigue lives obtained varied from 182,000 cycles at 0° to greater than 1,350,000 at 45° with a value of 500,000 cycles occurring at 90° (Table 12, Figure 12). However, the 0° value is much lower than obtained in Phase I tests (182,000 vs. 975,000 cycles). Reasons for this difference were not determined. Microscopic examination of the fatigue specimens showed no visible differences in failure mode which could be correlated with the differences in fatigue life.

6.4.2) Style PWA Carbon Fabric

The ultimate shear strengths of the style PWA/ADX-653 combination, when tested at various orientation angles, were about 4100 psi, approximately 20% lower than those seen in Phase I. There were slight differences in ultimate shear strength between 0° and 90° when compared to the 45° fabric orientation. The 3 data sets were considered as one and the fatigue test conducted at 50% of the grand average of 2080 psi. 2635 psi fatigue loading was used in Phase I work.

The fatigue data (Figure 12) showed no large effect due to fabric orientation angle. The test values ranged from 61,000 to 179,000 cycles. The results at 0° and 45° were nearly equivalent. The minimum value was found at a 90° orientation. Although these fatigue cycles to failure were similar to Phase I data, they were obtained using a 550 psi lower stress level. Microscopic examination and comparison of the two test sets have shown no visible differences. In all instances failure occurred at the resin-metal interface.

6.4.3) Type AS Randomly Distributed Fiber Mats

ADX-653 reinforced with Type AS fiber mats gave ultimate shear strengths which varied by approximately 25% when tested at different orientations (Table 12). These values varied from 4750 psi, equivalent to Phase I data, to 3540 psi. There was a 2 mil difference in average bond line thickness. A difference of this magnitude is usually accepted as being experimental difference usually resulting in no performance difference.

These mats were manufactured by dispersing the fibers in water at approximately 0.5 wt % concentration followed by a rapid water removal. Because of the preparation technique there should not be any specific orientation of the fibers. The observed variation in shear strength with test direction of the supplied adhesive mat should not be due to varied fiber orientation. However, the difference in static strengths obtained was too great to allow an averaging for fatigue testing purposes. Therefore, the 0° specimens were stressed at 2375 psi for fatigue testing and the 90° group at 1770 psi.

This system, when fatigue tested at 0° to the arbitrarily chosen mat orientation, failed in an average of 9000 cycles, roughly 50 times lower than that observed in the Phase I testing (Figure 12). When fatigue tested at 90° the result of 30,000 cycles to failure was about 15 fold less than Phase I results. Visual examination and comparison of the fatigue failure surfaces gave no indication as to the cause of the fatigue strength difference.

There being no experimental or visual reason for this gross difference in fatigue life, the tests were repeated at an orientation of 0° using specimens from both Phase I and Phase II. The ultimate shear strengths (Table 13) increased to approximately 4900 psi, roughly equivalent to the strength seen in Phase I. When fatigued at 50% of this strength, 2400 psi, fatigue improved as compared to the earlier Phase II work, but not to the level of Phase I. This difference between Phase I and Phase II, therefore, is real and appears to be due to some unknown variable in the manufacture of the mat supported adhesive.

6.5) CONCLUSIONS

The fatigue life improvement due to reinforcement with high modulus fibers appears to have a minimal dependance on reinforcement orientation. The PWA graphite system shows only a small dependance. The results using the style 120 Kevlar-49 was confused by the unexpected low data point at 0°. If this data is combined with earlier Phase I data, no significant dependance on fatigue life on fabric orientation was indicated. The random fiber distribution of the type AS graphite mat reinforced system precludes any conclusions as to its orientation effect.

The style 120 Kevlar-49 and the style PWA graphite reinforced ADX-653 were selected to investigate fatigue life improvement using composite adherends.

7.0 PHASE II, TASK 2, FATIGUE LIFE WITH COMPOSITE ADHERENDS

7.1) BACKGROUND

Structural members consisting of both graphite/epoxy and boron/epoxy composites are becoming common on current advanced aircraft. Any program which evaluates fatigue improvement of an adhesive should include these materials as adherends in addition to the metallic materials commonly used. These composite members should be of a type and design representative of those used on current advanced aircraft. The two adhesive/reinforcement systems which exhibited the least dependance of fatigue life on stress direction were examined using both graphite/epoxy and boron/epoxy composite adherends.

7.2) RESIN/REINFORCEMENT SELECTION

ADX-653 reinforced with either style 120 Kevlar-49 or style PWA graphite fabrics were selected to conduct the evaluation of fatigue improvement using composite adherends. These systems were selected during the stress orientation phase as having the highest combination of initial ultimate shear strength as well as retention of fatigue life under 50% of that stress level. The third system evaluated, ADX-653 reinforced with type AS carbon fiber mats, was eliminated due to poor fatigue properties.

7.3) EFFECT OF COMPOSITE PLY ORIENTATION

The composite adherends for this task were typical of those used for advanced aircraft applications. With some reduction in total number of plies to reduce cost and fabrication time. The graphite/epoxy adherends were 11 ply (±45,0,0,0,0,90,0,0,0,0±45) AS/SP286 (Figure 13). The boron/epoxy adherends were 13 ply (±45,0,0,0,0,90,0,0,0,0±45), AVCO 5505 (Figure 14). The metal adherend in both cases was Ti-6Al-4V. The adherends were stiffness balanced and lap length was chosen to assure failure in the bond line at a load well below the ultimate strength of the adherends. Initial double lap shear strengths with style 120 Kevlar-49, style PWA Carbon, nylon knit reinforced ADX-653 were unrealistically low when tested with the composite adherends (Table 14). As an example of these low strengths, the nylon knit supported adhesive control gave 2600 psi with the boron/epoxy composites and 2790 psi with the graphite/epoxy composite. Tensile shear strengths of 5360 psi were obtained when the test specimen was made completely of titanium. The style 120 Kevlar-49 gave 1950, 2460 and 4040 psi tensile strengths with the boron, graphite and titanium specimens respectively. A similar decrease in strength using the composite adherends was seen with the style PWA graphite.

The probable cause for the low strengths was the orientation of the outer plies of the composite adherends used. A composite with an outer ply of ±45° is typical of composite to composite joints. However, when used in a composite to metal joint this 45° ply causes a modification of the stress transfer type from a shear into a peeling mode. A 0° outer ply design should give a shear mode of stress transfer and consequently a higher joint strength.

New composite to titanium double lap shear specimens were, therefore, constructed using the Phase I type of double strap specimen (Figure 15). The composite adherends were constructed with a 0° outer ply and have the following construction: graphite/epoxy (0,0,0,0 Narmco 5208/T-300. Because of time and financial considerations, boron/epoxy adherends were not manufactured in this phase. The fatigue demonstration phase, Phase III, will include a large amount of testing using boron/epoxy/titanium adherends. In addition, a non-stiffness balanced 4 ply composite design was chosen over a stiffness balanced 3 ply to insure that composite failure would not occur.

7.4) RESULTS

Ultimate shear strengths equivalent to those found with all titanium specimens were obtained when the new 0° composite specimen was tested (Table 15). Specifically, the style 120 Kevlar-49 reinforced adhesive gave 3540 psi with 0° composite vs. 2460 psi for the 45° outer ply adherend. The style PWA carbon gave 4540 psi vs. 1710 psi for the 45° composite. The nylon control exhibited strengths of 5200 psi and 2790 psi for the 0° and 45° outer ply composites respectively. This data strongly reinforced the hypothesis that a 45° outer ply was not optimum for composite to metal joints.

The fatigue life times of the 3 systems, tested at 50% of their ultimate shear strengths were longer than those obtained with all-metal joints. This comparison of the composite to all metal joints was respectively style 120; 1,120,000 cycles vs. 976,000 style PWA 462,000 cycles vs. 128,000 cycles, and nylon knit 11,000 vs. 5,000 cycles. This comparison was drawn with tests conducted at 0° to the major axis of the fabric in the same specimen design. The style 120 Kevlar-49 reinforced specimens were removed from the fatigue machine after an average of 1,300,000 cycles and restressed at 60% of the systems ultimate shear strength. At this stress the average fatigue life was 194,000 cycles.

7.5) CONCLUSIONS

The improvement in fatigue life produced by bond line reinforcement with high modulus high strength fibers appeared to be real for not only titanium-titanium joints but also joints using titanium and graphite/epoxy composite adherends. The ultimate shear strengths for the composite-metal joint were approximately the same as with the all-titanium joints. The improvement in fatigue life time appears to be somewhat greater with the titanium-composite specimens than with the all titanium system.

The style PWA carbon was selected as the optimum reinforcement for use in the Phase III fatigue demonstration for the following reasons:

1) Greater ultimate shear strength (4540 psi vs. 3450 psi for style 120 Kevlar-49)
2) A better combination of fatigue life and high ultimate shear strength. The style PWA exhibited a fatigue life of 462,000 cycles at an applied stress of 2270 psi. The nylon control had a fatigue life of 11,000 cycles at a loading of 2570 psi.

3) Better adhesion of resin to fabric than with style 120 Kevlar-49.

8.0 PHASE III DEMONSTRATION OF FATIGUE RESISTANCE

8.1) BACKGROUND

A significant increase of the 10^7 cycle fatigue strength is the necessary proof of the concept of fatigue life improvement by high modulus fiber reinforcement of the bond line. The gain in terms of advanced aircraft manufacture and performance cannot be gauged without this value.

From the results of Phase I and Phase II screening tests, the ADX-653 resin system reinforced with style PWA graphite fabric was chosen to determine the extent of fatigue life improvement over that obtained with conventional nylon knit supported adhesives. Both graphite/epoxy and boron/epoxy to titanium adherends were used due to their increasing importance in advanced aircraft. The fatigue tests were conducted at both 0° and 45° fabric orientations to further determine the degree of isotropicity.

8.2) SPECIMEN DESIGN

Double lap shear test specimens were used to determine the fatigue strengths (Figure 15). They were manufactured using the optimized composite/titanium design, used in Phase II, Task 2 work. The composites had the following constructions: boron/epoxy - 4 ply (0,0,0,0 AVCO 5505), graphite/epoxy - 4 ply (0,0,0,0, Narmco 5208 T-300). A style 104 glass scrim cloth used as a carrier in the uncured boron/epoxy prepreg, was cured into the test specimen in contact with the adhesive. No adverse effects on fatigue properties have been ascribed to the presence of this glass fabric

The composite/titanium double lap shear specimens were not stiffness balanced due to required specimen design modification described in Phase II work. The composite adherend thickness had to be increased beyond the stiffness balanced state in insure sufficient tensile strength. Use of thicker titanium adherends; ie., 0.078 inch for the boron/epoxy specimen to reestablish the stiffness balanced state was not possible due to time and cost considerations. According to the design staff of McDonnell, the ultimate shear strength of the boron/epoxy and graphite/epoxy specimens were 65% and 82%, respectively, of the expected strengths of stiffness balanced specimens of the same type. The lack of balance has, in past studies, shown no observable effects on fatigue resistance.

8.3) RESULTS

8.3.1) Ultimate Shear Strength

The ultimate tensile shear strengths of the style PWA reinforced specimens were very similar to those of the nylon knit control (Table 16). The strengths varied from 4320 psi (0° orientation PWA/graphite/epoxy adherends) to 4915 psi (45° orientation PWA/boron/epoxy adherends). A comparison of fatigue strength on the basis of both equivalent percent of ultimate strength and equivalent applied fatigue stress was made possible by these equivalent ultimate strengths.

The -65°F ultimate strengths of the nylon control system (Table were 1000 psi lower than those determined using style PWA (ie; 3890 psi compared to 4910). The 350°F strengths of the control, in contrast were 400 to 600 psi greater than the PWA reinforced system. The type of adherend influenced the levels of strength at 350°F. The strengths determined using the graphite/epoxy adherend specimen were consistantly 700 psi greater than those of the boron/epoxy specimen.

8.3.2) Fatigue Resistance

The results of the fatigue testing are presented in Table 17 and Figures 16 to 21. Data was scattered and individual fatigue life values within a test set varied from one half to a full order of magnitude. Statistical analysis of the data was difficult due to the small data set (5 specimens) and the fact that a number of tests were stopped before failure when they had fatigue lives much beyond 10^7 cycles. In comparison of the fatigue results two criteria were used which caused a bias in the reduced data. These were:

a) Smooth curves describing the fatigue life of a system were drawn using the arithmetic mean of each data set. Shorter lifetime specimens in a set were emphasized by the use of the mean, especially in the data sets with a large degree of scatter.

b) In several sets, the data included 10^7 cycle runout points. In determination of the mean with this data, the number of cycles at which the specimen was removed from the test machine was used as a real data point.

This criteria biased the mean toward shorter lifetimes. The results from the PWA reinforced specimens and one nylon system were influenced by this bias. Therefore, with one exception, actual differences in fatigue strength between the two reinforcements were larger than indicated. The following table lists the expected bias due to inclusion of runout data.

Expected Bias in Fatigue Data Reduction

Reinforcement	Adherend	Support Fabric Orientation	Fatigue Stress Percent of Ultimate	Bias Due To Above Described Data Treatment
Nylon	boron/epoxy	0°	40	None
Nylon	boron/epoxy	0°	36.6	None
Nylon	boron/epoxy	0°	30	Low
Nylon	graphite/epoxy	0°	45	None
Nylon	graphite/epoxy	0°	40	None
Nylon	graphite/epoxy	0°	30	None
PWA	boron/epoxy	0°	50	None
PWA	boron/epoxy	0°	45	None
PWA	boron/epoxy	0°	40	Low
PWA	boron/epoxy	45°	50	None
PWA	boron/epoxy	45°	45	None
PWA	boron/epoxy	45°	40	Low
PWA	graphite/epoxy	0°	60	None
PWA	graphite/epoxy	0°	55	None
PWA	graphite/epoxy	0°	50	Low
PWA	graphite/epoxy	45°	55	None
PWA	graphite/epoxy	45°	50	None
PWA	graphite/epoxy	45°	45	Low

Reasons for the large data scatter are not known at this point. Microscopic examination of the failure surfaces of one test set which varied in fatigue resistance by two orders of magnitude did not reveal any observable differences.

Initially a significant amount of metal fatigue failures in the grip area occurred. These were the result of testing at high stress levels for unusually long lifetimes (as compared to the state of the art adhesives). The notch sensitivity of titanium has been offered as the reason for this occurrence. Such metal fatigue problem was essentially eliminated by the use of a fiberglass composite bonded onto the gripping surface of the test specimen. This precured reinforcement, a 9 ply laminate of F-161 (Hexcel) was bonded to the glass shot-peened titanium surface with EC-2216 (3M) or FM-123-2 (American Cyanamid).

8.3.2.1) Knitted Nylon Control Reinforcement The fatigue life (Table 17, Figure 16) of boron/epoxy adherends bonded with ADX-653 reinforced with the nylon knit varied from a mean of 128,000 cycles at 1870 psi applied fatigue stress to greater than ten million at 1400 psi. Long and short lifetime values could be eliminated from these data sets by using the Dixon criteria(7) for elimination of outliers. An incorrect loading of the test specimen was considered as the most plausible reason for the long life values. These values were not eliminated because of the small (2%) variation in loading accuracy that has been determined with this test equipment. The one short lifetime value was eliminated because it (714,000 cycles) was so uncharacteristic of the set (four values greater than 10^7 cycles). The 10^7 cycle fatigue strength of this combination was thus determined to be 1400 psi of 30% of the ultimate shear strength.

The fatigue life times of the ADX-653/nylon knit combination, (Figure 17) using graphite/epoxy adherends, varied from a mean of 28,000 cycles at 2200 psi to 4,050,000 cycles at 1470 psi. All data points were used in the determination of these means. The 10^7 cycle fatigue strength was shown to be 1450 psi or 28.5% of the ultimate shear strength.

8.3.2.2) Style PWA Graphite When used to bond boron/epoxy adherends to titanium at a fabric orientation of 0°, the mean fatigue lifetimes of the PWA/ADX-653 combination varied from 109,000 cycles at 2320 psi to 6,000,000 cycles at 1860 psi. This latter value had been biased toward shorter lifetimes by use of 10^7 cycle runout data. The 10^7 cycle fatigue strength was 1900 psi 40% of its ultimate shear strength (Figure 18).

The mean fatigue lifetimes of the same system with the PWA oriented at 45° varied from 55,000 cycles at 2460 psi applied fatigue stress to 8,670,000 cycles at 1970 psi (Figure 19). Again the latter value was biased low by use of runout data. The 10^7 cycle fatigue strength was 1950 psi (40% of ultimate strength).

Using test specimens consisting of graphite/epoxy and titanium adherends, the range of mean fatigue lifetimes of the PWA/ADX-653 combination were determined as; with the 0° orientation, 98,000 cycles at 2590 psi to 6,130,000 cycles at 2160 psi and with the 45° orientation, 193,000 cycles at 2480 psi to 7,730,000 cycles at 2030 psi. The same statistical analysis and rejection criteria were applied as in other data sets. None of the individual data was eliminated. 10^7 cycle bias appears in both data sets. The 10^7 cycle fatigue strengths thus determined were; at 0° orientation, 2150 psi and 50% of ultimate strength, and at 45° orientation, 2000 psi and 45% of ultimate strength.

8.4) DISCUSSION

8.4.1) Fatigue Strength Comparisons with the Nylon Knit Control

A comparison of the fatigue strengths of the nylon control and style PWA reinforced ADX-653 on the basis of both equivalent fatigue stress and percent of ultimate shear strength was made possible because the ultimate shear strengths were essentially equal.

8.4.1.1) Equivalent Fatigue Stress The reinforcement of the ADX-653 with style PWA graphite fabric increased the 10^7 cycle fatigue life over the knitted nylon support from 1400 psi to 1950 psi using boron/epoxy adherends (Figure 22). This final value was an average of the 1900 psi determined at a reinforcement orientation of 0° and 2000 psi determined at 45°.

The 10^7 cycles fatigue strength of ADX-653 was thus increased by 36% due to inclusion of the PWA graphite fabric. A comparison of fatigue lives at equivalent stress levels indicated a 50 fold improvement in 10^7 cycle fatigue life due to use of the PWA graphite reinforcement.

When tested with graphite/epoxy adherends the reinforcement with PWA resulted in an increase of the 10^7 fatigue strength from 1400 psi to 2080 psi, an increase of 49% (Figure 23). Comparison at equivalent stress levels indicated an approximate 50 fold increase in 10^7 cycle fatigue resistnace.

8.4.1.2) Equivalent Percent of Ultimate Strength Comparison of the Style PWA reinforced ADX-653 with the nylon knit supported system at equivalent percent of ultimate shear strength, using boron epoxy adherends, showed an increase of the 10^7 cycle fatigue strength from 30% of the ultimate strength in the case of the knit fabric to 41.5% for the PWA support (Figure 24). This latter value was an average of the 40% and 41 % values observed when the PWA was oriented at 45° and 0° to the axis of stress application. This amounted to a 35% increase in the percent of ultimate shear strength which could withstand a fatigue exposure of 10^7 cycles.

An increase from 28.5% to 47.3% (average 0° and 45° values) of ultimate strength which could survive 10^7 fatigue cycles was observed when PWA was substituted for the nylon support in ADX-653 using graphite epoxy adherends (Figure 25). This increase in the percent of ultimate strength amounted to a 66% increase in fatigue resistance (at 10^7 cycles).

8.4.2) Effect of Reinforcement Orientation

Only a minimal effect on 10^7 cycle fatigue strength could be ascribed to the change of reinforcement orientation from 0° to 45°. This amounted to an increase of 100 psi (a change from 40 to 41% in the percent of ultimate strength which will withstand 10^7 cycles) when boron/epoxy adherends were used.

Using graphite/epoxy adherends, a change in orientation from 0° to 45° resulted in a decrease of 10^7 cycle fatigue strength from 2150 to 2020 psi, a decrease from 49.5% to 45% of the ultimate shear strength. These results reinforce the findings of Phase II, Task I that the angle at which this PWA fabric reinforcement was oriented to the stress application direction had little affect on the fatigue resistance of the adhesive.

8.4.3) Effect of Adherend Type

There was a small but real difference in the fatigue life of the PWA/ADX-653 combination depending on whether the composite adherend was boron/epoxy or graphite/epoxy. At 0° to the stress, the fatigue strength using graphite/epoxy adherends was 2150 psi compared to 1900 psi for the boron/epoxy substrate (Table 18, Figure 26). On a basis of percent of ultimate strength the 10^7 cycle fatigue strength of the graphite adherend system was 49.5% compared to 40% for the boron. This large difference is in part due to the greater ultimate strength of the boron adherend system (4645 psi) compared to the 4320 psi of the graphite adherends.

At a fabric orientation of 45° the difference measured was smaller. No significant difference (Table 18, Figure 27) was measured on a stress basis; 2020 psi and 2000 psi for the graphite and boron adherend systems respectively. Measured on the basis of percent of ultimate strength in 10^7 cycles fatigue tests values of 45 and 40% were determined for the graphite and boron systems respectively.

There was apparently, an interaction between the type of adherend and the orientation of the fabric. The difference in fatigue life between the two adherends was accentuated by the angle of the major axis of the bondline reinforcing fabric makes with the axis of the adherend reinforcement. The PWA reinforcement appears to transfer stresses more efficient when parallel to the major axis of the adherends.

8.5) ADHESIVE PEEL STRENGTH

The peel strength of an adhesive can be significantly affected by modification of the type of support fabric and the fiber/resin volume ratio. This change is usually due to a change in the type or amount of honeycomb fileting or the type of fracture within the adhesive. The effect of substituting style PWA graphite for the nylon knit was estimated by comparing both the honeycomb and metal to metal peel strengths.

The honeycomb peel strengths observed were 7.4 in.lb/in. with the nylon support and 6.4 in.lb/in. with the PWA support. The values were lower than usually found with 350°F service adhesives due to the small size of the honeycomb filets. An increase in adhesive weight should increase the level of peel strength. The metal to metal climbing drum peel strengths of the two systems were 4.6 lb./in. and 8.3 lb./in for the nylon and PWA respectively. These values were in the range usually found with this adhesive resin system. Therefore, little reduction in peel properties of ADX-653 was shown by substitution of PWA support fabric for the nylon knit.

8.6) CONCLUSIONS

Initial conclusions from 10^5 cycle screening tests indicating improvement in fatigue resistance by inclusion of high modulus fibers in the adhesive bondline have been confirmed in fatigue tests extended to over 10^7 cycles. A significant improvement in fatigue life has been demonstrated over the nylon control on the basis of equivalent fatigue stress (36 to 49% increase in the 10^7 cycle fatigue stress) and at equivalent percent of ultimate stress (35 to 66% increase in the percent of ultimate strength which will survive 10^7 cycles). When compared on the basis of the number of cycles survived at the same stress, this difference amounts to a 50-fold increase over the nylon control.

Very similar results were observed whether the PWA reinforcing fabric was oriented at 0° or 45° to the axis of stress application. However, there appears to be some interaction with the type of adherend. The graphite/epoxy adherends apparently couple with the reinforced bond lines more efficiently then do the boron/epoxy. This results in a consistantly larger fatigue resistance when tested with graphite/epoxy adherends.

Substitution of style PWA graphite for the knitted nylon had essentially no effect on the honeycomb and metal to metal peel strength of the system.

9.0 REFERENCES

1) Merriman, H. R., "Research on Structural Adhesive Properties Over a Wide Temperature Range," WADC 56-320, April, 1957.

2) Boller, Kenneth H., "Effect of Single-Step Change in Stress on Fatigue Life of Plastic Laminates Reinforced with Unwoven "E" Glass Fibers," Technical Report, AFML-TR-66-220, September, 1966.

3) Dauksys, R. J., Pagano, N.J., Spain, R.G., "Graphite Fiber/Epoxy Resin Matrix Composites," 12th National SAMPE Symposium, Volume 12, Page AC.-9, October, 1967.

4) Hoggatt, J. T., "High Performance Filament Wound Composites for Pressure Vessel Applications," National SAMPE Technical Conference, Volume 3, Pg. 157, October, 1971.

5) Hanson, Morgan P., "Tensile and Cyclic Fatigue Properties of Graphite Filament Wound Pressure Vessels at Ambient and Cryogenic Temperatures," 15th National SAMPE Symposium & Exhibition, Pg. 249, April, 1969.

6) Frazier, Tom B., "A Computer Assisted Thick Adherend Test to Characterize the Mechanical Properties of Adhesives," Volume 2, pg. 71, 10th National SAMPE Technical Conference, October 7-10, 1970.

7) United States Department of Commerce, National Bureau of Standards, "Experimental Statistics," Handbook 91, October, 1966, Pg. 17-3.

APPENDIX

SECTION A.1) HIGH MODULUS FIBER REINFORCED ADHESIVE FILM MANUFACTURING TECHNIQUES

A.1.1) GRAPHITE TOW UNIDIRECTIONAL ADHESIVE FILM

A.1.1.1) Material Selection

The high modulus graphite fiber reinforced unidirectional adhesive films were manufactured using style HTS graphite tow made by Hercules. This material was selected for the following reasons:

a) It was material with which the concept was first demonstrated.

b) Material is readily available and in a convenient form

A.1.1.2) Assembly of tow into unidirectional form

The graphite tow was assembled into a unidirectional form using a pin jig. Removable pins were designed so that unidirectional tapes varying from 3 to 6 tow/in. could be assembled. The tow was wound onto the jig, secured with metal tabs and spread into as uniform a distribution as possible.

A.1.1.3) Fiber Consolidation

The unidirectional fibers were consolidated by impregnating with a dilute solution in acetone of the adhesive resin system. This was done by placing the pin jig with the fibers attached into a shallow pan and spreading a calculated amount of the solution over them. The amount of solution added was calculated to just fill the interstitial space within the unidirectional tow. The solvent was flashed off at a temperature of 200°F for 30 minutes. The flashing process was completed by exposure in a vacuum oven at 180°F for 20 minutes and 29 inches of mercury.

A.1.1.4) Adhesive Film Manufacture

The final adhesive film was manufactured from the consolidated unidirectional tow and an unsupported adhesive film by a heat lamination technique. This was performed in an electric press at an experimentally determined time, temperature and pressure. The laminate was placed under vacuum to avoid trapping air. Screening tests on the completed adhesive film were adhesive weight, volatile level, fiber/resin volume ratio and single overlap shear strength at 75° and 350°F.

A.1.2) ADHESIVE FILMS MANUFACTURED FROM HIGH MODULUS FIBER WOVEN FABRICS

A.1.2.1) Material Selection

Six woven fabrics manufactured from high modulus high strength fibers were selected for the fiber distribution study. They were selected with the criteria that the fabric thickness be between 5 and 15 mils. These fabrics are listed in Table 4 of the main body of the report and included the following fabrics: style WCG carbon fabric, a plain weave 3.0 ounce material, style PWA graphite fabric, a plain weave 3.35 ounce material, style 120 Kevlar-49, a plain weave 1.8 ounce fabric, and style 220 Kevlar-49, a plain weave 2.2 ounce fabric. All these materials have a uncompressed thickness of less than 15 mils. Unidirectional tow boron and randomly distributed graphite fiber constructions were also included.

A.1.2.2) Calculations of Finished Adhesive Film Weight

The final film weight was calculated with the criteria that there would be only enough resin present to; 1) completely fill the interstitial space of the fabric and 2) an excess on the surface to insure sufficient flow during the cure cycle for good bond formation.

A.1.2.3) Manufacture of Adhesive Resin/Fiber Combination

The completed adhesive films were manufactured via a solvent impregnation technique using a 70% solid solution of the resin in acetone as the impregnant. The wet adhesive films were dried for 30 minutes at 200°F. Subsequent quality control testing involved adhesive fiber volume and volatile determination as well as single overlap shear strength at both 75° and 350°F.

A.1.3) MANUFACTURE OF ADHESIVE FILM REINFORCED WITH RANDOMLY DISPERSED HIGH MODULUS GRAPHITE FIBER

A.1.3.1) Material Selection

The randomly dispersed fiberous mats were manufactured from AS graphite fiber which has been chopped by the manufacturer to a nominal 1/8" length. This material was selected as the only material of this type readily available.

A.1.3.2) Manufacture of Randomly Dispersed Fiberous Mat

The fiberous mats were manufactured using a paper hand sheet technique. The desired quantity of fiber was dispersed at an approximate 0.5 weight percent concentration in water using a Waring blender. The water was removed using a deckle box and leaving the fiber randomly distributed on a piece of nylon tricot. Drying was accomplished in two stages 1) blotting onto absorbent paper and 2) overnight at a temperature of 180°F.

A.1.3.3) Adhesive Mat Film Combination Manufacture

Mat was consolidated by spraying with a dilute solution of the adhesive resin in acetone and drying at 200°F for 20 minutes. The final film was manufactured using unsupported adhesive film, using the same techniques as described in section A.1.1.4.

A.1.4) MANUFACTURE OF UNIDIRECTIONAL BORON FILAMENT REINFORCED ADHESIVE

A.1.4.1) Material Selection

The type HS 4 mil boron filament was supplied by the Air Force Materials Laboratory.

A.1.1.2) Adhesive Film Manufacture

The unidirectional adhesive films were manufactured by winding the type HS boron filaments onto a 4" diameter drum at a spacing of 250 ends per inch. A ply of unsupported adhesive film was laminated onto the surface of the unidirectional filament by the technique described in Section A.1.1.4. The film was then cut off the drum, laid and a second ply added to the opposite side by the same technique. Quality control testing consisted of adhesive weight measurement and single overlap strengths at both 75° and 350°F.

A.2) TEST SPECIMEN CURING CONDITIONS

All double overlap shear test specimens were autoclave cured against a metallic tool for 60 minutes at 350°F and 50 psi. Normal cool down techniques under pressure were used. The aluminum single overlap shear specimens were oven cured for 60 minutes at 350°F at approximately 20 psi using aircraft style clamps.

A.3) TEST TECHNIQUES

A.3.1) VOLATILE DETERMINATION

Percent weight loss of film after exposure to 110°C for 30 minutes at 29 inches Mercury.

A.3.2) FIBER RESIN VOLUME CONTENT

A.3.2.1) Removal of metallic adherend by chemical milling.
Aluminum was removed by chemical milling in 30% Potassium Hysroxide at 200°F.

A.3.2.2) Removal of cured resin by exposure to concentrated Nitric Acid at 200°F.

A.3.2.3) Calculation of volume ratio

A.3.3) SINGLE OVERLAP SHEAR STRENGTH

Determined per MMM-A-132 using 2024-T3 Bare aluminum adherends. Tests at 350°F were allowed to equilibriate 15 minutes before testing. All testing was performed using a "Cal-Tester" and a Misimers environmental chamber.

A.3.4) DOUBLE OVERLAP SHEAR STRENGTH

The ultimate shear strengths were determined per MMM-A-132, using a Baldwin 30,000 pound capacity testing machine. Tests at -65° and 350°F were conducted per the above federal specification using a "standard" environmental chamber.

A.3.5) FATIGUE RESISTANCE

Fatigue resistance was determined using Sonntag universal testing machines. Tests specimens were stressed between the desired level (P_{MAX}) and (0.1) (P_{MIN}) in tension, at a frequency of 30 H_Z.

A.3.6) PEEL STRENGTH

Honeycomb and metal to metal peel resistance were determined per McDonnell Aircraft Company Specification MMS-307.

PHASE I

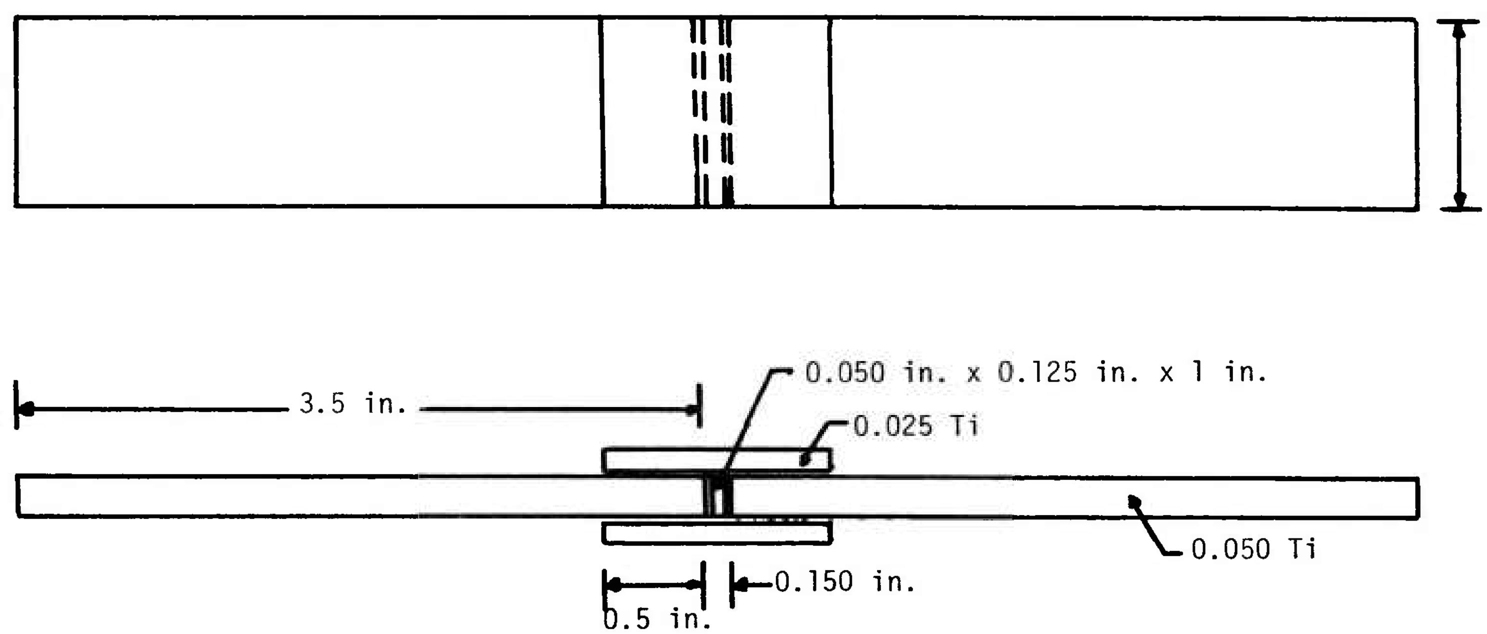


FIGURE 1. Titanium Double Lap Shear Specimen Used in the Screening of Fatigue Properties.

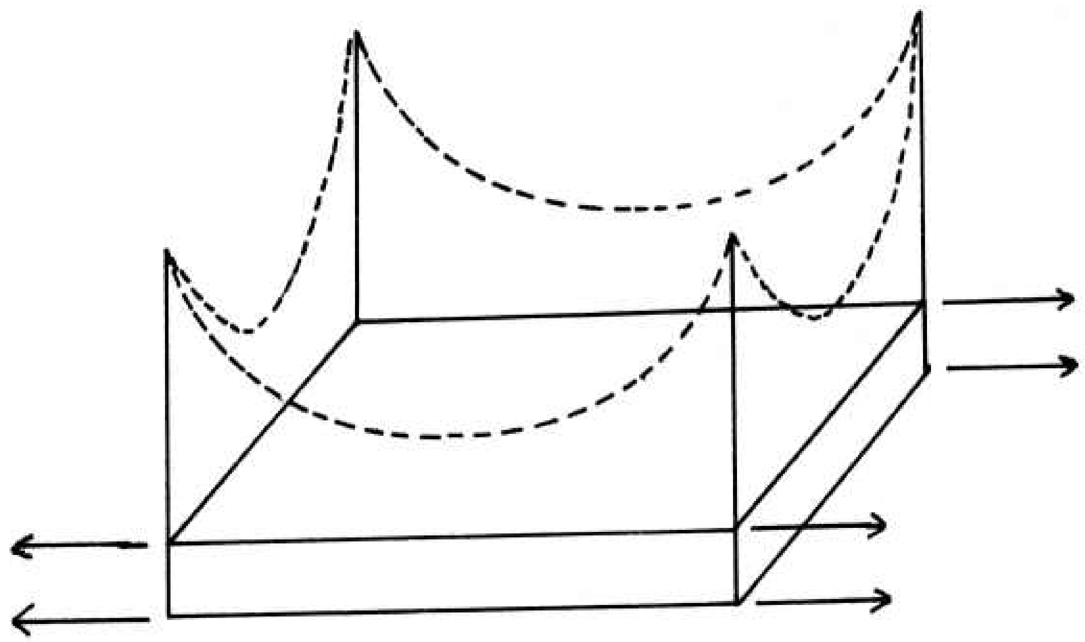
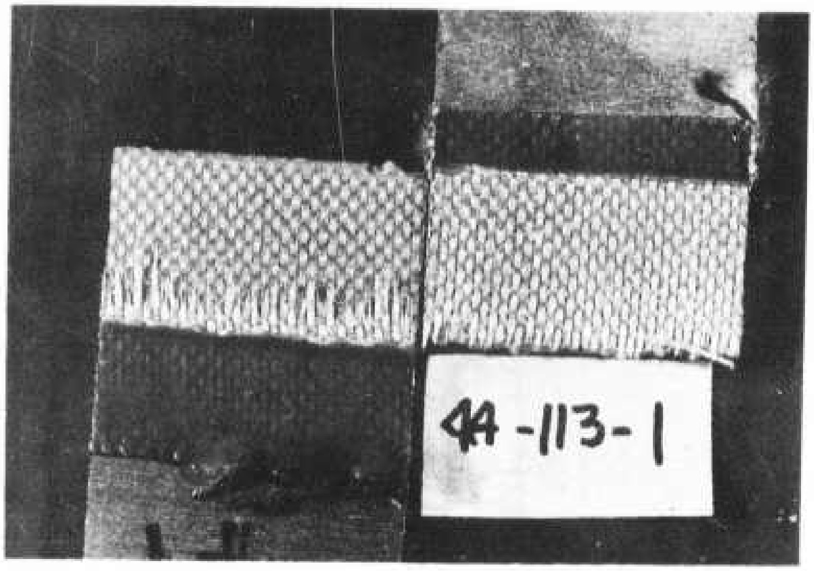
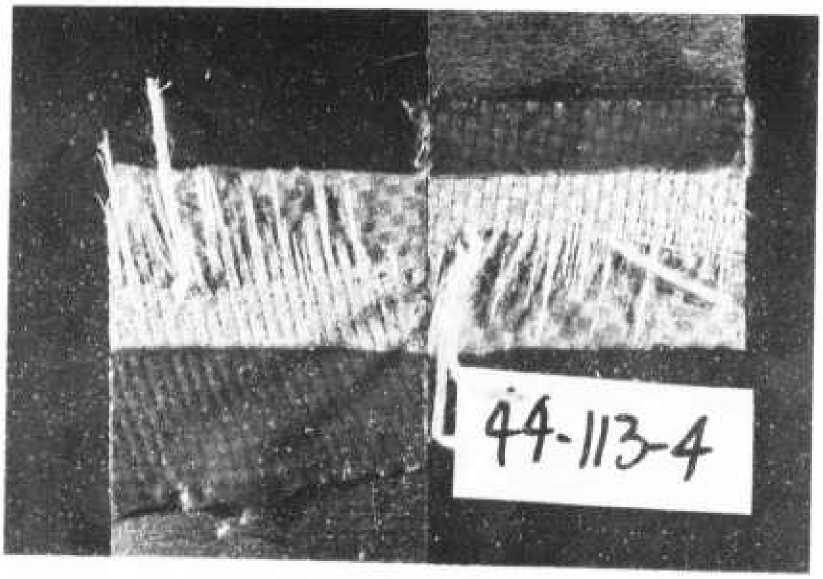


FIGURE 2. Shear Stress Distribution in a Lap Joint.



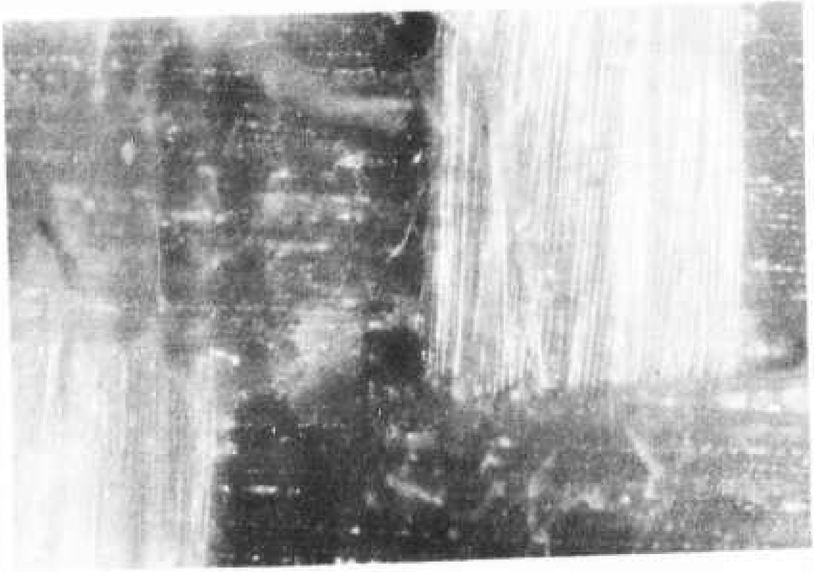
3-a) Kevlar^R-49, Style 120



3-b) Kevlar^R-49, Style 220

FIGURE 3. Microphotographs (1.7X) of Kevlar-49 Supported Adhesive Failure Surfaces.

4-a) Fabric Surface



4-b) Resin Surface

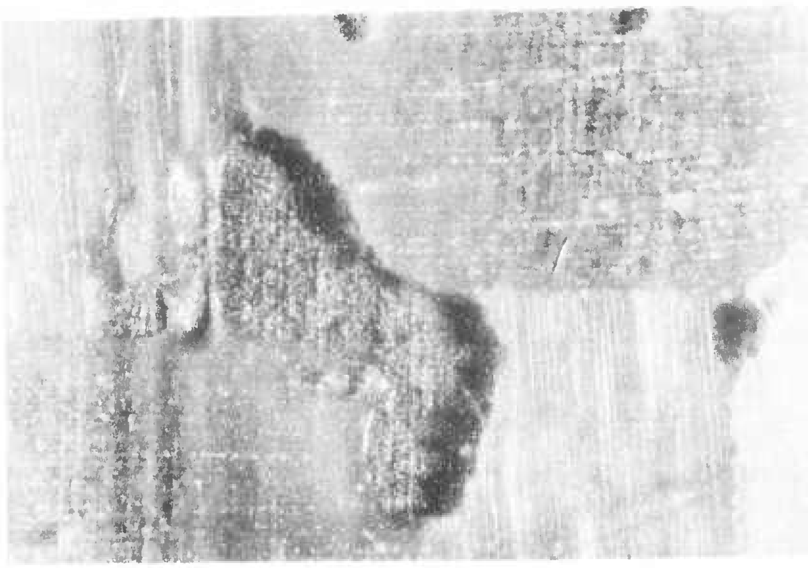
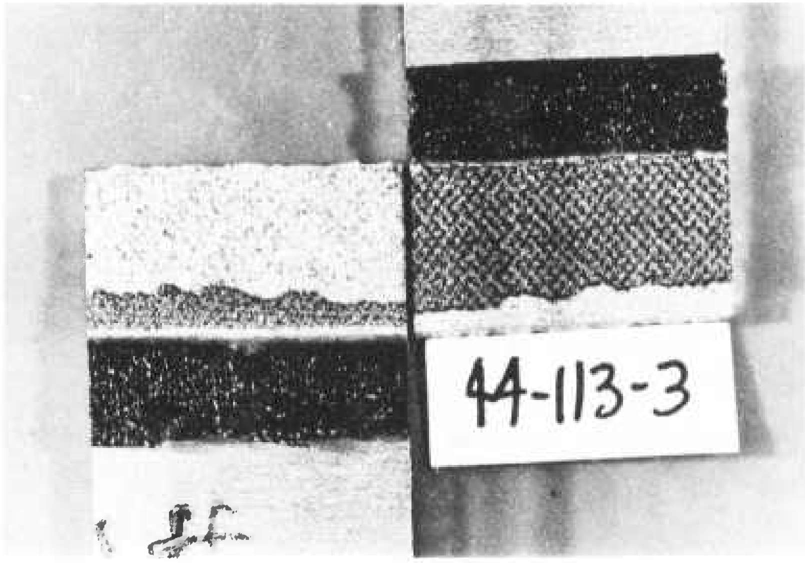
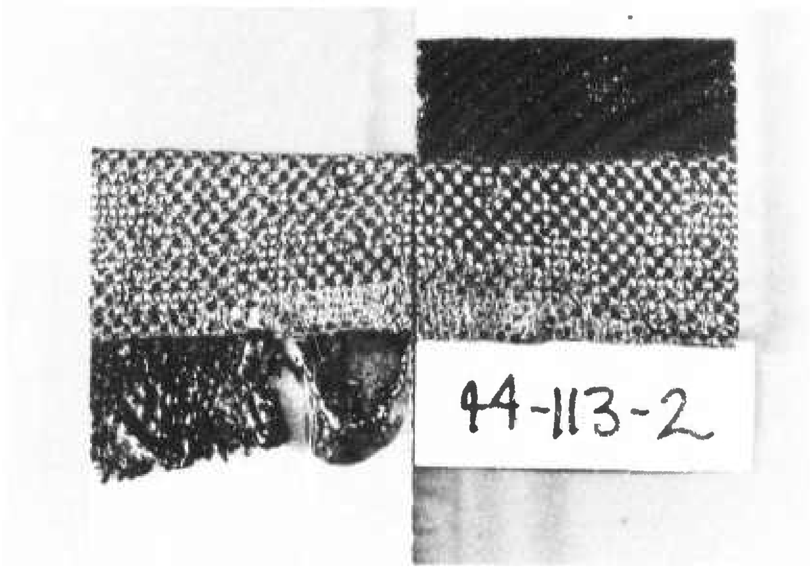


FIGURE 4: Photomicrographs (50 x) of Failure Surface of ADX-653/ Style 120 Kevlar^{R}-49 Single Overlap Shear Bonds.



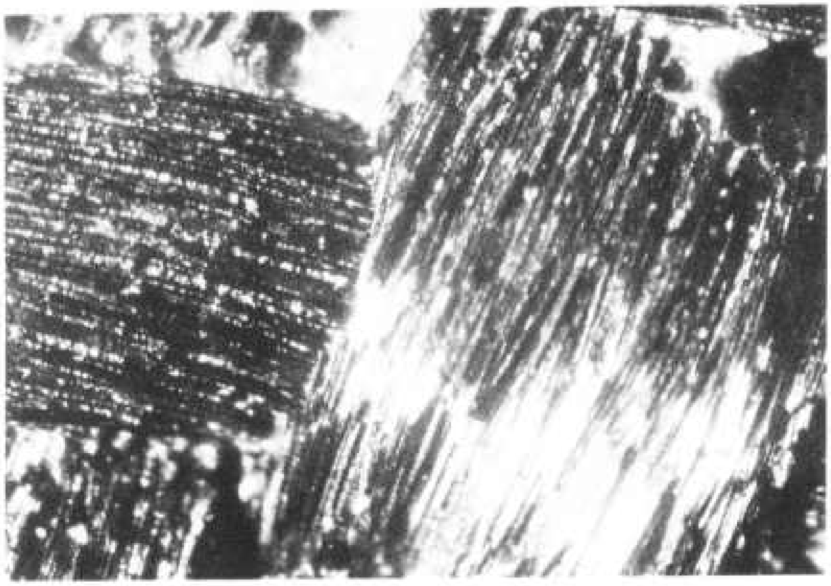
5-a) PWA



5-b) WCG

FIGURE 5: Macrophotographs (1.7 X) of the Failed Single Overlap Shear Specimens of Both PWA and WCG Supported ADX-653.

6-a Side a



6-b) Side b

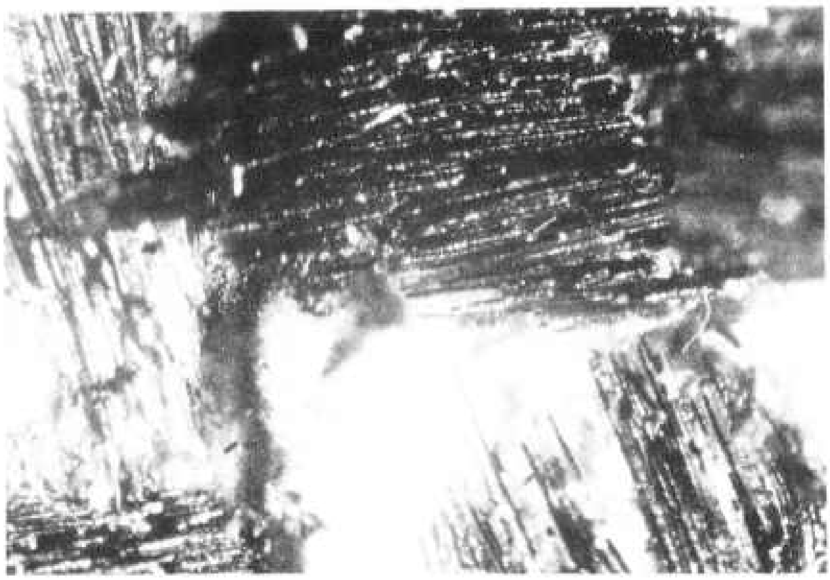
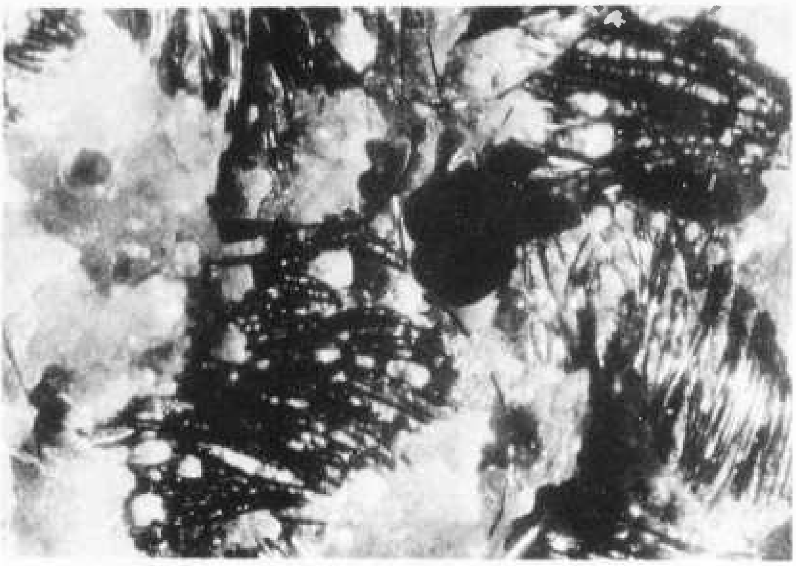


FIGURE 6: Photomicrographs (50 X) of the Failure Surface of ADX-653/ Style WCG Carbon Fabric Single Overlap Shear Bonds.

7-a) Fabric Side



7-b) Resin Side

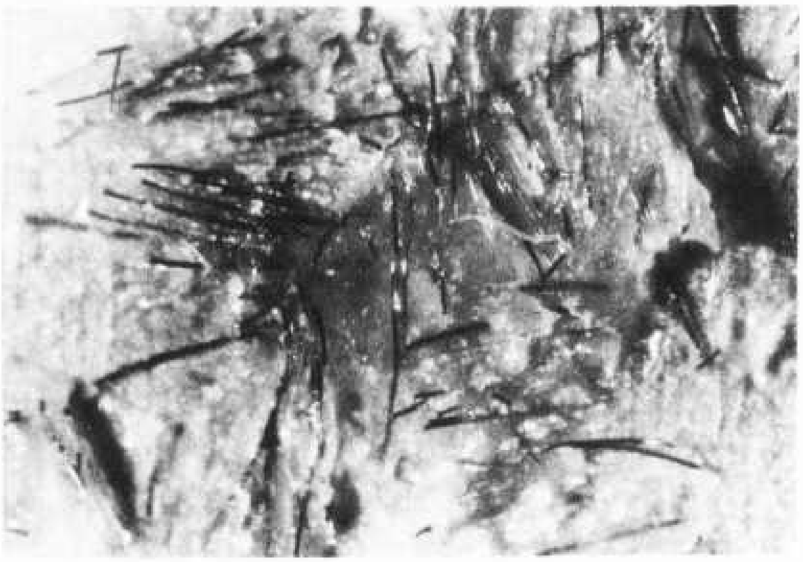


FIGURE 7. Photomicrographs (50 X) of the Failure Surface of ADX-653/PWA Carbon Fabric Single Overlap Shear Bonds.

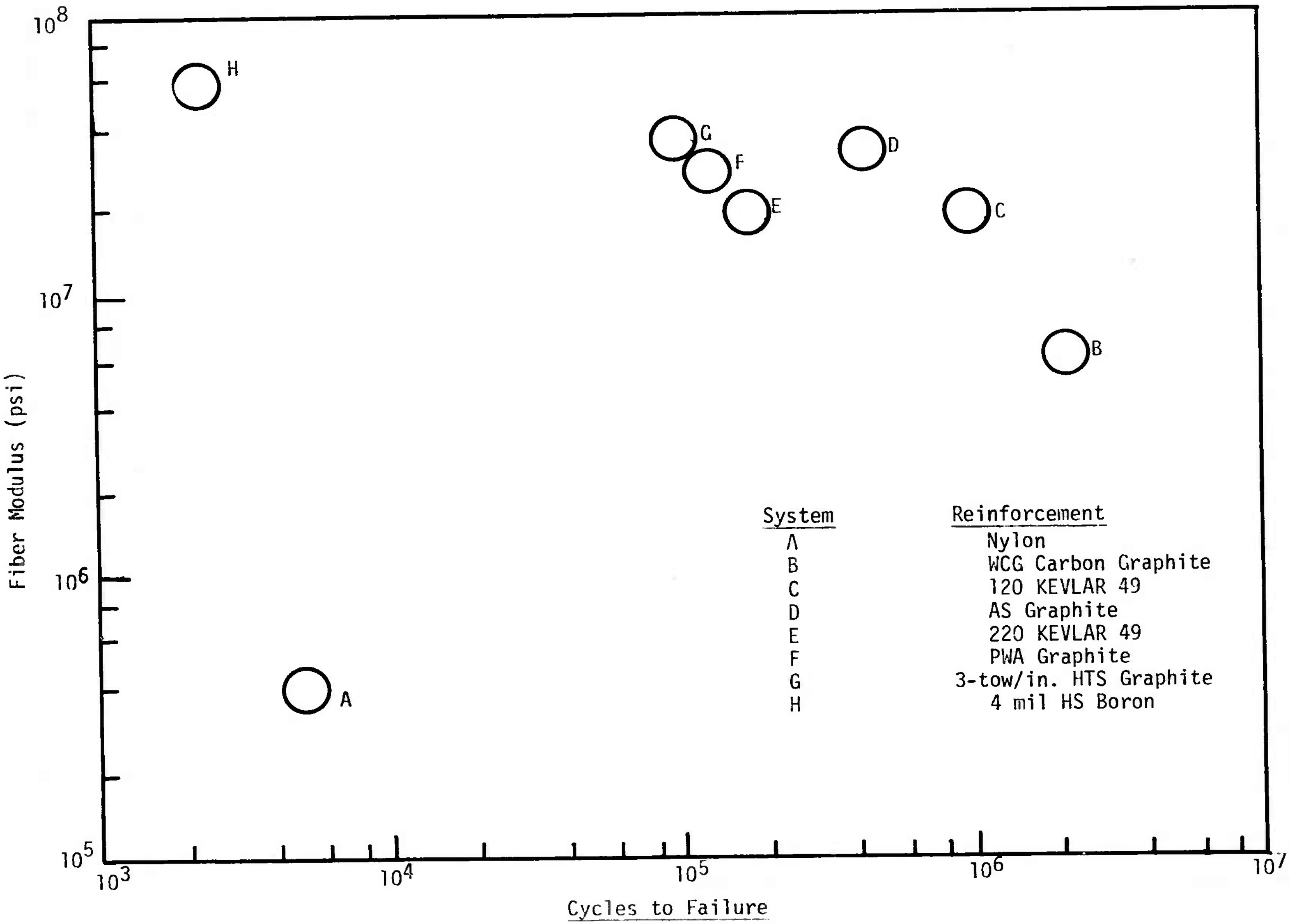


FIGURE 8: Correlation of Fatigue Strength and Reinforcing Fiber Modulus.

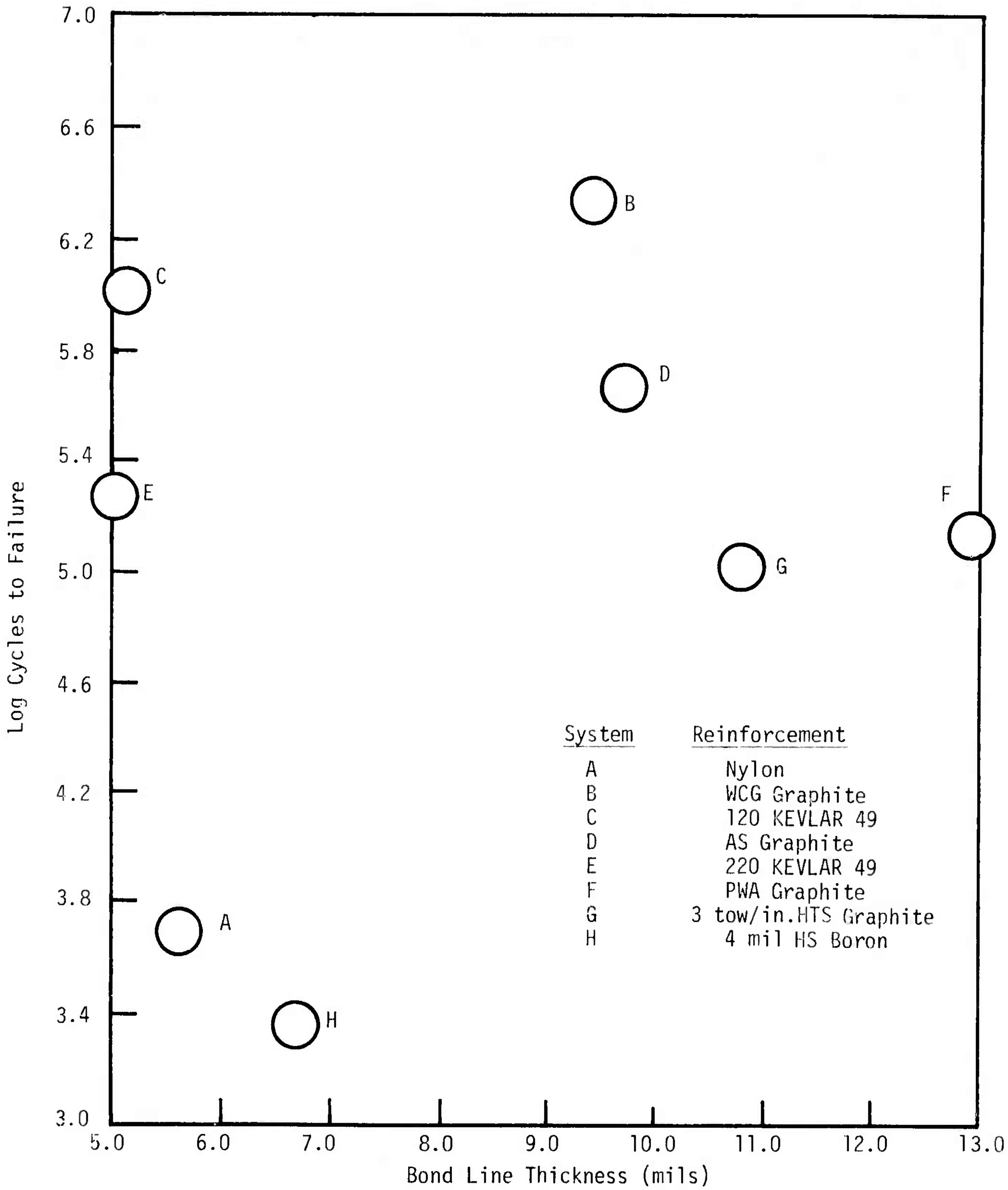


FIGURE 9. Correlation of Fatigue Resistance with Adhesive Bond Line Thickness.

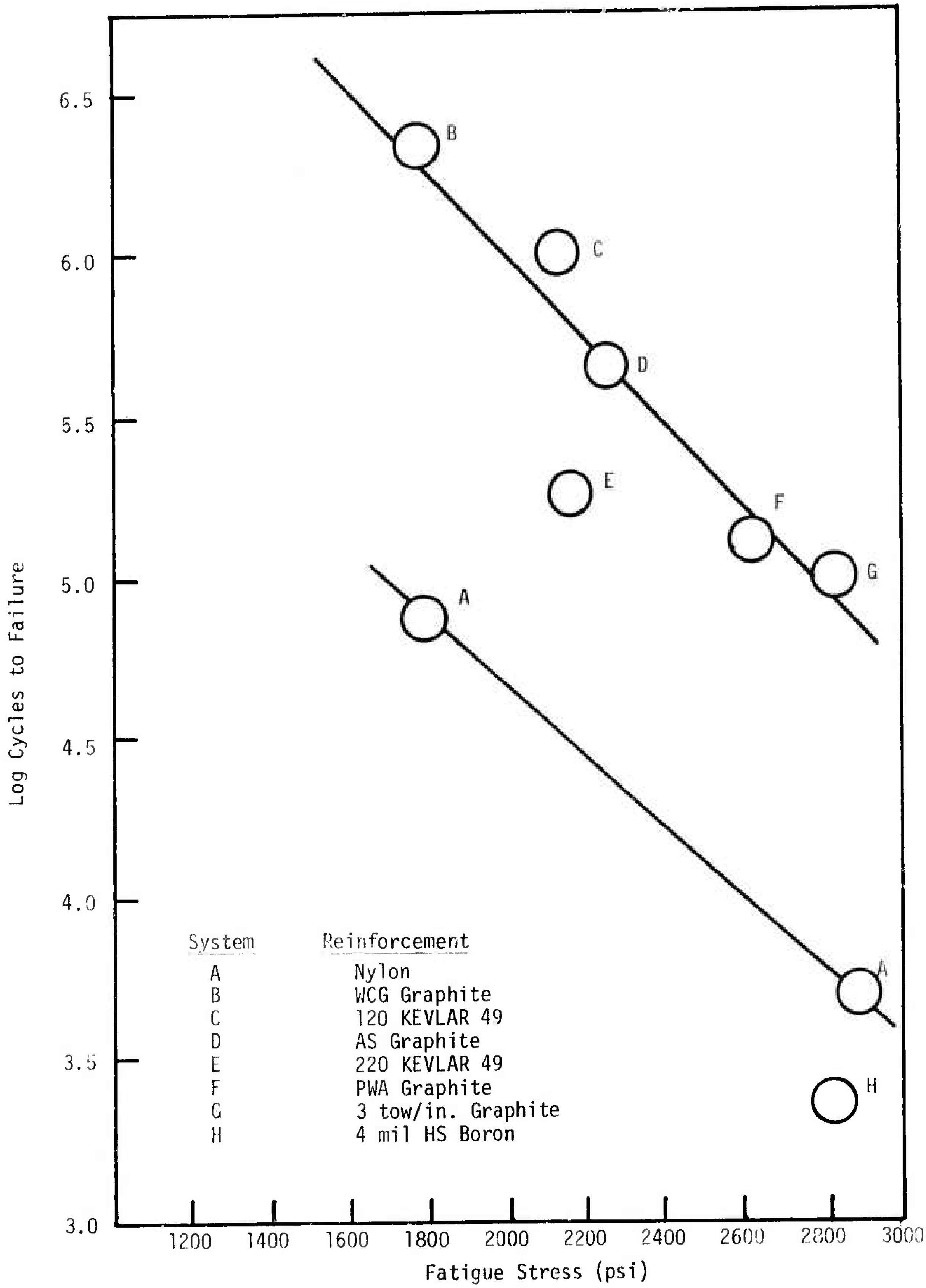


FIGURE 10. Correlation of Fatigue Resistance with Fatigue Stress Level.

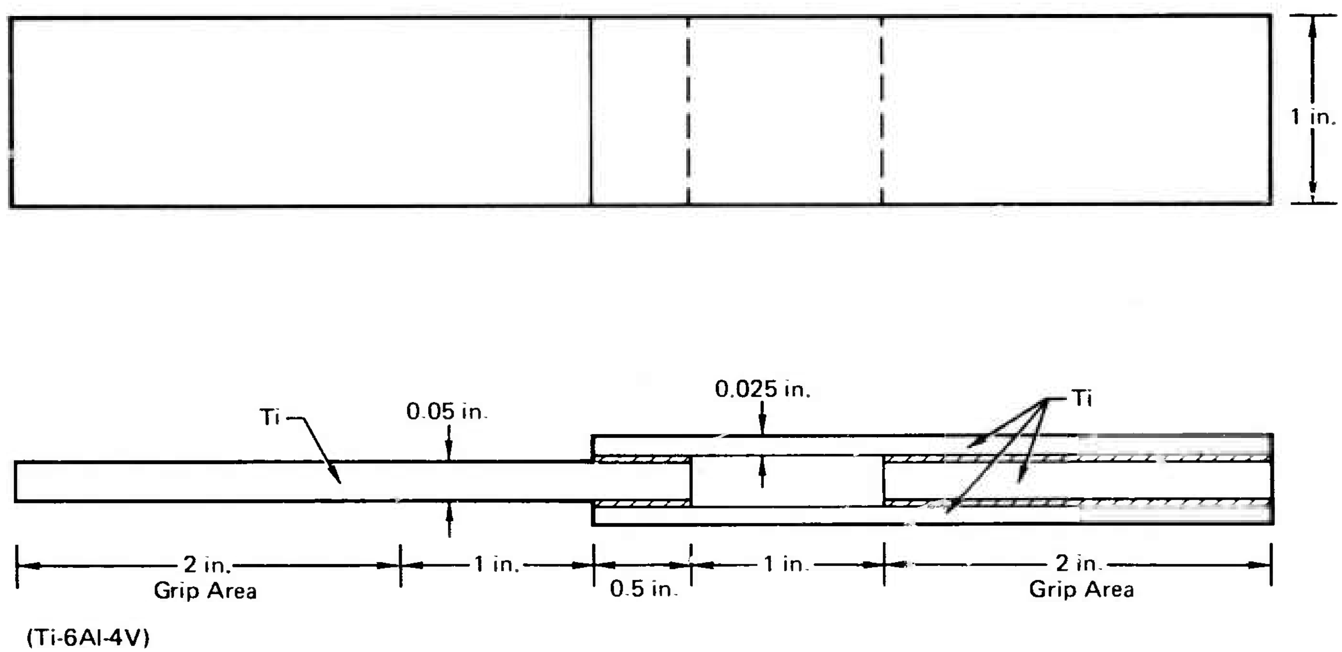


FIGURE 11. Titanium Double Lap Shear Specimen Used in Determination of Load Orientation Effects.

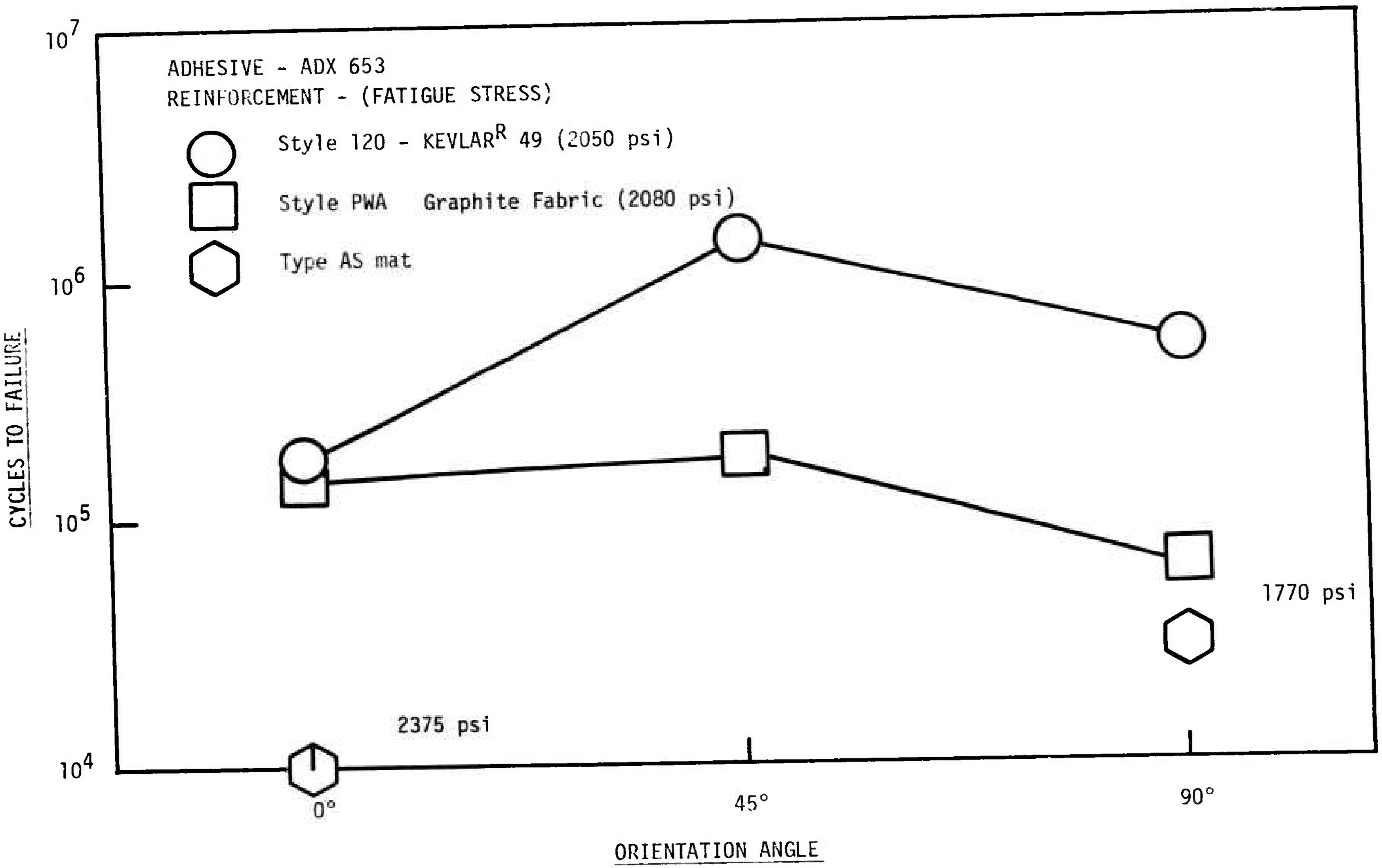


FIGURE 12: Effect of Reinforcement Orientation on Adhesive Bond Fatigue Life.

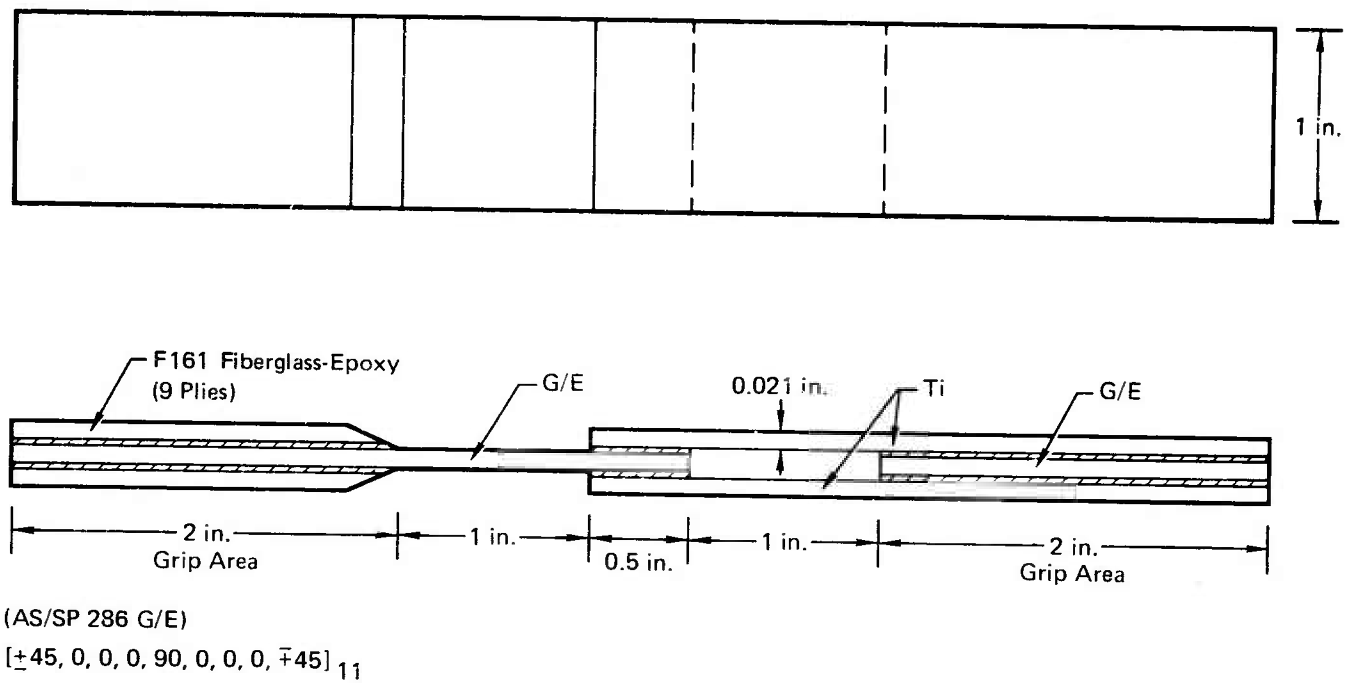


FIGURE 13. GRAPHITE EPOXY TO TITANIUM DOUBLE LAP SHEAR SPECIMEN

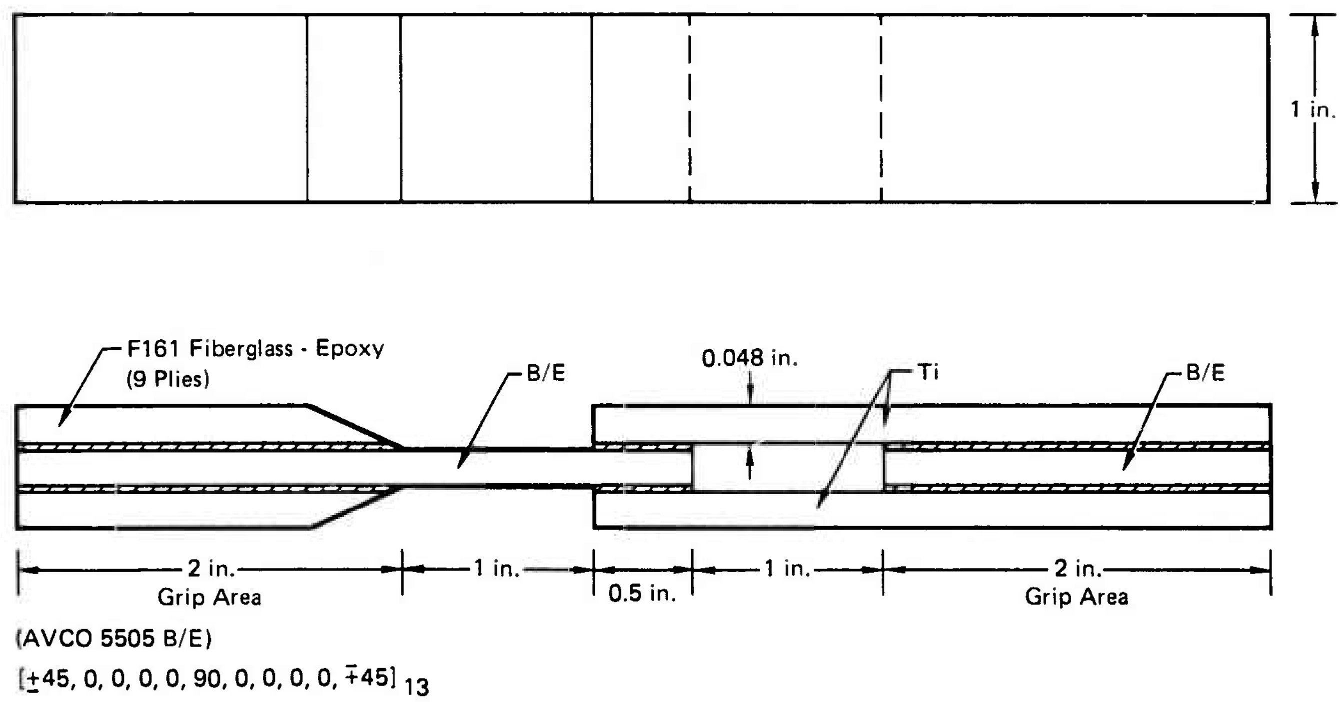


FIGURE 14. BORON EPOXY TO TITANIUM DOUBLE LAP SHEAR SPECIMEN

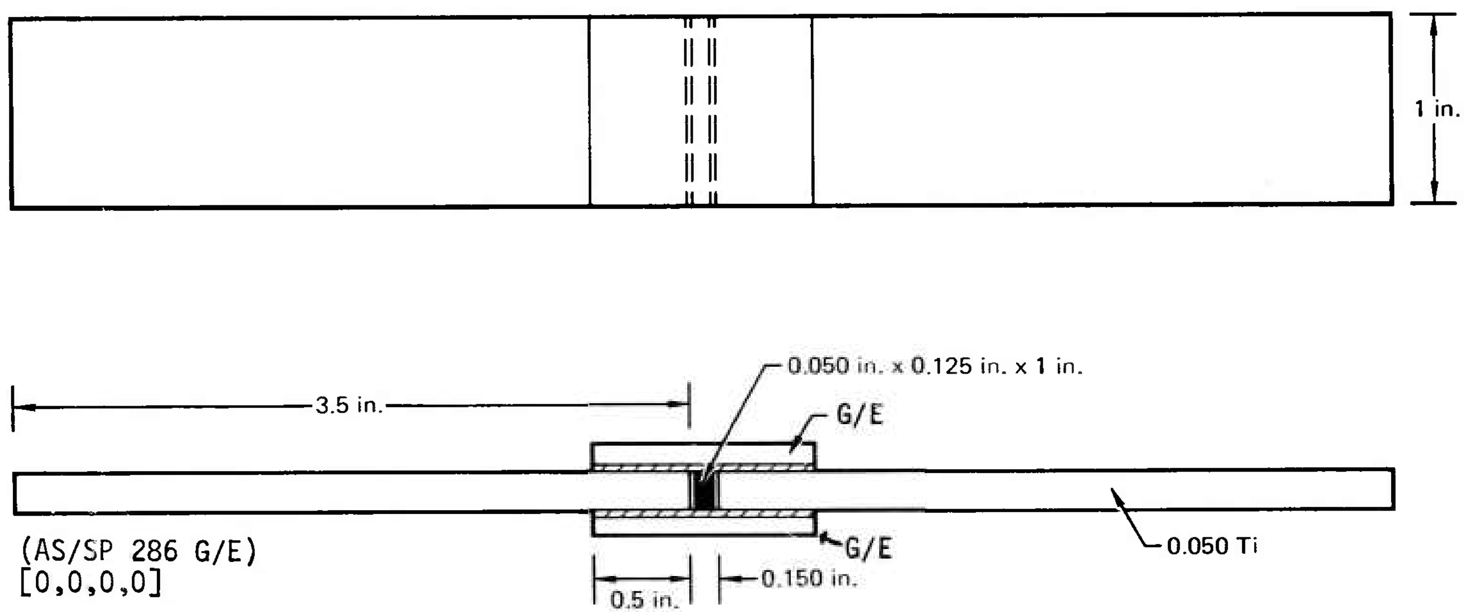


FIGURE 15. GRAPHITE EPOXY TO TITANIUM DOUBLE LAP SHEAR SPECIMEN

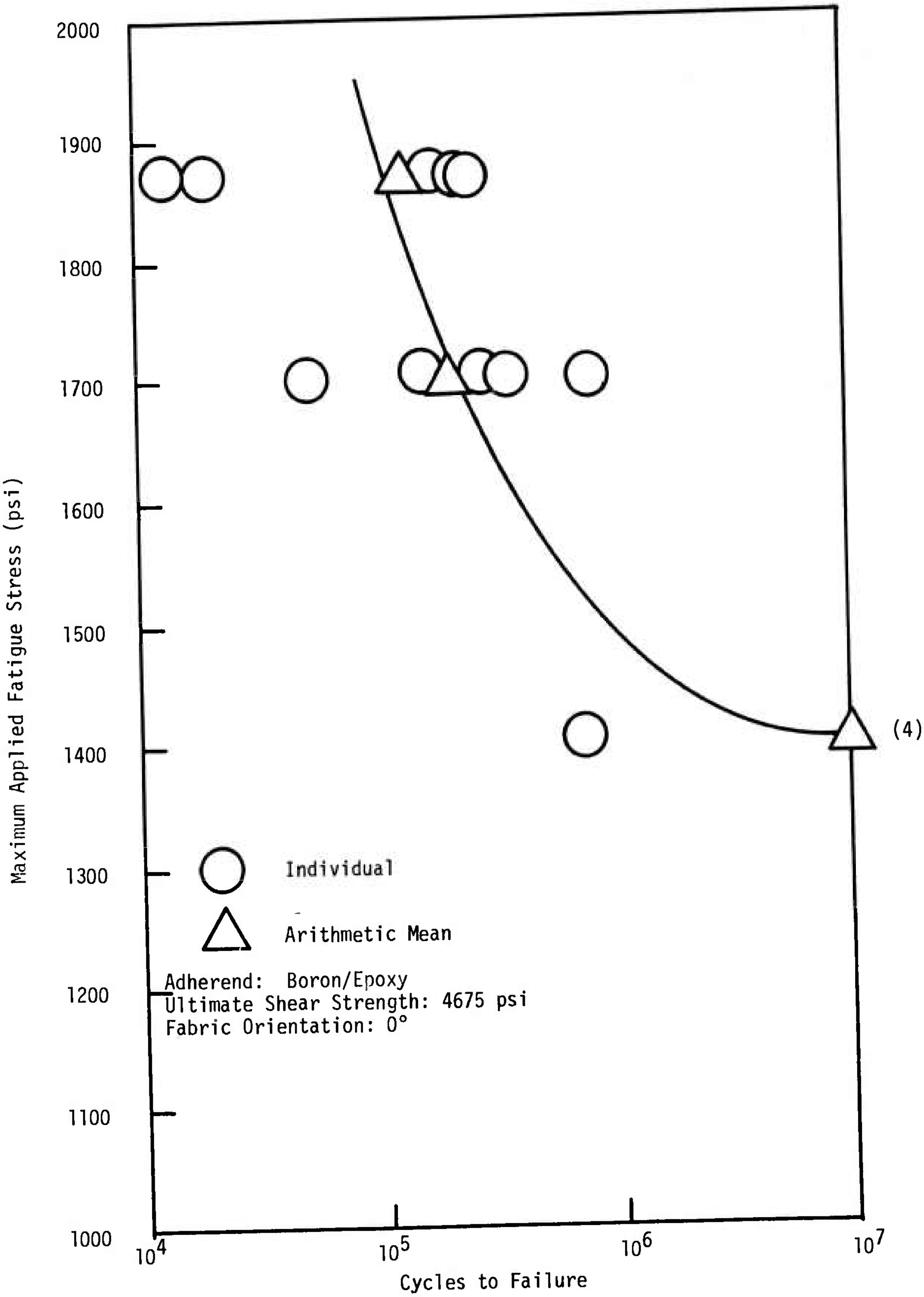


FIGURE 16: Fatigue Resistance of Nylon Knit Supported ADX-653.

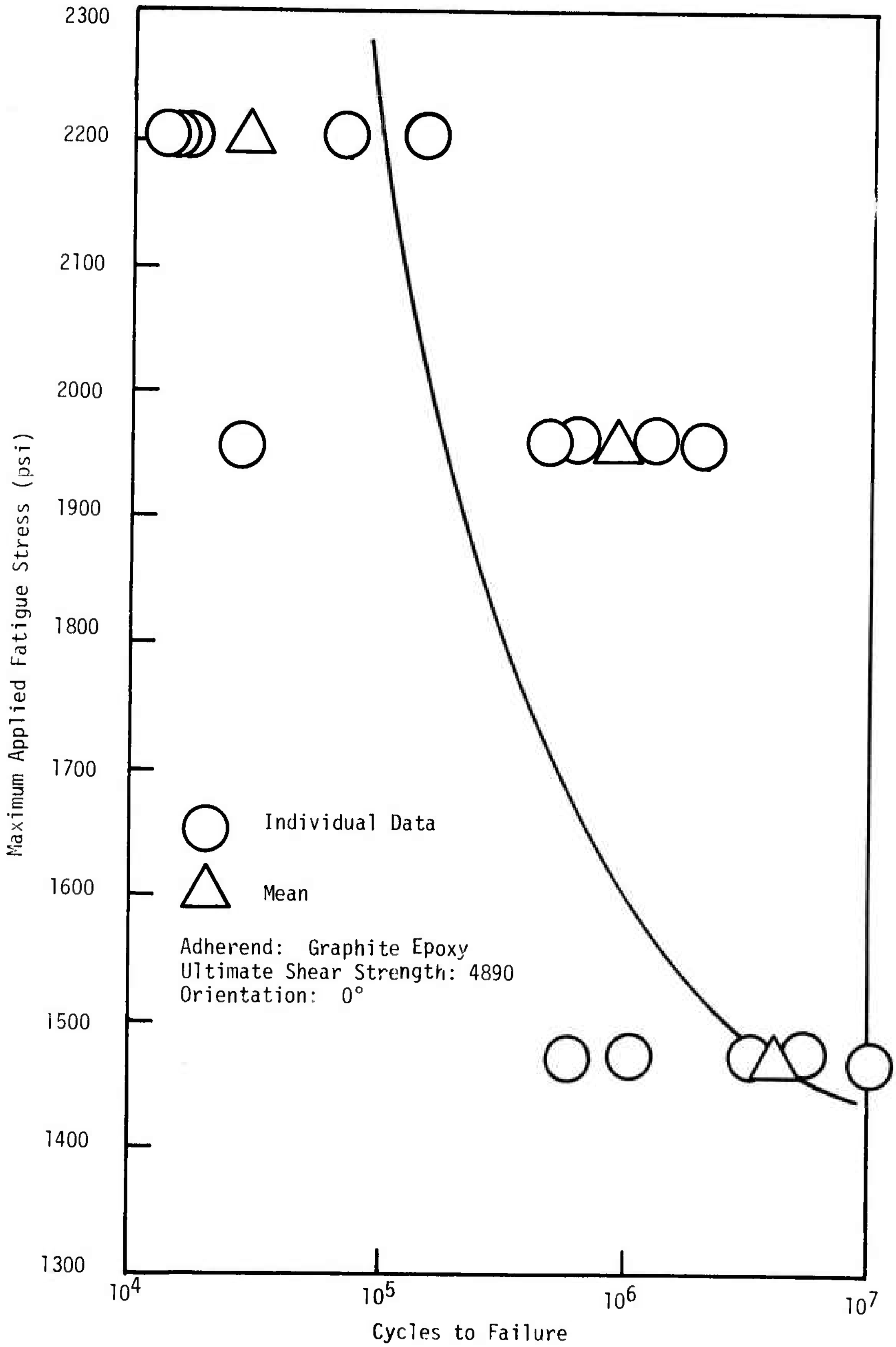


FIGURE 17: Fatigue Resistance of Nylon Knit Supported ADX-653

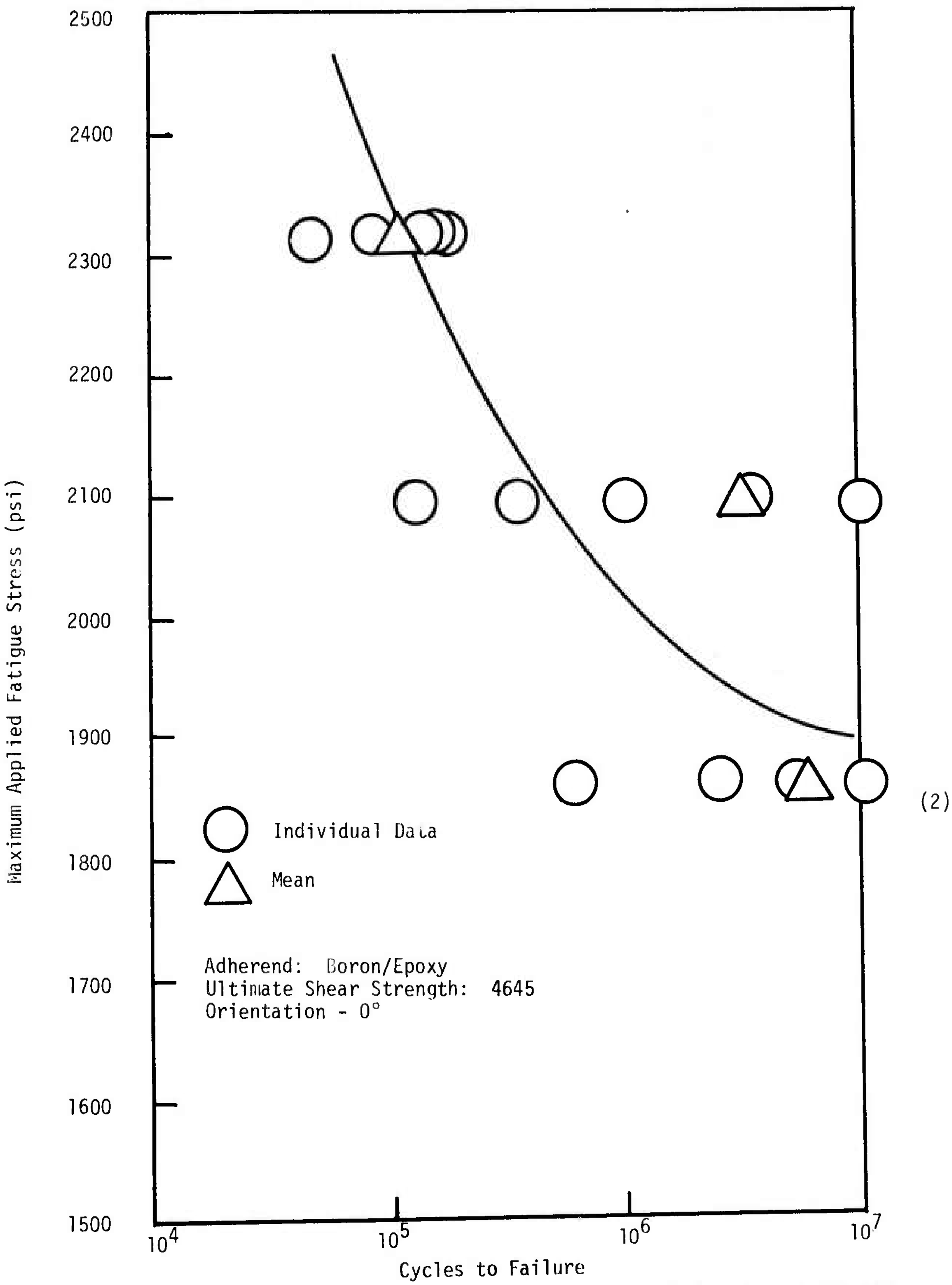


FIGURE 18: Fatigue Resistance of the Style PWA Graphite Reinforced ADX-653

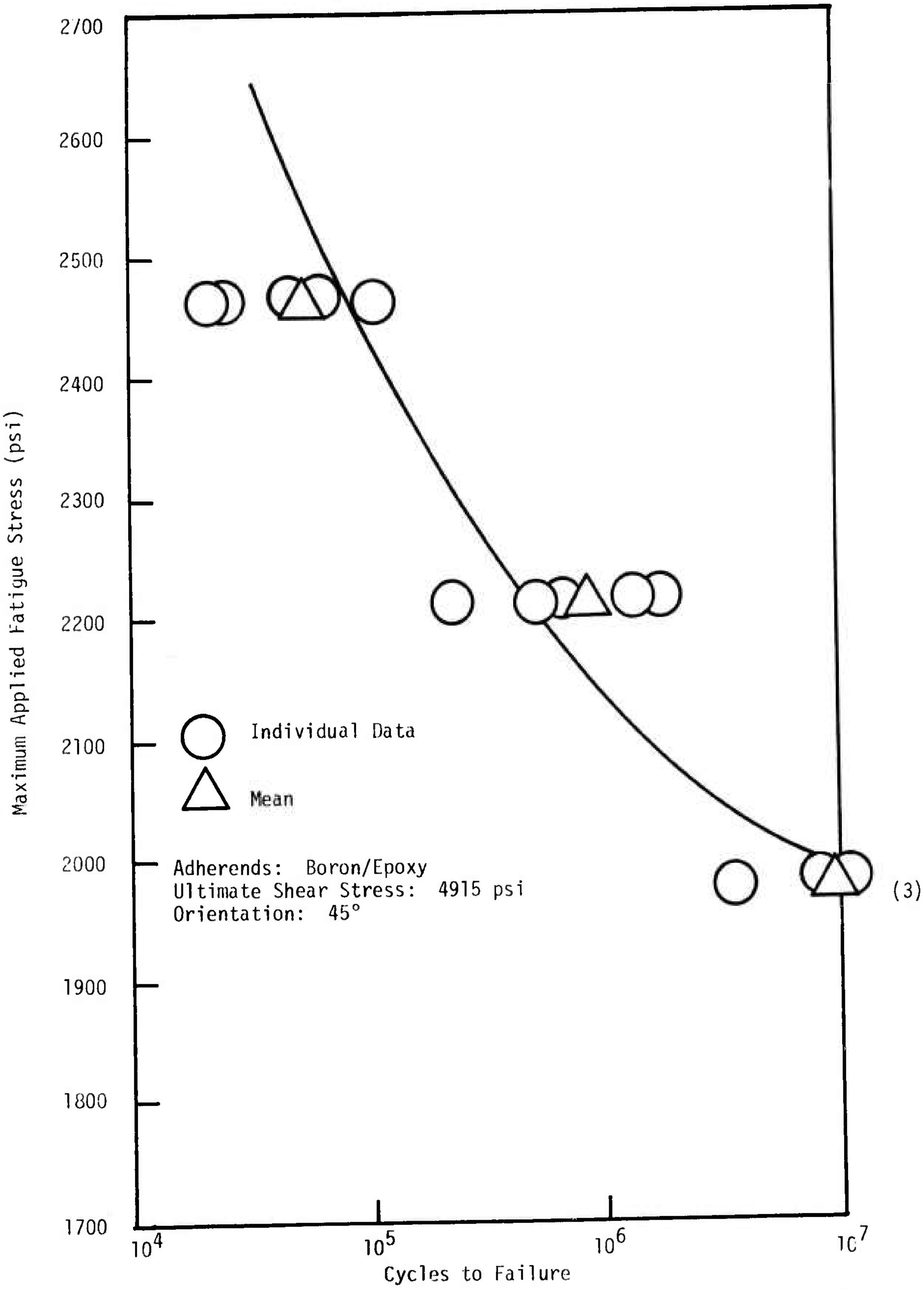


FIGURE 19: Fatigue Resistance of Style PWA Graphite Reinforced ADX-653

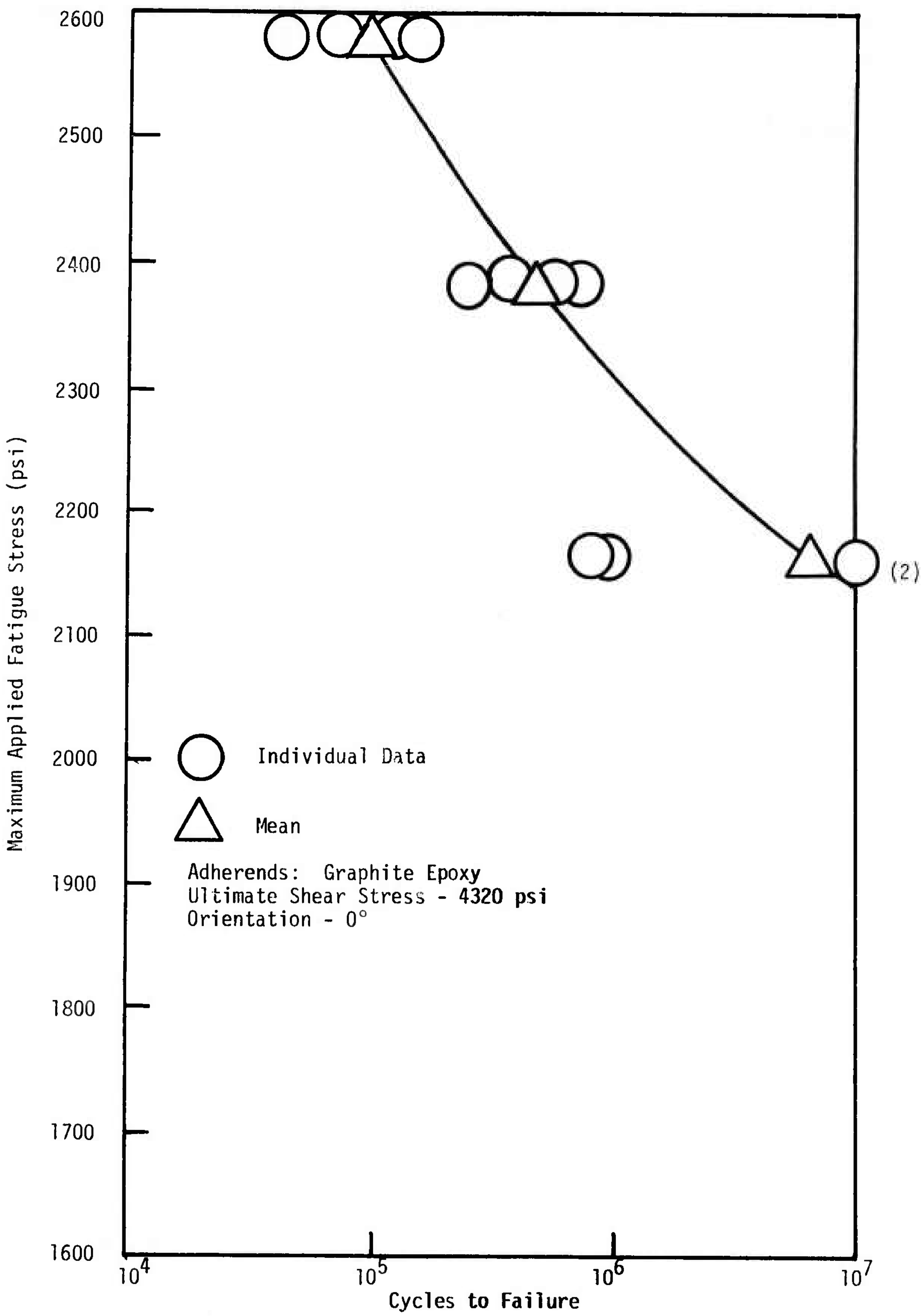


FIGURE 20. Fatigue Resistance of Style PWA Graphite Reinforced ADX-653.

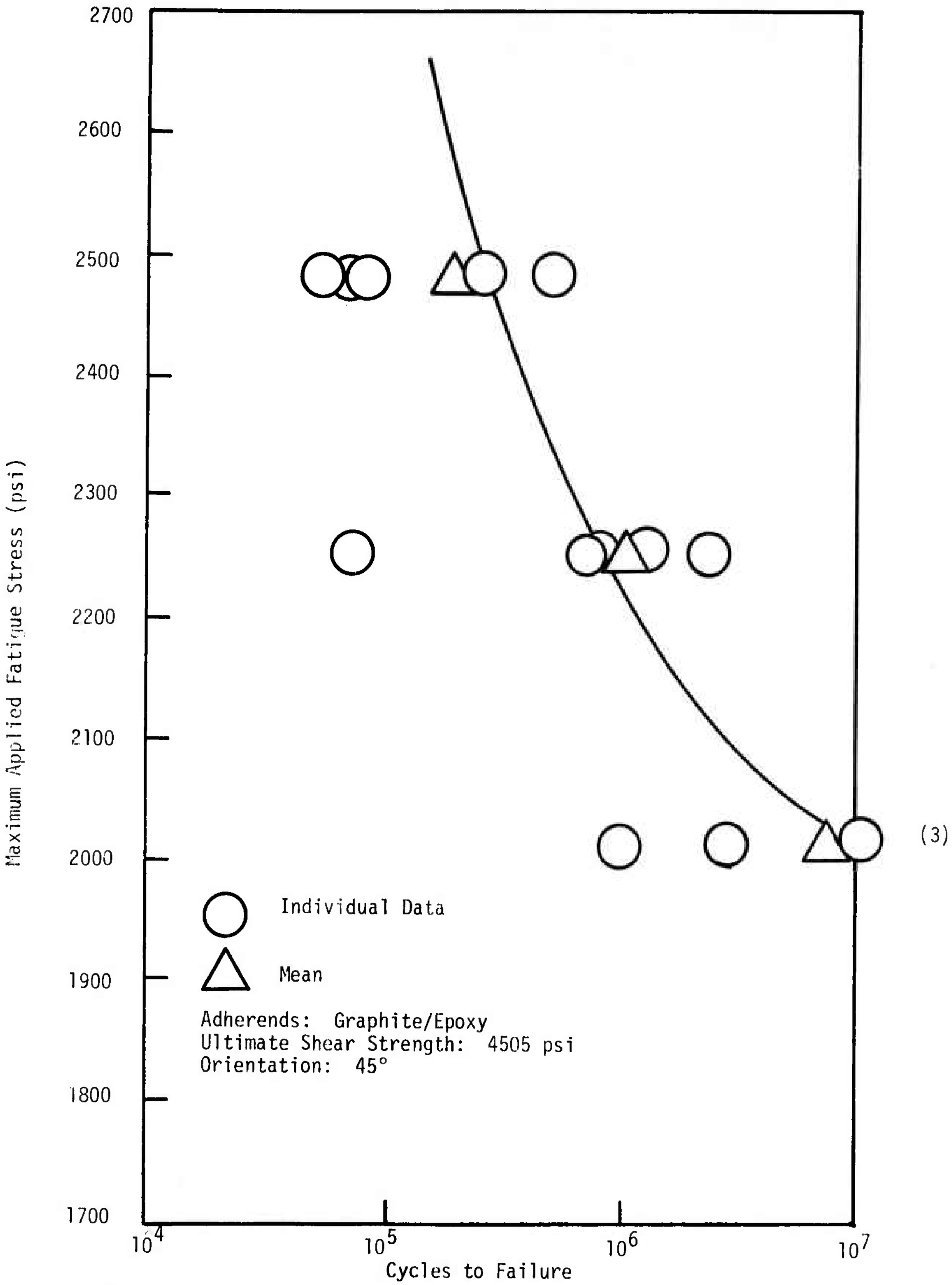


FIGURE 21: Fatigue Resistance of Style PWA Reinforced ADX-653

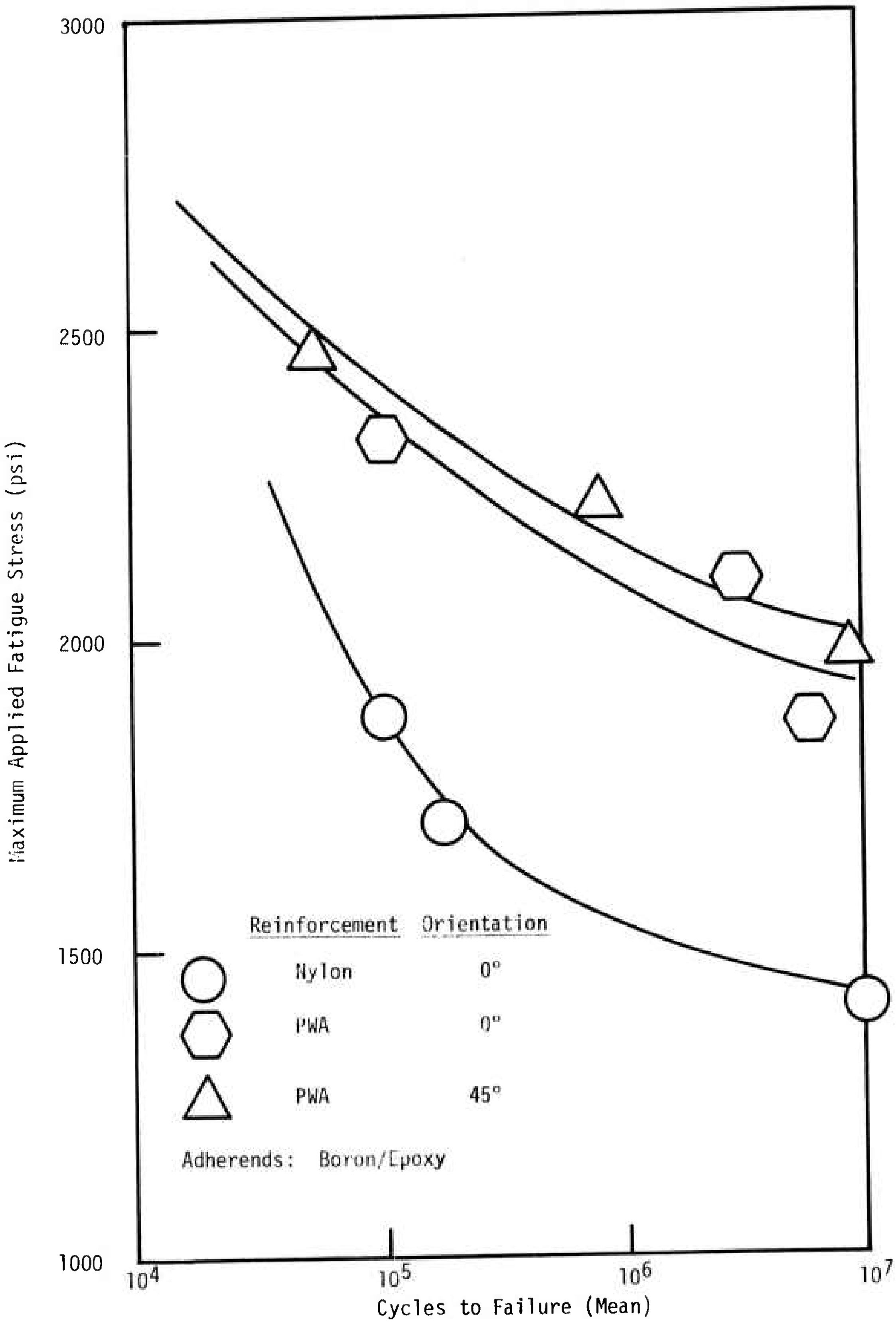


FIGURE 22: Comparison of the Fatigue Resistance of ADX-653 Reinforced with both PWA Graphite and Nylon Knit

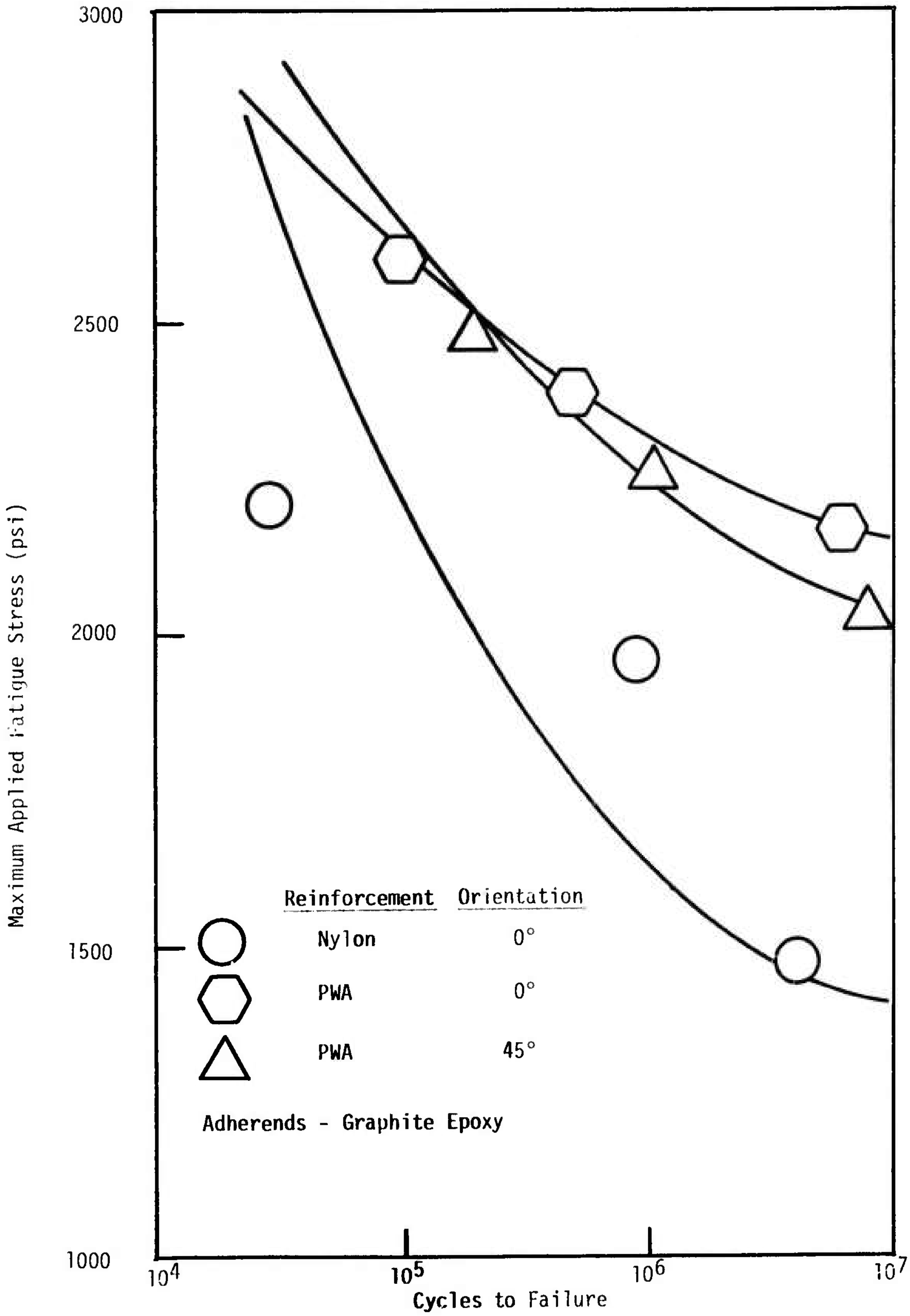


FIGURE 23: **Comparison of the Fatigue** Resistance of ADX-653 Reinforced **with both PWA Graphite** and Nylon Knit.

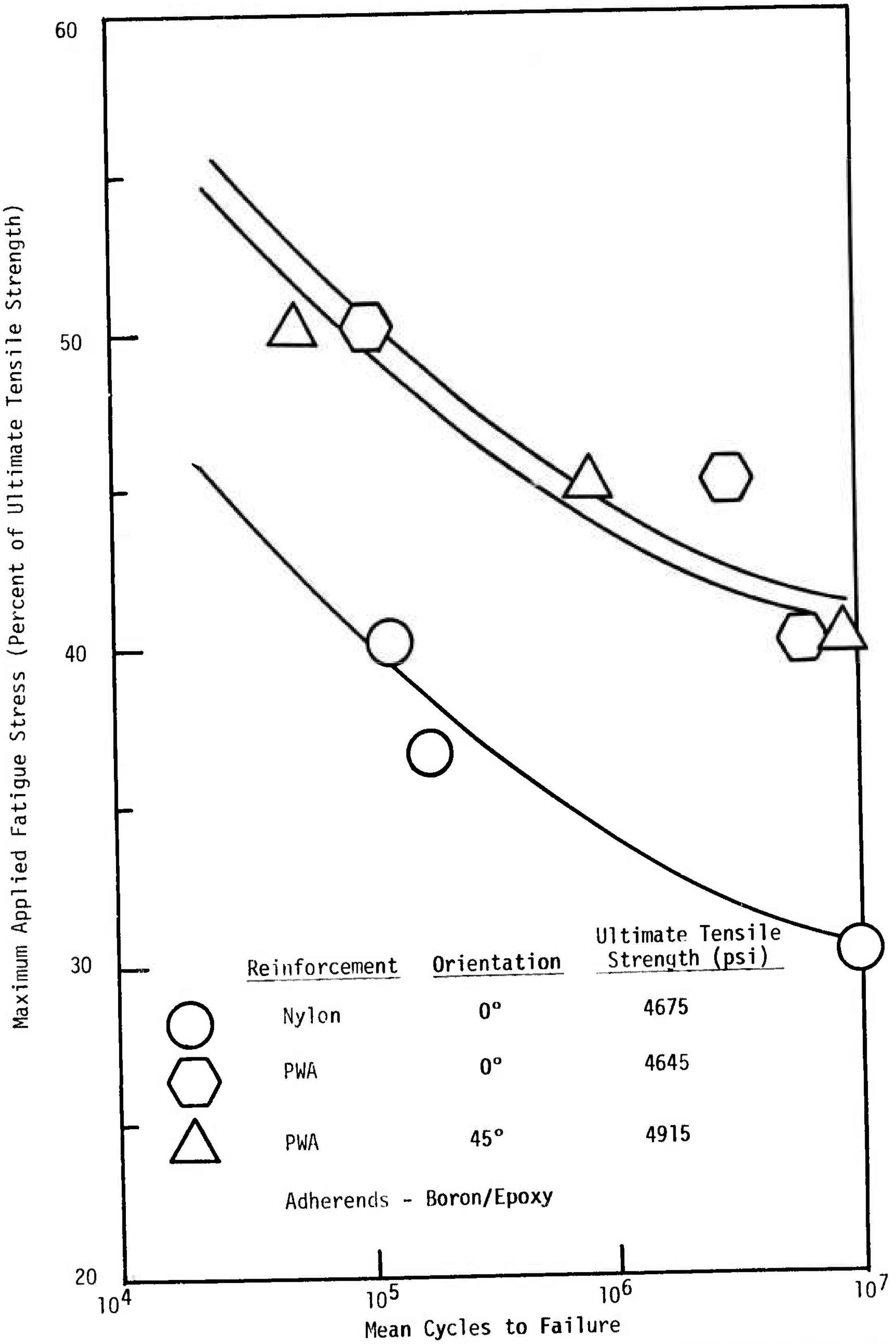


FIGURE 24: Comparison of the Fatigue Resistance of ADX-653 Reinforced with both PWA Graphite and Nylon Knit

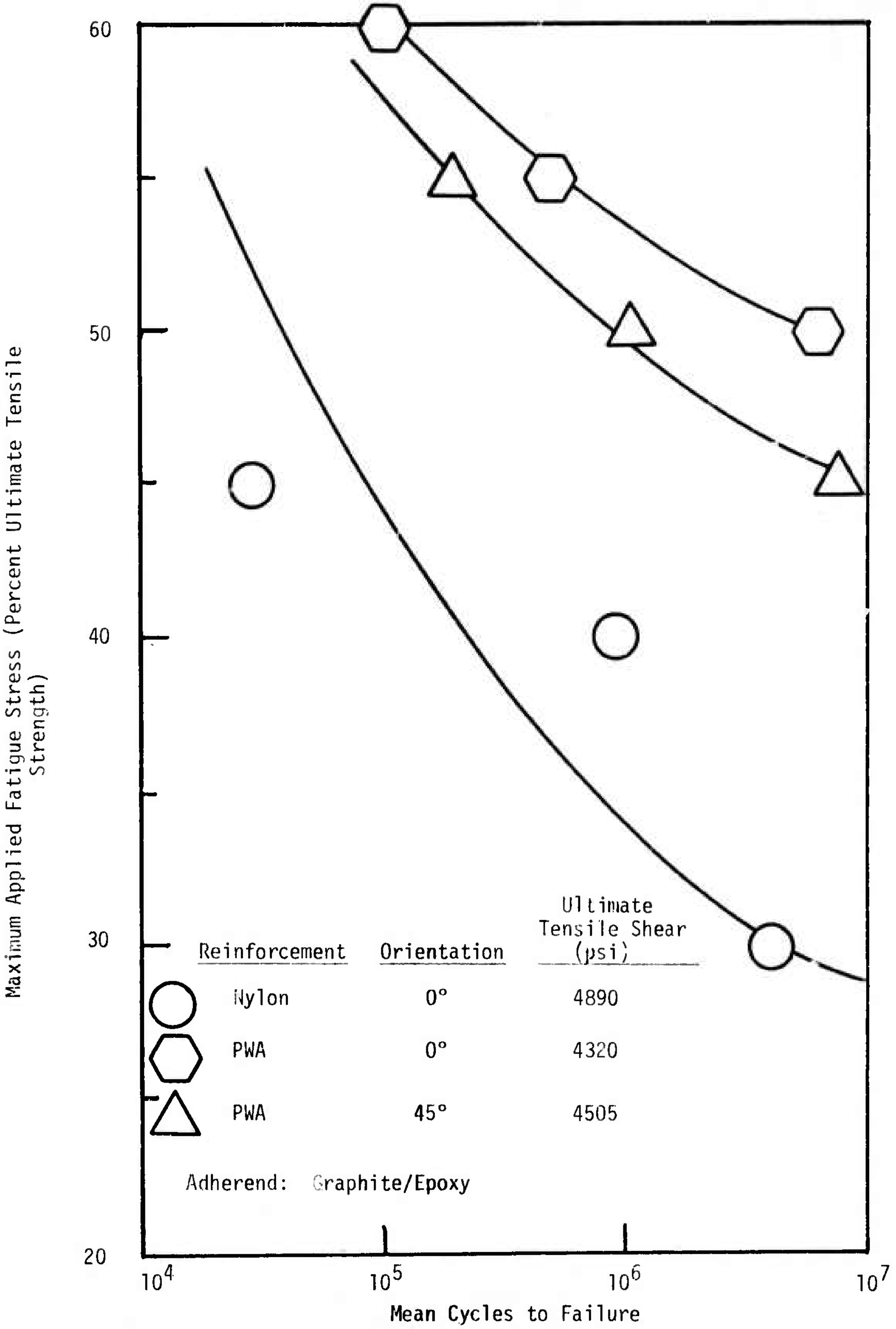


FIGURE 25: Comparison of Fatigue Resistance of ADX-653 Reinforced with both PWA Graphite and Nylon Knit.

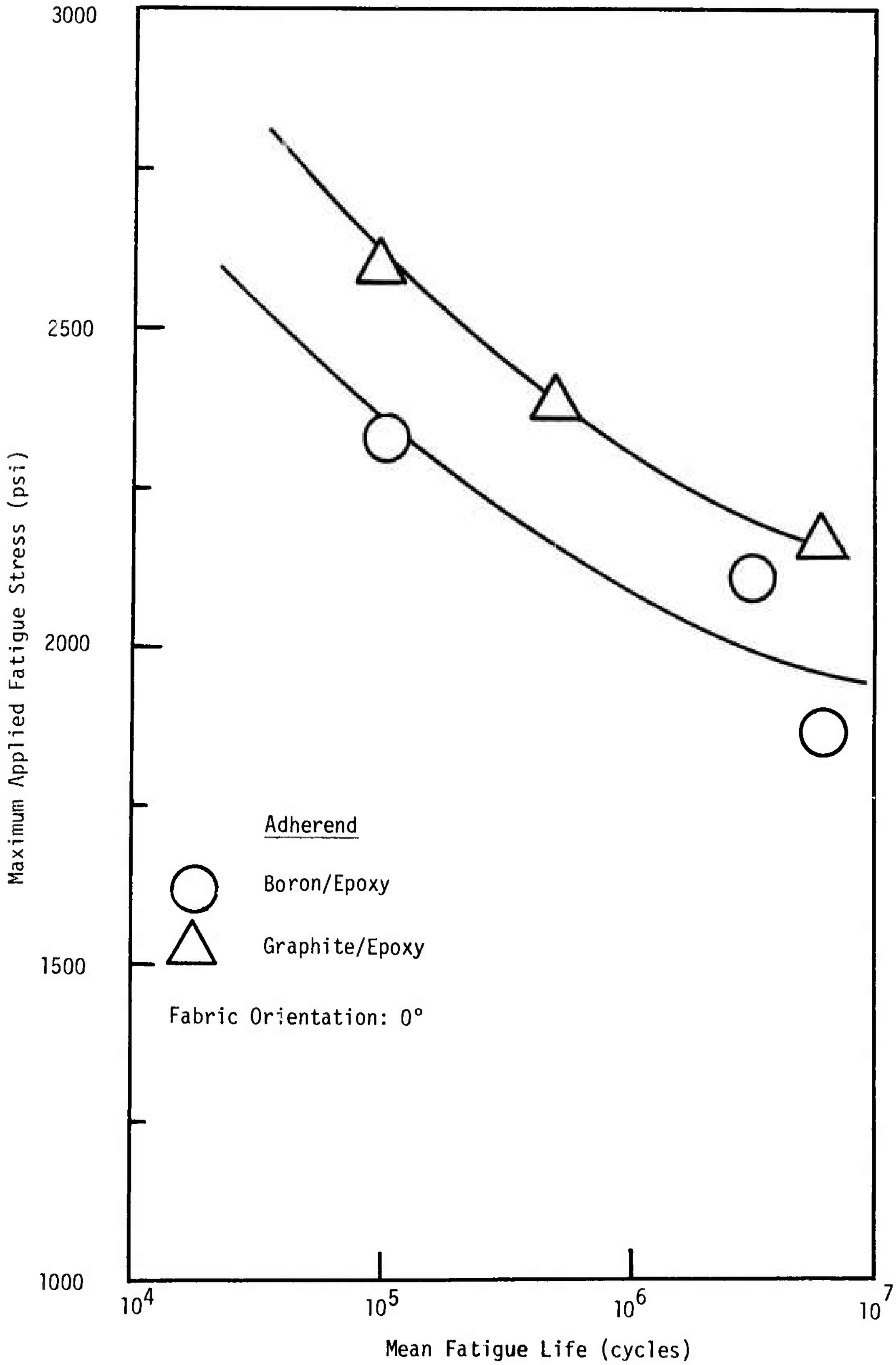


FIGURE 26: Effect of Adherend Type on the Fatigue Performance of Style PWA Graphite Reinforced ADX-653

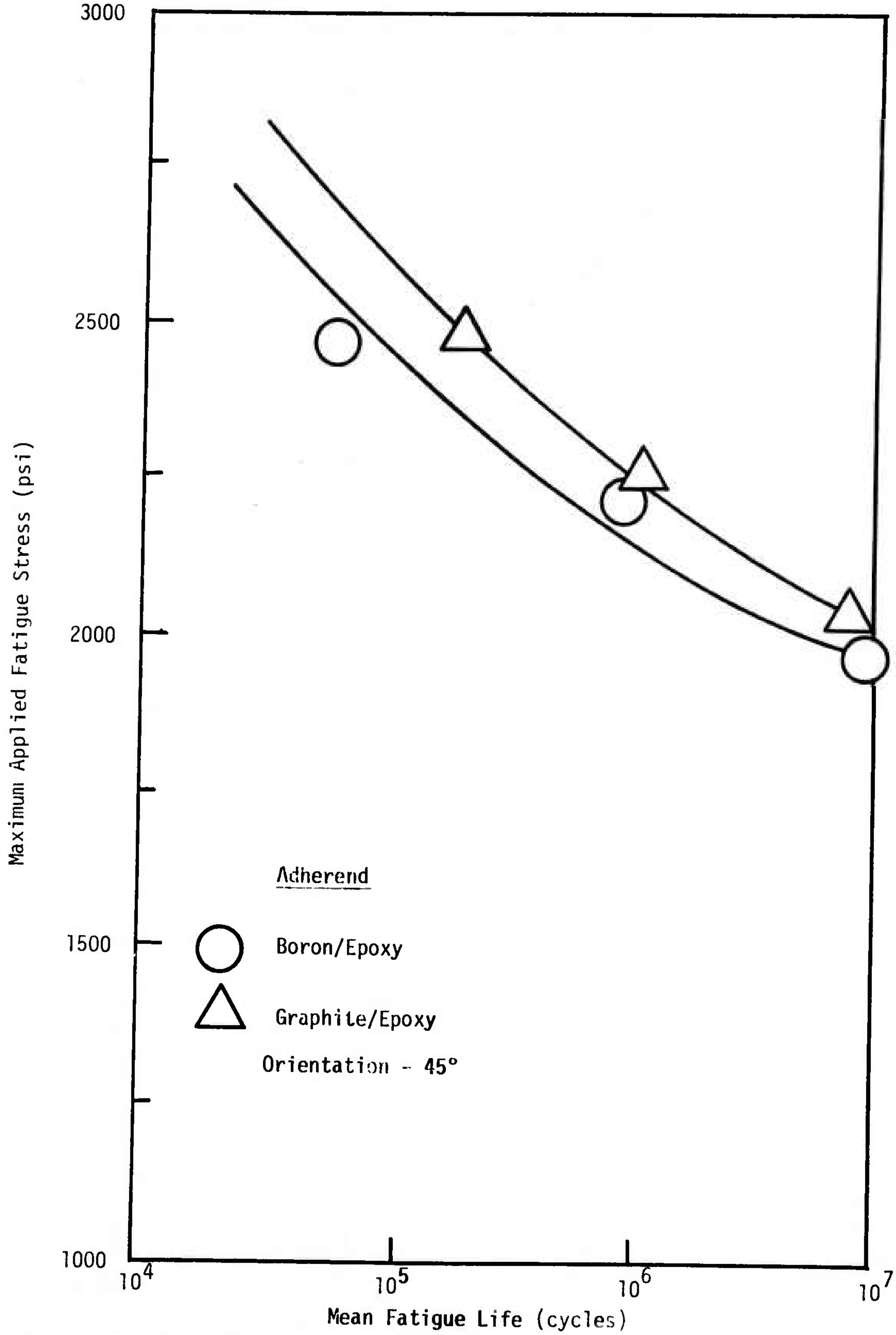


FIGURE 27: Effect of Adherend Type on the Fatigue Resistance of Style PWA Graphite Reinforced ADX-653.

Table 1: Adhesive Properties of ADX-653, ADX-655, and ADX-523

Adhesive Resin System	EA 9648		ADX-655		ADX-523	
Designation	EA 9648	ADX-653	ADX-655	-	ADX-523	-
Form	Adhesive Film					
Metallic Filler Present	Yes	No	Yes	No	Yes	No
Film Weight, lb/ft^2	0.1	0.045	0.1	0.045	0.1	0.047
Support	Glass	Nylon	Nylon	Nylon	Nylon	Nylon
Shear strength[2], 75°F, psi	4700	3400	4000	2500	3600	1900
" " 350°F, "	2700	2450	2600	2850	2500	2850
" " 420°F, "	1900	-	1450	-	2100	-
Shear strength after aging 10 hrs at 420°F, psi	1700	-	1050	-	1350	-
Honeycomb peel[3], 75°F, in.lb./3 in.	40	25	50	32	55	-
Bell peel[4], 75°F, lb/in.	8	6	5	3	10	-
Durability under stress (2000 psi, 140°F, 95% + RH) Failure time, hrs.	>900	-	>900	-	<150	-

(1) Cured 60 min. at 350°F and 50 psi.

(2) 2024 T3 bare aluminum single overlap shear panels.

(3) Skins - 0.020" thick 2024 T3 bare aluminum.
Core - 5052, 3/16" cell, 0.002" foil, non-perforated.

(4) 0.025" and 0.063" 2024 T3 bare aluminum.

Table 2: Effect of Resin Modification on the Adhesive Properties of ADX-523

[Resin Modification - Reaction of 7.5% of available epoxy with aromatic amine to improve the uncured, unfilled film handling properties]

Resin System	ADX-523	Modified ADX-523
Support	Nylon	Nylon
Tensile shear strength[1],		
75°F, psi	1600	1850
350°F, psi	2900	2850

[1]Aluminum (2024 T3 bare) single lap shear specimens, cured 60 mins. at 350°F.

Table 3: Results of Fatigue Screening Tests on Selected Resin Systems

Resin System	ADX-653			ADX-655			Modified ADX-523	
Support	HTS[1]	Nylon[4]	Nylon	HTS[1]	HTS[1]	Nylon	HTS[1]	Nylon
% Fiber[2] (w/w)	35.5	-	-	40.3	40.3	-	40.1	-
% Fiber (v/v)	26.9	-	-	30.9	30.9	-	31.3	-
% Volatiles[3]	0.6	Hot Melt	Hot Melt	0.7	0.7	Hot Melt	0.9	Hot Melt
Tape Wt. (lb./ft^2)	-	0.047	0.047	-	-	0.049	-	0.055
Specimen Preparation Technique[5]	1	1	1	1	2	1	1	
Ultimate Shear Strength, psi[6]	3620	5400	5400	3000	3960	4000	1980	2390
Fatigue Screening								
% Ultimate Strength	50	50	33	50	50	50		
Maximum Applied Stress, psi	1810	2700	1800	1500	1980	2000		
Cycles to Failure	118,000	2930	72,000	425,000	164,000	2730	(7)	(7)
Standard Deviation	78,000	2500	(8)	510,000	1700	1870		

(1) Adhesive tape, unidirectional HTS carbon tow, made with 3 tow/inch width.

(2) Acetone extraction of the resin in the uncured tape.

(3) Weight loss after 1 hour at 300°F.

(4) Nylon tricot (0.005 lb/ft^2)

(5) Technique 1 - used titanium spacers and shim.
Technique 2 - used titanium spacers and a teflon shim.

(6) Determined at 75°F, using titanium (6Al-4V) double lap shears.

(7) Not determined.

(8) One value.

Table 4: Fabrics Used in the Fiber Distribution Study

Fabric Designation	Source	Fiber	Fiber Modulus (x 10^6 psi)	Construction (Type/count)	Thickness (mils)	Weight Oz./Yd.^{2}	% Voids[(1)]
WCG	Union Carbide	Carbon	6	Plain (33 x 30)	11	3.0	79.8
PWA	Stackpole	Carbon	30	Plain (48 x 44)	15	3.35	83.2
120	DuPont	Kevlar[R]-49	19	Plain (34 x 34)	5	1.8	67.3
220	DuPont	Kevlar-49	19	Plain (22 x 22)	5	2.2	60.0
Tricot		Nylon	0.4	Knit	5	0.7	85.1
HS	Hercules	Boron	58	Unidirectional (250)	4	6.1	22.5
AS	Hercules	Carbon	30	Random Mat	18	2.4	89.9

(1) Calculated: % Voids + % Fiber (v/v) = 100

Table 5: Screening Test Results of Fabric Reinforced Adhesive Films

Adhesive System - ADX-653
Adherends - 2024 T3 bare aluminum (0.063" thick)
Test - Single lap shear (per MMM-A-132)
Cure - 60 minutes at 350°F and 25 psi

Reinforcement Designation	Fiber	Adhesive Tape Wt. (lb./ft^2)	Tensile Shear Strengths (psi) @ 75°F	Tensile Shear Strengths (psi) @ 350°F
Tricot	Nylon	0.047	2750	3030
120	Kevlar[R]-49	0.047	2600	2600
220	Kevlar-49	0.044	2350	2550
WCG	Carbon	0.099	2050	2100
PWA	Carbon	0.101	2740	2350
AS	Carbon	0.085	2350	2400
HS	Boron	0.075	2670	2700

Table 6: Comparison[1] of the Adhesion of Several Resin Systems to Style 120 Kevlar-49 Fabric

Resin System	Cure Temp., °F	Tensile Shear Strength, 75°F, psi	Bond Failure Type
ADX-653	350°	2300	Adhesive - resin to fiber surface
Commercial Adhesive A	250°F	2800	Adhesive - resin to fiber surface
Commercial Adhesive B	350°F	2200	Adhesive - resin to fiber surface

(1) The comparison was conducted on 2024 T3 bare aluminum panels cured at the temperature appropriate to the resin system.

TABLE 7. Results of the Fatigue Screening of Various Fibers and Woven Fabrics (Phase I, Task 2.)

Resin System - ADX-653

Reif.	BLT[4] (mils)	Fiber[3] Vol. (%)	Ult. Shear [1] Str. (psi)	Fatigue Load (psi)	Cycles to fail
Nylon	5.6	14.9	5810	2905	4,900[2]
WCG-Carbon	9.4	23.7	3545	1775	2,089,000
PWA Carbon	12.9	19.3	5270	2635	128,000
120/Kevlar-49	5.1	32.1	4285	2140	976,000
220/Kevlar-49	5.0	40.0	4320	2160	177,000
AS Carbon	9.7	-	4530	2265	445,000
HTS Carbon	10.8	-	5665	2830	99,000
HS Boron	6.7	47.5	5670	2835	2,300

(1) All testing performed on titanium (6-4) double lap shear specimens.

(2) One sample failed at 1.7 million cycles, other two stopped at 2.0 and 2.5 million cycles respectively.

(3) Calculated

(4) Bond Line Thickness

Table 8. Correlation of Fatigue Strength with Fracture Type

Reinforcement	Fatigue Stress (psi)	Cycles to Fail	Fracture Type
Nylon	2905	5,000	Resin
WCG-Carbon	1775	2,089,000	Fabric
PWA-Carbon	2635	128,000	Resin
120-Kevlar-49	2140	976,000	Adhesive/resin-fiber
220-Kevlar-49	2160	177,000	Adhesive/resin-fiber
AS-Carbon	2265	445,000	Resin
HTS-Carbon	2830	99,000	Adhesive/resin-fiber
HS Boron	2835	2,000	Adhesive/resin-fiber

Table 9. Attempts to Vary Cured Bondline Fiber Volume

Resin System: ADX-653
Reinforcement: HTS[R] Carbon Tow

a) Variation in wet adhesive fiber volume[1].

Fiber, % v			
In Uncured Tape	50.0	30.8	14.3
In Cured Bondline	54.9	46.6	47.0
Shear Strength, 75°F, psi	1070	2600	2700

b) Variation in cure pressure[2].

Cure Pressure, psi	15	50	75
Fiber, % v			
In Uncured Tape	30.8	30.8	30.8
In Cured Bondline	42.9	46.6	44.0
Shear Strength, 75°F, psi	2350	2600	2600

c) Variation in cure heatup schedule.

Schedule	30/15/210°[3] +30/60/350°	30/60/210° +30/60/350°	45/60/350°
Fiber, % v			
In Uncured Tape	14.3	14.3	14.3
In Cured Bondline	39.2	37.7	40.6
Shear Strength, 75°F, psi	2850	3150	3200

(1) Aluminum single overlap shear specimens cured 1 hour at 350°F and 50 psi.

(2) Aluminum single overlap shear specimens cured for 1 hour at 350°F.

(3) 30/15/210° + 30/60/350° means that the specimens were heated from ambient to 210°F in 30 minutes, held at 210°F for 15 minutes, heated from 210°F to 350°F in 30 minutes, and then held at 350°F for 60 minutes. All cures conducted under 15 psig autoclave pressure.

Table 10. Effect[1] of Tow Packing On Cured Fiber Contents

Resin System: ADX-653
Reinforcement: HTS (R) Carbon Tow

No. tow/in. width	3	3	4	4	6	6
Fiber, % V, in uncured tape	11.2	11.2	14.5	14.5	15.4	15.4
Shim thickness (in.)	0	0.0105	0	0.0105	0	0.0105
Fiber, % V, in cured tape	45.9	16.7	45.1	23.0	49.6	40.2
Shear Strength, 75°F, (psi)	3050	3050	3050	2800	2850	2700
Bond Line Thickness (in.)	0.0055	0.011	0.0065	0.0145	0.009	0.0125

(1) Aluminum (2024-T3 Bare) single lap shear specimens cured 60 minutes at 350°F and 50 psi.

Table 11. Fatigue Test Results with HTS^R Carbon Unidirectional Tapes Made at Various Tow/Inch Width

Resin: ADX-653

No. of Tow/Inch Width of Tape	3	4	6	0
Fiber, % v				
In Uncured Tape	11.2	14.5	15.4	-
In Cured Bondline	(1)	(1)	(1)	-
Cured Bondline Thickness, in.	0.008	0.012	0.020	0.008
Ultimate Shear Strength psi[2]	3600	4700	4200	5400
Fatigue Screening[2], Cycles to Failure				
Loaded at 50% of Ultimate Strength	118,000	257,000	26,000	2930
Maximum Loaded Stress, psi	1800	2350	2100	2700

(1) Not determined to date.

(2) Determined using Titanium (6Al, 4V) double lap shear specimens cured for 60 minutes at 350°F and 50 psi.

Table 12. Effect of Reinforcement Orientation of Fatigue and Ultimate Shear Properties

Reinforcement[1]	Orientation[2]	Ultimate Shear[4] Strength (psi) @ 75°F	Ultimate Shear[4] Strength (psi) @ 350°F	Fatigue Properties[4] at 75°F Stress(psi)	Fatigue Properties[4] at 75°F Life (cycle)
Style 120 Kevlar R 49	0°	4040	1555	2050	182,000
	45°	4170	1490	2050	>1,350,000
	90°	4090	1640	2050	500,000
Style PWA Carbon	0°	3930	1950	2080	151,000
	45°	4390	2380	2080	179,000
	90°	3950	2530	2080	61,000
Type AS Fiber mat	0° [3]	4750	3020	2375	9,000
	90°	3540	2950	1770	30,000
Nylon Knit	0°	5360	1860	2680	3,000

Phase I Data Reinforcement	Ultimate Shear (psi) at 75°F	Fatigue Stress (psi)	Fatigue Life cycle
Nylon Knit	5810	2905	5,000
Style 120	4285	2140	976,000
Style PWA	5270	2635	128,000
Type AS mat	4530	2265	445,000

1) ADX-653 Resin system used.

2) The angle the major axis of the support makes with the direction of stress application.

3) Major axis arbitrarily chosen.

4) Determined using titanium double lap shear. See Figure 11 for design.

TABLE 13. Effect of the Variation of Adhesive Lot and Test Specimen Type on the Ultimate Shear Strength and Fatigue Resistance of Type AS Mat Supported ADX-653.

Lot No.	Specimen Type	Orientation(3)	Ultimate Shear Strength (psi)	Fatigue Life @ 50% of Ultimate (cycles)
2	Phase II(1)	0° 90°	4750 3540	9,000 30,000
3	Phase II	0°	4930	22,000
3	Phase I(2)	0°	4680	89,000
1	Phase I	0°	4530	445,000

(1) See Figure 11 for design.

(2) See Figure 1 for design.

(3) Orientation to an arbitrarily chosen direction.

TABLE 14. Ultimate Shear Strengths of High Modulus Fiber Reinforced ADX-653 Joints Using Composite Adherends with Inferior Layup Configuration and Phase II Specimen Design[2].

Reinforcement	Composite[1]	Ultimate Shear Strength (75°F) psi
Style 120 Kevlar-49	Graphite/Epoxy	2460
	Boron/Epoxy	1950
	None	4040
Style PWA Carbon	Graphite/Epoxy	1710
	Boron/Epoxy	1560
	None	3930
Nylon Knit	Graphite/Epoxy	2790
	Boron/Epoxy	2260
	None	5360

1) Composites were constructed with ± 45,0,0,0, 90, 0,0,0, ± 45 ply design.

2) See Figures 13, 14 and 15 for design.

TABLE 15. Adhesive Properties of High Modulus Fiber Reinforced ADX-653 Using Composite Adherends[1)] with Refined Layup Configuration and Phase I Specimen Design.[2)]

Adhesive Reinforcement	Ultimate Shear Strength (psi)		Fatigue Properties at 75°F Stress (psi)	Lifetime (cycles)
Nylon Knit	5200		2600	11K
Style 120 Kevlar[R] 49	3540		1770	> 1,300 K
		then	2125	194 K
Style PWA Carbon	4540		2270	462 K

1) Four ply Narmco 5208 (T-300) Graphite Epoxy with a 0,0,0,0 layup configuration.

2) See Figure 15 for design.

Table 16: STATIC ULTIMATE STRENGTHS OF STYLE FABRIC PWA GRAPHITE REINFORCED ADX-653

Reinforcement	Nylon Knit		PWA	
Adherend	Boron/Epxoy	Graphite/Epxoy	Boron/Epxoy	Graphite/Epoxy
Ultimate Shear[1] Strength (psi)				
@-67°F	3690	3890	4800	4910
@ 75°F	4675	4890	4645	4320
@ 350°F	1780	2630	1390	2000

[1] Determined with a fabric orientation of 0°

Table 17: Demonstration of Fatigue Improvement[1)]

Part A: Reinforcement - Nylon knit
Orientation - 0°

Adherend[2)]	Ultimate Shear Strength, psi	Fatigue Stress, psi	Percent of Ultimate Strength	Fatigue Life	Mean Life
Boron/epoxy[3)]	4675	1870	40	13,000	
				222,000	
				19,000	
				228,000	
				159,000	128,200
Boron/epoxy	4675	1700	36.6	776,000	
				267,000	
				165,000	
				49,000	
				355,000	184,000
Boron/epoxy	4675	1400	30	714,000	
				>15,507,000	
				>10,354,000	
				>10,290,000	
				>15,506,000	$>10^7$
Graphite/epoxy[4)]	4890	2200	45 4	147,000	
				71,000	
				13,000	
				14,000	
				15,000	28,300
Graphite/epoxy	4890	1955	40	27,000	
				486,000	
				631,000	
				1,310,000	
				2,031,000	897,000
Graphite/epoxy	4890	1470	30	610,000	
				1,039,000	
				3,502,000	
				4,207,000	
				10,879,000	4,047,000

Table 17: Demonstration of Fatigue Improvement (Cont'd.)

Part B: Reinforcement - Style PWA Graphite
Orientation - 0°

Adherend	Ultimate Shear Strength, psi	Fatigue Sress, psi	Percent of Ultimate Strength	Fatigue Life	Mean Life
Boron/epoxy	4645	2320	50	49,000	
				92,000	
				124,000	
				131,000	
				149,000	109,000
Boron/epoxy	4645	2090	45	130,000	
				364,000	
				1,045,000	
				3,351,000	
				11,105,000	3,199,000
Boron/epoxy	4645	1860	40	613,000	
				2,569,000	
				5,509,000	
				>10,349,000	
				>10,898,000	5,988,000
Graphite/epoxy	4320	2590	60	44,000	
				79,000	
				109,000	
				158,000	98,000
Graphite/epoxy	4320	2380	55	262,000	
				386,000	
				587,000	
				735,000	493,000
Graphite/epoxy	4320	2160	50	817,000	
				921,000	
				>10,252,000	
				>12,541,000	6,133,000

Table 17: Demonstration of Fatigue Improvement (Cont'd.)

Part C: Reinforcement - Style PWA Graphite
Orientation - 45° [5]

Adherend	Ultimate Shear Strength, psi	Fatigue Stress, psi	Percent of Ultimate Strength	Fatigue Life	Mean Life
Boron/epoxy	4915	2460	50	22,000	
				26,000	
				54,000	
				61,000	
				111,000	55,000
Boron/epoxy	4915	2210	45	230,000	
				528,000	
				662,000	
				1,347,000	
				1,472,000	839,000
Boron/epoxy	4915	1970	40	>10,544,000	
				>10,420,000	
				8,533,000	
				>10,288,000	
				3,578,000	8,670,000
Graphite/epoxy	4505	2480	55	55,000	
				73,000	
				80,000	
				256,000	
				500,000	193,000
Graphite/epoxy	4505	2250	50	73,000	
				717,000	
				833,000	
				1,271,000	
				2,374,000	1,054,000
Graphite/epoxy	4505	2030	45	>14,759,000	
				>10,006,000	
				>10,113,000	
				2,759,000	
				1,019,000	7,730,000

1) Determined Using the ADX-653 Resin System
2) See Figure 15 for Design.
3) 4 ply (0,0,0,0) Avco 5505
4) 4 ply (0,0,0,0) Narmco 5208 (T-300)
5) Orientation of Major Axis of Fabric to the Direction of Stress Application.

Table 18: Effect of Reinforcement Orientation on the 10^7 Cycle Fatigue Strength of Style PWA Reinforced ADX-653

Orientation	Adherend	Ultimate Shear Strength, psi	10^7 Cycle Fatigue Strength psi	% UTS (1)
0°	Boron/epoxy	4645	1900	41
45°	Boron/epoxy	4915	2000	40
0°	Graphite/epoxy	4320	2150	49.5
45°	Graphite/epoxy	4505	2020	45

(1) Percent of ultimate shear strength.

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