UNCLASSIFIED

AD NUMBER
ADB009505
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies only; Test and Evaluation; DEC 1975. Other requests shall be referred to Air Force Materials Lab., Wright-Patterson AFB, OH 45433.**
AUTHORITY
AFWAL ltr 6 Oct 1981

THIS PAGE IS UNCLASSIFIED

AFML-TR-74-169

Part II

IMPROVED FATIGUE STRENGTH ADHESIVE
Part II – ADHESIVE OPTIMIZATION

THE DEXTER CORPORATION, HYSOL DIVISION

DECEMBER 1975

TECHNICAL REPORT AFML-TR-74-169, Part II
REPORT FOR PERIOD JUNE 1974 – JUNE 1975

Distribution limited to U.S. Government agencies only; Test and Evaluation; ~~November~~ Dec. 1975. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Composite and Fibrous Materials Branch, AFML/MBC, Wright-Patterson Air Force Base, Ohio 45433

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any was be related thereto.

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

T. J. APONYI
Project Monitor

FOR THE COMMANDER

T. J. REINHART, JR., Chief
Composite and Fibrous Materials Branch
Nonmetallic Materials Division

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AIR FORCE - 5-2-76 - 250

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

18

1. REPORT NUMBER: AFML-TR-74-169, Part 2

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

6

4. TITLE (and Subtitle): IMPROVED FATIGUE STRENGTH ADHESIVE PART II. ADHESIVE OPTIMIZATION.

9

5. TYPE OF REPORT & PERIOD COVERED: Technical Report, June 1974 to June 1975.

6. PERFORMING ORG. REPORT NUMBER

10

7. AUTHOR(s): David K. Klapprott, C. Lynn Mahoney, (Hysol) Paul M. Stifel, Eugene R. Fannin (McDonnell)

15

8. CONTRACT OR GRANT NUMBER(s): F33615-73-C-5133

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Hysol Division The Dexter Corporation, 2850 Willow Pass Road, Pittsburg, California 94565. Subcontractor: McDonnell Aircraft Company, St. Louis, Missouri 63166

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Project 7340, Task 734002

11. CONTROLLING OFFICE NAME AND ADDRESS: AFML/MBC, Wright Patterson Air Force Base, Ohio 45433

11

12. REPORT DATE: December 1975

12

89p.

13. NUMBER OF PAGES: Eighty-eight

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

16

AF-7340

17

734000

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution limited to U. S. Government agencies only; (test evaluation) December 1975. Other requests for this document must be referred to Air Force Materials Laboratory, Nonmetallic Materials Division, Plastics & Composites Branch, AFML/LNC, Wright Patterson Air Force Base, Ohio 45433.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Adhesives - improved fatigue
Adhesives - reinforcement
metal to metal bonding
metal to graphite/epoxy composite bonding fiber nylon
fiber - graphite
fiber - Kevlar 49
fiber - E-Glass

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

In spite of their high static strengths over a wide temperature range, present 350°F service adhesive systems must be limited in maximum structural design loadings to as little as 30% of static ultimate strength if fatigue lives in the order of 10^7 cycles are required. This situation has limited the use of high temperature adhesives in bonding such fatigue resistant materials as graphite-epoxy composites. However, addition of high strength, high modulus fibers, such as graphite, to the adhesive system has been found to improve the

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

10 to the 7th power

390 000

1/B

fatigue durability of such assemblies. An increase in allowable fatigue loading to as much as 50% of static strengths was demonstrated in the initial portion of this contract by addition of PWA, a graphite fiber fabric, to ADX-653, a 350°F service system. The object of this continued effort has been to optimize and define a practical adhesive system. To this end, the adhesion of resin to fiber, the effect of resin and fiber modulus, and the influence of fiber volume content and bondline thickness were examined.

The fatigue resistance of the ADX-653/PWA combination, as measured by a single load test, was doubled by the application of a silane finishing agent to the graphite surface prior to resin impregnation. Fatigue durability improvements due to high modulus fiber are limited to the 350°F service adhesive system. These systems show an increasing fatigue life with increasing fiber modulus. The high fatigue resistance of a high toughness, 250°F service system was not improved by the addition of such fibers. Improved fatigue resistance with increasing fiber volume content was shown. Using higher modulus fiber, higher fiber volume graphite fabrics gave no improved performance over PWA fabric. The improvements in the PWA/ADX-653 adhesive system gave constant amplitude 10^7 cycle fatigue strengths of 2550 psi or 50% of ultimate using a titanium-graphite epoxy double lap shear specimen.

A five-fold increase in the expected bond lifetime under advanced fighter aircraft spectrum fatigue testing was demonstrated using the PWA reinforced ADX-653 system as compared to a state of the art nylon fabric supported system. A titanium/graphite-epoxy multiple step splice plate test specimen representative of the end use of these materials in advanced aircraft design was used. This high modulus fiber reinforcement also resulted in a significant increase in the resistance to high loadings (>90% of ultimate during spectrum testing).

The ADX-653/PWA system, although showing significantly improved spectrum fatigue resistance over a control, is inferior in this parameter to an adhesive system currently used in constructing an advanced fighter aircraft. Analysis of the results strongly suggest that this difference is due to the lower static ultimate strengths of the ADX-653/PWA combination rather than an inefficiency of the reinforcement mechanism. There are strong indications that if the ultimate strength of this system were increased, significant and practical improvements of fatigue resistance would result.

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 Non-Metallic Materials Division.

This report covers the product optimization phase of the contract work. The results of the original exploration and demonstration of the concept of adhesive fatigue life improvement via high modulus fiber addition to the adhesive may be found in AFML-TR-74-169.

This report covers the work performed between June 1974 and June 1975.

The authors are D. K. Klapprott and C. L. Mahoney of the Hysol Division, The Dexter Corporation, and P. M. Stifel and E. R. Fannin of the McDonnell Aircraft Company. The report was submitted for approval of 6 October 1975.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (continued)

LIST OF TABLES

1.0 PROGRAM OBJECTIVE

The technical objective of this program was to maximize the adhesive fatigue life improvement obtainable by bondline reinforcement with high modulus fibers. This was attempted by further examination of the bond line parameters controlling this phenomenon. The objective also includes use of the above information to formulate a practical 350°F service adhesive system having good handling and cure properties, good environmental resistance and optimized fatigue resistance. The level of improvement of fatigue resistance was to be demonstrated as an increase in the percent of static ultimate strength at which the system will survive 10^7 cycles when used in complex bonded structures.

2.0) SUMMARY AND CONCLUSIONS

High performance composites are being used in more numerous applications and larger amounts in advanced aircraft due to the significant improvements in both performance and economics they afford. A significant impediment to their full use, however, has been a concern for the durability of joining techniques used with them. Whereas some composite materials can be stressed up to 90% of their ultimate strength and survive 10^7 fatigue cycles, most high temperature epoxy adhesives will survive only at 20 to 30% of ultimate.

Initial work on this contract, published in AFML-TR-74-169, demonstrated that the fatigue durability of a 350°F service adhesive can be increased to approximately 50% of ultimate strength by bondline reinforcement with a graphite fiber fabric. This improvement amounted to a 50% increase in the long term usable strength of the adhesive system. There was a need, however, to optimize the adhesive system in terms of fiber-resin adhesion and bondline properties such as cured thickness and fiber volume. This contract continuation has served this function.

Resin washes were applied to both the style PWA graphite and style 120 Kevlar 49 fabrics in an attempt to improve fiber-resin adhesion. These washes were selected from a group of reactive resins and polymers designed to bond to active sites by either physical or chemical mechanisms. An increase in adhesion as detected by increased resistance of composites to boiling water exposure was not detected. However, treatment of the PWA graphite with Z-6040 silane did result in the increase of the 10^5 cycle fatigue life of this system. The Kevlar 49 fabric was not responsive to these treatments.

Attempts to define the influence of adhesive bondline thickness, at constant fiber volume, on fatigue properties were unsuccessful due to an inability to independantly control these variables. Any future attempts to do so will have to be made with fabrics designed and constructed specifically for this task. A correlation of the level of fatigue improvement with increasing fiber volume was detected by reducing the fiber packing of the PWA graphite system. Experiments with the style 120 Kevlar 49 fabric at higher fiber volumes were inconclusive perhaps due to either the much thinner bond lines or the characteristic adhesive failure of resin from fiber.

The improvement of fatigue properties by bondline reinforcement with high modulus fibers appears to be most effective with the stiffer 350°F service adhesive systems. Experiments with two such resin systems, ADX-653 and ADX-646, revealed a trend of increasing fatigue resistance with higher fiber modulus reinforcements. This trend was absent when EA 9628, a tough, 250°F service adhesive, was used as the matrix. In this instance the 10^5 cycle fatigue strength of the control nylon knit system was equivalent to that of the PWA graphite reinforced adhesive. These results led to the development of a rationale concerning the mechanism of fatigue improvement. The two important parameters in this concept are the degree of reinforcement, i.e., the level of decrease in strain to a specific stress, and the inate crack or flaw resistance of the resin system.

Treatment of the PWA graphite fabric with Z-6040 silane resulted in the increase of the stress level which would survive 10^7 cycles of fatigue, when tested as a reinforcement for ADX-653, from 2150 psi (as determined in AFML-TR-74-169) to 2550 psi. However, this amounts to an increase in fatigue strength from 47.5% of ultimate to only 51.5% due to a significant increase in the strength of the titanium-graphite/epoxy double lap shear test specimens. Initial estimates of the fatigue strength of the ADX-653/Nylon knit system (1400 psi may have been low. Repetition of this experiment resulted in a 2000 psi value. No viable reasons for this discrepency were found.

Titanium-graphite/epoxy step-lap splice plate specimens were used to measure the level of fatigue performance improvement in terms more representative of advanced aircraft design. Constant amplitude fatigue testing of these specimens was aborted after significant problems with metal fatigue were found. At high stress levels, 50% of ultimate, the specimens were adhesive critical and failed in the bondline. However, at slightly lower stresses (40 to 45% of ultimate), the titanium failed by a simple fatigue mechanism. The small amount of data did reveal a two-fold improvement in fatigue resistance due to the high modulus fiber reinforcement.

A five-fold increase in fatigue resistance due to bondline reinforcement with PWA graphite was demonstrated using the multiple step specimen in a spectrum fatigue test. Thus, using a test limit load of 13,500 pounds, the PWA reinforced system survived 1.63 simulated fighter flight lifetimes while the nylon knit supported control failed at 0.32 lifetimes. Using a 12,000 pound test limit load, the expected life was 3.02 and 0.63 lifetimes for the PWA and nylon systems respectively. Bondline reinforcement with high modulus fibers also results in resistance to high (>90% of ultimate) loading during fatigue testing. A 125% test limit load was applied periodically during the 12,000 pound test. The ADX-653/nylon system predominantly failed during the application of this load while the PWA reinforced system survived between 3 and 8 load application. Additionally, no failure occurred during 125% test limit load application.

The ADX-653/PWA system, although showing a large increase in fatigue resistance over a ADX-653/nylon knit containing control, has inferior spectrum fatigue resistance, compared to 350°F service used in fighter aircraft construction (using the 13,500 pound test). Whereas, the ADX-653/PWA system failed at 1.63 lifetimes, the commercial adhesive failed at 2.52 lifetimes. Analysis of the results indicated that the lower ultimate strength of the ADX-653 system (16,000 pounds) compared to the commercial adhesive (20,000 pounds) may be a major factor in this discrepency. This results in the testing centering around 85% of ultimate in the case of the ADX-653/PWA combination and only 67.5% for the commercial adhesive. Another possible reason for this discrepancy lies in the fact that the test specimen was designed for this specific commercial adhesive and does not reflect the stress-strain properties of the ADX-653/PWA adhesive system.

This analysis also suggests that increasing the ultimate strength of the ADX-653/PWA combination would produce significant and practical increases in the fatigue resistance.

3.0 PHASE I, TASK 1 IMPROVED FIBER - RESIN ADHESION

The initial experimental effort in this contract[1]) defined two types of high strength, high modulus fibers which appreciably improved the fatigue resistance of ADX-653, a 350°F service adhesive system. Graphite, in the form of style PWA fabric (fiber modulus $\sim 30 \times 10^6$ psi), was the superior of the two and was used to effect a 49% increase, compared to a state of the art nylon knitted scrim, in the applied stress which survived 10^7 cycles of constant amplitude fatigue. A square weave fabric of Kevlar 49 ($E_f = 19 \times 10^6$ psi) gave, in screening tests, fatigue resistance better than the PWA graphite, but significantly lower ultimate strength (4285 vs. 5270 psi). The Kevlar 49 reinforced adhesive was considered inferior because of this lower strength.

One of the initial goals of this supplemental effort was to improve the ultimate strength performance of Kevlar 49 reinforced ADX-653. Examination of the bond failure revealed that the bond failed at the adhesive resin-fiber interface (Figure 1). Conceivably, this low level of fiber-resin adhesion could be associated with premature bond failure, resulting in low ultimate strength levels. Using this rationale, an increase in the specific adhesion of the ADX-653 resin system to the Kevlar fiber could result in higher levels of static strength. Viewing this lack of adhesion as a "defect", fatigue resistance should not be impaired by this lack in adhesion.

For the purposes of this experiment, the low level of adhesion was viewed as an insufficiency in either the level of resin "wetting" of the fiber or in the number and/or type of adhesive bonding sites. The Kevlar 49 fabric was woven from 195 deneir yarn which has 134 fiber filaments. Application of a viscous resin solution, such as ADX-653, could result in significant levels of non-wetted (i.e., non-bonded) surface in the interior of the yarn bundle. These defects, under stress could extend to the bundle surface giving an adhesive failure of the bond. Adhesive bonding with epoxies usually occurs through highly polar dipoles. The number of these in the high temperature service formulation used, prior to cure, is not great due to the nature of the resins. Lack of specific adhesion between the resin and the dipole structure in the Kevlar (i.e., amide bonds) could result in some unbonded areas acting as surface "defects".

A number of high molecular weight polymers containing highly polar dipoles were selected as resinous washes for the fiber. In addition, several reactive surface finishes used in the commercial fabric market (i.e., melamine and silanes) were also studied. These systems were applied to the fiber under conditions designed to maximize wetting. The change in composite interlaminar shear strength due to 24 hours exposure to boiling water was used as a guage of finish effectiveness.

This series of resinous washes were also applied to the PWA graphite fabric. Although adhesion of ADX-653 to this fiber surface is considered good, a small amount of adhesive failure, resin from fiber, is noticed. The graphite surface contains both acidic and basic sites and the fabric is constructed of multi-filament yarns. These two facts suggest the possibility of property improvement by resin wash application.

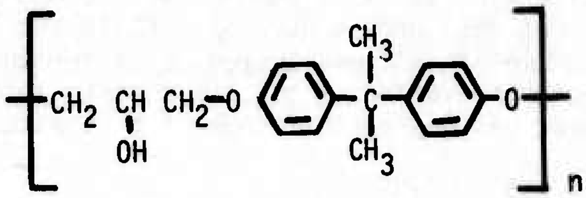
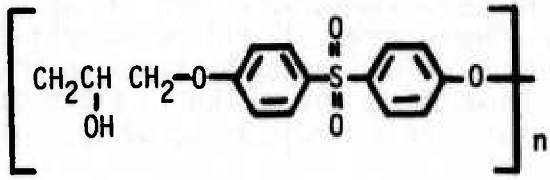
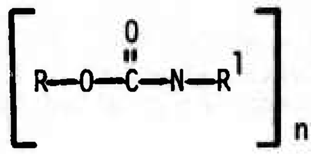
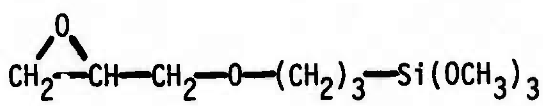
The intent of this experiment is to investigate the use of resin washes to facilitate improved adhesive bonding of the ADX-653 to the fiber surfaces. It was not designed to develop a finishing agent. As such, the effectiveness of the agents was guaged by performance testing levels and not by direct observation of the fiber-resin interface. Such a study, although needed, was beyond the scope of this effort.

3.1) SELECTION OF RESIN WASHES

Two general types of resin washes were used in the attempt to improve fiber-resin adhesion. These were: 1. polymeric resins with groups within the molecule which could interact by hydrogen bonding with the amide group of the Kevlar and the acidic and basic sites on the surface of the graphite and, 2. reactive silanes, designed to bond to the acidic sites of the graphite

To augment the information gained from these washes, a silicone release agent was included to guage the effect of a total loss of fiber-resin adhesion. Also the fabrics were vacuum dried to determine the role of surface moisture on adhesion.

Specifically, these washes were:

Resin	Resin Structure	Comments
ADX-653	-	-
PAHJ		Hydrogen bonding through hydroxyl group. Difficult to displace entirely from surface. Capable of accomodating thermal strains through yielding.
KSLA		Higher Tg than PAHJ, Experimental
Estane 5703		Commercial Thermoplastic polyurethane. Lower Tg than PAHJ
Aerotex M-3	-	Commercial "melamine" fabric finish
Z-6020	$H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$	Reactive through hydrolized Si-OCH3 sites and the N-H sites.
Z-6040		Reactive through both hydrolized Si-OCH3 and epoxide sites.
Ram 225	-	Commercial silicone release agent. Attempt to destroy all adhesion.
Air Dry	-	Dried 18 hours @ 121°C. Eliminate surface moisture.

3.2) EXPERIMENTAL

The resin washes were applied to the fabrics from 1% solids (w/w) solutions in either acetone or acetone/dimethylformamide, depending on solubility needs. The only exceptions were the Aerotex M-3 (water) and Ram 225 (Toluene).

Fabric interstitial air was eliminated by evacuation of the sample in a bell jar. The resin solution was then applied and the vacuum broken only after complete contact with the fabric. The washes were allowed to equilibrate on the surface for 30 minutes under ambient conditions (T = 20-22°C). The fabrics were then removed, excess solution removed by draining the solvent and flashed for 30 minutes at 200°F in a forced air oven. The Aerotex M-3 treated specimens were given a 60 minute at 350°F cure.

The polymeric resin washes were absorbed onto the Kevlar-49 surface in a range of 0.6 to 1.3% (w/w) as determined by fabric weight increase (Table 1). The reactive silanes and the silicone release agent were absorbed at less than 0.01% (w/w). The same trend was noticed with respect to the treated PWA samples. The polymeric resins were absorbed at 1.9 and 5.3 weight percent, the exception being ADX-653 (0.01% [w/w]). The reactive silanes and Ram 225 added less than 0.01% to the fabric weight. The finished adhesive films were then manufactured by solvent impregnation with ADX-653 (70% w/w solution in acetone). The final weight of the adhesive (0.050 lb/ft^2 for the Kevlar and 0.100 lb/ft^2 for the PWA) was designed to allow enough resin for flow and wetting of the adherends and to fill the interstitial voids of the fabric.

3.3) EFFECT OF RESINOUS WASHES

The effect of the fiber washes on the adhesion of ADX-653 to both graphite and Kevlar 49 was guaged by determining the 75°F interlaminar shear strength (short beam method) of a 0.080 inch thick composite specimen after a 24 hour water boil. For test method, see Appendix.

3.3.1) Style 120 Kevlar-49

The performance of the Kevlar 49 control system was not exceeded by any of the resin wash treated systems (Table 2). The initial interlaminar shear strength varied from 5700 psi (KSLA) and 5600 psi (untreated control) to 4600 psi (Aerotex M-3). This variation of strength could not be correlated with either the type of finish or the volume fraction of fiber in the composite. The retention of strength after a 24 hour water boil varied from 100% (PAHJ and untreated control) to 63.5% (Aerotex M-3). In general the polymeric resin treated systems performed better (80-90% retention) than did reactive silanes (66-72% retention). The Ram-225 release agent heated treated system exhibited poor performance (65.8% retention) but no poorer than the Aerotex M-3 (63.5%) or the air dried system (71.7%). The level of Ram 225 add-on (0.01%) may have been too low to be effective. The reason for the poor performance of the air dried system is not known.

Microscopic examination of the failed short beam specimens also indicated that the level of adhesion had not been improved. When dry, the specimens failed by a combination of interlaminar (usually in the tension face) and across ply failure modes (Figure 2). After a 24 hour boiling water exposure, a less distinct failure mode was evident but what was seen with the same combination of interlaminar and cross laminar fracture (Figure 3) with most of the failure being the former. These was no significant differences in this failure phenomenon as evidenced by comparing the failure surfaces of fabric treated with either Phenoxy PAHJ or Estane 5703 (Figure 4).

3.3.2) Style PWA Graphite

The already high level of resin-fiber adhesion of the ADX-653/PWA system was not increased by any of the fabric washes used. The interlaminer shear strength retention after water boil of the control system was not exceeded by any of the resin wash treated systems (Table 3). This control retained 98.6% of its initial strength (3480 psi) while the performance of the treated systems varied from 100% (Aerotex M-3) to 80.9% (ADX-653 dilute solution). The higher level of initial strength of the treated systems as compared to the control might be construed as evidence for better adhesion but it is felt that this is an artifact as reflected by the high strength levels of both the dilute solution ADX-653 and air dried systems.

The type of failure morphology before and after boiling water exposure was not modified by any fiber surface treatment. In all cases, the failure occured by cross laminar failure (Figure 5). Additionally a small amount of bare graphite fiber was always seen at the tension surface but the amount of this did not vary with any fabric treatment (Figure 6).

3.3.3) Conclusions

The level of adhesion of the ADX-653 resin system to both Kevlar 49 and PWA graphite fibers was not increased by treatment of the fiber surfaces with various resin washes. This conclusion was reached after comparing both the percent retention of ultimate interlaminar shear strength and failure morphology after 24 hours water boil. In both cases, untreated control systems retained the maximum level of strength.

3.4) SYSTEM SELECTION FOR FATIGUE SCREENING

The interlaminar shear testing mentioned above was used as a convenient and effecient screening tool for fiber resin adhesion. The performance test of interest in this work is fatigue resistance. Since there was no resin wash which improved fiber-resin adhesion as guaged by interlaminar shear strength retention, several systems for each fiber were selected which best exemplified the range of shear strength retention behavior seen.

3.4.1 Style 120 Kevlar 49

Systems exhibiting extremes of shear strength retention were selected for fatigue testing. These were PAHJ (a phenoxy polymer, 100% retention) and Z-6040 (the epoxy functional silane, 72% retention). In addition, the ADX-653 treated system was included as a control and the RAM 225 (a silicone release agent) was tested to investigate the effect of total loss of adhesion.

3.4.2) Style PWA Graphite

Representatives of the two major types of washes investigated (polymeric and silane) which exhibited a large retention of shear strength and which are commercially available and easily applied were selected for fatigue testing. These were: PAHJ, 88.6% retention; Estane 5703, 89.7% retention; and Z-6040, 97.1% retention. Again, the ADX-653 treated specimen was included as a control.

3.5) FATIGUE SCREENING

Constant amplitude fatigue screening was performed on both the ADX-653/Kevlar 49 and PWA graphite systems at 2600 psi maximum applied fatigue stress. This stress level was selected as being 55% of the ultimate strength of the ADX-653/PWA graphite control system. At this stress level, ADX-653 reinforced with PWA has historically failed at 100,000 cycles. The fatigue screening was conducted using a Titanium-Titanium double lap shear specimen (Figure 7).

3.5.1) Style PWA Graphite

ADX-653 reinforced with style PWA which had been treated with the resin washes gave ultimate tensile shear strengths at 75°F (Table 4) which were equivalent to that of the control system (4700 to 5300 psi). These values ranged from 4680 psi, given by the PAHJ phenoxy treated system to the 4810 psi of the Estane polyurethane system.

Application of both the Z-6040 epoxy silane and the Estane 5703 polyurethane to the PWA fabric resulted in an increase in fatigue resistance by a factor of approximately two (both systems failed at 200,000 cycles) as compared to the control. The PAHJ phenoxy and ADX-653 treated systems gave fatigue resistance equivalent to the control (100,000 cycles). Microscopic examination of the failed fatigue specimens revealed no morphological differences in resin-fiber adhesion which correlated with the increase in fatigue resistance. The major failure mode was in the resin near the metal interface.

3.5.2) Style 120 Kevlar 49

All resin wash treated ADX-653/Style 120 Kevlar 49 adhesive systems gave 75°F ultimate shear strengths equivalent to the previously determined value of the control (4285 psi, Table 4). These strengths ranged from 4070 psi (RAM 225 treatment) to 4320 psi (PAHJ treatment). All systems were fatigue tested at 2600 psi, 60 to 65% of their ultimate shear strength. The fatigue resistance was decreased considerably at this stress level as compared to the previously determined control (976,000 cycles at 2140 psi). Maximum fatigue resistance (47,000 cycles) was given by the ADX-653 treated control system (Table 4). The other treatments gave fatigue lives varying from 33,000 cycles (Z-6040 treatment) to 13,000 cycles (RAM 225). Microscopic examination of the failed specimens did not reveal any improvement of the resin to fiber adhesion. A complete adhesive failure of resin from fiber surface persisted.

3.5.3) Effect of Resin Washes on Elevated Temperature Shear Strengths

The presence of thermoplastic resin such as PAHJ phenoxy and Estane polyurethane at the resin/fiber interface might have a deleterious effect on shear strength at temperatures above their Tg, expecially at 350°F. No such effect has been noticed (Table 5). The 350°F blister shear strength of the resin treated PWA/ADX-653 systems ranged from 2100 psi to 2350 psi, essentially that of the ADX-653 treated control (2280 psi). The ADX-653/Kevlar 49 system appears to have been affected adversely at 350°F by the presence of the PAHJ phenoxy resin wash. The blister shear strength at this temperature (1510 psi) was significantly lower than either the ADX-653 control (1970 psi) or the other resin washes (>2100 psi, Table 4).

3.5.4) Conclusions

The fatigue resistance of the ADX-653/style PWA graphite adhesive system was increased by a factor of approximately 2 by the use of a dilute resin wash of either Z-6040, epoxy silane, or Estane 5703, thermoplastic urethane. There were no visual differences in adhesion at failure, however. The presence of a thermoplastic resin at the resin-fiber interface did not affect the shear strength of the system at temperatures much above the thermoplastic resin's glass transition temperature. This possibly could be due to a solution of the thermoplastic by the ADX-653 resin system. All following work with graphite fibers used a wash of Z-6040 silane on the fiber surface. This wash was selected over the Estane 5703 because of its established performance in improving the adhesion of epoxy resins to glass fabrics. The adhesion of ADX-653 to the Kevlar 49 fiber surface was not improved to any significant extent as guaged by microscopic examination of the failed fatigue fracture surfaces. All specimens examined showed an almost complete absence of resin adhering to the fabric surface. Interpretation of the fatigue results has been complicated by the high stress level at which the tests were conducted (60-65% of the systems ultimate shear strength). At this level, fatigue results were low (less than 50,000 cycles to failure) and no control exists for this stress level. The system treated with the RAM 225 release agent, designed to destroy all adhesion, failed at 13,000 cycles. This level was only slightly less than one third of the maximum resistance shown by the ADX-653 treated system. These results, possibly, reflect the poor level of adhesion of ADX-653 to the Kevlar 49 surface. All following tests using Kevlar 49 had a dilute resin wash of ADX-653 applied to the fiber surface.

4.0 PHASE I, TASK 2 VARIATION IN BONDLINE THICKNESS

A significant variation of static adhesive properties such as ultimate shear strength with variations in test specimen bondline thickness has been established by more than one investigator [2,3]. To date there has been no consistent data which would define the effect of this variable on fatigue resistance. Preliminary examination of this variable in the initial part of the present effort[1] suggested that fatigue properties were little affected below a specific but undetermined bondline thickness.

4.1) MATERIALS SELECTION

A more detailed examination of the effect of adhesive bondline thickness on fatigue resistance was attempted. Control of bondline thickness is at best difficult short of use of insert shims. Use of shims is controversial due to some doubt as to the level of bond pressure after the adherends have reached the shim. Additionally, the use of shims is not practicable with the double lap shear test panel. In the present effort, it was decided that the most practicable means of bondline control would be the use of a tightly woven, reinforcing fabric manufactured from high modulus fibers. During the resin flow stage of cure, the bond thickness would diminish to the thickness of the fabric. Further shrinkage would then be strongly retarded because of the dimensional stability of the fabric. A good estimate of the cured bondline thickness would then be the "as molded" per ply thickness of the fabric as supplied by the manufacturer.

Three fabrics each of graphite ($E = 30 \times 10^6$) and Kevlar 49 were selected with as wide a range of molded thickness as possible under the constraint of constant fiber volume. Because of the limited number of graphite and Kevlar 49 fabrics available, cured fiber volume, as estimated from the combination of cured ply thickness and fabric construction, could not be held constant. However, the fiber volume was held to ± 3% over the thickness range selected.

The fabrics used were:

Fiber	Style	wt (oz/yd^2)	Thickness (in)	Theoretical Fiber Volume (%v/v)	Average	Desired Adhesive wt(lb/ft^2)
Graphite Thornel 300	1065	6.75	0.013	38.5		0.112
	1509	9.00	0.016	41.8		0.138
	1522	10.25	0.017	44.8	41.7	0.147
Kevlar 49	220	2.20	0.005	43.1		0.037
	281	5.00	0.010	46.1		0.079
	328	6.80	0.013	48.2	45.8	0.102

Prior to adhesive resin impregnation, the fabrics were treated with the fiber resin wash determined to be optimum in Task 1 of this effort. These washes were: Thornel 300, Z-6040 epoxy functional silane and; Kevlar 49, dilute ADX-653 adhesive system. Adhesive films were manufactured from the fabrics by solvent impregnation. The finished tape weights were selected to provide enough resin to fill interstitial voids and allow for flow and wetting. These tape weights are listed in the above table.

4.2 RESULTS

Titanium-Titanium double lap shear specimens (Figure 7) were manufactured from each adhesive/fabric combination.

4.2.1 Ultimate Shear Strength

Ultimate strength testing of the graphite reinforced adhesives gave quite variable results, all of which were significantly lower than the PWA system, examined in previous work (Table 6). The values of strength and bondline thickness were: Style 1065, 1995 psi and 11 mils; Style 1509, 3800 psi and 16 mils; Style 1522, 4160 psi and 15 mils. PWA graphite reinforced ADX-653, when similarily tested, yields 4700 psi and 8 mils bondline thickness. The low strength of the Style 1065 was unexpected as quality assurance testing of the lots did not predict any large difference between it and Style 1509. The Style 1065 reinforced adhesive gave a failure surface within the fabric while the styles 1509 and 1522 gave failure morphologies similar to the PWA; a resin failure near the metal interface. Because of the low strength and unusual failure morphology, Style 1065 graphite reinforced ADX-653 was eliminated from the program.

ADX-653 reinforced with the three Kevlar 49 fabrics gave ultimate strengths and failure morphologies similar to the Style 120 Kevlar used earlier. The strengths and bondline thicknesses were: Style 220, 4320 psi and 5 mils, Style 281, 4020 psi and 12 mils; Style 328, 3540 psi and 11 mils (Table 6). The Style 120 reinforced ADX-653 has consistantly given 4000 to 4300 psi. All failures were of the adhesive type between the resin and fiber surface and were consistent with past experience with other Kevlar 49 reinforced adhesives.

4.2.2) Fatigue Screening

The fatigue screening tests were conducted at 2180 psi maximum applied stress rather than the 2600 psi used in Task 1 because at the rather low fatigue lifetimes expected at the higher stress levels (50,000 cycles) any differences due to bondline thickness could be masked by the normal amount of data scatter. Testing at 2180 psi, 55% of the grand average of ultimate strength os all systems, should extend the fatigue lifetimes into a region when significant differences would be more easily detected.

The fatigue lives of the graphite reinforced adhesives were unexpectedly short for the low maximum applied stress (29,000 and 100,000 cycles to failure for the styles 1509 and 1522 fabrics respectively, Table 7). In contrast, PWA reinforced ADX-653 failed at 200,000 cycles when tested at 2600 psi maximum stress, 400 psi greater than the present experiment (Table 4).

Microscopic examination of the PWA specimens showed a great deal more surface area generated upon failure with the fracture surface transferring from one side of the fabric to the other near the mid point of the bond. In contrast, the 1509 and 1522 reinforced systems exhibited a smooth fracture surface with no transfer from one side to the other.

The three Kevlar 49 reinforced adhesive systems gave fatigue resistance at the level which was expected for the test stress level (2180 psi). Specifically, ADX-653 reinforced with style 220 Kevlar 49 failed at 2,303,000 cycles and 0.012" bondline and style 328 at 73,000 cycles and 0.011" bond. Previous experience using Style 120 Kevlar 49 reinforced ADX-653 has yielded a fatigue life of 976,000 cycles when tested at 2140 psi. All failure surfaces were adhesive; resin from fiber.

4.3) CONCLUSIONS

The dependance of adhesive fatigue resistance, as guaged by a single load level screening test, upon the bond line thickness was not established by this experimental work.

The ability to predict cured bondline thickness for fabric cured ply thickness is poor. As an example, this method predicted cured bondlines for styles 281 and 328 Kevlar 49 fabric reinforced ADX-653 of 0.010 and 0.013 inches respectively. Actually, the style 281 gave a bond thickness of 0.0123 inches and the 328, 0.011 inches. Apparently, some unknown variable has a large controlling effect.

Because the poor ultimate strength of the 1065 style graphite fabric system eliminated this data point from consideration, little information was obtained from the experiments using graphite. The style 1509 and 1522 graphite reinforced adhesives varied significantly in fatigue resistance (respectively, 29,000 and 100,000 cycles to failure) but at equivalent cured bondline thickness (0.0157 and 0.0153 inches).

A correlation of fatigue resistance with adhesive bondline thickness was possible in the case of the Kevlar 49 reinforced systems. Both large variations in fatigue resistance and bond thickness existed and appeared to indicate a trend of declining durability with increasing thickness. However, a plot of these two variables (Figure 8) shows this correlation to be somewhat tenuous.

A strong correlation was found between fatigue resistance and the percent of each system's ultimate strength at which it was tested (Figure 9). Additionally, the pair of data points from the graphite reinforced systems form a parallel curve at a lower fatigue resistance level. It thus appears that what fatigue variations which were noticed in this experiment are generally resultant from variations in the percent of ultimate strength at which the systems were tested. Whatever effect that bond thickness exerted on these results was smaller and submerged by the controlling variable

The level of ultimate strength of the systems does not appear to be dependant upon the bond thickness or fiber volume. This parameter is, more likely, dependant upon fiber-resin adhesion and the weave of the fabric. This latter variable can control the locus of failure.

Any future attempts to define the dependancy on bondline thickness must be done using equivalent fiber types and constructions as well as with adhesives of similar ultimate strength.

5.0) PHASE I, TASK 3 VARIATION IN BOND FIBER VOLUME

Many of the physical properties of materials which use a reinforcing fiber can be predicted by use of the rule of mixtures. The improvement of fatigue resistance by incorporation of high modulus fibers has been rationalized to exist because of the reinforcing action of the fibers. If this is indeed the case, the volume percentage of fiber in the bond would be a very important variable.

An investigation into the effect of bondline fiber volume on fatigue resistance was made. Three fabrics each of graphite and Kevlar 49 were used. In order to maintain a constant bondline thickness, the fabrics were modifications of the PWA graphite and 120 Kevlar 49 materials. The changes were made by removing a known amount of the fill yarns. Maintenance of the number and distribution of warp yarns would control, it was rationalized, the cured bondline thickness.

The fabrics used were:

Fiber	Fabric	Construction	Comments
Graphite	PWA	48 x 44	Unmodified fabric
Graphite	PWA	48 x 29	33% removal of filling yarns
Graphite	PWA	48 x 22	50% removal of filling yarns
Kevlar 49	120	34 x 34	Unmodified fabric
Kevlar 49	120	34 x 26	25% removal of filling yarns
Kevlar 49	120	34 x 23	33% removal of filling yarns

The PWA fabric was modified by the manufacturer by dropping 1/3 and 1/2 of the filling yarns during weaving. The Kevlar 49 fabric was modified subsequent to manufacture by carefully removing, by hand, the required number of filling yarns. The fabrics were impregnated with ADX-653 by solvent techniques with the final adhesive weight kept constant, reflecting the increased amount of resin needed to fill the larger interstitial volume. Titanium-titanium double lap shear test panels were assembled with the warp oriented at 0° to the direction of stress application.

5.1) RESULTS

Significant variations in bondline fiber volume were achieved by reducing the fabric fill fiber content in both the PWA graphite and 120 Kevlar 49 systems. The fiber volume of the PWA reinforced ADX-653 ranged from 31.8% to 23.9% while that of the Kevlar 49 ranged from 37.4 to 49% fiber (Table 8). However, these variations were not obtained at constant BLT. Those of the PWA systems ranged from 0.0065" for the 48 x 29 construction (33% reduction in fill fiber content) to 0.0082" for the control 48 x 44 construction. The bondline thickness of the control and the 48 x 22 construction were practically equivalent, varying only 0.0004 inches. The Kevlar 49 reinforced ADX-653 systems ranged in bondline thickness from

0.0029 inches (the 34 x 23 construction) to 0.0045 inches for the 34 x 34 control. The thinner bondlines of the Kevlar 49 systems with lower levels of filling yarn count resulted in increasing bond fiber volume contents as contrasted to the anticipated reduction of this parameter.

The ultimate shear strength of the PWA graphite reinforced systems range from the 4415 psi of the 31.8% fiber (v/v) system to 4840 psi for the 23.9% fiber system. These values and the 4825 psi of the control are at the lower end of the strength range expected for the PWA system, but their small spread allowed fatigue comparison both on the basis of percent of ultimate strength and actual fatigue stress. The control (34 x 34) 120 Kevlar 49/ADX-653 system gave significantly higher strength (5400 psi) than in the past (4200-4500 psi). The reason for this is not known. The Kevlar systems with reduced fill counts gave strengths (both at 4470 psi) in the expected range.

All systems were fatigue tested at a maximum applied stress of 55% of the individual ultimate strength. The ADX-653/PWA control system (30.3% fiber) failed at 89,000 cycles, only slightly lower than the historical 100,000 cycles to failure at this stress level. The 31.8% fiber system failed at 58,000 cycles while the 23.9% system failed at 8,000 cycles.

The 120 Kevlar 49/ADX-653 control system [37.4% fiber (v/v)] failed at 21,000 cycles when tested at the unusually high stress level of 2970 psi. This level has never before been used, the system more normally being tested in the 2000 to 2400 psi range. The higher fiber volume systems (41.5 and 49.0%) were both tested at 2460 psi, due to their equivalent failure stress and both failed at 130,000 cycles.

5.2) CONCLUSIONS

Some insight into the effect of bondline fiber volume on the fatigue resistance of high modulus fiber reinforced adhesive systems has been gained by this experiment. Although control of bondline thickness was not as reliable as would be liked, data from both the PWA graphite and 120 Kevlar 49 reinforced systems is available with similar bondlines which indicate a trend of increasing fatigue resistance (when determined at 55% of ultimate strength) with higher volume loadings of fiber.

The graphite reinforced ADX-653 using PWA at 100 and 50% fill fiber counts have bond thicknesses varying by only 0.0004 inches and fiber volumes of 30.0 and 23.9% respectively. The control system failed at 89,000 cycles when tested at 2655 psi (Table 8) while the 23.9% system failed at 8,000 cycles when tested at 2660 psi. This indicates the desirability of higher fiber volume loadings (Figure 10). The 33% fill removal system (31.8% fiber volume) had a bond thickness 0.0017 inches lower than the control and failed at 58,000 cycles. With the large data scatter typical of the test, the difference between this system and the control may be small, however, this data point also indicates a trend of increasing fatigue resistance with higher fiber volumes.

The results from the Kevlar 49 variations is less clear cut. The ultimate shear strength of the control (5400 psi) is significantly higher than the past (4200-4400 psi). This system when fatigue tested at 2970 psi failed at 21,000 cycles. This is considerably lower than the modified systems which both failed at 130,000 cycles when tested at 2460 psi. This difference in fatigue resistance could be due to the large difference in maximum applied fatigue stress. This conjecture was affirmed by adding data on the Kevlar 49 control acquired in task 3A (see section 6 and Table 9). This test set resulted in an ultimate strength of 4340 psi and failed at 84,000 cycles when tested at 2385 psi. If this data is used in place of the first control, a flat response of fatigue resistance to high fiber loadings is noticed (Figure 10).

Why the behavior of the Kevlar 49 systems is different than that of the PWA can only be conjectured. The bondline thicknesses of the three Kevlar 49 systems varied by 0.001 inch. Whether this difference is significant is not known but it would be very difficult to reproducibly manufacture bondlines with differences less than this. It is the authors opinion that this data can be accepted as being of constant thickness.

Another possible explanation for the difference in behavior between the Kevlar 49 and PWA systems is derived from the fracture modes by which they fail. The PWA fails predominately in the resin with a small amount of fiber-resin adhesion failure. Kevlar 49 reinforced systems fail exclusively by the loss of adhesion between fiber and resin. This latter mechanism implies that at some stress level, the stress can no longer be transmitted from fiber to fiber via the resin. Perhaps this loss of reinforcement on the part of the Kevlar nullifies the dependance on the rule of mixtures.

In summary, some evidence indicating a trend of increasing fatigue resistance of high modulus fiber reinforced adhesives with increasing bondline fiber volume has been found. The evidence has not been substantiated because of problems in controlling bondline thickness and somewhat conflicting data using a Kevlar 49 fiber. Establishing this relationship securely will have to be done with fabrics woven specially for the experiment using fibers with excellent adhesion qualities.

6.0) PHASE I, TASK 3A EFFECT OF FIBER AND RESIN MODULUS

Throughout the course of this experimental effort, the action of the high modulus, high strength fibers has been assumed to be that of reinforcement of the adhesive resin system; that is, a composite system. Some of the properties of composites are a function of the modulii of both the resin and the fiber and are described by the rule of mixtures. It has been shown [4,5,6] that the properties of the fiber are important to the fatigue resistance of composites. For instance, 10^7 cycle fatigue strength of epoxy composites increased from the 40% of ultimate strength of E-glass (E=10 x 10^6 psi) to 50% when Kevlar 49 (E=19 x 10^6 psi) and 90% when graphite (E-30 to 50 x 10^6 psi) fibers are used as reinforcing agents. During the initial portion of this contract, attempts to define the relationship of adhesive fatigue resistance and the modulii of the component fiber and resin[1] were confused by the uncontrolled variation of fiber-resin volume content, bondline thickness, and fabric type. This work has been repeated with fabric made of different modulus fibers which are as consistent as possible in weave type, molded thickness and fiber volume.

6.1) EXPERIMENTAL

6.1.1) Fabrics

The reinforcing fabrics were selected both to represent as wide a range of fiber modulus as possible and to approach a constant fiber volume and weave type. The limited number of weave types available precluded a constant bondline thickness. The fabrics used were:

Fabric	Fiber	Fiber Modulus (psi)	Weave Type	Fiber Volume Content (%)	Molded Thickness (in)
1675	E-Glass	10 x 10^6	Plain	31.9	0.0045
120	Kevlar 49	19 x 10^6	Plain	36.9	0.0045
PWA	Graphite	30 x 10^6	Plain	28.8	0.0085
1009	Graphite	50 x 10^6	8 Harness Satin	34.1	0.0012

In addition to these, a nylon tricot fabric (nylon 6, E=0.4 x 10^6) was used to gauge the level of performance of state of the art adhesives.

6.1.2) Resin Systems

The modulus of adhesives of equal temperature resistance does not vary to a great extent[7]. In order to examine as broad a modulus range as possible, adhesive resin systems of varying temperature capabilities have been used. These systems were:

Resin System	Temperature Capability	Adhesive Quasielastic Stiffness (psi)
EA 9628	250°F	2.85
ADX-653	420°F	3.07
ADX-646 (AF-A-3639)[8]	350°F	5.08

ADX-646 was chosen because of its extremely high modulus. All resin systems received the same cure, 60 minutes at 350°F, with the exception of the ADX-646 which was given a total of 2 hours at 350°F. This was necessary to fully develop its high temperature properties.

6.1.3) Fatigue Screening

Single load level fatigue screening tests were conducted at 55% of each systems' ultimate shear strength. This technique was chosen over a fixed stress level because of the great range of strengths seen. Titanium-Titamium double lap shear specimens (Figure 7) were used.

6.2) RESULTS

6.2.1) Ultimate Shear Strengths

A large range in ultimate shear strengths was exhibited by the different resin/fabric combinations (Table 9). The level of strength appears to be mainly a function of the type of fiber used with the type of resin being important in specific instances. This is most readily seen by examining the ADX-653 systems. The ultimate strength of the E-glass and PWA graphite reinforced bonds, to which the resin exhibits good adhesion, was 5480 and 5360 psi respectively. The strength of the Kevlar 49 reinforced bond was 4340 psi and, as usually occurs with this system, a complete failure of resin adhesion to the fiber surface was noticed. The bond reinforced with the style 1099 graphite failed at 2280 psi with the fracture propagating through the fabric itself, leaving graphite on both surfaces. The bond containing the nylon tricot failed at 4960 psi, somewhat lower than usual.

In general, the strength relationships between fabrics using EA 9628 and ADX-646 were as illustrated above. The only notable exceptions were the EA 9628/Kevlar 49 and the ADX-646/tricot bonds. The Kevlar 49 reinforced EA 9628 failed at 5700 psi compared to the 4300 psi of both the ADX-653 and ADX-646. This higher bond strength appears to be the result of a much higher level of fiber-resin adhesion. EA 9628 is unique among the resin systems examined throughout this contract in that the bond failure occurred in the resin and near the resin-metal interface. The Kevlar fiber-resin bond remained intact. Very poor adhesion appears to be the cause of the low bond strength of the ADX-646/tricot system.

The ultimate strength of the adhesives, with respect to the different resins, increase in the following order. ADX-653, EA 9628 and ADX-646. This is illustrated by the ultimate strengths of the style 1675 E-glass reinforced bonds with the ADX-653 system failing at 5480 psi, the EA 9628 at 5980 psi and the ADX-646, at 6170 psi.

6.2.2) Fatigue Screening

The effect of variations in adhesive resin and fiber on fatigue resistance was screened by a single load level fatigue test. All systems were stressed to a maximum of 55% of each system's ultimate strength and cycled to failure.

The ADX-653, resin system, when reinforced with the three fibers, gave fatigue lives ranging from a low of 15,700 cycles with the E-glass to a high of 87,000 cycles with the PWA graphite. Previous testing of this ADX-653 PWA system has given approximately 100,000 cycles under similar conditions. The Kevlar 49 system failed at 84,000 cycles. The nylon tricot control failed at 3900 cycles.

The EA 9628 system gave, respectively; 164,000 cycles with the nylon tricot, 79,000 cycles with the 1675 glass, 142,000 cycles with the Kevlar 49 and 92,900 cycles with the PWA graphite. ADX-646 reinforced with 1675 glass failed at 35,300 cycles, style 120 Kevlar 49 at 490,000 cycles and PWA graphite at 28,700 cycles. The nylon tricot supported system failed at 10,500 cycles. The only unexpected failure morphologies occurred with the ADX-646/PWA graphite and ADX-646/nylon tricot systems which showed a significantly lower degree of adhesion of resin to fabric than experienced with the other resin systems.

The bonds reinforced with the style 1099 graphite ($E=50 \times 10^6$ psi) were not fatigue tested because of the low ultimate strength.

6.3) DISCUSSION

The mechanism of fatigue life improvement by the incorporation of high modulus fiber into a 350°F service adhesive system appears to be that of the resin reinforcement. This is strongly suggested by the fatigue screening response of both the ADX-653 and ADX-646 resin systems to the modulus of the fibers incorporated (Figure 11). A correlation of increasing fatigue durability with increasing fiber modulus is seen for both resin systems over a fiber modulus range of 0.4×10^6 psi (Nylon 6) to 19×10^6 psi (Kevlar 49). This change in fiber modulus resulted in a 30 to 40 x fatigue life increase (Table 9). This trend of increasing fatigue resistance did not continue beyond the 19×10^6 psi modulus level for either system. The PWA reinforced ADX-653 system produced fatigue resistance similar to the Kevlar 49 system. The ADX-646/PWA combination exhibited significantly lower fatigue life than the Kevlar 49 system (29,000 vs. 192,000 cycles to failure).

Whether this abrupt shift in behavior is an artifact is not known. It might be expected that the correlation might continue to the level of resistance that graphite/epoxy composites exhibit. That the behavior may be an artifact is suggested by the high amount of fiber-resin adhesion failure in the ADX-646/PWA graphite specimens.

The fact that the type of resin system also influences the fatigue improvement phenomenon is made very evident by the response of EA 9628 to large variations in fiber modulus. In contrast to the ADX-653 and ADX-646 systems, this resin system exhibits essentially the same fatigue life over the fiber modulus range of 0.4 to 30×10^6 psi (79,000 to 164,000 cycles to failure). The actual differences in resistance could be explained by small variations in maximum applied stress (Figure 12). In contrast, the ADX-646 and ADX-653 systems exhibit higher fatigue resistance at higher stress levels, an indication that some variable other than stress level is controlling the response.

EA 9628 is a 250°F service adhesive system designed for high toughness rather than thermal resistance. The difference in toughness of the systems can be seen in the metal to metal peel strength of the systems. Whereas ADX-646 and ADX-653 exhibit peel strengths of less than 15 in-lb/in. width, in their unreinforced forms, EA 9628 has a peel strength in excess of 60 in-lb/in. This difference in behavior between the two types of resin systems suggests that the phenomenon of fatigue life improvement by use of high modulus fibers should be viewed as a "toughening" action. There is a distinct possibility that its usefulness may be limited to the less tough. 350°F service systems.

6.4) CONCLUSIONS

The results of this experiment suggest a very qualitative "equation of state" concerning the phenomenon of adhesive fatigue life improvement by incorporation of high modulus fibers into the adhesive bondline. With resin systems of higher stiffness, an increase of the fiber modulus results in increased fatigue resistance of the adhesive bond. The upper and lower bounds of this phenomenon have yet to be defined. The experimental data suggests that the behavior peaks near 19 x 10^6 psi (Kevlar 49) although data from experiments on epoxy composites, suggest better results should have been found using higher modulus fibers. Perhaps a combination of poor fiber-resin adhesion and a mismatch of the weave of the fabric precluded obtaining these improved results.

This phenomenon of fatigue improvement appears to be operative only with the 350°F service resin systems. Using EA 9628, a 250°F service system, there was no observable effect on fatigue resistance due to an increase in fiber modulus. Where the breakoff point for fatigue improvement is and how to define it is completely unknown at this point. The initial modulus of the system does little to define the difference. EA 9628 has a modulus of 2.85 x 10^6 psi while ADX-653 has 3.07 x 10^6 psi. Perhaps the distinguishing differences are in total elongation or energy to failure.

These results suggest the following mechanistic "rationale". The test specimen fails when the size of prexisting or generated flaws reach a critical size above which the resin system can no longer sustain the applied loads and catastrophic failure results. These flaws can grow to the critical size either rapidly, as in a test to ultimate strength, or slowly, as in a fatigue test. In either case, there is a strain level, characteristic of the resin system, below which the flaws will not grow to critical size. The action of the high modulus fiber is to reinforce the bond line; i.e., reduce the amount of strain to any stress level. By reinforcing the bondline, the stress required to reach the resin's critical strain is increased, resulting in improved fatigue resistance.

The effect that the type of resin system imparts to the phenomenon lies in the level of critical strain. The high toughness of the EA 9628 system is demonstrated by its metal to metal peel strength, a test showing, in qualitative manner, the crack resistance of the adhesive. In other words, the critical strain level for this adhesive is greater than the ADX-653 and ADX-646. This difference is reflected in the high fatigue resistance of the EA 9628/Nylon knit system. Apparently, the amount of strain imparted on this essentially unreinforced system is still below the critical level of EA 9628. The upper and lower bounds of this phenomenon using EA 9628 are still undefined, although it is felt that the unreinforced (no fabric) system would have good fatigue resistance also.

This rationale has been advanced on the basis of a single load level fatigue test. Before a great deal of credence is lent to it, it should be demonstrated using a full S/N fatigue curves.

It does appear, however, that significant improvements in adhesive fatigue resistance via reinforcement with high modulus fibers is limited to the lower crack resistant, 350°F service adhesive systems.

In addition, EA 9628 appears unique among the resins examined in this contract with respect to its high degree of adhesion to the Kevlar fiber. In contrast to the other 250°F and 350°F service adhesives[1], the bond of EA 9628 to the Kevlar 49 surface survives ultimate shear strength testing; the failure locus being transferred into the resin and the shear strength being increased by 35%.

7.0 PHASE II, Task 1 EVALUATION OF OPTIMIZED ADHESIVE

7.1) BACKGROUND

Phase I of this experimental work was structured to investigate and suggest optimum settings of several potentially important material variables such as fiber-resin adhesion, bond thickness, etc. The decisions made in Phase I were based on the results of a screening test; a single bond level fatigue life determination. The present task was included to insure that any optimized system did indeed possess 10^7 cycle fatigue strength at least equivalent to the successful ADX-653/PWA graphite adhesive of the first half of this contract[1].

To demonstrate that the new adhesive system was indeed optimized, the stress at which it will survive 10^7 fatigue cycles will be determined and compared to both the ADX-653/nylon knit and PWA graphite reinforced systems.

7.2) SELECTION OF ADHESIVE SYSTEM

Style PWA graphite fabric, surface treated with the Z-6040 silane, in combination with the ADX-653 resin system was chosen for use in Phase II. This fabric was selected over the Kevlar 49 system because of its consistent ability to achieve high fatigue resistance (ca. 100,000) cycles) at higher fatigue stresses (2700 to 3000 psi). The Kevlar 49 systems have given equivalent fatigue resistance ($>$ 100,000 cycles) but at a significantly lower stress level (ca. 2400 psi). The other fabrics examined were eliminated because of poor fatigue performance.

ADX-653 was chosen as the resin system because of its practical service temperature, 350°F. The EA 9628 system, although offering equivalent to better fatigue performance, is only a 250°F service system and not practical for the desired end use. The ADX-646 resin system has poor performance in combination with the PWA graphite fabric.

Although positive indications were given for the desirability of a higher cured bond fiber volume, such a fabric is not readily available. It would have had to be designed and manufactured from scratch. This was beyond the scope of the contract.

7.3) EXPERIMENTAL

Titanium-graphite/epoxy double lap shear specimens were used to determine the full S/N curves (Figure 13). These were manufactured with the following construction: Titanium 6-4 alloy (surface preparation per McDonnell-Douglas specification PS 12037, graphite/epoxy composite - 4 plies $[0°]_4$, Narmco 5208 T-300. The adhesive and prepreg skin were cocured at 350°F for one hour and 50 psi in an autoclave. All specimens were assembled with the warp direction of the fabric oriented 0° to the direction of test.

The test specimen was almost exactly stiffness balanced. In order to exactly stiffness balance the specimens, 0.0593" titanium members would have had to have been used in place of the 0.060 inch pieces actually used. An epoxy-glass composite (Hexcel F-161) gripping surface was bonded to the titanium in all fatigue specimens to insure that metal fatigue failure would not occur.

7.4) RESULTS

Similar 75°F ultimate shear strengths were exhibited by both systems. The PWA graphite reinforced ADX-653 failed at 4950 psi while the nylon knit containing system failed at 5165 psi. The ADX-653/PWA specimens exhibited a mixed failure mode. A good deal of the bond failed in the resin (Figure 14) but a significant amount of adhesive type failure both from the titanium and graphite composite was also seen (Figure 14). The ADX-653/Nylon knit fracture morphology appeared to be mainly an adhesive failure from both the substrates. The surface of the adhesive itself appears to be little disturbed (Figure 15) while only small amounts of resin are seen on either the metal or composite surfaces (Figure 15).

The stress level which will withstand 10^7 cycles of fatigue was determined on each system (Table 10, Figures 16 to 18). As this was a screening test to determine if the ADX-653/PWA systems were really optimum, testing was limited to a specimen population of three (3) per data point. The results, within a test set, varied considerably; up to an order of magnitude. The arithmetic mean of the data was used to describe the results. In those cases where the specimens were removed intact after 10^7 cycles, the number of cycles at which it was removed was used in the caluclation of the mean. This results in some bias towards lower fatigue results with the ADX-653/PWA system when tested at 50% and the ADX-653 Nylon system at 40% of ultimate. Smooth curves were then drawn using the arithmetic means to describe the fatigue behavior.

The fatigue life (Table 10, Figure 16) of the ADX-653/PWA graphite bonded specimens varied from 710,000 cycles at 2970 psi maximum applied stress (60% of ultimate) to greater than 9,700,000 cycles at 2480 psi (50% of ultimate). The fatigue life of the ADX-653/Nylon knit control varied from 309,000 cycles at 2570 psi (50% of ultimate) (Figure 17) to greater than 9,300,000 cycles at 2070 psi (40%). The fracture surfaces of the fatigue specimens were essentially the same as was described for the static ultimate testing. The ADX- 653/PWA system failed primarily in the resin with some adhesive failure from both substrates. The ADX-653/Nylon system fractured primarily at the resin-substrate interface. The type of fracture mechanism, for either system did not vary with the number of cycles at which the system failed.

7.5) CONCLUSIONS

The fatigue strength; i.e., that stress which will survive 10^7 cycles, of the treated ADX-653/Style PWA graphite fabric system was determined to be 2550 psi (Figure 16) or 51.5% of the system's ultimate strength. This stress level is significantly greater than the 2050 psi (39.7% of ultimate) determined for the ADX-653/Nylon knit system. At equivalent stress, this difference amounts to a 20 fold increase in fatigue durability due to bondline reinforcement.

The fatigue strength of the Z-6040 epoxy silane treated PWA system is 400 psi greater than that found for the ADX-653/PWA system (2150 psi) in the initial stages of this work[1]. However, because the ultimate shear strength of this system was 600 psi greater than the untreated PWA (4950 vs. 4320 psi) the percent of ultimate strength which will withstand 10^7 cycles increased by only 4% (from 47.5 to 51.5%). It thus appears that the major effect of the Z-6040 silane treatment of the PWA fabric may have been an increase in ultimate strength rather than any increase in fatigue resistance.

The fatigue resistance of the ADX-653/Nylon knit system was appreciably higher than that value determined in the initial portion of this work[1] (2050 vs. 1400 psi). This increase amounts to an increase of the percent of ultimate strength which will withstand 10^7 cycles from 29.0 to 39.7%. It thus appears that the initial determination of this value was significantly low.

8.0 PHASE II, TASK 2 DETERMINATION OF FATIGUE IMPROVEMENT USING COMPLEX ADHEREND GEOMETRY

8.1) BACKGROUND

Although the double lap shear specimen being used in this program is balanced and utilizes realistic adherend thicknesses, it is not rigorously representative of the types of joints currently used to link titanium and high modulus composites on advanced aircraft. The load which an overlap joint can carry does not continue to increase forever as lap length increases. An effective load free zone develops after a certain point, and load carrying capacity remains constant regardless of the increase in lap length. Load can be increased only by using a wider bond.

The reason for this phenomena is that the metal adherend elongation at the edge of the bond where the greatest load transfer takes place eventually causes failure at the metal-composite interface (Figure 19). The theoretical method of avoiding this problem is to use a tapered metal adherend and composite layup as shown in Figure 19. The composite thickness increases as the level of load transferred increases, while the metal thickness decreases as the load carried by the metal decreases. This permits essentially constant elongation in the metal, and the most efficient load transfer. However, the precision tapering of titanium and the tapering of composites during layup have significant cost disadvantages in production application.

A third joint design, multiple step splice plates, allows load transfer which is comparable to tapered joints in many cases yet has significant cost advantages over tapered joints. The number and configuration of the steps used is adjusted to the load to be transferred.

A six step splice plate was used in this program in order to determine the increase in fatigue resistance caused by reinforcement of ADX-653 with the silane treated PWA graphite fabric. Full S/N fatigue curves were developed, using a constant amplitude test, comparing the high performance system with the ADX-653/knitted nylon combination.

8.2) SPECIMEN DESIGN

Rigerous design criteria for the stepped splice plate require that the stress-strain properties (as determined by torsion tests) for the individual adhesive be used. The geometry of the specimen is modified subtly to allow for these properties. In the absence of stress-strain data for the adhesive systems under study, design of an optimized specimen for these systems was not possible. A joint design optimized for a current 350°F service adhesive in use on advanced aircraft was selected (Figure 20). This specimen was optimized for strength and had been utilized extensivley in spectrum fatigue tests simulating advanced fighter service. It is the optimum for the adhesive and adherends for which it was designed.

8.3) EXPERIMENTAL

The six step lap joint specimens were assembled using ADX-653 containing either the knitted nylon, state of the art fabric, or the Z-6040 silane treated PWA graphite. The adherends were made up from titanium (6Al/4V alloy) and Narmco 5208-T300 graphite epoxy prepreg. During the layup of the composite, debulking occurred 4 times. The specimens were vacuum bagged and autoclave cured for 120 minutes at 350°F and 85 psi. A 30 minute hold at 270°F under slight vacuum was included during the heatup to densify the composite. A post cure of 8 hours at 350°F completed the cure schedule. The cured test panel was then machined into 1 inch wide test specimens using a combination of machine cutting (on the titanium) and diamond saw (for the composite) techniques.

The cured test panels were subjected to the ultrasonic and X-radiographic non-destructive inspection techniques used by McDonnell in their production of aircraft. Only a few composite voids and no debonds were detected by this inspection.

8.4) RESULTS

The step lap joints of both the ADX-653/PWA and nylon combinations were loaded to failure. The ultimate failure load of the ADX-653 reinforced with the silane treated PWA graphite was 15,960 pounds, while the ADX-653/nylon system failed at 16,000 pounds (Table 11).

When both systems were subjected to constant amplitude fatigue at 50% of their ultimate strength, the ADX-653/nylon system failed at 60,000 cycles and the PWA reinforced counterpart at 178,000 cycles. All three nylon supported test specimens failed in the bond while only two of the three PWA reinforced specimens failed in the bond (at 205,000 and 140,000 cycles). The third specimen exhibited a metal failure (at 196,000 cycles).

When the loading of the ADX-653/nylon system was decreased to 40% of ultimate (6400 pounds) all failures occurred by metal fracture (at 562,000 and 499,000 cycles). Likewise, one specimen bonded with the PWA reinforced adhesive tested at 45% of ultimate (7180 pounds) failed by metal fracture at 372,000 cycles.

The specimens which failed in the metal were subjected to a detailed failure analysis. The laboratory report concluded that the failure did not occur because of a surface or edge defect in the specimen but rather a simple fatigue failure of the metal. Electron micrographs of the fracture surface did have indications of fatigue failure.

Stress analysis of the specimen indicates that the highest stresses are at the first step (nearest the center of the specimen). So, if the metal is fatigue critical, it should fail at this point. Several specimens failed at steps more removed (i.e., higher) from the center. Unfortunately, those specimens which failed on higher steps were damaged by the fatigue machine before it could stop. Analysis of these specimens would be fruitless.

Possible causes of failures on higher steps could include: 1) edge or radius defects, 2) large disbonds on the lower steps which dump the load onto higher steps and, 3) laminate defects which concentrate loads on higher steps. N.D.T. and post failure analysis did not indicate that any of these causes were present on the group of specimens failing on higher steps. It is not possible, then, to positively assign a particular cause for these non-standard failure modes.

8.5) CONCLUSIONS

Fatigue life improvement by bondline reinforcement was not shown by constant amplitude fatigue testing of the step lap splice plate specimens. At high loads (50% of ultimate), the specimen was adhesive critical, failures occurring in the bond. However, at slightly lower loading (40% to 45%) the metal proved to be fatigue critical. This limited the amount of comparative data available. These were the first constant amplitude tests to be run with this specimen design. The point at which a specimen becomes fatigue critical in the metal can not be projected without a precise knowledge of the stress-strain (torsion ring) and S/N properties of all joint elements. This stress-strain data for the two adhesives was not avilable for this effort.

Thus in order to obtain comparative constant amplitude fatigue properties of the two systems, the stress-strain properties would have to be determined and the step lap joint specimen designed to account for the magnitude of these properties, especially the point of transition from elastic to plastic deformation. This effort is beyond the scope and timing of the contract. Because of this, it was decided to compare the nylon and PWA reinforced ADX-653 in spectrum fatigue using the step lap joint specimens. This program used a spectrum fatigue program used in the development of an advanced fighter aircraft.

Even though the complete comparative S/N constant amplitude fatigue properties of ADX-653 reinforced with both a nylon knit and PWA graphite fabric was not developed with the step lap joint specimen, a three-fold increase in fatigue life due to the PWA was indicated at 50% of the systems ultimate strength (8000 pounds).

9.0 PHASE II, TASK 2A DETERMINATION OF FATIGUE IMPROVEMENT USING RANDOM SPECTRUM FATIGUE TESTING

9.1) BACKGROUND

As utilization of advanced technology materials, such as high modulus fiber composites, in high performance aircraft has progressed towards primary, safety of flight structure, knowledge concerning the durability of these materials has become of prime importance. Constant load amplitude fatigue testing, even though useful in distinguishing between materials of differing fatigue resistances, gives little information concerning the expected response of such structures under flight conditions. This is true even when assemblise such as the step lap splice plate are used for testing.

A new test methodology; random spectrum fatigue, has been developed by the Air Force and the airframe industry to provide the durability information required by these advanced aircraft. McDonnell Aircraft Company has developed such a program for the F-15 air superiority fighter. This test scheme was developed by combining:

A) An aircraft lifetime mission profile which included data on the type of mission, number of missions, vehicle configuration and expected vehicle performance envelop.

B) Cumulative load exceedence curves for the structure of interest. These load exceedence curves were approximated with random load level application data on a flight by flight basis. The random load wave shapes were determined from actual aircraft maneuver time histories recorded during combat training.

The detailed technical approach for matching the cumulative load exceedence curves and aircraft maneuver wave shapes using random noise theory described in Reference 9.

The multiple step splice plate test specimen was used in successfully extablishing the spectrum fatigue performance of composite to titanium bonded structure on the F-15. As such, it should not be subject to the metal fatigue problems which arose during the constant amplitude testing of the ADX-653/PWA adhesive as described in Section 8. In addition, use of the spectrum fatigue program will allow the evaluation of any fatigue improvements due to bondline reinforcement with high modulus fibers to be made under more realistic test conditions.

9.2) EXPERIMENTAL

9.2.1) Test Specimens

Details of the assembly and cure of the six step splice plate test specimens (Figure 20) are found in Section 8.3.

9.2.2) Random Spectrum Fatigue Testing

The spectrum fatigue test procedure is characterized by a load level, called the test limit load (TLL). Applied loads during the program are usually at this level or lower. However higher loads (up to 105% of TLL) are randomly applied. This loading pattern was impressed onto the step lap splice plate test specimen using a 150,000 pound fatigue machine equipped with hydraulic load cylinders which were controlled by a load feedback servo system. This system was in turn programmed by a magnetic tape function generator. Details of this procedure can be found in Reference 9. In addition, a manually applied maximum load (125% TLL), hereafter called the load spike, was applied during some spectrum testing every 2000 equivalent flight hours. The loading pattern is random over a two lifetime (8000 equivalent flight hours) period as dictated by the magnetic tape function generator. If additional testing is desired, the tape is rerun.

The tests were conducted with a test population of 3 specimens under ambient conditions in late spring in St. Louis, Missouri.

9.3 RESULTS

The ADX-653 reinforced with both the nylon tricot and the style PWA graphite fabric were initially tested with a test limit load of 13,500 pounds with no maximum load spikes (Table 12). This test limit load was 84.4% of the two systems ultimate strength. The nylon knit/ADX-653 combination failed at a mean lifetime of 1271 equivalent flight hours or 0.32 lifetimes. The highest loading stresses in the splice plate specimen have been analyzed to occur at the first step (i.e., closest to the center line of the specimen) and bond failure at this point occurred at the metal-adhesive interface. As failure progressed to high steps, the failure location migrated to the adhesive/composite interface. On the highest steps, a considerable amount of fiber pull out from the composite was seen.

The ADX-653/PWA combination, when tested at the 13,500 pound TLL failed at a mean of 6536 equivalent flight hours on 1.63 lifetimes. The failure morphology in this instance, was the same as that of the ADX-653/Nylon specimens except that the failure on the first step was a mixture of fracture at both the adhesive/composite and adhesive metal interfaces.

All test specimens from both sets failed at less than test limit load, with values ranging from a low of 81.9% to a high of 99.3% of test limit load (Table 12).

Both adhesive systems were also tested at a test limit load of 12,000 pounds with a 125% TLL load spike applied every 2000 equivalent flight hours (Table 12). This test limit load is 95% of the systems' ultimate strength.

The nylon knit supported ADX-653 failed at a mean of 2507 equivalent flight hours or 0.63 lifetimes. Only one specimen survived the 125% TLL load spike, subsequently failing at 3522 hours (80.0% of test limit load). The other two specimens both failed at 2000 hours during the application of the load spike (at 103.5 and 104.1% TLL, respectively).

Bond failure morphology was similar to that noticed in the 13,500 pound TLL testing. At the highest stress points, the bond failed at the metal/adhesive interface. At progressively higher steps, fracture migrated to the composite/adhesive interface with some composite fracture (fiber pull-out) occurring at the highest steps.

The ADX-653 reinforced with style PWA graphite failed at a mean of 12,095 equivalent flight hours (3.02 lifetimes) when tested with a test limit load of 12,000 pounds (with load spikes). All specimens successfully survived at least three of the 125% TLL spikes with no failure occurring during their application. Two specimens failed at 12,651 and 7,624 hours at 91.3 and 97.5% TLL respectively. The third specimen survived 4 lifetimes (16,000 hours) without failure and yielded a residual ultimate strength of 13,800 pounds of 86.5% of its initial strength. Bond failure morphology was similar to the earlier 13,500 pound test limit load testing with a mixture of adhesive/composite and adhesive/metal interfacial failure. This changed to exclusively adhesive/composite interfacial failure at higher steps and finally to a mixture of this and composite fiber pullout at the highest steps.

9.4) CONCLUSIONS

Reinforcement of the ADX-653 bondline with PWA, a graphite fabric, has resulted in the improvement of fatigue life, as measured in a random spectrum fatigue test, by a factor of five times as compared to a state of the art knitted nylon support fabric. Thus, then tested at a test limit load of 13,500 pounds without high load spikes, fatigue resistance increased from 0.32 to 1.63 lifetimes. When tested with a 12,000 pound TLL with a 15,000 pound load spike, the presence of the PWA resulted in an increase in resistance from 0.63 to 3.02 lifetimes.

Another positive benefit of the graphite reinforcement is a much higher resistance to high stress loadings. Whereas the nylon knit supported system survived only one of the 125% TLL loadings out of a total of three specimens, all the PWA specimens survived at least 3 loadings with one surviving a total of 8. In a majority of cases, the 125% loading cycle failed the nylon supported systems while none of the PWA systems failed at this time.

Therefore, reinforcement of an adhesive bondline could give significantly longer fatigue lifetimes and a greater resistance to the random specification exceedance loadings experienced during flight.

9.5) INTERPRETATION AND RECOMMENDATIONS

Use of the spectrum fatigue test has permitted an insight into the usefulness of the ADX-653/PWA combination as a practical adhesive system. The adhesive presently used on the F-15 has also been tested with the 13,500 pound test limit load (no load spikes). A comparison of the two systems is as follows:

Adhesive System	Ultimate Strength (Lb)	Test Limit Load (% Ult)	Fatigue Life Time
ADX-653/Nylon	16,000	84.4	0.32
ADX-653/PWA	15,960	84.6	1.63
F-15 Adhesive	20,000	67.5	2.52

This data indicates that the ADX-653/PWA system, although being a five times improvement in fatigue resistance over its baseline adhesive system, does not have the fatigue resistance of the F-15 adhesive. Part of this difference may be due to the fact that the test specimen was designed with the material considerations of the F-15 system in mind. However, the controlling factor in this difference is probably that the 13,500 pound test limit load represents 84.6% of the ADX-653/PWA ultimate strength and only 67.5% of that of the F-15 system. Some comparison can perhaps be made under more equivalent conditions by comparing the performance of the ADX-653/PWA system in the 12,000 pound test limit load test with the 13,500 pound test of the F-15 system. In this case the ADX-653/PWA system was tested at 75% of its ultimate strength, the F-15 system at 67.5%. While the latter system fails in an average of 2.52 lifetimes, the ADX-653 specimens yielded a 3.02 lifetime result.

Therefore, it appears that the difference in spectrum fatigue results seen between the ADX-653/PWA and the F-15 adhesive systems is due not to the inefficiency of the fiber reinforcement concept but rather to the large difference in system ultimate strength. For F-15 applicability, all adhesive systems must perform at the 13,500 pound test limit load as this factor reflects a 35% safety factor on the 10,000 pound design limit load calculated for this portion of the F-15 structure.

Successful implementation of the phenomenon of fatigue life improvement by bondline reinforcement is not possible at this point. To do so would require that the ultimate strength of the adhesive system be increased by 25 to 30% over that of the ADX-653/PWA candidate. This possibly could be done by either modification of the adhesive resin system to increase the inherent strength of the system and/or design and construction of a new high modulus fiber fabric.

10.0) COMMENTS AND RECOMMENDATIONS

This contract effort has shown that the usable strength in fatigue of adhesively bonded metal to metal and metal to composite structures can be significantly increased by the addition to the adhesive of a high modulus, high strength fiber such as graphite or Kevlar 49.

Addition of style PWA graphite fabric ($E = 30 \times 10^6$ psi) to ADX-653, a 350°F service resin system produced a 30% increase of the useable strength in fatigue. With double lap shear specimens, the stress which would withstand 10^7 fatigue cycles was increased to 2550 psi from the 2050 psi characteristic of this system using a knitted nylon support fabric. This represents an increase in the ultimate strength of the system from 39.7 to 51.5%.

Significant fatigue life benefits were also demonstrated using a spectrum fatigue program designed for an advanced fighter aircraft. Using a titanium to graphite-epoxy composite multiple step splice plate specimen, representative of a possible use of the adhesive in the aircraft, a five-fold increase in the expected lifetime of the system due to the high modulus fabric was shown. With a 13,500 pound test limit load, fatigue resistance increased to 1.63 equivalent flight lifetimes from 0.32. Using a 12,000 pound test limit load, this difference was 3.02 and 0.63 lifetimes for the PWA and nylon knit supported system, respectively. Another benefit due to the inclusion of the high modulus fiber fabric was increased resistance to very high loadings. Whereas all but one of the nylon knit supported specimens failed during the application of a 125% test limit load, none of the PWA specimens failed during the application of this load. All of the PWA specimens survived at least three and as many as 8 of these load applications.

Appreciation of bonded assembly fatigue life was limited to the low elongation to failure 350°F service adhesive systems. Addition of the PWA fabric to EA 9628, a high peel 250°F service adhesive system, did not result in any increase of fatigue resistance. These data, in conjunction with those from ADX-653 suggested a rationale for this phenomenom which has as its central feature the concept that damage in a resin system due to fatigue cycling will not occur below a system specific critical level of strain. Without damage, i.e., cracking of the resin system, fatigue lives of 10^7 cycles or greater result. The function of the high modulus fiber in improving fatigue resistance is one of resin reinforcement, i.e., reducing the strain level to any specific stress level. The resinforcement is effective in the 350°F service resin systems due to the low critical strain level of these systems. They are not effective in the 250°F service adhesive systems probably because, at the stress levels examined, the critical strain load was not exceeded. However, the reinforcement concept could be effective in increasing the fatigue resistance of these systems, at higher stress levels. Also supporting this rationale, is some evidence that higher fiber volume loadings result in increased fatigue resistance. Exact definition of this parameter as well as the effect of adhesive bondline thickness was severly limited by the inability to vary each independantly of the other. This was the result of a paucity of the types of fabrics, both of graphite and Kevlar 49 available. This type of information is necessary in designing the optimum adhesive system and should be acquired by designing and manufacturing specific fabrics.

The PWA graphite reinforced ADX-653 adhesive, however, appears to be somewhat inferior to the adhesive system used on the F-15 aircraft, when compared on the basis of these specific spectrum fatigue test conditions. Using the 13,500 test limit load program, the ADX-653/PWA system failed at 1.63 lifetimes while the F-15 system failed at 2.52. Two reasons for this difference have been suggested.

First, the test specimen was designed for the F-15 adhesive system with experimentally determined stress-strain properties being considered. This specimen design was used for the ADX-653/PWA testing without modification. The impact of this non-ideal specimen design on the test results is unknown and cannot be determined without actual testing, a task beyond the scope of the present work.

Secondly, the testing was done at significantly higher percent of ultimate loadings on the ADX-653/PWA system. The 13,500 test limit load represents 84.5% of this system's ultimate strength but only 67.5% of that of the F-15 system. Using a 12,000 pound test limit load with the ADX-653 system (75% of ultimate) resulted in 3.02 expected lifetimes, superior to the F-15 system (tested at 13,500 pounds).

The resin systems of both adhesives appear to have similar fatigue resistances. The F-15 adhesive uses a synthetic support fabric and contains a metallic filler. When ADX-653 is manufactured with these components present, equivalent ultimate strengths result (6520 for the ADX-653 vs. 6480 for the F-15 system). Using a titanium-titanium double lap shear test specimen, both systems produce equivalent fatigue resistance when tested at 55% of ultimate (770 cycles for the ADX-653 and 500 cycles for the F-15 system). These results are approximately 5 times less than what was produced by the ADX-653/nylon knit system (4900 cycles) without the metallic filler, but are only a reflection of the higher ultimate strengths produced by the filler. Plotting the logarithm of the fatigue resistance against the maximum applied fatigue stress yields a smooth curve running through these three points (Figure 22). The differences, therefore, appear to be due to the varying levels of maximum applied fatigue stress.

This curve lies approximately 1.5 orders of magnitude below a similar curve describing the results of ADX-653 reinforced with different high modulus fibers. From this, it appears that the superior spectrum fatigue performance of the F-15 system is only a reflection of the significantly higher ultimate strength of the system and is not a reflection on the usefulness of the principal of high modulus fiber reinforcement of ahdesives.

To more fully define the usefulness of the ADX-653/PWA graphite system at its present stage of development for an application such as the F-15, a spectrum fatigue specimen specifically designed for this systems stress-strain properties should be used. A side by side comparison with the presently used F-15 adhesive would then be more meaningful.

In general, addition of metallic fillers significantly increases the ultimate strength of 350°F service adhesive resin systems. The present F-15 adhesive depends largely on this approach to attain its high ultimate strength. Addition of such fillers may not be compatible with high levels of high modulus fibers. Therefore, additional effort may have to be spent in developing new methods of increasing the base resin system ultimate strength, i.e., toughening, without reducing the glass transition temperature of the system. In addition, new high modulus fiber fabrics may have to be designed and manufactured to investigate the effect of weave type, fiber volume, and fabric thickness on ultimate strength and fatigue resistance. Upon successful completion of this task, the effectiveness of this system would be guaged by a spectrum fatigue comparison with the state-of-the-art adhesive system.

11.0) REFERENCES

1) The Dexter Corporation, Hysol Division, "Improved Fatigue Strength Adhesive", AFML-TR-74-169, November 1974.

2) Bikerman, J.J., "The Science of Adhesive Joints", Academic Press, New York, 1961, Pg. 2.

3) Bryant, R.W. and Dukes, W.A., "Structural Adhesive Bonding", (Bodnar, M.J., Ed.), Interscience, New York, 1966, Pg. 81.

4) Hogatt, J.T., "High Performance Filament Wound Composites for Pressure Vessel Applications", National SAMPE Technical Conference, Vol. 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 and Exhibition, Pg. 249, April, 1969.

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

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

8) Klapprott, D.K., Mahoney, C.L., and Mika, T.F., "Exploratory Development of Structural Adhesives Having Improved Toughness Properties, AFML-TR-71-256.

9) McDonnell Aircraft Company, McDonnell Douglas Corporation, "Reliability of Step Lap Bonded Joints", AFFDL-TR-75-26, April, 1975.

APPENDIX

A.1) FATIGUE LIFE VARIABILITY WITH TYPE AS GRAPHITE NON-WOVEN MAT

In earlier work on this contract[1], bondline reinforcement with a type AS graphite non-woven resulted in significant fatigue life improvement (445,000 cycles at 2265 psi maximum applied fatigue stress compared to 4900 cycles at 2905 psi shown by the nylon knit control). This improvement coupled to the ready variation of such important bondline parameter such as thickness and fiber volume made possible by use of the mat, led to further investigation of this reinforcement. Subsequent testing of the ADX-653/Type AS non-woven mat did not result in such high fatigue resistance fibers with lifetimes as low as 9000 cycles (2375 psi)(Table 13). Additional testing (Table 13) revealed that this variability was due to lot by lot variations in the adhesive and not to variation of the test specimen type. Because the use of the non-woven mat was important to the contract combination, further experimentation was undertaken aimed at determining the causes of fatigue life variation.

A.1.1) POSSIBLE CONTROLLING PARAMETERS

Four parameters were selected for further examination as possibly controlling and increasing fatigue resistance. These were:

1) The weight of the fibrous mat in the bondline - tested by increasing the amount of reinforcing material in the bond line.
2) Increase the weight of adhesive resin to produce a bond with fewer flaws and voids.
3) Fiber Finish - to improve the adhesion of resin to fiber by application of:
   a) ADX-653 containing curing agents.
   b) ADX-653 resin system only.
   c) Z-6020, an amino silane to the fiber from dilute solution.
4) Addition of metallic filler to the adhesive system.

A.1.2) RESULTS

A.1.2.1) Variable Mat Weight

Titanium to titanium double lap shear specimens (Figure 7) were manufactured using uncured adhesive systems containing 16.7, 23.1 and 26.8% (w/w) graphite fiber and fatigue tested at 55% of their ultimate shear strength. A Decrease in ultimate shear strength with increasing mat weight (5400, 4910 and 4390 psi respectively) was obtained (systems A, B. C, Table 14). The variation in fatigue resistance (3100, 3600, 9800 cycles to failure respectively) can be accounted for by the variation in fatigue stress alone (Figure 21).

A.1.2.2) Variable Adhesive Resin Weight

An increase in the resin weight fraction of the uncured tape resulted in increased fatigue resistance (Table 14). A plot of the fatigue life with the maximum applied fatigue stress (Figure 21) shows two groups of data, one from each of the two unsupported adhesive resin weights used (0.030 and 0.060 lb/ft^2) to manufacture the final adhesive films. Within each group, the variation of fatigue performance appears to be due only to the variation in maximum applied fatigue stress. This phenomenom may be due to the ability of the more resin rich systems to eliminate bondline flaws.

A.1.2.3) Application of Resin Washes

Three resin washes, ADX-653, ADX-653 Resin System and Z-6020, an amino silane, were applied to the graphite mat from dilute solution in acetone in an attempt to improve the level of adhesion of the resin to the fiber. All attempts (Table 14, E through J) proved unsuccessful with the improvements of fatigue resistance over the control more easily accounted for by variations in the maximum applied fatigue stress (Figure 21).

A.1.2.4) Addition of Metallic Filler

In many instances, the addition of a metallic filler to a high temperature adhesive system results in the increase in the system's ultimate strength properties. Such a filler was added to the type AS mat reinforced ADX-653 in an attempt to improve fatigue resistance. 50 and 100 phr were used and an increase of ultimate shear strength from 5000 to 5600 psi resulted in both cases (Table 14, Systems D. K. and L). This latter value is very close to that of the nylon supported control, 5800 psi. However, the level of fatigue resistance remained unchanged, the variation of results being accountable by differences in applied fatigue stress (Figure 21).

A.1.3) CONCLUSIONS

The poor fatigue resistance (50,000 cycles to failure) of the type AS graphite mat reinforced ADX-653 appears to be characteristic of the system. The reasons for the initial excellent fatigue resistance were not discovered. An increase in the weight fraction of the adhesive resin in the uncured film was the only parameter which positively controlled fatigue resistance, perhaps indicating a minimum level of resin necessary for flow and flaw elimination. However, the level of improvement was small, increasing fatigue resistance to only about 10% of the original results (50,000 vs. 450,000 cycles). Improvement in fatigue resistance of the ADX-653/Type AS random mat systems appears to require a much more extensive research effort than available. Consequently emphasis was changed from the random mat type of reinforcement to the woven forms of the high modulus films.

A.2) MANUFACTURE OF ADX-653 REINFORCED WITH HIGH MODULUS FIBER FABRICS

A.2.1) 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.2.2) 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.3) FATIGUE TEST METHOD

The double lap shear test specimens are fatigue tested using Sonntag universal fatigue testing machines. The specimens are cycled between a preselected stress level (P_{Max}) and 0.1 P_{Max} (P_{Min}). The test machine automatically maintains both a constant dynamic and static (P_{Max} and P_{Min} constant) load cycle at a cycle rate of 30 Hz. The arithmetic mean of the test results was used for data interpretation. The small test population (3) has, in the past, precluded use of statistical analytical techniques.

A.4) SHORT BEAM INTERLAMINAR SHEAR TEST METHOD

0.8 inch (nom) thick cured composites were manufactured from the ADX-653 impregnated fabrics (PWA/10 plies, Style 120 Kevlar 49/20 plies) using a parallel, nested layup. These composites were press cured at 350°F and 50 psi for 60 minutes. Interlaminar shear test specimens (0.60 inch x the 0.25 inch) were machined from the composites with the warp direction being the 0.60 inch direction.

Testing was performed using an Instron universal testing machine, a three point loading pattern and a 0.40 inch span. Specimens were loaded to failure at a crosshead speed of 0.05 inch/minute. The interlaminar shear stress at failure was calculated using the following:

$$\bar{\gamma}_I = \frac{3P}{4A}$$

where $\bar{\gamma}_I$ = interlaminar shear stress (psi)
P = total load at failure (pounds)
A = cross-sectional area (square inches)
b = specimen width (inches)
t = specimen thickness (inches)

A.5) DESCRIPTION OF MATERIALS

A.5.1) RESIN SYSTEMS

ADX-653: A 350°F service adhesive system - Hysol Division, The Dexter Corporation
ADX-646: A 420°F service adhesive system - Hysol Division, The Dexter Corporation
EA-9628: A 250°F service, high peel adhesive system - Hysol Division, The Dexter Corporation

A.5.2) FABRICS

Style 120 Kevlar 49: A plain weave (34 x 34) fabric weighing 1.8 oz/yd^2 and having a nominal thickness of 0.0045 inches - DuPont.

Style 220 Kevlar 49: A plain weave (22 x 22) fabric weighing 2.2 oz/yd^2 and having a nominal thickness of 0.0047 inches - DuPont.

Style 281 Kevlar 49: A plain weave (17 x 17) fabric weighing 5.0 oz/yd^2 and being 0.010 inches thick - DuPont.

Style 338 Kevlar 49: A plain weave (17 x 17) fabric weighing 6.8 oz/yd^2 and being 0.013 inches thick - DuPont.

Style 1065 Graphite: A plain weave fabric weighing 6.75 oz/yd^2 and being 0.013" thick. The warp yarns are T-300 ($E=30x10^6$ psi) graphite and the filling yarns are polyester - Prodesco.

Style 1509 Graphite: A plain weave (40 x 16 fabric weighing 10.25 oz/yd^2 and being 0.015 inches thick. The warp yarns are T-300 and the fill are nylon - Prodesco.

Style 1522 Graphite: A plain weave (42 x 6) fabric produced of T-300 graphite. It weighs 10.25 oz/yd^2 and is 0.017 inches thick - Prodesco.

Style 1675 E-Glass: A plain weave (40 x 32) fabric weighing 3.0 oz/yd^2 and being 0.0043" thick - Clark Schwebel.

Style PWA Graphite: A plain weave (48 x 44) fabric consisting of $E=30 \times 10^6$ psi graphite fibers in a staple form. The fibers are graphitized in the woven form by a special process. The fabric weighs 3.25 oz/yd^2 and is 0.013" thick - Stackpole.

A.5.3) ADHEREND MATERIALS

Titanium - 6 Al/4V Alloy

Graphite/Epoxy Composite - produced from 5208-T300, 350°F service prepreg - Narmco Materials Company.

A.5.4) RESINOUS WASHES

PAHJ: Union Carbide

ADX-653: Hysol Division, The Dexter Corporation

KSLA: Shell Chemical Company

Estane 5703: B. F. Goodrich Company

Z-6020: Dow Corning Corporation

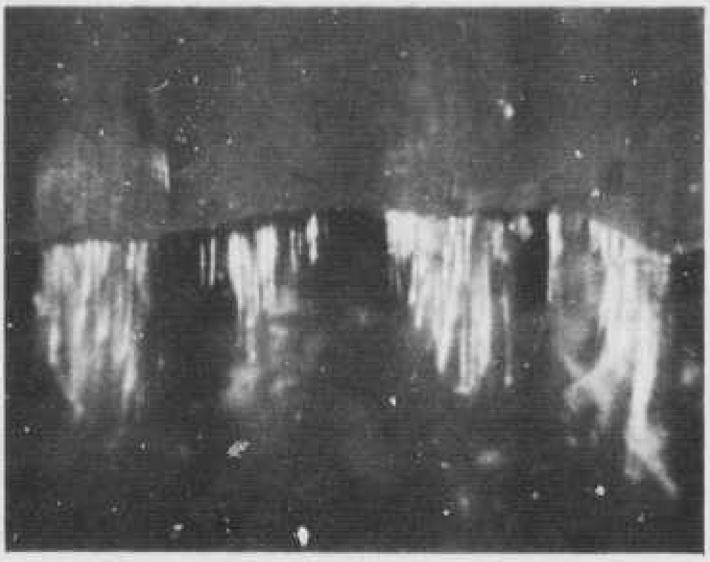
Z-6040: Dow Corning Corporation

Ram-225: Ram Chemicals Company

A) Fabric Surface

B) Resin Surface

Figure 1. Failure surface of ADX-653/Style 120 Kevlar 49 Fatigue Test Specimens

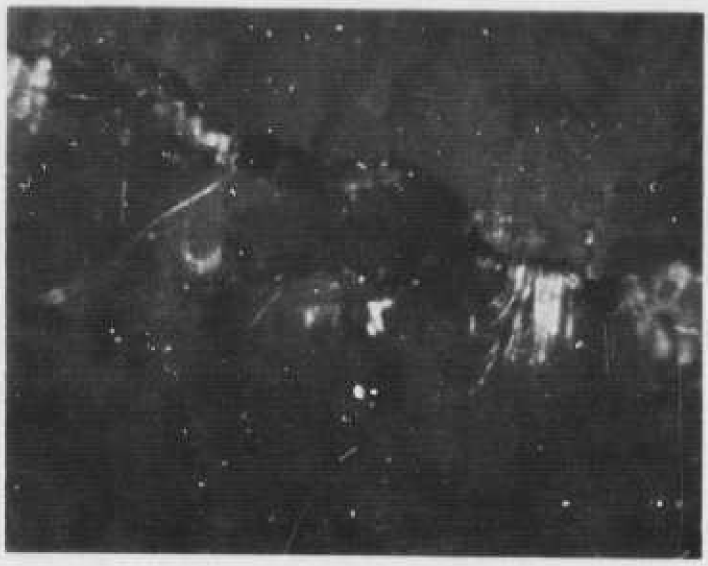


A) Interlaminar Failure

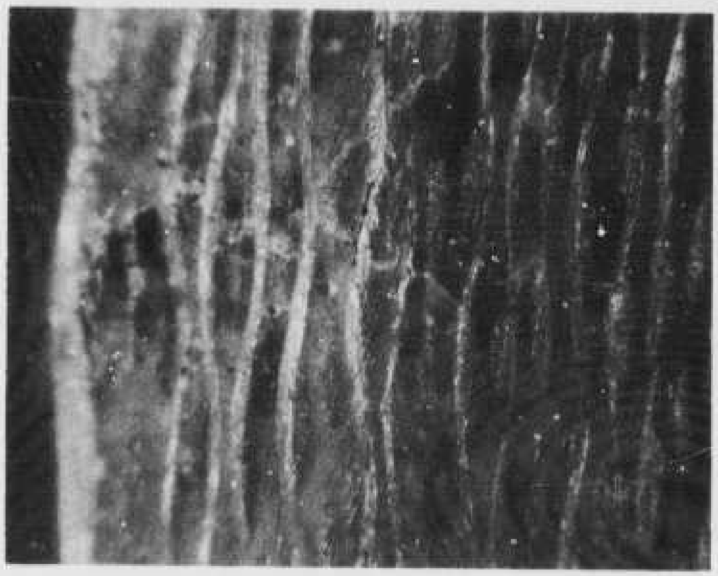
B) Transverse Failure

Figure 2. Failure Modes of Style 120 Kevlar 49 Reinforced ADX-653

PAHJ Surface Treatment
Interlaminar Shear Test - Dry Condition



A) Surface Failure



B) Transverse Failure

Figure 3. Failure Modes of Style 120 Kevlar 49 Reinforced ADX-653

PAHJ Surface Treatment
Interlaminar Shear Test - Wet (24 hours/100°C/H_2O) Condition

A) Interlaminar

B) Transverse

Figure 4. Failure Modes of Style 120 Kevlar 49 Reinforced ADX-653

Z-6040 Surface Treatment
Interlaminar Shear Test - Wet (24 hours/100°C/H_2O) Condition

A) Dry

B) Wet (24 hours/100°C/H_2O)

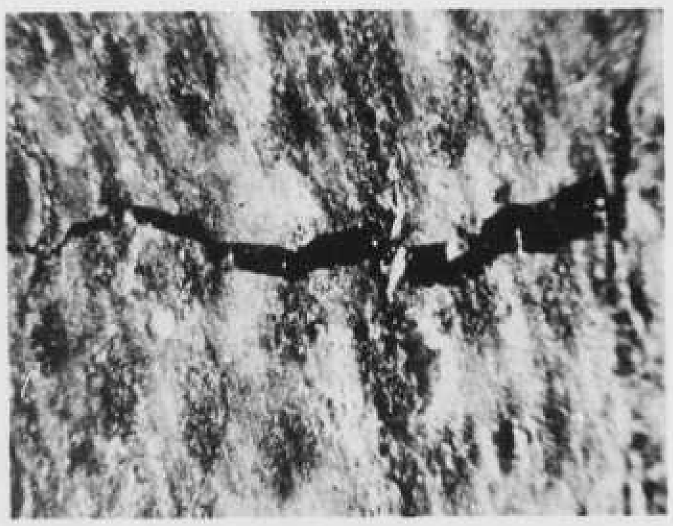


Figure 5. Failure Modes of Style PWA graphite reinforced ADX-653
Z-6040 Surface Treatment
Interlaminar Shear Test - Dry and Wet Conditions

A) Dry

B) Wet (24 hours/100°C/H_2O)

Figure 6. Failure Modes of Style PWA Graphite Reinforced ADX-653

PAHJ Surface Treatment
Interlaminar Shear Test

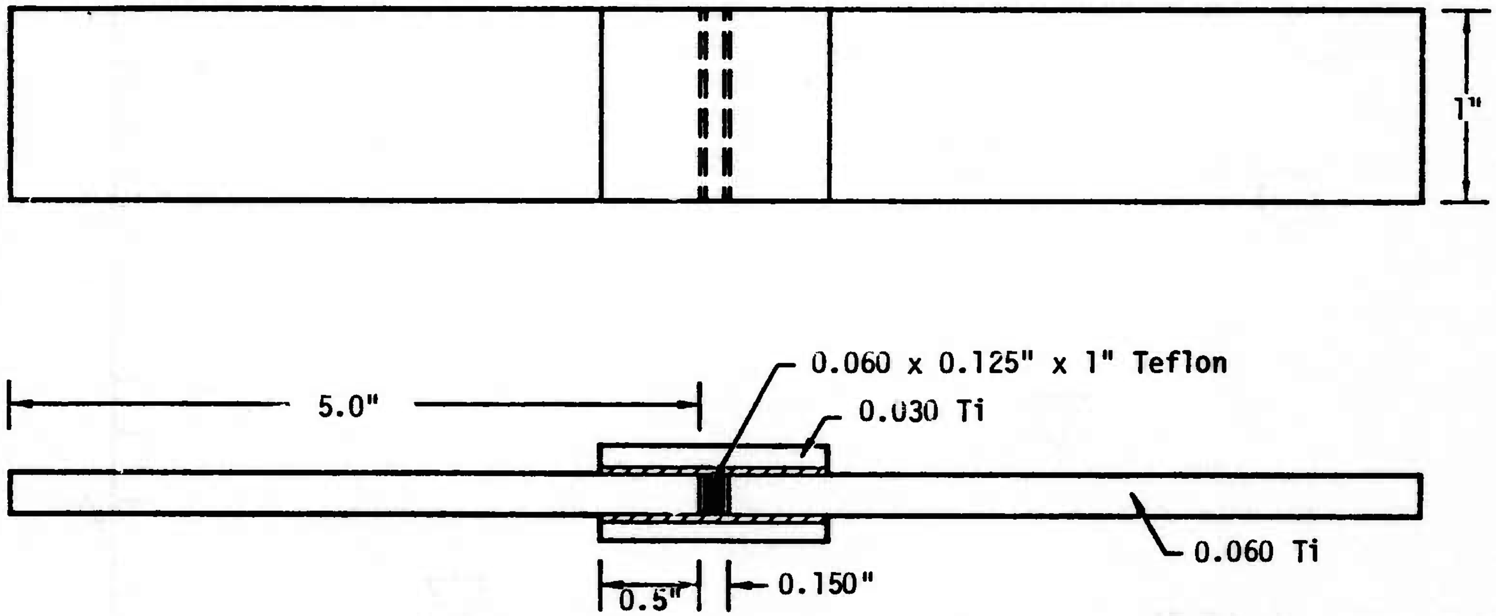


Figure 7. Titanium Double Lap Shear Specimen Used in the Screening of Fatigue Properties

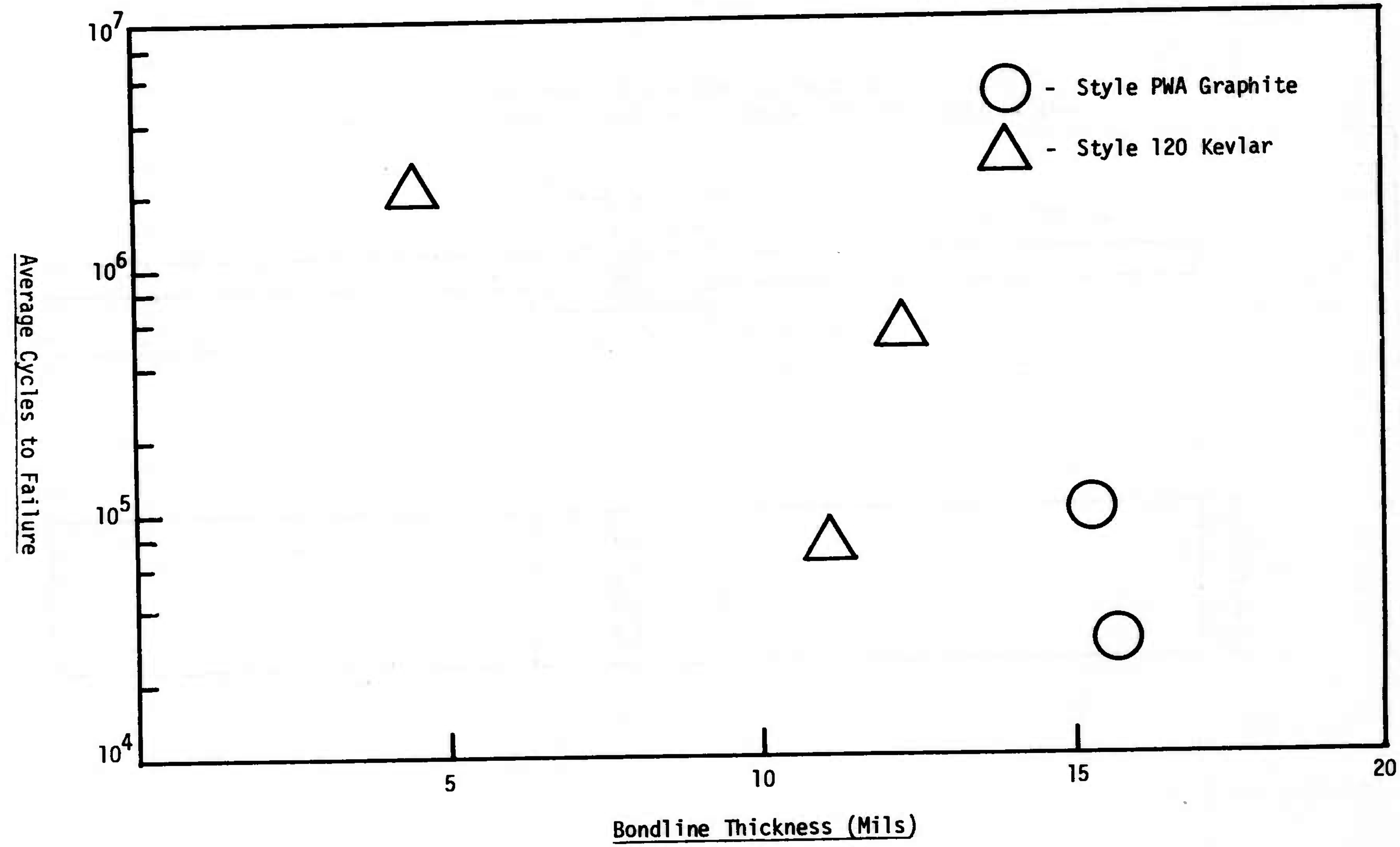


Figure 8. Fatigue Resistance Correlation with Bondline Thickness

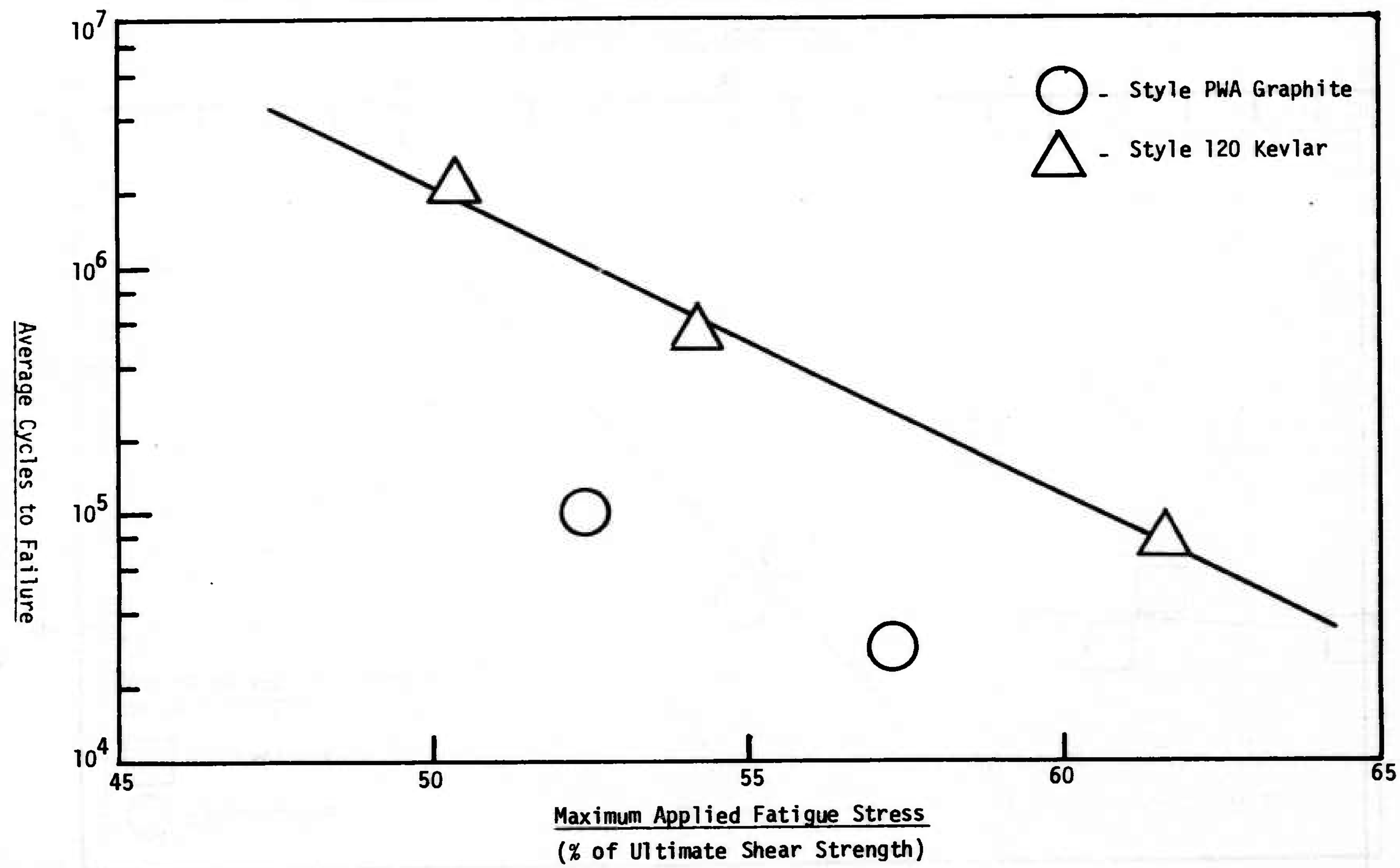


Figure 9. Fatigue Resistance Correlation with Percent of Ultimate Strength

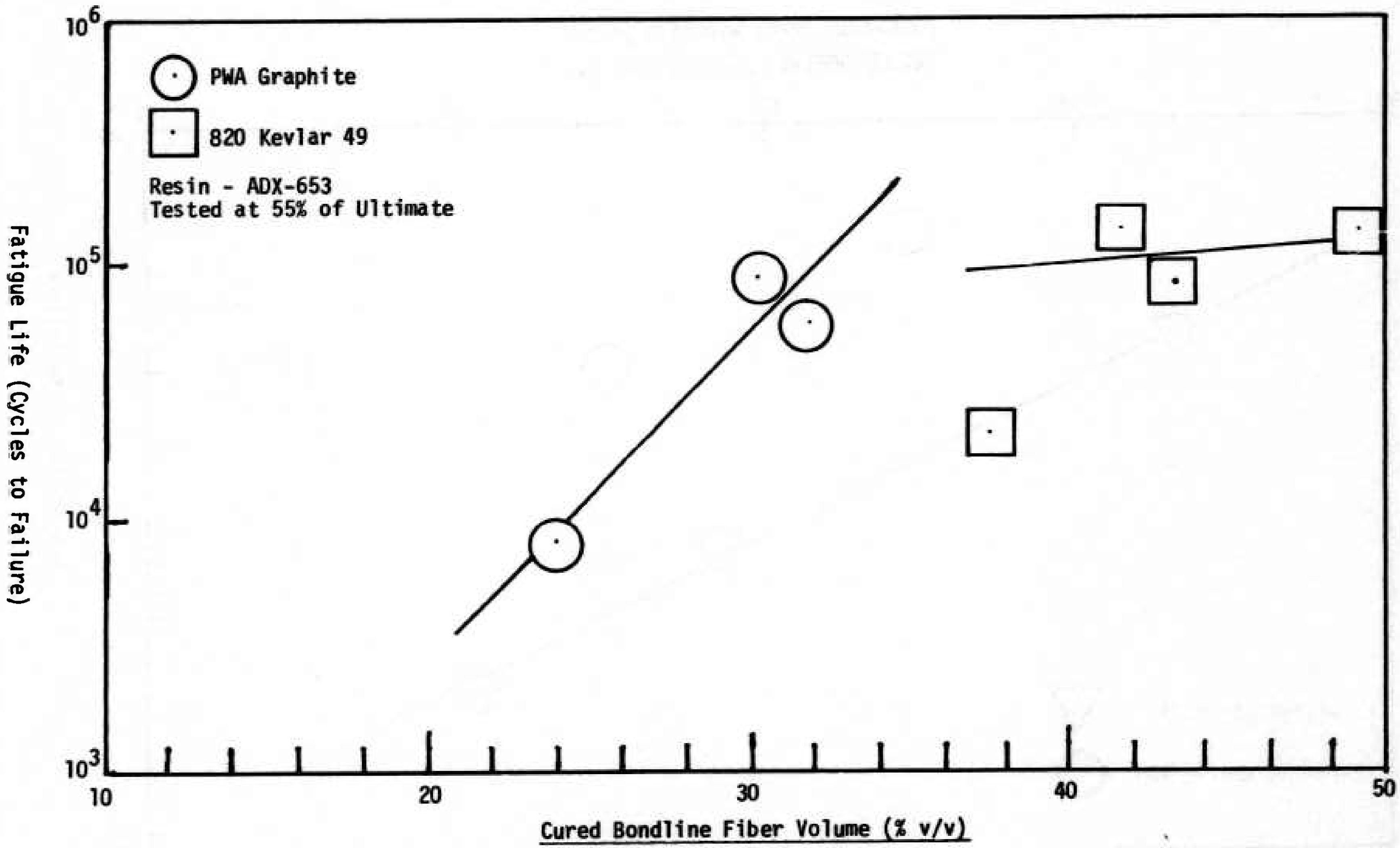


Figure 10. Variation of Adhesive Fatigue Resistance with Cure Bondline Fiber Volume

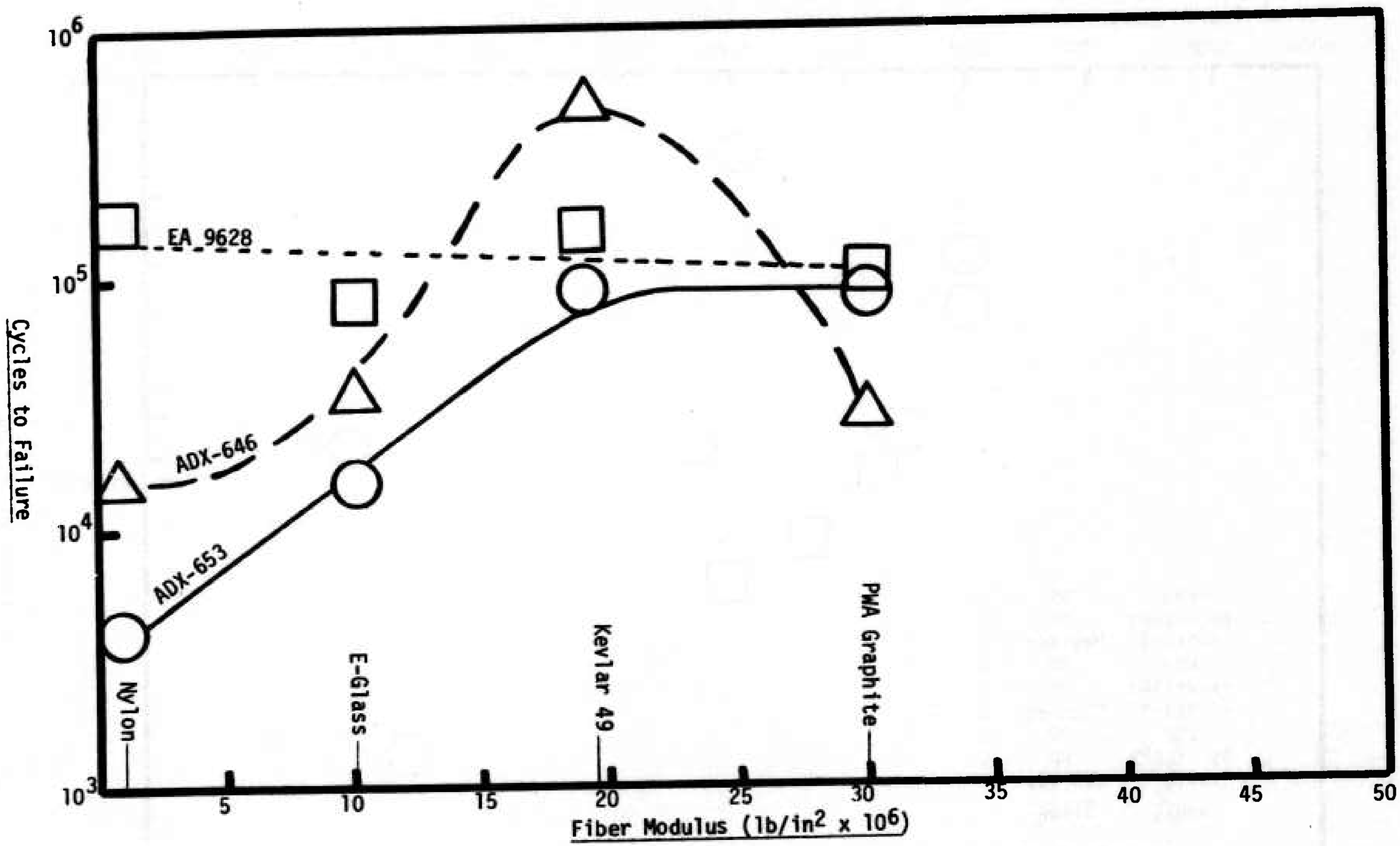


Figure 11. Fatigue Results with Various Fabrics and Matrix Resin Systems

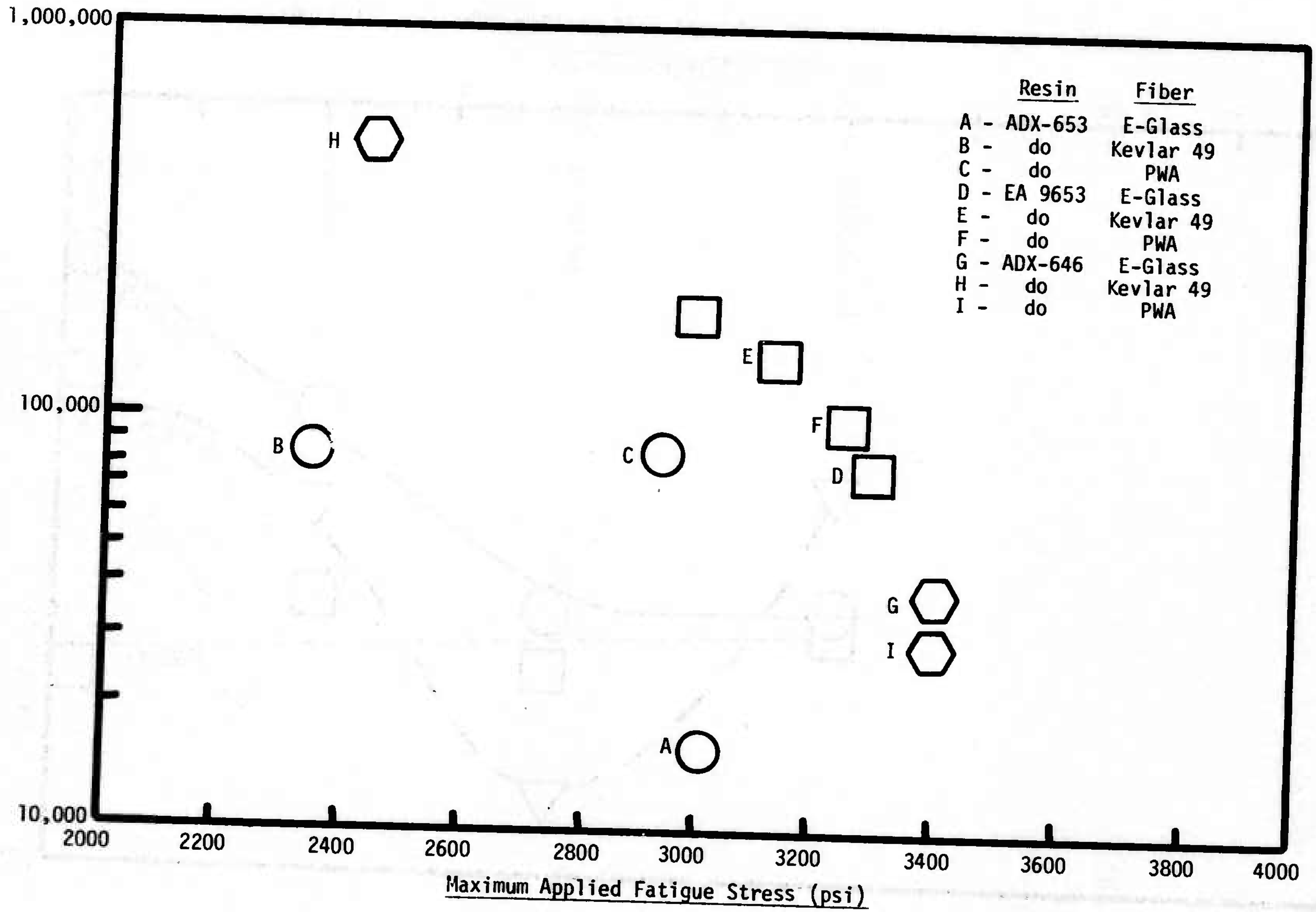
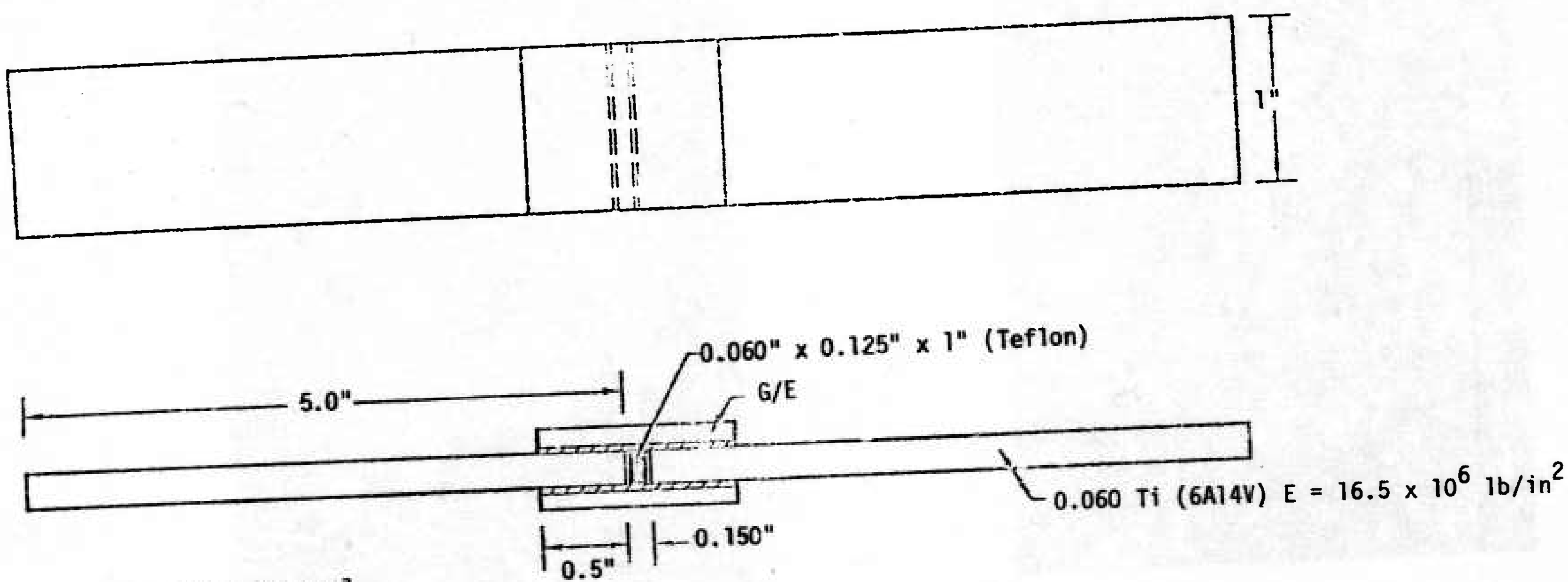


Figure 12. Variation of Fatigue Resistance With Increasing Maximum Applied Stress

$E_1 t_1 = E_2 2 t_2$



[Narmco 5208 (T-300) G/E]
(0,0,0,0)
$E - 21 \times 10^6$ lb/in^2(nom)

Figure 13. TITANIUM TO GRAPHITE/EPOXY DOUBLE LAP SHEAR SPECIMEN

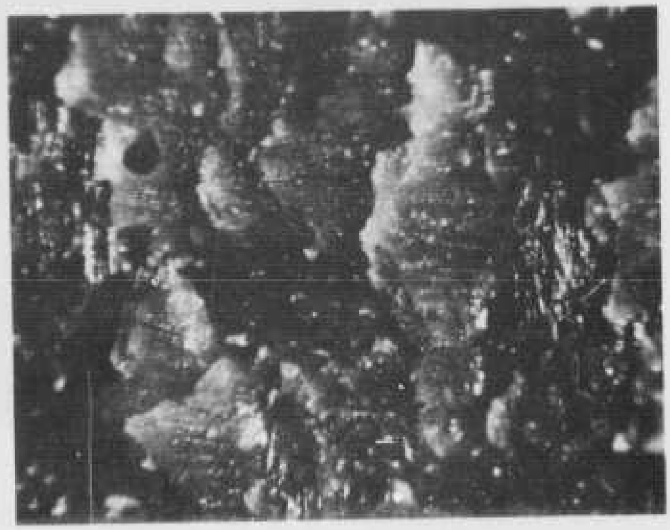
A) Graphite/Epoxy Composite Surface

B) Titanium Surface

Figure 14. Failure Surfaces of Titanium-Graphite/Epoxy Double Lap Shear Specimens Bonded with ADX-653/Style PWA Graphite

Figure 14 - Continued

C) Adhesive Surface



A) Graphite/Epoxy Composite Surface

B) Titanium Surface

Figure 15. Failure Surfaces of Titanium-Graphite/Epoxy Double Lap Shear Specimens Bonded with ADX-653/Nylon Knit

Figure 15 - Continued

C) Adhesive Surface

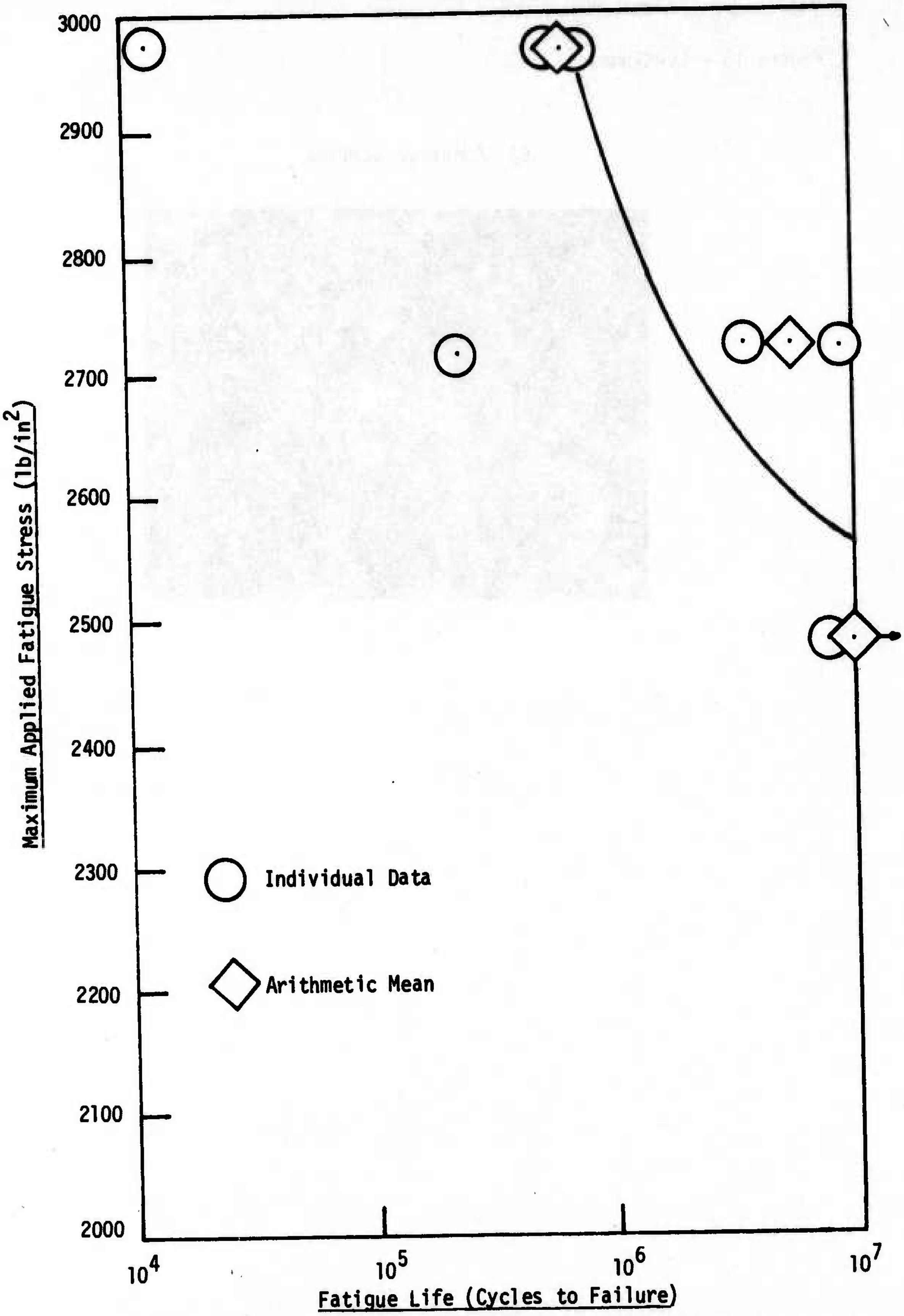


Figure 16. 10^7 Cycle Fatigue Resistance of ADX-653 Reinforced with the Z-6040 Silane Treated PWA Graphite Fabric

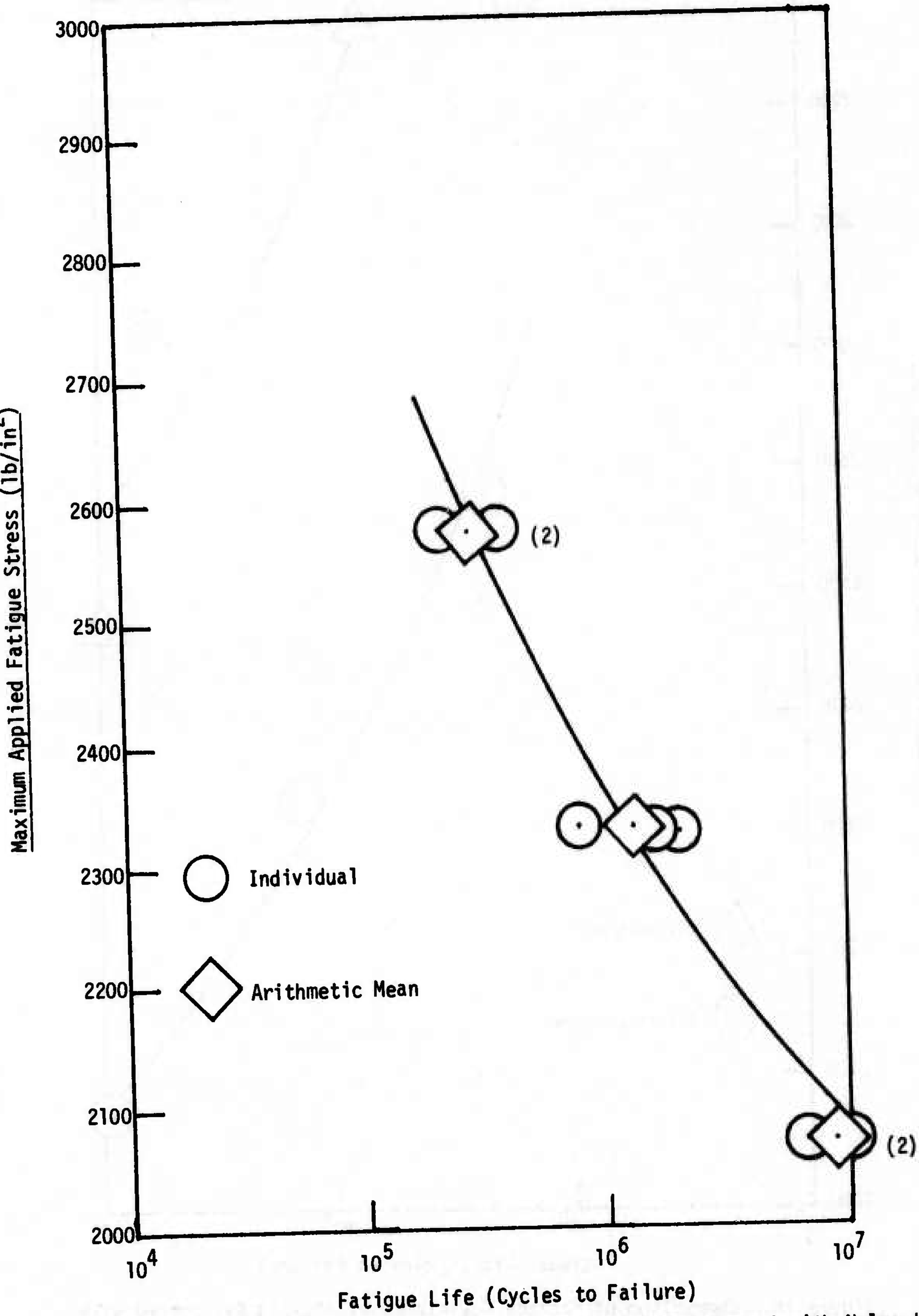


Figure 17. 10^7 Cycle Fatigue Resistance of ADX-653 Reinforced with Nylon Knit

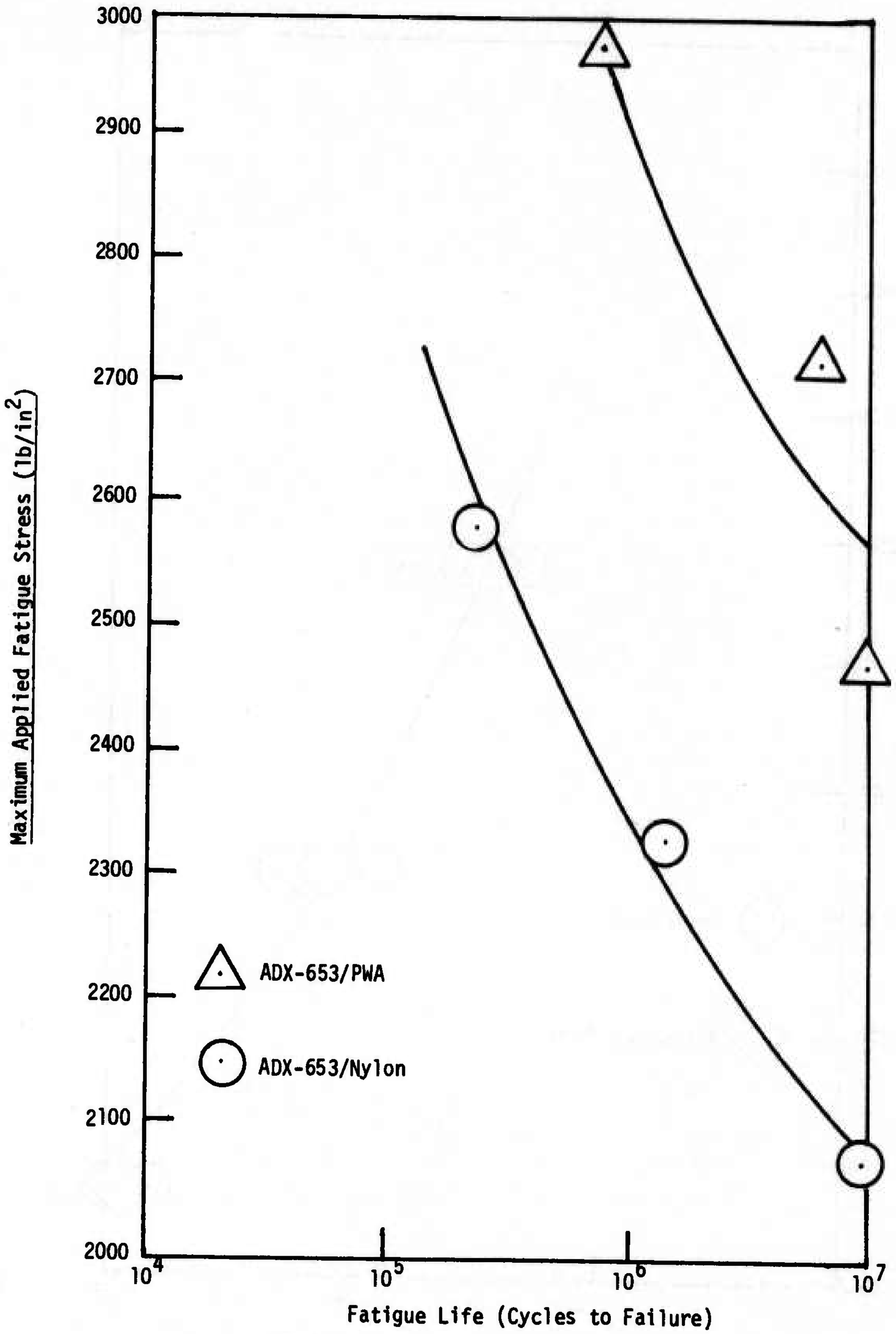


Figure 18. Comparison of Fatigue Resistance of ADX-653 Reinforced With Silane Treated PWA Graphite and Nylon Knit Fabrics

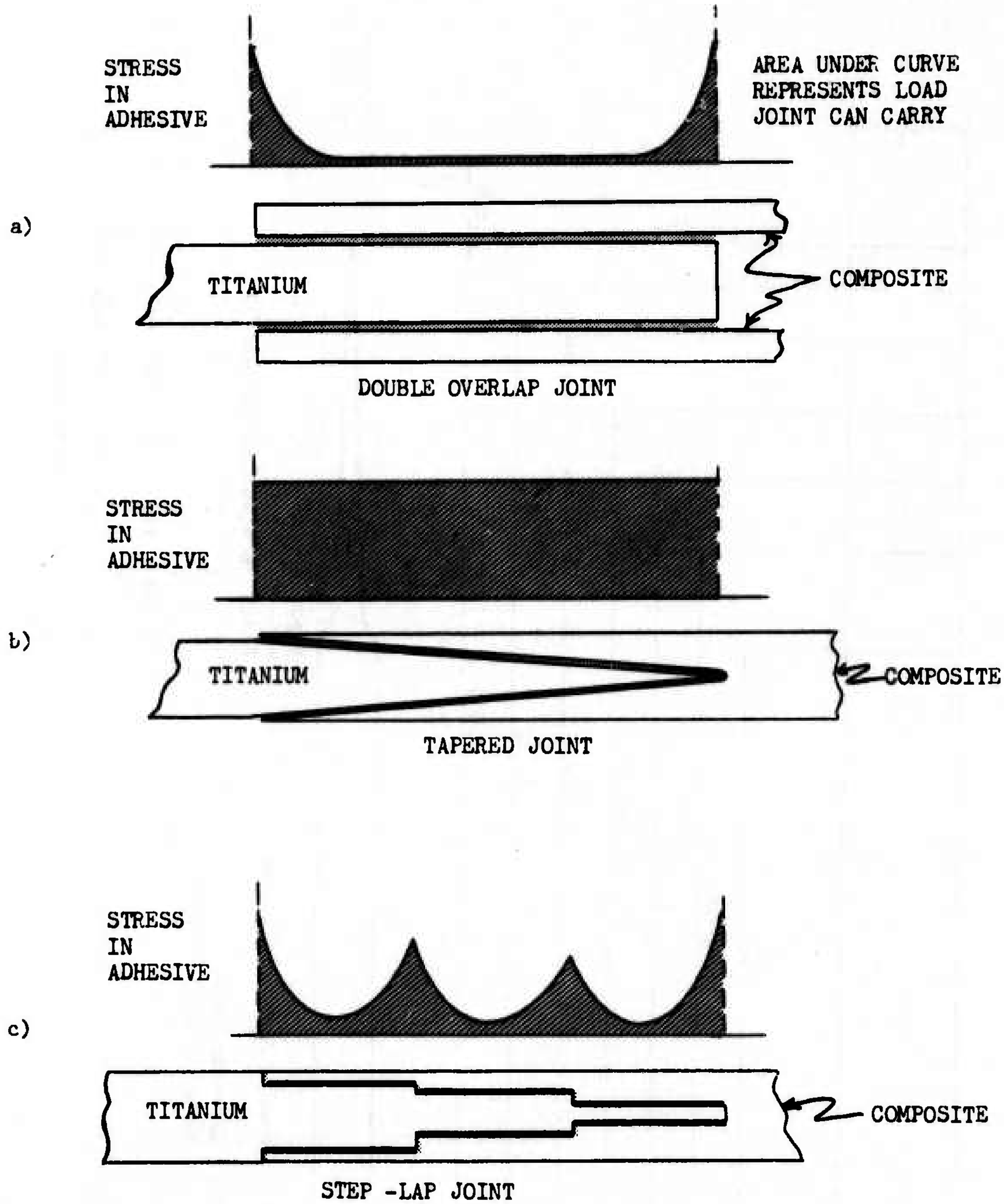
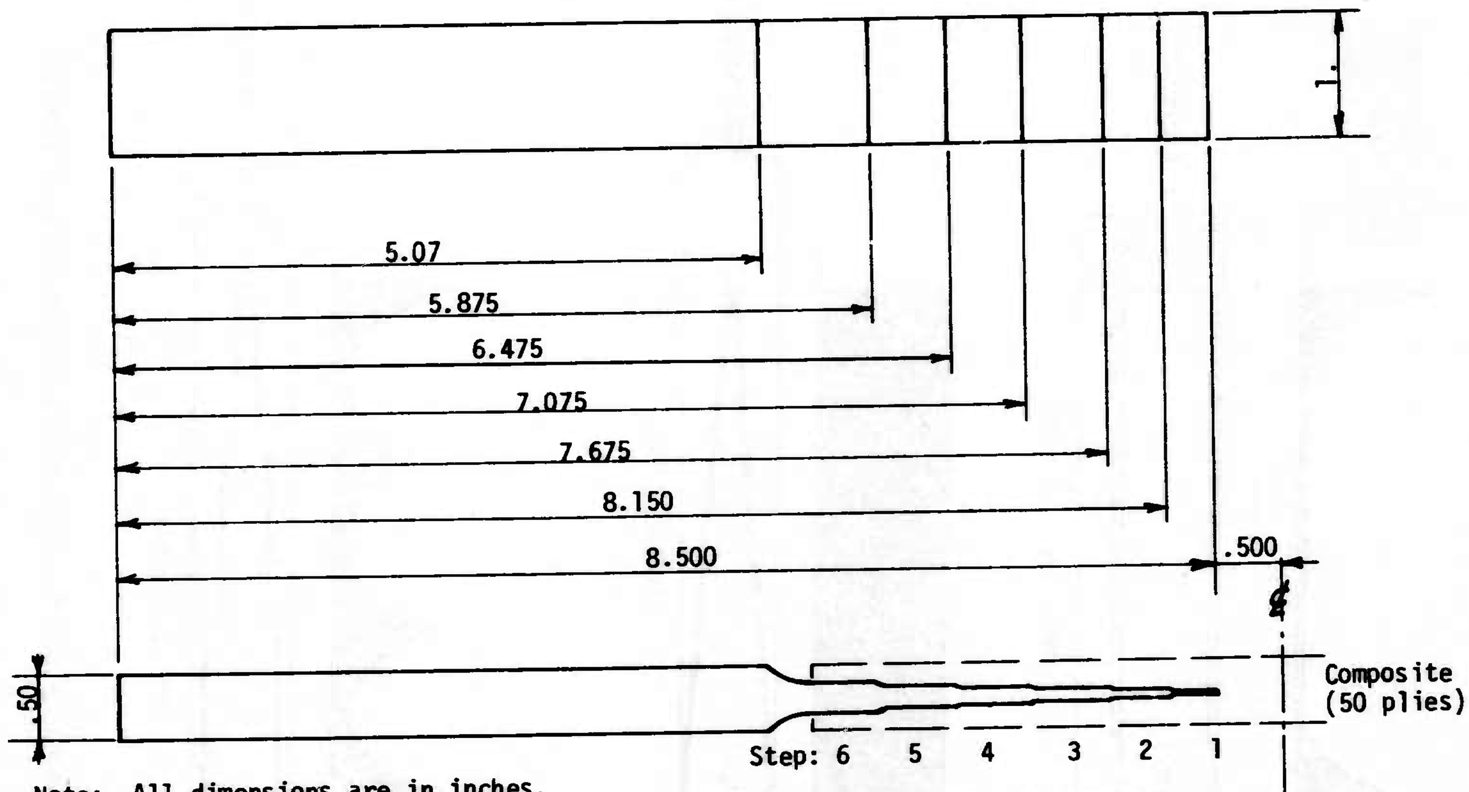


FIGURE 19. DEPENDENCE OF STRESS DISTRIBUTION PATTERN ON BOND GEOMETRY

Figure 20. Step Lap Joint



Note: All dimensions are in inches.

Composite: Graphite/Epoxy
Narmco T-5208 (T-300)

Plies Terminating at Step No.

1	2	3	4	5	6
0	0	0	0	0	0
-45	+45	-45	+45	-45	-45
0	0	0	0	0	0
		90	90	+45	+45

Both Sides

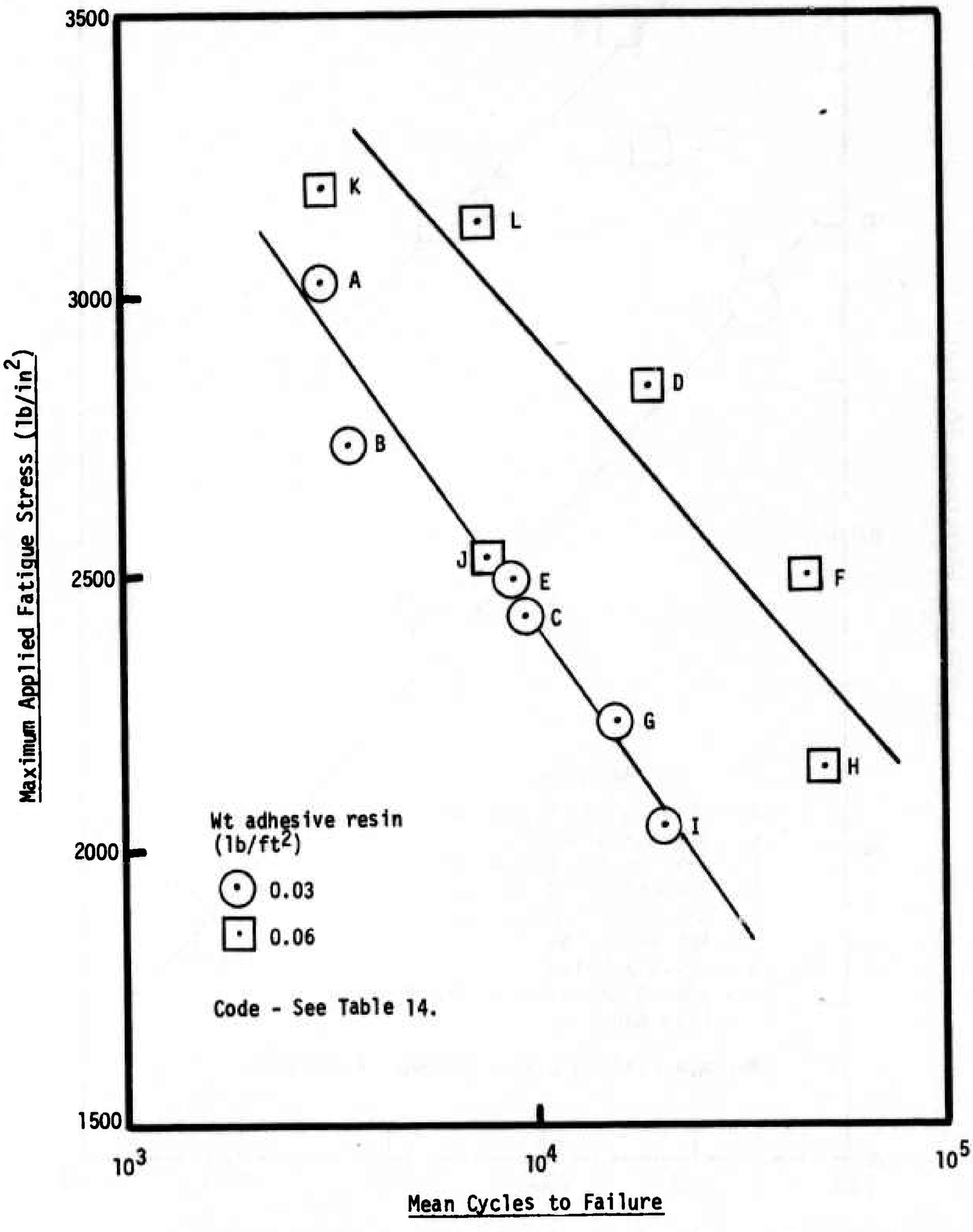


Figure 21. Variation of Fatigue Life with Applied Fatigue Stress

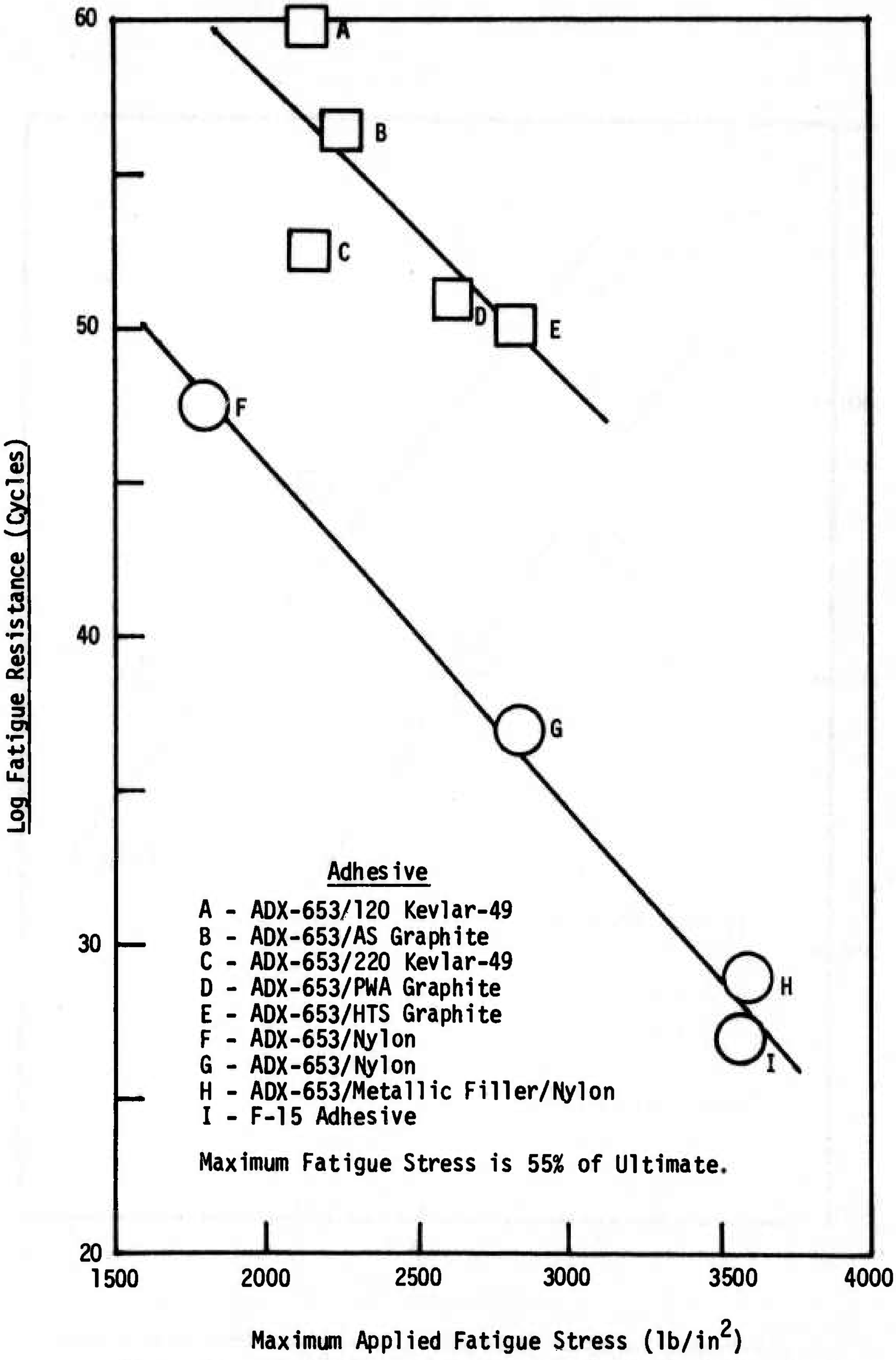


Figure 22. Comparison of Fatigue Resistance of High Modulus Fiber and Nylon Supported Adhesives

TABLE 1. RESIN WASH PICKUP OF KEVLAR 49 AND PWA GRAPHITE FABRICS

	% Weight Pickup	
Finish	Style 120 Kevlar 49	PWA Graphite
PAHJ	1.11	1.93
ADX-653	1.30	<0.01
KSLA	0.87	2.16
Estane 5703	0.93	1.97
Aerotex M-3	0.61	5.26
Z-6020	<0.01	<0.01
Z-6040	<0.01	<0.01
Ram 225	<0.01	0.1

TABLE 2. EFFECT OF RESIN WASHES ON THE INTERLAMINAR SHEAR PROPERTIES OF AN ADX-653/STYLE 120 KEVLAR 49 COMPOSITE

Finish[1]	Pickup (% w/w)	Adhesive Film wt (lb/ft^2)	Volatiles (% w/w)	Volume Fraction Fiber[2]	Interlaminar[3] Shear Strength (lb/in^2) Initial	Exposed[4]	% Retention
1. None	-	0.051	0.92	0.336	5600	5750	102.7
2. PAHJ	1.11	-	-	0.339	5150	5150	100.0
3. ADX-653	1.30	0.047	0.85	0.393	5320	4510	84.8
4. KSLA	0.87	-	-	0.303	5700	5015	88.0
5. Estane 5703	0.93	-	-	0.421	5610	4570	81.5
6. Aerotex M-3	0.61	-	0.41	0.418	4590	2914	63.5
7. Z-6020	<0.01	0.049	-	0.383	4690	3100	66.1
8. Z-6040	<0.01	0.052	-	0.382	5000	3600	72.0
9. Ram 225	<0.01	0.050	-	0.385	4970	3270	65.8
10. Dry	-	0.046	0.32	0.450	5080	3640	71.7

1) For chemical structure - see section 3.1
2) Calculated (based on cured laminates)
3) For test details, see Appendix
4) Exposed to boiling water for 24 hours

TABLE 3. EFFECT OF RESIN WASHES ON THE INTERLAMINAR SHEAR PROPERTIES OF AN ADX-653/STYLE PWA GRAPHITE COMPOSITE.

					Interlaminar[3)] Shear Strength		
Finish[1)]	Pickup (% w/w)	Adhesive Film wt (lb/ft^2)	Volatiles (% w/w)	Volume Fraction Fabric[2)]	Initial	Exposed[4)]	% Retention
None	-	0.114	1.02	-	3480	3430	98.6
PAHJ	1.93	0.108	0.40	0.201	4750	4210	88.6
ADX-653	<0.01	0.111	0.50	0.167	5070	4100	80.9
KSLA	2.16	0.114	0.66	0.189	4560	4130	90.6
Estane 5703	1.97	0.111	0.71	0.179	4840	4340	89.7
Aerotex M-3	5.26	-	-	0.208	3980	4150	104.3
Z-6020	<0.01	0.114	-	0.205	4610	4130	89.6
Z-6040	<0.01	0.108	-	0.214	4130	4010	97.1
Ram 225	0.1	0.113	0.59	0.235	4620	4180	90.5
Dry		0.111	0.55	0.193	4410	3990	90.5

1) For chemical structure, see section 3.2
2) Calculated (based on cured laminates)
3) For test method, see Appendix
4) Exposed to boiling water for 24 hours

TABLE 4. EFFECT OF RESIN WASHES ON THE FATIGUE RESISTANCE OF PWA GRAPHITE AND 120/KEVLAR 49 REINFORCED ADX-653

Maximum Applied Fatigue Stress - 2600 psi

Reinforcement	Resin Wash	Ultimate Shear Strength (75°F, lb/in^2)	Fatigue Life[4] (cycles)
PWA	PAHJ	4680	114,000
	ADX-653	4690	129,000
	Z-6040	4750	200,000
	Estane 5703	4810	205,000
	None[2]	5270	128,000[1]
	None[2]	4720	105,000
Kevlar 49	PAHJ	4320	21,000
	ADX-653	4140	47,000
	Z-6040	4270	33,000
	RAM 225	4070	13,000
	None[2]	4285	976,000[3]

1) Determined at 2635 psi fatigue stress
2) Determined in first part of contract with different batches of adhesive
3) Determined at a maximum applied fatigue stress of 2140 psi
4) Determined using a titanium to titanium double lap shear specimen (Figure 7)

TABLE 5. EFFECT OF RESIN WASHES ON THE 350°F SHEAR STRENGTH OF PWA GRAPHITE AND 120/KEVLAR 49 REINFORCED ADX-653

Reinforcement	Finish	Blister Shear Strength[1] (psi)	
		@ 75°F	@ 350°F
PWA	PAHJ	2260	2170
	ADX-653	2430	2280
	Z-6040	2430	2100
	Estane 5703	2520	2350
Kevlar 49	PAHJ	2160	1510
	ADX-653	2220	1970
	Z-6040	2270	2170
	RAM 225	2250	2180

1) Determined using 2024-T3 Bare aluminum blister detection specimens (0.5 inch overlap). All adhesives cured for 60 minutes at 350°F and 50 psi.

TABLE 6. PHASE I, TASK II - VARIATION IN BONDLINE THICKNESS - ULTIMATE SHEAR PROPERTIES

Reinforcement (Style)	Fiber Type	Cured Thickness (in)	Adhesive[1] wt (lb/ft^2)	Ultimate Shear Strength (lb/in^2) @ 75°F Al/Al[2]	Ti/Ti[3]
1065	Graphite, Thornel 300	0.011	0.120	1830	1955
1509	Graphite, Thornel 300	0.016	0.173	2250	3800
1522	Graphite, Thornel 300	0.015	0.196	3000	4160
220	Kevlar 49	0.005	0.513	2150	4320
281	Kevlar 49	0.012	0.076	2570	4020
328	Kevlar 49	0.011	0.092	1900	3540

1) Adhesive weight was calculated to fill the voids in the fabric and leave an excess on the surface for adhesive flow and wetting during cure.
2) 2024-T3 Bare Aluminum Lap Shear specimens per MMM-A-132
3) Titanium (6-Al/4V) Double Lap Shear specimens per Figure 7.

TABLE 7. PHASE I, TASK II - VARIATION IN BONDLINE THICKNESS - FATIGUE RESULTS

Maximum applied fatigue stress - 2180 psi

Reinforcement (Style)	Fiber Type	Cured Bondline Thickness (inch)	Ultimate Shear Strength (lb/in^2)	Fatigue (% of UTS)	Lifetime (cycles to fail)
1065	Graphite, Thornel 300[1]	0.0113	1995	-	Not Tested
1509	Graphite, Thornel 300	0.0157	3800	57.3	17,000 43,000 27,000
				$\bar{x}/\sigma x$[3]	29,000/ 13,000
1522	Graphite, Thornel 300	0.0153	4160	52.4	128,000 98,000 75,000
				$\bar{x}/\sigma x$	100,000/ 27,000
220	Kevlar 49	0.0045	4323	50.4	3,583,000 2,554,000 774,000
					2,303,000/ 1,421,000
281	Kevlar 49	0.0123	4020	54.2	706,000 365,000 489,000
				$\bar{x}/\sigma x$	520,000/ 173,000
328	Kevlar 49	0.011	3542	61.6	91,000 80,000 47,000
				$\bar{x}/\sigma x$	73,000/ 23,000
PWA[2]	Graphite[1]	0.0085	4750	55	258,000 204,000 138,000
				$\bar{x}/\sigma x$	200,000/ 60,000

1) Modulus = 30×10^6 psi
2) The PWA reinforced adhesive was fatigue tested with a maximum applied fatigue stress of 2600 psi.
3) $\bar{x} \equiv$ Statistical Mean
$\sigma x \equiv$ Standard Deviation

TABLE 8. RESULTS OF THE INVESTIGATION OF THE EFFECT OF BONDLINE FIBER VOLUME ON FATIGUE RESISTANCE

Adhesive Resin - ADX-653

Fabric	Construction	Bond[1] Fiber Volume (% v/v)	Bond Thickness (in)	Ultimate[2) 4)] Strength (lb/in^2)	Fatigue[3)] Stress (lb/in^2)	Mean[2) 4)] Cycles to failure
PWA	48 x 44	30.3	0.0082	4825	2655	89,000
PWA	48 x 29	31.8	0.0065	4415	2430	58,000
PWA	48 x 22	23.9	0.0078	4840	2660	8,000
120 Kevlar 49	34 x 34	37.4	0.0045	5400	2970	21,000
120 Kevlar 49	34 x 34[5)]	43.1	0.0039	4340	2385	84,000
120 Kevlar 49	34 x 26	41.5	0.0036	4475	2460	131,000
120 Kevlar 49	34 x 23	49.0	0.0029	4470	2460	133,000

1) Calculated (based on cured specimen)
2) Determined on Titanium-Titanium double lap shear specimens (Figure 7)
3) 55% of Ultimate
4) Tested with adhesive fabric warp 0° to direction of applied stress
5) Data from Task 3A

TABLE 9. SUMMARY OF PERFORMANCE RESULTS WITH RESIN SYSTEMS AND FABRIC FIBER MODULII VARIATION

Resin System[1]	Resin Modulus[2] (psi 10^6)	Fiber: Fabric	Fiber: Type	Fiber: Modulus (psi)	Ultimate Shear Strength[4] (psi)	Maximum Applied Fatigue Stress (psi)[3]	Fatigue Life (Cycles)[4]
ADX-653	3.07	Tricot	Nylon	0.4×10^6	4960	2730	3,900
		1675	E-Glass	10×10^6	5480	3015	15,700
		120	Kevlar 49	19×10^6	4340	2385	84,000
		PWA	Graphite	30×10^6	5360	2945	87,000
		1099	Graphite	50×10^6	2280	Not Tested	Not Tested
EA 9628	2.85	Tricot	Nylon	0.4×10^6	5410	2980	164,000
		1675	E-Glass	10×10^6	5980	3290	79,000
		120	Kevlar 49	19×10^6	5700	3135	142,000
		PWA	Graphite	30×10^6	5910	3250	92,000
		1099	Graphite	50×10^6	3380	Not Tested	Not Tested
ADX-646	5.08	Tricot	Nylon	0.4×10^6	3375	1890	10,500
		1675	E-Glass	10×10^6	6170	3395	35,300
		120	Kevlar 49	19×10^6	4480	2465	490,000
		PWA	Graphite	30×10^6	6150	3385	28,700
		1099	Graphite	50×10^6	2260	Not Tested	Not Tested

1) All systems cured 60 minutes at 350°F except ADX-646 (120 minutes)
2) Quasielastic stiffness, see reference 7.
3) 55% of ultimate strength
4) Specimen, see Figure 7.

TABLE 10. DEMONSTRATION OF FATIGUE IMPROVEMENT

Test Specimen - Double Lap Shear[1)]
Adhesive Resin - ADX-653
Orientation - 0°[2)]
Adherends - Ti (6,4) and Graphite Epoxy Composite

Reinforcement	Ultimate Shear Strength (psi)	Fatigue Stress (psi)	Percent of Ultimate Strength	Fatigue Life (Cycles)	Mean Life
Nylon Knit	5165	2070	40	>10,121,000[3)]	
				7,960,000	
				>10,087,000[3)]	>9,333,000
		2325	45	829,000	
				2,160,000	
				1,616,000	1,425,000
		2580	50	217,000	
				366,000	
				373,000	309,000
PWA Graphite[5)]	4950	2480	50	8,737,000	
				>10,295,000[3)]	
				>10,276,000[3)]	>9,742,000
		2720	55	232,000	
				3,843,000	
				9,100,000	5,914,000
		2970	60	733,000	
				688,000	
				12,000[4)]	710,000

1) See Figure 13 for design
2) Orientation angle of warp direction of fabric to test application direction
3) Specimens removed from testing without bond failure
4) Value not included in arithmetic mean
5) Fabric treated with Z-6040 epoxy silane prior to impregnation

TABLE 11. FATIGUE LIFE IMPROVEMENT DUE TO PWA REINFORCEMENT OF STEP LAP JOINT SPECIMENS

Test Specimen - Multiple Step Lap Splice Plate[1)]
Fatigue - Constant Amplitude[2)]

Adhesive Reinforcement	Load	Percent Ultimate	Cycles To Failure	Comments
Nylon	16,000		-	Ultimate Strength
	8,000	50	65,000	Adhesive Failure
			66,000	Adhesive Failure
			49,000	Adhesive Failure
			60,000 (Mean)	
	6,400	40	562,000	Titanium Failure[3)] in Radius of Step 2
			499,000	Titanium Failure[3)] in Radius of Step 2
	4,800	30	85,075,000	No Failure
PWA	15,960		-	Ultimate Strength
	7,980	50	205,000	Adhesive Failure
			140,000	Adhesive Failure
			196,000	Titanium Failed in Radius of Step 3
PWA	7,180	45	372,000	Titanium Failed in Radius of Step 1

1) For design see Figure 20

2) Constant Load Amplitude

3) The steps are numbered in ascending order, from the center of the specimen out.

TABLE 12. RANDOM SPECTRUM FATIGUE TESTING OF ADX-653 REINFORCED WITH BOTH NYLON KNIT AND PWA GRAPHITE FABRICS

Test Specimen: Multiple Step Lap Splice Plate[1)]
Fatigue: F-15 Random Spectrum
Adhesive Resin System: ADX-653

Reinforcement	Ultimate Strength (Lbs)	Test Limit Load (TLL) (Lbs)	Load Spike[2)] Applied (?)	Failure Time (Hours)[3)]	Failure Location (% TLL)	Mean Failure Time ($\bar{x}/\sigma x$)[7)] (Hours)	Mean Failure Time (Lifetimes)[4)] ($\bar{x}/\sigma x$)[7)]
Nylon	16,000	13,500	No	1070	89.3		
				1616	83.9		
				1127	84.4	1271/300	0.32/0.08
PWA	15,960	13,500	No	8737	86.8		
				6125	99.3		
				4745	81.9	6536/2027	1.63/0.51
Nylon	16,000	12,000	Yes	2000[5)]	103.5%		
				3522	80.0%		
				2000[5)]	104.1%	2507/879	0.63/0.22
PWA	15,960	12,000	Yes	12651	91.3%		
				16000	No Failure[6)]		
				7634	97.5%	12095/4210	3.02/1.05

1) For design see Figure 20.
2) A manually applied 125% (TLL) applied every 2000 hours.
3) Equivalent flight hours,
4) Aircraft flight lifetime = 4000 hours
5) Failed during application of 125% TLL spike.
6) Tested for residual strength at ambient. Strength was 13,800 lbs (86.5% of ultimate strength)
7) $\bar{x} \equiv$ Statistical mean
$\sigma x \equiv$ Standard Deviation

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[1)]	Orientation[2)]	Ultimate Shear Strength (psi)	Fatigue Life @ 50% of Ultimate (cycles)
2	A	0°	4750	9,000
		90°	3540	30,000
3	A	0°	4930	22,000
3	B	0°	4680	89,000
1	B	0°	4530	445,000

1) Specimen Type
   A) Titanium-Titanium Double Lap Shear - for design see Figure 23
   B) Titanium-Titanium Double Lap Shear - for design see Figure 7
2) Orientation to an arbitrarily chosen direction

TABLE 14. AN INVESTIGATION INTO THE CAUSES OF THE LACK OF REPRODUCIBILITY OF FATIGUE PERFORMANCE USING THE TYPE AS GRAPHITE RANDOM MAT/ADX-653 COMBINATION

Code[1]	Mat Wt. (lb/ft^2)	Total Wt.[2] (lb/ft^2)	Fiber[3] Finish	Filler Conc. (phr)	Shear Stress[4] (psi) Ultimate	Shear Stress (psi) Fatigue	Fatigue Life Cycles To Fail
A	0.006	0.036	None	None	5400	2970	3,100
B	0.009	0.039	None	None	4910	2700	3,600
C	0.011	0.041	None	None	4390	2420	9,800
D	0.009	0.069	None	None	5090	2800	20,000
E	0.009	0.039	ADX-653	None	4515	2480	9,200
F	0.009	0.069	ADX-653	None	4515	2480	50,000
G	0.009	0.039	ADX-653 Resin	None	4080	2245	16,000
H	0.009	0.069	ADX-653 Resin	None	3910	2150	53,000
I	0.009	0.039	Z-6020[5]	None	3720	2045	23,000
J	0.009	0.069	Z-6020[5]	None	4560	2505	8,400
K	0.009	0.079	None	50	5685	3130	3,130
L	0.009	0.089	None	100	5595	3080	7,600
M	Nylon Control	-	-	-	5810	2900	4,900

1) Corresponds to data points in Figure 21.
2) Corresponds to impregnation with 0.030 and 0.060 lb/ft^2 unsupported ADX-653
3) Calculated to give 1.0 wt percent add-on
4) Titanium-Titanium double lap shear test specimens used (for design see Figure 7)
5) An amino silane $H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$

☆ U. S. GOVERNMENT PRINTING OFFICE: 1976 — 657-630/385

UNCLASSIFIED

AD B009505

AUTHORITY: AFWAL

ltr, 6 OCT 81

UNCLASSIFIED