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EVALUATION OF HIGH TEMPERATURE STRUCTURAL ADHESIVES FOR EXTENDED SERVICE – PHASE III

S. G. Hill and C. L. Hendricks

Boeing Aerospace Company
Seattle, Washington 98124

Contract NAS1-15605
July 1983

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National Aeronautics and
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Langley Research Center
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Evaluation of High Temperature Structural Adhesives for Extended Service - Phase III

Sylvester G. Hill and Carl L. Hendricks

The Boeing Company

1.0 SUMMARY AND INTRODUCTION

Summary

This report documents the work performed by The Boeing Aerospace Company for the National Aeronautical and Space Administration, Langley Research Center, under Contract NAS1-15605—Phase III. The primary objective of this program was to evaluate NASA Langley-developed polymers as structural adhesives for joining titanium (6Al-4V) to titanium for applications requiring long-term (thousands of hours) stability at 450K (350°F) to an hour or less at 811K (1000°F). Four (4) polymers were evaluated for adhesive properties, they were: crosslinked polyphenylquinoxaline (X-PPQ), thermoplastic polyimide (LARC-TPI), ethynyl terminated polysulfone (ETPS), and crosslinked polyimide (X-PI). Surface preparation for titanium was 10 volt chromic acid anodize (CAA) and phosphate fluoride (Boeing process BAC 5514). The test matrix originally consisted of lap shear, crack extension and T-peel specimens of all four adhesives on both surface preparations to be evaluated at 450K, 505K, 589K, 644K, 700K, and 811K. Additional exposure and test included stressed and unstressed Skydrol exposure and combined high temperature and high humidity.

The four adhesive resins exhibited varying strengths when exposed to the different thermal and environmental conditions. In general, none of the systems as supplied and processed were capable of maintaining structural bonds above 644K (700°F). X-PPQ, LARC-TPI, and X-PI exhibited good adhesive performance at 505K (450°F) after extended exposure (to 3000 hours) at 505K. These three polymers also performed well after exposure to combined elevated temperature/high humidity and also to Skydrol while under stress. ETPS gave good ambient temperature adhesive properties but performed poorly under all other exposure conditions, presumably due to inadequate chain extension and crosslinking.

Introduction

The purpose of this program was to evaluate NASA Langley Research Center developed polymers for use as structural adhesives in high temperature applications. These new adhesive systems require evaluation with respect to processing and determination of bond performance under different test conditions. The polymers selected for evaluation were crosslinked polyphenylquinoxaline (X-PPQ), thermoplastic polyimide (LARC-TPI), ethynyl terminated polysulfone (ETPS), and crosslinked polyimide (X-PI). These systems offer the potential for processing into large area bond structures with stability at temperatures above those for epoxy resins.

The basic approach to this study was to convert the supplied polymers to a usable thin adhesive film by impregnating on 112 E glass with A1100 finish. Test specimens were prepared using 10 volt chromic acid anodize and phosphate fluoride titanium surface treatments. Initial cure processes for specimen preparation were supplied by NASA for each of the four candidate resins. Lap shear specimens were exposed to specific environmental conditions and tested for bond degradation. The failed test specimens were examined for mode and type of failure. Boron powder was formulated into X-PPQ in an attempt to improve the high temperature stability.

The original test plan for this program included crack extension and T-peel, as well as, testing at temperatures of 700K (800°F) and 811K (1000°F). However, unplanned process development studies for each of the four resins absorbed program resources that resulted in testing of lap shear specimens only. None of the adhesive systems performed at temperatures above 644K (700°F). Therefore, tests above that temperature were not conducted.

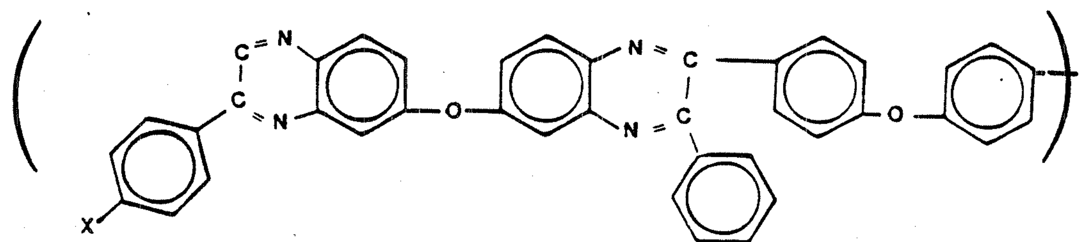
This report is organized to describe the separate work performed on each of the four resins. Average test values, as well as individual specimen values, are tabulated along with conclusions on bond performance.

2.0 TECHNICAL DISCUSSION

This section describes the detailed technical effort that was conducted on this program.

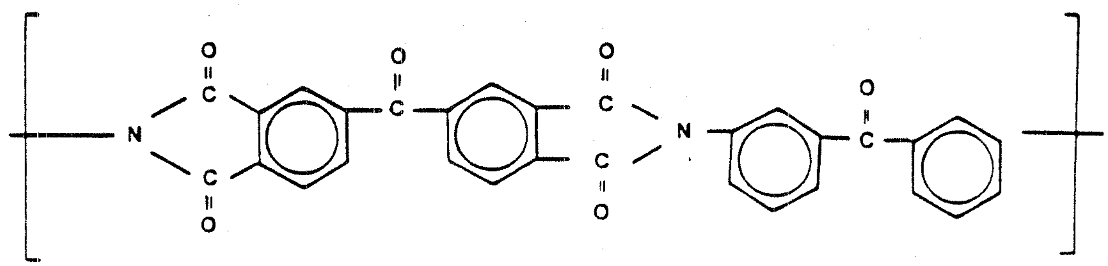
2.1 ADHESIVE RESIN CANDIDATE SELECTION

The adhesive resin candidates were selected from new polymers developed by NASA Langley personnel. Those selected were X-PPQ, LARC-TPI, ETPS, and X-PI. The X-PPQ polymer is shown below. This polymer was prepared by reacting 3,3',4,4'-teta-aminodiphenyl ether with 4,4'-oxydibenzil and 4,4'-oxybis(4"-phenyl-ethynylbenzil) in a 1:1 mixture of m-cresol and mixed xylenes (ref. 1).

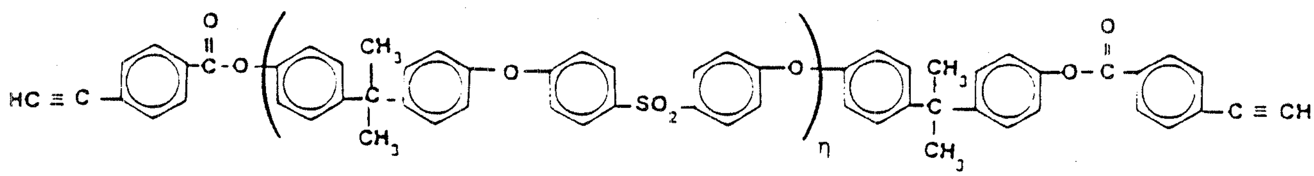


X = H (90%), C ≡ C ϕ (10%)

LARC-TPI is synthesized from benzophenone tetracarboxylic acid dianhydride (BTDA) and 3,3'-diaminobenzophenone (ref. 2).

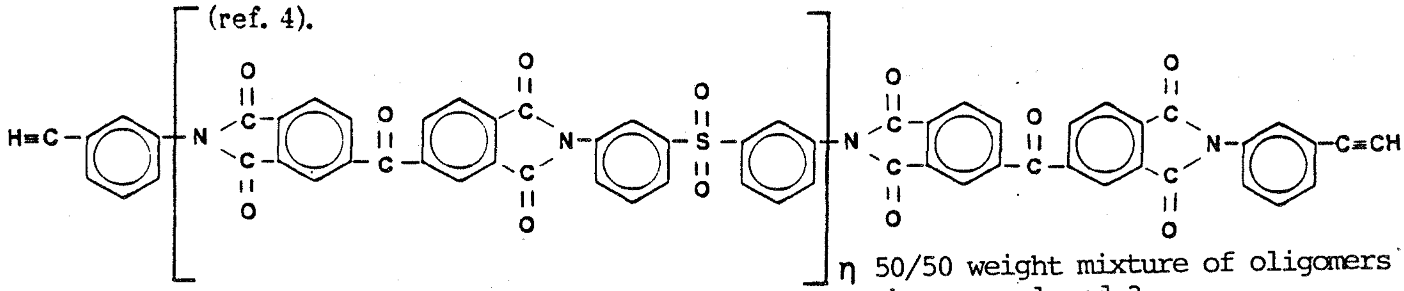


Ethynyl terminated polysulfone structure is shown below (ref. 3).



n = 53 $\overline{M_n} \cong 12{,}000$ g/mole

The chemical structure of X-PI supplied by NASA for evaluation is as follows (ref. 4).



50/50 weight mixture of oligomers where n = 1 and 3

2.2 PREPARATION OF ADHESIVE FILMS

Subsequent to receipt of candidate adhesive resin samples they were processed into film form using 112 E glass fabric with A1100 finish. Each resin required individual processing to achieve desired film properties. Variables such as solution preparation, resin application to the glass, and drying cycles for the film were different for each system.

2.2.1 X-PPQ Adhesive Films

Five quarts of X-PPQ were received from NASA Langley as a 19.7% solids content solution in a 50:50 mixture of m-cresol-xylene. The film was initially prepared using the resin solution unfilled and undiluted. An aluminum frame was used to tautly hold a 24" x 30" section of E glass scrim cloth as the resin solution was brush coated. After each coating application the adhesive scrim was oven dried in 28K (50°F) increments up to 477K (400°F). The film was held at each increment for one hour. Eight coats were required to achieve an adhesive film thickness of 0.3 mm (0.012 inch). The film volatile content was measured gravimetrically before and after exposure to 505K (450°F) for 60 minutes and 616K (650°F) for 120 minutes. Volatile content was 1.1% wt. after 505K (450°F) and 2.5% wt. after 616K (650°F) exposures.

2.2.2 LARC-TPI Adhesive Films

Two pints of LARC-TPI were received from NASA Langley as a 15.0% solution in diglyme. All films from this resin were prepared using the resin solution undiluted and unfilled. An aluminum metal frame was used to hold the 112 E glass scrim while the resin was brush coated. The film was oven dried in 28K (50°F) increments from ambient to 477K (400°F). At each increment the film was held for 30 minutes. Twenty brush coats were required to achieve an adhesive film thickness of 0.02 mm (0.009 inch). The adhesive film was subjected to 505K (450°F) for 60 minutes and 616K (650°F) for 120 minutes to determine volatile content. The measured volatile content after these exposures was 2.5% wt. and 5.8% wt. respectively.

2.2.3 ETPS Adhesive Films

ETPS was received as a dry white powder (250 gms). It was dissolved in a mixture of 90 volume % methylene chloride and 10 volume % toluene to a 15% wt. solids content. This solution was brush coated to 112 E glass, ambient air dried for 15 minutes, and then oven dried by gradual heating to 373K (212°F). The film was held at this temperature for 30 minutes. Approximately six coats were required to achieve a film thickness of 0.3 mm (.012"). Film volatile contents after exposure to 505K (450°F) for 60 minutes and 616K (450°F) for 120 minutes were 7.2% wt. and 7.5% wt. respectively.

2.2.4 X-PI Adhesive Films

The X-PI was received as a one pint solution containing 40% by weight resin solids (NMP and Diglyme). The solution was brush coated to 112 E glass fabric and ambient temperature air dried for one hour followed by one hour oven dry at 352K (175°F). The oven temperature was then increased in 28K (50°F) increments (held one hour at each) to 422K (300°F) and held for one hour. Approximately seven coats were required to achieve a film thickness of 0.36 mm (0.014"). Film volatile content was measured after exposure to 505K (450°F) for 60 minutes and after 616K (650°F) for 120 minutes. Volatile contents were a high 7.0% wt. and 10.8% wt. respectively.

2.2.5 Adhesive Films Flow Results

Each of the adhesive resin films were tested for resin flow using a 35.5 mm (1.40 inch) diameter film disk pressed between two sheets of 1 mm (0.040 inch) aluminum. The flow test conditions and test results (as determined by increase in film disk diameter) are listed below.

Adhesive	Flow Pressure MPa (Psi)	Flow Temperature, K (°F)	Flow Time	Disk Diameter Before mm (inch)	Disk Diameter After mm (inch)
X-PPQ	1.38 (200)	616 (650)	1 Hour	35.5 (1.4)	39.4 (1.55)
LARC-TPI	1.38 (200)	616 (650)	1 Hour	35.5 (1.4)	35.5 (1.40)
ETPS	1.38 (200)	588 (600)	1 Hour	35.5 (1.4)	55.9 (2.20)
X-PI	0.34 (50)	588 (600)	1 Hour	35.5 (1.4)	81.3 (3.20)

2.3 PREPARATION OF TEST SPECIMENS

This section describes the preparation of lap shear test specimens. The single adherend was 6Al-4V titanium alloy. Surface preparation for bonding was 10 volt chromic acid anodize (CAA) and phosphate fluoride. Lap shear test specimen configuration is shown in Figure 2.3-1.

The original plan for this section of work was to use NASA supplied cure cycles for each resin system. However, the initial lap shear values from these cures indicated the need for process studies to improve strength values to levels required for structural bonding. It was further determined that possibly two cure cycles would be required; a moderate cure for lower temperature performance (to 588K (600°F) and a higher cure temperature for conditions exceeding 588K. Further cure cycle variables that were critical included use of postcuring to improve high temperature performance and air cure in a press to enhance crosslinking. The impact of this unplanned activity was to gain valuable data on processing to improve adhesive performance of the candidate resins. It did, however, absorb program funds that were intended for crack extension and T-peel testing.

2.3.1 X-PPQ Specimens

Surface preparation of the 6Al-4V titanium alloy adherend was accomplished using BAC 5890 for 10 volt chromic acid anodize and BAC 5514 for phosphate fluoride. The lap shear specimens were prepared from five finger panels mounted in bonding jigs.

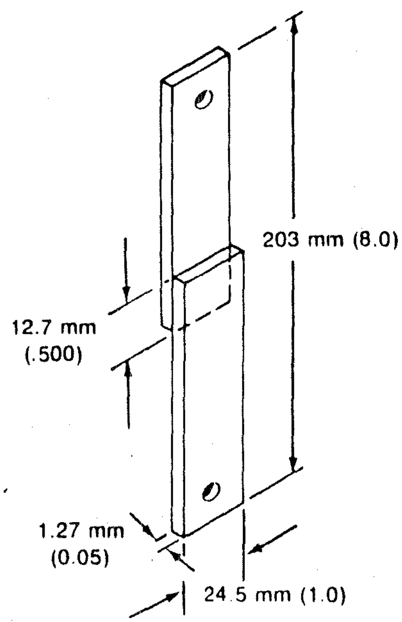


Figure 2.3-1. Titanium (6Al-4V) Adherend Lap Shear Test Specimen

The initial cure cycle (conducted in an autoclave) for X-PPQ was as follows:

1) Heat from ambient temperature to 588K (600°F) at 1-2K per minute.
2) Maintain full vacuum bag pressure + 1.4 MPa (200 psi) throughout cure.
3) Hold at 588K (600°F) for 120 minutes.
4) Cool to 388K (150°F) at 1K per minute before releasing pressure.

A second cure (conducted in a press) was used for the preparation of lap bonds with 30 PHR boron powder and without boron powder additive.

1) Place lap shear specimens (in jigs) in a press without a vacuum bag.
2) Apply 1.4 MPa (200 psi) press pressure.
3) Heat specimens from ambient temperature to 588K (600°F) at 1-2K per minute.
4) Hold at 588K (600°F) for 120 minutes.
5) Cool to 388K (150°F) at 1K per minute before releasing pressure.

In general, the press cured specimens did not perform nearly as well as the autoclave cured specimens (without boron). This is discussed later in the section on lap shear strength determinations.

2.3.2 LARC-TPI Specimens

Surface preparation of titanium adherend was as discussed in Section 2.3.1. The initial cure cycle for LARC-TPI was:

1) Apply full vacuum and 1.4 MPa (200 psi).
2) Heat from ambient temperature to 616K (650°F) at 1-2K per minute.
3) Hold at 616K (650°F) for 60 minutes.
4) Cool to below 388K (150F) and release pressure.

A second cure cycle was used in an attempt to improve thermal properties. The regular cure cycle was completed then followed by a 240 minute dwell at 616K (650°F) while maintaining 1.4 MPa (200 psi) pressure.

2.3.3 ETPS Specimens

Surface preparation of titanium adherend was as discussed in Section 2.3.1 The initial cure cycle for ETPS was:

1) Apply full vacuum plus 1.4 MPa (200 psi).
2) Heat from ambient temperature to 588K (600°F) at 1-2K per minute.
3) Hold at 588K (600°F) for 30 minutes.
4) Cool to below 388K (150°F) and release pressure.

A postcure consisting of 1.4 MPa (200 psi) plus 588K (600°F) for 120 minutes was also evaluated. A second postcure of 1.4 MPa (200 psi) plus 577K (580°F) for 240 minutes was evaluated.

Another cure cycle was conducted as follows:

1) Apply .24 MPa (35 psi) press pressure without vacuum bag.
2) Heat from ambient temperature to 588K (600°F) at 1-2K per minute.
3) Hold at 588K (600°F) for 30 minutes.
4) Cool to 388K (150F) before releasing pressure, cooling rate at 1K per minute.

The press cured lap shear specimens did not perform as well as the autoclave processed specimens in lap shear at ambient and elevated temperature.

2.3.4 X-PI Specimens

Surface preparation of titanium adherend was as discussed in Section 2.3.1. The initial cure cycle for X-PI was:

1) Apply full vacuum and 0.30 MPa (50 psi).
2) Heat from ambient temperature to 498K (437°F) at 1-2K per minute.
3) Hold at 498K (437°F) for 15 minutes.
4) Heat from 498K (437°F) to 548K (527°F) at 1-2K per minute.
5) Hold at 548K (527°F) for 30 minutes.
6) Heat from 548K (527°F) to 573K (572°F) at 1-2K per minute.
7) No hold at 573K (572°F), cool to 388K (150°F) and release pressure.

An additional postcure was evaluated which consisted of 0.34 MPa (50 psi) pressure and 672K (750°F) hold for 240 minutes.

The latter postcure resulted in failure of the chromic acid anodize oxide layer characteristic of previous high temperature cures attempted in other work on this program.

2.4 LAP SHEAR STRENGTH DETERMINATIONS

Lap shear strengths were determined for each of the four adhesive resins using 10 volt chromic acid anodize treated titanium. X-PPQ and LARC-TPI adhesive systems were also evaluated with phosphate fluoride treated titanium. Shear strengths were determined at ambient temperature, 450K (350°F), 505K (450°F), 589K (600°F) and 644K (700°F). Testing at 589K (600°F) and 644K (700°F) was conducted with an induction heater set up as shown in Figures 2.4-1 and 2.4-2.

The data shown in Tables 2.4-1 - 2.4-8 lists initial and 10 minute exposure test results that actually are 2-3 minute and approximately 12 minute exposures. Normal testing procedures allow about a 10 minute soak at the initial test temperature before applying load. However, the test of lap shear specimens in this program requires short soak times to more accurately assess effects of high temperature exposure. The use of induction heating allowed close control of these exposure times. Heat-up rates are extremely fast to minimize degradation of specimen before they reach test temperature.

In addition, the long term 505K (450°F) exposure of LARC-TPI was completed. This work was started in Phase II, Task II - Environmental Exposure Data.

2.4.1 X-PPQ

This resin was processed using autoclave - vacuum bag and press cure without vacuum bag to determine the crosslink dependence upon exposure to air during cure.

Initial Ambient Test

Autoclave cured lap shear specimens prepared using 10 volt CAA (Table 2.4-1) exhibited relatively good strengths of 32.1 MPa (4650 psi) for the initial specimens and 35.9 MPa (5200 psi) for a later set of specimens. The autoclave cured specimens with phosphate fluoride surface treatment (Table 2.4-2)

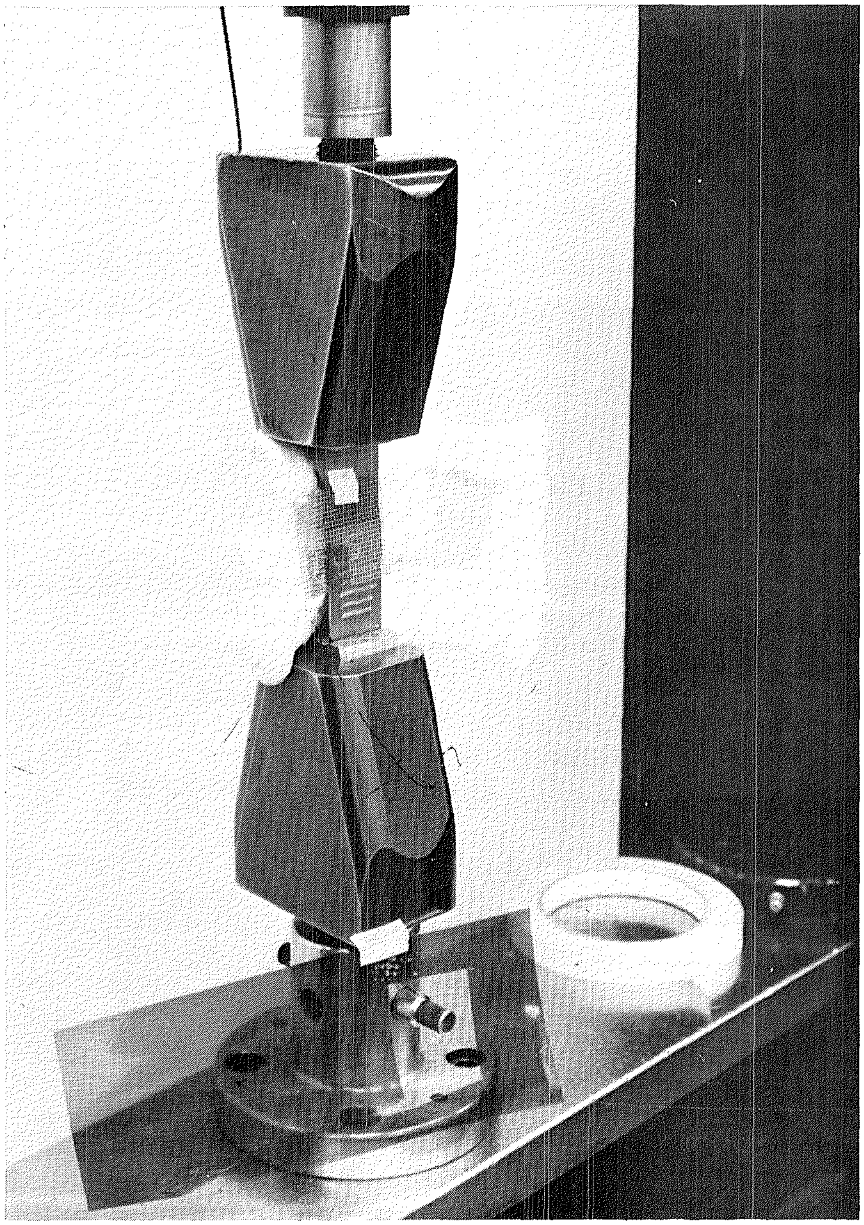


Figure 2.4-1 Lap Shear Specimen Setup for Induction Heating/Test

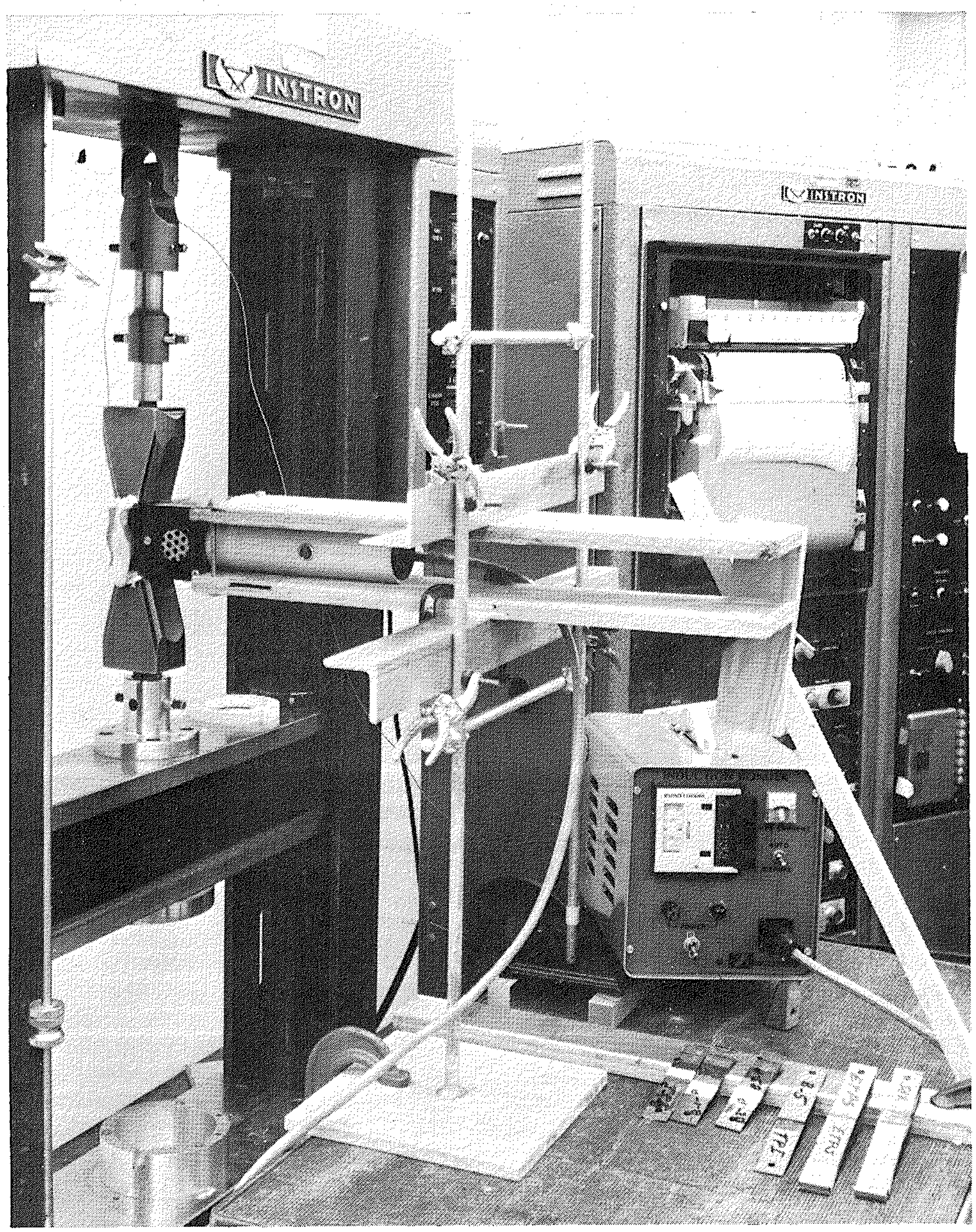


Figure 2.4-2 Induction Heating/Test of Lap Shear Specimen

TABLE 2.4-1

ELEVATED TEMPERATURE TEST RESULTS

LAP SHEAR, Mpa (Psi)

X-PPQ (Ti-Ti/10 VOLT CAA)

	AMBIENT	450K (350F)	505K (450F)	589K (600F)
	INITIAL	INITIAL	INITIAL	INITIAL
	31.3 (4540)	14.8 (2140)	15.9 (2310)	1.0 (150)
	32.8 (4750)	30.8 (4460)	14.9 (2160)	1.6 (230)
	32.2 (4670)	-	-	2.0 (285)
	-	-	-	1.2 (175)
Avg.	32.1 (4650)	22.8 (3300)	15.4 (2240)	1.4 (210)
		10 MINUTES	10 MINUTES	10 MINUTES
		28.0 (4060)	13.7 (1990)	1.8 (260)
		28.6 (4140)	10.3 (1500	4.4 (640)
		28.7 (4160)	9.4 (1360	5.8 (840)
		29.0 (4200)	12.1 (1750)	1.9 (280)
		26.2 (3800)	12.2 (1770)	
Avg.		28.1 (4070)	11.6 (1675)	3.5 (505)
		3000 HRS.	1000 HRS.	10 HRS.
	33.8 (4900)	28.3 (4100)	16.3 (2360)	7.4 (1080)
	34.3 (4980)	28.6 (4150)	12.7 (1840)	6.6 (960)
	38.2 (5540)	25.8 (3740)	9.2 (1340)	8.0 (1160)
	40.1 (5820)	32.7 (4740)	12.6 (1820)	11.9 (1720)
	32.8 (4760)	29.9 (4340)		
Avg.	35.9 (5200)	29.1 (4215)	12.7 (1840)	8.5 (1230)
			3000 HRS.	100 HRS.
			22.8 (3300)	2.9 (416)
			19.3 (2800)	3.8 (556)
			15.7 (2280)	3.8 (556)
			17.2 (2490)	4.1 (594)
			19.3 (2800)	3.6 (520)
Avg.			18.9 (2735)	3.6 (520)
				300 HRS.
				1.5 (220)
				1.7 (244)
				1.8 (264)
				1.4 (210)
				1.5 (220)
Avg.				1.6 (230)

TABLE 2.4-2

ELEVATED TEMPERATURE TEST RESULTS

LAP SHEAR, Psi

X-PPQ (Ti-Ti/PHOSPHATE FLUORIDE)

	AMBIENT	450K (350F)	505K (450F)	589K (600F)	644K (700F)	700K (800F)
	INITIAL	INITIAL	INITIAL	INITIAL	INITIAL	
	20.1 (2910)	25.5 (3700)	15.6 (2170)	2.1 (300)	1.0 (143)	
	22.9 (3320)	26.5 (3840)	12.1 (1760)	0.8 (120)	0.9 (136)	
	24.6 (3560)	25.9 (3760)	15.7 (2280)	0.8 (110)	0.9 (128)	
	22.9 (3320)	27.3 (3960)	14.1 (2040)	1.0 (140)	1.1 (160)	
	23.9 (3460)	27.9 (4040)	16.6 (2400)	1.0 (140)	1.0 (144)	
Avg.	22.8 (3310)	26.6 (3860)	14.7 (2130)	1.1 (160)	1.1 (155)	
		10 MINUTES	10 MINUTES	10 MINUTES	10 MINUTES	10 MINUTES
		16.7 (2420)	14.5 (2100)	2.2 (320)	0.8 (110)	0.6 (86)
		23.9 (3460)	16.9 (2440)	1.0 (140)	0.9 (125)	0.5 (66)
		23.6 (3420)	12.0 (1740)	1.1 (160)	0.8 (115)	0.7 (100)
		22.5 (3260)	11.6 (1680)	1.8 (260)	0.8 (110)	0.6 (90)
		24.5 (3550)	17.7 (2560)	4.1 (600)	0.9 (125)	0.6 (90)
Avg.		22.2 (3221)	14.5 (2106)	2.1 (300)	0.8 (115)	0.6 (85)
		1000 HRS.	1000 HRS.	10 HRS.	1 HR.	
		18.1 (2630)	22.8 (3300)	3.0 (440)	1.1 (165)	
		16.1 (2330)	19.0 (2750)	4.1 (600)	1.1 (155)	
		20.1 (2920)	19.1 (2770)	8.1 (1180)	1.4 (210)	
		17.1 (2490)	16.3 (2360)	8.6 (1250)	1.4 (200)	
		23.9 (3460)	16.1 (2330)	7.0 (1020)	1.4 (200)	
Avg.		19.2 (2780)	18.6 (2700)	6.2 (900)	1.3 (185)	
		3000 HRS.	3000 HRS.	100 HRS.	10 HRS.	
		21.0 (3040)	18.6 (2700)	4.4 (640)	1.0 (148)	
		14.3 (2080)	25.5 (3708)	8.1 (1180)	1.3 (186)	
		21.0 (3050)	29.6 (4300)	8.8 (1280)	0.9 (128)	
		22.1 (3200)	29.0 (4200)	6.3 (910)	1.1 (160)	
		16.3 (2360)	23.1 (3350)	10.2 (1480)	1.0 (144)	
Avg.		18.9 (2745)	25.2 (3650)	7.6 (1100)	1.1 (155)	
				300 HRS.	50 HRS.	
				0.9 (132)	0.5 (75)	
				1.1 (164)	0.8 (120)	
				1.2 (174)	0.8 (115)	
				1.7 (242)	0.8 (110)	
				1.9 (280)	0.5 (75)	
Avg.				1.3 (190)	0.7 (100)	

produced lower shear strengths which averaged 22.8 MPa (3310 psi). A third set of test specimens prepared in a press without a vacuum bag (Table 2.4-3) produced values at ambient temperature of 25.9 MPa (3750 psi). Table 2.4-4 lists the test values obtained with 30 PHR boron filled X-PPQ cured in a press without a vacuum bag. Ambient temperature test values were 33.9 MPa (4920 psi). All ambient temperature tested specimens failed cohesively.

450K (350°F) Exposure and Test

Vacuum bag—autoclave cured 10 volt CAA and phosphate fluoride specimens were tested at 450K (350°F). The initial values at 450K on phosphate fluoride as shown in Table 2.4-2 are higher than those obtained at ambient temperature. This apparent discrepancy is due to the testing of two separate batches of specimens. The initial ambient temperature tests were conducted on "first try" processed panels. A later batch of specimens was prepared and tested at the remaining elevated temperatures. In the case of 450K, the values appeared higher than the initial ambient temperature results due to the fact that different specimen cure batches were involved.

The extended (3000 hours) exposure to 450K (350°F) for both 10 volt CAA and phosphate fluoride produced no drop in lap shear strengths from prior 1000 hour exposure data. All shear failures were cohesive.

505K (450°F) Exposure and Test

Thermal performance of X-PPQ at 505K (450°F) was evaluated for both 10 volt CAA and phosphate fluoride specimens. Phosphate fluoride prepared specimens exhibited significantly higher shear values after 1000 hours exposure than 10 volt CAA treated specimens. The press cured specimens (both filled and unfilled) produced cohesive failures at 12.6 MPa (1820 psi) and 12.7 MPa (1840 psi) respectively (initial tested only). These results indicated that to 505K (450°F), X-PPQ performed well with phosphate fluoride surface treatment cured by an autoclave-vacuum bag process. The 3000 hour aged specimens show a significant increase in strength over the 1000 hour specimens as shown in Tables 2.4-1 and 2.4-2. This increase in strength is attributed to crosslinking of the polymer. The 25.2 MPa (3650 psi) values obtained on phosphate fluoride are considered good structural bonds. Process studies to tailor postcure parameters for improvement in initial exposed

TABLE 2.4-3

ELEVATED TEMPERATURE TEST RESULTS OF NON-BAG PRESS CURED X-PPQ (Ti-Ti/10 Volt CAA)

Coupon No.	Bondline Thickness, mm (inches)	Test Temperature, K (°F)	Lap Shear Strength, MPa (Psi)	Failure Mode
A-26	0.17 (0.0065)	Ambient	23.9 (3,460)	Cohesive
A-27	0.19 (0.0075)	Ambient	22.9 (3,320)	Cohesive
A-28	0.19 (0.0075)	Ambient	27.2 (3,940)	Cohesive
A-29	0.18 (0.0070)	Ambient	29.5 (4,280)	Cohesive
Average	--	—	25.9 (3,750)	
A-30	0.14 (0.0055)	505 (450)	16.3 (2,360)	Cohesive
A-31	0.13 (0.0050)	505 (450)	9.2 (1,340)	Cohesive
A-32	0.13 (0.0050)	505 (450)	9.2 (1,340)	Cohesive
A-33	0.13 (0.0050)	505 (450)	12.6 (1,820)	Cohesive
Average	--	-	12.7 (1,840)	
A-34	0.13 (0.0050)	589 (600)	1.0 (150)	Adhesive
A-35	0.15 (0.0060)	589 (600)	1.6 (230)	Adhesive
A-36	0.17 (0.0065)	589 (600)	2.0 (285)	Adhesive
A-37	0.17 (0.0065)	589 (600)	1.2 (175)	Adhesive
Average	--	-	1.4 (210)	

A-36

Not tested at 644K (700°F) and 700K (800°F) due to previous low test values at 589K (600°F)

A-45

Elevated temperature for testing was achieved with an induction heater.

TABLE 2.4-4

ELEVATED TEMPERATURE TEST RESULTS OF 30 PHR BORON FILLED X-PPQ*
(Ti-Ti/10 Volt CAA)

Coupon No.	Bondline Thickness, mm (inches)	Test Temperature, K (°F)	Lap Shear Strength, MPa (Psi)	Failure Mode
A/B-1	0.10 (0.0040)	Ambient	35.9 (5,200)	Cohesive
A/B-2	0.11 (0.0042)	Ambient	34.8 (5,040)	Cohesive
A/B-3	0.09 (0.0035)	Ambient	32.6 (4,720)	Cohesive
A/B-4	0.11 (0.0045)	Ambient	32.4 (4,700)	Cohesive
Average	--	—	33.9 (4,920)	
A/B-5	0.14 (0.0055)	505 (450)	16.1 (2,340)	Cohesive
A/B-6	0.15 (0.0060)	505 (450)	13.4 (1,940)	Cohesive
A/B-7	0.15 (0.0060)	505 (450)	11.3 (1,640)	Cohesive
A/B-8	0.14 (0.0055)	505 (450)	9.4 (1,360)	Cohesive
Average			12.6 (1,820)	
A/B-9	0.13 (0.0050)	589 (600)	1.5 (215)	Adhesive
A/B-10	0.09 (0.0035)	589 (600)	1.6 (235)	Adhesive
A/B-11	0.13 (0.0050)	589 (600)	1.9 (270)	Adhesive
A/B-12	0.10 (0.0040)	589 (600)	1.1 (160)	Adhesive
Average	--	—	1.5 (220)	

A/B-13

Not tested at 644K (700°F) and 700K (800°F) due to previous low test values at 589K (600°F)

A/B-20

*Press cured without bag - Elevated temperature for testing was achieved with an induction heater.

strength values was not attempted on this program. All failures were cohesive at this temperature.

589K (600°F) Exposure and Test

The lap shear specimens tested at 589K (600°F) exhibited thermoplastic failure. That is, the bond failed by extreme adhesive film distortion at this higher temperature. No failure of the titanium surface preparation was apparent. The test values tended to increase with exposure time indicating that some additional crosslinking (raising the Tg) was occurring.

For both the 10 volt CAA and phosphate fluoride autoclave processed test specimens there was an initial very low shear strength at 589K (600°F) of 1.4 MPa (200 psi). As the exposure progressed to 300 hours there was a peak value encountered at 100 hours for phosphate fluoride 7.6 MPa (1100 psi) and a peak value at 10 hours for 10 volt CAA 8.5 MPa (1230 psi). The 300 hour values were again in the range ~ 1.4 MPa (200 psi). This indicates that a proper postcure, that is, one specifically tailored for a short time at high temperature 505K (450°F) can improve shear strength to significantly above that shown for no special postcure. All tests at 589K (600°F) and above were conducted using an induction heater.

644K (700°F) Exposure and Test

As with the 589K (600°F) tested specimens, failure at 644K (700°F) was primarily through a thermoplastic mode. Tests at this temperature were conducted with phosphate fluoride prepared specimens only. A measurable strength 0.7 MPa (100 psi) was found as shown in Table 2.4-3. Without additional postcure studies or other means to improve crosslinking, this system could not be used for 644K (700°F) exposure service conditions.

700K (800°F) Exposure and Test

One set of test specimens with phosphate fluoride surface treatment were evaluated after 10 minutes exposure to 700K (800°F). The test average was a measurable 0.6 MPa (85 psi), far below that considered structural.

2.4.2 LARC-TPI

Stressed environmental exposure data from Phase II, Task II is summarized in Table 2.4-5. The stressed lap shear data displayed very little change from initial data through 5000 hours aging at 219K (-65°F) and ambient exposure and test conditions. Specimens exposed and tested at 505K (450°F) showed an increase in shear strength after 1000 hours of aging and then started to show a small decrease after 5000 hours. The increase in strength after 1000 hours is probably due to crosslinking of the polymer. Initial low test values were the result of insufficient post-cure of the specimens for 505K (450°F) testing and exposure. Apparently, the 1000 hour aging provided the necessary post-cure for the specimens.

The average of five LARC-TPI unstressed lap shear specimens exposed at 505K (450°F) for 9500 hours and tested at 505K (450°F) was 20.7 MPa (3000 psi). See Table 2.4-6 and Figure 2.4-3. The unstressed lap shear specimens at 9500 hours compared favorably with the 5000 hour specimens (21.7 MPa, 3140 psi) indicating no problems at 505K (450°F) with the adhesive or adherend surface preparation. Phase III PAA treated specimens that were aged at 450K (350°F) and tested at 450K (350°F) after 1000 hours showed a significant increase in shear strength from the initial tested specimens. Again, this increase was due to a post-cure effect prior to testing at 505K (450°F) elevated temperature. This same condition is true with specimens aged and tested at 589K (600°F). An increase in shear strength from 1.8 MPa - 7.6 MPa was noted for specimens aged 10 minutes and 100 hours at 589K (600°F), respectively. These data are reported in Table 2.4-6. The failures were cohesive for ambient and 10 minutes at 589K (600°F) test but exhibited 85-95% cohesive failure for the longer aging tests.

Lap shear specimens bonded with phosphate fluoride surface treatment failed at much lower shear strengths than the CAA specimens. However, the trend of the data was similar to the CAA. The data is summarized in Tables 2.4-7 and 2.4-8.

TABLE 2.4-5

PHASE II STRESSED THERMAL AGING—LARC-TPI INDIVIDUAL TEST VALUES — LAP SHEAR

Stress Percent of Ultimate	Stress Load		Exposure & Test Temperature		Initial		1000 Hours		3000 Hours		5000 Hours	
	MPa	psi	K	(°F)	MPa	psi	MPa	psi	MPa	psi	MPa	psi
25	8.28	(1200)	219	(-65)			29.4	(4260)	35.9	(5120)	32.5	(4710)
25	8.28	(1200)	219	(-65)	*		33.6	(4880)	35.2	(5100)	30.9	(4480)
25	8.28	(1200)	219	(-65)			35.9	(5200)	31.3	(4540)	30.3	(4400)
Average					32.8	(4760)	34.0	(4780)	33.9	(4920)	31.2	(4530)
30	10.3	(1500)	219	(-65)			35.2	(5100)	33.9	(4290)	31.8	(4610)
30	10.3	(1500)	219	(-65)	*		36.1	(5240)	31.6	(4580)	30.9	(4480)
30	10.3	(1500)	219	(-65)			31.0	(4500)	30.5	(4420)	29.0	(4210)
Average					32.8	(4760)	34.1	(4950)	32.0	(4640)	30.6	(4430)
25	8.28	(1200)	Ambient				33.2	(4820)	29.6	(4300)	31.8	(4160)
25	8.28	(1200)	Ambient		*		29.5	(4280)	27.6	(4010)	27.3	(3960)
25	8.28	(1200)	Ambient				28.0	(4060)	27.7	(4020)	29.5	(4280)
Average					29.7	(4310)	30.3	(4390)	28.3	(4110)	28.5	(4130)
30	10.3	(1500)	Ambient				27.4	(3980)	28.0	(4060)	27.2	(3940)
30	10.3	(1500)	Ambient		*		32.6	(4720)	30.0	(4350)	24.8	(3600)
30	10.3	(1500)	Ambient				30.1	(4360)	30.6	(4430)	29.4	(4260)
Average					29.7	(4310)	30.0	(4350)	29.5	(4280)	27.1	(3930)
25	5.1	(740)	505	(450)			21.7	(3150)	20.6	(2980)	12.6	(1820)
25	5.1	(740)	505	(450)	*		22.3	(3240)	22.3	(3240)	20.2	(2930)
25	5.1	(740)	505	(450)			23.4	(3390)	18.1	(2620)	15.7	(2280)
Average					14.8	(2150)	22.5	(3260)	20.3	(2950)	16.1	(2340)
50	10.2	(1480)	505	(450)			19.8	(2870)	22.2	(3220)	18.3	(2660)
50	10.2	(1480)	505	(450)	*		24.8	(3600)	17.8	(2580)	17.1	(2480)
50	10.2	(1480)	505	(450)			21.5	(3120)	24.1	(3490)	18.9	(2740)
Average					14.8	(2150)	22.1	(3200)	21.4	(3100)	18.6	(2690)

* Average obtained from initial unstressed lap shear data.

TABLE 2.4-6

PHASE II UNSTRESSED THERMAL AGING — LARC-TPI INDIVIDUAL TEST VALUES — LAPSHEAR

Initial Values

	219K (-65°F)		Ambient		422K (300°F)		505K (450°F)		533K (500°F)	
	MPa	Psi	MPa	Psi	MPa	Psi	MPa	Psi	MPa	Psi
	34.8	(5040)	32.1	(4660)	21.9	(3180)	13.5	(1960)	6.6	(960)
	36.0	(5220)	33.4	(4840)	22.0	(3190)	15.8	(2290)	4.3	(630)
	32.3	(4680)	28.3	(4100)	21.6	(3130)	11.1	(1610)	7.0	(1010)
	33.5	(4860)	26.2	(3800)	26.2	(3800)	15.4	(2240)	6.9	(1000)
	34.8	(5040)	26.2	(3800)	24.8	(3590)	18.1	(2620)	7.8	(1130)
	33.8	(4900)	28.8	(4180)	21.6	(3130)	16.0	(2320)	8.0	(1160)
	28.6	(4140)	30.1	(4360)	22.1	(3200)	12.7	(1840)	9.0	(1310)
	31.0	(4500)	31.7	(4600)	22.1	(3210)	13.2	(1920)	7.6	(1100)
	30.5	(4420)	30.3	(4400)	26.3	(3810)	17.1	(2480)	6.2	(900)
	32.9	(4770)	29.8	(4320)	27.6	(4010)	15.0	(2180)	6.7	(980)
Average	32.8	(4760)	29.7	(4310)	23.6	(3420)	14.8	(2150)	7.0	(1020)

1000 Hours Aging at 505K (450°F)

	MPa	Psi	MPa	Psi	MPa	Psi	MPa	Psi
	30.6	(4430)	24.6	(3560)	23.2	(3370)	19.4	(2810)
	32.0	(4640)	24.1	(3500)	25.0	(3630)	20.6	(2990)
	31.6	(4580)	25.1	(3640)	25.9	(3760)	18.6	(2700)
	29.7	(4310)	25.2	(3650)	20.1	(2920)	20.7	(3000)
	33.6	(4880)	24.6	(3970)	22.2	(3220)	19.4	(2810)
Average	31.5	(4570)	25.2	(3660)	23.3	(3380)	19.7	(2860)

2000 Hours Aging at 505K (450°F)

	MPa	Psi	MPa	Psi	MPa	Psi	MPa	Psi
	28.6	(4140)	27.1	(3930)	16.4	(2380)	21.7	(3150)
	28.7	(4160)	26.1	(3780)	23.9	(3470)	22.6	(3280)
	28.6	(4140)	25.2	(3660)	25.9	(3760)	19.0	(2750)
	28.4	(4120)	23.2	(3360)	18.5	(2680)	22.7	(3290)
	25.8	(3740)	20.3	(2940)	22.2	(3220)	17.6	(2560)
Average	28.0	(4060)	24.3	(3530)	21.4	(3100)	20.8	(3010)

TABLE 2.4-6

PHASE II UNSTRESSED THERMAL AGING — LARC-TPI
INDIVIDUAL TEST VALUES — LAPSHEAR (Cont.)

5000 Hours Aging at 505K (450°F)

	219K (-65°F)		Ambient		422K (300°F)		505K (450°F)	
	MPa	Psi	MPa	Psi	MPa	Psi	MPa	Psi
	30.8	(4460)	28.3	(4100)	27.6	(4000)	23.6	(3420)
	29.2	(4240)	28.8	(4170)	24.9	(3610)	23.6	(3430)
	32.4	(4700)	27.0	(3910)	28.3	(4100)	17.6	(2560)
	32.6	(4720)	27.6	(4000)	27.0	(3920)	21.1	(3060)
	28.3	(4100)	29.2	(4230)	24.7	(3580)	22.3	(3230)
Average	30.6	(4440)	28.1	(4080)	26.5	(3840)	21.6	(3140)

9500 Hours Aging at 505K (450°F)

	MPa	Psi
	18.0	(2610)
	21.0	(3050)
	17.3	(2510)
	25.0	(3620)
	22.1	(3200)
Average	20.7	(3000)

PHASE II UNSTRESSED THERMAL
EXPOSURE, LARC-TPI

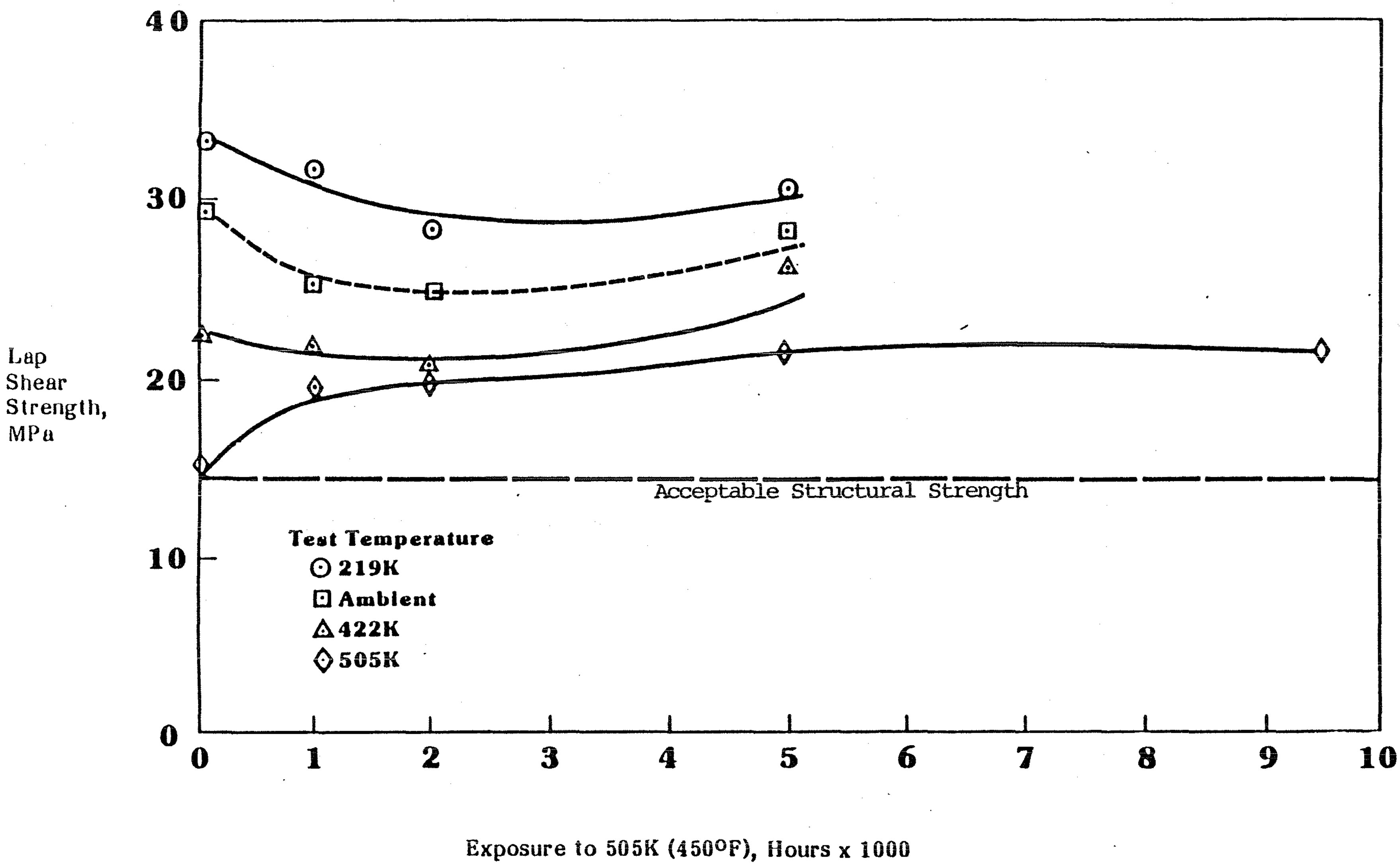


Figure 2.4-3

TABLE 2.4-7

ELEVATED TEMPERATURE TEST RESULTS

LAP SHEAR, Mpa (Psi)

LARC-TPI (Ti-Ti/10 VOLT CAA)

	AMBIENT	450K (350F)	505K (450F)	589K (600F)
	INITIAL	INITIAL	INITIAL	INITIAL
	22.5 (3260)	23.2 (3370)	9.7 (1410)	27.2 (3940)
	24.0 (3480)	21.2 (3080)	12.8 (1860)	27.6 (4000)
	22.4 (3250)	-	-	32.6 (4720)
	-	-	-	31.4 (4560)
	-	-	-	29.2 (4240)
Avg.	23.0 (3330)	22.2 (3220)	11.3 (1640)	29.6 (4290)
		10 MINUTES		10 MINUTES
	27.2 (3940)	24.1 (3500)		1.1 (160)
	27.6 (4000)	22.1 (3200		4.0 (576)
	32.6 (4720)	27.6 (4000)		1.2 (180)
	31.4 (4560)	26.5 (3840)		0.9 (130)
	29.2 (4240)	-		No Test
Avg.	29.6 (4290)	25.1 (3635)		1.8 (260)
		1000 HRS.		10 HRS.
		26.3 (3820)		0.7 (100)
		23.7 (3440)		2.5 (360)
		27.0 (3920)		3.1 (450)
		25.0 (3620)		2.9 (420)
		29.0 (4200)		
Avg.		26.2 (3800)		2.3 (330)
		3000 HRS.		100 HRS.
		24.8 (3600)		1.4 (200)
		26.2 (3800)		6.6 (960)
		23.5 (3400)		12.8 (1860)
		27.6 (4000)		10.5 (1520)
		20.1 (2920)		6.9 (1000)
Avg.		24.5 (3545)		7.6 (1110)
				672 HRS.
				3.2 (470)
				2.8 (400)
				3.0 (440)
				3.0 (430)
				- -
Avg.				3.0 (430)

TABLE 2.4-8

ELEVATED TEMPERATURE TEST RESULTS

LAP SHEAR, MPa (Psi)

LARC-TPI (Ti-Ti/PHOSPHATE FLUORIDE)

	AMBIENT	450K (350F)	505K (450F)	589K (600F)
	INITIAL	INITIAL	INITIAL	INITIAL
	9.9 (1440)	17.5 (2540)	18.2 (2640)	0.6 (90)
	10.9 (1580)	19.0 (2760)	18.1 (2620)	0.6 (90)
	12.4 (1800)	16.8 (2440)	14.6 (2120)	0.8 (110)
	10.5 (1520)	17.0 (2460)	17.4 (2620)	1.0 (140)
	11.2 (1630)	12.8 (1850)	17.1 (2480)	0.8 (110)
Avg.	11.0 (1590)	16.6 (2410)	17.1 (2480)	0.8 (110)
		10 MINUTES		10 MINUTES
		18.0 (2610)		0.6 (80)
		18.8 (2720)		1.4 (200)
		19.2 (2790)		4.4 (640)
		18.9 (2740)		0.8 (120)
		19.9 (2885)		4.6 (660)
Avg.		19.0 (2750)		2.3 (340)
		1000 HRS.		10 HRS.
		16.3 (2370)		4.4 (640)
		18.2 (2640)		4.7 (680)
		14.6 (2110)		2.5 (360)
		15.7 (2280)		5.8 (840)
		11.2 (1620)		5.5 (800)
Avg.		15.2 (2200)		4.6 (660)
		3000 HRS.		100 HRS.
		12.8 (1850)		6.6 (950)
		12.1 (1760)		5.0 (720)
		10.8 (1560)		6.7 (970)
		12.7 (1840)		6.1 (880)
		12.1 (1760)		5.0 (720)
Avg.		12.1 (1755)		5.9 (850)
				300 HRS.
				4.3 (622)
				5.1 (742)
				3.7 (540)
				2.0 (290)
				3.1 (444)
Avg.				3.6 (523)

2.4.3 ETPS

Lap shear strength of CAA bonded ETPS specimens was good at ambient temperatures. However, when specimens were tested at elevated temperatures from 450K (350°F) to 589K (600°F) the strength dropped significantly (Table 2.4-8). These specimens failed 100% cohesively.

In an effort to alleviate the low shear strength problem, a new batch of specimens were bonded in the press without a bag in hope of increasing the crosslink density of the polymer. The test results in Table 2.4-9 shows that improved thermal performance did not occur. The failure modes of the press cured specimens were cohesive.

Early NASA Langley work reported respectable ETPS lap shear strength of 16.9 MPa (2445 psi) at 450K (350°F) (ref. 2). Since our work on ETPS failed to provide similar performance it was important to determine the reason for this difference. In discussions with NASA Langley researchers, it was disclosed that the ETPS involved in the early NASA work was prepared by a multi-step synthesis where a bromo-terminated polysulfone was converted to an ethynyl-terminated polysulfone (ETPS) using a palladium catalyst. A significant amount of palladium remained in the ETPS. NASA found that palladium effects the cure of ETPS, providing a cured material with a higher Tg and better solvent resistance than that from ETPS containing little or no palladium. The NASA supplied ETPS used in our work was made by a direct route where hydroxy-terminated polysulfone was reacted with 4-ethynylbenzoyl chloride to yield ETPS. This route provided an essentially palladium free ETPS. Although not conclusive, it appears that the difference in adhesive performance at 450K (350°F) was due to the palladium content which effects the cure chemistry. In addition, the ETPS supplied by NASA for our evaluation may not have been properly end-capped with acetylanic groups.

TABLE 2.4-9

ELEVATED TEMPERATURE TEST RESULTS OF AUTOCLAVE CURED ETPS

LAP SHEAR, Mpa (Psi)

(Ti-Ti/10 VOLT CAA)

	AMBIENT	450K (350F)	505K (450F)	589K (600F)
	INITIAL	INITIAL	INITIAL	INITIAL
	32.4 (4700)	10.6 (1540)	1.0 (140)	-
	31.9 (4620)	8.3 (1200)	0.4 (60)	-
	29.9 (4340)	8.1 (1180)	0.6 (80)	-
	28.8 (4180)	5.0 (730)	0.3 (40)	-
	32.4 (4700)	9.3 (1350)	0.3 (40)	-
Avg.	31.1 (4510)	8.3 (1200)	0.5 (70)	
		10 MINUTES	10 MINUTES	10 MINUTES
	25.1 (3640)	0.3 (44)	1.2 (180)	-
	34.9 (5060)	4.8 (700)	2.0 (290)	-
	37.7 (5400)	7.4 (1080)	2.8 (400)	-
	35.3 (5120)	3.1 (450)	0.7 (100)	-
	29.0 (4200)	2.8 (400)	0.7 (100)	-
Avg.	32.3 (4680)	3.7 (535)	1.5 (215)	
		1000 HRS.	1000 HRS.	10 HRS.*
		4.2 (610)	3.3 (480)	0.8 (110)
		4.4 (640)	7.3 (1060)	1.0 (140)
		4.6 (660)	7.8 (1125)	1.8 (260)
		4.4 (640)	1.3 (190)	2.1 (300)
		5.2 (750)	1.0 (150)	4.1 (600)
Avg.		4.5 (650)	4.1 (585)	1.9 (280)
		3000 HRS.	3000 HRS.	
		5.8 (840)	5.2 (760)	
		5.9 (860)	4.7 (680)	
		10.1 (1460)	6.5 (940)	
		6.1 (890)	7.3 (1060)	
		7.5 (1080)	5.5 (795)	
Avg.		7.1 (1025)	5.8 (845)	

*These specimens were run to determine possible additional crosslinking.

TABLE 2.4-10

ELEVATED TEMPERATURE TEST RESULTS OF PRESS CURED ETPS (Ti-Ti/10 Volt CAA)

Coupon No.	Bondline Thickness, mm (inches)	Test Temperature, K (°F)	Lap Shear Strength, MPa (Psi)	Failure Mode
C-26	0.13 (0.0050)	Ambient	25.1 (3,640)	Cohesive
C-27	0.10 (0.0040)	Ambient	34.9 (5,060)	Cohesive
C-28	0.09 (0.0035)	Ambient	37.2 (5,400)	Cohesive
C-29	0.08 (0.0030)	Ambient	35.3 (5,120)	Cohesive
C-30	0.09 (0.0035)	Ambient	29.0 (4,200)	Cohesive
Average	--	—	32.3 (4,680)	
C-31	0.08 (0.0030)	450 (350)	3.8 (555)	Cohesive
C-32	0.08 (0.0030)	450 (350)	4.6 (660)	Cohesive
C-33	0.06 (0.0025)	450 (350)	4.3 (630)	Cohesive
C-34	0.06 (0.0025)	450 (350)	5.3 (775)	Cohesive
C-35	0.08 (0.0030)	450 (350)	3.3 (485)	Cohesive
Average	--	—	4.3 (620)	
C-36	0.08 (0.0030)	505 (450)	0.3 (45)	Cohesive
C-37	0.05 (0.0020)	505 (450)	0.3 (50)	Cohesive
C-38	0.06 (0.0025)	505 (450)	0.3 (40)	Cohesive
C-39	0.06 (0.0025)	505 (450)	0.3 (50)	Cohesive
C-40	0.06 (0.0025)	505 (450)	0.3 (45)	Cohesive
Average	--	—	0.3 (45)	

Elevated temperature for testing was achieved with an induction heater.

TABLE 2.4-11

ELEVATED TEMPERATURE TEST RESULTS

LAP SHEAR, Mpa (Psi)

X-PI (Ti-Ti/10 VOLT CAA)

	AMBIENT	450K (350F)	505K (450F)	589K (600F)	644K (700F)
	INITIAL	INITIAL			
	16.9 (2450)	16.3 (2360)			
	16.3 (2370)	16.3 (2360)			
	17.9 (2600)	16.1 (2340)			
	18.3 (2660)	15.0 (2170)			
	17.6 (2560)	16.0 (2320)			
Avg.	17.4 (2530)	15.9 (2310)			
		10 MINUTES	10 MINUTES		
	14.8 (2140)	11.8 (1704)	14.5 (2100)		
	17.4 (2520)	15.2 (2200)	15.4 (2240)		
	16.1 (2340)	16.4 (2380)	15.7 (2270)		
	15.9 (2300)	14.6 (2120)	14.1 (2040)		
	14.2 (2060)	14.6 (2120)	13.5 (1960)		
Avg.	15.7 (2270)	14.5 (2105)	14.6 (2120)		
		1000 HRS.	1000 HRS.		
	15.8 (2290)	13.1 (1900)	11.9 (1720)		
	16.3 (2370)	15.0 (2170)	12.5 (1815)		
	16.1 (2340)	12.2 (1770)	12.6 (1830)		
	15.0 (2290)	13.5 (1960)	12.3 (1780)		
	16.0 (2360)	13.1 (1900)	-		
Avg.	16.1 (2330)	13.4 (1940)	12.3 (1785)		
		3000 HRS.	3000 HRS.	100 HRS.	10 HRS.
		16.8 (2440)			
		12.4 (1800)	9.8 (1420)	13.4 (1950)	10.1 (1465)
		14.8 (2150)	9.6 (1390)	13.4 (1930)	11.2 (1625)
		13.0 (1890)	8.6 (1250)	13.8 (2000)	9.5 (1380)
		13.0 (1890)	9.8 (1420)	12.7 (1840)	11.1 (1615)
Avg.		14.0 (2035)	9.5 (1370)	13.3 (1930)	10.5 (1520)
					50 HRS.
					*Failed
					2.0 (295)
					1.8 (255)
					1.9 (275)
Avg.					1.9 (275)

2.4.4 X-PI

The lap shear strength of CAA bonded X-PI specimens was not significantly changed when tested at ambient temperature through 505K (450°F). Specimens that were thermally aged for 1000 hours each at 450K (350°F) and 505K (450°F) and tested at these temperatures displayed a slight loss in shear strength (Table 2.4-10). After 100 hours at 589K (600°F), the shear strengths were approximately 13.3 MPa (1930 psi). Specimens that were thermally aged at 644K (700°F) for 10 hours exhibited shear strength of 10.5 MPa (1520 psi). A very significant drop in shear stress was noted after 50 hours at 644K. These results are also summarized in Table 2.4-10. All X-PI failures were 95-100% cohesive.

2.5 MOISTURE RESISTANCE DETERMINATIONS

Lap shear specimens for each adhesive system on CAA surface titanium were exposed in a humidity environment of 322K/95% relative humidity. Test results for these systems are reported in Table 2.5-1.

2.5.1 X-PPQ

X-PPQ bonded specimens were affected slightly by humidity exposure. A 20% reduction in lap shear strength was seen (Table 2.5-1) after 1000 hours exposure with the failure mode changing from 100 cohesive initially to approximately 95% cohesive failure after 100 hours.

2.5.2 LARC-TPI

LARC-TPI bonded specimens showed a 18% decrease in shear strength after 1000 hours of exposure to humidity. However, with the decrease in shear strength, the failure mode was 100% cohesive. The color of the adhesive did not change in the environment.

2.5.3 ETPS

The conditioning of ETPS in the humidity chamber reduced the lap shear strength of ETPS bonded specimens by 30% after 1000 hours of exposure. The failures remained 100% cohesive.

TABLE 2.5-1

MOISTURE RESISTANCE TEST RESULTS (322K/95% RH)

LAP SHEAR, Mpa (Psi)

Ti-Ti/10 VOLT CAA

Exposure Time, Hours	X-PPQ		LARC-TPI		ETPS		X-PI	
0	33.8	(4900)	27.2	(3940)	19.7	(2890)	14.8	(2140)
0	34.3	(4980)	27.6	(4000)	25.3	(3670)	17.4	(2520)
0	38.2	(5540)	32.6	(4720)	24.6	(3560)	16.1	(2340)
0	40.1	(5820)	31.4	(4560)	25.1	(3640)	15.9	(2300)
0	32.8	(4760)	29.2	(4240)	24.6	(3560)	14.2	(2060)
Average	35.9	(5200)	29.6	(4290)	23.8	(3480)	15.7	(2270)
1000	27.0	(3900)	26.5	(3840)	17.1	(2840)	12.1	(1760)
1000	27.6	(4000)	22.9	(3320)	17.0	(2460)	13.0	(1880)
1000	29.7	(4300)	24.8	(3600)	16.1	(2330)	10.6	(1540)
1000	30.3	(4400)	21.7	(3150)	16.8	(2440)	14.1	(2040)
1000	28.3	(4100)	24.8	(3600)	16.8	(2440)	13.0	(1890)
Average	28.6	(4140)	24.1	(3500)	16.8	(2435)	12.6	(1820)
2000	24.8	(3600)	23.7	(3440)	13.4	(1940)	12.7	(1840)
2000	20.3	(2940)	21.4	(3100)	15.9	(2300)	13.0	(1880)
2000	25.9	(3760)	24.0	(3480)	16.8	(2440)	12.4	(1800)
2000	25.9	(3760)	21.6	(3140)	15.4	(2240)	15.6	(2260)
2000	26.9	(3900)	24.4	(3540)	13.4	(1950)	13.4	(1940)
Average	24.8	(3590)	23.0	(3340)	15.0	(2170)	13.4	(1944)

TABLE 2.5-2

MOISTURE RESISTANCE TEST RESULTS (322K/95% RH)

LAP SHEAR, Mpa (Psi)

Ti-Ti/Phosphate Fluoride

Exposure Time, Hours	X-PPQ	LARC-TPI
0	15.1 (2910)	
0	22.9 (3320)	No
0	24.6 (3560)	Data
0	22.9 (3320)	
0	23.9 (3460)	
Average	22.8 (3310)	
1000	2.76 (400)	21.4 (3100)
1000	5.10 (740)	16.6 (2400)
1000	4.96 (720)	14.5 (2100)
1000	4.07 (590)	16.3 (2360)
1000	6.07 (880)	16.0 (2320)
Average	4.62 (670)	17.0 (2460)
2000	4.7 (680)	14.4 (2090)
2000	4.5 (650)	16.7 (2418)
2000	5.9 (860)	15.7 (2280)
2000	3.9 (570)	15.4 (2240)
2000	5.3 (770)	14.2 (2060)
Average	5.0 (720)	15.3 (2220)

2.5.4 X-PI

A 20% reduction was observed in lap shear strength of X-PI bonded specimens after exposure to 322K/95% relative humidity. The failure mode of the specimens remained 100% cohesive after exposure. There appeared to be no color change in the adhesive after exposure.

2.6 SKYDROL RESISTANCE TESTING

Lap shear specimens for each adhesive system on CAA treated titanium were immersed in Skydrol in both the stress and unstressed conditions. The stressed specimens were stressed at 25% of their ultimate. Stressed levels were calculated as follows:

X-PPQ = [40 MPa (5800 psi) x 0.25 x 322 mm^2 (0.5 $in.^2$)] = 3225N (725 lbs)*
LARC-TPI = [32.1 MPa (4650 psi) x 0.25 x 322 mm^2 (0.5 $in.^2$)] = 2548N (581 lbs)
ETPS = [31.1 MPa (4510 psi) x 0.25 x 322 mm^2 (0.5 $in.^2$)] = 2504N (563 lbs)
X-PI = [16.8 MPa (2430 psi) x 0.25 x 322 mm^2 (0.5 $in.^2$)] = 1348N (303 lbs)

*The stress levels for X-PPQ were erroneously calculated from lap shear specimens that produced the highest ambient strength values obtained instead of being calculated from the ambient values obtained from the set of specimens subjected to stressed Skydrol. As a result, stress levels 25% of ultimate were placed upon X-PPQ specimens.

2.6.1 X-PPQ

X-PPQ lap shear strength was not significantly affected by exposure to Skydrol in both the stressed and unstressed conditions. The lap shear strength did not seem to decrease with time in aging under both conditions. Test results are presented in Tables 2.6-1 and 2.6-2. The failure mode for X-PPQ specimen were 95-100% cohesive within the adhesive system.

2.6.2 LARC-TPI

Lap shear strength of LARC-TPI was initially affected by exposure to Skydrol. This affect was noted in both the stressed and unstressed conditions.

However, the reduction in shear strength seemed to be stabilized after 500 hours of exposure (see Tables 2.6-1 and 2.6-2).

The failure mode of the specimens from both conditions were 90-100% cohesive. The 90% cohesive failures occurred in the unstressed condition with 0 hours of aging. However, this would be expected since the stress was greater for specimens without aging.

2.6.3 ETPS

Lap shear specimens bonded with ETPS were not resistant to Skydrol. Specimens in the unstressed condition retain very little strength after Skydrol exposure with some of the specimens failing while loading in the test machine.

Stressed Skydrol specimens failed immediately after immersion in the solution with 100% adhesive failures to the titanium.

2.6.4 X-PI

The shear strength of X-PI bonded specimens was not affected by exposure to skydrol in both the stressed and unstressed conditions. Test results are also summarized in Tables 2.6-1 and 2.6-2.

The failures were 90-100% cohesive. Most of the 90% cohesive failures were observed on specimens that were immersed in Skydrol for 500 hours. No logical explanation for less cohesive failures at 1000 hours aging than 500 hours aging was found. The shear strengths remained basically the same for all conditions.

TABLE 2.6-1

SKYDROL RESISTANCE TESTS (UNSTRESSED)

LAP SHEAR, Mpa (Psi)

Ti-Ti/10 VOLT CAA

Exposure Time Hours	X-PPQ		LARC-TPI		ETPS		X-PI	
0	33.8	(4900)	32.8	(4760)	25.1	(3640)	15.8	(2290)
0	34.3	(4980)	30.5	(4420)	34.9	(5060)	16.3	(2370)
0	38.2	(5540)	32.1	(4640)	37.2	(5400)	16.1	(2340)
0	40.1	(5820)	32.9	(4760)	35.3	(5120)	15.8	(2290)
0	32.8	(4760)	32.1	(4660)	29.0	(4200)	16.3	(2360)
Average	35.9	(5200)	32.1	(4650)	32.3	(4685)	16.1	(2330)
500	29.7	(4300)	28.3	(4100)		*	16.5	(2390)
500	30.3	(4400)	27.5	(3990)		*	12.1	(1750)
500	33.1	(4800)	27.4	(3980)	0.3	50	13.8	(2000)
500	32.3	(4680)	24.5	(3550)	0.9	130	13.8	(2000)
500	34.5	(5000)	26.2	(3800)		*	13.8	(2000)
Average	32.0	(4635)	26.8	(3885)	.6	(90)	14.0	(2030)
1000	30.6	(4440)	24.4	(3540)	2.1	(305)	15.4	(2240)
1000	31.7	(4600)	29.9	(4340)	0.6	(80)	13.3	(1930)
1000	36.3	(5260)	22.3	(3240)	1.2	(180)	15.4	(2240)
1000	33.5	(4860)	25.4	(3680)	2.0	(290)	15.1	(2190)
1000	37.2	(5400)	28.1	(4080)	0.5	(75)	16.0	(2322)
Average	33.9	(4910)	26.0	(3775)	1.3	(185)	15.0	(2180)
2000	35.4	(5140)	28.6	(4140)			16.3	(2360)
2000	32.6	(4720)	28.6	(4150)			16.1	(2340)
2000	32.4	(4700)	27.2	(3940)			15.6	(2270)
2000	32.8	(4750)	28.1	(4080)			15.4	(2230)
2000	32.1	(4660)	29.5	(4280)			16.0	(2320)
Average	33.0	(4790)	28.4	(4120)			15.7	(2280)

TABLE 2.6-2

SKYDROL RESISTANCE TESTS (STRESSED)

LAP SHEAR, Mpa (Psi)

Ti-Ti/10 VOLT CAA

Exposure Time Hours	X-PPQ		LARC-TPI		ETPS		X-PI	
0	28.3	(4100)	27.2	(3940)	20.6	(2980)	15.8	(2290)
0	31.0	(4500)	27.6	(4000)	25.3	(3670)	16.3	(2370)
0	29.3	(4250)	32.6	(4720)	24.6	(3560)	16.1	(2340)
0	28.4	(4150)	31.4	(4560)	25.1	(3640)	15.9	(2290)
0	31.7	(4600)	29.2	(4240)	24.6	(3560)	16.3	(2360)
Average	29.7	(4320)	29.0	(4290)	24.0	(3480)	16.1	(2330)
500	28.3	(4100)	22.3	(3240)	Specimens		13.4	(1950)
500	31.0	(4500)	24.8	(3590)			15.9	(2300)
500	29.3	(4250)	28.0	(4060)	failed		13.4	(1950)
500	28.6	(4150)	27.0	(3920)			16.1	(2330)
500	31.7	(4660)	28.1	(4080)	immediately		16.6	(2400)
Average	29.8	(4320)	26.0	(3780)			15.1	(2185)
1000	29.0	(4200)	28.6	(4140)			15.5	(2250)
1000	33.1	(4800)	25.2	(3660)			15.2	(2205)
1000	32.1	(4660)	18.9	(2740)			15.8	(2290)
1000	32.7	(4740)	25.8	(3740)			13.9	(2010)
1000	34.8	(5040)	26.5	(3840)			13.3	(1980)
Average	32.3	(4680)	25.0	(3620)			14.7	(2145)
2000	31.0	(4500)	27.6	(4000)			14.6	(2120)
2000	29.8	(4320)	27.6	(4000)			16.2	(2350)
2000	29.4	(4270)	21.8	(3160)			14.1	(2040)
2000	33.1	(4800)	28.3	(4100)			14.3	(2080)
2000	-	-	-	-			13.0	(1880)
Average	30.8	(4470)	26.3	(3820)			14.4	(2090)

3.0 CONCLUSIONS AND RECOMMENDATIONS

3.1 CONCLUSIONS

X-PPQ

The NASA supplied resin was easily converted to film form and fabricated into test specimens using normal processing techniques. The adhesive system was composed of unfilled X-PPQ, X-PPQ as primer, and 10 volt CAA on phosphate fluoride surface treatment on titanium. This system exhibited good adhesive properties to 450K (350°F) and 505K (450°F) on 10 volt CAA and phosphate fluoride respectively.

The lack of strength retention at higher temperature seemed to be caused by inadequate crosslinking. The press cure cycles without a vacuum bag to increase air exposure to promote crosslinking did not appear to have been successful. More extensive post-cure studies may have improved the thermal properties.

X-PPQ was only slightly affected by combined moisture and heat. This system was also not affected by unstressed or stressed exposure to Skydrol.

LARC-TPI

The preparation of adhesive film from this resin was accomplished easily using the procedures described previously. Fabrication of test specimens from the adhesive film, LARC-TPI primer and 10 volt CAA or phosphate fluoride was straight forward without complication.

However, the overall lap shear properties (though consistent with previous work) were lower. This may have been the result of a change in the monomer used for synthesis.

Thermal performance was demonstrated to 505K (450°F) especially with regard to the 9500 hour aging data which carried over from Phase II. Addition of a post-cure to processing of this system did improve the shear strengths, however, these studies were far from being optimized. LARC-TPI adhesive specimens exhibited good performance after exposure to combined moisture and heat and stressed and unstressed Skydrol.

ETPS

This system was easily processed into film form and used to prepare lap shear specimens. However, the cure cycles and post-cures attempted did not adequately crosslink the resin. The lack of trace palladium and/or improper end-capping was the probable cause for the poor performance. The inadequate crosslinking was reflected in low thermal test values at 450K (350°F) and above, plus a reduced stability in combined high humidity and heat and Skydrol exposure.

X-PI

This system was easily processed into film and test specimens. The lap shear strengths were generally lower than that characteristic of linear polyimide systems. However, some crosslinking was evident in the test results obtained at 589K (600°F) and 644K (700°F). Shear strengths could probably be improved if additional cure and post-cure studies were undertaken. This system exhibited little or no effects from exposure to humidity/heat and Skydrol.

3.2 RECOMMENDATIONS

X-PPQ

Further development and evaluation of X-PPQ, if continued, should proceed with investigation of post-cure cycles to increase crosslinking for improved initial high temperature bond strength. Data generated in this program indicates that this system offers the potential for use in aerospace vehicle bonded assemblies.

LARC-TPI

LARC-TPI, as an adhesive, is a relatively mature developmental material. This system can be used in aerospace vehicle applications if sufficient positive data is generated for each contemplated application. Questions as to material costs and potential suppliers will have to be resolved by each user company.

ETPS

This system did not receive a realistic evaluation of its potential as an adhesive due to incomplete crosslinking as discussed previously. Any further work on this material should include evaluation of the polymer that is crosslinkable to assess its capability to perform at elevated temperature and in other adverse environments.

X-PI

The evaluation of this system, although not as detailed as other systems on this program, indicated a potential for use in high temperature bonded structure. However, much more work will be required to determine its full potential in such applications.

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16. Abstract

The preliminary evaluation of crosslinked polyphenylquinoxaline (X-PPQ), LARC-TPI, ethynyl terminated polysulfone (ETPS), and crosslinked polyimide (X-PI) as adhesives is presented. Lap shear strength stability under thermal, combined thermal/humidity, and stressed and unstressed Skydrol exposure was determined.

X-PPQ, LARC-TPI, and X-PI exhibited good adhesive performance at 505K (450^{o}F) after 1000 hours at 505K. These three polymers also performed well after exposure to combined elevated temperature/high humidity, as well as, to Skydrol while under stress. ETPS exhibited good ambient temperature adhesive properties, but performed poorly under all other exposure conditions, presumably due to inadequate chain extension and crosslinking.

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