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EVALUATION OF Ti-6Al-4V SURFACE TREATMENTS FOR USE WITH A POLYPHENYLQUINOXALINE ADHESIVE

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INTRODUCTION

Quinoxalines, and in particular a monoether polyphenylquinoxaline (MEPPQ), have shown promise as high temperature polymers with good oxidative stability which, at reasonably high temperatures, exhibit thermoplasticity.[1] MEPPQ bonded titanium alloy (Ti-6Al-4V) has been shown to retain high lap shear strengths at 232°C (450°F) [23.1 MPa (3350 psi)] after 8000 hrs of thermal exposure at 232°C (450°F).[1]

The use of high temperature, high performance polymers as adhesives for aerospace applications is highly dependent on the durability of the surfaces joined by the adhesive. Recent efforts to determine a surface treatment with long term, high temperature performance for titanium alloy joints has met with limited success.[2,3,4] Titanium, and in particular the titanium alloy, Ti-6Al-4V, is a primary candidate material for spacecraft and high performance aircraft because of its high strength to weight ratio and its high temperature capabilities.

In this paper, three surface treatments for Ti-6Al-4V were evaluated with the MEPPQ adhesive: phosphate-fluoride (PF) etch, chromic acid anodization (CAA), and sodium hydroxide anodization (SHA). The SHA treatment has been shown to have excellent durability in low temperature adhesive joints as assessed by wedge specimens exposed to high humidity and 50°C (122°F) temperature.[5] In this application, the SHA treatment gave better results than the CAA treatment.

The primary criterion used to evaluate the MEPPQ/Ti system with three different surface treatments was their durability to long term thermal exposure in air at 232°C (450°F) based on lap shear strengths and the type of failure.

EXPERIMENTAL

Synthesis. The reaction scheme for the formation of MEPPQ is shown in figure 1. The chemicals used to prepare the polymer were obtained from commercial sources. The polymer was prepared by adding 3,3'-diaminobenzidine (0.49 mole) as a fine powder to a stirred solution of 4,4'-oxydibenzil (0.50 mole) in a 1:1 mixture of *m*-cresol and xylenes. The solids content, based upon the weight of the monomers, was 20% (w/v). The initial reaction exotherm was controlled by maintaining the temperature at < 40°C (104°F) by external cooling. After stirring for 18 hr, a viscous amber solution was formed. Polymer was isolated by adding a small volume of solution to methanol in a blender. The yellow fibrous material was boiled twice in methanol. The dried polymer had an inherent viscosity of 0.81 dl/g as measured on a 0.5% solution in *m*-cresol at 25°C (77°F). The glass transition temperature as measured by differential scanning calorimetry at 20°C/min (36°F/min) was 290°C (554°F). The polymer solution was stored in a brown bottle at ambient conditions.

The 20 wt % solids solution was diluted to 10 wt % by addition of 1:1 *m*-cresol/xylene to lower the viscosity for use as a primer for the 112-style glass cloth and as a primer for the Ti-6Al-4V adherends.

Characterization. Lap shear strength (LSS) was obtained according to ASTM D-1002 using a Model TT Instron universal testing machine. Elevated temperature tests were conducted in a clam-shell, quartz-lamp oven with temperatures controlled to within ±3°C (±5°F) for all tests. Specimens were held 10 mins at temperature prior to testing.

The average bondline thicknesses for the MEPPQ adhesive with the CAA and PF surface treated Ti-6Al-4V adherends were 0.26 mm (0.0104 in.) and 0.28 mm (0.0112 in.) respectively. The average bondline thickness for the SHA specimens was 0.18 mm (0.007 in.).

Glass transition temperature (Tg) of the adhesive from the fractured lap shear specimens was determined by thermomechanical analysis (TMA) on a DuPont 943 Analyzer. TMA was run on the fractured specimens in static air at a heating rate of 5°C/min (9°F/min) using a hemispherical probe with a 15 g load. A Tg of 290°C (554°F), as determined for this polymer by dynamic mechanical and dielectric relaxation measurements, was reported in reference 1.

Adhesive Tape Preparation. MEPPQ adhesive tape was prepared by brush coating a 10 wt % solids solution in 1:1 m-cresol/xylene onto a 112 E-glass cloth with an A-1100 finish (γ-aminopropylsilane). The glass cloth had been tightly mounted on a metal frame and dried in a forced-air oven for 30 min at 100°C (212°F) prior to coating. The 0.10 mm (0.004 in.) thick glass cloth served as a carrier for the adhesive as well as for bondline control and an escape channel for solvent. The coated cloth was then air dried overnight (approximately 16 hrs) and heated for 1 hr at each of three temperatures: 85°C (185°F), 140°C (284°F), and 185°C (365°F). Subsequently, each application of a 20 wt % solids solution was brush coated onto both sides of the cloth and the same heating schedule used until the thickness was approximately 0.30 mm (0.012 in.). The tape was then heated for 18 hrs at 185°C (365°F) and 9 hrs at 220°C (428°F) to reduce the volatile content to 2%. The percent volatiles was determined by heating a 2.54 cm x 2.54 cm

(1 in. x 1 in.) piece of tape in a forced-air oven at 399°C (750°F) for 30 min. The weight of the tape was determined before and after the heat treatment.

Ti-6Al-4V Surface Treatments. The adhesive tape was used to bond titanium alloy adherends (Ti-6Al-4V, per Mil-T-9046E, Type III Comp. C) with a nominal thickness of 1.27 mm (0.050 in.).

Three surface treatments were investigated: chromic acid anodization (CAA), developed by Boeing Aircraft Company;[6] phosphate-fluoride (PF) etch, and sodium hydroxide anodization (SHA). The CAA surface treated adherends were prepared for LaRC according to the Boeing process specification BAC 5890 using 10 vdc at 2 amp. The PF treatment of Ti-6Al-4V was also prepared by Boeing according to the BAC 5514 process specification. The surfaces treated by Boeing were immediately primed with MEPPQ solution supplied by LaRC. The SHA surface treatment was performed in our laboratories using the conditions which produced the best results in reference 5, i.e., 10 vdc for 30 min in 5M NaOH at 20 ±1°C (68 ±2°F) [actual temperatures used in our laboratory were 25 ±2°C (77 ±4°F)]. Adherends were grit blasted with 120 grit Al_2O_3 prior to the surface treatment. In general, stable oxides of titanium are formed by these processes which increase the durability of the adhesive joint to adverse environments, i.e., humidity and heat.

Bonding. The Ti-6Al-4V was supplied in a "four-fingered" configuration with each "finger" being 2.54 cm (1 in.) wide and approximately 12.7 cm (5 in.) long. Immediately after the surface treatments, the area to be bonded was primed with a 10 wt % solids solution of MEPPQ, air-dried for 30 min under a fume hood, placed in a forced-air oven, and held for 30 min at each of the three temperatures: 70°C (158°F), 140°C (284°F), and 180°C (356°F).

The primed adherends were placed in a sealed polyethylene bag and stored in a desiccator until needed.

The lap shear specimens were prepared by inserting the MEPPQ adhesive tape between the primed adherends using a 1.27 cm (0.5 in.) overlap (ASTM D-1002). A vacuum bag technique was used to bond the samples. Bonding temperature was monitored using a type K thermocouple spotwelded to the titanium adherend at the edge of the bond area. The following bonding process was used:

(1) Apply a full vacuum within the bag,
(2) Apply 1.37 MPa (200 psi) pressure (with a hydraulic press),
(3) Heat at approximately 20°C/min (37°F/min) to 371°C (700°F),
(4) Hold 371°C (700°F) for 20 min,
(5) Cool under vacuum and pressure to 150°C (302°F) and remove from bonding press.

RESULTS AND DISCUSSION

Bonding. The processability of MEPPQ is attributed to the thermoplastic nature of this type of polymer. The adhesive tape was processed to contain very little volatile material, 2% in this case, in order to avoid the formation of voids during bonding. Using the bonding schedule previously mentioned, the thermoplastic MEPPQ flowed sufficiently to provide a void free adhesive bond with a small amount of squeeze out. Microscopic examination of failed specimens verified the void free nature of the bonded joints.

Thermal Exposure Tests. The durability of the MEPPQ bonded joints with three different surface treatments was determined by exposing lap shear specimens in a forced-air oven at 232°C (450°F) for up to 12 months for the PF and CAA prepared specimens and for up to 18 months for the SHA specimens. Lap shear strengths were determined primarily at 232°C (450°F) before (control) and after thermal exposure. SHA lap shear strengths were also determined at RT before and after exposure.

Results are given in Table 1 and included in Figure 2 for MEPPQ/PF treated specimens. The RT LSS values were lower than expected for this adhesive, 19.6 MPa (2851 psi), compared to those in reference 1, 32.7 MPa (4740 psi). However, the adhesive type of failure indicates the adherend surface as the possible reason for the lower results. Low results were obtained after thermal aging with total loss of strength at some period between 6 months and 12 months (indicated by the dashed portion of the curve in Figure 2). Again, only adhesive type failures occurred.

Results for the CAA treated specimens are given in Table II and included in Figure 2. Higher LSS values were obtained for this system as compared to the PF system except for a slight difference for the 232°C (450°F) control values [23.1 MPa (3355 psi) versus 24.8 MPa (3608 psi)]. The CAA retains good strengths up to 6 months (4380 hr) but strength decreases significantly after a 12 month (8760 hr) exposure [5.8 MPa (838 psi)]. Failure modes were 100% cohesive for the control and 3 month tests but changed to adhesive failures for the 12 month tests. Examples of failed specimens are shown in Figure 3. The surfaces of these specimens were surface analyzed by Boeing Aerospace Company using x-ray photoelectron spectroscopy (XPS). The XPS data on the unexposed and 3 month exposure specimens indicate a disbond in the adhesive (cohesive failure) whereas the data for the 6 month exposure specimen implies that the disbonding occurred at the primer/oxide interface.[3] The low results after 12 months thermal exposure at 232°C (450°F) make the CAA surface treatment unacceptable for MEPPQ for long term durability at elevated temperatures. Similar results were obtained in a Boeing study where LSS values decreased significantly between 5000 and 10,000 hrs exposure at 232°C (450°F).[4]

Because of the encouraging results obtained with the SHA treatment by Kennedy, et. al., reference 5, this treatment was investigated for the MEPPQ adhesive after the poor results for the PF and CAA treatments were determined. Thermal aging test results are given in Table III and included in Figure 2 for the MEPPQ/SHA specimens. The LSS tests at RT and 232°C (450°F) were conducted after 6.7, 12, and 18 months. A significant improvement in LSS retention was obtained after the thermal aging with this treatment. The LSS values at 232°C (450°F) for the SHA tests after 12 months are significantly higher than the CAA and PF LSS values: 17.0 MPa (2465 psi), 5.8 MPa (838 psi), and 0 MPa, respectively. The failure mode for the SHA specimens tested at 232°C (450°F) after 12 months were primarily cohesive (Figure 4) whereas the CAA specimens failed adhesively and the PF specimens fell apart (adhesively) when removed from the oven. When the SHA specimens were tested at 232°C (450°F) after 18 months thermal exposure, the LSS values were lower than those after 12 months exposure, 12.1 MPa (1750 psi) compared to 17.0 MPa (2465 psi). Failure for the 18 month specimens were primarily adhesive (Figure 4).

RT LSS tests were also conducted for MEPPQ/SHA specimens before and after thermal exposure. A significant decrease in LSS was obtained between

6.7 and 12 months: 24.5 MPa (3560 psi) to 9.1 MPa (1318 psi). Associated with this decrease was a change in failure mode from primarily cohesive to a 100% adhesive failure. The reason for this change of failure mode is unknown at this time but a possible casue is discussed further below.

The Tg's of the MEPPQ adhesive from the fracture specimens are included in Table III. The measured Tg's range from 275°C (527°F) to 332°C (630°F). As noted before, reference 1 cites the Tg as 290°C (554°F) which was determined by dynamic mechanical and dielectric relaxation measurements.

A possible cause of the abrupt change in failure mode noted above is an interaction of the solvent system with the treated surfaces. A 1:1 mixture of *m*-cresol and xylene (mixed) solvent system was used for this polymer. *Meta*-cresol [b.p. 202°C (396°F)] is a difficult solvent to remove from the polymer system because it is tenaciously held by the polymer. Xylene [b.p. 137°C - 140°C (279°F - 284°F)] is more easily removed than *m*-cresol. Perhaps the solvent system interacts in some manner with time and temperature (high) to degrade the interface region or surface of the adherend to bring about an interfacial type failure. An analysis was made using mass spectrometry to determine if any of the solvent system, especially the *m*-cresol, was still evident in the adhesive of a fractured lap shear specimen of an as-fabricated as well as a specimen thermally aged for 18 months at 232°C (450°F). No evidence of the existence of either solvent was found. Perhaps surface analysis studies of the treated surface before testing and after failure could provide an explanation for the system's failure.

SUMMARY

Three surface treatments for Ti-6Al-4V adherends were evaluated using a thermoplastic polymer monoether polyphenylquinoxaline, MEPPQ, which had been shown in previous studies to have good potential as a high temperature adhesive for aerospace applications. Initial results based on long term thermal exposure at 232°C (450°F) using the phosphate-fluoride (PF) and chromic acid anodized (CAA) treatments with MEPPQ adhesive were not encouraging. A significant improvement in strength retention and a change in failure mode (cohesive) at 232°C (450°F) was found for the SHA treated specimens compared to the PF and CAA treatments. Although an improvement in long term thermal durability was obtained with the SHA treatment of Ti-6Al-4V, a change in failure mode from cohesive to adhesive was noted for the RT tests after 12 months exposure at 232°C (450°F). Such a change is indicative of a degradation of the adhesive-adherend interface. An improved surface treatment with better long term durability is still required for aerospace applications.

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TABLE I. THERMAL AGING* TEST RESULTS FOR PF TREATED Ti-6Al-4V BONDED WITH MEPPQ

THERMAL EXPOSURE, HR (MONTH)	BONDLINE THICKNESS,** MM (IN. X 10^{-3})	TEST TEMPERATURE, °C (°F)	LSS, MPa (psi)	COHESIVE FAILURE, %
0 (Controls)	0.30 (11.9)	RT (RT)	25.8 (3740)	40
	0.29 (11.6)	RT (RT)	20.5 (2970)	20
	0.30 (11.8)	RT (RT)	12.7 (1845)	0
			Avg. 19.6 (2851)	
	0.25 (9.8)	232 (450)	16.3 (3430)	100
	0.29 (11.6)	232 (450)	25.8 (3750)	100
	0.27 (10.6)	232 (450)	25.1 (3645)	100
			Avg. 24.8 (3608)	
2160 (3)	0.30 (11.7)	232 (450)	14.1 (2040)	0
	0.28 (11.2)	232 (450)	10.9 (1580)	0
	0.27 (10.6)	232 (450)	1.9 (275)	0
			Avg. 9.0 (1298)	
4380 (6)	0.32 (12.6)	232 (450)	4.3 (625)	0
	0.28 (11.1)	232 (450)	3.8 (550)	0
	0.26 (10.2)	232 (450)	3.3 (475)	0
			Avg. 3.8 (550)	
8760 (12)	0.30 (12.0)	--	0***	
	0.26 (10.2)	--	0	

*In air at 232°C

**Average bondline thickness was 0.28 mm (0.0112 in.)

***Failed when removed from aging oven

TABLE II. THERMAL AGING* TEST RESULTS FOR CAA TREATED Ti-6Al-4V BONDED WITH MEPPQ

THERMAL EXPOSURE, HR (MONTH)	BONDLINE THICKNESS,** MM (IN. X 10^{-3})	TEST TEMPERATURE, °C (°F)	LSS, MPa (psi)	COHESIVE FAILURE, %
0 (Controls)	0.25 (10.0)	RT (RT)	41.8 (6060)***	100
	0.25 (10.0) 0.28 (10.9) 0.26 (10.4)	232 (450) 232 (450) 232 (450)	24.6 (3565) 23.2 (3370) 21.6 (3130) Avg. 23.1 (3355)	100 100 100
2160 (3)	0.28 (10.9) 0.27 (10.5) 0.25 (10.0)	232 (450) 232 (450) 232 (450)	21.5 (3120) 24.8 (3600) 25.2 (3650) Avg. 23.8 (3457)	100 100 100
4380 (6)	0.25 (10.0) 0.25 (10.0) 0.26 (10.4)	232 (450) 232 (450) 232 (450)	23.2 (3370) 19.6 (2850) 13.5 (1965) Avg. 18.8 (2728)	80 20 30
8760 (12)	0.24 (9.3) 0.26 (10.2)	232 (450) 232 (450)	6.5 (950) 5.0 (725) Avg. 5.8 (838)	0 0

*In air at 232°C

**Average bondline thickness was 0.26 mm (0.0104 in.)

***Tested on a Cal-Tester testing machine

TABLE III. THERMAL AGING* TEST RESULTS FOR SHA TREATED Ti-6Al-4V BONDED WITH MEPPQ

THERMAL EXPOSURE, HR (MONTH)	BONDLINE THICKNESS,** MM (IN. X 10^{-3})	TEST TEMPERATURE, °C (°F)	LSS, MPa (psi)	COHESIVE FAILURE, %	GLASS TRANSITION TEMPERATURE, Tg,*** °C (°F)
0 (Controls)	0.19 (7.6)	RT (RT)	28.6 (4150)	60	278 (532)
	0.20 (7.8)	RT (RT)	29.4 (4270)	55	
	0.17 (6.7)	RT (RT)	26.0 (3780)	50	
	0.17 (6.6)	RT (RT)	26.2 (3800)	45	
			Avg. 27.6 (4000)		
	0.19 (7.4)	232 (450)	25.1 (3645)	100	275 (527)
	0.18 (7.1)	232 (450)	24.1 (3505)	100	
	0.16 (6.4)	232 (450)	23.8 (3450)	95	
	0.20 (7.7)	232 (450)	23.8 (3450)	95	
			Avg. 24.2 (3512)		
5000 (6.7)	0.16 (6.4)	RT (RT)	27.2 (3945)	90	303 (577)
	0.20 (7.9)	RT (RT)	26.5 (3850)	80	
	0.15 (6.1)	RT (RT)	23.4 (3390)	60	
	0.16 (6.5)	RT (RT)	21.1 (3055)	60	
			Avg. 24.5 (3560)		
	0.20 (7.7)	232 (450)	21.1 (3060)	95	332 (630)
	0.18 (7.1)	232 (450)	19.7 (2860)	80	
	0.17 (6.7)	232 (450)	23.8 (3450)	100	
	0.18 (7.1)	232 (450)	23.4 (3400)	100	
			Avg. 22.0 (3192)		
8760 (12)	0.14 (5.6)	RT (RT)	8.9 (1305)	0	311 (592)
	0.18 (7.0)	RT (RT)	10.1 (1465)	0	
	0.19 (7.5)	RT (RT)	9.3 (1350)	0	
	0.17 (6.6)	RT (RT)	7.9 (1150)	0	
			Avg. 9.1 (1318)		
	0.18 (7.1)	232 (450)	19.1 (2770)	80	325 (617)
	0.20 (7.8)	232 (450)	16.7 (2420)	50	
	0.15 (6.0)	232 (450)	14.1 (2050)	25	
	0.18 (6.9)	232 (450)	18.1 (2620)	85	
			Avg. 17.0 (2465)		

TABLE III. CONTINUED

13140 (18)	0.18 (7.2)	RT (RT)	7.3 (1060)	0	317 (602)
	0.19 (7.5)	RT (RT)	7.3 (1060)	0	
	0.18 (7.1)	RT (RT)	6.9 (1000)	0	
	0.20 (7.9)	RT (RT)	8.9 (1290)	0	
			Avg. 7.6 (1102)		
	0.17 (6.8)	232 (450)	10.8 (1570)	10	312 (594)
	0.19 (7.4)	232 (450)	14.8 (2150)	30	
	0.18 (7.2)	232 (450)	11.2 (1630)	5	
	0.18 (7.0)	232 (450)	11.4 (1650)	15	
			Avg. 12.1 (1750)		

*In air at 232°C (450°F)
**Average bondline thickness was 0.18 mm (0.007 in.)
***Single measurement

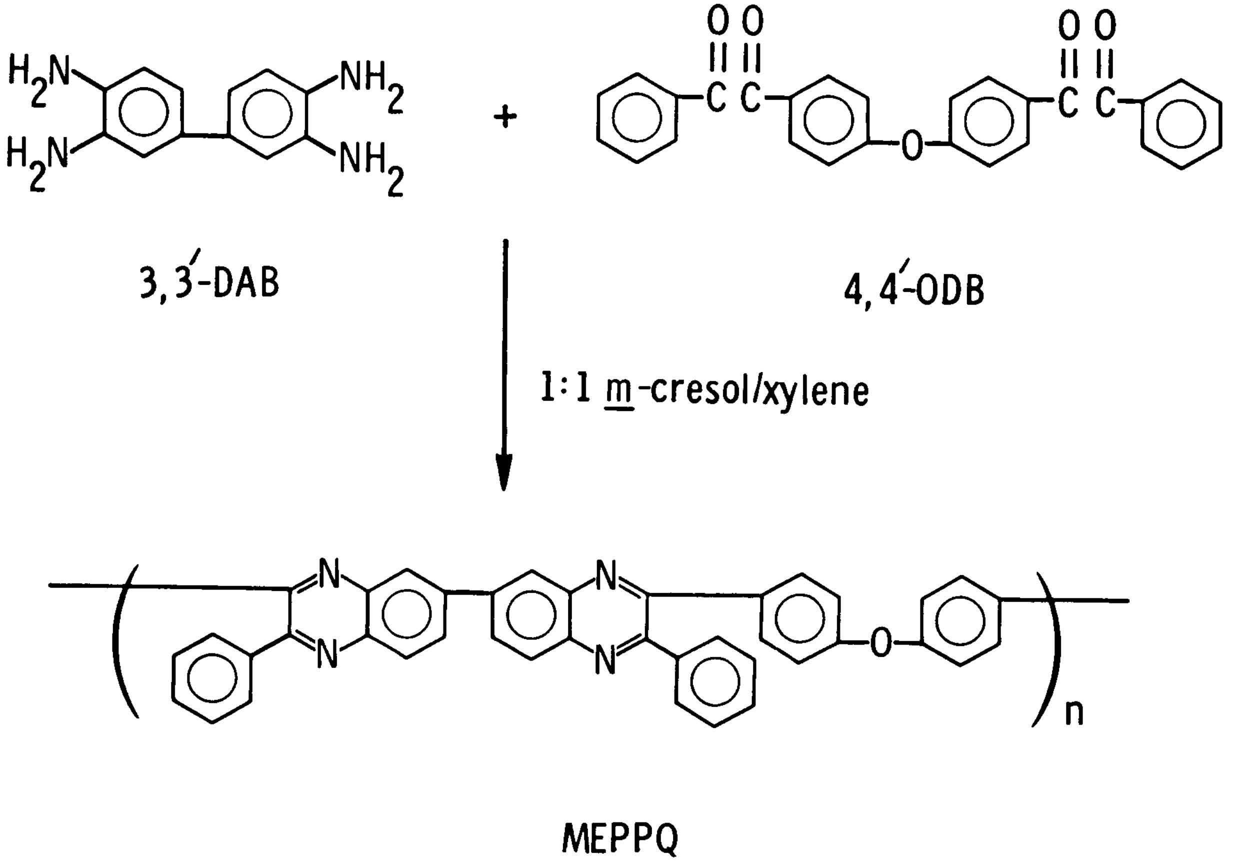

Figure 1. Reaction scheme for monoether polyphenylquinoxaline (MEPPQ).

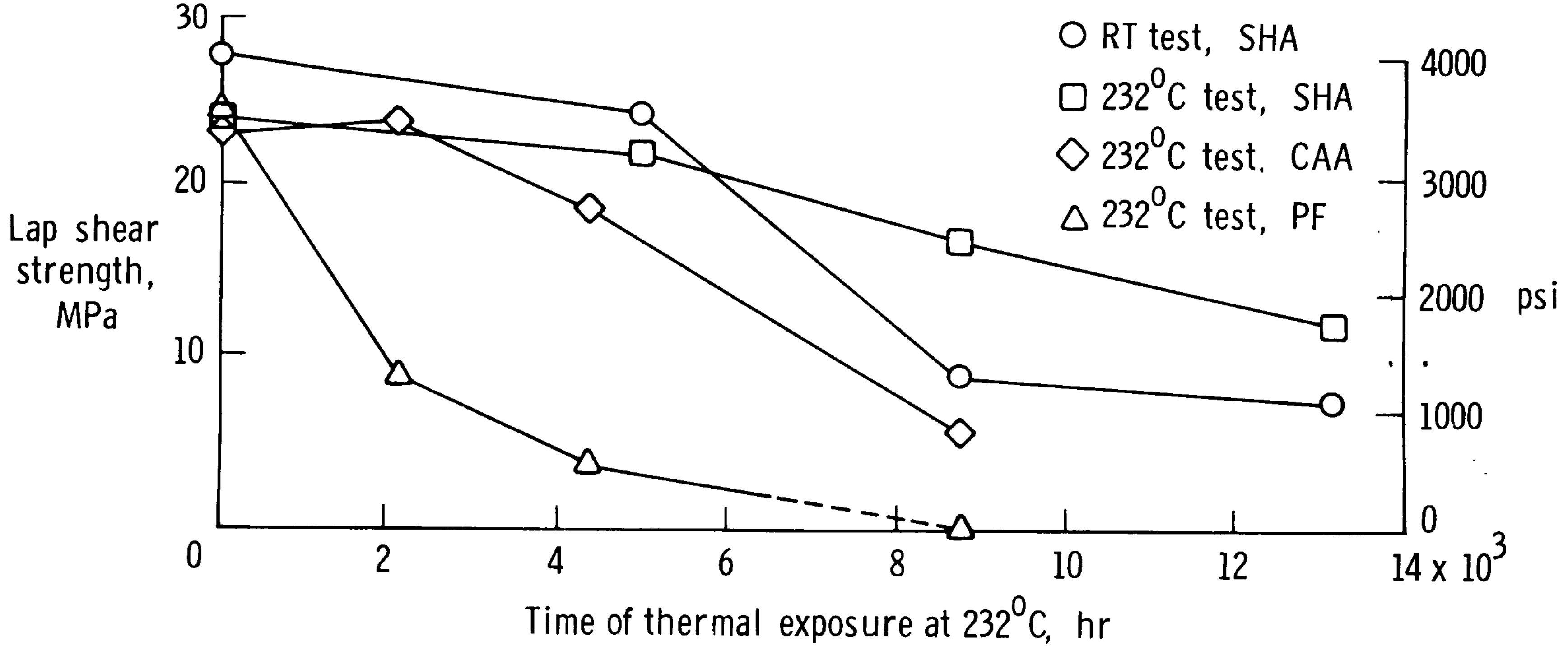

Figure 2. LSS test results after thermal exposure of MEPPQ bonded Ti-6Al-4V with various surface treatments.

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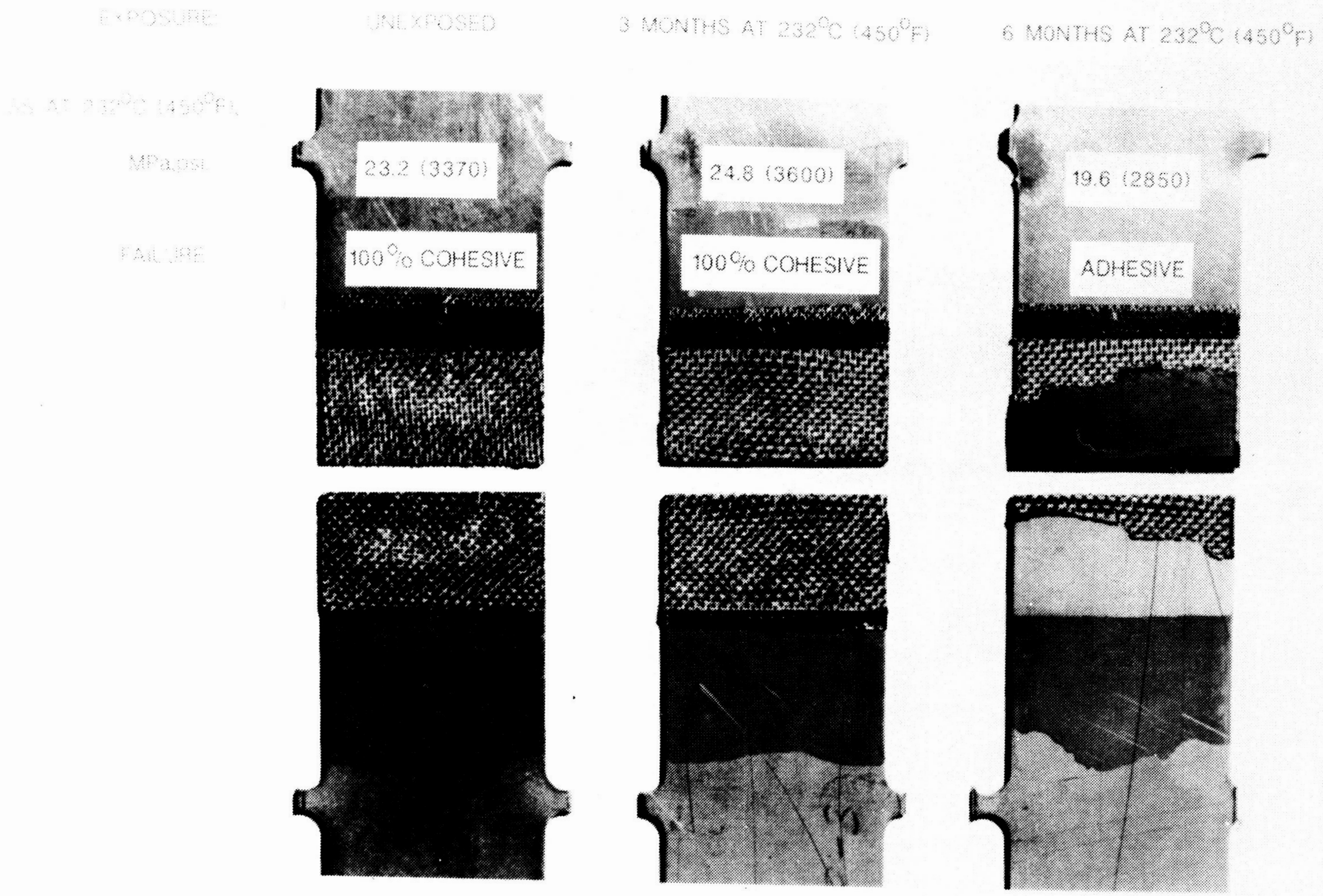

Figure 3. Failed MEPPQ-CAA lap shear specimens tested at 232°C (450°F) before and after thermal aging at 232°C (450°F).

EXPOSURE:	UNEXPOSED	6.7 MONTHS	12 MONTHS	18 MONTHS
LSS AT 232°C (450°F), MPa, psi:	26.2 (3800)	23.8 (3450)	19.1 (2770)	14.8 (2150)
FAILURE:	100% COHESIVE	100% COHESIVE	80% COHESIVE	30% COHESIVE

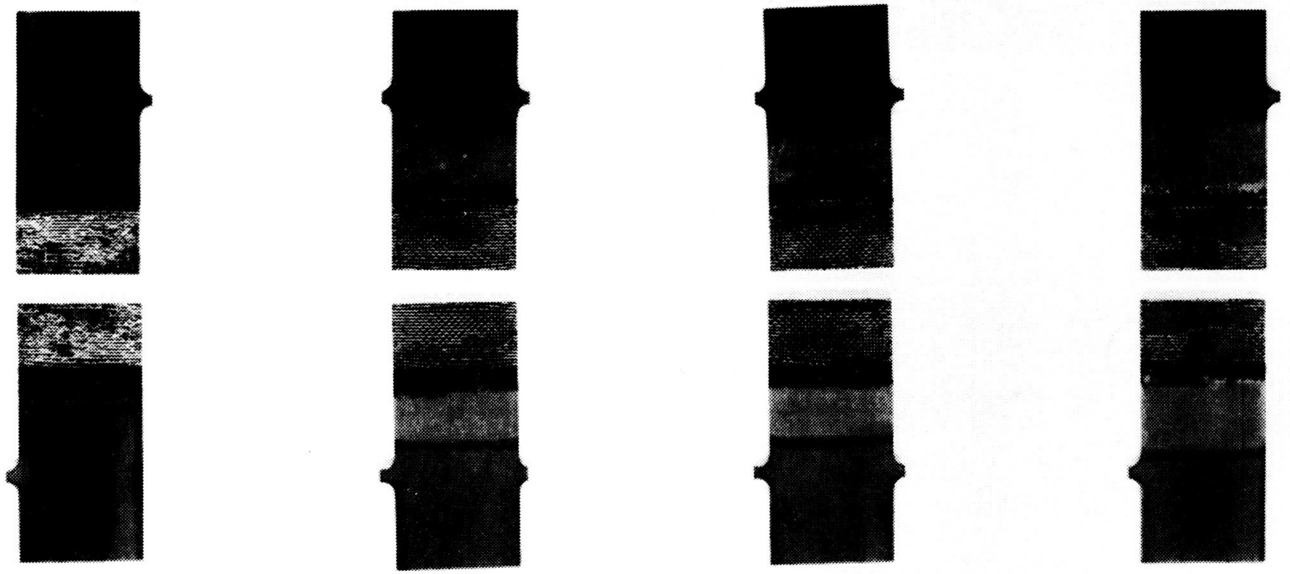

Figure 4. Failed MEPPQ/SHA lap shear specimens tested at 232°C (450°F) before and after thermal aging at 232°C (450°F).

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16. Abstract
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