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AFML-TR-74-88

DEVELOPMENT OF HIGH TEMPERATURE ADDITION-CURED ADHESIVES

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TECHNICAL REPORT AFML—TR—74—88

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AIR FORCE MATERIALS LABORATORY
WRIGHT—PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

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

T. J. Aponyi

T. J. APONYI
Project Monitor

FOR THE COMMANDER

T J Reinhart Jr

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

AIR FORCE/56780/8 November 1974 — 200

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FOREWORD

This technical report was prepared by Hughes Aircraft Company, Aerospace Group, Culver City, California under U.S. Air Force Contract Nr. F33615-73-C-5062. This contract was initiated under Project Nr. 7340, "Nonmetallic and Composite Materials," and Task Nr. 734002 "Structural Adhesives." The work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. T. J. Aponyi (AFML/MBC) as the Project Engineer.

This report covers the work performed from 1 March 1973 to 28 February 1974. It is submitted in partial fulfillment of the contract.

The work was performed in the Advanced Materials Department of the Materials and Processes Laboratory under the management of Mr. L. Brian Keller. The program manager was Dr. Norman Bilow, Senior Scientist for the Materials Technology Department. The principal investigator was Dr. Robert H. Boschan. Professional assistance was provided by Dr. Abraham Landis and Ms. Kathryn E. Van Buren, who assisted in synthesis of monomers and prepolymers, and professional consultation was provided by Mr. A. J. Tuckerman and Mr. Keller. Research assistance of very high caliber was provided by Mr. Raymond E. Lawrence and Mrs. Deborah Smythe.

This report was submitted by the authors in March, 1973.

ABSTRACT

Two systems were evaluated as adhesives which cure via addition reactions. These were (1) nitrile substituted polyphenyl ethers cured with terephthalonitrile N, N-dioxide (TPNO) and (2) acetylene terminated polyimide (HR600) cured thermally. The thermally cured acetylene terminated polyimide proved to be superior to the TPNO cured cyano substituted polyphenylene oxide. Lap-shear strengths of 6Al4V titanium bonded with HR600 adhesive exceeded 3000 psi at ambient temperature on powdered aluminum-filled specimens reinforced with heat cleaned 112 glass fabric and 2800 psi at ambient temperature, 2600 psi at 450°F and 2100 psi at 500°F on unfilled specimens bonded with 70 percent HR600 prepreg on 112 heat-cleaned glass fabric. Weld-bonding of titanium specimens using aluminum powder filled HR600 adhesive proved to be successful and showed superior fatigue resistance over spot-welded specimens.

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I. INTRODUCTION

The coming generation of supersonic aircraft will require structural adhesives capable of withstanding extended use in the 450-600°F temperature range. Such adhesives can be prepared only from polymers with aromatic structures. Most conventional aromatic polymers, however, are cured by condensation processes which produce volatile by-products. These volatiles tend to expel adhesive from the bond during cure, leaving voids in the adhesive, and thus impairing the strength of the bond.

A number of molecular features are required of a high temperature structural adhesive. For high cohesive strength, a high molecular weight crosslinked polymer is necessary, since forces of attraction between covalently bonded atoms are far greater than those between adjacent molecules. The chemical makeup of the polymer must be such that it consists of units having known resistance to bond rupture under extreme thermal, oxidative and hydrolytic conditions. The backbone of the polymer should contain structural units which prevent excess rigidity, so that stresses due to change in temperature are not created.

For optimum adhesive strength, the adhesive must have adequate fluidity prior to cure to provide for a low contact angle (good surface wetting) with the substrate, in addition to good flow properties for use with fillers and carrier cloths. Cure reactions involving strictly addition processes will, by eliminating volatile cure products, greatly reduce or eliminate formation of both adhesive-adherend interface voids and adhesive-matrix voids during cure. Furthermore, elimination of void formation during cure by utilization of addition type cure processes will greatly enhance hydrolytic stability by retarding entry of water vapor into the polymer matrix.

To meet the above requirements for a high temperature adhesive which cures by addition, two types of adhesive systems have been studied in this program. These are: (1) Cyano- or ethynyl-substituted polyphenylene oxide prepolymers cured with terephthalonitrile N,N'-dioxide(TPNO), (2) Homopolymerizable acetylene-terminated polyimide. Both of these systems cure to resonance-stabilized thermally stable aromatic polymers. Cross-linking reactions occur during high temperature cure in both systems. In addition, both systems feature aromatic ether units in the prepolymers and in the subsequently formed polymer matrix to lend a degree of flexibility and toughness to the polymeric adhesive.

Early in 1971 under AFML contract, Hughes Aircraft Company began the development of thermally stable adhesives that could be cured at readily attainable temperatures by addition reactions which liberated no gaseous by-products. The materials investigated were nitrile-substituted or nitrile-terminated polyphenylene oxides and nitrile-terminated polyimide oligomers containing terephthalonitrile N,N'-dioxide as a curing agent. Adhesive compositions were found that could be cured by heating to 80°C (176°F) without producing significant quantities of gaseous by-products. Titanium lap-shear specimens bonded with an adhesive of this type under a pressure of 15 psi had tensile strengths up to 2500 psi at 450°F. Thus, the adhesive was demonstrated to have considerable potential for meeting the stated objectives.

In a continuation of work on addition cured laminating resins, the discovery was made at Hughes that a difunctional acetylene substituted polyimide oligomer readily cured to an intractable polymeric resin at temperatures slightly above its melting point. This material, which has been designated as HR600, showed great success as a laminating resin in the preparation of glass fiber and graphite reinforced composites.

The extension of this technology to the application of HR600 as a thermally curing adhesive for titanium substrates was attempted and found to be successful, and effort was expended on the program to develop an adhesive system, based upon thermally curing HR600, for bonding of titanium.

The adhesive strengths of this polymer displayed a dependency upon the method of imidization of the amic acid precursor. Two methods of imidization have been utilized. These are: (1) refluxing in acetic anhydride and (2) refluxing in a cresol-benzene mixture. The imidized oligomers from these two methods of imidization were designated, respectively, HR 600A and HR 600C. Lap shear studies showed that a mixture of HR 600A and HR 600C was a superior adhesive to either of these alone.

Further development work on this adhesive system was necessary. The required studies included a study of fillers and carrier cloths, preparation of glass cloth prepreg adhesives, optimization of cure cycles, and a study of the use of this adhesive for titanium weldbonding applications. These studies were carried out during the past year.

II. SUMMARY

The work performed on high temperature adhesives during the past year is a continuation of the adhesive study previously combined with the development of high temperature laminating resins under Air Force Contract Number F33615-71-C-1228 entitled "Development of High Temperature Laminating Resins and Adhesives Which Cure Through Addition." The adhesive study part of this program subsequently was continued under Air Force Contract Number F33615-73-C-5062. The studies reported here are a continuation of those reported in the previous summary report, AFML-TR-72-57, Part II, June 1973.

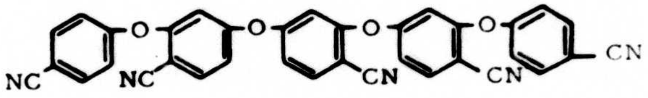
Two resin systems were examined as addition cured adhesives for titanium during the course of this program. The studies on nitrile substituted polyphenylene oxide cured with terephthalonitrile N,N'-dioxide were directed toward experiments on fillers, carrier cloths and thermal aging. Attempted preparation of a reactive diluent to replace the inert solvent xylene used in the adhesive formulation was not entirely successful due to difficulties encountered in purification of products.

Studies on TPNO cured polynitrile substituted polyphenylene oxide adhesives containing xylene in the adhesive formulation were discontinued at the request of the AFML project monitor. Developmental research on the Hughes developed acetylene terminated polyimide, designated as HR 600, as a high temperature adhesive was emphasized. Adhesive formulations containing glass carrier cloth and aluminum powder filler gave ambient temperature strengths in excess of 3000 psi. Glass carrier cloth impregnated with a N-methylpyrrolidinone solution of the polyimide served as an excellent prepreg adhesive. With an optimum cure cycle, adhesive lap shear strength in excess of 2800 psi at ambient, 2600 psi at 450°F and 2000 psi at 500°F were observed in the absence of fillers. Weldbond studies were made and preliminary S/N (fatigue) tests showed superior fatigue resistance of weld-bonded specimens over spotwelded specimens. Adhesive and weldbond studies with this thermally cured acetylene terminated polyimide are currently being extended under a continuation of Air Force Contract F33615-73-C-5062.

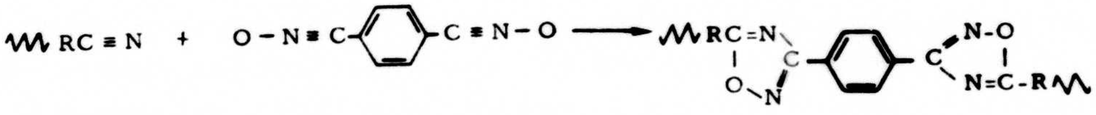
III. CYANO SUBSTITUTED POLYPHENYLENE OXIDE ADHESIVES CURED WITH TEREPHTHALONITRILE N,N'-DIOXIDE

A. BACKGROUND

Cyano substituted polyphenylene oxide prepolymer I was synthesized and research on its use as an adhesive was continued. The cure reaction involves the 1,3-cycloaddition of the cyano groups to terephthalonitrile N,N'-dioxide(TPNO)II to yield the resonance-stabilized oxadiazole derivative III.



I



II

III

Polymerization by reaction of the polycyano derivative I with the difunctional nitrile oxide II to yield a highly crosslinked polymer matrix having a structure comprised of stable aromatic segments showed promise as a basis for a cure process for an adhesive system having good thermal, oxidative and hydrolytic stability.

Our early experiments with mixtures of solid oligomer I and TPNO II demonstrated that they reacted with such vigor that the mixture could be expelled from the container. In addition, the fact that both I and II are solids made it necessary to use a solvent to provide the necessary flow and wetting characteristics for the adhesive in contact with the titanium substrate. The vehicle chosen for this purpose was xylene, due to the fact that it is an excellent solvent for the cyano-substituted polyphenylene oxide I and it has a boiling point substantially higher than the initial cure temperature of 80°C.

Thus, a low temperature curing, low void adhesive was formulated from I, II and xylene in the relative weight ratio 1:1:0.7. Initial cure was at 80°C (176°F), followed by postcure at 160°C (320°F) and 260°C (500°F). This adhesive system has been extensively tested for bonding 6Al4V titanium alloy.

Experiments performed on previous programs indicated that a 1:1:0.7 weight ratio of oligomer:TPNO:xylene was close to the optimum. Smaller amounts of xylene appeared to diminish the ability of the adhesive to wet the metal. Although the xylene remains dissolved in the adhesive during cure and did not cause channeling, it was desirable to reduce or eliminate the xylene so that a denser and stronger adhesive bond would be obtained. Microscopic voids are left in the adhesive after the xylene diffuses out during postcure, and the strength of the adhesive is adversely affected.

Thus, in order to improve the utility and reliability of the polycyano-substituted polyphenylene oxide adhesive system, it appeared necessary to replace the xylene with a reactive diluent, i.e., one which serves as a solvent for the prepolymer and which participates in the cure process by becoming an integral portion of the final polymeric matrix after postcure. Synthesis of one possible reactive diluent, 4,4'-diethynyl diphenyl ether, was attempted.

Preliminary studies on the use of fillers and carrier cloths had been made on the previous program and continuation of this effort was required. Thermal aging tests were also necessary and this additional work has since been carried out and is reported herein.

B. EFFECT OF CARRIER CLOTH ON LAP SHEAR STRENGTH

In order to determine the optimum carrier cloth for bonding of titanium substrates with cyano substituted polyphenylene oxide-TPNO copolymer, a study was made of the effect of carrier cloth on lap shear strengths. In all cases, the adhesive contained aluminum powder. As expected, the best of three carrier fabrics tried was 112E heat cleaned glass fabric. The results of these lap-shear tests are shown in Table I.

TABLE I. EFFECT OF CARRIER CLOTH UPON LAP-SHEAR STRENGTH OF TITANIUM SAMPLES BONDED WITH ALUMINUM-FILLED CYANO-SUBSTITUTED POLYPHENYLENE OXIDE TPNO COPOLYMER (1)

Specimen	Adhesive Thickness, in. x 10^3 (mils)	Test Temperature, °F	Carrier Cloth (2)	Lap-Shear Strength (k psi)	Average Lap-Shear Strength (k psi)
HR 52C 1	20	Ambient	a	1.3	1.4
2	16			1.4	
3	12			1.8	
4	20			1.1	
5	17			1.3	
HR 52C 6	17	450°F	a	1.0	1.2
7	16			1.5	
8	19			1.3	
9	18			1.1	
10	16			1.3	
HR 60A 1	14	Ambient	b	1.8	2.0
2	9			2.2	
3	7			2.1	
4	8			2.1	
5	15			1.8	

(Continued next page)

(Table I, concluded)

Specimen	Adhesive Thickness, in. x 10^3 (mils)	Test Temperature, ^{o}F	Carrier Cloth (2)	Lap-Shear Strength (k psi)	Average Lap-Shear Strength (k psi)
HR 60A 6	15	450°F	b	1.7	2.0
7	12			2.0	
8	10			2.3	
9	11			1.9	
10	9			2.0	
HR 60B 1	18	Ambient	c	1.6	1.5
2	20			1.5	
3	21			1.3	
4	17			1.7	
5	17			1.6	
HR 60B 6	14	450°F	c	1.6	1.4
7	19			1.0	
8	19			1.4	
9	15			1.2	
10	15			1.6	

(1) Cyano substituted polyphenylene oxide: TPNO: Xylene = 1:1:0.7 (wt. ratio)

(2) Carrier Cloth (a) 194/A1100 Glass Fabric. (b) 112E heat cleaned glass fabric. (c) 112E Volan A cleaned glass fabric.

C. THERMAL AGING TESTS

Thermal aging tests on TPNO cured cyano substituted polyphenylene oxide adhesive (CSPPO) have been completed. The tests were conducted at ambient, 450°F and 500°F, in 100 hour increments from 0 to 500 hours. All specimens were reinforced with glass cloth. The specimens represented by Figures 1 and 2 were reinforced with 904 scrim and aging was conducted with both filled and unfilled specimens. The filled specimens contained about 38% by weight of 325 mesh aluminum powder. All of these specimens appeared to

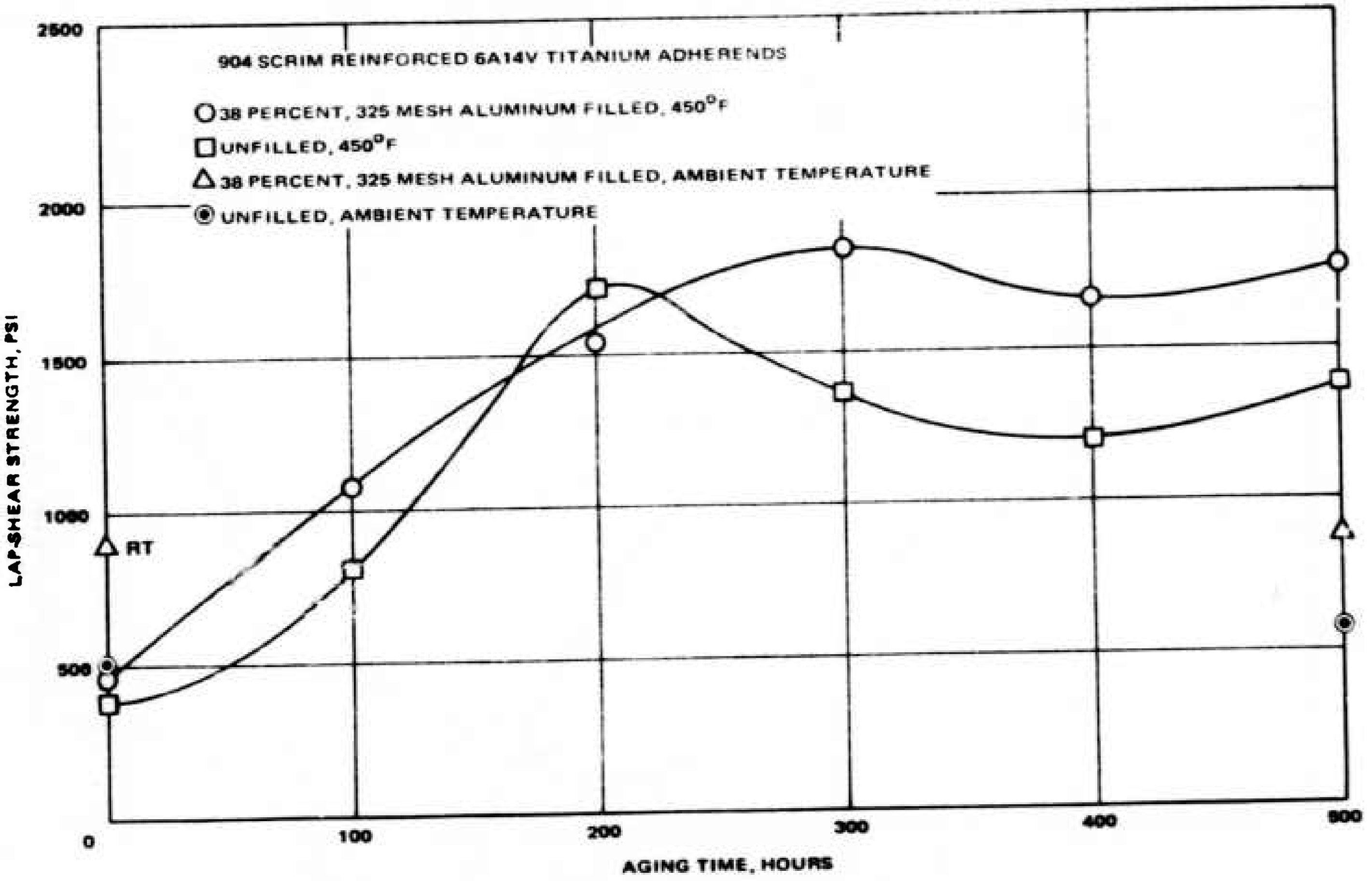


Figure 1. Lap Shear Strengths of Cyano Substituted Polyphenylene Oxide/TPNO Adhesive at 450°F

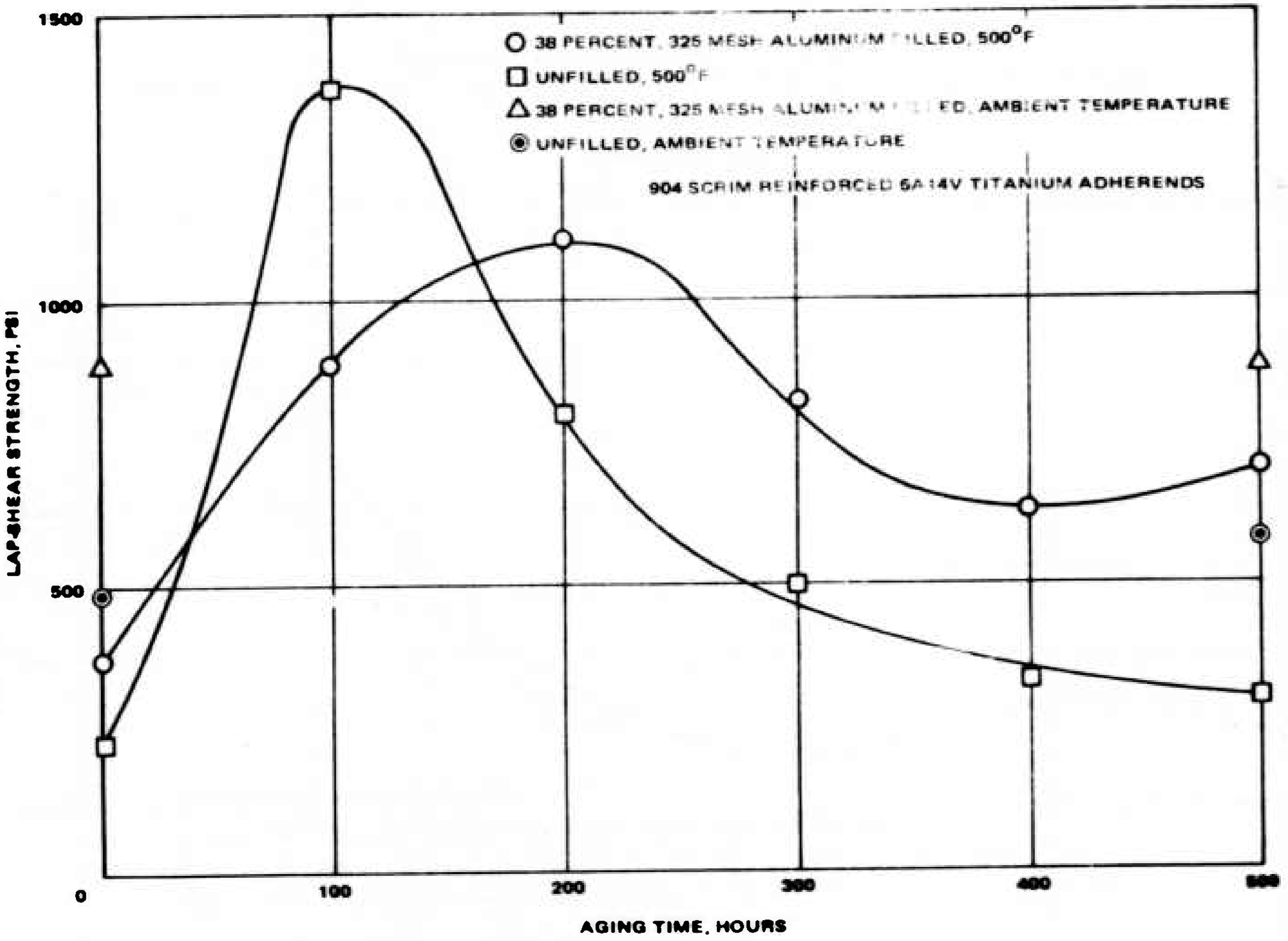


Figure 2. Lap Shear Strengths of Cyano Substituted Polyphenylene Oxide/TPNO Adhesive at 500°F

experience a gradual postcure over about the first 200 hours of thermal aging. As observed previously, 450°F appears to be the optimum temperature for continous use of this adhesive. A loss of about 60% in strength is observed in aging tests at 500°F compared to those at 450°F. Filled and unfilled specimens aged for 500 hours and tested at ambient temperature remained unchanged in strength.

The specimens represented by Figures 3 and 4 were reinforced with 112E heat cleaned glass cloth. Aluminum filler levels (325 mesh aluminum) studied were 0% (Figure 3), 25% (Figure 4) and 50% (Figure 5).

In contrast with the samples reinforced with 904 scrim, the strengths observed during aging in specimens reinforced with 112E cleaned glass cloth were somewhat more uniform. In general, it appears that lap-shear strengths at 450°F are somewhat enhanced after aging for 500 hours. At 500°F, there appears to be a slight drop in lap-shear strength. Figures 6 and 7 illustrate the effect of aluminum filler level on lap-shear strength in reinforced specimens aged at 450°F and 500°F, respectively.

It is clear from these figures that 25 weight percent aluminum powder approaches the optimum level for achieving highest heat resistance. This is particularly true on long time aging.

The absolute values of Figures 1 through 7 are not high. They do however, illustrate the unusual stability of this class of polyimide on temperature aging at temperatures up to 500°F, and particularly at 450°F, where the strength actually increases after 500 hours.

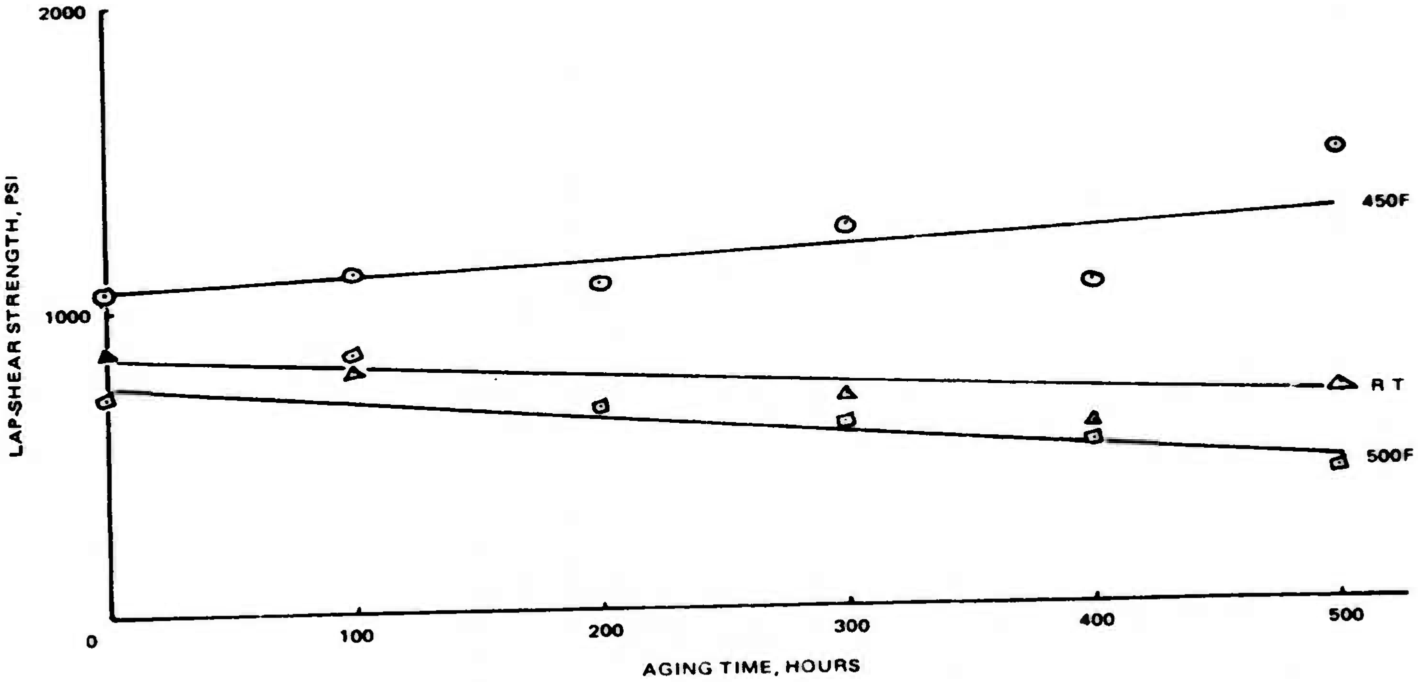


Figure 3. Lap Shear Properties, CSPPO/TPNO Polymer, Titanium Adherend, Unfilled Resin, Heat-cleaned 112E Glass Cloth Reinforced

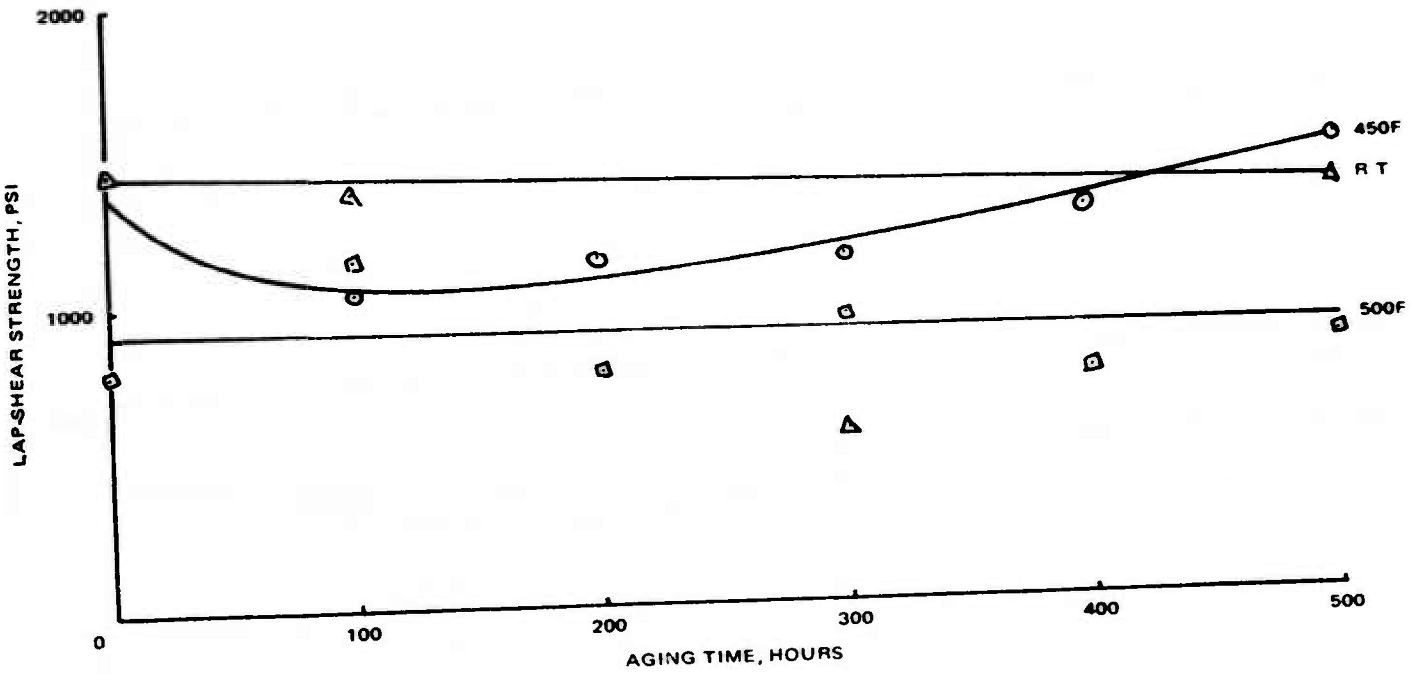


Figure 4. Lap Shear Properties, CSPPO/TPNO Polymer, Titanium Adherend, 25 Weight % Aluminum Powder Filled, Heat-cleaned 112E Glass Cloth Reinforced

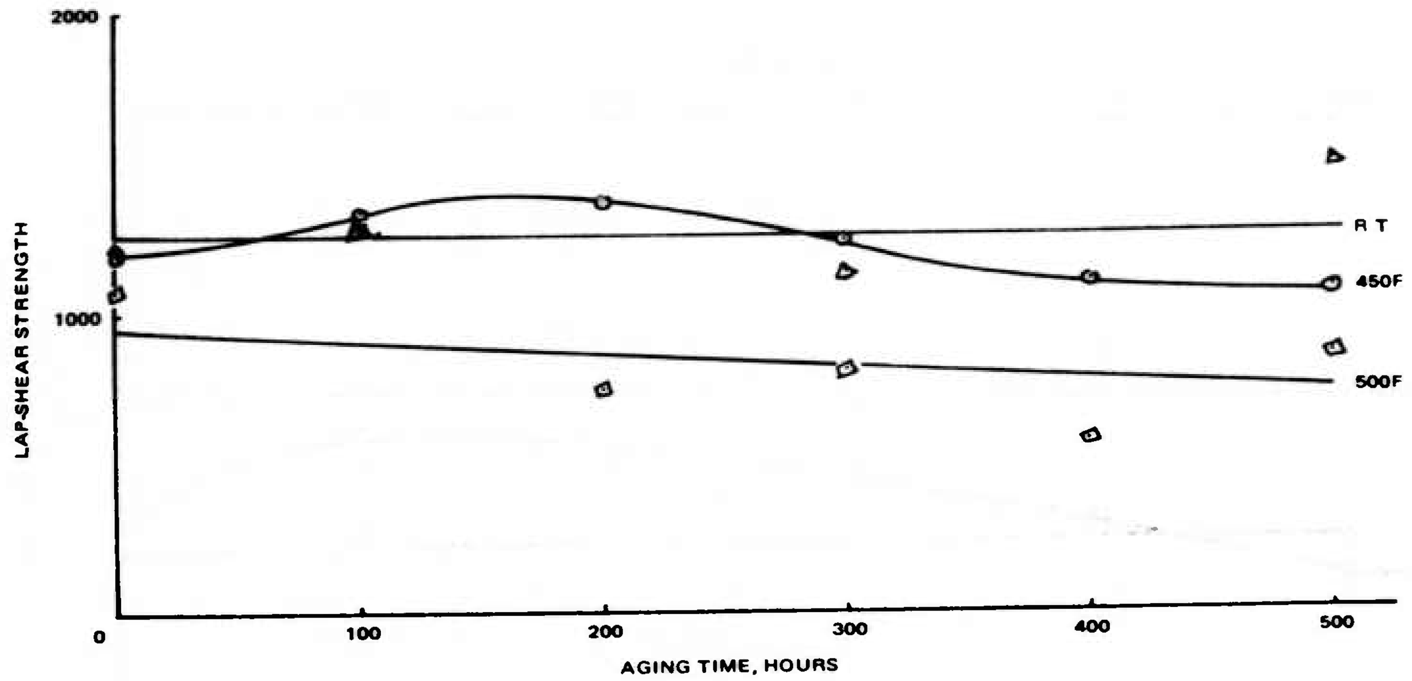


Figure 5. Lap Shear Properties, CSPPO/TPNO Polymer, Titanium Adherend, 50 Weight % Aluminum Powder Filled, Heat-cleaned 112E Glass Cloth Reinforced

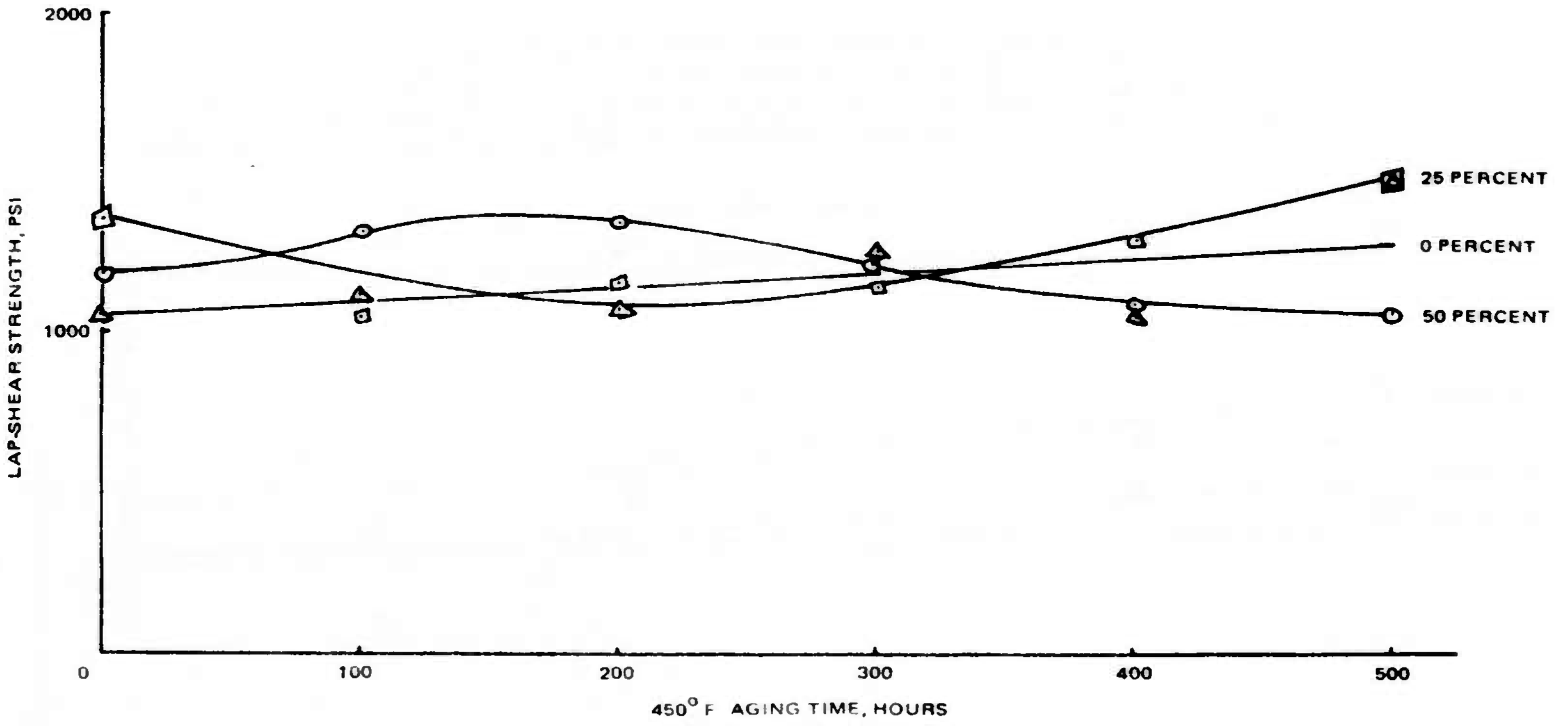


Figure 6. Lap Shear Strength of CSPPO/TPNO Bonded Titanium Adherends as a Function of Aging at 450°F. 0-50 Weight % Aluminum Powder Filled, Heat-Cleaned 112E Glass Cloth Reinforced, Aged and Tested at 450°F

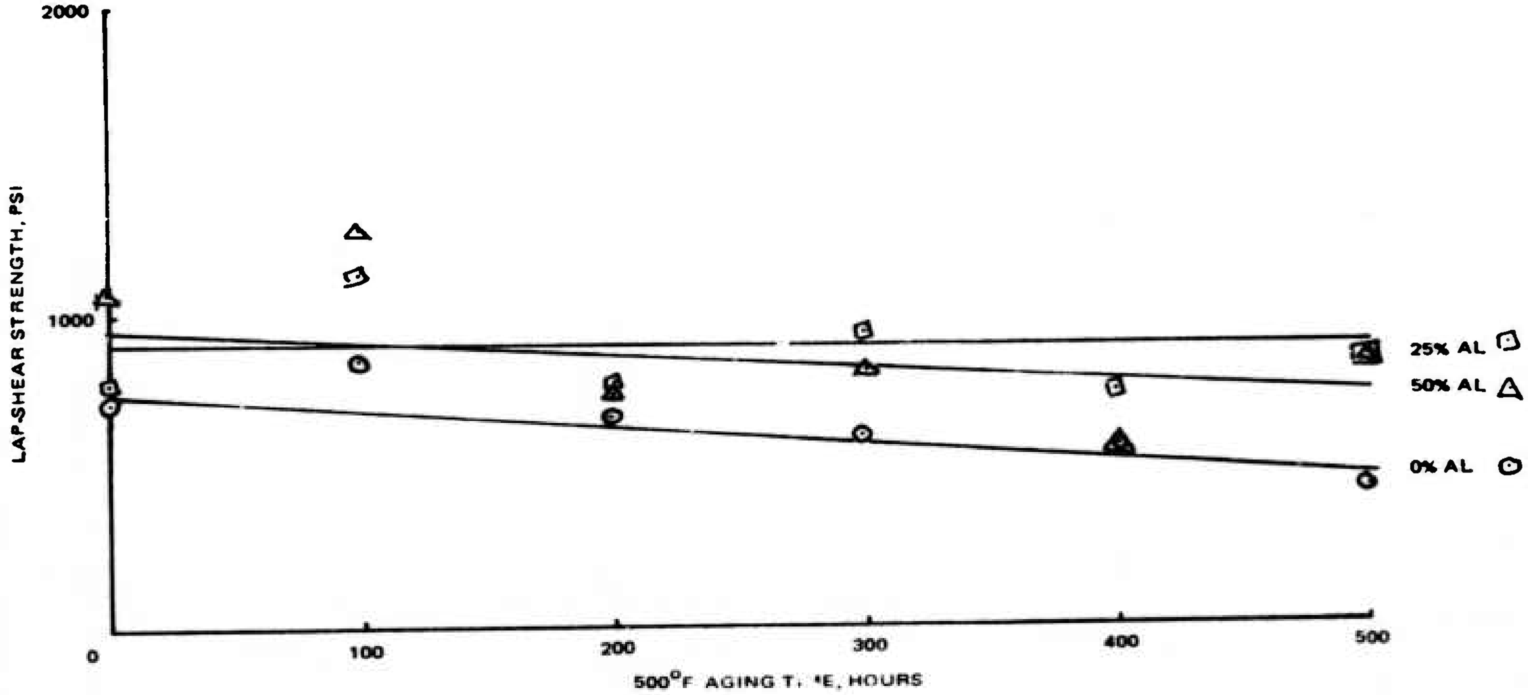


Figure 7. Lap Shear Strength of CSPPO/TPNO Bonded Titanium Adherends as a Function of Aging at 500°F. 0-50 Weight % Aluminum Powder Filled, Heat-Cleaned 112E Glass Cloth Reinforced, Aged and Tested at 500°F

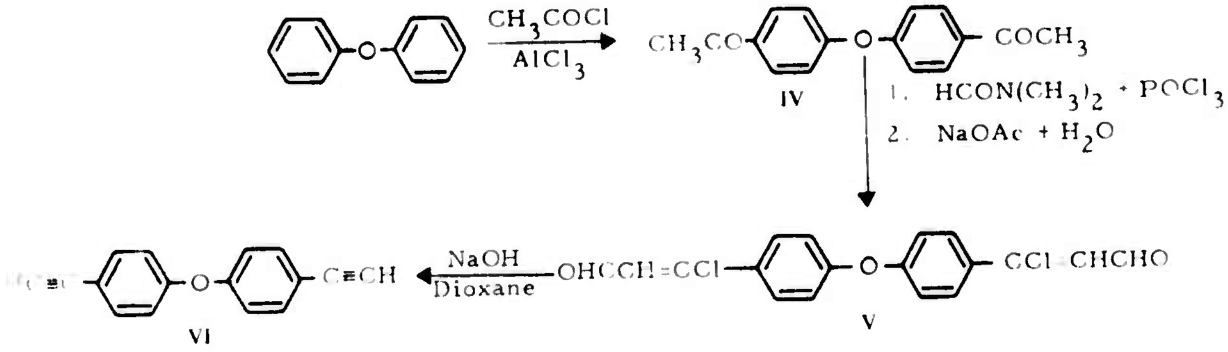
D. SYNTHESES OF REACTIVE DILUENTS

The strength and reliability of the TPNO cured cyano substituted polyphenylene oxide adhesives are severely limited by the fact that a volatile vehicle, i.e., xylene, is used in the adhesive formulation. While a low cure temperature, 80°C (176°F), is applicable in this system, the inert solvent may be responsible for the erratic lap shear strengths, possibly due to porous glue lines created when the solvent is driven off during postcure.

In an attempt to alleviate this difficulty, the synthesis of a reactive diluent to replace the xylene has been attempted. Its function would be to provide a solvent for the cyano substituted polyphenylene oxide oligomer so that adequate fluidity could be maintained in the monomeric state, allowing the adhesive to flow readily and adequately wet the adherends. In the cure process, this reactive diluent would then become part of the polymeric adhesive matrix, and no volatiles would be evolved during cure or postcure.

With these objectives in mind, the synthesis of the difunctional acetylenic monomer, 4,4'-diethynyl diphenyl ether VI, was undertaken. It was felt that, in addition to functioning as a reactive diluent for the cyano substituted polyphenylene oxide oligomer, VI might also be effective as a reactive diluent for the acetylene substituted polyimide discussed in Section IV of this report.

The synthesis of 4,4'-diethynyl diphenyl ether VI has been carried out as follows:



The infrared spectrum of the final product, 4,4'-diethynyl diphenyl ether, showing the C ≡ CH and C ≡ C stretching vibrations at 3300 cm^{-1} and 2110 cm^{-1} respectively, is consistent with the expected structure. However, considerable difficulty was encountered in the purification of the bis chloroacrolein derivative V and of the final acetylenic ether VI. The ether was never obtained in sufficiently high purity to warrant its evaluation, and inasmuch as work on the cyano substituted polyphenylene oxide adhesive system was discontinued, this effort has not been pursued further.

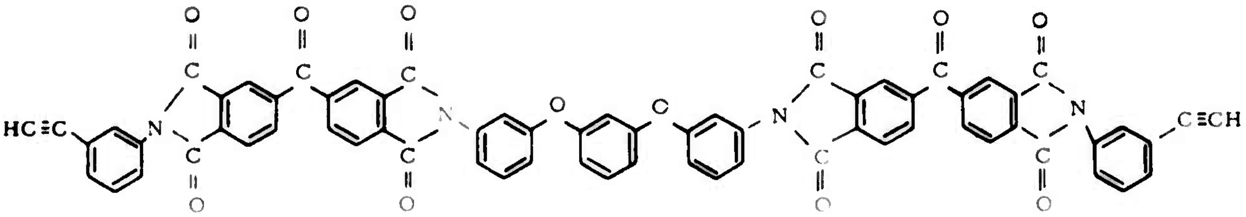
E. DISCONTINUATION OF WORK

Studies on the TPNO cured cyano substituted polyphenylene oxide adhesive system have resulted in adhesive compositions that could be cured at 80°C without producing significant quantities of gaseous by-products and in tensile shear strengths as high as 2500 psi at 450°F for titanium lap-shear specimens. However, there have been certain drawbacks to the TPNO cured cyano substituted polyphenylene oxide system. In addition to the problem of using xylene, certain difficulties are inherent in the use of the TPNO curing agent. These are the formation of homopolymer and insolubility of the monomer. For these reasons the AFML Project Monitor requested that the study of the TPNO cured substituted polyphenylene oxide adhesive be discontinued.

IV. THERMALLY CURED ACETYLENE TERMINATED POLYIMIDE ADHESIVES

A. BACKGROUND

The successful use of homopolymerizable acetylene-terminated polyimide VII, designated as HR 600, as a laminating resin in the preparation of glass cloth and graphite reinforced laminates led to the speculation that VII would function as a one-component adhesive for 6A14V titanium. As with the cyano-substituted polyphenylene oxide, adhesive tests using VII as an adhesive have been made at ambient and elevated temperatures and formulation studies were carried out with fillers and carrier cloths. Results of these tests have been sufficiently promising to justify a major emphasis being placed on the acetylenic polyimides and the de-emphasis of the cyano substituted polyphenyl ether/TPNO system.



VII

Two methods of imidization have been utilized in the synthesis of the acetylene terminated polyimide prepolymer. They differed in that a cresol-benzene mixture was used as a solvent in one case, whereas acetic anhydride was used in the other. Lap shear tests, using 1:1 mixtures of cresol-imidized (HR 600C) and acetic anhydride-imidized (HR 600A) oligomer, showed superior ambient temperature strength to that of mixtures containing predominantly acetic anhydride imidized material, where ambient temperature lap shear strengths in excess of 3000 psi were observed.

B. LAP SHEAR STRENGTHS OF ACETIC ANHYDRIDE AND CRESOL IMIDIZED POLYIMIDE

Lap-shear strengths have been measured with titanium adherends using varying mixtures of the acetic anhydride-imidized and cresol-imidized acetylene-terminated polyimide adhesive. Aluminum powder, 325 mesh, was used as the filler and heat cleaned 112E glass cloth was used as the reinforcement. From these results, it is clear that the method of imidization has a pronounced effect upon the lap-shear strength. The results of these tests are shown in Table II.

The results of these tests are illustrated graphically in Figure 8.

Figure 8 shows the lap shear strengths of titanium specimens bonded with mixtures of acetic-anhydride-imidized and cresol-imidized HR 600 reinforced with heat cleaned 112E glass fabric. The dramatic effect of using acetic anhydride imidized over cresol imidized HR 600 at ambient temperature is evident (Figure 8, Curve A). Also evident from Figure 8 is the fact that the lap shear strengths of these samples at 450°F show very little dependence upon method of imidization (Figure 8, Curve B). Note that these results contrast with those obtained at ambient temperature.

TABLE II. LAP-SHEAR STRENGTHS OF TITANIUM SPECIMENS BONDED WITH MIXTURES OF ACETIC ANHYDRIDE-IMIDIZED POLYIMIDE AND CRESOL-IMIDIZED POLYIMIDE.①

Specimen	Adhesive Thickness in. x 10^3 (mils)	Test Temperatures °F	Ratio a/b	Lap-Shear Strength (k psi)	Average Lap-Shear Strength (k psi)
HR 63 A1	6	Ambient	∞	3.1	3.1
2	6			3.1	
3	6			3.1	
4	7			2.7	
5	6			3.3	
HR 63 6	7	450°F	∞	1.1	1.2
7	6			1.2	
8	6			1.2	
9	7			1.6	
10	6			1.1	
HR 63 B1	7	Ambient	3/1	3.2	3.1
2	6			2.6	
3	8			2.9	
4	7			3.5	
5	7			3.1	
HR 63 B6	7	450°F	3/1	0.9	1.3
7	7			1.3	
8	7			1.5	
9	8			1.1	
10	7			1.5	
HR 63 C1	9	Ambient	1/1	2.2	2.2
2	10			2.3	
3	7			1.9	
4	8			2.2	
5	7			2.3	
C6	10	450°F	1/1	1.4	1.5
7	12			1.2	
8	15			1.5	
9	10			1.6	
10	12			1.9	

(Continued next page)

(Table II, concluded)

Specimen	Adhesive Thickness in. x 10^3 (mils)	Test Temperature °F	Ratio a/b ②	Lap-Shear Strength (k psi)	Average Lap-Shear Strength (k psi)
HR 63 D1	10	Ambient	1/3	2.0	2.2
2	8			2.1	
3	7			2.0	
4	10			2.5	
5	9			2.5	
D6	8	450°F	1/3	2.6	2.2
7	10			2.2	
8	12			1.8	
9	8			2.3	
10	10			2.2	
HR 63 E1	7	Ambient	0	1.5	1.4
2	5			0.9	
3	5			1.7	
4	6			1.8	
5	6			1.2	
HR 63 E6	6	450°F	0	0.6	1.1
7	7			1.0	
8	5			1.0	
9	6			0.9	
10	6			1.8	

Footnotes:

① The adhesive used for bonding these specimens contained 50% aluminum powder, 325 mesh. Reinforcement was provided by use of 112E heat cleaned fabric. After joining the specimens, the adhesive was cured 4 hours at 500°F.

② (a) - Acetic-anhydride-imidized acetylene terminated polyimide.

(b) - Cresol-imidized acetylene terminated polyimide.

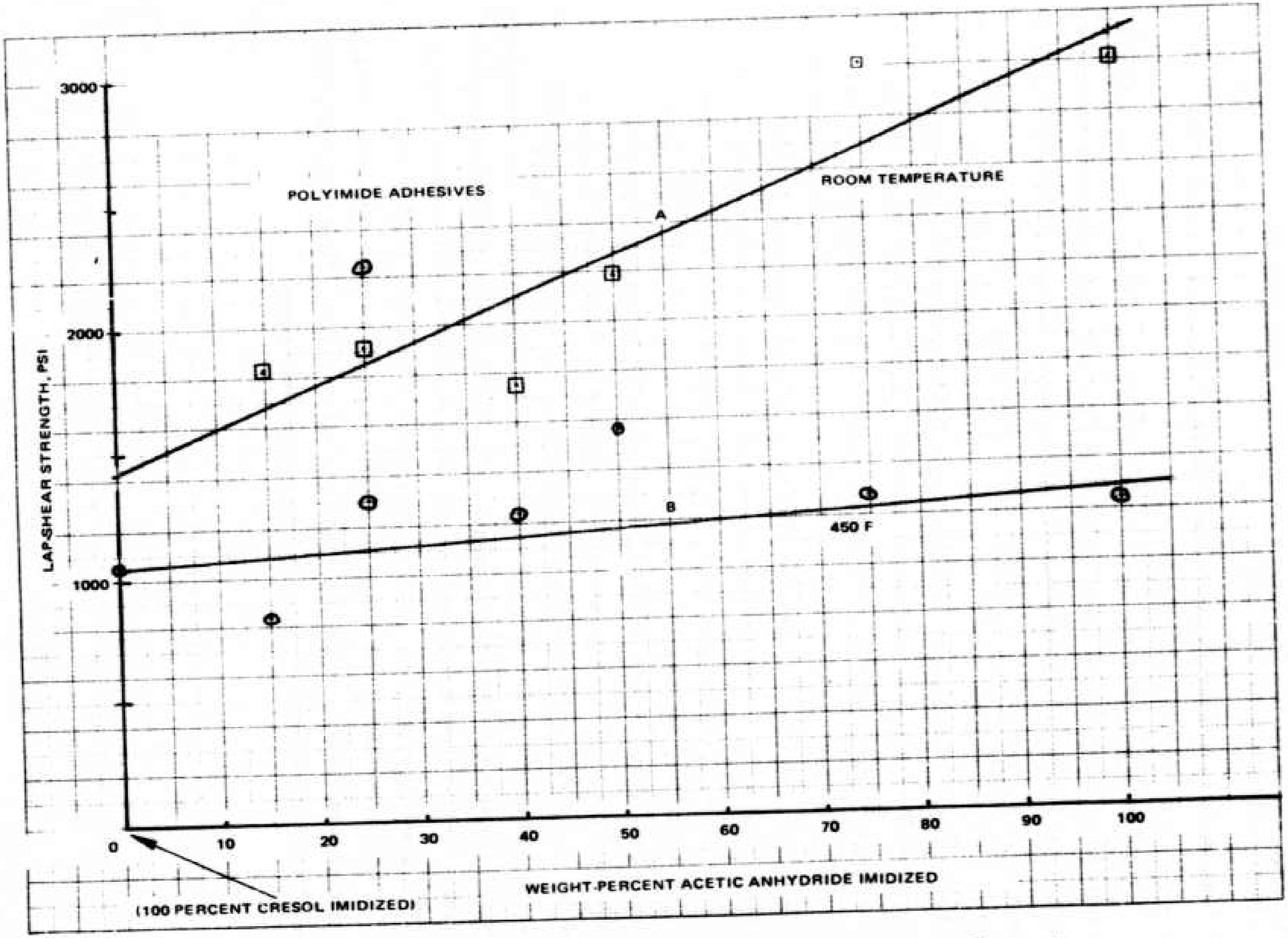


Figure 8. Influence of Imidization Method on Lap-shear Strength, 50 Weight % 325 Mesh Aluminum Filled, Heat-cleaned 112E Glass Cloth on Titanium Coupons

C. EFFECTS OF ALUMINUM FILLER LEVEL AND PRIMING UPON LAP SHEAR STRENGTH

Studies were made to show the effects of variation of aluminum filler level and of priming upon lap shear strength.

Figures 9 and 10 show the effect of aluminum filler level and priming upon lap shear strengths of titanium samples bonded with polyimide adhesive and reinforced with 112E heat cleaned glass cloth. The lap shear tests represented in Figure 9 were run at ambient temperature, while those in Figure 10 were run at 450°F. The specimens were primed by application of a 10% dimethylfomamide lacquer of the acetylene-terminated polyimide to the specimen, followed by removal of the solvent in a vacuum oven at 350°F. At ambient temperature, the lap shear strengths of unprimed specimens bonded with 50% acetic anhydride-imidized acetylene-terminated polyimide are nearly the same for 0, 25% and 50% by weight of aluminum powder (Curve A, Figure 9(. By comparison, in the primed specimens a definite drop in lap shear strength was noted for the same bonding conditions with increased aluminum powder filler level (Curve B, Figure 9). Samples containing 75% acetic anhydride-imidized polyimide displayed a sharp increase in lap shear strength at the 50% aluminum filler level (Curve C, Figure 9). At 450°F, the primed sample showed increased strength with increasing aluminum filler level (Curves A and B, Figure 10). The unprimed specimens bonded with 50% acetic anhydride-imidized polyimide showed, by contrast, a decreasing strength with increasing aluminum filler-level with a crossover point between 15% and 20% aluminum (Curve C, Figure 10).

It seems evident from these data that, in the elevated temperature lap shear tests, additional curing of the primer takes place. This indicates that a longer cure of the polyimide adhesive may be necessary.

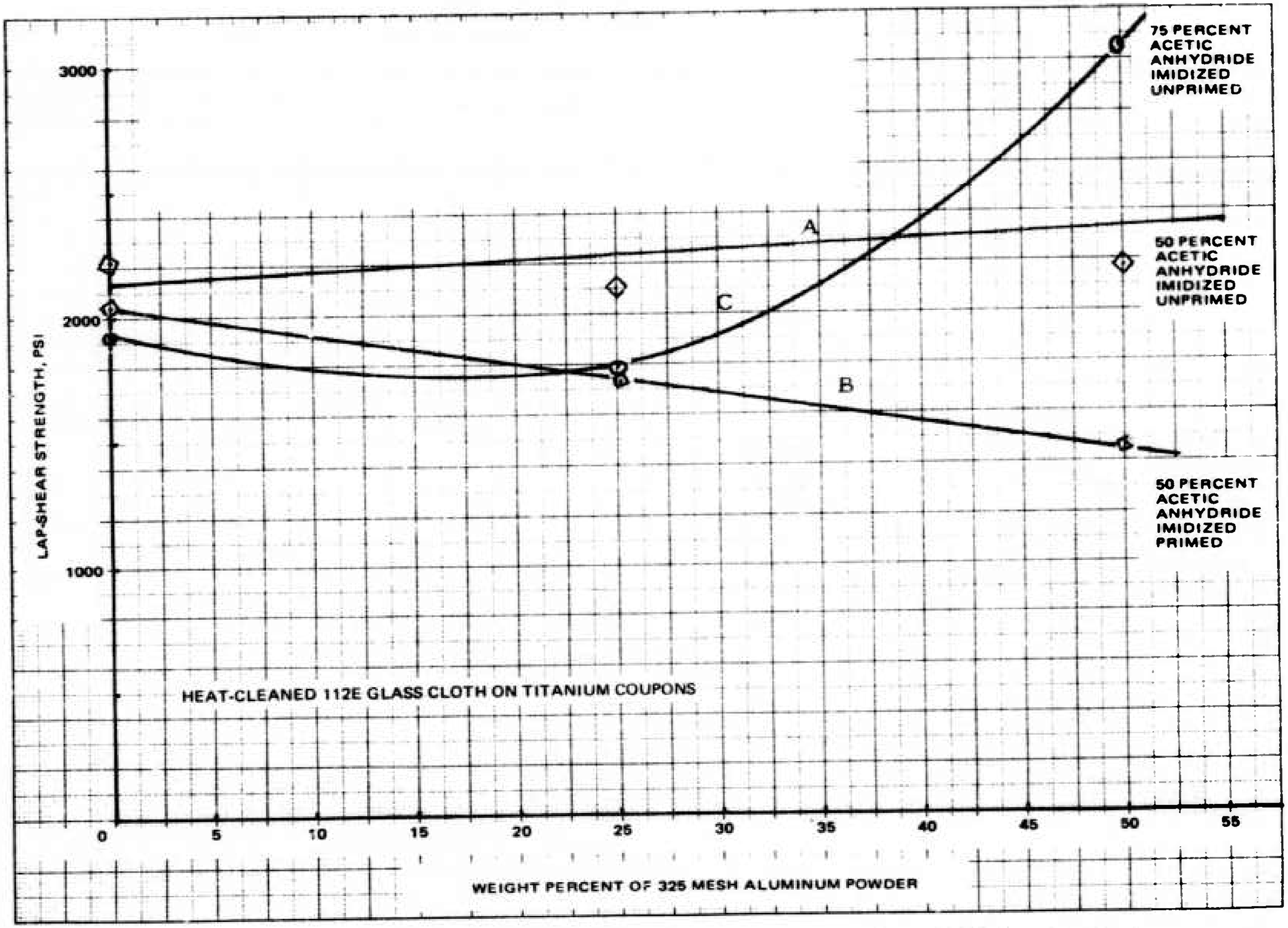


Figure 9. Lap Shear Strengths of HR 600AC as a Function of Filler Content - Ambient Temperature Tests

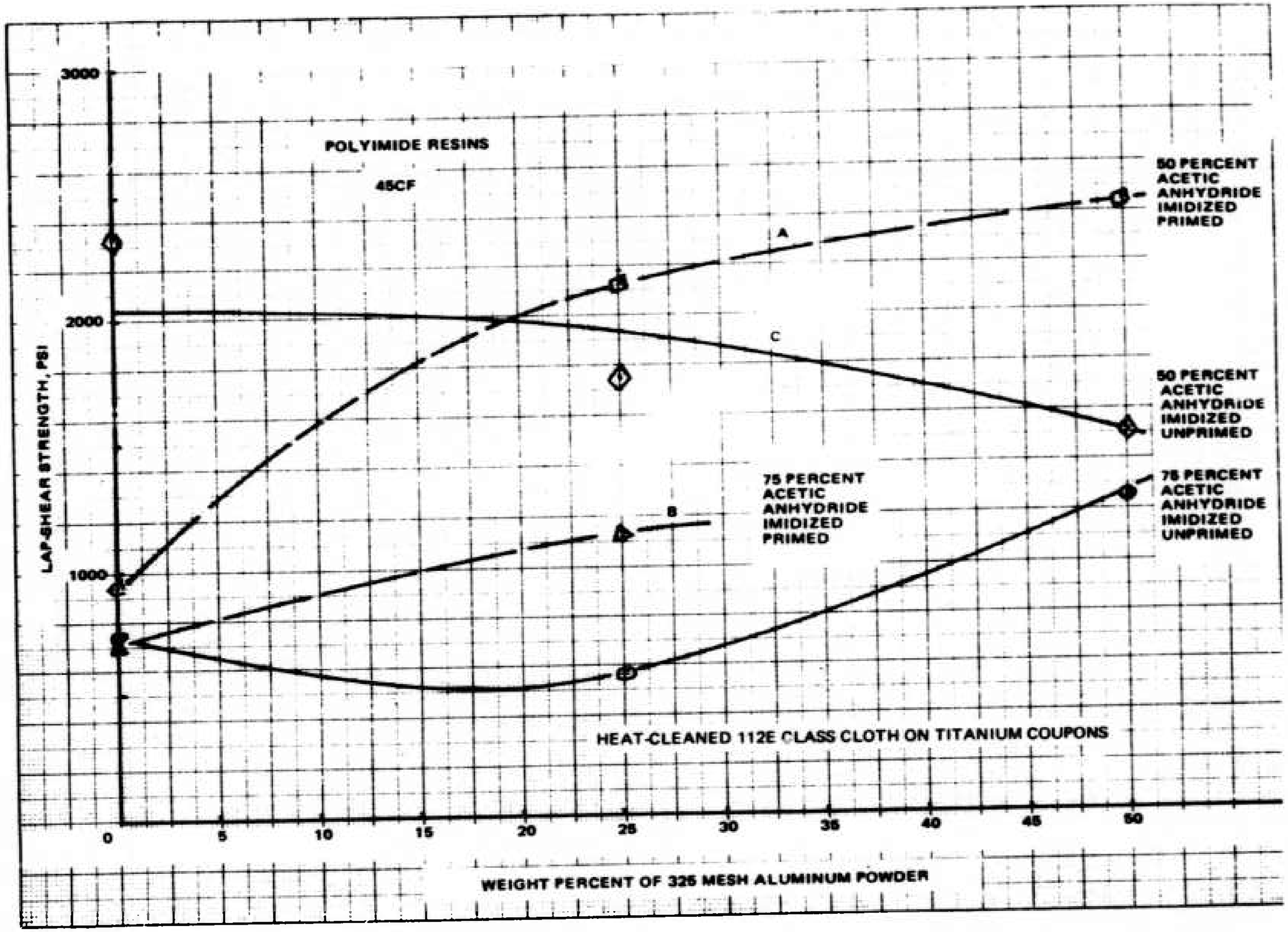


Figure 10. Effect of Filler Content on Lap Shear Strengths of HR 600AC Bonded Titanium-450°F Tests

D. ADHESIVE PREPREG STUDIES

A dimethylformamide solution of HR 600C oligomer was used to impregnate glass fabric. Lap shear strength data using this prepreg were compared with lap shear strength data obtained with powdered adhesive prepared from a 1:1 mixture of HR 600A and HR 600C, using (as reinforcement) heat cleaned 108 Volan A finished glass fabric (108 VHC), heat cleaned 112 Volan A finished glass fabric (112 VHC), and heat cleaned starch-oil finished 112 glass fabric (112 SHC). The results of these lap shear tests are shown in Figure 11. The prepreg was tested at ambient temperature and 450°F and the powder samples were tested at ambient temperature, 260°F and 450°F. The measured strengths at 260°F are represented by the dotted areas in the bar chart in Figure 11.

The data from Figure 11 indicates the following priorities for scrim at both ambient temperature and 260°F: 112 SHC >112 VHC >108 VHC.

At a 450°F test temperature, the prepreg adhesive system shows a clear superiority over specimens prepared from powdered adhesive and tested at the same temperature. This is shown in Figure 11, where the specimens prepared by powdered adhesive techniques have all declined in strength, but the prepreg sample increased slightly in strength.

In our previous work, we found that, in room temperature tests, adhesive formulations containing appreciable amounts of HR 600A resin had superior adhesive strengths over pure HR 600C. Thus, in view of the results with the HR 600C prepreg, a prepreg containing a 1:1 mixture of HR 600A and HR 600C on 112 SHC was prepared. Two prepregs were made, one containing 70 percent oligomer, and one containing 80 percent oligomer. Neither of these prepregs contained filler. The solvent used in preparing the prepregs was N-methylpyrrolidinone. This solvent was chosen because it was shown to be superior to dimethylformamide in the preparation of prepregs with HR600 when used in laminates.

An extensive set of titanium lap shear specimens has been made using these prepregs, with cure temperatures of 500°F, 525°F, 600°F, and 650°F. At the upper two temperatures, 600°F and 650°F, cure times of two hours and four hours were studied. At the 500°F and 525°F temperatures, longer cure times were used.

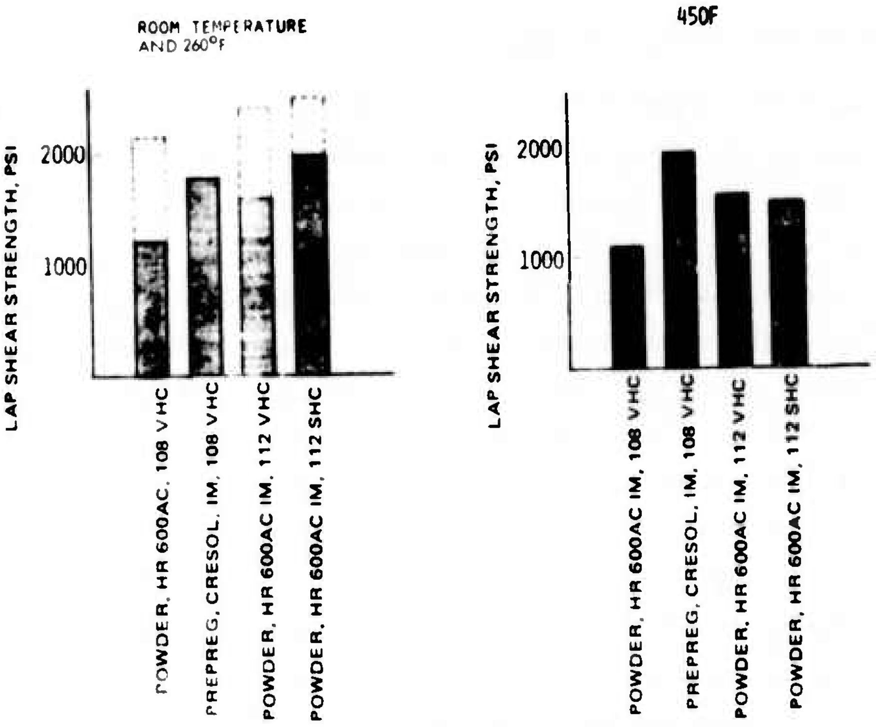


Figure 11. Influence of various parameters on lap shear strength of polyimide adhesive. (cured 4 hours at 500°F.)

The results of these studies are shown in Figures 12 through 22. In Figures 12 and 13 lap shear strengths are shown for samples cured at 500°F for 16, 20, and 24 hours with prepregs containing 70 and 80 percent oligomer.

The spread in the strengths observed with different cure times indicates that a slightly higher cure temperature, such as 525°F, may make strength less dependent upon cure time. The 525°F cure temperature was chosen because this was expected to cause an increase in cure rate without initiating the degradation of adhesive properties. Indeed, the 525°F cure temperature showed considerably less dependence of lap shear strength upon cure time at 450°F and maintained the same upper level of strength as at 500°F. This is illustrated in Figures 14 and 15.

Short cure times may be utilized at higher temperatures without much loss in lap shear strength. This is illustrated in Figures 16 through 19 for cure temperatures of 600° and 650°F and cure times of 2 and 4 hours. At the higher cure temperatures, the data points appear to be closer together, especially at the 450°F test temperature.

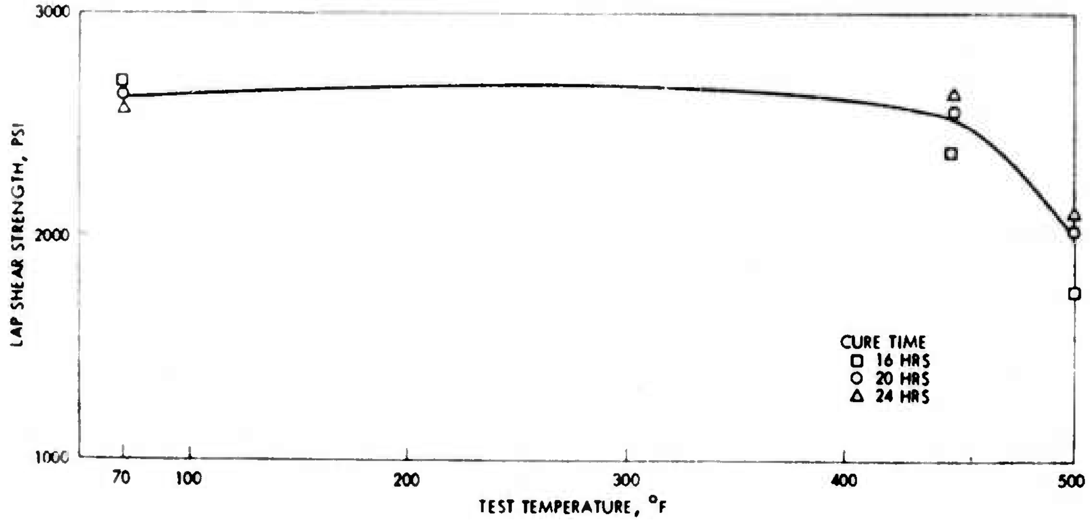


Figure 12. Influence of cure time on ambient and elevated temperature properties of 70 percent HR 600AC prepreg bonded titanium, 500°F cure.

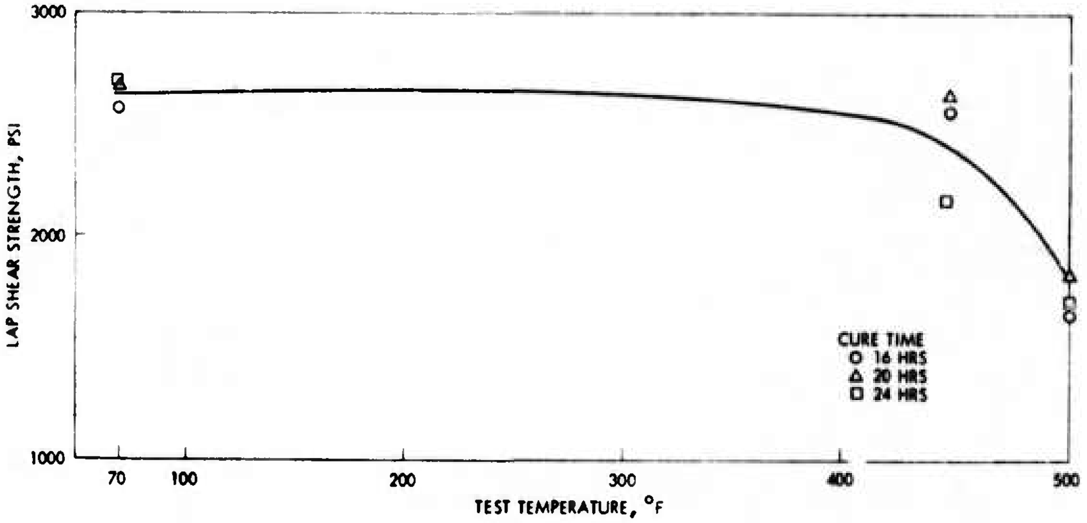


Figure 13. Influence of cure time on ambient and elevated temperature properties of 80 percent HR 600AC prepreg bonded titanium, 500°F cure.

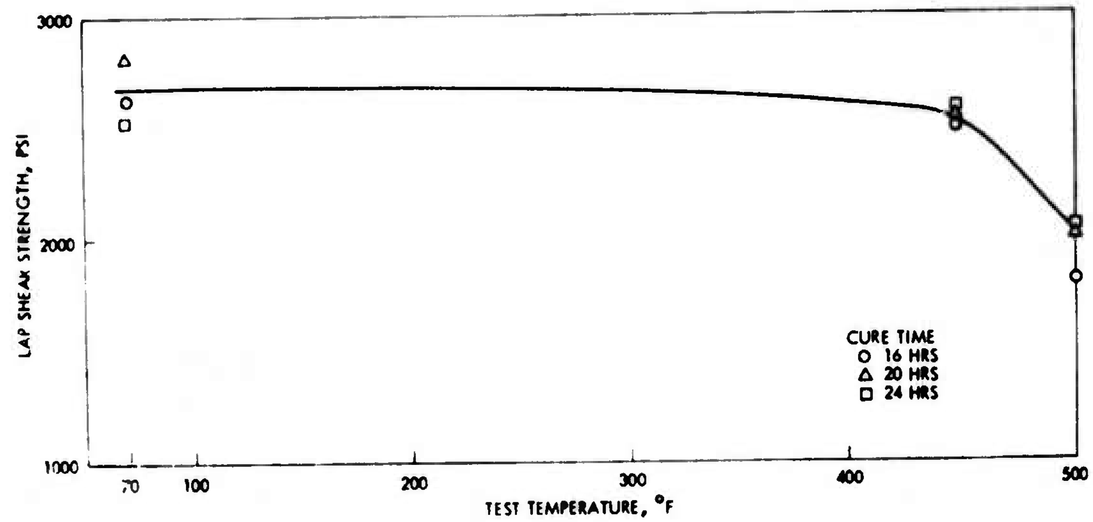


Figure 14. Influence of cure time on ambient and elevated temperature properties of 70 percent HR 600AC prepreg bonded titanium, 525°F cure.

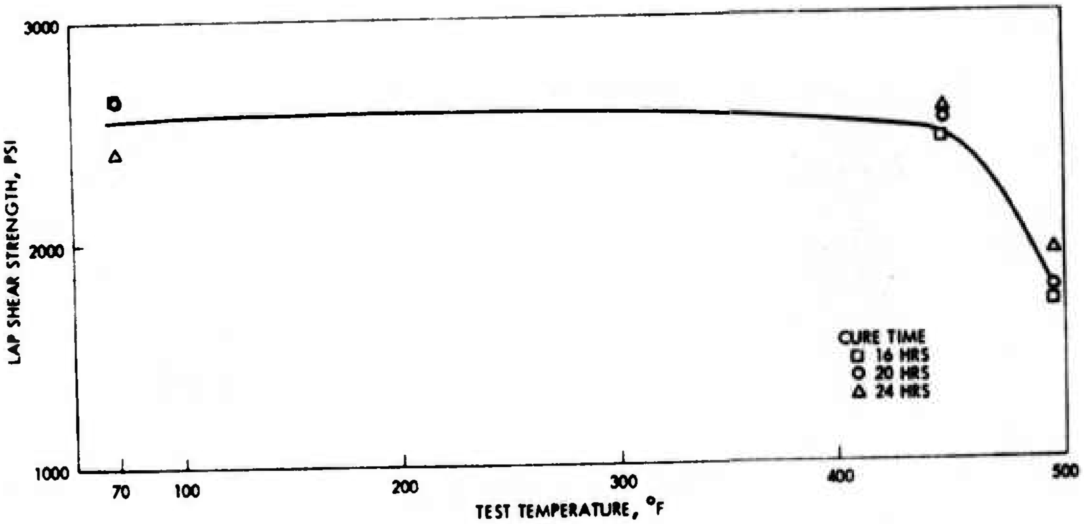


Figure 15. Influence of cure time on ambient and elevated temperature properties of 80 percent HR 600AC prepreg bonded titanium, 525°F cure.

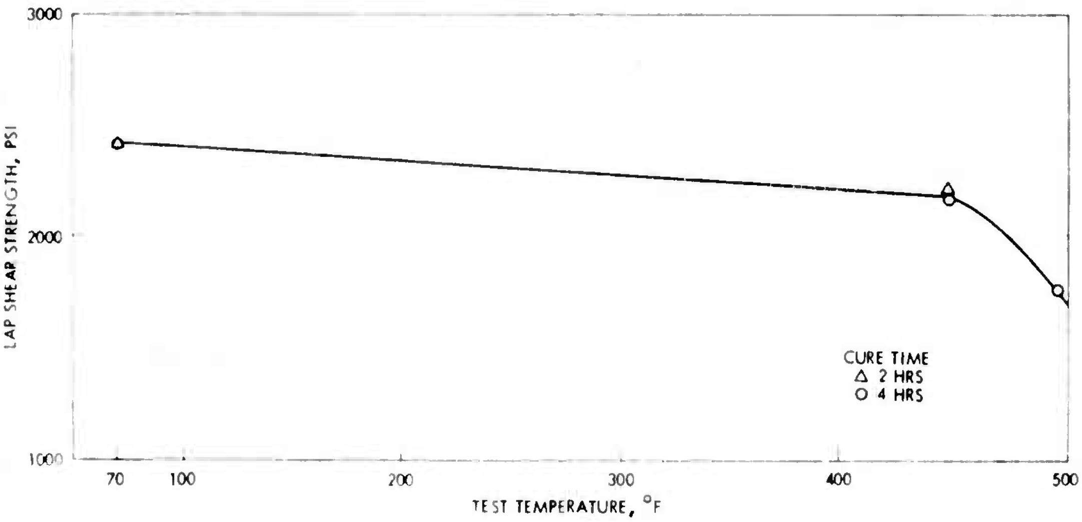


Figure 16. Influence of cure time on ambient and elevated temperature properties of 70 percent HR 600AC prepreg bonded titanium, 600°F cure.

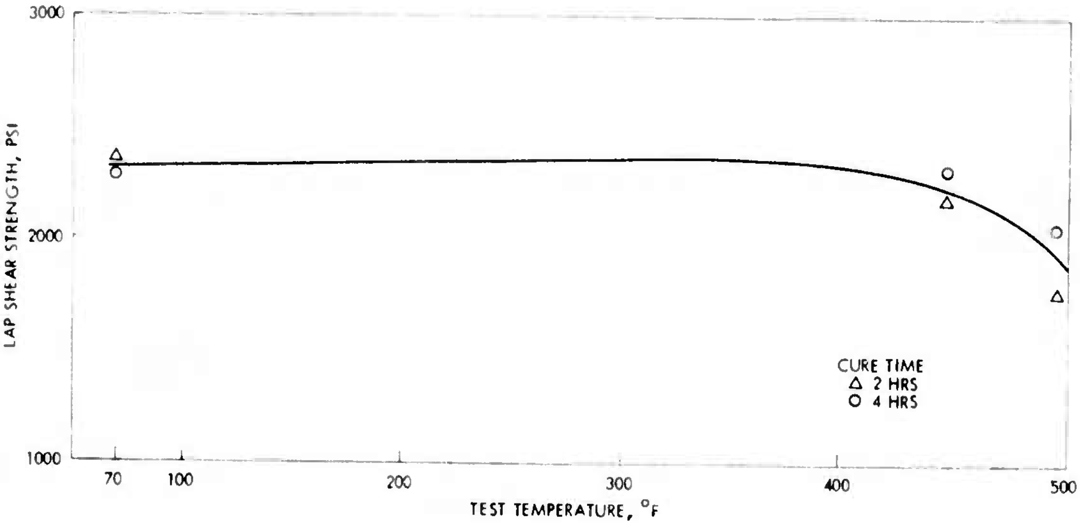


Figure 17. Influence of cure time on ambient and elevated temperature properties of 80 percent HR 600AC prepreg bonded titanium, 600°F cure.

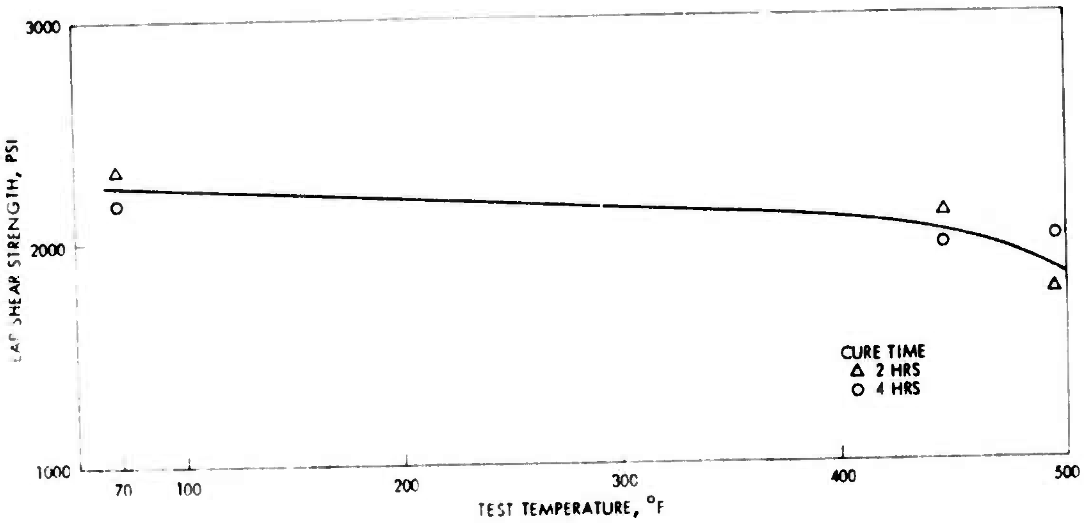


Figure 18. Influence of cure time on ambient and elevated temperature properties of 70 percent HR 600AC prepreg bonded titanium, 650°F cure.

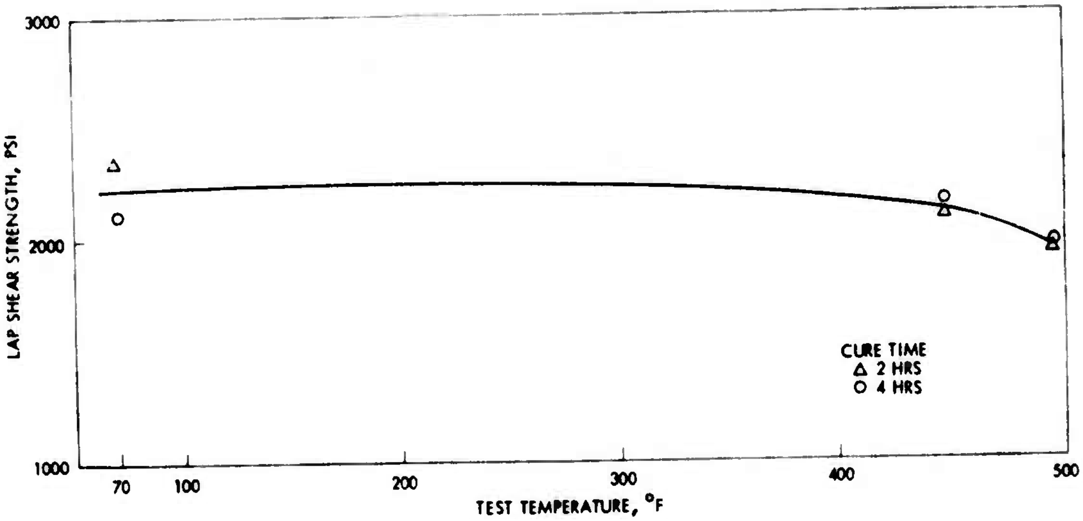


Figure 19. Influence of cure time on ambient and elevated temperature properties of 80 percent HR 600AC prepreg bonded titanium, 650°F cure.

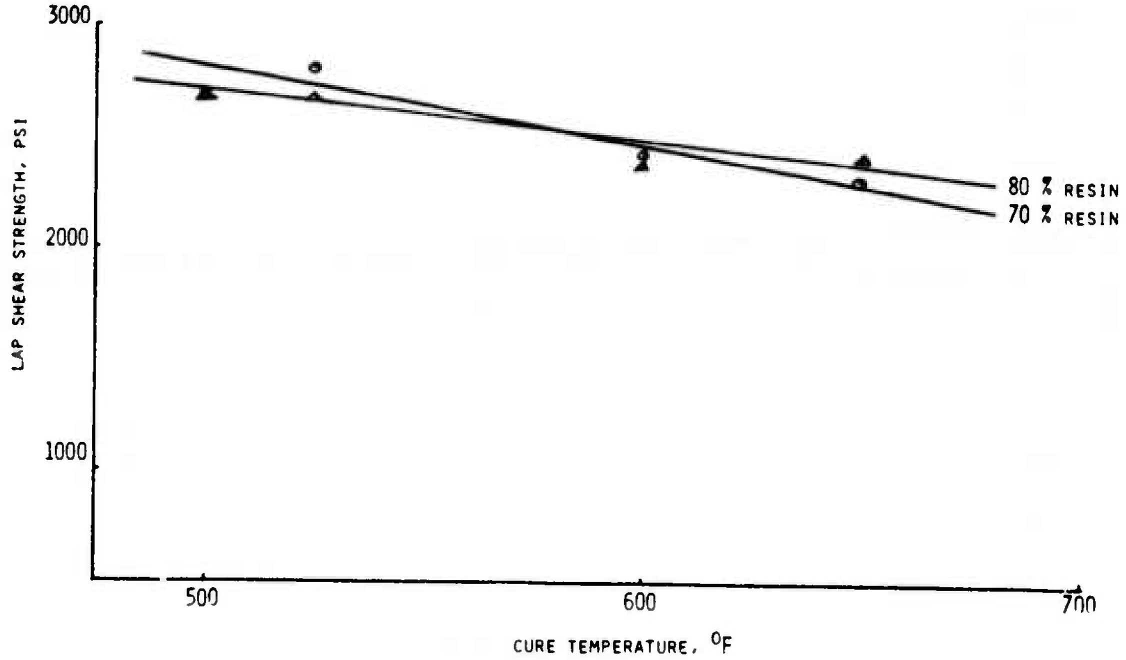


Figure 20. Influence of cure temperature on properties of HR 600AC prepreg bonded titanium - ambient temperature tests.

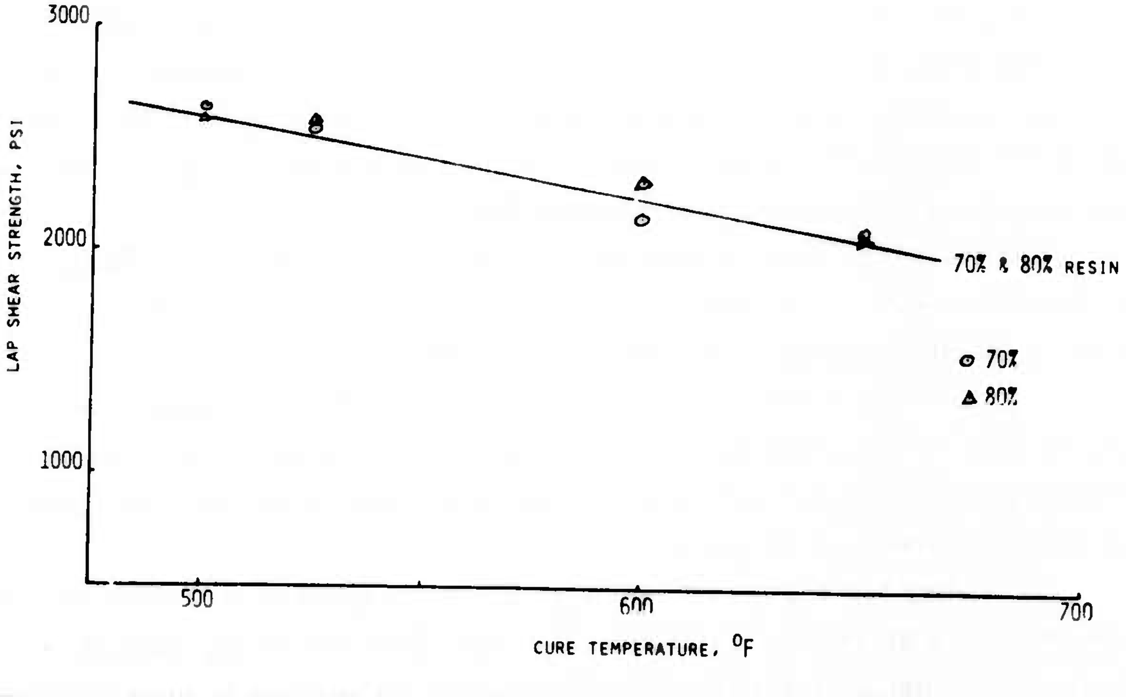


Figure 21. Influence of cure temperature on properties of HR 600AC prepreg bonded titanium - 450°F tests.

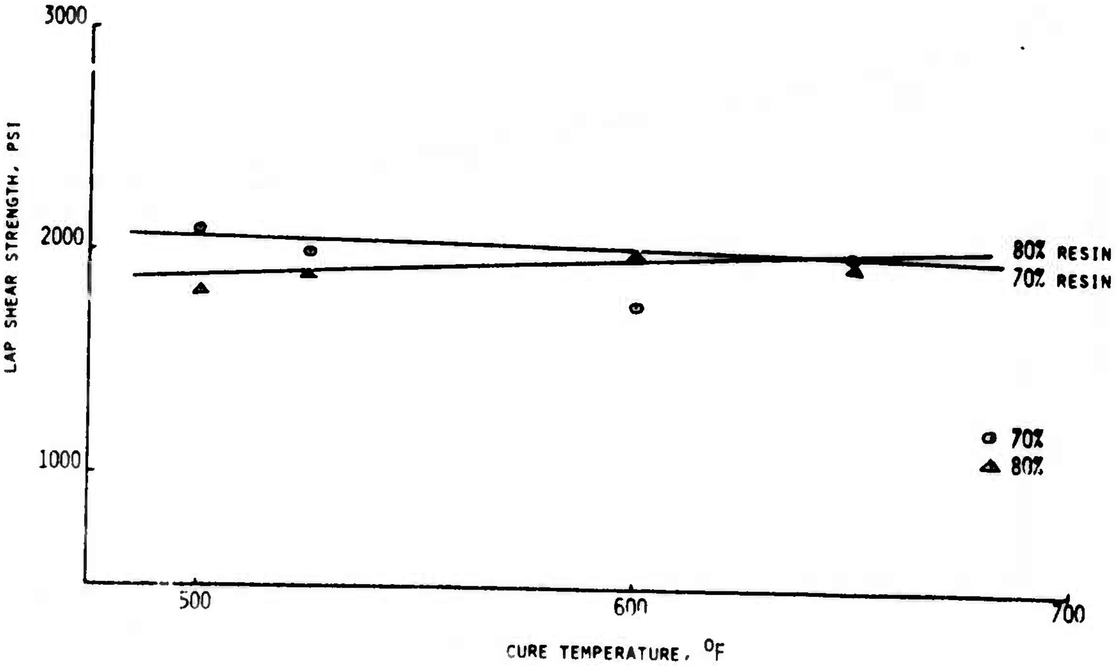


Figure 22. Influence of cure temperature on properties of HR 600AC prepreg bonded titanium-500°F tests.

Figures 20 through 22 show the variation of adhesive strength with cure temperature. The ambient temperature and 450°F strength is seen to decrease slightly with increasing temperature (Figures 20 and 21), while the 500°F lap shear strength, though starting at a lower level, is seen to remain approximately constant (Figure 22).

At the lower cure temperatures, longer cure times are necessary, but higher strengths are obtained. This same correlation exists for lap shear strengths measured at ambient and 450°F.

At 500°F test temperature there seems to be very little dependence of cure time and cure temperature on lap shear strength, i.e., lap shear strengths fall within a relatively narrow range when different cure times and temperatures are utilized.

The data for Figures 12 through 22 are presented in Tables III and IV. Note that for a given cure temperature, cure time and resin content, the lap shear strengths at 450°F range from about 80 percent to over 100 percent of the ambient temperature values, and the strengths measured at

TABLE III. LAP SHEAR STRENGTHS OF TITANIUM SPECIMENS BONDED WITH HR 600AC PREPREG*

Specimen No.	Cure Temp. (^{o}F)	Cure Time (Hrs.)	Test Temp. (^{o}F)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
68A				2760		
97	500	16	Ambient	2620	2690	100
78				2690		
59				Broken		
69	500	16	450	2380	2380	89
98				1820 (Bad Part?)		
91				—— (Bad Part)		
74	500	16	500	1780	1755	65
83				1730		
88				2630		
80	500	20	Ambient	2730	2663	100
94				2630		
60				2820		
51	500	20	450	2370	2595	97
95				2040 (Bad Part)		

*The adhesive prepreg consisted of 112 starch finished heat-cleaned glass cloth impregnated with a 1:1 mixture of HR 600A and HR 600C. The resin content was 70 percent.

The specimens consisted of 6A14V titanim alloy cleaned by Hughes Process (HP) 9-30.

(Continued on next page)

(Table III, continued)

Specimen No.	Cure Temp. (°F)	Cure Time (Hrs.)	Test Temp. (°F)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength
61	500	20	500	1980	2053	77
65				2140		
62				2040		
77A	500	24	Ambient	2410	2583	100
81				2790		
85				2550		
64	500	24	450	2800	2646	102
67				2750		
53				2390		
90	500	24	500	2040	2100	81
55				2160		
96				Bad Specimen		
56A	525	16	Ambient	2530	2683	100
79				2550		
52				2850		
58	525	16	450	2580	2483	92
102				2460		
72				2410		

(Continued on next page)

(Table III, continued)

Specimen No.	Cure Temp. (^oF)	Cure Time (Hrs.)	Test Temp. (^oF)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
50	525	16	500	1880	1810	67
63				1740		
103						
76	525	20	Ambient	2770	2813	100
100				2820		
89				2850		
92	525	20	450	2510	2513	89
93				2380		
57				2650		
73	525	20	500	2140	2040	73
101				Bad Part		
75				1940		
71A	525	24	Ambient	2530	2530	100
54				——— (Bad Specimen)		
99				——— (Missing Specimen)		

(Continued on next page)

(Table III. continued)

Specimen No.	Cure Temp. (°F)	Cure Time (Hrs.)	Test Temp. (°F)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
82	525	24	450	2570	2553	101
86				2420		
70				2670		
87	525	24	500	2080	2050	81
84				2090		
66				1980		
27	600	2	Ambient	2270	2407	100
31				2460		
35				2490		
14	600	2	450	2070	2173	90
17				2270		
3				2180		
40	600	2	500	1770	1757	73
5				1800		
38				1700		
30	600	4	Ambient	2460	2433	100
44				2420		
10				2420		

(Continued on next page)

(Table III, continued)

Specimen No.	Cure Temp. (°F)	Cure Time (Hrs.)	Test Temp. (°F)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
1	600	4	450	2160	2207	87
45				2150		
11				2310		
28	650	2	Ambient	2380	2337	100
9				2290		
19				2340		
41	650	2	450	2150	2103	90
24				2010		
33				2150		
21	650	2	500	1650	1767	76
4				1790		
32				1860		
36	650	4	Ambient	2290	2194	100
20				2111		
37				2180		
34	650	4	450	1780	1993	91
16				2160		
26				1860		

(Continued on next page)

(Table III, concluded)

Specimen No.	Cure Temp. (°F)	Cure Time (Hrs.)	Test Temp. (°F)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
39	650	4	500	2170	2017	92
42				1930		
43				1950		

TABLE IV. LAP SHEAR STRENGTHS OF TITANIUM SPECIMENS BONDED WITH HR 600AC PREPREG*

Specimen No.	Cure Temp. (°F)	Cure Time (Hrs.)	Test Temp. (°F)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
68B	500	16	Ambient	2410	2680	100
97				2880		
78				2750		
59	500	16	450	2000	2170	81
69				Bad Part		
98				2340		
91	500	16	500	1760	1700	63
74				Bad Part		
83				1640		
88	500	20	Ambient	2600	2673	100
80				2600		
94				2820		
60	500	20	450	2630	2630	98
51				(Bad Part)		
95				—		
61	500	20	500	1750	1836	69
65				1840		
62				1920		

*The adhesive prepreg consisted of 112 starch finished heat-cleaned glass cloth impregnated with a 1:1 mixture of HR 600A and HR 600C. The resin content of the prepreg was 80 percent.

The specimens consisted of 6A1V4 titanium alloy cleaned by Hughes Process (HP) 9-30.

(Continued on next page)

(Table IV, continued)

Specimen No.	Cure Temp. (°F)	Cure Time (Hrs.)	Test Temp. (°F)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
77B	500	24	Ambient	2750	2567	100
81				2420		
85				2530		
64	500	24	450	2610	2570	100
67				2390		
53				2710		
90	500	24	500	1760	1653	64
55				1670		
96				1530		
56B	525	16	Ambient	2760	2670	100
52				2910		
79				2340		
58	525	16	450	2460	2445	92
102				2430		
72				Bad Part		
50	525	16	500	Broken	1700	64
63				1750		
103				1650		

(Continued on next page)

(Table IV, continued)

Specimen No.	Cure Temp. (°F)	Cure Time (Hrs.)	Test Temp. (°F)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
76	525	20	Ambient	2750	2660	100
100				2710		
89				2520		
92	525	20	450	2590	2540	95
93				2490		
57				Bad Part		
73	525	20	500	1780	1777	67
101				1870		
75				1680		
71B	525	24	Ambient	2630	2407	100
54				2000		
99				2590		
82	525	24	450	2660	2580	107
86				2500		
70				Bad Part		
87	525	24	500	1690	1903	80
84				1930		
66				2090		

(Continued on next page)

(Table IV, continued)

Specimen No.	Cure Temp. (^oF)	Cure Time (Hrs.)	Test Temp. (^oF)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
27	600	2	Ambient	2530	2370	100
31				2060		
35				2520		
14	600	2	450	2210	2180	92
17				2140		
3				2190		
40	600	2	500	1730	1760	74
5				1570		
38				1980		
30	600	4	Ambient	2380	2293	100
44				2060		
10				2440		
1	600	4	450	2240	2317	101
45				2340		
11				2370		
15	600	4	500	2010	2060	90
12				2010		
18				2160		

(Continued on next page)

(Table IV. concluded)

Specimen No.	Cure Temp (^oF)	Cure Time (Hrs.)	Test Temp. (^oF)	Lap Shear Strength (psi)	Ave. Lap Shear Strength (psi)	Relative Strength (%) (of ambient temp. strength)
28	650	2	Ambient	2230	2360	100
9				2700		
19				2150		
41	650	2	450	2270	2097	89
24				1860		
33				2160		
21	650	2	500	2040	1933	82
4				1870		
32				2070		
36	650	4	Ambient	2150	2110	100
20				2270		
37				1910		
34	650	4	450	2230	2167	103
16				2220		
26				2050		
39	650	4	500	1970	1963	93
42				2010		
43				1910		

500°F range from above 60 percent to over 90 percent of the ambient temperature strengths.

E. ALUMINUM POWDER FILLED ADHESIVE PREPREG

Studies were conducted to examine the effect of 325 mesh aluminum powder filler on the strength of specimens bonded with HR 600AC prepreg. For the initial tests, prepregs of heat cleaned 112 glass cloth were prepared from a formulation of HR 600AC adhesive containing 25% of 325 mesh aluminum powder. The aluminum filled prepreg fabrics contained 81 and 89 percent adhesive (including the aluminum powder). The data are shown in Table V. Tests were run at ambient temperature.

TABLE V. AMBIENT TEMPERATURE LAP SHEAR STRENGTHS OF TITANIUM SPECIMENS BONDED WITH ALUMINUM FILLED* HR 600 AC PREPREG

Prepreg Composition	Sample Number	Bonding Area	Lap Shear Strength (psi x 10^3)	Average Lap Shear Strength (psi x 10^3)	Glue Line Thickness, Inch
81% Resin	1	0.559	1.31	1.36	0.007
81% Resin	2	0.554	1.35		0.006
81% Resin	3	0.552	1.33		0.009
81% Resin	4	0.540	1.46		0.007
81% Resin	5	0.519	1.37		0.008
89% Resin	1	0.575	1.80	1.70	0.009
89% Resin	2	0.534	1.77		0.007
89% Resin	3	0.540	1.65		0.009
89% Resin	4	0.565	1.65		0.008
89% Resin	5	0.494	1.62		0.009

*25% by weight of the adhesive.

The data indicated that the higher oligomer content prepreg gives better bonding. Thus, it is anticipated that a metal filled prepreg containing even lower aluminum content will result in even higher lap shear strength partly due to the resulting thinner glue lines.

Better bonding is expected with the aluminum filled prepreg because of the known enhancement in strength previously observed with aluminum filled reinforced specimens.

F. T-PEEL TESTS

T-peel specimens have been prepared by bonding one-inch strips of 16 mil 6A14V titanium alloy with the prepreg fabric. T-peel strengths were determined according to ASTM T-Peel Method D1876.

The peel distance in each case was five inches. The results of these tests are shown in Table VI. Testing was done at ambient temperature.

It is recognized that bonded aluminum will have comparatively more peel strength than bonded titanium due to the lower modulus of the aluminum, which permits it to bend more as it peels. The titanium T-peel specimens appear to have a relatively high initial peel strength, but a comparatively low average peel strength. Due to the relatively high modulus of titanium, it is

TABLE VI. RESULTS OF T-PEEL TESTS ON TITANIUM SPECIMENS BONDED WITH HR 600AC

Specimen	Sample T-Peel Strength (lbs)			
	Initial	High	Low	Average
1	3. 6	3. 6	1. 8	2. 7
2	7. 2	7. 2	2. 0	4. 6
3	4. 8	4. 8	2. 0	3. 0
4	6. 6	6. 6	2. 0	4. 3
5	5. 0	5. 0	2. 0	3. 5
Failures in all cases were cohesive				

apparent that T-peel tests on titanium specimens must be carried out with thinner titanium foil in order to get useful T-peel data. T-peel tests with thinner titanium foil will be run in future studies.

G. WELDBONDING

Weld schedules have been established for spotwelding of titanium specimens and both spotwelded and weldbonded specimens have been prepared. All spotwelded lap shear specimens had a one-inch overlap. Weld schedules were established on three phase Sciaky Spot Welders with solid state controllers, and both spotwelded and weldbonded specimens were prepared for S/N tests. The adhesive mixture used in the weldbonded specimens had the following composition by weight: HR 600A, 25%; HR 600C, 25%; aluminum powder, 325 mesh, 50%; dimethylformamide, sufficient to make a readily applicable paste. Good spotwelds were obtained on lap shear specimens containing this formulation.

H. S/N TESTS

S/N (fatigue) tests were run to evaluate the fatigue life of aluminum filled HR 600AC bonded spotwelded titanium. These tests were run on 1.0 inch overlap, 0.050 inch thick titanium specimens 1.0 inch wide. The specimens were adhesive bonded, spotwelded and weldbonded. The adhesive used in preparing the weld bond specimens was described in the previous section. The fatigue tests were run at 30 cycles per second. The S/N tests on the spotwelded, weldbonded and adhesive bonded specimens are shown in Figures 23, 24, and 25. The weldbonded specimens (Figure 24) clearly show increased fatigue resistance over the spotwelded specimens, particularly at the higher loads (above 2000 psi), where the number of cycles to failure for a given load is superior by about one order of magnitude, and at the lower loads (300+ psi), where failure occurred at 10^6 cycles in the spotwelded specimens, but did not occur at all in the weldbonded samples. No carrier cloth was used in any of the specimens used for the fatigue tests.

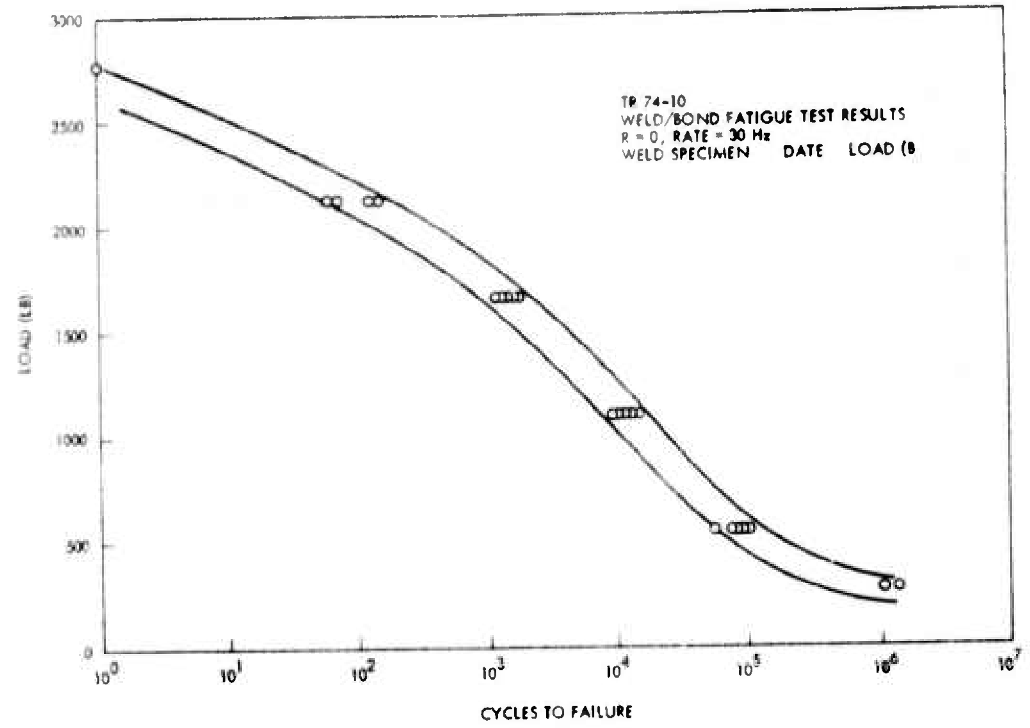


Figure 23. Fatigue (S/N) tests on spotwelded titanium specimens.

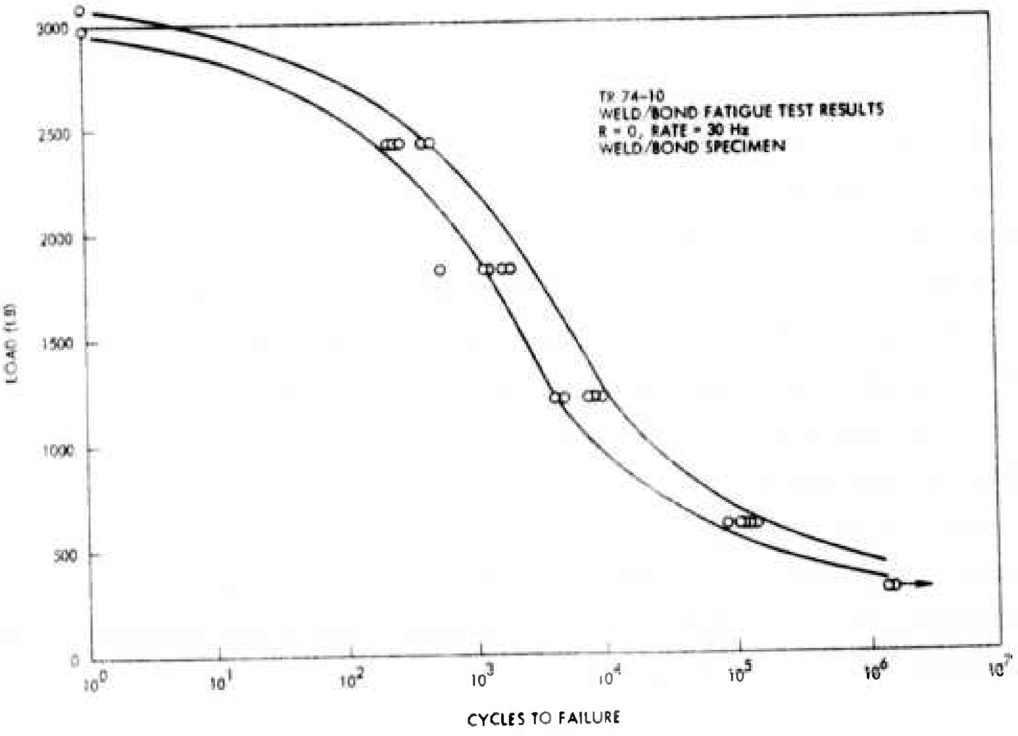


Figure 24. Fatigue (S/N) tests on spotwelded titanium specimens bonded with HR 600AC thermally cured acetylene terminated polyimide.

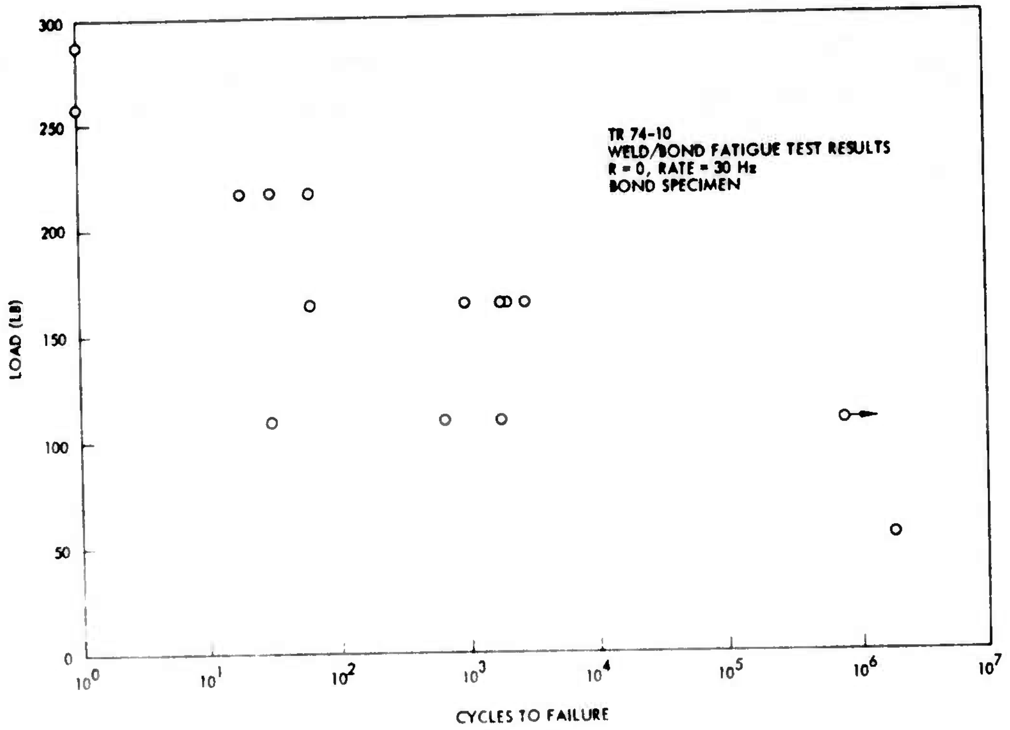


Figure 25. Fatigue (S/N) tests on titanium specimens bonded with HR 600AC thermally cured acetylene terminated polyimide.

The strengths of the adhesive bonded titanium specimens are surprisingly low, especially in view of past Instron lap shear strengths, where values in excess of 2000 psi were observed on bonded titanium specimens in the absence of carrier cloth.

As demonstrated in work with laminating resins, the cured HR 600 resin is a relatively high modulus material, and thus may display poor strength on the fatigue testing apparatus, particularly in view of the fact that the rate of application of load is greater in the fatigue tester by at least two orders of magnitude.

Lower modulus adhesives to be developed in the forthcoming program continuation should be less sensitive to this extremely high rate of load application and thus are expected to be considerably more tolerant of the test conditions in the fatigue tester.

Figure 26 shows the four observed types of failure modes and Tables VII, VIII, and IX contain the applied loads, cycles to failure, and failure modes for spotwelded, weld-bonded and adhesive bonded (no reinforcement) titanium specimens. At the lower applied loads, failure was a Type I sheet failure, whereas at the higher loads failure appeared to be by partial or complete nugget separation.

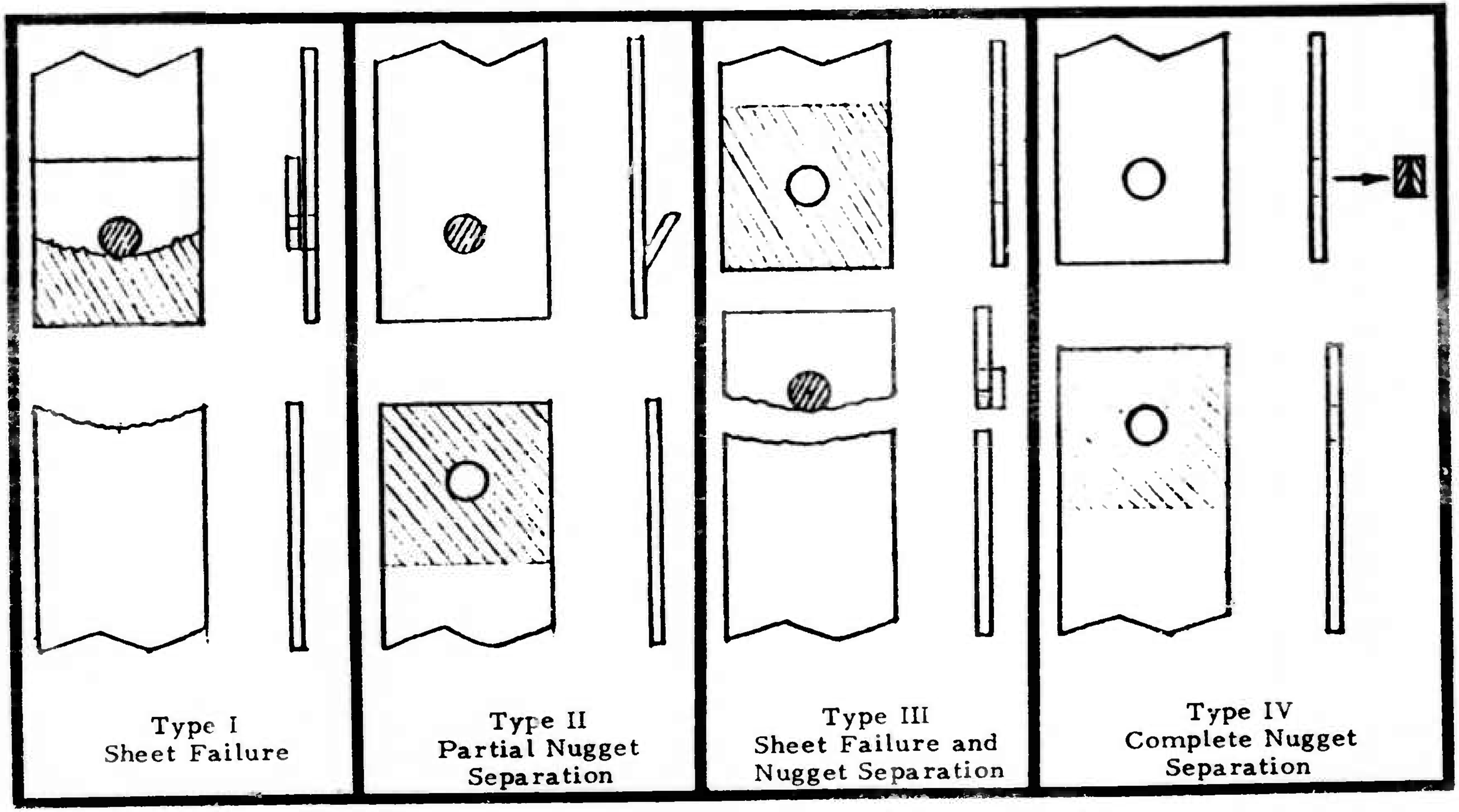


Figure 26. Failure modes observed on weldbonded titanium lap shear fatigue specimens.

TABLE VII. FATIGUE TEST SPOTWELDED TITANIUM SPECIMENS

Spec. No.	Load (lb)	N (cycles)	Failure Mode	Remarks
1	2760	–		Failed statically - No separation
2	0-2128	120	IV	
3	0-2128	150	IV	
4	0-2128	60	II	
5	0-2128	75	II	
6	–	–	IV	Wrong settings
7	0-1656	1890	IV	
8	0-1656	1080	II	
9	0-1656	1650	IV	
10	0-1656	1290	II	
11	0-1656	1320	IV	
12	0-1104	15,300	III	
13	0-1104	11,010	I	
14	0-1104	14,850	I	
15	0-1104	13,860	I	
16	0-1104	9,450	I	
17	0-552	80,500	I	
18	0-552	56,000	I	
19	0-552	91,000	I	
20	0-552	95,000	I	
21	0-552	79,000	I	
22	0-276	1,028,000	I	
23	0-276	1,303,000	I	
24	Not tested			
25	2760	–	II	Tested statically

TABLE VIII. WELD/BOND FATIGUE TEST WELDBONDED TITANIUM SPECIMENS (SPOTWELDED WITH ADHESIVE BOND)

Spec. No.	Load (lb)	N (cycles)	Failure Mode	Remarks
1	3075	1	II	Tested statically
2	2970	1	II	Tested statically
3	0-2417	270	IV	
4	0-2418	220	II	
5	0-2418	405	IV	
6	0-2418	410	IV	
7	0-2418	240	II	
8	0-1813	1410	II	
9	0-1813	1250	IV	
10	0-1813	1920	I	
11	0-1813	1260	II	
12	0-1813	520	II	Specimen weld/bond misaligned
13	0-1209	5000	I	
14	0-1209	10,600	I	
15	0-1209	4,530	II	
16	0-1209	8,940	I	
17	0-1209	10,000	I	
18	0-604	143,000	I	
19	0-604	87,000	I	
20	0-604	115,000	I	
21	0-604	217,000	I	
22	0-604	158,000	I	
23	0-302	1,662,000		No failure
24	0-302	1,685,000		No failure
25	Not tested			

TABLE IX. FATIGUE TEST BONDED TITANIUM SPECIMENS HR 600 AC ADHESIVE

Spec. No.	Load (lb)	N (cycles)	Bond Area (in^2)	Remarks
1	258		1.051	Tested statically
2	288		1.030	Tested statically
3	–	–	1.060	Broke while drilling
4	–	–	1.040	Broke while applying static load
5	0-218	60	1.051	
6	0-218	18	1.062	
7	0-218	30	1.092	
8	0-164	930	1.061	
9	0-164	60	1.061	Specimen misaligned
10	0-164	2910	1.061	
11	0-164	1890	1.061	
12	0-164	1980	1.061	
13	0-109	30	1.071	
14	0-109	75	1.040	
15	–	–	–	Missing
16	Not tested		1.071	
17	Not tested		1.051	
18	–	–	1.050	Broke while applying static load
19	0-109	30	1.133	
20	0-109	630	1.030	
21	0-109	1800	1.061	
22	0-109	713,000	1.040	No failure
23	Not tested		1.051	
24	Not tested		1.051	
25	0-55	1,839,000	1.052	

V. EXPERIMENTAL

Preparation of 4,4'-Diacetyl Diphenyl Ether (Experiment No. G1344-90)

The procedure for the preparation of this compound has been modified from that reported by Dilthey, Bach, Grütering and Hausdörfer[4] in that 1,2-dichloroethane was used as solvent in place of carbon disulfide.

To a solution of diphenyl ether (85 g, 0.50 mole) in 1,2-dichloroethane (150 ml) was added anhydrous aluminum chloride (270 g, 2.02 moles). The mixture was cooled to about -20°C and acetyl chloride (112 g, 1.43 moles) was added dropwise with vigorous stirring. Evolution of HCl was fairly vigorous, and it became necessary to add the acetyl chloride quite slowly. This addition required ca. 2-1/2 hours. After the addition was complete, the mixture was slowly allowed to rise to ambient temperature. This required an additional 3 hours, since HCl evolution was still quite vigorous during this period. Stirring was continued overnight at ambient temperature. The temperature was raised to 60°C on a water bath and kept at 60°C for 2 hours, and cooled. The contents of the flask were poured into about 2 trays of ice. A large amount of crystalline material appeared as the mixture became diluted with water. This crystalline precipitate was filtered off and recrystallized from ethanol to yield 89.3 g. (70 percent) of material, m.p. 100° - 101°. Reported m.p. for this material is 100° - 101°. The infrared spectrum is consistent with the structure.

(Experiment No. H1060-16)

Diphenyl ether, (85g, 0.50 moles) and 1,2-dichloroethane, 150 ml. were placed in a 1 liter 3 necked round bottomed flask fitted with thermometer and mechanical stirrer. The mixture was cooled with a cooling bath while aluminum chloride, 270 g. (2.0 moles) was added. The solution was stirred and maintained at about -20°C while acetyl chloride, 112 g. (1.43 moles) was added dropwise. After the addition of acetyl chloride was complete (about 1-1/2 hours), the temperature was slowly (ca. 2 hours) allowed to rise to ambient temperature while stirring continuously. If the temperature was allowed to rise too rapidly, evolution of hydrogen chloride became very vigorous. After the mixture reached ambient temperature, stirring was continued overnight. The flask was then heated slowly to about 55°C to drive off most of the remaining HCl and the product was poured over ice and water. The mixture was filtered and the yellow precipitate was washed with water. Recrystallization from ethanol yielded 89 g. (70%) of product, m.p. 100°C.

Attempted Preparation of 4,4'-Bis(1-chloro-2-formylvinyl) Diphenyl Ether and 4,4'-Diethynyl Diphenyl Ether (Experiments No. G1344-92 and -95)

Dimethylformamide (200 ml) was placed in a 500 ml round bottomed flask cooled to about 15°C. Phosphorus oxychloride, (153.3 g, 1 mole) was added slowly with stirring. To this solution was slowly added a solution of 4,4'-diacetyl diphenyl ether (101.5 g, 0.4 mole) in anhydrous dimethylformamide (250 ml). The temperature of the mixture was kept at 15° - 20°C with cooling during the exothermic reaction. After addition was completed, the mixture was gradually warmed to about 50 - 55°C. An additional exotherm appeared to occur during the heating. The temperature of the mixture was maintained at 50° - 60° for 2-1/2 hours, and then allowed to return to ambient. The contents of the flask were poured into a mixture of sodium acetate trihydrate (408 g, 3 moles), water (500 ml) and a tray of ice cubes. The mixture was extracted, first with ether and then with benzene to remove the organic portion. The combined extracts were dried with potassium carbonate, filtered and distilled on the rotary evaporator to remove solvents. The bulk of this yellow oily residue resisted attempts at crystallization.

A solution of this crude residue (53.5 g) in adequate dioxane to make 200 ml of solution was added slowly to a refluxing solution of sodium hydroxide (40 g, 1 mole) in water (200 ml). Addition was maintained at such a rate that refluxing was not interrupted. The addition required ca. 45 minutes and refluxing was continued for an additional 45 minutes. After cooling, the mixture was poured onto an ice-water slush and extracted in several portions with a total of about 1 liter of ether. The ether extract was dried over anhydrous potassium carbonate, filtered and distilled, leaving a dark yellow residue. Attempted molecular distillation of this residue at 10μ and about 75°C yielded no distillate.

Preparation of 4,4'Bis(1-chloro-2-formylvinyl) Diphenyl Ether (Experiment No. G1343-08)

Phosphorus oxychloride, 91.0 g, 54.5 cc (0.60 moles) was added to 80 ml. of anhydrous dimethylformamide at ca. 10°C. The mixture was stirred for an hour after the addition was complete. To this solution was added 50.8 g. (0.20 moles) of 4,4' diacetyl diphenyl ether dissolved in 90 ml. of dimethylformamide. The DMF had to be warmed slightly to dissolve the diacetyl diphenyl ether. The addition was carried out, keeping the reaction mixture at 15 - 20° by external cooling during the addition, which required about an hour. After addition was complete, the cooling bath was removed, and the exothermic reaction created a temperature rise to ca. 50°C. At this time the cooling bath was used to lower the temperature to ca. 40°C. After removal of the cooling bath, the temperature remained at 40° - 42°C for about an hour, then gradually dropped to ambient temperature. After standing at ambient temperature overnight without stirring, the mixture was slowly poured into cold aqueous sodium bicarbonate solution. A finely divided yellowish orange precipitate formed which was difficult to filter. The precipitate was removed and triturated with benzene. The aqueous solutions were extracted with benzene and the combined benzene extracts were dried over anhydrous magnesium sulfate and filtered to yield ca. 2-1/2 liters of benzene extract which was concentrated on the rotary evaporator to give a semicrystalline mass of material. This product, assumed to be a mixture of geometric isomers of 4,4'-bis(1-chloro-2-formylvinyl) diphenyl ether, was carried to the next step without further purification.

4,4'-Diethynyl Diphenyl Ether (Experiment No. G1343-11)

To a solution of 10 g. of sodium hydroxide in 80 ml. of water at reflux was added a solution of 23.3 g. (0.065 mole) of 4,4'-bis(1-chloro-2-formylvinyl) diphenyl ether in 125 ml. of dioxane. After the addition was complete, an additional 5 g. of sodium hydroxide was added and refluxing was continued for an additional 2 hours. Most of the dioxane and water were removed on the rotary evaporator and the residue was extracted with a total of ca. 300 ml. of ether. After drying the ether extract over magnesium sulfate, filtering and distilling the ether, a residue remained which was a semi-solid mass, yield 9.5 g. (67% crude yield). The residue failed to crystallize. The infrared spectrum showed the characteristic $C \equiv C-H$ stretch band at 3300 cm^{-1} and the $C \equiv C$ stretch band at about 2110 cm^{-1}. Further characterization of this material was not carried out.

General Procedure for Preparing Titanium Lap Shear Specimens Containing Cyano-Substituted Polyphenylene Oxide/TPNO Adhesive

Titanium coupons were cleaned as before in accordance with Hughes Process (HP) 9-30, as follows:

The titanium surfaces were first wiped with toluene using clean, silicone-free tissues. They were then pickled in the following solution at room temperature for 30 ± 2 seconds:

Nitric Acid, 70 percent	15 ± 1.5 Volume Percent
Hydrofluoric Acid, 50 percent	3 ± 0.3 Volume Percent
Water, deionized	82 ± 8.2 Volume Percent

Following this, the specimens were rinsed in tap water for two minutes. Next, titanium coupons were immersed in the following room-temperature solution for 2 - 2 1/2 minutes:

Trisodium Phosphate	5.0 ± 0.5 Volume Percent
Sodium Fluoride	0.9 ± 0.09 Volume Percent
Hydrofluoric Acid, 50 percent	1.6 ± 0.16 Volume Percent
Tap Water	92.5 ± 9 Volume Percent

Following this, the coupons were rinsed in tap water, then soaked in a fresh tap water bath at 150° ± 10°F (66° ± 6°C) for 15 minutes minimum. They were then spray rinsed with deionized water and dried at 120° to 150°F (49° - 66°C) in a circulating air oven.

A paste was made of oligomer/TPNO/xylene in the ratio 1:1:0.7 by blending with a spatula and carefully "buttered" on the open scrim which had been placed on a Teflon film. A second Teflon film was placed on top, then chilled with dry ice. Adhesive coupons approximately 1-1/8" x 5/8" were then cut out, the Teflon was stripped off and the coupon placed on one titanium substrate and covered by a second titanium substrate to achieve a 1/2 overlap. Pressure-sensitive tape was then used to align and hold the specimens in place.

Cure was conducted in a heated platen press at 15 psi according to the following schedule:

18 hours at 80°C followed by
4 hours at 160°C followed by
18 hours at 260°C.

Following this, specimens were conditioned 24 hours at room temperature and tested in shear. Five each were tested at room temperature, and five each were tested at 450°F after 1/2 hour conditioning at temperature.

Imidization of Amic Acid Precursor to Acetylene-Terminated Polyimide (Experiment No. G1344-94)

To 20 g. of acid amide (1996-62A) was added redistilled acetic anhydride (250 ml) and the mixture was heated at reflux for 48 hours. The major portion of the acetic anhydride was removed by evaporation on the rotary evaporator and the residue was poured into anhydrous ethanol (300 ml) and stirred for an hour, then filtered. The precipitate was resuspended in fresh ethanol and stirred with a high speed stirrer at about 20,000 RPM for 5 to 10 minutes, then filtered to yield a straw-colored finely powdered material. The yield was 13 g.

Preparation of HR 600AC Polyimide Prepregs

1. Materials

   a. 112 Glass Fabric, starch-oil finish, heat cleaned.
      Source – Clark-Schwebel Fiber Glass Corp.

   b. N,N-dimethyl formamide (DMF)

   c. N-methyl pyrrolidinone (NMP)

   d. Cresol imidized polyimide (HR 600C)

   e. Acetic anhydride imidized polyimide (HR 600A)

2. Process

   a. Formulation

      One part by weight HR 600C polyimide oligomer
      One part by weight HR 600A polyimide oligomer
      1.6 part by weight solvent (DMF or NMP)

   b. Method

      Prepare impregnation tank suitable for submerging glass fabric in strip form under the surface of the polyimide solution, in continuous single-pass impregnation mode. Heat solvent to 350°F, add polyimide and mix until dissolved. Place solution in impregnation tank.

      Cut glass fabric into strips of suitable proportions, and pass through solution in impregnation tank, in single pass.

      Hang in air circulating oven for 15 minutes at 350°F.

      Check resin content by weighing before and after prepregging. Redip if necessary. A single dip should yield a resin content of 50 percent - 70 percent resin by weight.

3. Lap-Shear Specimen Preparation

   a. Clean titanium specimens per HP 9-30.

   b. Cut prepreg to 1-1/8 inches x 5/8 inch coupon.

   c. Place prepreg between titanium coupons to achieve 1/2-inch lap.

   d. Hold in position using pressure sensitive tape.

   e. Using spring clips to achieve 15 psi pressure.

   f. Cure in air circulating oven.

VI. REFERENCES

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Two systems were evaluated as adhesives which cure via addition reactions. These were (1) nitrile substituted polyphenyl ethers cured with terephthalonitrile N,N-dioxide (TPNO) and (2) acetylene terminated polimide (HR600) cured thermally. The thermally cured acetylene terminated polyimide proved to be superior to the TPNO cured cyano substituted polyphenylene oxide. Lap-shear strengths of 6Al4V titanium bonded with HR600 adhesive exceeded 3000 psi at ambient temperature on powdered aluminum-filled specimens reinforced with

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heat cleaned 112 glass fabric and 2800 psi at ambient temperature, 2600 psi at 450°F and 2100 psi at 500°F on unfilled specimens bonded with 70 percent HR600 prepreg on 112 heat-cleaned glass fabric. Weld-bonding of titanium specimens using aluminum powder filled HR600 adhesive proved to be successful and showed superior fatigue resistance over spot-welded specimens.

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