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LARC-IA: A FLEXIBLE BACKBONE POLYIMIDE

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Abstract - A new linear, aromatic, thermoplastic polyimide, identified as LARC-IA, has been synthesized and evaluated, primarily as an adhesive, which is physiologically safe and relatively inexpensive. The polymer was prepared from oxydiphthalic anhydride (ODPA) and 3,4-oxydianiline (ODA) in diglyme. In order to promote optimal flow properties, which improves wetting, the molecular weight of the polymer was controlled by use of a monofunctional anhydride, phthalic anhydride (PA).

The polymer is of particular interest as a possible replacement for LARC-TPI, a commercially available polyimide with exceptional adhesive properties as well as being a highly thermooxidatively stable material. LARC-TPI is presently available in several forms: films, molding powder, 30 wt.% solids solution (varnish), and prepreg. However, the 3,3'-diaminobenzophenone component is expensive and its physiological effects are uncertain. LARC-IA is synthesized from noncarcinogenic, nontoxic chemicals which are relatively inexpensive.

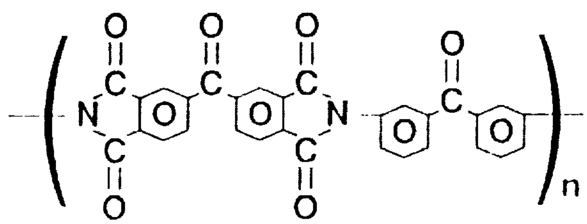
Adhesively bonded lap shear specimens, using Ti-6Al-4V adherends, were prepared and tested to assess its adhesive potential. Specimens were exposed to water boil and thermal aging to determine the adhesive system's durability. Results were compared to data for LARC-TPI previously generated in our laboratory and published earlier.

Preliminary results were also obtained for composites fabricated from LARC-IA (5% PA) and graphite fibers (AS4, 12K). Flatwise tensile strength and critical fracture energy were also determined.

Initial results of this study indicate considerable promise as a structural adhesive for applications for temperatures up to 200°C.

1. INTRODUCTION

Because of the anticipated needs of the aerospace industry for high temperature polymers for use in various applications, research has continued at Langley Research Center on the synthesis and development of new, inexpensive, flexible, aromatic, high temperature polymers. A recent result of that goal was the development of the thermoplastic, linear polyimide, LARC-TPI, that exhibited exceptional adhesive and other properties [1-3]. The polyimide is presently



LARC-TPI
T_g = 260°C (500°F)

produced by several suppliers in film, molding powder, prepreg, and solution (varnish) forms. However, present concern of the physiological effects due to the diamine component, 3,3'-diaminobenzophenone (DABP), and its relatively expensive cost tend to detract from its other excellent attributes. Therefore, a new polyimide with properties similar to LARC-TPI has been synthesized and evaluated. The polymer, identified as LARC-IA (Langley Research Center - Improved Adhesive), has been prepared in diglyme as a 15 wt.% solids solution from oxydiphthalic anhydride (ODPA) and 3,4'-oxydianiline (ODA). The molecular weight, and therefore, its flow, was controlled by use of a monofunctional anhydride [phthalic anhydride (PA)].

The adhesive evaluation of this new polyimide, LARC-IA with and without endcaps, is the primary subject of this report. The effects of an aluminum powder filler was also investigated. Preliminary results were also obtained for composites composed of LARC-IA with 5 wt.% PA endcap [LARC-IA (5% PA)] and graphite fiber (AS4, 12K). Flatwise tensile strength (FWT) and critical fracture energy (G_{1c}) were determined as well as several LARC-IA film properties.

2. EXPERIMENTAL

2.1 Materials and synthesis

The reaction scheme for the synthesis of LARC-IA is shown in Fig. 1. The chemicals used to prepare the polymer were obtained from commercial sources. The oxydiphthalic anhydride (ODPA) was supplied by OXY Chemical, Niagara Falls, NY. The 3,4'-oxydianiline (3,4'-ODA) was supplied by Kennedy and Klim Incorporated, Little Silver, NJ.

The polymer that was primarily used as the adhesive was prepared in reagent grade bis(2-methoxyethyl)ether (diglyme) at 16.5 percent solids. The ODPA (60.4935 g) was mixed with 3,4'-ODA (40.0480 g) in 515 g of diglyme at room temperature (RT). This mixture was stirred overnight and PA (1.4812 g) was added and stirring continued for an additional 1/2 hour. This solution was stored for 48 hours at 40°F and its inherent viscosity, η_{inh}, was determined to be 0.47 dL/g (0.5% in DMAc at 35°C). This afforded a polymer with a 2.5 percent molar excess of the diamine which was endcapped with 5.0 molar percent monofunctional PA. The unendcapped version of the polymer was prepared in the same manner with equimolar amounts of the ODPA and 3,4'-ODA (η_{inh} 0.63 dL/g). A 10 percent endcapped version was prepared in a like manner with a 5 percent molar excess of diamine and 10 mole percent of PA (η_{inh} 0.25 dL/g).

2.2 Characterization

Lap shear strength (LSS) was determined according to ASTM D1002 using an Instron Universal Testing Machine. The LSSs reported represent an average of four lap shear specimens per test condition except as noted in the tables. The range of LSSs is indicated by dashed lines in the bar graphs and is listed in the tables. Elevated temperature tests were conducted in a clam-shell, quartz-lamp oven with temperatures controlled to ± 3°C for all tests. Specimens were held 10 min at temperature prior to testing except for the water boil tests which were conducted upon reaching the test temperature (approximately 1-2 min).

Bondline thickness for the bonded titanium lap shear specimens is defined as the difference between the total joint thickness measured with a micrometer and the sum of the adherend thicknesses. The average bondline thickness for the thermally aged and water boil specimens was 0.023 cm for LARC-IA, 0.010 cm for LARC-IA (5% PA), and 0.017 cm for LARC-IA (5% PA) 50% Al powder.

Glass transition temperatures (Tg) were determined using a DuPont 990 Thermal Analyzer in conjunction with a DuPont Model 943 Thermal Mechanical Analyzer (TMA)*. TMAs for films were run in static air at a heating rate of 5°C/min with a load of 0.5 to 2.0 g. Tgs, determined by Differential Scanning Calorimetry (DSC), were obtained on a DuPont 1090 Thermal Analyzer in conjunction with a Model 910 Differential Scanning Calorimeter run at 20°C/min.

Inherent viscosity was determined using a Cannon-Ubbelohde viscometer in a 35°C water bath controlled to within ± 0.01°C. A 10 ml solution of 0.5 wt/vol% solids in dimethylacetamide (DMAc) was made and filtered.

*Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

The type of failure for lap shear tests was evaluated visually using a 10X magnification and estimating the percent area of each type of failure, cohesive or adhesive.

FWT was determined according to ASTM C297 using 5.1 x 5.1 cm specimens tested at RT.

Critical fracture energy was determined using a double cantilever beam specimen in accordance with ref. [4]. The film properties: yield strength, tensile strength, tensile modulus, and elongation were determined according to ASTM D882.

The mechanical properties, flexural strength and flexural modulus, were obtained for LARC-IA (5% PA)/AS4 12K composite according to ASTM D790.

The solvent resistance of LARC-IA film was evaluated by immersing a strip of film, 0.64 cm x 1.27 cm, in several different solvents for 72 hours, removing the film and assessing the results visually as well as determining the Tg by TMA and DSC techniques.

2.3 Adhesive tape

The adhesive tapes were prepared by brush coating the polymer solution [15 wt% for LARC-IA, η_{inh} 0.63 dL/g; 16.5 wt% for LARC-IA (5% PA), η_{inh} 0.47 dL/g; and 16.9 wt% for LARC-IA (10% PA), η_{inh} 0.25 dL/g] in diglyme onto a 112 E-glass cloth with an A-1100 finish (γ-aminopropylsilane) (Union Carbide). The glass cloth had been tightly mounted on a metal frame and dried in a forced-air oven for 30 min at 100°C prior to coating. The 0.10 mm thick glass cloth served as a carrier for the adhesive as well as for bondline thickness control and an escape channel for the solvent. After a primer coat ($\approx$ 7.5 wt% solids solution) was applied and dried, several applications of the originally prepared solution were applied until the thickness of the tape was 0.20 - 0.30 mm. After each coat was applied, the tape was air-dried at ambient for 0.5 - 1.0 h, placed in a forced-air oven, and exposed to the following schedule:

(1) RT → 100°C, hold 1 h;

(2) 100°C → 150°C, hold 1 h; and

(3) 150°C → 175°C, hold 1 h.

The procedure used to prepare the tapes was required to drive off the solvent and reaction product volatiles when converting the polyamic acid resin to the polyimide. Imidization of most polyamic acids to polyimides generally occurs in the 160°C range, with the degree of conversion being a function of time and temperature. The prepared tapes were stiff and boardy with no tack or drape.

The same procedure was used to prepare the powdered aluminum filled tapes. The aluminum was added to the polymer solution at 50% by weight of the polymer solids content.

2.4 Adhesive bonding

The prepared adhesive tapes were used to bond lap shear specimens with titanium adherends (Ti-6Al-4V, per Mil-T-9046E, Type III Comp. C) that were a nominal 1.27 mm thick. The four-fingered Ti-6Al-4V panels were grit-blasted with 120 grit aluminum oxide, washed and rinsed with methanol, and surface treated with Pasa-Jell 107* treatment to form a stable oxide on the surface. The adherends were primed with a 7.5 wt% solution of the same resin that was used to prepare the tape. The primer was air-dried 0.5 h, then heated in a forced-air oven for 15

*Trade name for a titanium surface treatment available from Semco, Glendale, CA.

min at 100°C and 15 min at 150°C prior to bonding. Lap shear specimens were prepared by inserting the adhesive tape between the primed adherends using a 12.7 mm overlap. Each adhesive system was bonded using three different bonding conditions. Bonding temperature was monitored using a type K thermocouple spotwelded next to the bond area. Selection of the optimized bond condition was based on that giving the highest LSSs. The selected bonding condition was then used to prepare specimens for the aging and water boil tests.

FWT specimens for LARC-IA (5% PA) and LARC-IA (5% PA) 50% Al were prepared from titanium honeycomb core (≈ 2.71 mm thick) and Ti-6Al-4V facesheets (≈ 0.51 mm thick). Both the core and facesheets were given a Pasa-Jell 107 surface treatment and primed prior to bonding. Bonding conditions were: 8°C/min heating rate, 0.34 MPa pressure, RT → 371°C held 1 h. 5.1 x 5.1 cm specimens were cut and bonded to the test blocks with HT-424 adhesive (American Cyanamid Company). Tests were performed at RT.

Double cantilever beam (DCB) specimens, also bonded with LARC-IA (5% PA) and LARC-IA (5% PA) 50% Al, were prepared using 1.27 mm thick Ti-6Al-4V with a Pasa-Jell surface treatment and primed prior to bonding. The DCB configuration, testing, and calculations are presented in ref. [4]. Bonding conditions were: 8°C/min heating rate, 2.07 MPa pressure, and RT → 371°C held 1 h.

2.5 Thermal and water boil exposure

A bonding cycle was selected which was based on the highest LSS and was used to prepare specimens to determine the effects of thermal exposure in a forced-air oven at 204°C ± 2°C for up to 5000 h. Lap shear tests were conducted at RT, 177, 204 and 232°C before (controls) and after exposure.

A 72-h water boil test was conducted in laboratory glassware containing boiling distilled water. Lap shear specimens were immersed above the bonded area during a 72-h period. LSSs were determined at RT, 177, 204 and 232°C.

2.6 LARC-IA film solvent resistance

A nominal 0.025 mm thick LARC-IA film was prepared by doctoring a 15 wt% solids solution in diglylme on a glass plate and curing in a forced-air oven for 1 h at each temperature of 100, 200 and 300°C. Films were soaked at RT for a 72-h period in methylene chloride, diglyme, DMAc, m-cresol and N-methyl-2-pyrrolidone. Films were patted dry with hand wipes and visually evaluated. Tg was then determined by TMA and DSC.

3. RESULTS AND DISCUSSION

3.1 Chemistry

The adhesive properties of LARC-TPI have been attributed to the high degree of flexibility in the polymer backbone afforded by the bridged dianhydride and the meta-linked diamine [5]. The 3,3'-BTDA diamine is expensive to synthesize (> $50/lb.) Also, because it has been shown to give a positive Ames test, this material must be handled with great care which adds to the cost of the resulting adhesive. However, once the diamine has been reacted into the polymer backbone it should no longer pose a hazard.

The novel diamine 3,4'-ODA has been commercially developed in Japan for potential use in high modulus aromatic polyimides. This diamine has been tested and shown to have very low mutagenic activity in the Ames test [6]. Also the monomer, ODPA, has become commercially available. The combination of these two monomers in diglyme affords a polyimide which has exceptional adhesive properties especially when its molecular weight is controlled. Examination of molecular models shows this new polyimide, LARC-IA, to have similar chain flexibility to LARC-TPI.

3.2 Bonding temperature and pressure

Selection of the optimum bonding conditions for each polymer was based on obtaining the best compromise of high LSS for tests at RT, 177, 204 and 232°C. Results are expressed in graphical form for those interested in obtaining a quick pictorial summary of the results, and in tabular form for those interested in more detail and additional information not included in the graphs.

In general, the LSSs decrease with test temperature with a drastic decrease as the Tg is approached. Therefore, in most cases, the 232°C strength is greatly reduced from that at 204°C.

3.2.1 LARC-IA

As shown in Fig. 2 and given in Table 1, three combinations of temperature and pressure were evaluated using either 2.07 or 3.45 MPa pressure and 343 or 371°C temperature. Little flashing or squeeze-out was observed for the polymer after bonding, indicating poor flow properties. The best compromise of LSSs was obtained with 2.07 MPa and 371°C. A significant increase in LSS was noted for the 204 and 232°C tests (21.1 MPa versus 15.7 and 14.7 MPa for the 204°C tests and 9.1 MPa versus 5.6 and 5.8 MPa for the 232°C tests). Therefore, specimens for thermal aging and water boil were prepared using 2.07 MPa pressure and 371°C temperature conditions.

3.2.2 LARC-IA (5% PA)

LSS results for LARC-IA (5% PA) adhesive are shown in Fig. 3 and Table 2. The same three bonding conditions used for LARC-IA were again used to evaluate LARC-IA (5% PA). This time squeeze-out was evident indicating improved flow due to the control of the molecular weight by endcapping with phthalic anhydride. The best compromise of LSS values was again evident for the 2.07 MPa and 371°C bonding conditions. Excellent LSSs were obtained at RT, 177 and 204°C for all three bonding conditions (RT, 44.0 to 45.6 MPa; 177°C, 32.5 to 36.6 MPa;and 204°C 23.9 to 28.4 MPa).

3.2.3 LARC-IA (10% PA)

Because of the increase in the percent of endcapping, greater flow was to be expected during bonding and, therefore, in two cases, a lower bonding pressure was used. Test results for LARC-IA (10% PA) are shown in Fig. 4 and given in Table 3. Greater squeeze-out was noticed for this polymer which was also more brittle than LARC-IA and LARC-IA (5% PA). However, although the RT LSS is slightly lower for the 0.69 MPa/371°C condition than for the other two conditions evaluated, the 232°C strength increased by ≈ 3 MPa and the 177 and 204°C strengths remained the same. Because the 5% PA endcapped adhesive provided higher strengths than the 10% PA endcapped adhesive, no thermal aging or water boil tests were conducted with the 10% PA endcapped adhesive.

3.2.4 LARC-IA (5% PA) 50% Al

The addition of aluminum powder filler to the LARC-IA (5% PA) material was investigated because past experience has shown that improvement in strength and use temperature were realized by this technique [7]. As shown in Fig. 5 and Table 4, excellent LSSs were obtained for all test temperatures and bond conditions. An improvement in strength for the 232°C tests was evident (13.6 MPa versus 9.3 MPa previously obtained). The best results for the LARC-IA (5% PA) 50% Al adhesive were obtained using the 2.07 MPa and 371°C bonding conditions.

3.2.5 LARC-IA (10% PA) 50% Al

Only one bonding condition was used for LARC-IA (10% PA) 50% Al because of the results mentioned earlier for the same polymer which provided excess flow without the aluminum filler. Fig. 6 shows a comparison of the LSSs for the LARC-IA 5% and 10% PA endcap with 50 wt % of aluminum powder filler. The LSSs for the 10% PA adhesive were lower than the 5% PA adhesive for all test temperatures, a similar trend obtained earlier for the same polymers without the aluminum filler. No thermal aging or water boil tests were attempted with this adhesive system.

3.3 Thermal exposure

The effects on LSS due to thermal exposure in a forced-air oven at 204°C are shown in Fig. 7 and given in Table 5 for LARC-IA, LARC-IA (5% PA), LARC-IA (5% PA) 50% Al, and LARC-TPI. LSS tests were performed at RT, 177, 204 and 232°C. Strength results for LARC-TPI, reported previously, are included for comparison [2].

A beneficial effect of the thermal exposure was experienced for the LARC-IA system. Significant increases in LSS were obtained for 177, 204 and 232°C tests (177°C, from 25.5 to 29.4 MPa; 204°C, 21.1 to 26.2 MPa; and 232°C, 9.1 to 14.0

MPa). However, RT strengths decreased from 31.8 to 27.8 MPa. Further exposure at 204°C for 5000 h resulted in no change in LSS for tests conducted at 204°C (1000 h, 26.2 MPa; 5000 h, 26.9 MPa).

After 1000 h at 204°C, the LSSs for the LARC-IA (5% PA) system decreased from 44.2 to 35.0 MPa for the RT tests and from 36.6 to 33.4 MPa for 177°C tests. LSSs at 204 and 232°C were unchanged. Continuing the exposure for 5000 h, the RT strength decreased to 29.0 MPa, the 177°C strength decreased slightly to 30.9 MPa, the 204°C strength remained the same and the 232°C was slightly lower at 7.9 MPa. These LSSs, except for the 232°C test, are excellent considering the time and temperature of exposure. Comparing these results with LARC-TPI data, the strengths for LARC-IA (5% PA) are higher at RT, 177°C and 204°C but significantly lower than LARC-TPI at 232°C, probably due to the higher Tg of the LARC-TPI polymer.

The addition of aluminum powder filler to the 5% PA endcapped system resulted in an adhesive that retained the original strengths at all test temperatures after the 1000 h exposure. After 5000 h, the RT strength decreased from 43.8 MPa to 34.1 MPa, the 177°C strength decreased from 33.2 MPa to 28.3 MPa, the 204°C strength decreased from 28.7 MPa to 24.5 MPa and the 232°C strength decreased from 13.6 MPa to 7.7 MPa. The strengths retained after 5000 h are still excellent except for that tested at 232°C (7.7 MPa). Comparing the 5000 h aging data of LARC-IA (5% PA) 50% Al with the LARC-TPI data indicates higher strengths at RT and 177°C, essentially the same strength at 204°C, and a lower strength at 232°C. The higher strength of LARC-TPI at 232°C is again probably due to its higher Tg.

The LARC-TPI adhesive data which had been reported earlier, indicated some increase in the strengths at 204 and 232°C after thermal exposure. As noted, the LSS test at 232°C was conducted after 2260 h at 232°C and still resulted in a significant increase (17.5 to 23.3 MPa). The strengths for the 232°C tests are much higher for the LARC-TPI than for the variations of LARC-IA primarily due to a higher Tg for LARC-TPI. The initial and 1000 h exposure strengths at RT, 177 and 204°C are higher for LARC-IA (5% PA) 50% Al than the LARC-TPI.

Lap shear test failures after thermal exposure were primarily cohesive except for the RT test of LARC-IA and the 232°C tests for LARC-IA (5% PA) for 1000 and 5000 h exposure which were thermoplastic and a combination of cohesive/adhesive, respectively.

3.4 72-h Water boil exposure

Lap shear specimens were exposed to a rather severe 72-h water boil to determine the bonded system's resistance to a high humidity type condition. LSS test results are shown in Fig. 8 and given in Table 6 for the LARC-IA polymers and compared with earlier reported results for LARC-TPI.

Most of the adhesive systems show greatly reduced strengths for all test temperatures after the water boil exposure. Water is known to plasticize most polymers and, therefore reduce their strength properties. LARC-IA and LARC-IA (5% PA) provide similar results to the LARC-TPI. Strength retention for those two systems ranged from 77% to 95% at RT, 59% to 80% at 177°C, 25% to 40% at 204°C and 38% to 41% at 232°C. LARC-TPI retained 84, 67, 40 and 30% at RT, 177, 204 and 232°C respectively. The LARC-IA (5% PA) 50% Al bonded system was similar to all others; however, it retained 52% of its original strength at 232°C or 7.0 MPa. The aluminum additive provided a slight improvement in strength retention at the 232°C test temperature.

3.5 Flatwise tensile strength and fracture energy

Results of the FWT strength tests for LARC-IA (5% PA) with and without aluminum filler are given in Table 7 along with the fracture energy, G_{1c}.

Although the FWT strengths were less than expected, ranging from 1.7 to 2.6 MPa, they show promise since this was a preliminary attempt to prepare the specimens and not an optimization of tape preparation and bonding conditions. Also, core cell size influences the bond strength obtained, the smaller the cell size, the greater the contact bond area and, therefore, the greater the strength. The cell size of the titanium core used to prepare these specimens was rather large, 0.95 cm. Failures were between the core cell edges and the adhesive. Minimal filleting was observed around the core cells. No apparent improvement in strength was obtained as a result of aluminum powder addition.

The fracture energy of LARC-IA (5% PA), 560 and 438 J/m^2, was approximately double that of the LARC-IA (5% PA) 50% Al system, 298 and 210 J/m^2, as determined by the DCB technique at RT. Although these G_{1c} values for LARC-IA (5% PA) are not as high as desired, they are higher than most epoxies and bismaleimides but less than polyimidesulfones [8]. The glass cloth, that the polymer had been supported on, could account for the lower than expected G_{1c} values.

3.6 Film properties and solvent resistance

The mechanical properties of LARC-IA films were obtained according to ASTM D882. Results are given in Table 8. Yield strength was obtained by taking the tangent of the curve from zero. Overall mechanical properties were in line with other aromatic polyimides with flexible backbones. The tensile strength, which is quite sensitive to molecular weight, was found to be almost 18 Ksi at RT and the modulus was a nominal half million Ksi.

The mechanical properties decrease significantly at higher temperatures or as the Tg of the material is approached. Elongation will generally increase with increased temperature. All measured values are reasonable and typical of linear aromatic polyimides.

The resistance to several typical organic solvents is shown in Table 9. A visual observation of the film after a 72-h period soak in the solvents is noted. Methylene chloride was the only solvent that effected the LARC-IA film as indicated by the curling of the film and the increase in Tg. All others retained the same Tg and film appearance.

3.7 Polyimide/graphite composite

Composites were fabricated from LARC-IA (5% PA) polyimide and AS4 12K graphite fibers. Results of mechanical properties testing (ASTM D790) are given in Table 10. No attempt was made to optimize the processing conditions when fabricating the composite. The composite was laid-up as a unidirectional, 10 ply (≈ 1.75 mm thick) configuration. Fabrication conditions were: 1 h heat up, 2.07 MPa (300 psi) pressure applied at 232°C (485°F); continued heating to 349°C (660°F), held for 1 h and cooled under pressure.

4. SUMMARY

The synthesis and evaluation of a new linear, aromatic, thermoplastic polyimide, prepared from oxydiphthalic anhydride and 3,4'-oxydianiline and identified as LARC-IA, have been performed. The flow properties were optimized by controlling the molecular weight by use of a monofunctional anhydride, phthalic anhydride (PA). The polymer, which is prepared from physicologically safe and inexpensive monomers, was of interest as a possible substitute or replacement for existing expensive and possibly carcinogenic monomers used to prepare commercially available polymers.

The polymer, a high temperature thermoplastic adhesive, was evaluated using lap shear strength (LSS) tests involving adhesive tape preparation, bond condition optimization, endcapping optimization for improved flow, thermal exposure and water boil tests. A comparison was made with LARC-TPI data previously generated in our laboratory and reported earlier.

Limited studies were conducted on film mechanical properties and solvent resistance, composite mechanical properties, flatwise tensile strength and fracture energy.

The polymer with the 5% PA endcap provided the best compromise of the three polymers prepared and evaluated to optimize flow and strength properties. The addition of aluminum powder filler to the LARC-IA (5% PA) polymer enhanced the control LSS at 232°C as well as improved its strength retention after 1000 h exposure at 204°C and a 72-h water boil. After 5000 h, the test results are essentially the same with or without the aluminum powder.

Preliminary results of the flatwise tensile strength tests indicate promising strengths but further improvement could most likely be achieved with refined processing procedures.

Fracture energy, G_{1c}, determined by the double cantilever beam technique for LARC-IA (5% PA) with and without aluminum powder filler, was higher than most epoxies and bismaleimides but less than the polyimidesulfones. The glass cloth in the bond could account for the lower than expected values.

The LARC-IA film mechanical properties obtained were typical of linear aromatic polyimides. Film mechanical properties decreased when the film was tested at 200°C. This is typical when the glass transition temperature (Tg) of the material is approached.

LARC-IA film was resistant to degradation when exposed to most of the solvents investigated, i.e., diglyme, dimethyl acetamide, m-cresol and N-methyl-2-pyrrolidone. Methylene chloride produced an increase in Tg as well as causing the film to curl after the 72-h soak.

Preliminary mechanical property measurements for a 10 ply, unidirectional LARC-IA (5% PA)/AS4 12K composite indicates promise (flexural modulus of 195,500 psi) but improvements are definitely possible with further optimization studies.

The new polyimide, LARC-IA, which is "safe" and potentially inexpensive, shows excellent promise as an adhesive, film and composite matrix; and compares favorably with LARC-TPI for future applications in aerospace and industry.

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Table 1. LSS results for LARC–IA bonded Ti–6Al–4V

Bonding pressure [MPa (psi)]	Bonding temperature [°C (°F)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode[a]
2.07 (300)	343 (650)	4	RT (RT)	37.2 (5390)	34.8-38.3 (5050-5550)	Co
		4	177 (350)	25.0 (3620)	24.5-25.4 (3550-3680)	Co
		4	204 (400)	15.6 (2260)	14.1-16.5 (2040-2400)	Co
		4	232 (450)	5.6 (820)	4.9 - 6.3 (710 - 920)	Ad
3.45 (500)	343 (650)	4	RT (RT)	34.5 (5000)	29.6-39.6 (4290-5750)	Co
		4	177 (350)	27.8 (4030)	27.4-28.5 (3970-4130)	Co
		7	204 (400)	14.7 (2130)	13.0-16.3 (1880-2370)	Co
		5	232 (450)	5.8 (850)	5.2 - 6.5 (750 - 950)	Ad
2.07 (300)	371 (700)	4	RT (RT)	31.8 (4620)	30.3-32.6 (4400-4730)	Co
		4	177 (350)	25.5 (3700)	25.0-26.5 (3630-3840)	Co
		7	204 (400)	21.1 (3060)	20.2-21.7 (2930-3150)	Co
		5	232 (450)	9.1 (1320)	7.2-10.6 (1040-1540)	Ad

[a] Cohesive-Co, adhesive-Ad

Table 2. LSS results for LARC−IA(5%PA) bonded Ti−6Al−4V

Bonding pressure [MPa (psi)]	Bonding temperature [°C (°F)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode[a]
2.07 (300)	343 (650)	4	RT (RT)	44.0 (6390)	43.4-44.8 (6300-6500)	Co
		4	177 (350)	32.5 (4710)	29.4-34.4 (4270-4990)	Co
		4	204 (400)	23.9 (3470)	23.2-24.9 (3370-3610)	Co
		4	232 (450)	9.0 (1310)	7.6 - 9.6 (1100-1390)	Ad
3.45 (500)	343 (650)	4	RT (RT)	45.6 (6620)	44.3-46.8 (6430-6790)	Co
		4	177 (350)	33.3 (4830)	32.2-34.5 (4670-5010)	Co
		4	204 (400)	25.4 (3690)	24.5-26.7 (3560-3880)	Co
		4	232 (450)	6.8 (990)	5.7 - 7.8 (830-1130)	Ad
2.07 (300)	371 (700)	4	RT (RT)	44.2 (6420)	43.7-45.3 (6340-6570)	Co
		4	177 (350)	36.6 (5310)	35.5-39.0 (5150-5660)	Co
		4	204 (400)	28.4 (4120)	27.3-29.7 (3960-4310)	Co
		4	232 (450)	9.3 (1350)	8.5-10.6 (1240-1540)	Ad

[a] Cohesive-Co, adhesive-Ad

Table 3. LSS results for LARC-IA(10%PA) bonded Ti-6Al-4V

Bonding pressure [MPa (psi)]	Bonding temperature [°C (°F)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode[a]
0.69 (100)	343 (650)	4	RT (RT)	38.8 (5630)	38.0-39.4 (5510-5710)	Co
		4	177 (350)	26.1 (3790)	25.6-26.8 (3720-3890)	Co
		4	204 (400)	18.9 (2740)	17.8-19.3 (2580-2800)	Co/Ad
		4	232 (450)	5.4 (780)	4.9 - 5.4 (710 - 850)	Co/Ad
2.07 (300)	343 (650)	3	RT (RT)	37.3 (5420)	34.3-39.4 (4980-5710)	Co
		4	177 (350)	27.6 (4010)	26.4-28.3 (3830-4110)	Co
		4	204 (400)	19.3 (2800)	16.9-21.2 (2450-3070)	Co/Ad
		4	232 (450)	4.9 (710)	4.0 - 5.7 (580 - 830)	Ad
0.69 (100)	371 (700)	4	RT (RT)	30.7 (4450)	29.2-33.0 (4240-4780)	Co
		4	177 (350)	26.6 (3860)	25.1-27.5 (3640-3990)	Co
		4	204 (400)	22.0 (3190)	21.0-23.0 (3050-3330)	Co/Ad
		4	232 (450)	8.1 (1180)	7.2 - 8.7 (1040-1260)	Co/Ad

[a] Cohesive-Co, adhesive-Ad

Table 4. LSS results for LARC–IA(5%)50%AL Powder bonded Ti–6Al–4V

Bonding pressure [MPa (psi)]	Bonding temperature [°C (°F)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode[a]
2.07 (300)	343 (650)	4	RT (RT)	43.0 (6240)	41.0-44.0 (5950-6380)	Co
		4	177 (350)	31.5 (4570)	30.2-32.3 (4380-4680)	Co
		4	204 (400)	27.2 (3940)	26.7-27.6 (3870-4010)	Co
		4	232 (450)	10.1 (1470)	9.4-11.6 (1360-1690)	Co
3.45 (500)	343 (650)	4	RT (RT)	42.5 (6170)	41.3-43.8 (5990-6350)	Co
		4	177 (350)	33.5 (4860)	32.4-34.1 (4700-4950)	Co
		4	204 (400)	27.5 (3990)	26.5-28.5 (3840-4130)	Co
		4	232 (450)	11.2 (1620)	10.3-12.5 (1490-1810)	Co
2.07 (300)	371 (700)	4	RT (RT)	43.8 (6350)	42.7-45.3 (6200-6570)	Co
		4	177 (350)	33.2 (4820)	32.5-34.0 (4710-4940)	Co
		4	204 (400)	28.7 (4160)	27.7-29.2 (4020-4240)	Co
		4	232 (450)	13.6 (1970)	13.2-14.7 (1910-2130)	Co

[a] Cohesive-Co, adhesive-Ad

Table 5. LSS results of thermal exposure in air at 204°C for bonded Ti–6Al–4V[a]

Adhesive	Thermal exposure hr	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode[b]
LARC-IA	0	4	RT (RT)	31.8 (4620)	30.3-32.6 (4400-4730)	Co
		4	177 (350)	25.5 (3700)	25.0-26.5 (3630-3840)	Co
		7	204 (400)	21.1 (3060)	20.2-21.7 (2930-3150)	Co
		5	232 (450)	9.1 (1320)	7.2-10.6 (1040-1540)	Ad
	1000	4	RT (RT)	27.8 (4030)	26.1-29.4 (3790-4260)	Co/Ad
		4	177 (350)	29.4 (4260)	25.9-31.0 (3760-4500)	Co
		4	204 (400)	26.2 (3800)	23.3-29.1 (3380-4220)	Co
		4	232 (450)	14.0 (2030)	13.5-14.7 (1960-2130)	Co
	5000	4	204 (400)	26.9 (3900)	24.7-27.8 (3590-4040)	Co
LARC-IA (5% PA)	0	4	RT (RT)	44.2 (6420)	43.7-45.3 (6340-6570)	Co
		4	177 (350)	36.6 (5310)	35.5-39.0 (5150-5660)	Co
		4	204 (400)	28.4 (4120)	27.3-29.7 (3960-4310)	Co
		4	232 (450)	9.3 (1350)	8.5-10.6 (1240-1540)	Ad
	1000	4	RT (RT)	35.0 (5080)	34.0-35.8 (4930-5190)	Co
		3	177 (350)	33.4 (4850)	31.2-35.2 (4530-5100)	Co
		4	204 (400)	30.4 (4410)	29.6-31.6 (4300-4590)	Co
		4	232 (450)	9.7 (1410)	8.0-12.6 (1160-1830)	TP
	5000	4	RT (RT)	29.0 (4200)	27.4-31.3 (3970-4540)	Co
		4	177 (350)	30.9 (4480)	29.6-31.6 (4300-4550)	Co
		4	204 (400)	30.4 (4410)	29.0-32.0 (4200-4640)	Co
		4	232 (450)	7.9 (1150)	6.7- 8.7 (970-1260)	Co/Ad

[a] Bonding conditions: 2.07 MPa (300 psi) pressure from start, heating rate of 8°C/min (14°F/min), RT → 371° C (700°F), held 1 hr

[b] Cohesive-Co, adhesive-Ad, thermoplastic-TP

[c] Data previously reported by our laboratory. Bonding conditions: 2.07 MPa; 343°C held 1 hr

[d] 2260 hr at 232°C (450°F)

[e] 5000hr at 232°C (450°F)

Table 5. LSS results of thermal exposure in air at 204°C for bonded Ti–6Al–4V[a] concluded

Adhesive	Thermal exposure hr	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode [b]
LARC-IA (5% PA) 50% Al powder	0	4	RT (RT)	43.8 (6350)	42.7-45.3 (6200-6570)	Co
		4	177 (350)	33.2 (4820)	32.5-34.0 (4710-4940)	Co
		4	204 (400)	28.7 (4160)	27.7-29.2 (4020-4240)	Co
		4	232 (450)	13.6 (1970)	13.2-14.7 (1910-2130)	Co
	1000	4	RT (RT)	42.9 (6220)	41.1-43.8 (5960-6360)	Co
		4	177 (350)	34.3 (4980)	33.8-34.9 (4900-5060)	Co
		4	204 (400)	31.3 (4540)	29.9-31.8 (4340-4610)	Co
		4	232 (450)	12.9 (1870)	11.6-14.2 (1680-2060)	Co
	5000	5	RT (RT)	34.1 (4950)	33.1-35.4 (4800-5130)	Co
		4	177 (350)	28.3 (4100)	26.3-29.6 (3820-4300)	Co
		3	204 (400)	24.5 (3560)	23.7-25.5 (3440-3700)	Co
		3	232 (450)	7.7 (1120)	7.6 - 7.8 (1100-1140)	TP
LARC-TPI[c]	0	4	RT (RT)	33.0 (4790)	32.3-33.5 (4680-4860)	Co
		4	177 (350)	29.5 (4280)	28.8-30.7 (4180-4450)	Co
		4	204 (400)	25.2 (3660)	25.0-25.4 (3620-3690)	Co
		8	232 (450)	17.5 (2540)	14.8-19.7 (2150-2860)	Co
	1000	4	RT (RT)	32.9 (4780)	32.3-34.4 (4690-4980)	Co
		4	177 (350)	29.9 (4340)	28.5-31.0 (4140-4490)	Co
		4	204 (400)	27.8 (4020)	27.2-28.6 (3940-4160)	Co
		3	232 (450)[d]	23.3 (3380)	21.8-24.5 (3160-3550)	Co
	5000	4	RT (RT)	27.1 (3930)	26.0-28.1 (3760-4080)	Co
		4	177 (350)	25.7 (3730)	24.5-26.4 (3550-3820)	Co
		4	204 (400)	26.0 (3770)	24.7-26.9 (3580-3900)	Co
		4	232 (450)	23.7 (3440)[e]	22.8-24.6 (3300-3570)	Co

[a] Bonding conditions: 2.07 MPa (300 psi) pressure from start, heating rate of 8°C/min (14°F/min), RT → 371° C (700°F), held 1 hr

[b] Cohesive-Co, adhesive-Ad, thermoplastic-TP

[c] Data previously reported by our laboratory. Bonding conditions: 2.07 MPa; 343°C held 1 hr

[d] 2260 hr at 232°C (450°F)

[e] 5000hr at 232°C (450°F)

Table 6. LSS results of a 72–hour water boil for bonded Ti–6Al–4V

Adhesive [a]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode [b]
LARC-IA	4	RT (RT)	30.1 (4370)	25.6-33.8 (3720-4900)	Co
	4	177 (350)	20.4 (2960)	19.8-20.7 (2870-3000)	Co
	4	204 (400)	9.4 (1360)	8.4-10.0 (1220-1450)	Co
	4	232 (450)	3.4 (500)	2.8 - 4.1 (410 - 600)	Ad
LARC-IA (5% PA)	4	RT (RT)	34.2 (4960)	32.9-35.4 (4780-5130)	Co
	4	177 (350)	21.7 (3150)	21.3-22.3 (3090-3230)	Co
	4	204 (400)	7.2 (1040)	3.9 - 9.2 (560-1330)	Ad
	4	232 (450)	3.8 (550)	3.0 - 4.6 (440 - 660)	Ad
LARC-IA (5% PA) 50% Al powder	4	RT (RT)	36.4 (5280)	35.6-37.9 (5160-5500)	Co
	4	177 (350)	22.2 (3220)	20.0-25.0 (2900-3620)	Co
	4	204 (400)	11.0 (1590)	8.9-14.2 (1290-2060)	Co
	4	232 (450)	7.0 (1020)	5.6 - 7.6 (810-1100)	Co
LARC-TPI [c]	4	RT (RT)	27.8 (4030)	26.7-28.8 (3870-4180)	Co
	4	177 (350)	19.7 (2860)	19.1-20.3 (2760-2950)	Co
	4	204 (400)	10.1 (1470)	9.4-11.0 (1360-1600)	Co
	4	232 (450)	5.2 (760)	4.6 - 5.6 (670 - 810)	Co

[a] Bonding conditions: 2.07 MPa (300 psi) pressure from start, heating rate of 8° C/min (14° F/min), RT → 371° C (700° F), held 1 hr

[b] Cohesive-Co, adhesive-Ad

[c] Data previously reported by our laboratory. Bonding conditions: 2.07 MPa; 343° C held 1 hr

Table 7. Flatwise tensile strength and critical fracture energy

Adhesive	FWT [a] [MPa (psi)]	G_{1c} [b] $\left[J/m^2 \left(\frac{in.\ lb}{in.^2}\right)\right]$
LARC-IA (5% PA)	1.7 (247)	560 (3.2)
	2.6 (378)	438 (2.5)
LARC-IA (5% PA) 50% Al powder	2.3 (340)	298 (1.7)
	2.4 (355)	210 (1.2)

[a] Specimens were fabricated from Ti-6Al-4V facesheets [0.05 cm (0.020 in.)] and Ti core [0.95 cm (0.37 in.) cell size] given a Pasa Jell 107 surface treatment before priming and bonding

[b] Specimens were fabricated from Ti-6Al-4V 0.13 cm (0.050 in.) thick and given a Pasa Jell 107 surface treatment before priming and bonding

Table 8. LARC–IA film properties[a]

Sample #	Yield strength, psi	Tensile strength, psi	Tensile modulus, psi	Elongation, %
Test temperature, RT				
1	11 097	16 645	439 883	5.14
2	10 625	17 375	426 136	6.30
3	10 000	17 882	464 396	7.17
4	8 625	17 250	597 610	5.64
5	11 733	19 333	490 798	7.12
	Avg 10 416	Avg 17 697	Avg 483,764	Avg 6.27
Test temperature, 200° C				
6	5067	7000	285 714	6.21
7	6400	7667	306 513	22.80
8	5200	6600	306 513	6.37
9	5379	7034	266 105	9.36
10	5286	6714	295 567	23.20
	Avg 5466	Avg 7003	Avg 292 082	Avg 13.59

Glass transition temperature, T_g = 243°C (469°F)

[a] An amorphous, transparent, amber film 1.6 mils thick

Table 9. LARC–IA solvent resistance[a]

Solvent	Visual observation	T_g after exposure, °C (°F)	
		DSC	TMA
None	---	243 (469)	---
Methylene chloride	Curling	256 (493)	250 (482)
Diglyme	No change	242 (468)	240 (464)
Dimethyl acetamide	No change	243 (469)	242 (468)
m-cresol	No change	242 (468)	241 (466)
N-methyl-2-pyrrolidone	No change	243 (469)	239 (462)

[a] Conducted at room temperature for 72 hours

Color - amorphous, transparent, amber film
Dielectric constant - 3.06 at 10 GHz

Table 10. LARC–IA(5%PA)/AS4 12K polyimide/graphite composite[a]

Sample	FLEX. STR. psi	FLEX. MOD. psi
1	213,400	13.9×10^6
2	177,700	14.3×10^6
Avg	195,500	14.1×10^6

[a] Unidirectional, 10 ply, ~1.75 mm (0.069 in.) thick; fabrication conditions: 1 hr heat-up, 349°C (660°F) for 1 hr, pressure 2.07 MPa (300 psi) applied at 252°C (485°F), cool under pressure

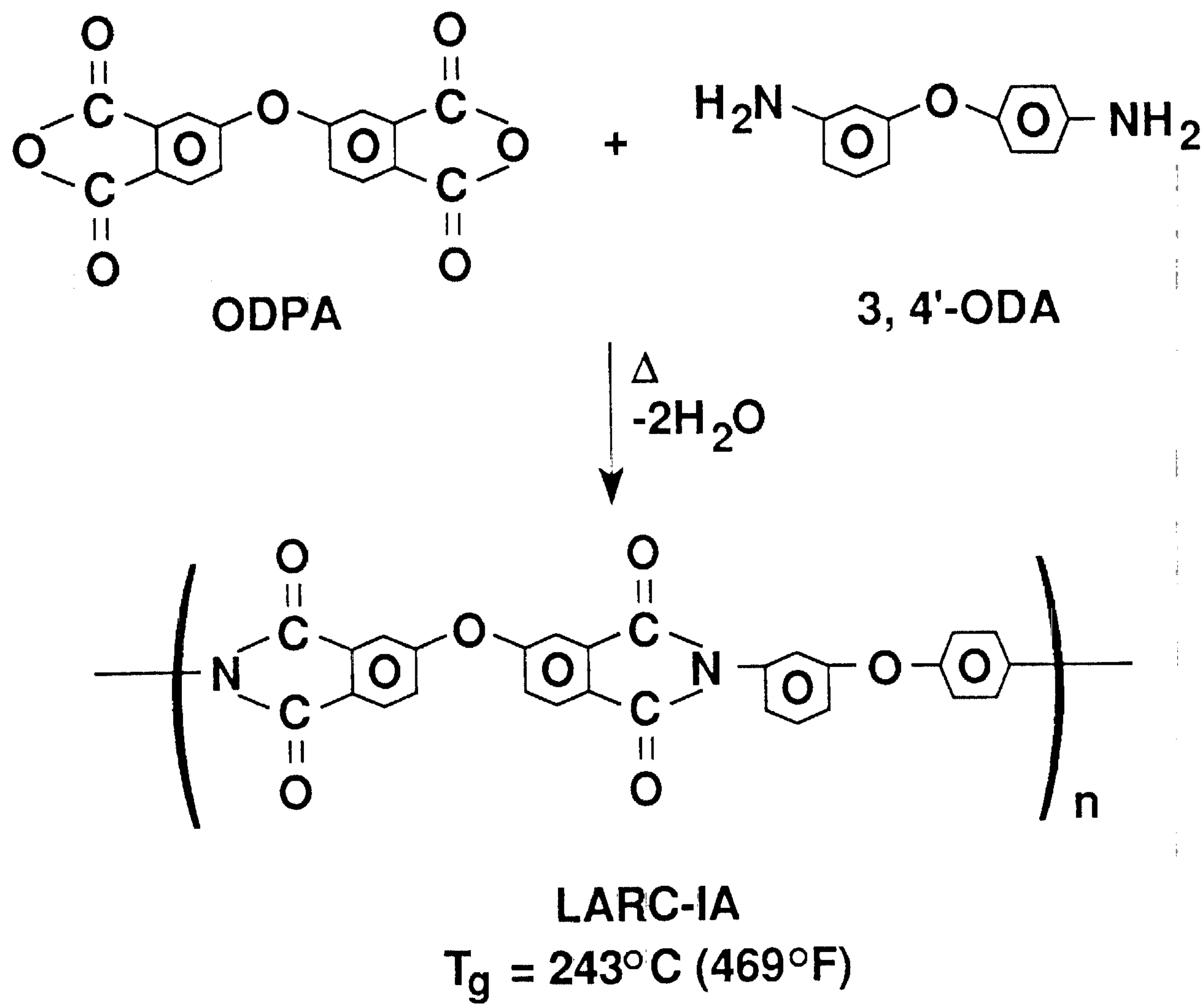


Figure 1. Reaction scheme for LARC–IA.

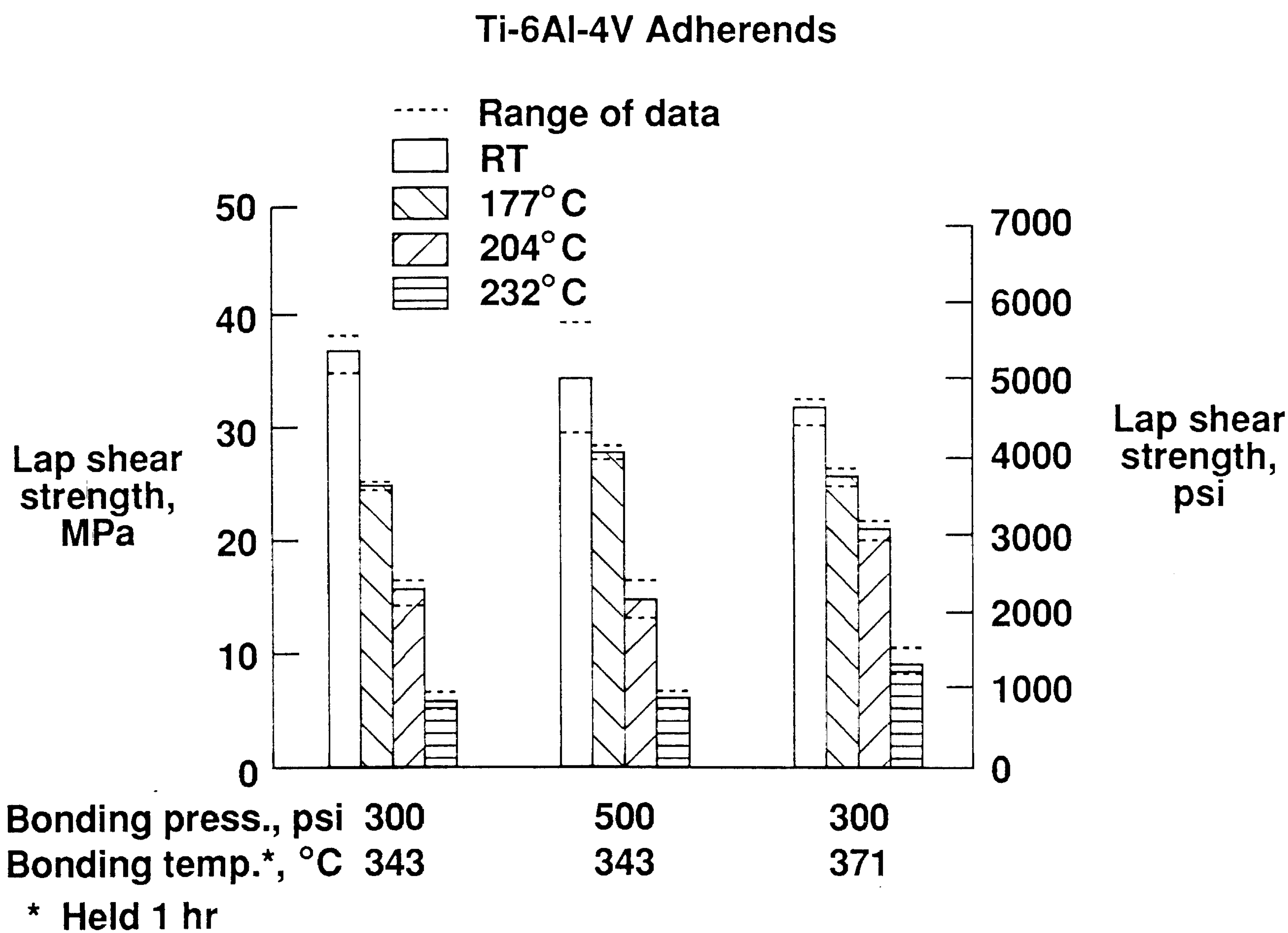


Figure 2. Effect of bonding conditions on the lap shear strengths of LARC-IA bonded Ti-6Al-4V specimens.

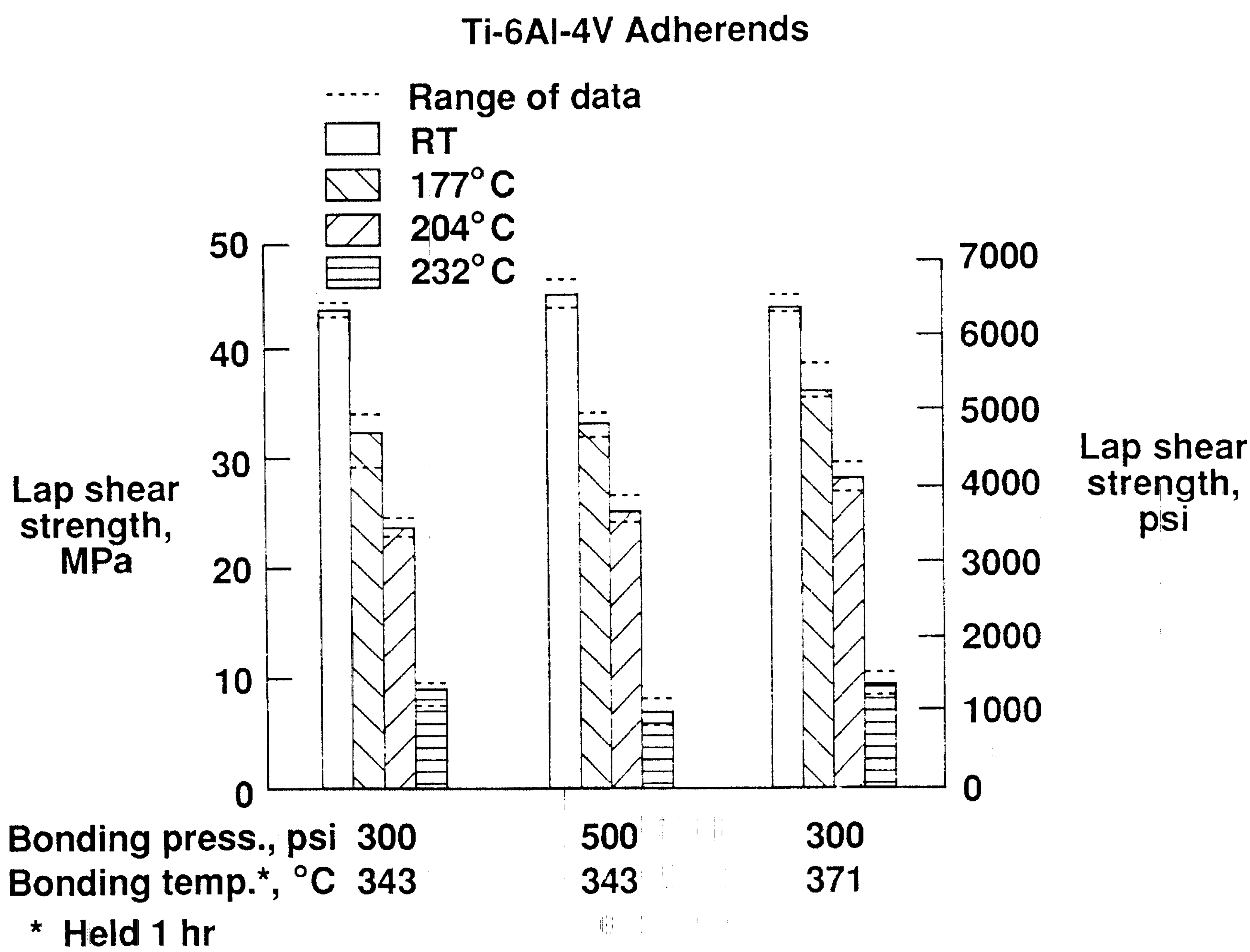


Figure 3. Effect of bonding conditions on the lap shear strengths of LARC-IA(5%PA) bonded Ti-6Al-4V specimens.

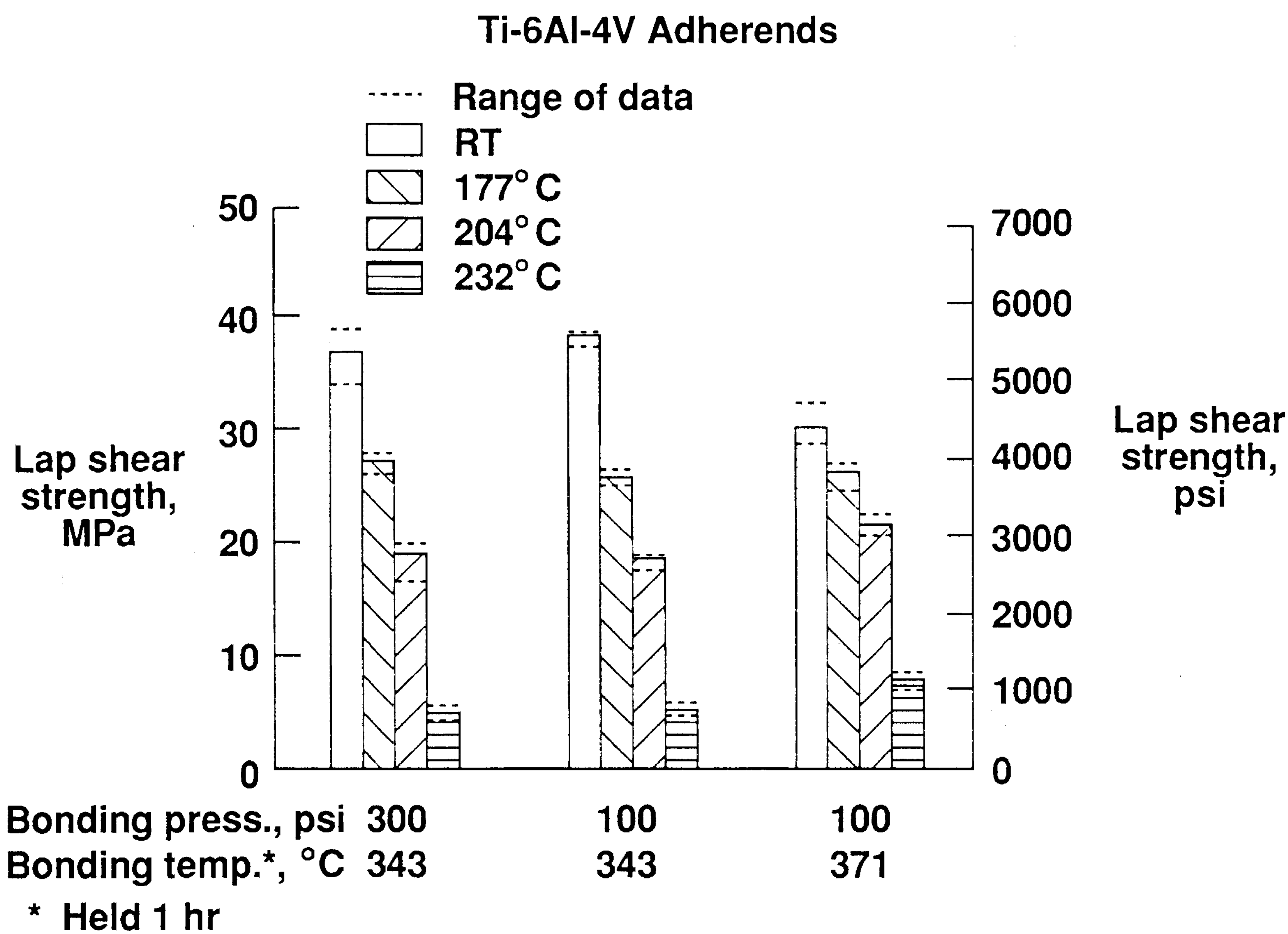
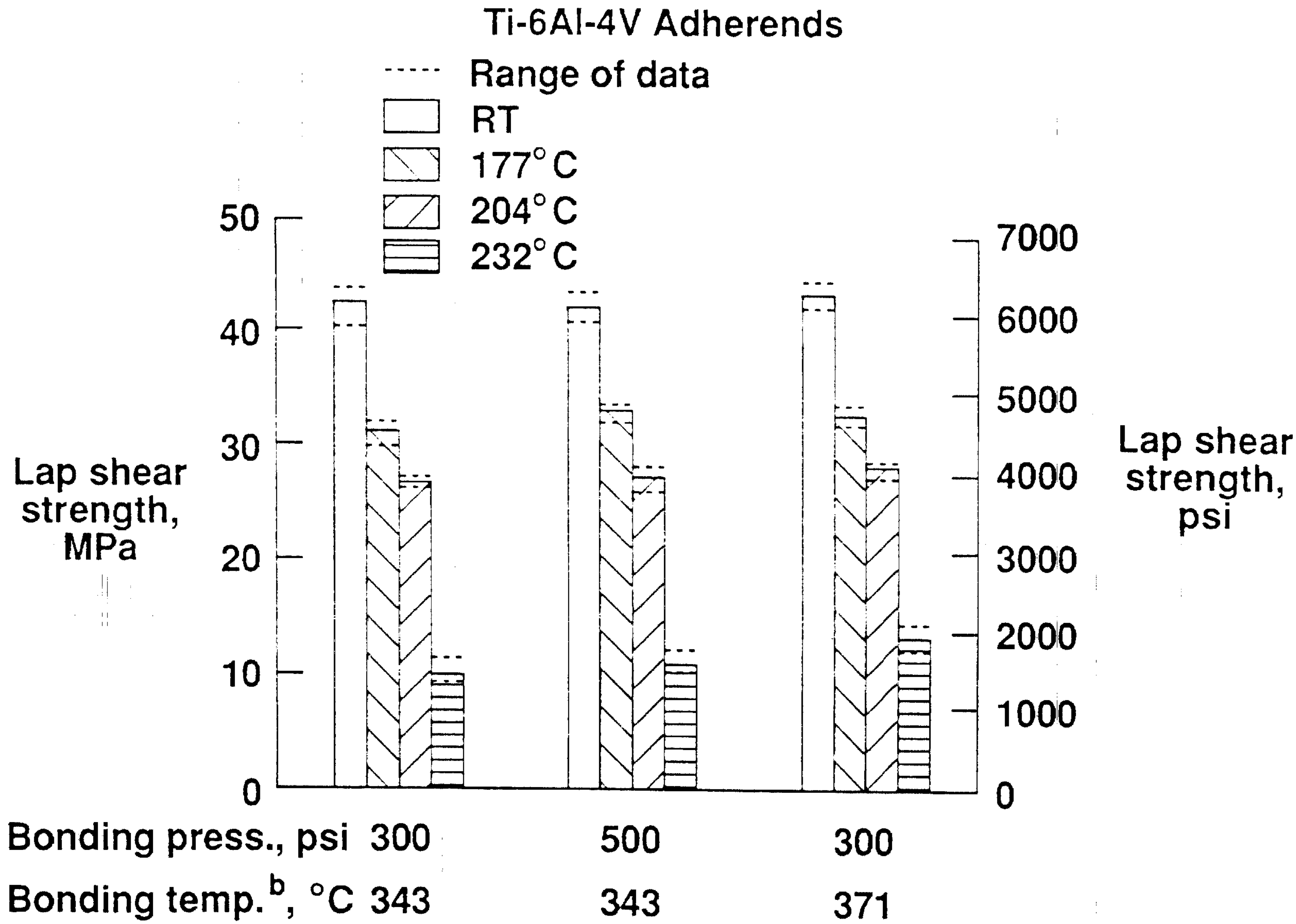


Figure 4. Effect of the bonding conditions on the lap shear strengths of LARC–IA(10%PA) bonded Ti–6Al–4V specimens.



[a] Alcan Aluminum Corp., grade MD105, 98% min. Al content, 4.5-6.45μ particle size
[b] Held 1 hr

Figure 5. Effect of bonding conditions on the lap shear strengths of LARC-IA(5%PA)50%Al bonded Ti-6Al-4V specimens.

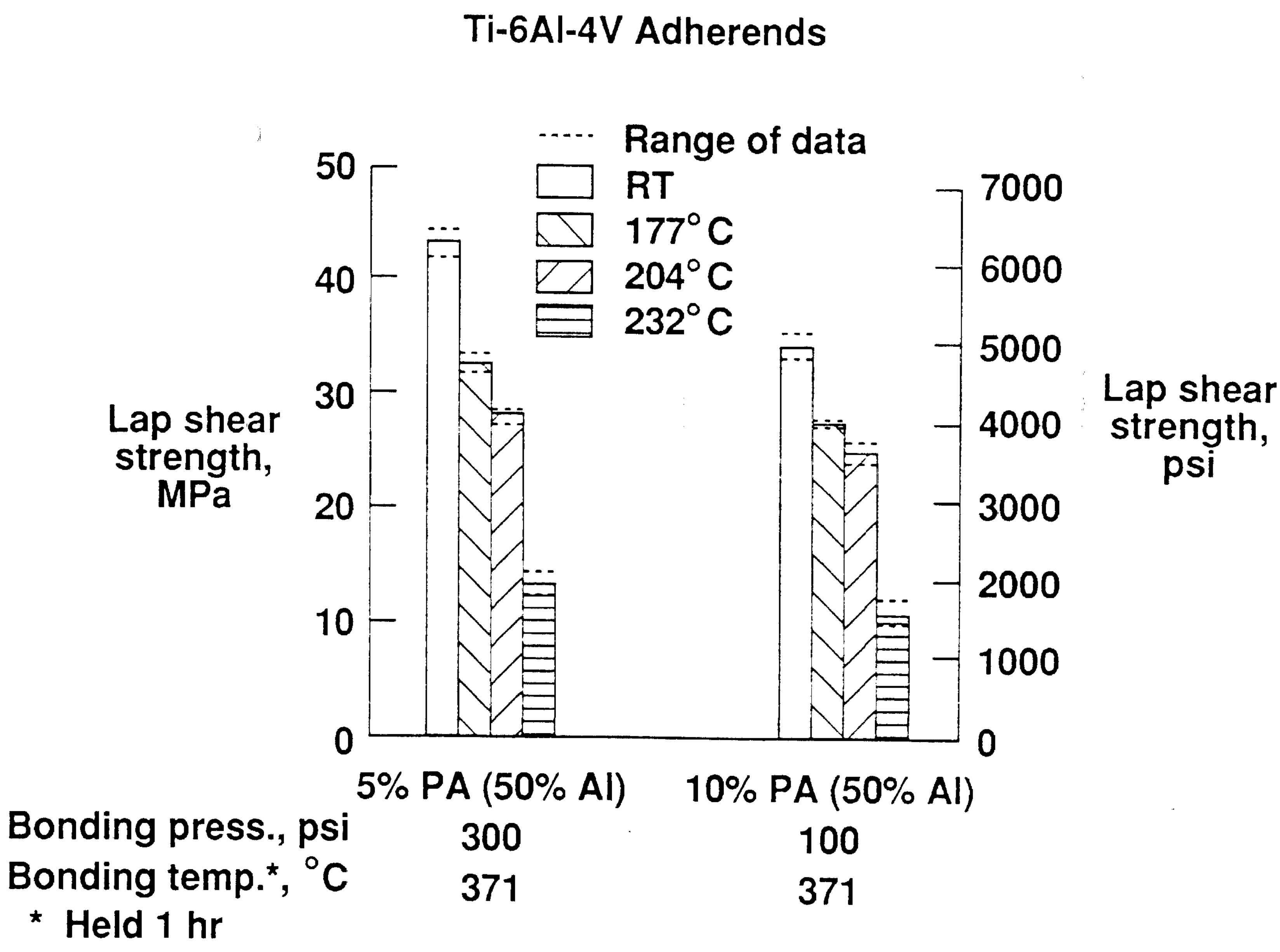


Figure 6. Lap shear strengths for LARC–IA 5% and 10%PA endcap with 50 wt.% aluminum powder filler.

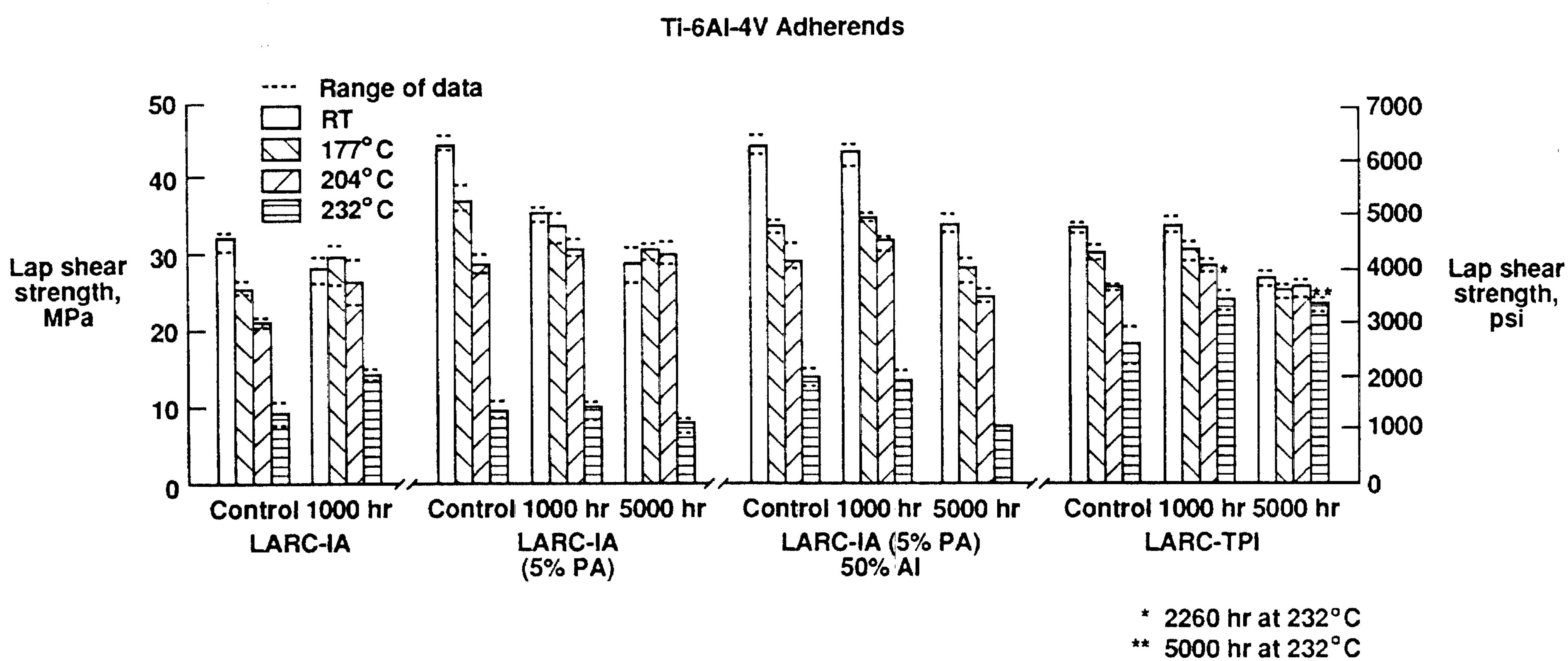


Figure 7. Lap shear strengths for thermal exposure in air at 204°C for Ti–6Al–4V bonded with LARC–IA adhesives and compared with LARC–TPI adhesive.

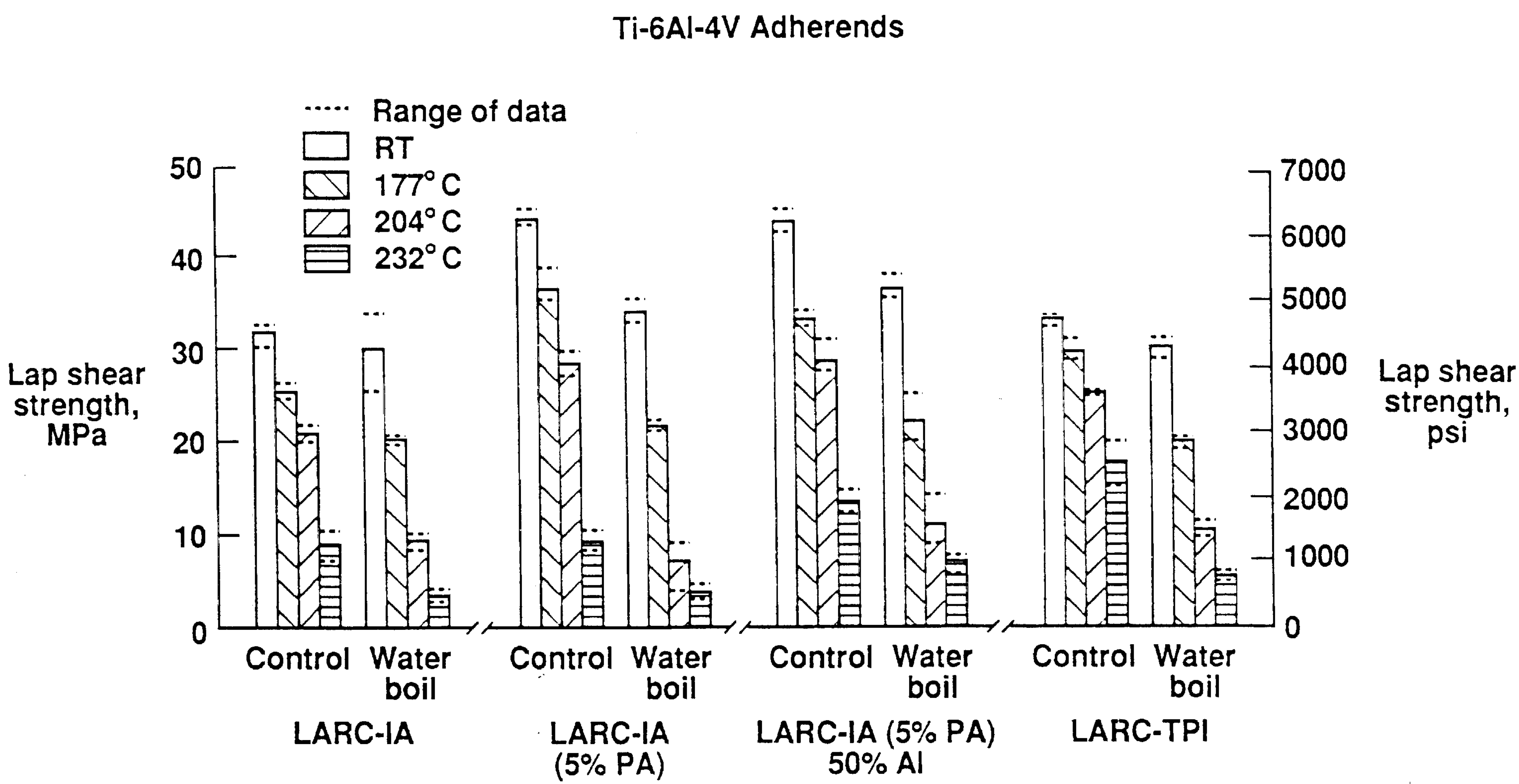


Figure 8. Lap shear strengths for Ti−6Al−4V bonded with LARC−IA adhesives and LARC−TPI exposed to a 72−hour water boil.

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16. Abstract

A new linear, aromatic, thermoplastic polyimide, prepared from oxydiphthalic anhydride (ODPA) and 3,4'-oxydianiline (ODA) in diglyme and identified as LARC-IA, has been synthesized and evaluated. The monomers are relatively inexpensive and physiologically safe. Molecular weight was controlled by use of a monofunctional anhydride, phthalic anhydride (PA), in order to promote controlled flow and wetting properties.

The polymer is considered a safe alternative to commercially available LARC-TPI which is prepared with an expensive diamine of uncertain carcinogenicity.

The evaluation was based primarily on the polymer's adhesive properties as determined by thermal and water boil exposure of lap shear specimens. Strengths were determined at room temperature, 177, 204 and 232°C before and after exposure to determine the adhesive system's durability to adverse environments over a period of time.

Other properties (FWT, G_{1c}, film and composite properties) were examined which were determined to be typical of a high temperature polyimide.

Results of the study show a favorable comparison to LARC-TPI, a commercially available polyimide.

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