HIGH-TEMPERATURE ADHESIVE DEVELOPMENT AND EVALUATION

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ABSTRACT

High-temperature adhesive systems were evaluated for short- and long-term stability at temperatures ranging from 232°C to 427°C. The resins selected for characterization included: NASA Langley developed polyphenylquinoxaline (PPQ), and commercially available polyimides (PI). The primary method of bond testing was single lap shear. The PPQ candidates were evaluated on 6Al-4V titanium adherends with chromic acid anodize and phosphate fluoride etch surface preparations. The remaining adhesives were evaluated on 15-5 PH stainless steel with a sulfuric acid anodize surface preparation. Preliminary data indicate that the PPQ adhesives tested have stability to 3000 hours at 450°F with chromic acid anodize surface preparation. Additional studies are continuing to attempt to improve the PPQ's high-temperature performance by formulating adhesive films with a boron filler and utilizing the phosphate fluoride surface preparation on titanium. Evaluation of the polyimide candidates on stainless-steel adherends indicates that the FM-35 (American Cyanamid), PMR-15 (U.S. Polymeric/Ferro), TRW partially fluorinated polyimide and NR 150B2S6X (DuPont) adhesives show sufficient promise to justify additional testing.

Objective

To evaluate and test various polymers as adhesives for potential high temperature (450 ^{o}F – 800 ^{o}F) aerospace vehicle applications

INTRODUCTION

Increasing demands for improved structural performance and efficiency of advanced aerospace vehicle systems have severely stressed existing material designs. For additional improvement in this area, new materials and processes must be developed to meet these stringent requirements. High-temperature adhesives could be utilized to improve the reliability and durability of advanced composite, metallic, and ceramic designs.

The purpose of this effort is to evaluate and test various available polymers as adhesives for potential high-temperature applications. The two candidate polymers are polyphenylquinoxaline and polyimide. The three PPQ polymers, designated X-PQ, PPQ-2501 and PPQ-HC, are currently under evaluation as adhesives for long-term 232^{o}C applications under contract NAS1-15605. The six PI candidates, designated FM-35, PMR-15, TRW-PFPI, NR150B2S6X, LARC-TPI, and IP-600, are also candidates for short-term applications (15 minutes) at temperatures ranging from 316^{o}C to 427^{o}C.

The following presentation details some of the work accomplished by the Materials and Processes Group of the Boeing Aerospace Company.

Polymers Selected for Study

1. Polyphenylquinoxalines (NAS1-15605)
- **A. X-PQ (NASA Langley)**
- **B. PPQ-2501 (King Mar Laboratories)**
- **C. PPQ-HC (Hunt Chemical)**

2. Polyimides (IR&D)
- **A. PMR-15 (U.S. Polymeric)**
- **B. FM-35 (American Cyanamid)**
- **C. TRW-PFPI (TRW)**
- **D. NR150 (DuPont)**
- **E. LARC-TPI (Mitsui Toatsu)**
- **F. IP-600 (National Starch and Chemical)**

Selected Polymers

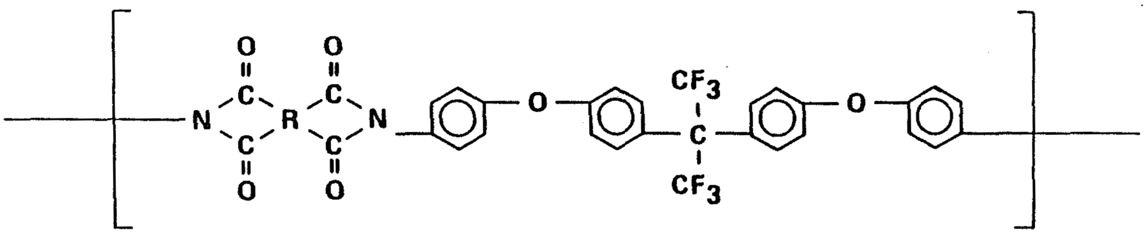
The polymers selected for study as high-temperature adhesives include polyphenylquinoxaline (PPQ) and polyimide (PI).

The PPQ adhesive candidates are currently under evaluation as 232°C structural adhesives on NASA Contract NAS1-15605. In this study, titanium lap shear, crack extension and climbing drum peel specimens were fabricated and then subjected to various environmental conditions before testing. These conditions included temperature ranges from -54°C to 232°C, humidity exposure (49°C/95% R.H.) and aircraft fluid immersion (Skydrol). Exposure times in these environments ranged from 0-3000 hours.

In addition, boron-filled PPQ adhesives are being evaluated on a Boeing Independent Research and Development (IR&D) Program to improve their high-temperature (427°C) performance. This is being done in conjunction with a phosphate fluoride titanium surface preparation.

All PI candidates are being evaluated on a Boeing (IR&D) Program. These adhesives are being assessed for short-term stability at high temperatures (above 316°C) on stainless-steel adherends. The surface preparation is sulfuric acid anodize. A majority of this testing was completed on single lap shear specimens at test temperatures from -54°C to 427°C.

TRW-PFPI (4BDAF/PMDA)
Partially Fluorinated Polyimide

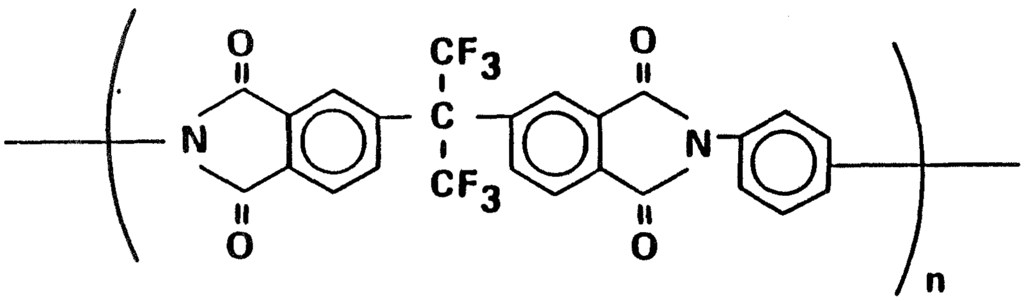


Where R = aromatic ring structure

This figure shows the general molecular structure of the partially fluorinated polyimide, a linear aromatic condensation polyimide that can be utilized as a thermo-oxidative/corrosive protective coating. The glass transition temperature for this polymer is approximately 390°C (734°F).

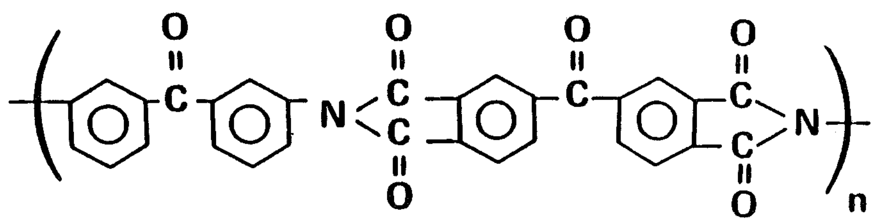
DuPont NR150 B2S6X

Thermoplastic Polyimide



This figure shows a NR 150 condensation polyimide from DuPont supplied as a precursor solution in diglyme solvent; it is a polymer that exhibits excellent thermal and oxidative stability with a glass transition temperature of approximately 375°C (707°F).

Mitsui Toatsu LARC-TPI Thermoplastic Polyimide



This figure shows the molecular structure of a NASA Langley-developed linear thermoplastic polyimide produced by Mitsui Toatsu Chemicals, Inc., Japan. In its fully imidized form, LARC-TPI exhibits excellent toughness and thermo-oxidative stability. This condensation polyimide has a glass transition temperature of 259°C (498°F).

PPQ Processing Parameters

- **Adhesive tape preparation: Polymer solution was applied to 112 E-glass scrim. Individual coats of polymer were dried at 65 °C/1 hour; tape thickness was built up to .010". Final film was cured at 185 °C/1 hour. Flow and volatile tests were conducted to check processing techniques.**
- **Adherend: Adherend was 6Al-4V titanium.**
- **Adherend surface preparation: It was 10V chromic acid anodize, primed immediately with a dilute solution consisting of 3 parts solvent (1:1 mixture of m-cresol/xylene) and 1 part polymer solution.**
- **Bonding conditions: All specimens were autoclave cured under 22 in. Hg vacuum and 200 psi for 90 minutes at 329 °C.**

The processing conditions for the PPQ polymer system were characterized in earlier work (Ref. 1). Processes optimized included adhesive film preparation techniques, surface preparation methods and cure cycles.

The PPQ polymers were supplied in solutions of M-cresol and xylene solvent with a solid content of approximately 20% by weight. Adhesive film construction involved applying layers of the polymer solution to a 112 E-glass scrim. Typically the fiberglass was stretched in an aluminum frame and the polymer solution was spread onto the surface by either brush or squeegee application. Each layer of polymer solution was subsequently oven dried to remove the majority of the residual solvent. After the desired film thickness (.010") has been acheived, the film is then oven cured at 185°C for 1 hour to further reduce the volatile content. Flow and volatile tests were then conducted to check the processing methods. After processing the PPQ films usually exhibited very little melt flow at 600°F/200 psi and a volatile content of from 0.5% to 3.0% by weight.

Surface preparation of the titanium adherends included the following process steps:

1. Trichloroethylene degrease
2. Alkaline clean
3. Nitric-hydrofluoric acid etch
4. Chromic acid anodize

After surface preparation, the adherends are immediately primed with a dilute polymer solution, and then oven dried at 163°C for one hour.

Fabrication of the test specimens (lap shear, crack extension and climbing drum peel) required the assembly of appropriately sized adhesive films and the primed titanium adherends. All specimens were subsequently vacuum bagged and autoclave cured at 329°C for ninety minutes.

Data Summary for X-PQ Adhesive

Test Condition	Lap Shear MPa (psi)	Crack Extension mm (inches)	Climbing drum peel, N-M (in/lb)
Ambient (68° F) Initial	26.6 (3850)	22.1 (.87) 24.1 (.95) 1/	1.3 (11.7)
219 K (-67° F) Initial	29.9 (4340)	–	–
450 K (350° F) Initial	25.5 (3700)	23.9 (.94)	–
505 K (450° F) Initial	16.1 (2330)	24.6 (.97)	5.6 (49.7)
Ambient after exposure to 322 K (120° F)/95% R. H. 1000 hrs	16.6 (2400)	34.8 (1.37)	0.4 (3.5)
450 K (350° F) after exposure to 322 K (120° F)/95% R. H. 1000 hrs	17.6 (2550)	64.9 (2.55)	–
Ambient after exposure to Skydrol at ambient stressed to 25% of ultimate	28.2 (4090)	–	–
450 K (350° F) after exposure to to Skydrol at ambient stressed to 25% of ultimate 1000 hrs		–	–
450 K (350° F) after exposure to 450 K (350° F) in air 1000 hours 3000 hours	 24.6 (3570) 20.6 (2980)	 25.7 (1.01) 25.9 (1.02)	 – –
505 K (450° F) after exposure to 505 K (450° F) in air 1000 hours 3000 hours	 13.4 (1950) 4.7 (680) 2/	 28.1 (1.11) 44.2 (1.74)	 – –
450 K (350° F) stressed to determine creep resistance	N		
505 K (450° F) stressed to determine creep resistance	F		

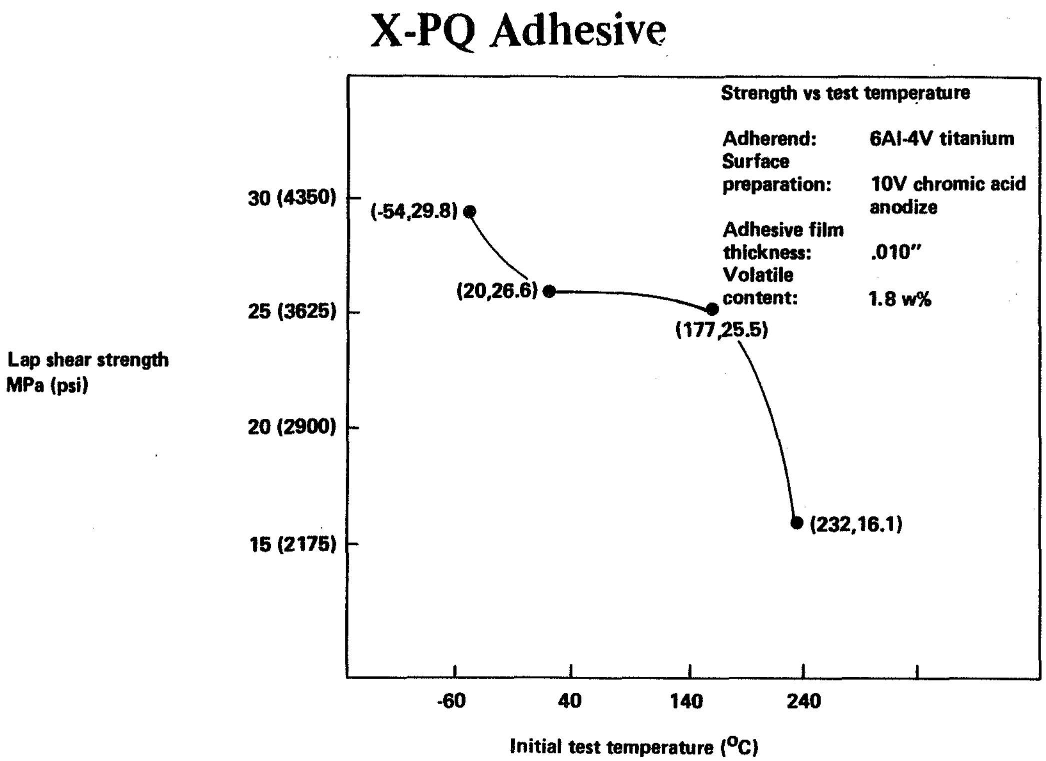
1/ Crack length measured after 1000 hours exposure.
2/ 2 specimens failed prematurely.

F – Failed at 2832 hours.
N – No creep recorded at 3000 hours.

Data Summary (X-PQ)

Examination of the data generated for the X-PQ adhesive supplied by NASA Langley reveals the following trends:

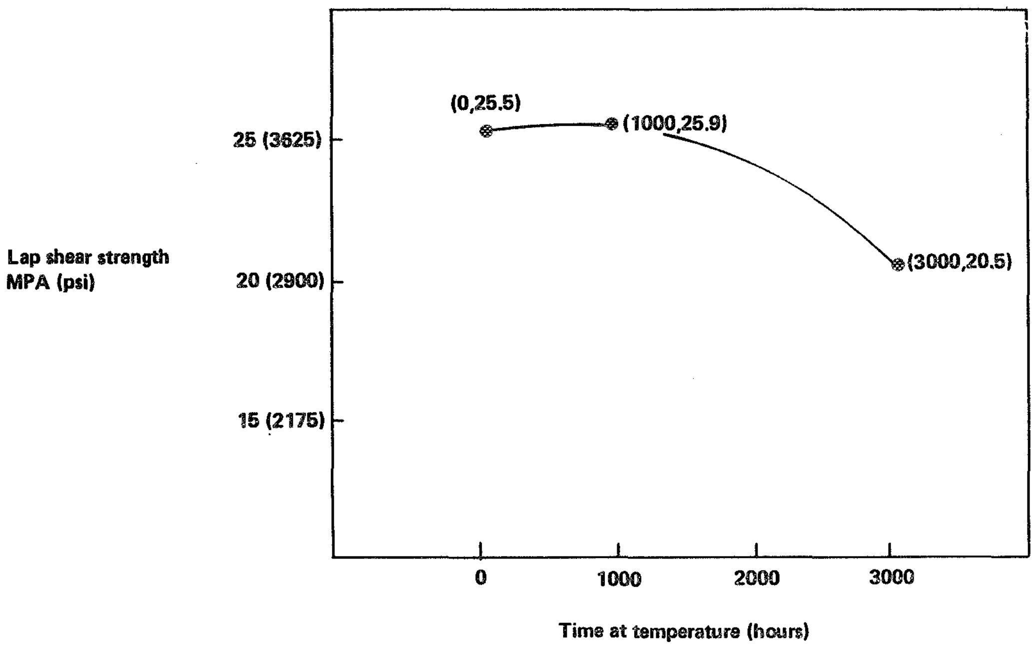
- Shear-strength and toughness decrease with increasing temperature.
- After 1000 hours humidity exposure, shear strength, peel strength, and toughness all decrease.
- X-PQ adhesive lap shear strength is very stable in Skydrol.
- X-PQ has excellent retention of shear strength and toughness after long-term exposure (3000 hours) at 177°C in both stressed and unstressed conditions.
- X-PQ has substantial degradation of shear strength and toughness after long-term exposure (3000 hours) at 232°C, especially the specimens stressed at 25% of ultimate strength.



Lap Shear Strength Versus Temperature (X-PQ)

As expected, the lap shear strength of the X-PQ adhesive decreases with increasing temperature. At 177°C, the test specimens retained 96% of the room temperature properties. However, at 232°C, the room temperature retention was only 60%. Improvements in the lap shear strength at temperature could probably be achieved by reducing the volatile content and post-curing the test specimens.

X-PQ Adhesive Strength at 177 ^{o}C



Lap Shear Strength Versus Exposure Time at 177^{o}C (X-PQ)

The excellent thermo-oxidative stability of X-PQ at 177^{o}C is apparent from this figure. Exposure for a period of 3000 hours resulted in only a 20% decrease in lap shear strength.

Data Summary for PPQ-2501 Adhesive

Test Condition	Lap Shear MPa (psi)	Crack Extension mm (inches)	Climbing drum peel, N-M (in/lb)
Ambient (68° F) Initial	21.1 (3060)	22.8 (0.90) 28.1 (1.11) 1/	0.6 (5.1)
219 K (-67° F) Initial	25.2 (3650)	–	–
450 K (350° F) Initial	20.0 (2900)	25.4 (1.00)	0.2 (2.0)
505 K (450° F) Initial	8.1 (1180)	29.0 (1.14)	–
Ambient after exposure to 322 K (120° F)/95% R. H. 1000 hrs	16.9 (2450)	36.6 (1.44)	0.4 (3.2)
450 K (350° F) after exposure to 322 K (120° F)/95% R. H. 1000 hrs	15.3 (2220)	40.9 (1.66)	–
Ambient after exposure to Skydrol at ambient stressed to 25% of ultimate	F	–	–
450 K (350° F) after exposure to to Skydrol at ambient stressed to 25% of ultimate 1000 hrs	F	–	–
450 K (350° F) after exposure to 450 K (350° F) in air			
1000 hours	21.2 (3080)	30.5 (1.20)	–
3000 hours	24.1 (3490)	30.5 (1.20)	–
505 K (450° F) after exposure to 505 K (450° F) in air			
1000 hours	15.6 (2260)	39.1 (1.54)	–
3000 hours	13.4 (1950)	39.1 (1.54)	–
450 K (350° F) stressed to determine creep resistance	N		
505 K (450° F) stressed to determine creep resistance	F		

1/ Crack length measured after 1000 hours exposure

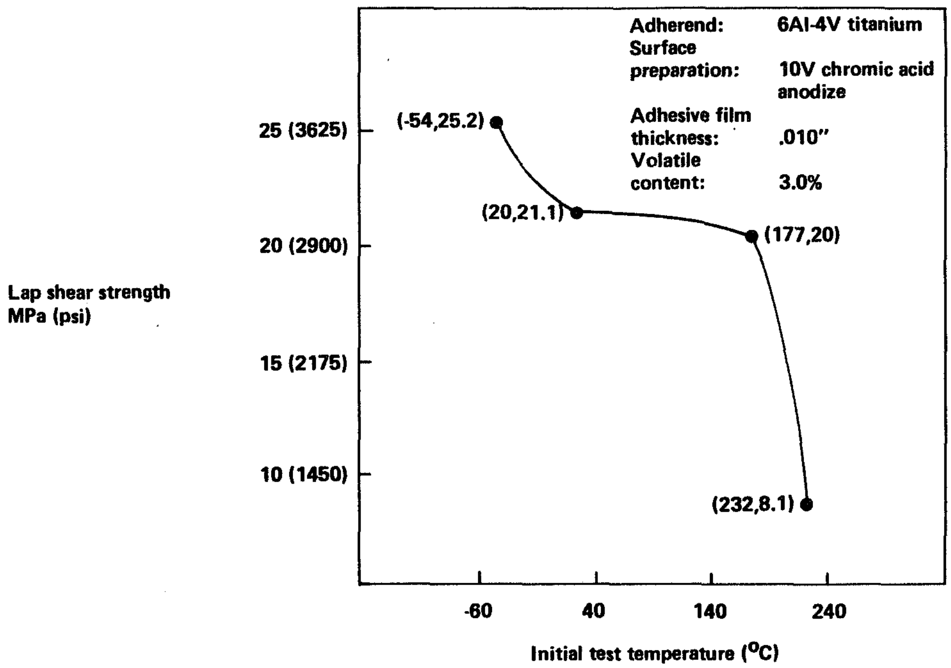
F – Specimens failed after 120 hour exposure
N – No creep recorded at 3000 hours

Data Summary (PPQ-2501)

The following observations can be made from the data generated from King Mar Laboratories PPQ-2501:

- A decrease in shear strength and toughness generally with increasing temperature
- A noticeable decrease in shear strength and toughness after humidity exposure
- Premature lap shear specimen failure in stressed Skydrol condition, suggesting a sensitivity to this fluid
- Increased shear strength after 1000 hour exposure at both 177°C and 232°C exposure temperatures, possibly indicating the need for additional post-cure

PPQ-2501 Adhesive Strength vs Test Temperature



Lap Shear Strength Versus Temperature (PPQ-2501)

As expected the lap shear strength of the PPQ-2501 adhesive decreases with increasing temperature. At 177°C, the test specimens retained 95% of their room temperature properties. And at 232°C, retention was 38%. Additional data indicate that these properties could be improved by post-curing the test specimens.

Data Summary for PPQ-HC Adhesive

Test Condition	Lap Shear MPa (psi)	Crack Extension mm (inches)	Climbing drum peel, N-M (in/lb)
Ambient (68° F) Initial	22.8 (3300)	21.8 (.86) 26.1 (1.03) 1/	1.4 (12.5)
219 K (-67° F) Initial	25.1 (3640)	–	–
450 K (350° F) Initial	19.4 (2820)	23.1 (.91)	1.9 (17.0)
505 K (450° F) Initial	12.3 (1790)	22.1 (.87)	–
Ambient after exposure to 322 K (120° F)/95% R. H. 1000 hrs	21.9 (3170)	31.8 (1.25)	1.9 (16.6)
450 K (350° F) after exposure to 322 K (120° F)/95% R. H. 1000 hrs	8.8 (1280)	36.8 (1.45)	–
Ambient after exposure to Skydrol at ambient stressed to 25% of ultimate	12.8 (1860)	–	–
450 K (350° F) after exposure to to Skydrol at ambient stressed to 25% of ultimate 1000 hrs	1.4 (210) 2/	–	–
450 K (350° F) after exposure to 450 K (350° F) in air			
1000 hours	29.7 (4300)	27.4 (1.08)	–
3000 hours	25.3 (3670)	31.5 (1.24)	–
505 K (450° F) after exposure to 505 K (450° F) in air			
1000 hours	13.9 (2020)	32.5 (1.28)	–
3000 hours	14.6 (2110)	32.6 (1.29)	–
450 K (350° F) stressed to determine creep resistance	N		
505 K (450° F) stressed to determine creep resistance	F		

1/ Crack length measured after 1000 hours exposure.
2/ Premature failure of 2 specimens.

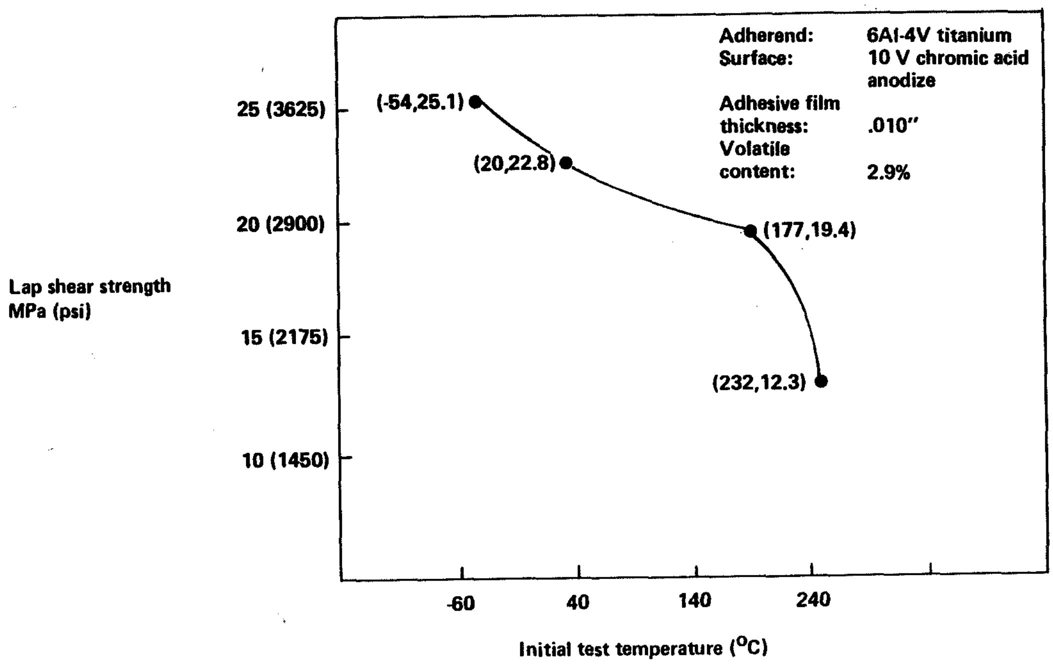
F – Specimens failed after 120 hour exposure.
N – No creep recorded at 3000 hours.

Data Summary (PPQ-HC)

Examination of the data generated for PPQ-HC supplied by Hunt Chemical indicates the following trends:

- The shear strength decreases with increasing temperature; however, the crack extension values (toughness) remain stable over the same temperature range
- After a 1000-hour humidity exposure, shear strength and toughness both decrease
- Stressed exposure in Skydrol results in a substantial decrease in shear strength
- An increased shear strength after 1000 hour exposure at 177°C and 232°C conditions is seen, possibly indicating the need for additional post-cure
- The premature failure of all test specimens at the stressed 232°C condition indicates some potential thermal stability problems

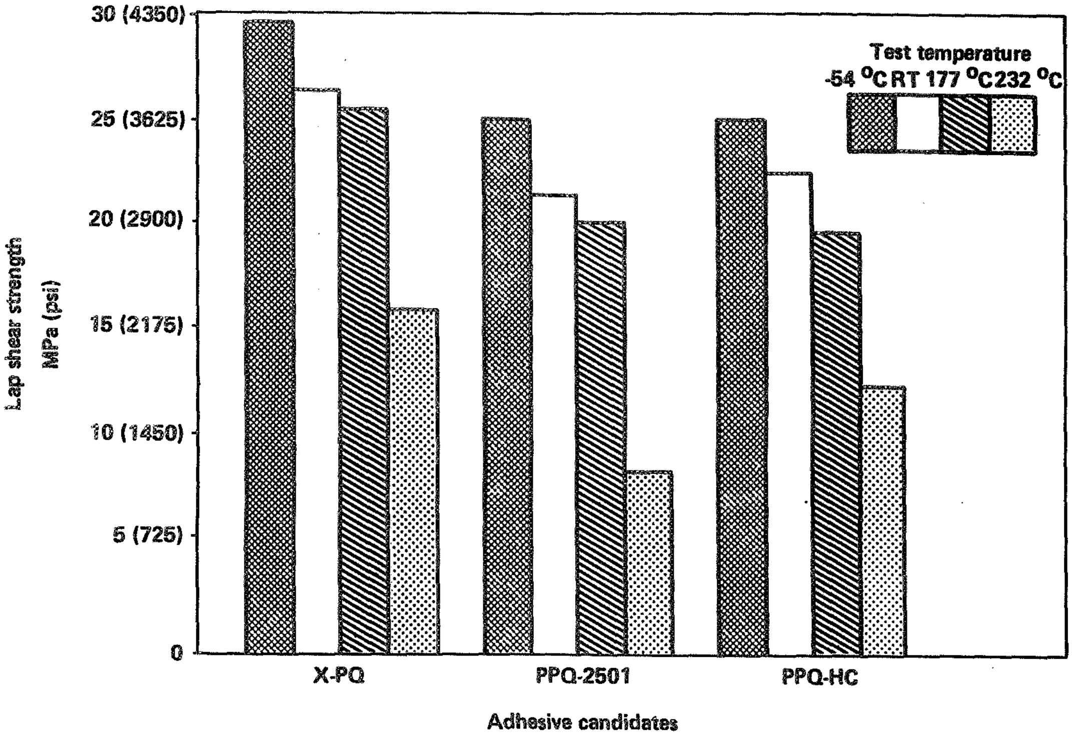
PPQ-HC Adhesive Strength vs Test Temperature



Lap Shear Strength Versus Temperature (PPQ-HC)

As found with the other PPQ candidates, a general decrease in shear strength is observed with increasing test temperature. Retention of room temperature properties at 177°C and 232°C was 85% and 54% respectively.

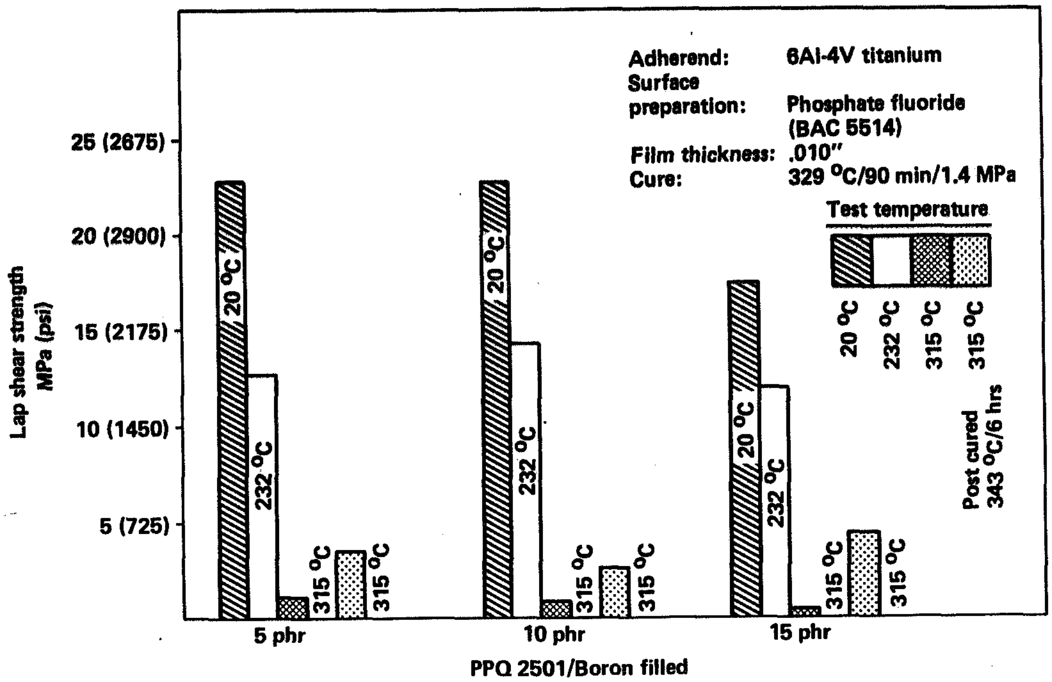
Comparison of Initial Lap Shear Data



Comparison of Initial Lap Shear Data

The best overall lap shear strength properties are clearly exhibited by X-PQ. However, conclusions should not be drawn based solely on lap shear data. To select an adhesive for high-temperature/high-performance applications, careful consideration must be given to all available data.

PPQ-2501/Boron Filled System



Boron-Filled PPQ-2501 System

To improve the high-temperature performance (above 232°C) of the PPQ adhesive systems, additional studies were conducted by formulating adhesive films with an amorphous boron filler and utilizing a phosphate fluoride surface preparation for titanium. Previous work (Ref. 2) conducted by Boeing Aerospace has shown that the chromic acid anodize surface preparation can produce adhesive failure when exposed to temperatures above 700°F.

The boron filler improves bond strengths probably through improvement of the differential coefficient of thermal expansion between the titanium and the adhesive layers, and an improvement in the thermo-oxidative stability of the adhesive.

Analysis of the room temperature and 232°C data shows a general improvement in shear strength at all filler loading levels, except 15 phr (room temperature). Additional testing done at 315°C indicates only a 10% to 20% retention of room temperature properties.

Polyimide Processing Parameters

Adherend: 15-5 PH stainless steel

Surface preparation: Sulfuric acid anodize

Adhesive cure schedule:

FM-35/PMR-15	**– 329 °C/1.4 MPa/2 hours/full vacuum**
TRW-PFPI	**– 454 °C/.7MPa/15 minutes/full vacuum Post-cure 371 °C/6 hours**
NR150-B2S6X	**– 371 °C/1.4 MPa/30 minutes/full vacuum**
X-PQ	**– 329 °C/1.4 MPa/1.5 hours/full vacuum**
IP-600	**– 260 °C/.7 MPa/2 hours/full vacuum**

Polyimide Processing Parameters

For the preliminary analysis of the PI candidates, manufacturers recommendations for processing were followed except for FM-35/PMR-15. Previous processing optimization for these two candidates has been completed on an Independent Research and Development Program. The polyimide polymers were supplied as follows:

- FM-35 - Aluminum-filled supported film, primer
- PMR-15 - resin, supported film
- TRW-PFPI - resin, unsupported film
- NR150-B2S6X - resin
- LARC-TPI - resin
- IP-600 - powder

Adhesive film construction was as previously described.

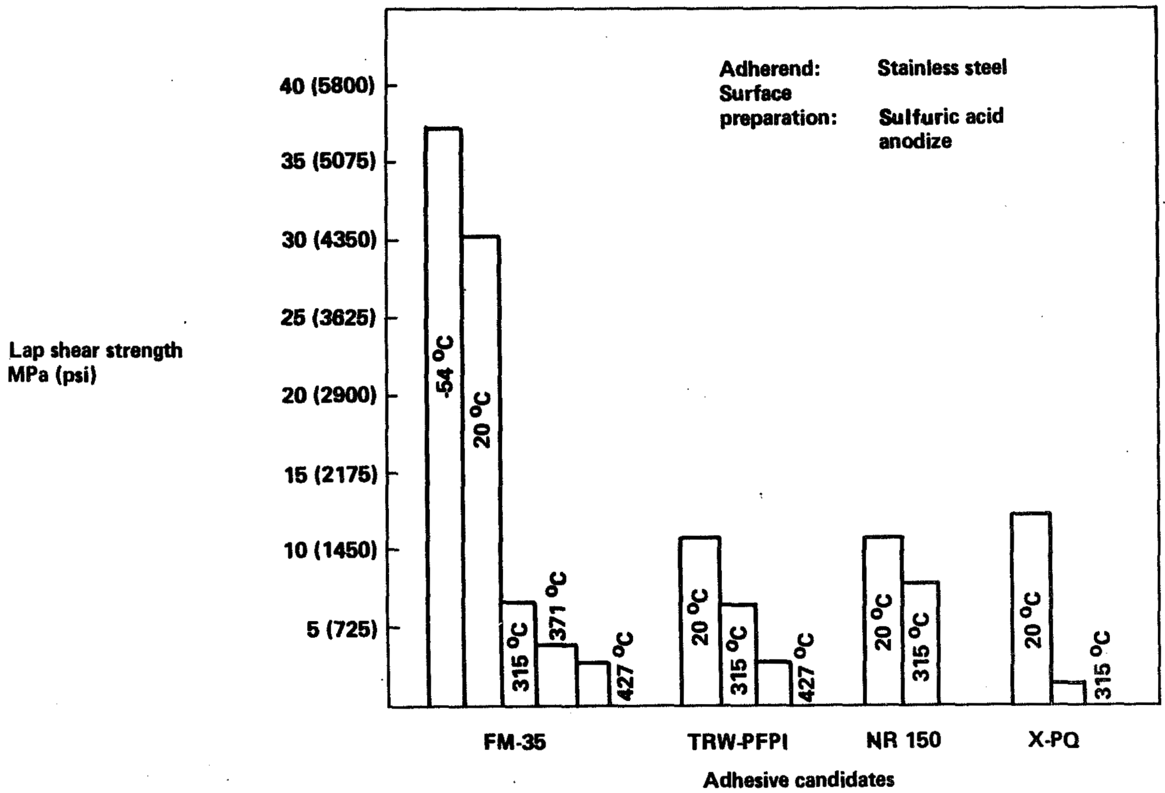
Surface preparation of the stainless-steel adherends included the following process steps:

1. Trichloroethylene Degrease
2. Alkaline Clean
3. Sulfuric Acid Anodize

After surface preparation, the adherends are immediately primed with a dilute polymer solution and then oven dried.

Fabrication of the lap shear test specimens required the assembly of the primed adherends and the adhesive film. All specimens were then vacuum bagged and autoclave cured according to schedule.

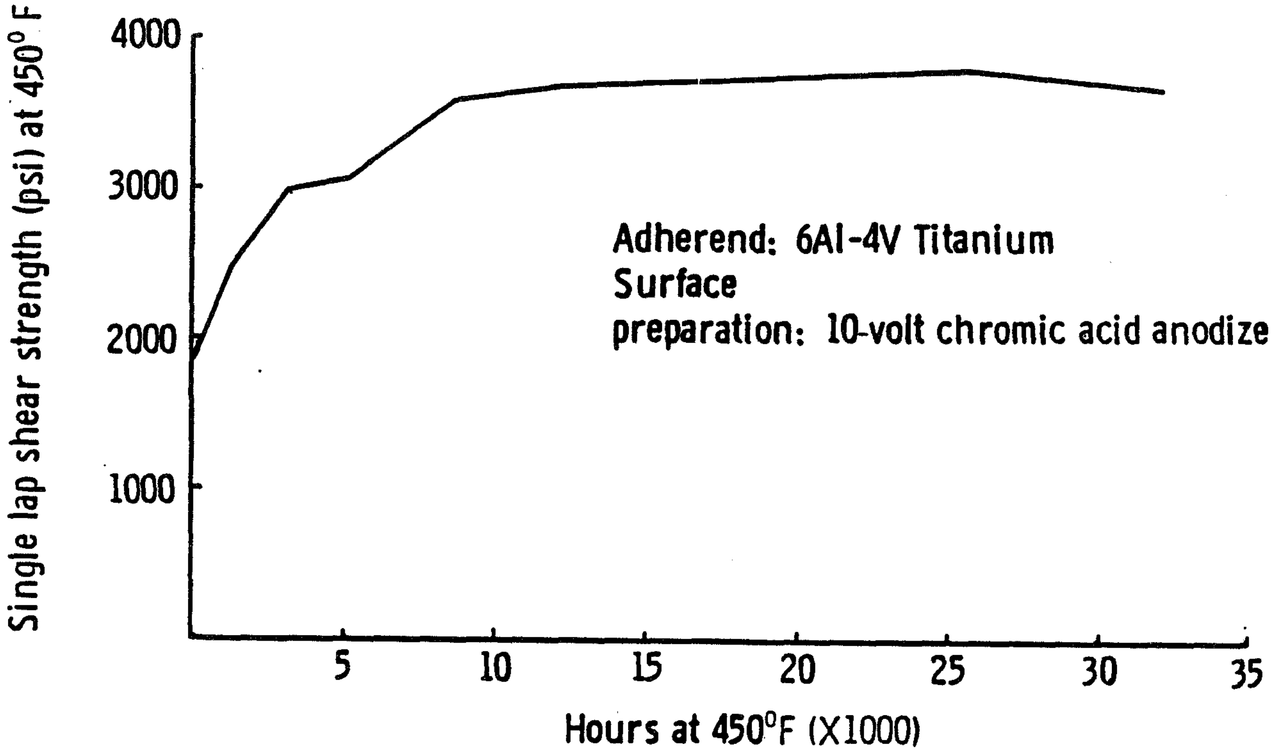
Comparison of Polyimide candidates: Lap Shear Strength vs Test Temperature



Comparison of Polyimide Candidates

Of the candidates tested, FM-35 exhibits the best overall lap shear strength at room temperature. However, at 315°C the three polyimide candidates (FM-35, TRW-PFPI, NR150) show similar strengths.

EXTENDED AGING OF LARC-2 POLYIMIDE ADHESIVE



LARC-2 Aging Studies

Thermal aging of LARC-2 (TPI) adhesively bonded titanium with a chromic acid anodize surface preparation is shown in this figure. The excellent thermal stability of the LARC-TPI adhesive over 32,000 hours is clearly exhibited.

CONCLUSIONS/RECOMMENDATIONS

Various polymers have been evaluated and tested for potential high-temperature (232°C to 427°C) aerospace vehicle applications.

Three PPQ polymers (X-PQ, PPQ-2501, PPQ-HC) have been evaluated as high-temperature structural adhesives on NASA Contract NAS1-15605. X-PQ exhibits the best overall adhesive properties of the three polymers tested. Although some problems are noted with the bond stability of X-PQ at 232°C (stressed/unstressed exposure), this could be resolved by further optimization of the film processing, surface preparation and post-curing methods.

Significant problems were also noted with the commercially produced PPQ-2501 and PPQ-HC, specifically, with thermo-oxidative stability, solvent and humidity exposure sensitivity. The PPQ polymers appear to be excellent candidates for metal-to-metal adhesive bonding; however, further work is necessary to optimize this adhesive system

Several PI polymers were also evaluated on Boeing Aerospace IR&D Programs. Preliminary testing of these candidates reveals several promising commercially available polymers. These include FM-35, PMR-15, NR150, TRW-PFPI and LARC-TPI. Further evaluation is continuing in the area of large area bonds, dissimilar material bonding and filler loading.

REFERENCES

1. S. G. Hill, P. D. Peters, and C. L. Hendricks, "Evaluation of High-Temperature Structural Adhesives for Extended Service," NASA Contractor Report 165944, July 1982.

2. Boeing Company 1985 IR&D Technical Plan, Document Number D1-8299-3.