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LARC-13 ADHESIVE DEVELOPMENT

S.G.Hill, C.H.Sheppard, and J.C. Johnson

BOEING AEROSPACE COMPANY
Seattle, Washington 98124

Contract NAS1-15562

NASA
National Aeronautics and
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FOREWORD

This work was conducted under the technical direction of Dr. T. St. Clair of NASA Langley Research Center, Hampton, Virginia. The Materials and Processes Department of the Boeing Aerospace Company was responsible for the work performed under this contract. Mr. J. T. Hoggatt, Mr. W. A. Symonds, and Mr. J. C. Johnson were program managers and Mr. S. G. Hill was technical leader. Acknowledgement is made of the technical assistance provided during the program by the following Boeing Aerospace Company personnel:

- C. H. Sheppard—Resin Synthesis, Materials and Processes
- J. V. Jaquish—Resin Synthesis
- W. C. DuMars—Materials and Processes
- R. A. Hodges—Materials and Processes

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1.0 INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

This report presents the work accomplished by the Boeing Aerospace Company for the National Aeronautics and Space Administration, Langley Research Center, under Contract NAS1-15562 during the period from November 1978 through April 1980. This program consisted of experimental studies to develop an improved adhesive for 589K (600°F) application by chemical or physical modification of NASA's LARC-13 resin. The program was accomplished under four separate tasks as follows:

- Task 1—Resin and Adhesive Formulation Study
- Task 2—Fabrication Study
- Task 3—Adherend Surface Preparation Study
- Task 4—Final Thermal Aging and Deliverable Items

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1.2 SUMMARY

This report documents work performed by the Boeing Aerospace Company for the National Aeronautics and Space Administration under NASA Contract NAS1-15562. The objectives of the program were as follows:

1. Development of an improved adhesive for 589K (600°F) application by chemical and/or physical modification of NASA's LARC-13 resin
2. Optimization of the adhesive film and bonding processes
3. Identification of compatible surface treatments for titanium and composite substrates

The work was performed in four separate tasks over a 21-month period. Task 1, Resin and Adhesive Formulation Study, was the primary effort of the program. This task was conducted under three separate headings: (1) resin synthesis and LARC-13 modification, (2) amide-imide copolymer study, and (3) adhesive compounding.

Four modified LARC-13 resins (Table 1) were synthesized by partial substitution of m,m'-methylene dianiline (m,m'-MDA). The first two resins (BAC-2 and BAC-3) were modified by substituting with 60 and 40 weight percent meta-phenylene diamine for m,m'-MDA. The third and fourth resins (BAC-4 and BAC-5) had 60 and 40 weight percent of 2,4-bis (para amino-benzyl) aniline (2,4-BABA) substituted for m,m'-MDA, respectively. The four modified LARC-13 resins were chemically characterized and evaluated as adhesives in lap-shear and crack extension tests.

During the Task 1 amide-imide copolymer study, three different copolymers (Table 2) were evaluated. The first, A7F, was a blend of LARC-13 and AMOCO's AI1130L. The second and third were, respectively, blends of BAC-3 resin with 25 and 50 PHR of AMOCO's Torlon 4000T amide-imide resin.

In Task 2, the parameters of film thickness, film B-staging, and cure conditions were evaluated for their effect upon bond strength of titanium-bonded lap-shear specimens at room temperature and 589K (600^{o}F).

In Task 3, a surface preparation study was conducted that evaluated four different surface pretreatments for titanium bonding. The surface treatments evaluated were:

1. Chromic acid anodize—5 volts
2. Chromic acid anodize—10 volts
3. Phosphate fluoride
4. Pasa-Jell 107

In Task 4, BAC-3 resin with 50 PHR amide-imide was evaluated on anodized titanium (10-volt chromic acid anodize) and graphite adherends. Crack extension, lap-shear, "T" peel, and flatwise tensile specimens were fabricated and tested to determine bond properties and the effect of thermal aging on bond strength.

2.0 TECHNICAL DISCUSSION

The objectives of this program were as follows:

1. Development of an improved adhesive for 589K (600°F) application by chemical and/or physical modification of NASA's LARC-13 resin
2. Optimization of the adhesive film and bonding processes
3. Identification of compatible surface treatments for titanium and composite substrates

To accomplish these objectives, the program was divided into four tasks:

- Task 1—Resin Formulation Study
- Task 2—Fabrication Study
- Task 3—Adherend Surface Preparation Study
- Task 4—Final Thermal Aging and Deliverable Items

2.1 TASK 1—RESIN FORMULATION STUDY

The goal of this study was to synthesize resins with higher temperature stability by modifying LARC-13 resin with increased aromatic structure in an attempt to raise its glass transition temperature (T_g). The initial plan was to raise the glass transition temperature by partial substitution with meta-phenylene diamine (MPDA) and 3,5-diaminobenzamidobenzene (3,5-DABAB) as codiamines.

2.1.1 Diamine Substitution Study

The initial plan called for partial substitution of m,m'-methylene dianiline (m,m'-MDA) with MPDA and 3,5-DABAB, as shown in Figure 1. The four resins that were to be synthesized are shown in Figure 2. However, 3,5-DABAB was not available from the chemical suppliers, and neither were 1,3,5-triamino benzene or 2,4,6-triamino toluene, considered to be good starting compounds for the synthesis of the 3,5-DABAB. Due to the unavailability of these starting materials, the use of 3,5-DABAB was deleted from the program.

To ensure that there were no problems in the synthesis procedure, a control batch of LARC-13 (BAC-1) was synthesized and tested along with the first two diamine-substituted resins (BAC-2 and BAC-3) shown in Figure 1. Chemical testing of these

three resins and a NASA-prepared LARC-13 resin was accomplished with no anomalies detected. Therefore, titanium lap-shear panels using the three BAC resins were fabricated. Ten- to twelve-mil films were made using 112E glass/A-1100 finish and the resins formulated with 60 PHR Plasmalloy 100 aluminum powder. LARC-13 was used as a baseline. After testing, it was readily apparent that the BAC resins yielded lower properties than the LARC-13 resin. These test results are reported in Table 3, items 1 through 4. A revised synthesis was developed and a second series of resins prepared and tested with the same low results (Table 3, items 5 through 7). It was decided to synthesize only LARC-13 until the Boeing procedures produced resins comparable to NASA-prepared LARC-13. The initial resin using the approved procedures was prepared and tested along with NASA's LARC-13. These results are reported in Table 1, items 8 through 10. Since Boeing's LARC-13 (BAC-1) resin was still very low in shear strength, it was obvious that more than one problem existed. Some of the potential problems encountered with Boeing's synthesis are summarized as follows:

1. Use of N_2 containing moisture instead of dry nitrogen
2. Addition of anhydrides from 50 percent solution of DMF instead of solid mixtures
3. The rate of addition of anhydrides (anhydrides were initially added slowly from DMF solution and this procedure was changed to adding the anhydrides as powder in equal increments)
4. Use of technical grade DMF in place of reagent grade DMF
5. Use of a different grade of aluminum filler in the film adhesives, Plasmalloy 100 versus Alcoa 101

The more detailed resin synthesis procedure and correct aluminum filler were obtained from NASA and another batch of LARC-13 resin synthesized. The NASA aluminum filler (Alcoa 101) was added and titanium-titanium lap-shear panels were fabricated, along with titanium-titanium lap-shear panels using NASA-prepared LARC-13 adhesive. The resulting test data demonstrated no difference in the two adhesive batches (Table 3, items 11 and 12). Based on these data, the next two resin batches (BAC-2 and BAC-3) were made substituting MPDA for m,m'-MDA as shown in Figure 1. From the resulting adhesive films, four lap-shear assemblies and one 6 x 6-inch wedge were bonded. In addition, a companion set of lap-shear and wedge assemblies were bonded using NASA-prepared LARC-13 adhesive. Following are the cure cycles used in making the bonded assemblies.

NASA LARC-13

- o Cure Cycle

  Apply full vacuum plus 0.068 MPa (10 psi) and heat assembly to 575K (575°F) at 2.2-3.3K (4-6°F) per minute. Hold at 575K (575°F) for 60 minutes and apply 1.38 MPa (200 psi). Heat to 602K (625°F) at 2.2-3.3K (4-6°F) per minute and hold 2 hours. Cool assembly to below 339K (150°F) before removing pressure.

- o Postcure Cycle

  Free standing, heat at 589K (600°F) for 6 hours.

Boeing Cure Cycle (BAC-2, BAC-3, BAC-4, and BAC-5)

- o Cure Cycle

  Apply full vacuum plus 0.068 MPa (10 psi) and heat assembly to 477K (400°F) at 2.2-3.3K (4-6°F) per minute. When assembly reaches 477K (400°F), apply 1.38 MPa (200 psi) positive pressure and hold 60 minutes. Heat assembly to 602K (625°F) at 2.2-3.3K (4-6°F) per minute and hold for 2 hours. Cool assembly to below 339K (150°F) before removing pressure.

- o Postcure Cycle

  Free standing, heat at 477K (600°F) for 6 hours.

Test results from tested lap-shear and crack extension specimens are reported in Table 4 and Figures 3 and 4.

As a check on the Boeing resin synthesis procedure, another batch of BAC-2 was prepared and tested. The initial titanium-titanium lap-shear properties using this batch of resin were far superior (Table 5) with respect to the system's 589K (600°F) properties than those of the previous resin batch (Table 4).

Based upon lap-shear properties obtained with a different titanium cleaning procedure on another NASA program (NAS1-15605), phosphoric acid anodize was used to evaluate the BAC-2 resin for direct comparison with the chromic acid anodize. These test results are reported in Table 5. The specimens prepared with phosphoric acid anodized titanium appeared to have better shear strength initially and after 100 hours of aging than specimens made with chromic acid anodized titanium. However, data on the the phosphoric acid anodized system obtained from Contract NAS1-15605 showed that the oxide is thinner and less stable in a heat environment, and further testing with phosphoric acid was terminated.

With synthesis problems solved for making LARC-13 resin, new batches of BAC-1, BAC-2, BAC-3, resins were synthesized as previously shown in Figure 1 and evaluated for lap-shear strength at room temperature, 589K (600°F), 589K (600°F) after 100 hours at 589K (600°F), and 589K (600°F) after 200 hours at 589K (600°F). These data are reported in Table 4 and were somewhat lower than expected. BAC-4 and BAC-5 resins were synthesized by substituting 2,4-BABA amine for the 3,5-DABAB, as previously shown in Figures 1 and 2 and evaluated with BAC-1, BAC-2, and BAC-3. The test results of BAC-4 and BAC-5 also are reported in Table 4. After 200 hours of aging at 589K (600°F), specimens from BAC-5 resin fell apart while loading. The failure mode of these specimens was adhesive and precluded the true evaluation of the thermal mechanical properties. After careful analysis, the trend of the data indicated that BAC-2 and BAC-3 resins were slightly better than BAC-4 and BAC-5 resins.

In the evaluation of the thermal gravimetric analysis (TGA) data of BAC-2 resin (Fig. 5), the decomposition temperature was 772K (932°F), whereas the comparable temperature of BAC-4 and BAC-5 resins was 752K (896°F). These data indicate that BAC-2 resin should be more thermally stable than BAC-4 and BAC-5 resins. After consultation with the program monitor, the resin evaluation plan that was previously presented (Fig. 1) was modified as shown in Figure 6. The 2,4-BABA amine was deleted and AMOCO's 4000T amide-imide was added to BAC-2 or BAC-3 resins in the copolymer studies for the rest of the program.

To solve the adhesive failure problem, a small test experiment was conducted using two different voltages and lap-shear specimen configurations. Titanium adherends were chromic acid anodized using both 5 and 10 volts. Specimens were evaluated using single and double laps. These test results are reported in Table 6. The lap-shear specimens fabricated with the 5-volt anodized adherends failed adhesively. The 10-volt anodized specimens failed cohesively with both configurations (single and double lap).

2.1.2 Amide-Imide Copolymer Study

This study was initiated to increase the bond strength of modified LARC-13 adhesives to honeycomb core by restricting or controlling the adhesive flow to improve filleting around the core cells. The addition of an AI 1130L (amide-imide) to LARC-13 adhesive made adhesive films easier to prepare by restricting flow and blistering

during the drying process. The addition of the amide-imide also restricts the flow of the LARC-13, improves filleting and bond strength to honeycomb core. Three different copolymers were evaluated during this study: A7F, BAC-3 with 25 PHR amide-imide, and BAC-3 with 50 PHR amide-imide. These resins were bonded with the previously presented cure cycle for BAC resins. The resins were formulated as follows:

A7F

- 50 PHR LARC-13
- 50 PHR amide/imide 1130L
- 16 PHR aluminum powder (Alcoa 101)
- 5 PHR Cab-o-Sil

BAC-3/50 percent amide/imide

- 50 PHR BAC-3
- 50 PHR Torlon 4000T
- 60 PHR Alcoa 101

BAC-3/25 percent amide/imide

- 50 PHR BAC-3
- 25 PHR Torlon 4000T
- 60 PHR Alcoa 101

Adhesive films were prepared from each formulated copolymer, and lap-shear, flat-wise tension, and crack extension specimens were bonded and tested. The composite-to-composite lap shear specimens were bonded as standard over-lap specimens. The addition of the amide-imide to the adhesives prevented the bonding of wide area lap shear specimens. The test results from the specimens are presented in Tables 7, 8, and 9. The initial lap-shear strength of LARC-13, BAC-2, BAC-3, and BAC-3 with 25 PHR amide/imide were lower than expected; however, BAC-2 and BAC-3 exhibited excellent 589K (600°F) strength. These low values were initially thought to be due to inadequate curing. However, through work on another contract (NAS1-15605), it was found that the chromic acid anodize bath was the major cause of these low numbers. After the bath has been used for a period of time, the current density must be kept on the high side of the specification to produce good bondable oxides. The failures of

these specimens were in the weak oxide layer. The increase in voltage moderately improved the lap-shear value. These data are shown in Table 15.

2.1.3 Adhesive Compounding

The goal of this phase of Task 1 was to improve the high-temperature performance of the adhesive by reducing the thermal stresses in the adhesive/substrate interface. Stress reduction was attempted by physical modification of the adhesive through the use of fillers. Previous work in this task was conducted with Alcoa 101 aluminum powder for filler material. This phase evaluated the use of elemental titanium powder (Penn Nuclear's 100), silica (JT Baker's reagent grade), and graphite flock (Union Carbide's Thornel Carbon Fiber Mat VMT-75 ground to powder). This selection of fillers was an attempt to match the thermal expansion coefficient (CTE) of the substrate materials with minimum effect on flow and adhesion characteristics. BAC-3 resin was selected for this study based on initial lap-shear strength. It was felt that the differences in honeycomb flatwise tensile strength and initial elevated-temperature properties were due to adhesive uniformity and cure/postcure conditions.

The initial titanium lap-shear values from the silica-filled material showed some loss of strength when tested at 589K (600°F) (Table 10), but recovered during the 125 hours of thermal aging. This lowering of strength initially was probably due to inadequate postcuring or nonuniform adhesive parts. Polyimide laminate notched lap-shear specimens and flatwise tensile specimens showed some degradation when tested at 589K (600°F) and at 589K (600°F) after 125 hours at 589K (600°F). However, the lap-shear specimens failed in the composite adherends. Honeycomb sandwich flatwise tensile specimens failed at the adhesive-core interface because of inadequate filleting to the core.

Adhesive test results, Table 10, showed that titanium and graphite were good filler materials for the adhesive in thermal aging environments for 125 hours at 589K (600°F).

CTE was measured on bonded specimens that were fabricated with the titanium, graphite, and silica filled adhesives. The coefficient of thermal expansion was measured using a Thermo Physics dilatometer. The system used involves a quartz specimen holder and pushrod and is routinely calibrated using an NBS platinum

specimen. For very accurate measurements, a quartz correction is used to correct for the dimensional changes in the quartz (approximately 10^{-7} in./in./°C). It was interesting to note that the test results (Table 11) showed no significant CTE difference on titanium adherends, while there are significant differences among thermal expansion coefficients on the PMR-15 composite adherends. The CTE for titanium is evidently 10 times that for the adhesive on graphite/PI adherends.

2.2 TASK 2—FABRICATION STUDY

This task was directed at improving adhesive performance by improving control over bondline thickness and filleting behavior. A process optimization study was conducted on adhesive thickness, B-staging conditions, cure conditions, cure time, cure temperature, postcure time, and postcure temperature. Adhesive tape preparation and bonding processes were run concurrently using the fractional factorial test matrix (Table 12). This test matrix was selected because it can screen numerous samples with relatively few experiments. A total of eight experiments were run on titanium lap-shear specimens and tested at room temperature using the following film preparation procedures:

Adhesive Film B-Staging

- B-Stage No. 1
  - 30 minutes at 325K (125°F)
  - 45 minutes at 339K (150°F)
  - 120 minute at 408K (275°F)
  - 10 minutes at 436K (375°F)
- B-Stage No. 2
  - 30 minutes at 325K (125°F)
  - 45 minutes at 339K (150°F)
  - 120 minutes at 323K (250°F)
  - 30 minutes at 422K (300°F)
  - 10 minutes at 463K (375°F)

Adhesive Cures

- Cure No. 1

  Parts were placed in an autoclave at room temperature under 660 mm (26 inches) of mercury vacuum and raised to 575K (575°F) at a rate of 1.65-2.75K (3-5oF) per minute. After 60 minutes at 575K (575°F), 0.52 MPa (75 psi) pressure was applied and the temperature raised to 600K (620°F) at a rate of 1.65-2.75K (3-5°F) per minute. Parts were held at 600K (620°F) for 120 minutes and then cooled to 339K (150°F) before releasing pressure.

- Cure No. 2

  Parts were placed in an autoclave at room temperature under 660 mm (26 inches) of mercury vacuum and raised to 477K (400°F) at a rate of 1.65-2.75K (3-5°F) per minute. When the temperature reached 477K (400°F), 1.38 MPa (200 psi) pressure for laminate or 0.52 MPa (75 psi) pressure for honeycomb sandwich parts was applied and the temperature held for 60 minutes. The temperature then was raised to 600K (620°F) at a rate of 1.65-2.75K (3-5°F) per minute and held for 120 minutes. Parts were cooled to 330K (150°F) before releasing pressure.

Adhesive Postcures

- Postcure No. 1—6 hours at 589K (600°F)
- Postcure No. 2—10 hours at 589K (600°F)

Test results of these specimens are presented in Table 13. The failures were 90-95 percent cohesive on all the tested specimens and showed good adhesive coverage. The failure modes of all the specimens appeared to be equally cohesive; however, the shear strength varied from 18 to 27 MPa (2635 to 3915 psi).

The bonding parameters selected for BAC-3 resin were B-stage no. 2, cure cycle no. 2, and postcure no. 1, with either adhesive thickness. PMR-15 polyimide notched laminate lap-shear and flatwise tensile specimens were bonded using these parameters. Data are reported in Table 14. The failures for lap-shear specimens were 90-95 percent cohesive failures. Polyimide honeycomb flatwise tensile specimens failed 95-100 percent adhesively to the core.

2.3 TASK 3—ADHEREND SURFACE PREPARATION STUDY

The objective of this task was to choose, based on lap-shear and wedge test results, the optimum surface preparation procedures for both the titanium and composite adherends for use in 589K (600°F) aging tests. Titanium surface treatments up to this point were chromic acid anodize, with the exception of one experiment with phosphoric acid anodize evaluated earlier in Task 1. However, phosphoric acid anodize was dropped in Task 1 due to the lack of thermal aging stability at elevated temperatures of 589K (600°F) or greater.

Under this task, four different surface treatments for titanium were evaluated at 589K (600°F) in lap-shear and crack extension tests. Chromic acid anodize was the baseline. The four different surface treatments evaluated were:

1. Phosphate fluoride
2. Pasa-Jell 107
3. Chromic acid anodize—10 volts
4. Chromic acid anodize—5 volts

Titanium lap-shear and crack extension specimens were bonded with BAC-3/50 PHR amide/imide adhesive and 60 PHR Alcoa 101 aluminum filler. Test results of these specimens are reported in Table 15.

The data demonstrated that 10-volt chromic acid anodize was the superior surface treatment, followed by phosphate fluoride, 5-volt chromic acid anodize, and Pasa-Jell 107. The failure modes of all four surface treatments were 85-95 percent cohesive, with some oxide failures of specimens treated with 5-volt chromic acid anodize. From these test results and data from previous tasks, 10-volt chromic acid anodize was selected for Task 4—Thermal Aging Study.

No screening of adherend surface preparation was conducted on the graphite composite adherends. The composite adherends were solvent cleaned, vacuum blasted followed by solvent cleaning, and primed with a dilute coat of the adhesive resin (BAC-3 with 50 PHR AI).

2.4 TASK 4—FINAL THERMAL AGING AND DELIVERABLES

The objective of this task was to evaluate the resin formulation identified in Task 1 as having the greatest potential for long-term (125-200 hours) 589K (600°F) use. The solution was to be based upon the mechanical properties of the adhesive system before and after thermal aging at 589K (600°F).

Resin BAC-3 with 50 PHR amide-imide, 6 PHR graphite flock, was selected for Task 4 evaluation. This adhesive system was very similar in propertites to LARC-13 and other modifications of LARC-13 adhesive, and either of the other systems could have been selected. Differences noted in some of the mechanical properties are probably caused by batch-to-batch variations in resins and adhesive film making or inadequate surface preparation, rather than differences in resin formulation.

Lap-shear, polyimide honeycomb sandwich flatwise tensile, crack extension, and T-peel specimens were fabricated using adhesive film made from BAC-3 resin blended with 50 PHR Torlon 5000T amide-imide, 6 PHR graphite flock on 112E-glass with A-1100 finish. Specimens were bonded using the cure cycle selected in Task 2 and tested according to the test matrix shown in Table 16. A complete listing of the test data is contained in Table 17, and Table 18 is a summary of the data from the thermal aging evaluation.

The quality of the bonded lap-shear specimens was good with initial titanium and composite lap-shear speicmens failing at 21.4 MPa (3100 psi) and 16.2 MPa (2345 psi), respectively. When tested at 589K (600°F), these specimens failed at 11.5 MPa (1665 psi) and 11.2 MPa (1620 psi). After thermal aging 200 hours at 589K (600°F) and tested at 589K (600°F), specimens failed at stresses of 10.2 MPa (1485 psi) and 7.8 MPa (1125 psi). The polyimide honeycomb flatwise tension specimens failed at 4.7 MPa (675 psi) at RT and 1.3 MPa (190 psi) after cycling 200 hours at 589K (600°F) and tested at 589K (600°F).

Figures 7, 8, and 9 show typical failed flatwise tensile, lap-shear, and peel specimens. The failures were cohesive and did not change with the different aging conditions and test temperatures.

Additional test specimens for delivery to NASA were fabricated using the same adhesive formulation, surface preparation, and bonding parameters. However, three batches of Torlon 4000T amide-imide were received before a usable batch was obtained. This usable batch did not blend with the LARC-13 adhesive to give the same properties as the batch used in the aging study. The materials were either insoluble because the polymers were advanced too much, or the polymers had not reached the correct B-staging to give good thermal properties.

3.0 CONCLUSIONS AND RECOMMENDATIONS

The primary objectives of this program were to develop an improved adhesive for 589K (600°F) application, to identify compatible surface treatments, and to optimize the adhesive film and bonding processes. The program objectives were successfully achieved by the studies conducted.

3.1 CONCLUSIONS

1. Partial substitution of m,m'-MDA with MPDA in the LARC-13 resin chemistry produced two new resins (BAC-2, BAC-3) that were equivalent to or better than the original LARC-13. The resins were easier to process as an adhesive film than LARC-13.
2. BAC-4 and BAC-5 resins were not improvements over the LARC-13 resin.
3. The addition of amide-imide polymers to the base resins (LARC-13 and BAC-3) improves the adhesive properties of sandwich structure by improving the filleting of the adhesive.
4. The addition of the AI 1130L amide-imide polymer to the base resins appears to make them less attractive for wide-area bonding.
5. Thick adhesive films produced better room-temperature flatwise tensile and lap-shear strengths when processed with B-stage 2 (heated 30, 45, 120, and 10 minutes at 325, 339, 408, and 436K (125, 150, 275, and 375°F), respectively) and cure cycle 2 (RT to 477K under vacuum, 1.65-2.75K (3-5°F)/min., apply 1.38 MPa (200 psi) for laminates or 0.62 MPa (75 psi) for honeycomb sandwich, hold 60 minutes, raise temperature to 600K (620°F) at 1.65-2.75K (3-5°F)/min., hole 120 minutes, cool to 330K (150°F) before releasing pressure).
6. Thin adhesive film should be used for composite-to-composite bonding.
7. LARC-13 and modified LARC-13 resins were compatible with Pasa-Jell 107, chromic acid anodize, and phosphate fluoride titanium surface treatments, but 10 volt chromic acid anodizing produced the best bonding surface.

3.2 RECOMMENDATIONS

Based upon this study program, the following recommendations are offered:

1. Optimize resin formulations to achieve the best adhesive properties after thermal aging (1000 hrs).

2. Determine the long-term thermal stability of LARC-13, BAC-3, and A7F adhesives at 589K (600°F).
3. Establish design allowables for the BAC-3 and modified BAC-3 resins with respect to their mechanical properties and environmental stability in honeycomb sandwich and laminate structural elements.
4. Develop and optimize a titanium cleaning procedure to be used in conjunction with BAC-3 that will exhibit long-term stability in high-temperature environments.

4.0 REFERENCES

1. T. L. St. Clair and D. J. Progar, SAMPE Symposium, 24, May 1979.

2. C. H. Shephard, J. T. Hoggatt, and W. A. Symonds, "Manufacturing Processes for Fabricating Graphite/PMR-15 Polyimide Structural Elements," Final Report, Contract NAS1-15009, Boeing Aerospace Company, Seattle, WA, Feb. 1979.

3. R. W. Vaughn, C. H. Shephard, and M. K. O'Rell, "Weld Bonding of Titanium with Polyimides Adhesives," NASA CR-132665, Jan. 1975.

Table 1. Adhesive Formulations

Constituents	Resin Formulation Constituents (wt %)				
	BAC-1	BAC-2	BAC-3	BAC-4	BAC-5
1. Benzophenone tetracarboxylic dianhydride (BTDA)	385.3	429.1	45.69	29.77	26.23
2. Nadic anhydride (NA)	23.55	21.96	21.88	23.76	23.86
3. 3,3'-methylenedianiline (3,3'-MDA)	37.92	25.36	17.84	19.58	12.21
4. Metaphenylene diamine (MPDA)		9.37	14.59		
5. 2,4-bis(para amino-benzyl) aniline (2,4-BAB)				26.88	37.71

NOTE: All formulas contained DMF at 50% resin solids and Alcoa 101 aluminum powder at 60% resin solids + aluminum.

Table 2. Amide-Imide Copolymer Adhesive Formulations

Constituent	Resin Formulation Constituents (wt %)		
	A7F	50% 4000T	25% 4000T
1. Benzophenone tetracarboxylic dianhydride (BTDA)	19.26	22.84	34.27
2. Nadic anhydride (NA)	11.77	10.94	16.41
3. 3,3'-methylenedianiline (3,3'-MDA)	18.96	8.92	13.38
4. Metaphenylene diamine (MPDA)		7.30	10.94
5. Torlon 4000T		50.00	25.00
6. AI 1130L	50.00		

NOTE: All formulas contained DMF at 50% resin solids and Alcoa 101 aluminum powder at 60% resin solids + aluminum.

Table 3. Summary Lap-Shear Data, Titanium Substrate

Item No.	Resin No.	Batch No.	Test Temperature, °F	Shear Strength, MPa (psi)
1	BAC-1(a)	1	RT	11.8 (1705)
2	BAC-2	1	RT	11.4 (1655)
3	BAC-3	1	RT	13.0 (1885)
4	LARC-13 (NASA)	--	RT	26.3 (3815)
5	BAC-1(b)	2	RT	12.9 (1875)
6	BAC-2	2	RT	12.4 (1795)
7	BAC-3	2	RT	11.2 (1625)
8	LARC-13 (NASA)	--	RT	27.3 (3960)
9	BAC-1(c)	3	RT	13.9 (2010)
10	BAC-1(d)	3	RT	12.9 (1875)
11	LARC-13 (NASA)	4	RT	27.2 (3950)
12	BAC-1(e)	4	RT	27.3 (3960)

Table 4. Summary Lap-Shear Properties

	Lap-Shear Properties, MPa (psi)				
	LARC-13	BAC-2	BAC-3	BAC-4	BAC-5
After postcure					
RT initial	20.1 (2920)	13.2 (1910)	12.1 (1760)	8.4 (1220)	7.3 (1060)
589K (600°F)	8.1 (1180)	9.3 (1350)	6.7 (970)	7.8 (1130)	6.1 (880)
After 100 hours 589K (600°F)					
589K (600°F)	8.8 (1280)	9.3 (1350)	8.7 (1260)	8.2 (1195)	5.1 (740)
After 200 hours 589K (600°F)					
589K (600°F)	4.6 (670)	3.9 (570)	3.4 (500)	2.3 (330)	1/

1/ Specimen broke prior to loading.

Table 5. Surface Preparation Study,
Summary Lap-Shear Properties, BAC-2 Resin

	Lap-Shear Properties, MPa (psi)	
	Chromic Acid Anodized	Phosphoric Acid Anodized
After postcure		
RT	13.8 (2000) 1/	15.0 (2170) 1/
589K (600°F)	13.6 (1980)	14.5 (2100)
After 100 hours 589K (600°F)		
589K (600°F)	15.0 (2170)	19.6 (2840)

1/ Specimens not postcured before test.

Table 6. LARC-13 Titanium Bond Properties
Chromic Acid Anodize, 5 volts versus 10 volts

Surface Treatment and Coupon Configuration	Lap Shear Strength, MPa (psi)		
	Without Postcure	Postcured	
	RT	RT	589K (600°F)
LARC-13			
10 volts, single lap shear	23.7 (3440)	20.5 (2975)	11.3 (1645)
10 volts, double lap shear	30.8 (4460)	30.8 (3600)	9.5 (1380)
5 volts, single lap shear	16.7 (2420)	14.7 (2135)	8.5 (1235)

Table 7. Summary Data, Titanium/Titanium Lap Shear

	Titanium/Titanium Lap Shear, MPa (psi)					
	LARC-13	A7F	BAC-2	BAC-3	BAC-3 25 PHR AI	BAC-3 50 PHR AI
RT initial	15.8 (2290)	28.5 (4130)	15.4 (2235)	17.0 (2470)	13.9 (2010)	19.4 (2810)
589K (600°F) initial	8.1 (1180)	8.1 (1180)	13.2 (1910)	13.9 (2015)	5.4 (780)	3.3 484)
RT after 125 hours at 589K (600°F)	8.8 (1280)	---	---	---	---	---
589K (600°F) after 125 hours at 589K (600°F)	4.6 (670)	7.5 (1090)	8.2 (1190)	8.8 (1270)	10.7 (1555)	10.2 (1475)

Table 8. Summary Data, PI Sandwich Flatwise Tensile

	PI Sandwich Flatwise Tensile, MPa (psi)					
	LARC-13	A7F	BAC-2	BAC-3	BAC-3 25 PHR AI	BAC-3 50 PHR AI
RT initial	4.0 (575)	5.9 (855)	5.0 (730)	5.5 (790)	1.7 (245)	1.5 (215)
589K (600°F) initial	2.9 (420)	4.1 (590)	2.2 (315)	1.9 (270)	1.2 (180)	1.8 (255)
RT after 125 hours at 589K (600°F)	---	---	---	---	---	---
589K (600°F) after 125 hours at 589K (600°F)	1.6 (235)	2.8 (400)	2.2 (315)	1.9 (280)	0.9 (125)	1.3 (185)

Table 9. Summary Data, Titanium/Titanium Crack Extension

	Titanium/Titanium Crack Extension, mm (inch) (Total Crack Growth)					
	LARC-13	A7F	BAC-2	BAC-3	BAC-3 25 PHR AI	BAC-3 50 PHR AI
RT initial crack length	30.5 (1.20)	29.7 (1.17)	29.7 (1.18)	29.7 (1.18)	38.4 (1.51)	27.2 (1.07)
589K (600°F) after 1 hour	12.7 (0.50)	2.5 (0.10)	2.8 (0.11)	3.6 (0.14)	---	---
589K (600°F) after 3 days	12.9 (0.51)	4.3 (0.17)	3.6 (0.14)	5.1 (0.20)	8.1 (0.32)	7.1 (0.28)
589K (600°F) after 5 days	13.2 (0.52)	5.8 (0.22)	5.6 (0.22)	6.4 (0.25)	9.4 (0.37)	8.1 (0.32)

Table 10. Summary Data, Adhesive Filler Evaluation
(BAC-3 with 50 PHR Al, Graphite Filler)

	Aluminum	Titanium	Silica	Graphite
Ti/Ti Lap Shear, MPa (psi)				
RT initial	19.4 (2810)	22.4 (3250)	16.6 (2410)	21.1 (3055)
589K (600°F)	3.3 (484)	13.5 (1965)	8.5 (1235)	13.0 (1885)
RT after 125 hours at 589K (600°F)		15.7 (2270)	15.0 (2180)	16.1 (2335)
589K after 125 hours at 589K (600°F)	10.2 (1475)	11.0 (1600)	9.4 (1370)	10.6 (1540)
PI/PI Notched Lap Shear, MPa (psi)				
RT initial		11.7 (1700)	10.4 (1515)	10.9 (1585)
589K (600°F)		5.4 (785)	5.9 (855)	6.5 (910)
589K after 125 hours at 589K (600°F)		8.9 (1290)	7.4 (1070)	6.6 (960)
PI Sandwich Flatwise Tension, MPa (psi)				
RT initial	1.5 (215)	2.2 (325)	1.7 (240)	1.4 (200)
589K (600°F)	1.8 (255)	1.9 (270)	1.5 (220)	1.5 (215)
589K after 125 hours at 589K (600°F)	1.3 (185)	0.8 (120)	0.6 (90)	0.8 (110)
Ti/Ti Crack Extension, mm (in.)				
RT initial	27.2 (1.07)	3.0 (1.18)	3.4 (1.34)	3.4 (1.28)
589K (600°F), 72 hours 1/	7.1 (0.28)	0.3 (0.11)	0.3 (0.11)	0.2 (0.09)
589K (600°F), 125 hours 1/	8.1 (0.32)	0.4 (0.17)	0.4 (0.15)	0.3 (0.11)

1/ Crack growth after aging.

Table 11. Coefficient of Thermal Expansion (CTE) Data

Bonding Adherend	Filler	Adhesive	Thermal Expansion Coefficient, in./in./°F
6Al-4V titanium	Aluminum	LARC-13	5.4×10^{-6}
6Al-4V titanium	Aluminum	BAC-3 with 25 PHR AI	5.5×10^{-6}
6Al-4V titanium	Aluminum	BAC-3 with 50 PHR AI	5.5×10^{-6}
6Al-4V titanium	Graphite	BAC-3 with 50 PHR AI	5.5×10^{-6}
6Al-4V titanium	Silica	BAC-3 with 50 PHR AI	5.4×10^{-6}
6Al-4V titanium	Titanium	BAC-3 with 50 PHR AI	5.4×10^{-6}
PMR-15/CE 6000 graphite	Silica	BAC-3 with 50 PHR AI	0.60×10^{-6}
PMR-15/CE 6000 graphite	Titanium	BAC-3 with 50 PHR AI	0.51×10^{-6}
PMR-15/CE 6000 graphite	Graphite	BAC-3 with 50 PHR AI	0.49×10^{-6}
PMR-15/CE 6000 graphite	Aluminum	BAC-3 with 50 PHR AI	0.31×10^{-6}

NOTE: Titanium and silica fillers were 60 PHR; graphite filler was 6 PHR.

Table 12. Task 2 Test Matrix

		Cure No. 1		Cure No. 2	
Thickness	Postcure	B-Stage 1	B-Stage 2	B-Stage 1	B-Stage 2
Thick	No. 1	x			x
	No. 2		x	x	
Thin	No. 1		x	x	
	No. 2	x			x

Table 13. Fabrication Study—Room-Temperature Titanium Lap-Shear Data (BAC-3 with 50 PHR AI, Graphite Filler)

Thickness, mm (mil)	Postcure	Titanium Lap-Shear, MPa (psi)			
		Cure No. 1		Cure No. 2	
		B-Stage 1	B-Stage 2	B-Stage 1	B-Stage 2
0.28-0.53 (15-21)	No. 1	24.1 (3500)			27.0 (3915)
	No. 2		20.1 (2915)	18.6 (2700)	
0.25-0.36 (10-14)	No. 1		18.2 (2635)	18.7 (2710)	
	No. 2	23.8 (3450)			24.2 (3510)

Table 14. Fabrication Study, Room-Temperature Lap-Shear and Flatwise Tensile Data (BAC-3 with 50 PHR AI, Graphite Filler)

	Adhesive Thickness, mm (in.)	Ultimate Strength	Failure Mode
PI/PI Notched Lap-Shear, MPa (psi)	0.25-0.36 (0.010-0.014)	19.3 (2800)	90-95% composite
	0.38-0.53 (0.015-0.021)	18.5 (2680)	90-95% composite
PI Sandwich Flatwise Tension, MPa (psi)	0.25-0.36 (0.010-0.014)	3.1 (460)	95-100% adhesive to core
	0.38-0.53 (0.015-0.021)	4.2 (610)	95-100% adhesive to core

Table 15. Surface Preparation Study,
Crack Extension and Lap-Shear Strength at 589K (600°F)
BAC-3 with 50 PHR AI

Aluminum Filler	Phosphate Fluoride	PasaJell 107	Chromic Acid Anodize	
			10 volts	5 volts
Lap-Shear Strength, MPa (psi)	10.1 (1470)	8.1 (1180)	12.4 (1800)	8.5 (1240)
Crack Extension, mm (in.)	35.6 (0.14)	43.2 (0.17)	22.9 (0.09)	38.1 (0.15)
Graphite Filler				
RT	18.2 (2645)			
589K (600°F)	15.7 (2270)			

Table 16. Task 4 Test Matrix

Specimen		Control		After 125 hours at 589K (600°F)		After 200 hours at 589K (600°K)	
		RT	589K (600°F)	RT	589K (600°F)	RT	589K (600°F)
Lap-Shear	Titanium	4	4	4	4	4	4
	Composite	4	4	4	4	4	4
Flatwise Tension	Polyimide Honeycomb Sandwich	4	4	4	4	4	4
Peel	Titanium to titanium	--	4	--	4	--	4
Wedge	Titanium to titanium	--	4	--	4	--	4

Table 17. Thermal Data (BAC-3 with 50 PHR Al, Graphite Filler)

Specimen		Control Values		After 125 hours at 589K (600°F)		After 200 hours at 589K (600°F)	
		Ambient	589K (600°F)	Ambient	589K (600°F)	Ambient	589K (600°F)
Lap-Shear, MPa (psi)	Titanium	18.8 (2720)	10.8 (1560)	14.1 (2040)	11.4 (1650)	13.2 (1910)	11.7 (1700)
		21.5 (3120)	9.0 (1310)	12.4 (1800)	11.5 (1670)	12.3 (1790)	9.7 (1410)
		20.5 (2970)	12.8 (1850)	14.8 (2140)	12.1 (1750)	11.9 (1720)	9.4 (1370)
		24.8 (3590)	13.3 (1930)	15.5 (2250)	13.2 (1910)	10.7 (1550)	10.1 (1460)
	x	21.4 (3100)	11.5 (1665)	14.2 (2060)	12.0 (1745)	12.0 (1745)	10.2 (1485)
	Composite	15.6 (2260)	11.4 (1660)	9.6 (1390)	10.1 (1460)	8.9 (1290)	8.0 (1160)
		16.1 (2340)	11.4 (1660)	10.4 (1510)	9.9 (1430)	8.0 (1160)	7.5 (1090)
		18.2 (2640)	11.9 (1720)	10.1 (1460)	9.0 (1300)	7.5 (1090)	7.9 (1150)
		14.8 (2140)	9.9 (1430)	8.8 (1270)	10.0 (1450)	7.7 (1120)	7.6 (1100)
	x	16.2 (2350)	11.2 (1620)	9.7 (1410)	9.7 (1410)	8.0 (1165)	7.8 (1125)
"T"-Peel, MPa (psi)	Titanium		51.1 (1.8)		51.1 (1.8)		36.9 (1.3)
			56.7 (2.0)		42.6 (1.5)		31.2 (1.1)
			53.9 (1.9)		48.2 (1.7)		34.0 (1.2)
			62.4 (2.2)		39.7 (1.4)		31.2 (1.1)
			56.7 (2.0)		45.4 (1.6)		34.0 (1.2)
Flatwise Tension, MPa (psi)	Composite	5.2 (750)	2.6 (380)	2.3 (335)	1.9 (270)	1.8 (260)	1.6 (230)
		4.6 (665)	2.2 (325)	2.2 (315)	2.1 (305)	1.3 (190)	1.2 (170)
		4.9 (710)	3.0 (435)	2.1 (300)	2.0 (285)	1.4 (200)	1.2 (175)
		3.9 (570)	3.0 (435)	2.1 (300)	1.9 (280)	1.4 (200)	1.3 (190)
		4.7 (675)	2.7 (395)	2.2 (315)	2.0 (285)	1.5 (215)	1.3 (190)
Crack Extension, cm (in.)	Titanium	3.2 (1.27)	0.3 (0.10)		0.4 (0.14)		0.4 (0.14)
		2.9 (1.14)	0.2 (0.09)		0.4 (0.16)		0.5 (0.21)
		3.2 (1.27)	0.2 (0.07)		0.3 (0.12)		0.4 (0.16)
		2.8 (1.11)	0.3 (0.10)		0.5 (0.18)		0.6 (0.22)
		3.0 (1.20)	0.2 (0.09)		0.4 (0.15)		0.5 (0.18)

Table 18. Summary Data (BAC-3 with 50 PHR Al, Graphite Filler)

			After 125 hours at 589K (600 F)		After 200 hours at 589K (600 F)	
	RT Initial	589K (600°F) Initial	RT	589K (600°F)	RT	589K (600°F)
Ti/Ti Lap-Shear, MPa (psi)	21.4 (3100)	11.5 (1665)	14.2 (2060)	12.0 (1745)	12.0 (1745)	10.2 (1485)
PI/PI Lap-Shear, MPa (psi)	16.2 (2345)	11.2 (1620)	9.7 (1410)	9.7 (1410)	8.0 (1165)	7.8 (1125)
Ti/Ti "T" Peel, g/2.54 cm (lb/in.)		56.7 (2.0)		45.4 (1.6)		34.0 (1.2)
PI Sandwich Flatwise Tension, MPa (psi)	4.7 (675))	2.7 (395)	2.2 (315)	2.0 (285)	1.5 (215)	1.3 (190)
Ti/Ti Crack Extension, cm (in.)	3.0 (1.20)	0.2 (0.09) 1/		0.4 (0.15) 1/		0.5 (0.18) 1/

1/ Crack growth after exposure.

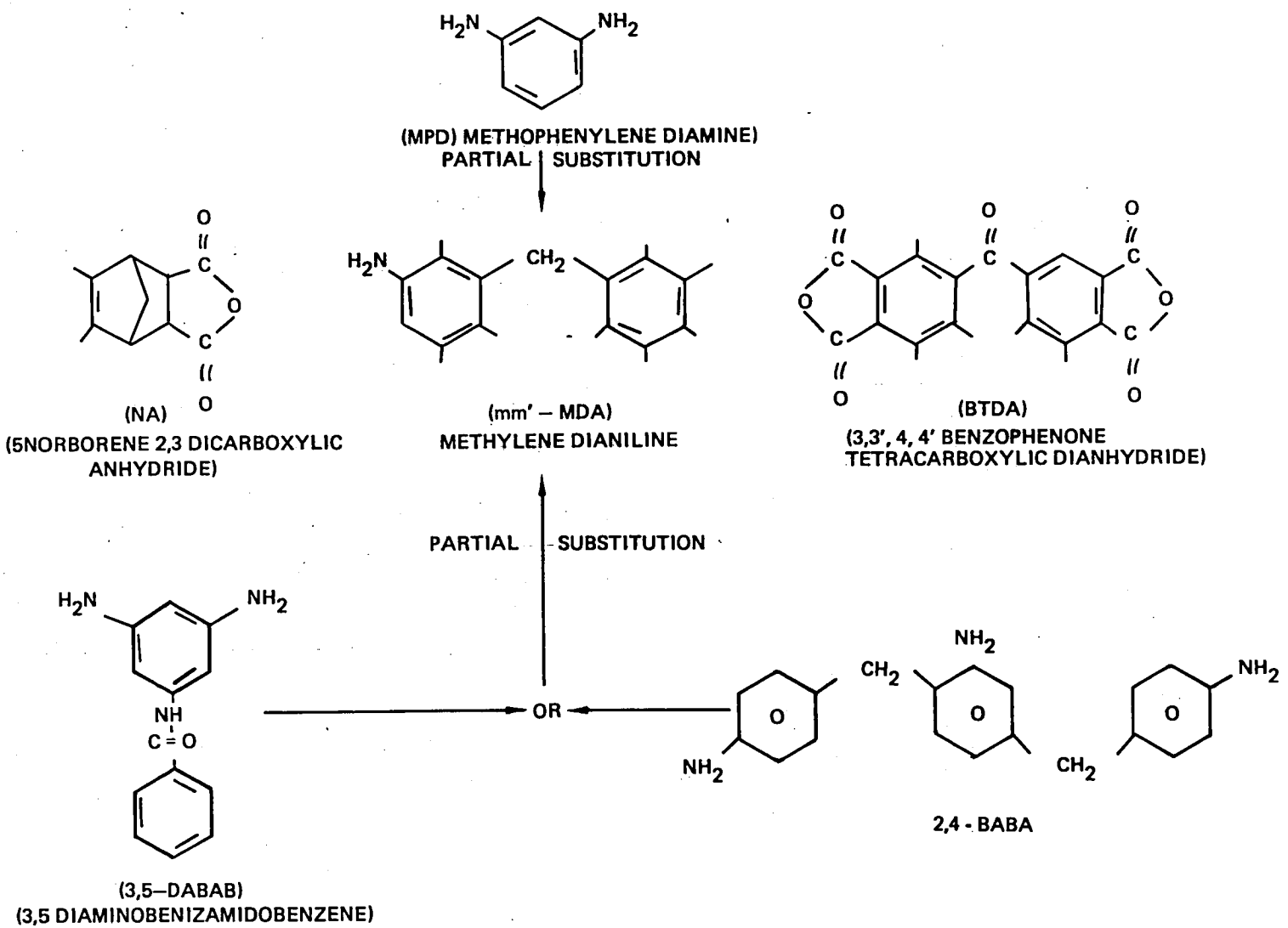
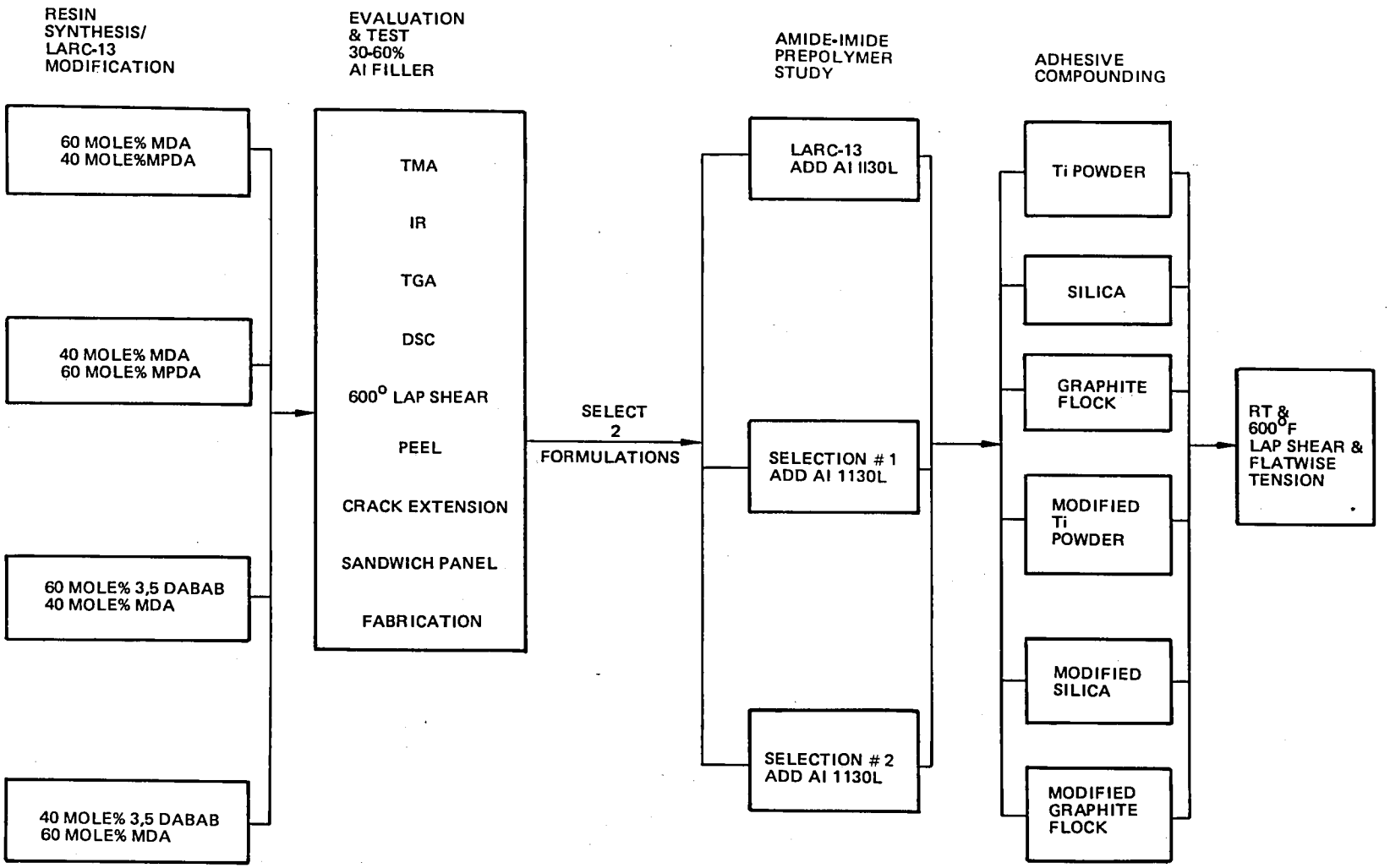


Figure 1: Daimine Substitution Scheme



NOTE: 2,4 BABA AMINE WAS SUBSTITUTED FOR 3,5 DABAB SYNTHESIS SCHEME

Figure 2: Task 1 Resin Formulation Study

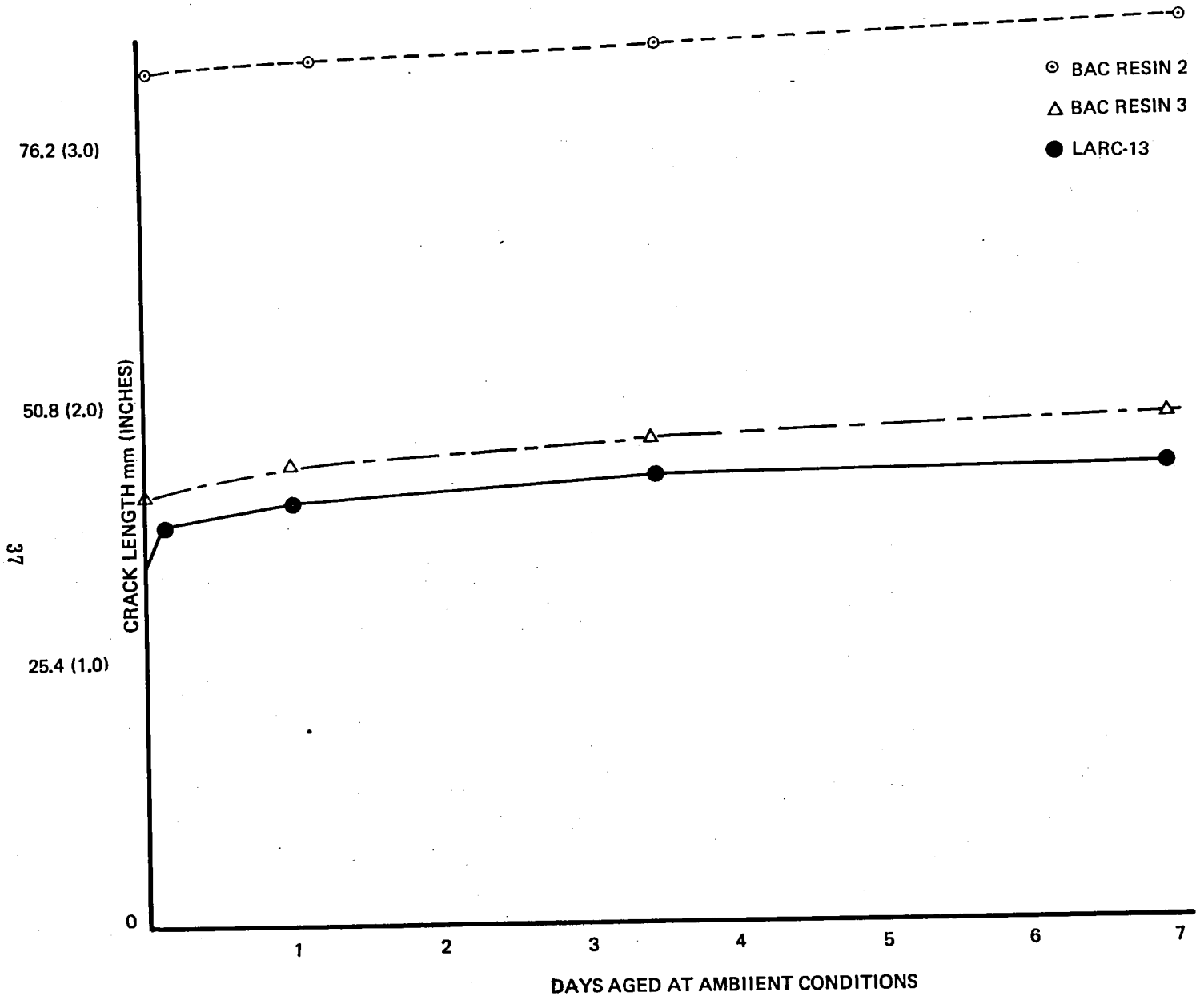


Figure 3: Crack Extension Data

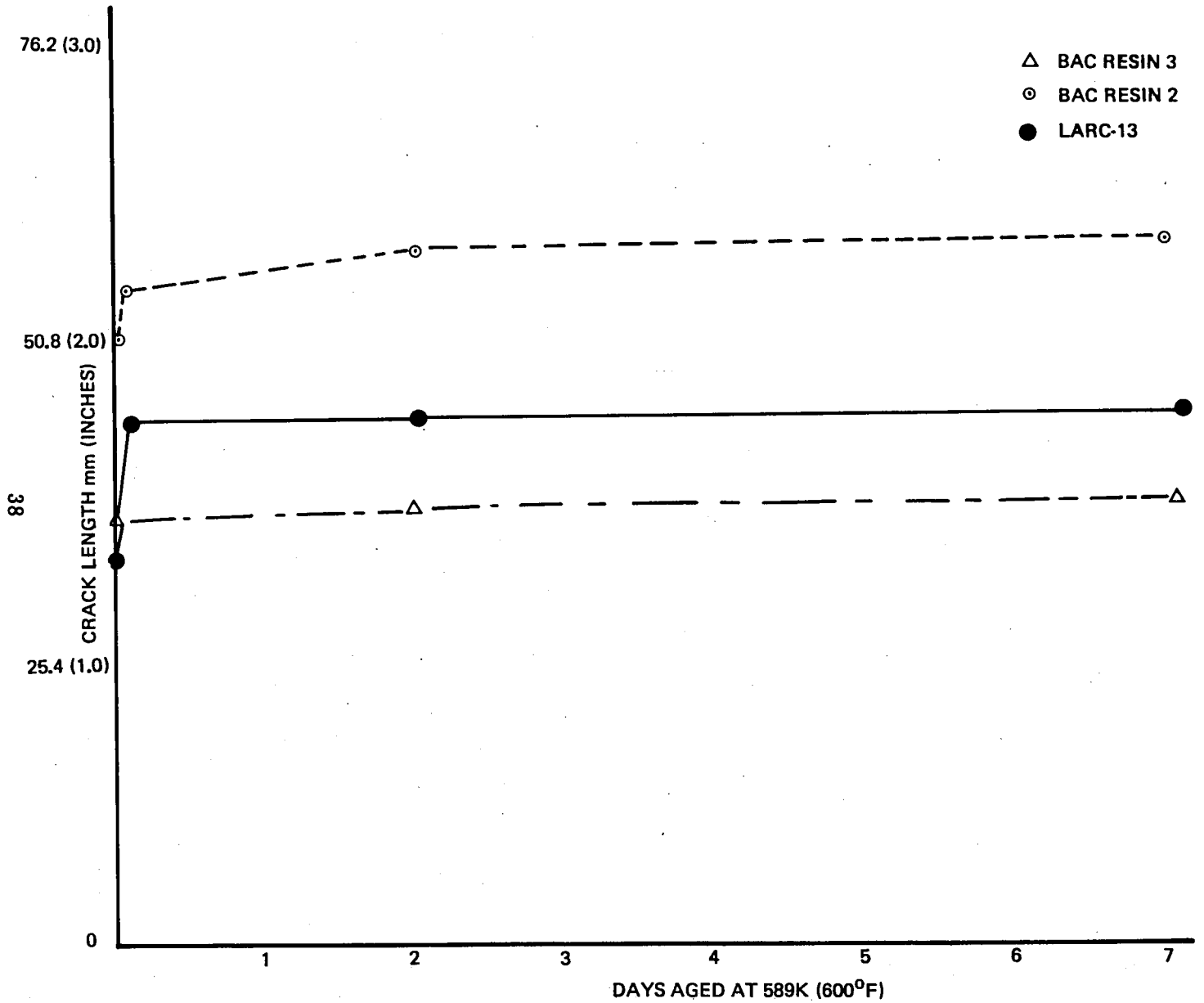


Figure 4: Crack Extension Data

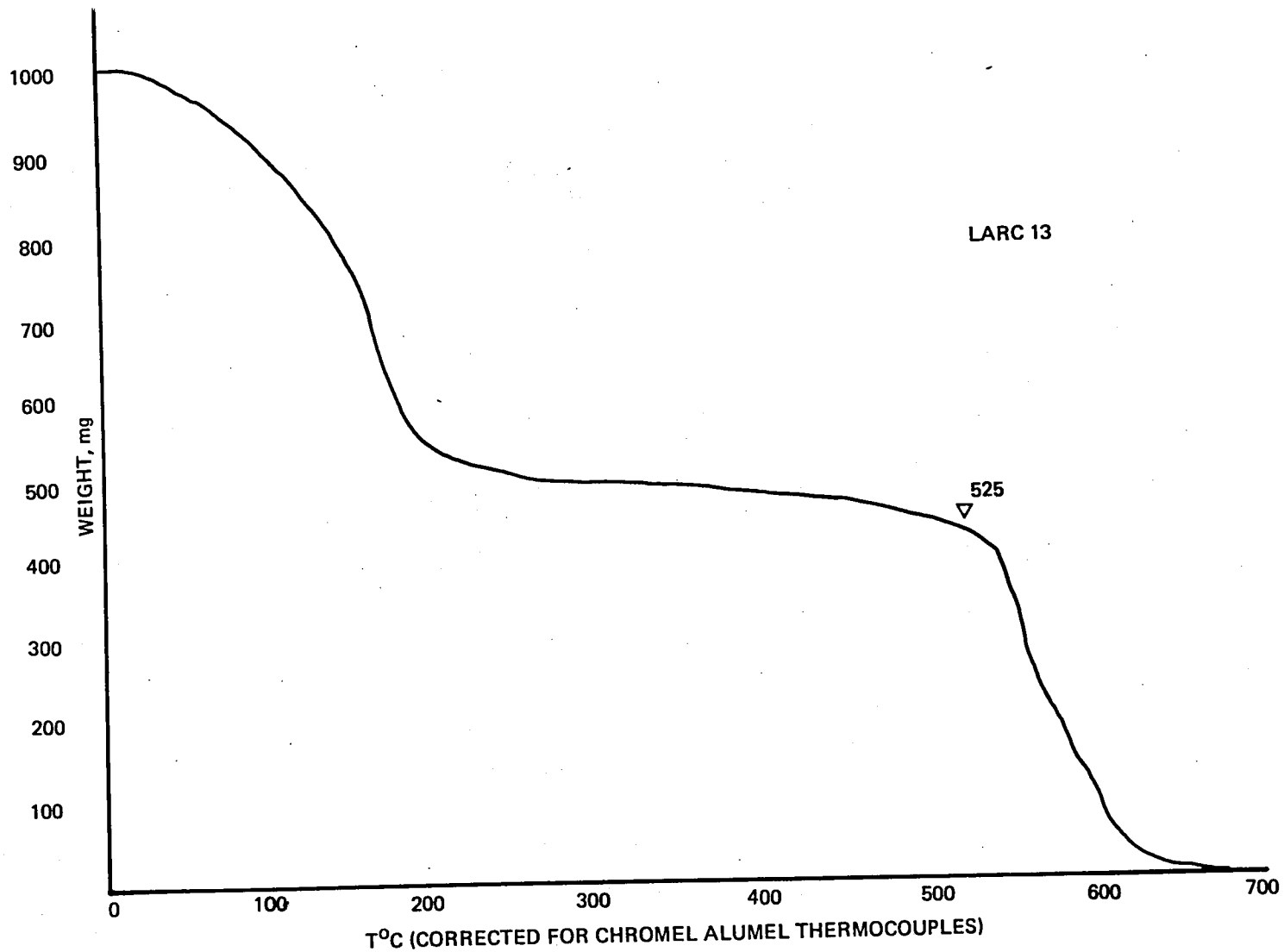


Figure 5: Thermal Gravimetric Analysis

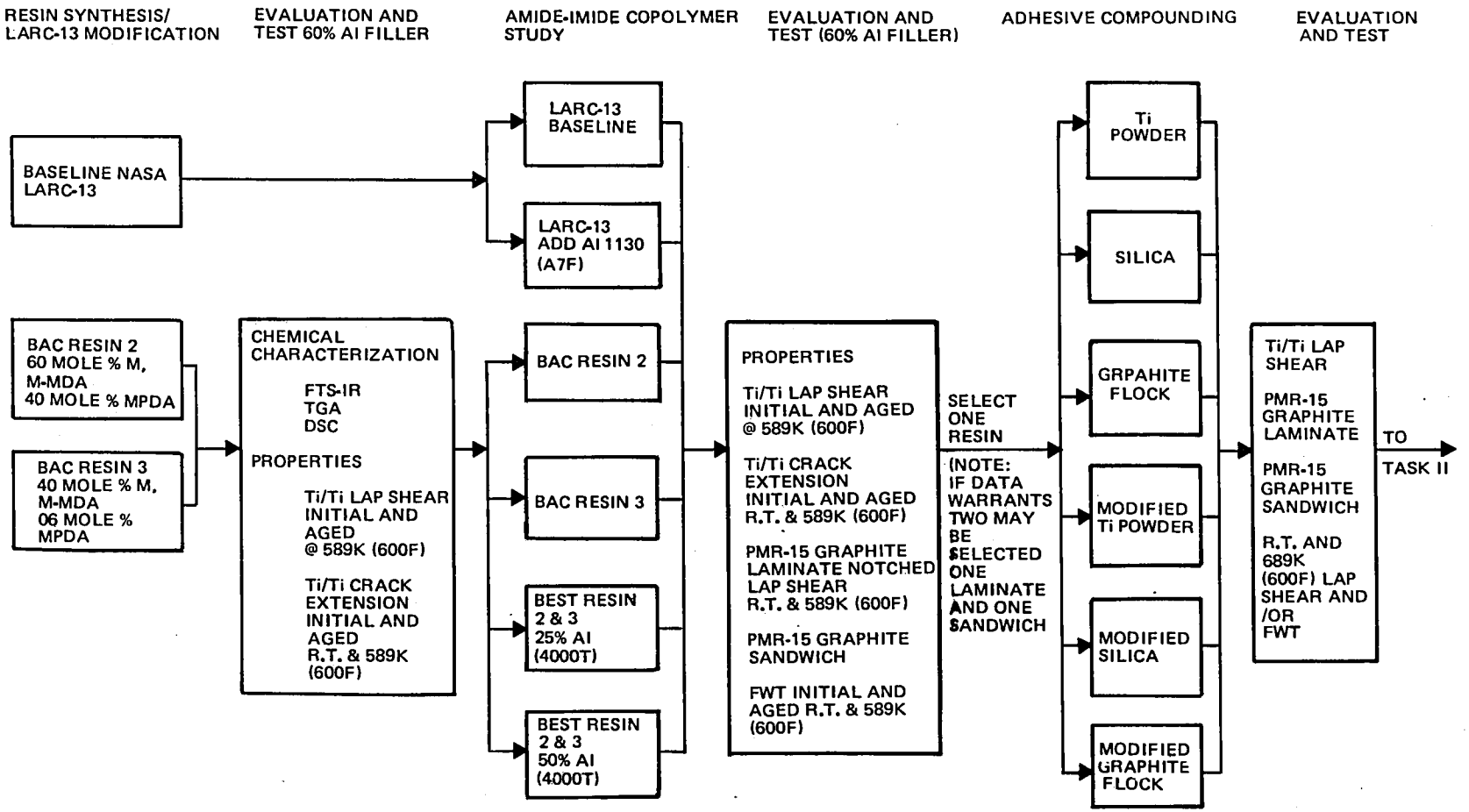


Figure 6: Task I Resin Formulation and Adhesive Development

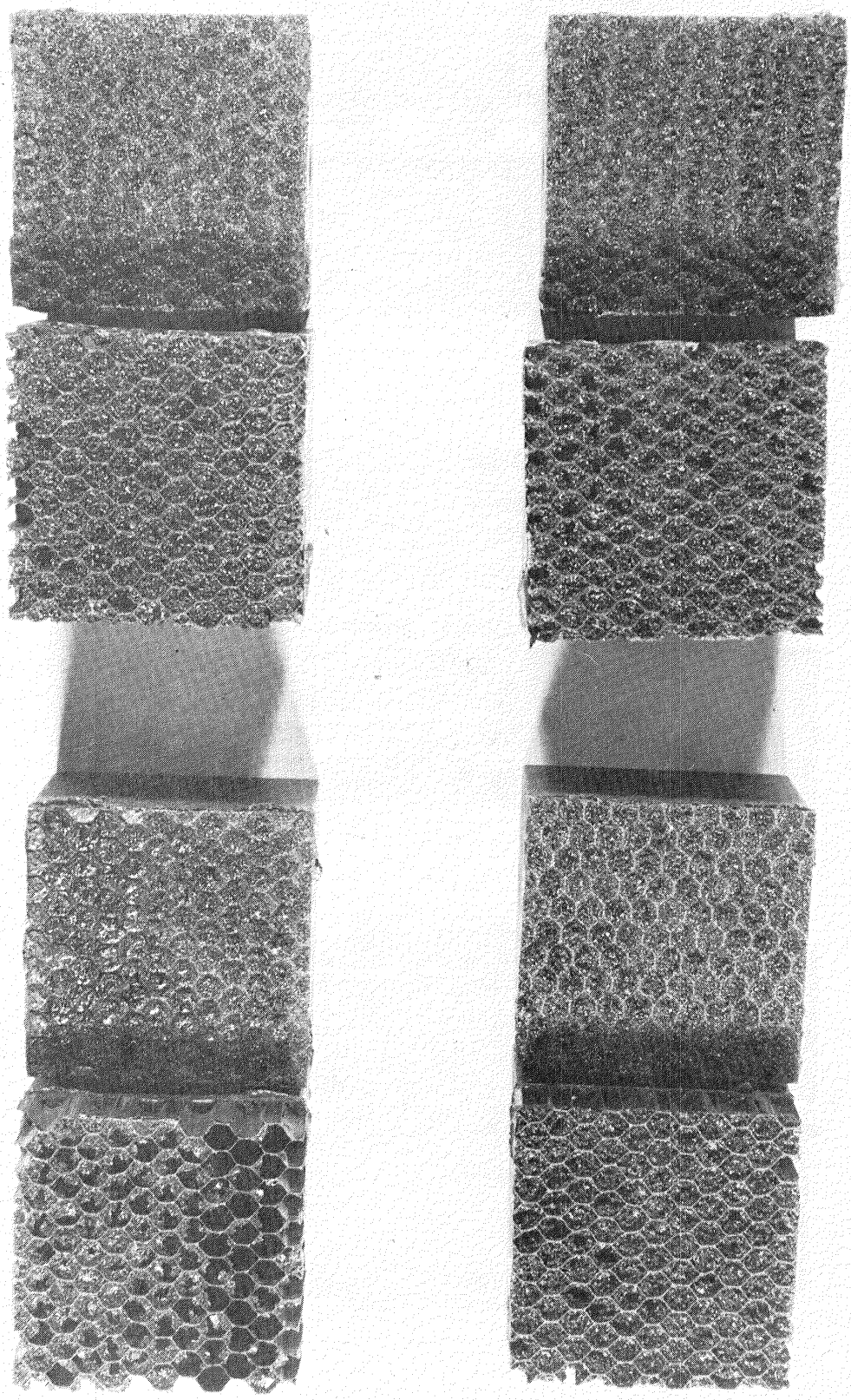


Figure 7: Failed Flatwise Tensile Specimens

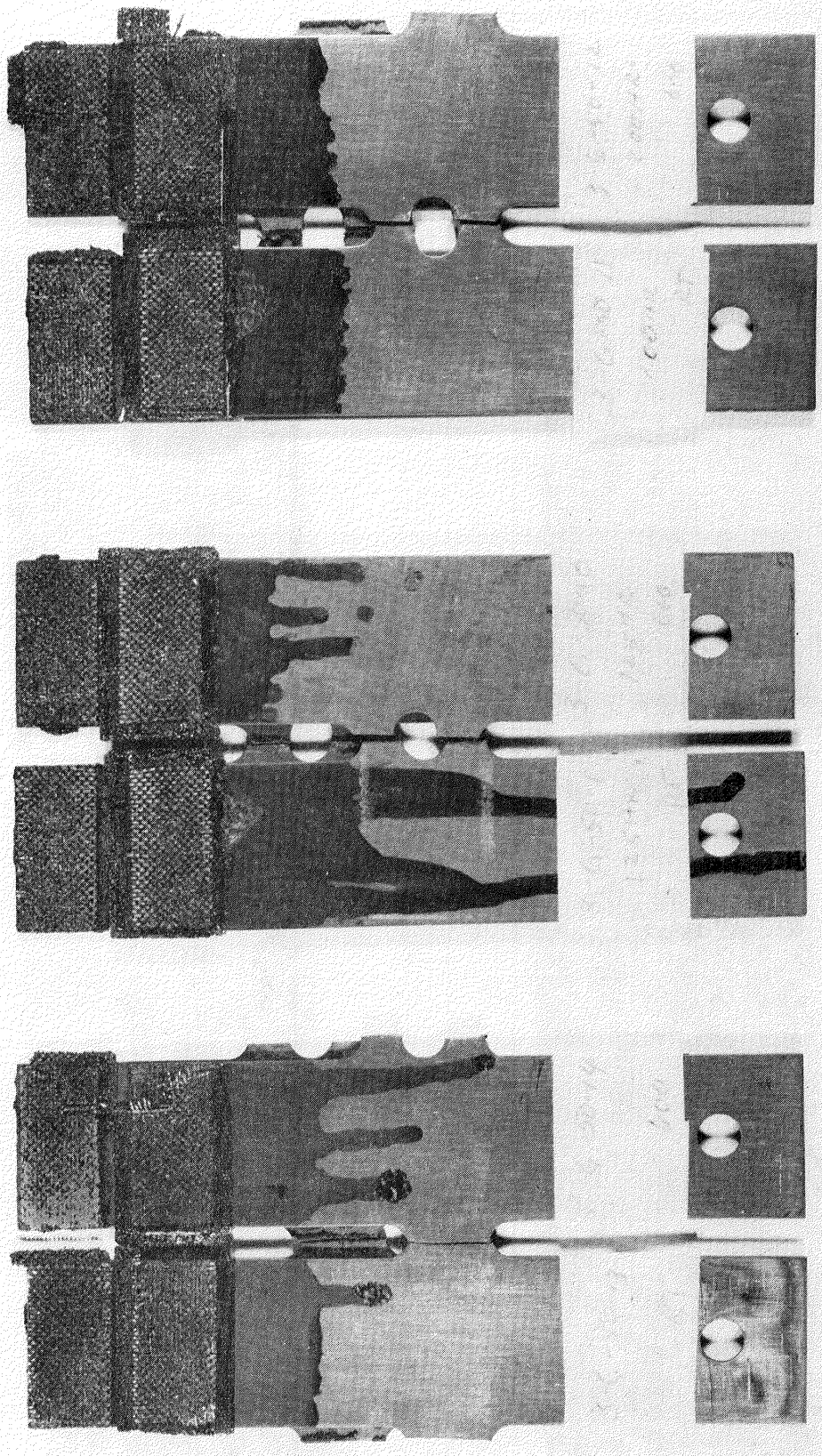


Figure 8: Failed Titanium Lap Shear Specimens

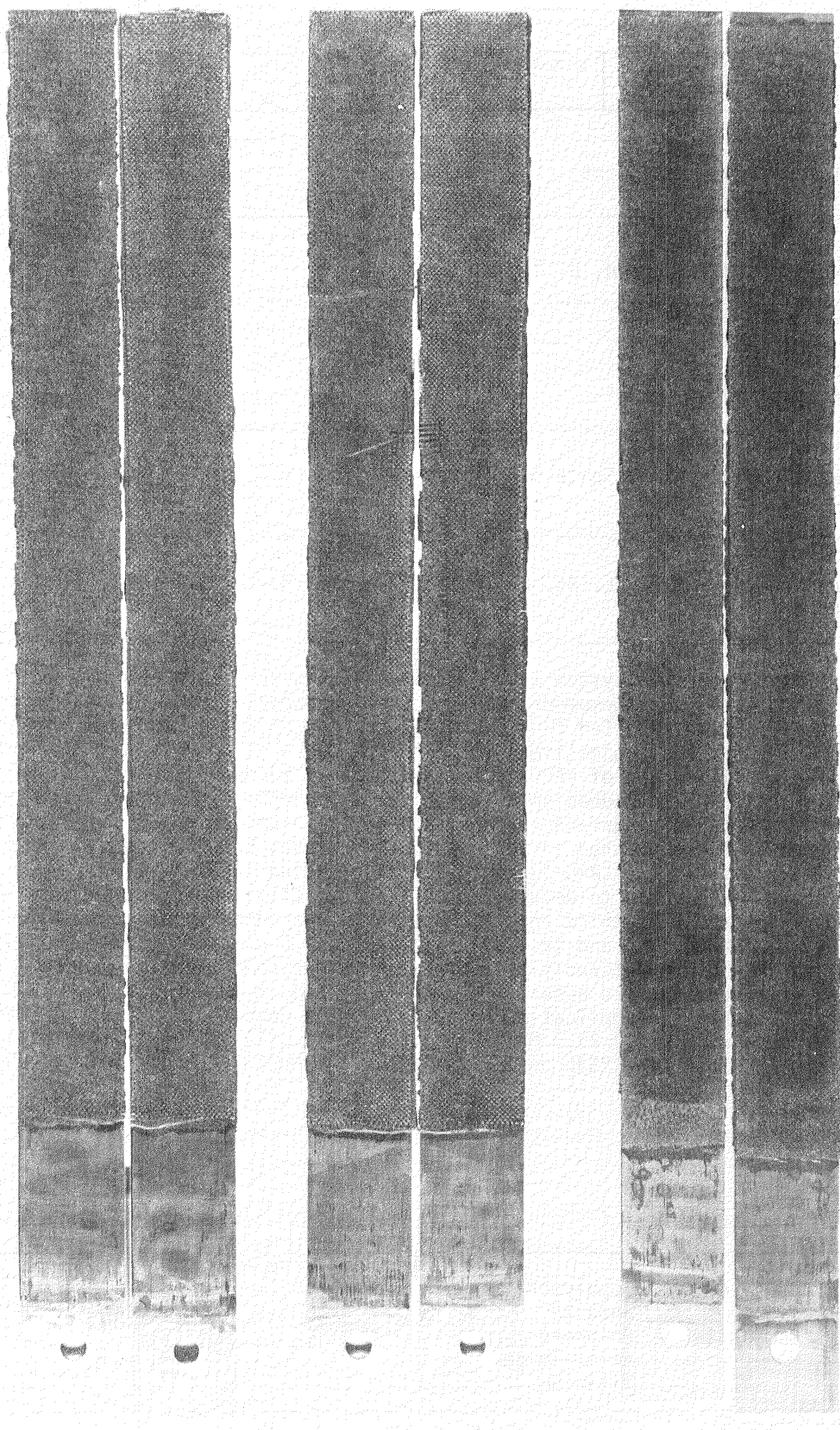


Figure 9: Failed Titanium Metal-to-Metal Peel Specimens

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15. Supplementary Notes

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Final Report

16. Abstract

A LARC-13 type adhesive system was developed and property data obtained that demonstrated improved thermomechanical properties superior to base LARC-13 adhesive. The adhesive system resulted from studies performed at Boeing under a NASA supported program. The original objectives of the program were (1) development by physical or chemical modification of LARC-13, of an improved adhesive for 589 K (600°F) use, (2) optimization of the adhesive for titanium and composite bonding, (3) identification of a compatible surface preparation for titanium and composite substrates. The program was accomplished in three separate phases; the first was devoted to chemically modifying the LARC-13 resin and/or blending it with another resin. The second phase was devoted to developing an adhesive film, substrate preparation and bonding processes. The third phase demonstrated the adhesive system and bonding processes by fabricating and testing Ti/Ti and PRM-15 composite/composite lap shear panels and PMR-15 graphite/polyimide fiberglass honeycomb sandwich panels. The data obtained with the improved adhesive system indicated it would meet the 589 K (600°F) properties desired for application on Space Shuttle Components. Average titanium lap shear data were: (1) 21.1 MPa (3355 psi) at RT, (2) 13.0 MPa (1881 psi) at 600°F, and (3) 16.4 MPa (2335 psi) after aging 125 hours at 600°F and tested at 600°F.

17. Key Words (Suggested by Author(s))		18. Distribution Statement
LARC-13 Adhesive A7F Adhesive Graphite Composite Silica Scrim	Copolymers Anodize Polymers Amide-Imide Titanium	Unclassified - unlimited subject category 24

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