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A NOVEL ADDITION POLYIMIDE ADHESIVE

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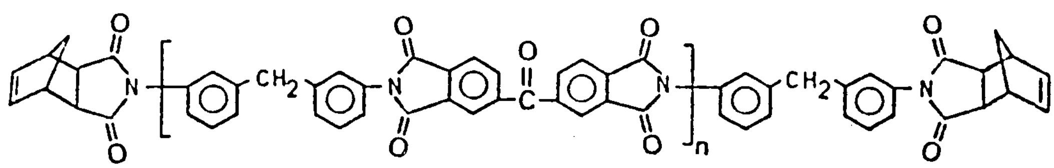
1. INTRODUCTION

The currently available high-temperature resistant (533-589K) adhesives were developed for bonding either steel or titanium. In order to fabricate structural components from polyimide composites, an adhesive was needed which would be compatible both chemically and thermally with polyimide matrix resins. An addition polyimide adhesive, LARC-13 (LARC for Langley Research Center), was designed to be chemically similar to existing high temperature matrix systems and to interact with these materials during a bonding cycle to form a continuum bond of high strength.[1,2] Commercially available high temperature adhesives frequently yield poor results when used for bonding large areas because a large volume of volatiles is given off during the cure process. LARC-13 was designed to solve this problem. It has an addition-type cure which results in the evolution of few volatiles and, consequently, should be satisfactory for large-area bonding. Its unique molecular building blocks (see below), incorporating meta-linkages and oligomeric chains, afford a relatively low polymer softening temperature and permit the adhesive to be easily processed at temperatures between 533K and 598K. Because of the above features, LARC-13 is also attractive for bonding metals. The purpose of this paper is to discuss the synthesis and formulation of this adhesive and present data on its suitability as a high temperature adhesive for bonding titanium, stainless steel and high temperature composites for structural applications.



LARC-13

2. EXPERIMENTAL

2.1 SYNTHESIS OF LARC-13 ADHESIVE

2.1.1 MATERIALS

Flake benzophenone tetracarboxylic dianhydride (BTDA) was used as received from Gulf Chemicals*, m.p. 488-493K(419°-428°F). Powdered BTDA is not

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recommended because of a tendency to form lumps in solution which are difficult to break up and dissolve. The flake BTDA dissolves more slowly and is easier to handle.

Glass-distilled dimethylformamide (DMF) was used as received from Burdick and Jackson. Nadic anhydride was used as received from Eastman or Fallek, m.p. 435-437K(324-327°F). 3,3'-Methylenedianiline (3,3'-MDA) was used as received from Ash-Stevens, Inc. m.p. 348-351K(167-172°F). Alcan MD 105 aluminum powder of 325 mesh was used as received.

2.1.2 PROCEDURE

A wide-mouth resin kettle was utilized for convenience so that the viscous liquid could easily be removed after the aluminum powder had been added. No heating or cooling was required since the reaction exotherm was slight. Thus, the reaction can easily be scaled as required. Using mechanical stirring, MDA (11.8 grams) was dissolved in 445 grams of DMF in a one-liter resin kettle. Nadic anhydride (73.8 grams) was added in ten equal portions alternately over a period of 5-6 hours. The time between subsequent additions was increased since material in later additions dissolved more slowly in the more concentrated medium. Stirring was continued until complete solution was obtained, usually 24-36 hours. Aluminum powder (134 grams) was then added in ten equal portions and slurried. The adhesive was stored in a refrigerator at approximately 277K(40°F).

2.2 ADHESIVE SCRIM PREPARATION

The LARC-13 resin was supported on Type 112 E-glass carrier cloth with an A-1100 finish. The cloth was stretched tightly in an aluminum frame and brush-coated with the adhesive. In order to prepare an adhesive cloth with good texture, the desired scrim thickness was built up through five to eight applications. After each application the cloth was heated in a forced-air oven to 373K(212°F) and held at that temperature for one-half hour. Next, the scrim was staged for one hour at 423K(302°F), one hour at 473K(392°F), and one hour at 508K(455°F). This procedure afforded cloth with very little tack and drape because the resin had been staged to a point where practically no volatiles remained. An accurate determination of volatiles was precluded by the evolution of cyclopentadiene which occurs when the resin is not cured under pressure. A more flexible LARC-13 tape was made by allowing a small amount of solvent (DMF) to be retained. Consequently, by adjusting its solvent content, scrim with a range of tack, drape and flow properties may be prepared.

2.3 ADHERENDS

Titanium (6Al-4V) adherends [per Mil-T-9046E, Type III Com. C.] with a nominal thickness of 0.127 cm(0.050 inch) were employed. Four-fingered panels with one-inch-wide adherend sections and the peel adherends were cleaned by the Pasa Jell 107 acid surface treatment.* Composite adherends were either unidirectional graphite/polyimide (PMR-15 or NR-150B2) or cross-plied $(0,+45,90,-45)_S$ graphite/PMR-15.[13] The unidirectional panels had a nominal thickness of 0.280 cm (0.110 inch) and the crossplied panels a nominal thickness of 0.114 cm (0.045 inch). The PMR-15/Celion 6000 panels were fabricated with a void content of less than 2%. Ultrasonic "C"-scans indicated these panels to be of high quality and excellent uniformity. The NR-150B2/HTS I panels[4] had some variability in quality as indicated by ultrasonic "C"-scans. The resin content of the composite adherends was 32-37% by weight, as determined by sulfuric acid digestion. The composite panels were lightly grit-blasted with 120 aluminum oxide and solvent-wiped with acetone or alcohol prior to bonding.

2.4 BONDING

The adherends were primed with the LARC-13 resin with 30% aluminum powder and placed in an air oven at 373K(212°F) and held for one hour. The adhesive scrim was placed in the bondline and cured according to the following cycle:

RT→477K (400°F) at 5K/minute; hold one hour.

477K(400°F)→ 580°F) at 5K/minute; hold one hour.

Apply 345 kPa (50 psi).

580K(585°F)→603K(625°F) at 5K/minute; hold one hour.

Cool at 5K/minute to 423K (302°F).

Postcure: RT→616K (650°F) at 7K/minute; hold 16 hours.

The postcure at 616K (650°F) was not necessary for materials with use temperature below 561K (550°F).

2.5 TESTING

Isothermal aging of bonded specimens was conducted in a forced-air oven, with the indicated temperature controlled to within ±1 percent. Lap shear tests were conducted on an Instron Universal Testing Instrument according to ASTM D-1002 at a crosshead speed of 0.127 cm/min (0.05 in/min). Each lap shear data point represents an average of four test results. Flat-wise tensile strengths represent an average of three data points and were obtained according to ASTM-C-297 at a crosshead speed of 0.127 cm/min (0.05 in/min). Elevated

*Commercial surface treatment for titanium from American Cyanamid.

temperature tests were performed after the samples were conditioned by holding at the test temperature for 10 minutes. "T"-peel tests were performed according to ASTM D-1876 using 0.025 cm (0.010 inch) titanium (6Al-4V) peel strips.

3. RESULTS AND DISCUSSION

3.1 POLYMER CHEMISTRY

The imide oligomer was formulated to have an average molecular weight of 1300, similar to P13N polyimide resin.(5) Of the other molecular weight materials (between 300 and 2000) that were prepared and evaluated, the 1300 molecular weight material yielded the best lap shear strengths at room temperature and 533-589K. The prepolymer system is end-capped with norbornene moieties which crosslink when heated to 561-616K to form a thermally stable polymer with the evolution of few volatiles. During the cure of LARC-13, as well as any addition-polyimide system containing the norbornene, pressure must be maintained to avert the formation of cyclopentadiene via a reverse Diels-Alder reaction.(6) Cyclopentadiene did not form when the system was cured under pressure above 344kPa (50 psi) in a Differential Scanning Calorimeter. Data from this instrument showed that the exothermic reaction of the nadic end groups begins at approximately 473K (392°F). The glass transition temperature (T_g) of LARC-13 was determined by thermomechanical analysis to be 566-580K(559-584°F). Conversion of the oligomeric amide-acid, as prepared in DMF, to the imide was accomplished by heating the adhesive on the carrier cloth to 423K(302°F), or slightly above, depending on the desired carrier characteristics.

3.2 ADHESIVE EVALUATION

Some general properties of LARC-13 adhesive (filled with 30% aluminum powder) are shown in Table 1. The wide range of lap shear strengths for bonded Ti 6Al-4V was due to variations in cure.

The highest room temperature strengths were obtained by curing the adhesive for short times to 589K(600°F). Longer times at 589K(600°F) and the use of higher cure and post-cure temperatures generally led to higher elevated temperature strengths at the expense of room temperature properties. The range of values obtained for composite lap shear strengths was attributed to variations in cure temperature and in adherend thickness (1.14 to 2.80 mm) which can introduce peel forces(7) that substantially affect the final shear strengths.

"T"-peel strengths for LARC-13 on titanium adherends were low (180-710 g/cm-g/cm-width) but were in the range expected for a highly crosslinked material. Titanium to glass/polyimide honeycomb climbing drum peel tests yielded strengths of 710-800 g/cm-width.

Flat-wise tensile samples bonded with LARC-13 exhibited excellent room temperature strengths ranging from 2.8-3.5 MPa (400-500 psi).

Table 2 is a compilation of lap shear strengths at room temperature and 533K(500°F) for various amounts of aluminum filler. The 30% aluminum loading was chosen for the best combination of flow control and strength characteristics. The optimum aluminum content should be determined for each bonding application. The lap shear strengths for unaged and aged titanium to titanium bonds are listed in Table 3. As previously noted, the cure temperature has an effect on the room temperature lap shear strengths as illustrated - 13.8 MPa vs. 20.1 MPa (2000 psi vs. 3000 psi) for 603K and 589K (625°F and 600°F) cures respectively. Higher lap shear strengths at 589K (600°F) were evident for the higher temperature cure - 11.7 MPa vs. 10.5 MPa (1700 psi vs. 1500 psi). The lap shear strengths after aging at 589K (600°F) indicate LARC-13 has at least short-term utility (in excess of 125 hours) at this temperature. When LARC-13 was used for bonding crosspplied graphite/PMR-15 composite panels, failures occurred at lower strengths than were expected (Table 4). In many of the tests the adherends failed prior to adhesive failure. In the cases where failure occurred in the adhesive, the flexing of the thin adherends (1.14 mm) probably initiated adhesive failure.

The exposure of graphite/PMR-15 lap shear samples to 589K (600°F) for 125 hours can cause degradation of the adherend surface which may lead to poor bond performance. The use of a high molecular weight linear polyimide (BR-34) as a protective coating for the adherend seemed to alleviate this problem, as illustrated by the higher strengths both at room temperature and 589K (600°F) after aging at 589K (Table 4).

Exceptional lap shear strengths were obtained when graphite/NR-150B2 laminates were bonded with LARC-13 (Table 5). In this case the laminates were sufficiently thick (0.280 cm) to reduce peel forces which can cause premature failures.(7) The data in Table 5 also illustrates the deleterious effect of curing for long times at elevated temperature (598K); room temperature lap shear strengths decreased from 34.5 MPa (5000 psi) to 19.3 MPa (2800 psi) with five hours additional cure at 598K (617°F).

Table 6 is a compilation of LARC-13 adhesive data as generated at NASA-Langley, Rockwell International, Downey, CA, and Boeing Aerospace, Seattle, WA. Boeing used adhesive resin made by NASA-Langley while Rockwell made its own. The prepreg was prepared in different ways by each organization and bonding cycles were also different. The high room temperature and 589K (600°F) titanium lap shear strengths generated by Boeing may be attributed to their unique surface preparation.(8)

Boeing has also successfully used LARC-13 to bond ceramic to titanium for a missile application where the adhesive must withstand a short thermal excursion (15 sec.) to approximately 867K(1100°F).

Figure 1 illustrates a current application at NASA-Langley for LARC-13 adhesive. As part of a program on Supersonic Cruise Aircraft Research (SCR), components for the YF-12 were fabricated of graphite/polyimide and bonded with LARC-13.[9]

Because the panel was closed-out around the edges an adhesive was needed which generated no volatiles during cure and yet had good thermal performance up to 533K (500°F). No high temperature adhesives were able to meet this particular requirement except LARC-13. The panel failed at loads in excess of the experimental design level when statically tested at room temperature and at 533K (500°F).

4. CONCLUSIONS

An addition-curing polyimide adhesive, LARC-13, has been developed which can be utilized for low pressure bonding without the generation of volatiles during cure. Its oligomeric nature allows for a high degree of melt flow, thus making it an excellent material for autoclave processing. LARC-13 exhibits high room temperature and elevated temperature strengths in bonding metals and composites, and can be utilized for short terms at temperatures up to 867K (1100°F). Excellent retention of both initial room temperature and 589K (600°F) lap shear strengths has been achieved after aging in air up to 125 hours at 589K.

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TABLE I

LARC-13 PROPERTIES*

Property	Test Temp	Test Value	
		MPa	psi
Lap Shear Strength			
Ti/Ti	RT	20 - 35	3000 - 5000
	533K (500°F)	14 - 20	2000 - 3000
Gr-PI/Gr-PI	RT	17 - 35	2500 - 5000
	533K	14 - 20	2000 - 3000
Flatwise Tensile Strength			
Gr-PI/Honeycomb	RT	2.8-3.5	400 - 500
		g/cm	lb/in
Peel Strength			
"T", Ti/Ti	RT	180-710	1 - 4
Climbing Drum, Ti/Honeycomb	RT	710-800	4.0 - 4.5
Glass Transition Temp.		565-580K	559-584°F

*Filled with 30% aluminum powder

TABLE 2

LAP SHEAR STRENGTHS OF TITANIUM BONDED WITH FILLED LARC-13

% FILLER*	LAP SHEAR STRENGTH, MPa (psi)	
	RT	533K (500°F)
0	18.6 (2700)	15.2 (2200)
15	13.8 (2000)	16.5 (2400)
30	20.7 (3000)	17.2 (2500)
45	19.3 (2800)	19.3 (2800)
60	22.8 (3300)	18.3 (2650)

* MD-105/Alcan Aluminum Powder, percent by weight

TABLE 3

LAP SHEAR STRENGTHS OF Ti ADHERENDS BONDED WITH LARC-13*

Exposure at 589K(600°F), hr	Lap Shear Strength, MPa (psi)	
	RT	589K(600°F)
0 (603K cure)	13.8 (2000)	11.7 (1700)
0 (589K cure)	20.1 (3000)	10.5 (1500)
50 (603K cure)	13.4 (1950)	13.1 (1900)
125 (603K cure)	11.4 (1650)	11.4 (1650)

*30% Aluminum filler

TABLE 4

LAP SHEAR STRENGTHS OF Gr/PI[a] BONDED WITH LARC-13

Adhesive System	Exposure at 589K, hr	Lap Shear Strength, MPa (psi)	
		RT	589K (600°F)
LARC-13	0	13.4 (1950)	10.3 (1500)
LARC-13 with BR-34[b]	0	14.8 (2150)	10.7 (1550)
LARC-13	125	8.3 (1200)	7.9 (1150)
LARC-13 with BR-34[b]	125	13.4 (1950)	10.3 (1500)

[a]Crosspiied Celion/PMR-15, $(0,+45,90,-45)_S$ layup with a nominal 0.114cm cured thickness
[b]Adherend surface primed with BR-34 (American Cyanamid)

TABLE 5

LAP SHEAR STRENGTHS OF Gr/PI* BONDED WITH LARC-13

Postcure Condition	Lap Shear Strength, MPa (psi)		
	RT	533K (500°F)	589K (600°F)
2 hours at 598K (617°F)	34.5 (5000)	20.7 (3000)	11.7 (1700)
7 hours at 598K (617°F)	19.3 (2800)	17.2 (2500)	11.7 (1700)

*Unidirectional HTS I/NR-150B2, nominal 0.280cm thickness

TABLE 6

LARC-13 LAP SHEAR STRENGTH

Laboratory	Adherend	Lap Shear Strength, MPa (psi)	
		RT	589K (600°F)
NASA-Langley	Gr/PMR-15	15.9 (2300)	13.1 (1900)
	Gr/NR-150B2	34.5 (5000)	11.7 (1700)
	Ti 6Al-4V	20.7 (3000)	10.3 (1500)
Rockwell International	Gr/NR-150B2	18.6 (2700)	12.4 (1800)
	17-7 PH Steel	16.9 (2450)	9.65 (1400)
Boeing Aerospace	Gr/PMR-15	13.8 (2000)	13.8 (2000)
	Ti 6Al-4V	27.6 (4000)	15.2 (2200)
	Glass/PMR-15	22.8 (3300)	15.2 (2200)

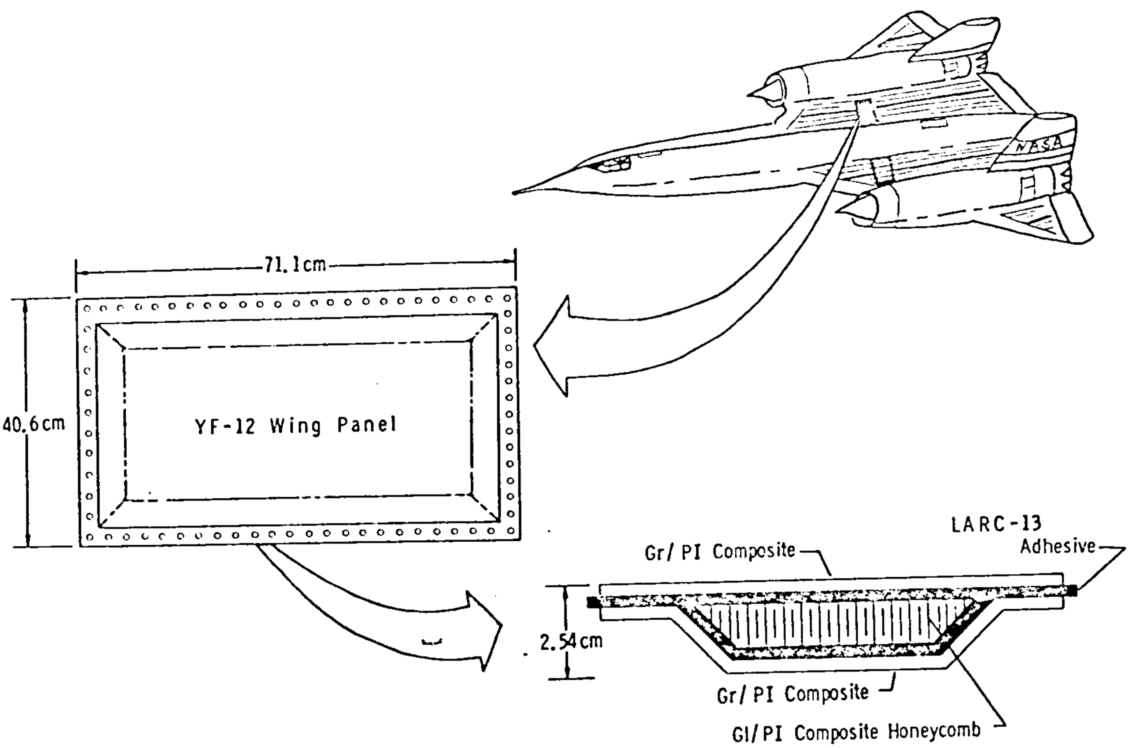

Figure 1. NASA YF-12 SCR Adhesively Bonded Gr/PI Wing Panel

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16. Abstract
A novel addition-polyimide adhesive, LARC-13, has been developed which shows promise for bonding both titanium and composites for applications which require service temperatures in excess of 533K (500°F). LARC-13 is based on an oligomeric bis-nadimide containing a meta-linked aromatic diamine. Due to its oligomeric nature the adhesive melts prior to polymerization, thereby allowing it to be processed at 344kPa (50psi) or less. Therefore, LARC-13 is ideal for the bonding of honeycomb sandwich structures. After melting, the resin thermosets during the cure of the nadic endcaps to a highly crosslinked system. Because of the cure mechanism associated with this adhesive, few volatiles are evolved, thus allowing large enclosed structures to be bonded. Preparation of the adhesive as well as bonding, aging and testing of lap shear and honeycomb samples are discussed.

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