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Flexibilized Copolyimide Adhesives*

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Two copolyimides, LARC-STPI and STPI-LARC-2, with flexible backbones were prepared and characterized as adhesives. The processability and adhesive properties were compared to those of a commercially available form of LARC-TPI.

Lap shear specimens were fabricated using adhesive tape prepared from each of the three polymers. Lap shear tests were performed at room temperature, 177°C, and 204°C before and after exposure to water-boil and to thermal aging at 204°C for up to 1000 hours.

The three adhesive systems possess exceptional lap shear strengths at room temperature and elevated temperatures both before and after thermal exposure. LARC-STPI, because of its high glass transition temperature provided high lap shear strengths up to 260°C. After water-boil, LARC-TPI exhibited the highest lap shear strengths at room temperature and 177°C, whereas the LARC-STPI retained a higher percentage of its original strength when tested at 204°C [68% versus 50% (STPI-LARC-2) and 40% (LARC-TPI)].

These flexible thermoplastic copolyimides show considerable potential as adhesives based on this study and because of the ease of preparation with low cost, commercially available materials.

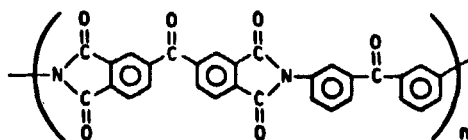
KEY WORDS Adhesive performance; flexibilized copolyimides; high temperature adhesives; polymer synthesis; processability; thermoplastic polyimides.

INTRODUCTION

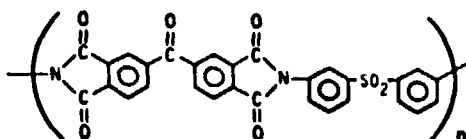
There are few materials available which can be used as aerospace adhesives at temperatures in excess of 200°C. During the past 10-15 years, the Materials Division at NASA Langley Research

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Center has developed several novel high temperature polyimide adhesives needed to fulfill the anticipated needs of the aerospace industry. These developments have resulted from fundamental studies of structure-property relationships in polyimides. Two materials that have exhibited exceptional adhesive properties are LARC-TPI (*Langley Research Center Thermoplastic Imide*)^{1,2} and PIS02 (a thermoplastic polyimidesulfone).³ The structures of these materials are illustrated below.

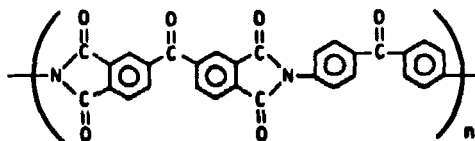


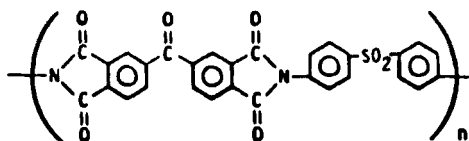
LARC-TPI



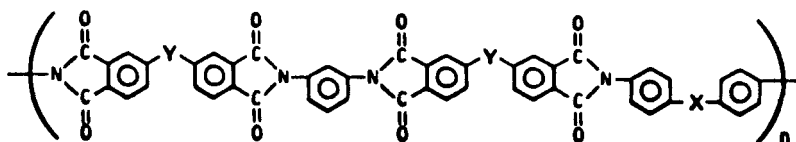
PIS02

In examining these structures one should note that the backbones are identical with one exception—a carbonyl group in LARC-TPI and a sulfone group in PIS02. The primary characteristic that imparts the thermoplastic nature, and hence good adhesive properties, to these systems is the degree of flexibility along the backbone. In this regard, the flexibility is introduced *via* the carbonyl bridging group in the anhydride-derived portion of the chain and from the sulfone and carbonyl groups in the diamine-derived portion of the chain.⁴ In addition, a key factor is the *meta*-oriented linkage to the benzene rings in the amine-derived segments. The corresponding systems with *para*-oriented linkages exhibit very little thermoplasticity. These structures are shown below for comparison.



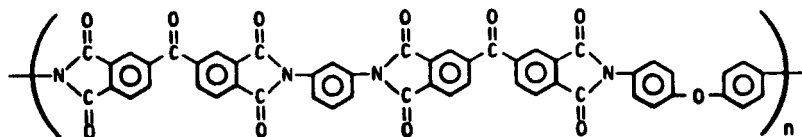


A recent research program at NASA Langley involved the synthesis and evaluation of copolyimides which incorporated both flexibilizing bridging groups and *meta*-linked benzene rings. This activity was undertaken in order to develop systems based on low cost, readily available monomers. The approach involved the preparation of copolyimides of the following structure:

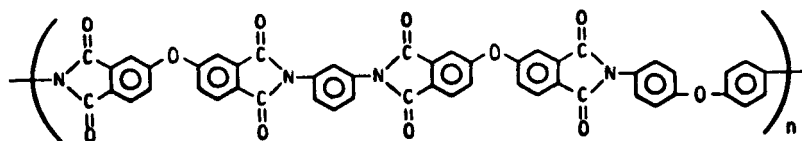


In the cases studied to date, x is an oxygen and y is either an oxygen or a carbonyl. Molecular models of this system and of the LARC-TPI/PIS02 were prepared and compared. Models of all systems exhibited similar long range flexibility with the LARC-TPI/PIS02 exhibiting more uniform short range flexibility. A study of the adhesive properties of copolypyromellitimides was published by Varma and Rao.⁵

The two copolyimides that have been evaluated as adhesives for bonding a titanium alloy (Ti 6Al-4V) are as follows:



LARC-STPI



STPI-LARC-2

EXPERIMENTAL

Materials

The chemicals were obtained from commercial sources. The list of chemicals, abbreviations, and their sources follows:

benzophenonetetracarboxylic acid dianhydride (BTDA), King Mar Laboratories; oxydiphthalic anhydride (ODPA), Ciba-Geigy (made on NASA contract); 4,4'-oxydianiline (ODA), Mallinckrodt, Inc.; *meta*-phenylenediamine (MPD), N,N-dimethylacetamide (DMAc), 2-methoxyethylether (diglyme), N-methylpyrrolidone (NMP), Fluka Chemical Co.; and phthalic anhydride (PA), Eastman Kodak Co.

Synthesis

The preparation of the copolyimides were carried out at room temperature in a 1000 ml cylindrical reaction flask with a removable, four-necked top. Stirring of the mixture was accomplished using an impeller blade driven by a constant-torque, overhead motor equipped with a variable speed control.

The BTDA or ODPA (0.050M) and PA (0.002M) were slurried in a mixed solvent system of diglyme with either NMP or DMAc. To this was added ODA (0.025M) and the mixture was allowed to stir for 15 min to form a solution. Next the MPD (0.025M) was added and the solution was stirred for an additional 35 min. The resin was decanted from the vessel. In this manner, a 15 wt% solids solution of LARC-STPI with a 3:1 ratio of amide/ether solvent was prepared. The STPI-LARC-2 was prepared as a 17.5 wt% solid solution with an approximate 1.6:1 ratio of amide/ether solvent. An inherent viscosity of 0.52 dl/g was obtained for the LARC-STPI resin and 0.65 for STPI-LARC-2.

Characterization

Lap shear strength was obtained according to ASTM D-1002 using a Model TT-C Instron Universal Testing Machine. The lap shear strengths reported represent an average of four lap shear specimens per test condition except where noted in the tables. The range of the lap shear strengths is indicated by dashed lines in the bar graph

figures and given in the tables. Bondline thickness was obtained as the difference between the total joint thickness measured with a micrometer and the sum of the adherend thicknesses. The average bondline thickness for LARC-STPI was 0.017 cm with a range of 0.014 cm to 0.020 cm. STPI-LARC-2 averaged 0.019 cm with a range of 0.015 cm to 0.021 cm. Due to the greater flow of the LARC-TPI adhesive, average bondline thickness for the LARC-TPI was 0.009 cm with a range of 0.007 cm to 0.011 cm. Specimens were heated in a clam-shell, quartz-lamp oven and were held at temperature for 10 minutes prior to testing except for the water-boil specimens which were tested as soon as the test temperature was reached. Temperatures were controlled to within $\pm 3^\circ\text{C}$ for all tests.

Glass transition temperatures (T_g) were determined by thermo-mechanical analysis (TMA) for the adhesive on fractured lap shear specimens and by differential scanning calorimetry (DSC) for films of the polymers, both methods using a DuPont† Thermal Analysis System. TMA measurements were performed in static air at a heating rate of $5^\circ\text{C}/\text{min}$ using a hemispherical probe with a 15 g load. DSC measurements were run in air at $50^\circ\text{C}/\text{min}$. The inherent viscosity reported is the average of three measurements on 0.5 wt% solids solutions in DMAc made at $35^\circ\text{C} \pm 0.01^\circ\text{C}$ using a Cannon Ubbelohde viscometer.

Adhesive bonding

Adhesive tape for the LARC-STPI was prepared by brush coating a primer solution of polyamic acid, diluted to approximately 7.5 wt% solids in diglyme/DMAc, onto 112 E-glass cloth with A-1100 finish (γ -aminopropylsilane). The glass cloth had been tightly mounted on a metal frame and dried in a forced-air oven for 30 min at 100°C prior to coating. The 0.01 cm thick glass cloth served as a carrier for the adhesive as well as for bondline control and an escape channel for solvent. The coated cloth was then air-dried for 1 hr and heated for 1 hr at each of three temperatures: 100°C , 150°C , and 175°C . Subsequently, each application of a 15 wt% solids solution was brush-coated onto the cloth and exposed to the following schedule

† Use of trade names or company names does not constitute an official endorsement by NASA, either expressed or implied.

until a thickness of 0.020–0.025 cm was obtained:

- (1) Room temperature, hold 1 hr
- (2) RT → 100°C, hold 1 hr
- (3) 100°C → 150°C, hold 2 hrs
- (4) 150°C → 175°C, hold 3 hrs

The involved procedure to prepare the tape was needed to drive off solvent and reaction product volatiles when converting the polyamic acid resin to the polyimide. Imidization of polyamic acids to polyimides generally occurs above 160°C with the degree of conversion being a function of time and temperature.

The same procedure was used for STPI-LARC-2 adhesive tape preparation except that a 17.5 wt% solids solution was applied for all coatings until a tape thickness of 0.022 cm was obtained. The solvent system used also contained a small amount of NMP. A final heat treatment of 15 min at 270°C was given to the tape used in this study.

Adhesive tape for the LARC-TPI was prepared in a similar manner to the LARC-STPI and STPI-LARC-2 in an attempt to

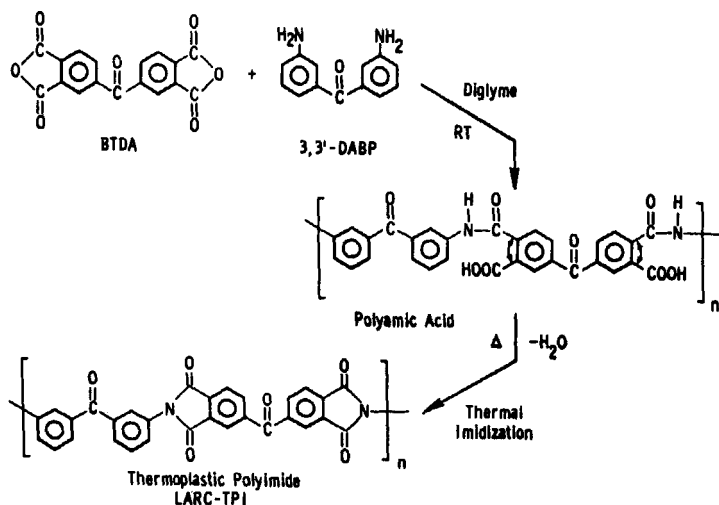


FIGURE 1 Reaction scheme for LARC-TPI.

standardize the tape preparations. The reaction scheme for LARC-TPI, developed at NASA Langley Research Center in the late 1970's from BTDA and 3,3'-diaminobenzophenone (3,3'-DABP) in diglyme solvent is shown in Figure 1.^{1,2} LARC-TPI, Lot No. 26-001, was supplied by Mitsui Toatsu Chemicals, Incorporated, Tokyo, Japan, as a 29.1 wt% solids polyamic acid solution in diglyme with an inherent viscosity of 0.54 dl/g (35°C). Brookfield viscosity was 24,600 cps (23°C). A solution, diluted to approximately 7.5 wt% solids, was applied as the primer to the glass cloth and treated as above. Due to the difficulty of applying the as-supplied 29.1 wt% solids solution, it was necessary to dilute the solution to approximately 24 wt% solids for easier application by brush to the glass cloth. Heat treatment of the applied resin solution was the same as that for LARC-STPI (for up to 175°C for 3 hrs) except fewer applications were necessary due to the higher solids content of the LARC-TPI solution. The adhesive tape thus prepared foamed slightly. All three tapes prepared were stiff and had no tack or drape.

The prepared adhesive tapes were used to bond titanium adherends (Ti 6Al-4V, per Mil-T-9046E, Type III Comp. C) with a nominal thickness of 0.13 cm for the adherends. The Ti 6Al-4V panels were grit blasted with 120 grit aluminum oxide, washed with methanol, and treated with Pasa-Jell 107† to form a stable oxide on the surface. The adherends were washed with water and dried in a forced-air oven at 100°C for 5 min. The treated adherends were primed within two hrs of the surface treatment by applying a thin coat of the polyamic acid solution of the respective adhesives on the surfaces to be bonded. After air-drying in a forced-air oven for 30 min, they were heated for 15 min at 100°C and 15 min at 150°C. The primed adherends were placed in a polyethylene bag and stored in a desiccator until needed. Lap shear specimens were prepared by inserting the adhesive tape between the primed adherends using a 1.27 cm overlap (ASTM D-1002) and applying 2.1 MPa pressure in a hydraulic press during the heating schedule. Bonding temperature was monitored using a type K thermocouple spot-welded to the titanium adherend at the edge of the bondline.

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

The following bonding cycles for the LARC-STPI adhesive were investigated during this study to determine a bonding process which produced good strengths.

Cycle 1

- (1) 2.1 MPa pressure, heating rate $\approx 8.2^\circ\text{C}/\text{min}$, RT \rightarrow 329°C
- (2) Hold 15 min at 329°C
- (3) Cool under pressure to $\approx 150^\circ\text{C}$ and remove from bonding press

Cycle 2

Same as Cycle 1 except RT \rightarrow 343°C

Cycle 3

Same as 1 except RT \rightarrow 343°C, hold 1 hr

A bonding cycle was selected from the above conditions and used to determine the effects of an additional heat treatment of the LARC-STPI adhesive tape prior to bonding based on the lap shear strengths. Next, lap shear specimens were prepared for thermal exposure for 500 and 1000 hrs at 204°C. Thermal exposure was performed in a forced-air oven controlled within $\pm 1\%$ of the desired exposure temperature. Lap shear tests were conducted at room temperature, 177°C, and 204°C before (controls) after exposure.

A 72-hr water-boil test was conducted in laboratory glassware containing boiling distilled water. Lap shear specimens were immersed (above the bonded area) during the 72-hr period. Lap shear strengths were subsequently determined at room temperature, 177°C, and 204°C.

The bonding cycle selected for the LARC-STPI was also used to prepare lap shear specimens with the STPI-LARC-2 and LARC-TPI adhesive tapes. The thermal exposure in air and water-boil exposure tests were the same as that for the LARC-STPI.

RESULTS AND DISCUSSION

Materials

The chemicals for this program were of very high purity and in most cases were used without further purification. The BTDA from King Mar Laboratories was originally prepared by Gulf Chemical (now Allco). King Mar Laboratories purified this material by recrystallizing it from a 90:10 mixture of anisole/acetic anhydride. The ODA from Mallinkrodt was a high purity grade. In some cases, where this material had aged in the light, a darkening occurred. This ODA was sublimed in order to obtain high purity. MPD from Fluka is an off-white crystalline material supplied in an opaque bottle. Prolonged exposure of this chemical to air and/or light will result in a severe darkening. The ODA, which had been prepared in the 1970's by Ciba-Geigy, was sublimed prior to use. Care was taken in drying and handling DMAc, PA, and diglyme, as all are capable of absorbing water if they are left open to the atmosphere for extended times. Water is, of course, deleterious to the reaction and usually results in a lower inherent viscosity (molecular weight).

Synthesis

The reaction schemes for LARC-STPI and STPI-LARC-2 are shown in Figure 2. The anhydride monomers had only partial solubility in the mixed solvent system of diglyme and DMAc (NMP). The difunctional anhydride allows for molecular weight buildup (chain growth); the PA was used as a method of controlling the molecular weight so that the level was high enough to yield tough, flexible polymers, but not so high as to inhibit the thermoplastic flow properties. The resulting polymer did afford a flexible film when cast and cured to 300°C. There was adequate thermoplastic flow as evidenced by the softening that occurred during the adhesive bonding operation.

The ODA was added initially because in a preliminary experiment a precipitation occurred when MPD was added first. Also, in preparing a random copolymer by the method that was used, there was no way of ensuring that block formation does not occur. From a

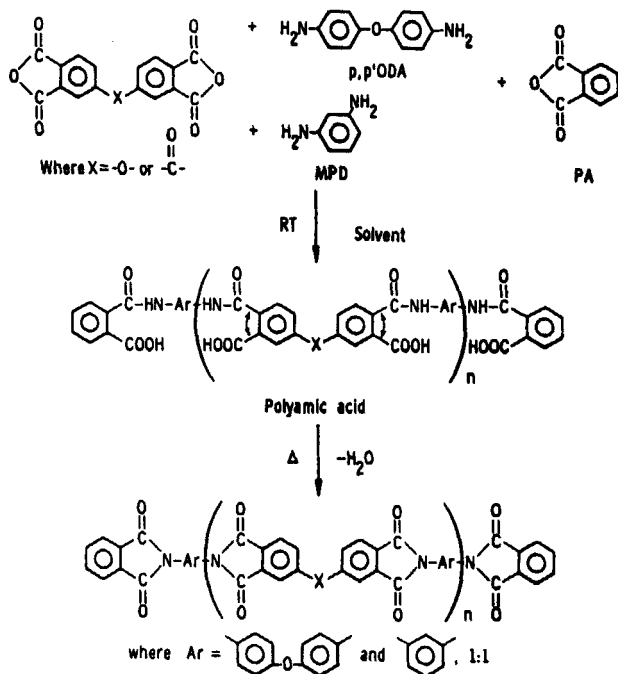


FIGURE 2 Reaction scheme for formation of LARC-STPI and STPI-LARC-2.

statistical standpoint this should not occur, but previous work in our laboratory had shown that diglyme may promote this behavior. For this reason, a mixture of diglyme, DMAc, and/or NMP was used in an effort to avoid block formation and to improve solubility. Other amide solvents such as dimethylformamide could also be used.

Bond cycle selection

Adhesive tape for the LARC-STPI was used to bond lap shear specimens using the three cycles mentioned previously. The bonding pressure was held constant for the three cycles while the temperature and time-held-at-temperature was varied. A higher than normal bonding pressure, 2.1 MPa, was used to assure sufficient flow of the polymer during bonding. Results on the effects of the bond cycle are shown in Figure 3 and Table 1 which includes

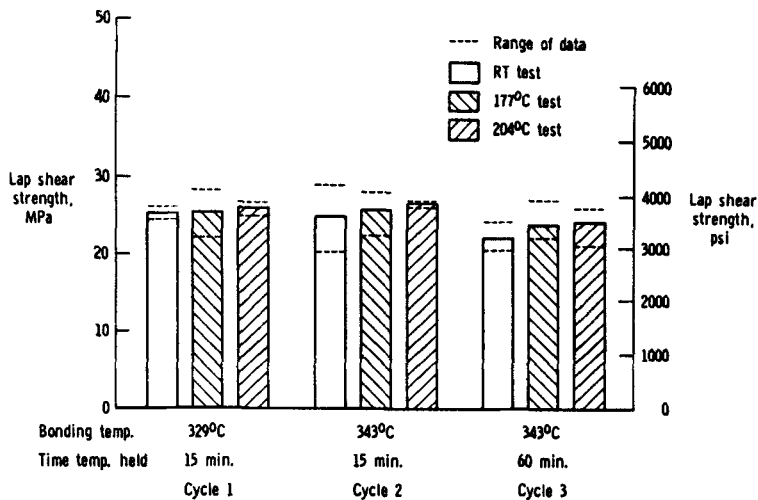


FIGURE 3 Effects of bonding temperature and time-temperature-held on lap shear strength of titanium bonded with LARC-STPI adhesive.

TABLE I
Effects of bonding cycle on LSS for LARC-STPI bonded TI 6-4

Bonding cycle	Number of specimens	Test temperature, °C	Average LSS, MPa	Range of LSS, MPa	Primary failure mode†	T_g , ‡ °C
1	2	RT	25.4	24.6–26.1	AD	222
	3	177	25.5	22.1–28.3	CO	—
	3	204	25.9	24.9–26.7	CO	—
2	3	RT	25.0	20.0–29.1	AD	240
	4	177	25.8	22.5–28.0	CO	—
	3	204	26.7	26.2–27.0	CO	—
3	4	RT	22.2	20.7–24.3	AD	266
	4	177	23.9	22.2–27.2	CO/AD	—
	4	204	24.3	21.2–26.2	CO	—

† AD—adhesive.

CO—cohesive (through glass cloth).

‡ Glass transition temperature, single measurement. T_g determined by DSC on a LARC-STPI film cured to 300°C was 283°C.

additional information, *i.e.* number of specimens tested, primary failure mode, and T_g . Lap shear strengths were determined at RT, 177°C, and 204°C. Results indicate very little difference in strengths for the three test temperatures. Average strengths at RT for the three cycles ranged from 22.2 to 25.4 MPa; at 177°C, from 23.9 to 25.8 MPa; and at 204°C, from 24.3 to 26.7 MPa. The RT test specimens failed primarily adhesively for all three cycles, changing to cohesive with increasing test temperature. The T_g 's, measured on the fractured RT test specimens, tended to increase as temperature and time-held-at-temperature increased, *i.e.* Cycle 1, 222°C; Cycle 2, 240°C; and Cycle 3, 266°C. Because all three cycles produced essentially the same lap shear strengths and because Cycle 3 had the highest T_g , 266°C, it was selected as the bonding cycle for use in the remainder of this study.

Past experience with these types of thermoplastic polyimides had shown a beneficial effect when heating the adhesive tape to higher temperatures for a period of time.⁶ Table II and Figure 4 show the effect on lap shear strength resulting from an additional heating of the adhesive tape prior to bonding. Specimens were bonded after

TABLE II
Effect on LSS of additional heat treatment to LARC-STPI adhesive tape

Additional heat treatment†	Number of specimens	Test temperature, °C	Average LSS, MPa	Range of LSS, MPa	Primary failure mode‡	T_g , § °C
1 hr at 200°C	4	RT	24.6	23.1–25.8	AD	265
	4	177	25.2	24.3–26.0	CO/AD	—
	4	204	26.2	24.5–27.8	CO	—
As above plus 1 hr at 225°C	4	RT	25.0	24.1–26.8	AD	265
	4	177	26.7	25.7–28.0	CO	—
	4	204	26.3	25.4–27.6	CO	—
As above plus 1 hr at 250°C	4	RT	26.6	24.2–29.6	CO	267
	4	177	27.0	23.6–30.0	CO	—
	4	204	25.0	24.1–26.0	CO	—

† Prior adhesive tape treatment was heating in forced-air oven at 100°C, 150°C and 175°C after each application until ≈ 0.025 cm thick.

‡ AD—adhesive.

CO—cohesive (through glass cloth).

§ Glass transition temperature, single measurement.

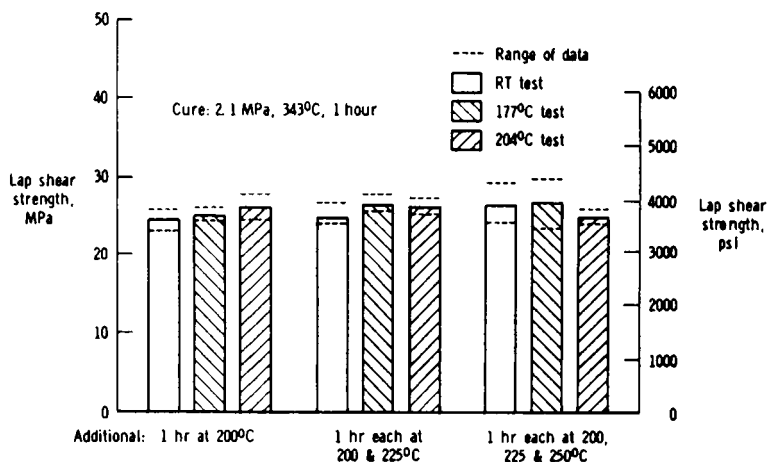


FIGURE 4 Effect on lap shear strength of additional heating (in air) of LARC-STPI adhesive tape prior to use for bonding titanium.

each of the successive heat treatments, *i.e.* 1 hr at 200°C, plus 1 hr at 225°C, and plus 1 hr at 250°C. Again lap shear strengths were determined at RT, 177°C, and 204°C. No significant differences in strengths were obtained at any test temperature due to the heat treatment of the adhesive tape. In fact, the average strength was essentially the same for all test temperatures and tape heat treatments. The T_g 's determined were also about the same, 265–267°C, as that of the adhesive tape used prior to the additional heat treatment, 266°C. The significant difference found was that the type of failure for the adhesive tape taken to 250°C for 1 hr was cohesive at all test temperatures, whereas, others changed from an adhesive failure to a cohesive failure. Due to the cohesive type of failure for the adhesive tape taken to 250°C for 1 hr, it was used for the LARC-STPI adhesive tape treatment to prepare lap shear specimen for the thermal exposure and water-boil tests.

Adhesive tape for the LARC-TPI was prepared in a similar manner to the LARC-STPI except no additional heat treatment above the 175°C for 3 hrs was performed. Cycle 3 was also used to fabricate lap shear specimens of LARC-TPI and STPI-LARC-2 for the thermal exposure and water-boil tests.

Thermal exposure tests

The stability of the adhesives to long term thermal exposure was determined for the three adhesive systems by exposing lap shear specimens for 500 and 1000 hrs at 204°C in a forced-air oven. Cycle 3 (2.17 MPa pressure, RT to 343°C, hold 1 hr) was used to bond the lap shear specimens for the thermal exposure study. Lap shear strengths were determined at RT, 177°C, and 204°C before (controls) and after exposure.

Results for LARC-STPI are given in Table III and Figure 5. Little change in lap shear strength was observed due to the thermal exposure. The 500 and 1000 hr exposure strengths, approximately 23 MPa, are the same, but slightly lower than the control strengths, approximately 26 MPa. The primary failure mode of the fractured specimens was cohesive except for the 500 and 1000 hr exposure specimens tested at RT which were adhesive/cohesive and adhesive, respectively. The T_g 's measured on the fractured adhesive surfaces were between 260°C and 267°C.

Results for STPI-LARC-2 adhesive are given in Table IV and Figure 6. Little change in lap shear strength was noted due to thermal exposure at 204°C. A general decrease in RT lap shear

TABLE III
Effects of thermal exposure (in air) on LSS for LARC-STPI bonded Ti 6-4

Thermal exposure at 204°C, hr	Number of specimens	Test temperature, °C	Average LSS, MPa	Range of LSS, MPa	Primary failure mode†	T_g , ‡ °C
0 [Controls]	4	RT	26.6	24.2–29.6	CO	267
	4	177	27.0	23.6–30.0	CO	—
	4	204	25.0	24.1–26.0	CO	—
500	4	RT	23.2	20.0–25.0	AD/CO	265
	4	177	23.9	23.2–24.6	CO	—
	4	204	23.4	22.4–24.5	CO	—
1000	4	RT	24.1	23.6–25.1	AD	260
	4	177	23.2	22.1–25.0	CO	—
	4	204	22.7	20.7–24.1	CO	—

† AD—adhesive.

CO—cohesive (through glass cloth).

‡ Glass transition temperature, single measurement.

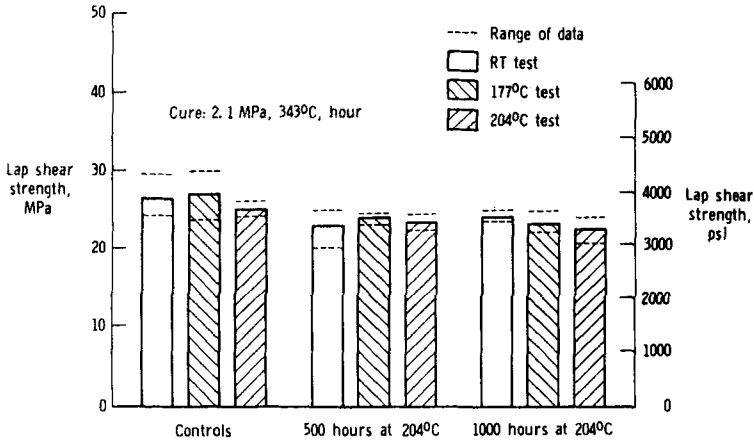


FIGURE 5 Effects of thermal exposure in air for 500 and 100 hours at 204°C on lap shear strength for titanium bonded with LARC-STPI adhesive.

TABLE IV
Effects of thermal exposure (in air) on LSS for STPI-LARC-2 bonded Ti 6-4

Thermal exposure at 204°C, hr	Number of specimens	Test temperature, °C	Average LSS, MPa	Range of LSS, MPa	Primary failure mode†	T _g , ‡ °C
0 [Controls]	4	RT	35.1	34.4–36.1	CO	225
	3	177	32.7	31.8–33.8	CO	220
	4	204	26.2	25.7–27.6	CO/AD	227
500	4	RT	32.5	28.2–34.6	CO/AD	235
	4	177	31.4	29.8–32.4	CO	236
	4	204	28.8	26.9–29.6	CO	239
1000	4	RT	28.6	27.2–30.7	AD	241
	4	177	30.1	30.0–30.9	CO	237
	4	204	28.8	28.3–29.5	CO	229

† AD—adhesive.

CO—cohesive.

‡ Glass transition temperature, single measurement.

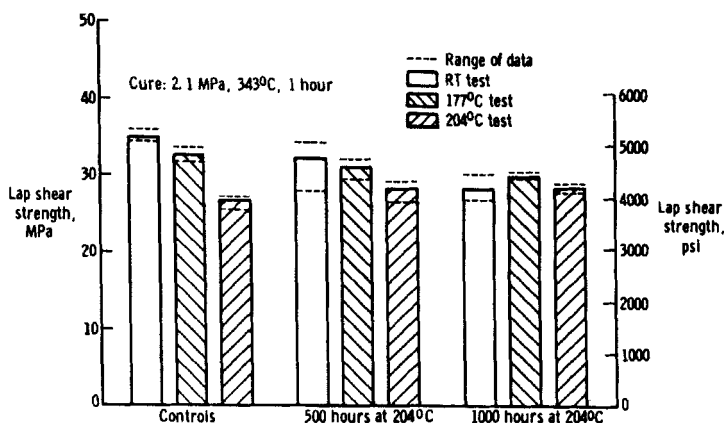


FIGURE 6 Effects of thermal exposure in air for 500 and 1000 hours at 204°C on lap shear strength for titanium bonded with STPI-LARC-2 adhesive.

strength from 35.1 MPa (controls) to 28.6 MPa (1000 hrs) was noted. Lap shear strength remained approximately the same at 177°C (30.1 MPa–32.7 MPa) and at 204°C (26.2 MPa–28.8 MPa). A slight decrease in lap shear strength with test temperature was shown for the control tests—RT, 35.1 MPa; 177°C, 32.7 MPa; and 204°C, 26.2 MPa. For the 500 hr exposure at 204°C, a small decrease, 11%, was noted for the 204°C test when compared to the RT lap shear strength. No changes in lap shear strength with test temperature were determined for the 1000 hr thermal exposure tests. Failures were primarily cohesive except for the RT test for those given a 1000 hr thermal exposure. A slight general increase in T_g with time of thermal exposure was shown—controls, 220–227°C; 500 hr, 235–239°C; and 1000 hr, 229–241°C. Results, not included in Table IV or Figure 6, show a 55% strength retention at RT and 73% retention at 204°C for specimens aged 5000 hrs at 204°C. The T_g also increased 33°C from approximately 226°C to approximately 259°C.

Results are given in Table V and Figure 7 for the LARC-TPI adhesive. No significant difference was found in the lap shear strength with time of thermal exposure up to 1000 hrs for any one temperature (RT, 32.9–34.1 MPa; 177°C, 29.0–29.9 MPa; and 204°C, 25.2–27.8 MPa). In all cases there is a general trend of

TABLE V
Effects of thermal exposure (in air) on LSS for LARC-TPI bonded Ti 6-4

Thermal exposure at 204°C, hr	Number of specimens	Test temperature, °C	Average LSS, MPa	Range of LSS, MPa	Primary failure mode†	T_g , ‡ °C
0 [Controls]	4	RT	33.0	32.3–33.5	CO	228
	4	177	29.5	28.8–30.7	CO	225
	4	204	25.2	25.0–25.4	CO	236
500	4	RT	34.1	32.7–35.3	CO	242
	4	177	29.0	27.5–30.5	CO	242
	4	204	26.9	26.6–27.1	CO	237
1000	4	RT	32.9	32.3–34.4	CO	242
	4	177	29.9	28.5–31.0	CO	246
	4	204	27.8	27.2–28.6	CO	238

† AD—adhesive.

CO—cohesive.

‡ Glass transition temperature, single measurement. T_g determined by DSC on a LARC-TPI film cured to 300°C was 260°C.

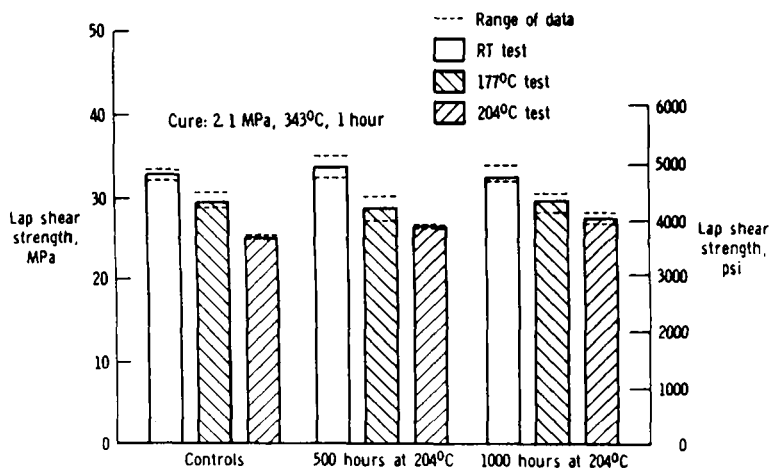


FIGURE 7 Effects of thermal exposure in air for 500 and 1000 hours at 204°C on lap shear strength for titanium bonded with LARC-TPI adhesive.

decreasing lap shear strength with increasing test temperature. However, the decrease is small, less than 24% for up to a 204°C test temperature, when compared to most adhesive systems for this temperature range. All failures were 100% cohesive. Data obtained but not shown here for 5000 hrs exposure show a small decrease at RT and 177°C but no change at 204°C. There appears to be a slight increase in T_g with thermal aging which is characteristic for these types of adhesives (polyimides).

Lap shear strengths up to 260°C were obtained for the three adhesive systems to determine their highest possible use temperature capabilities (Figure 8). Quite obviously, STPI-LARC-2 and LARC-TPI decrease drastically at the 260°C test temperature because the T_g of the adhesives were exceeded (all $\leq 246^\circ\text{C}$) as shown in Table IV and Table V (T_g determined by TMA of the adhesive on a fractured specimen). The T_g 's given in Figure 8 were determined by DSC on films heated for one hr each at 100°C, 200°C, and 300°C. Although the STPI-LARC-2 and LARC-TPI have high lap shear strengths at RT, 177°C, and 204°C, the LARC-STPI because of its higher T_g (267°C, Table III) has greater strength at 232°C and is the only one of the three with good strength at 260°C. All three systems show promising results for the thermal exposure investigated. In general, the LARC-TPI and STPI-LARC-2 had approximately the same range of lap shear strengths which

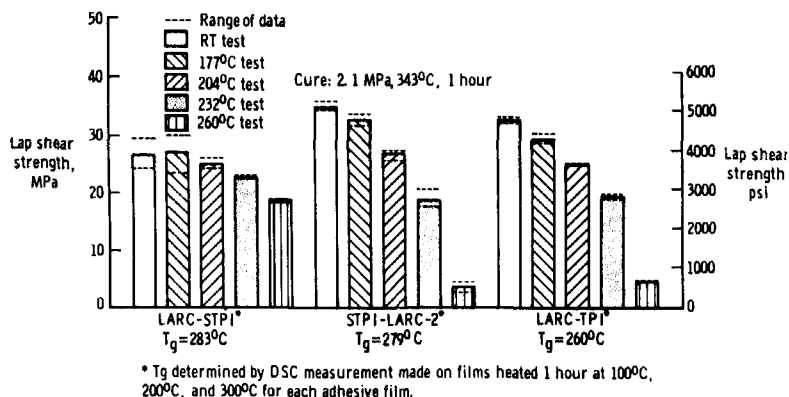


FIGURE 8 Lap shear strength comparison for the three adhesives tested up to 260°C.

were higher overall than the LARC-STPI system. However, the LARC-STPI system had a higher T_g than LARC-TPI and STPI-LARC-2 which generally indicates a higher potential use temperature. All failures for the LARC-TPI were 100% cohesive, whereas, the LARC-STPI and STPI-LARC-2 failed primarily cohesively with partial adhesive failures.

72-Hour water-boil

The resistance of the three adhesives to water (humidity) was determined by immersing lap shear specimens in distilled boiling water for a 72-hour period and subsequently testing their lap shear strengths at RT, 177°C, and 204°C. Results of those tests are given in Table VI and Figure 9 for the LARC-STPI adhesive system, Table VII and Figure 10 for STPI-LARC-2, and in Table VIII and Figure 11 for the LARC-TPI system.

The lap shear strengths of LARC-STPI specimens after water-boil were 88% of the control's RT strength, 62% of the control's 177°C strength, and 68% of the control's 204°C strength. The lap shear strengths for the STPI-LARC-2 were 52% of the control's RT strength and 50% of the control's 204°C strength. The lap shear strengths for the LARC-TPI were 84% of the control's RT strength, 67% of the control's 177°C strength, and 40% of the control's 204°C strength. From these results, it appears that the LARC-STPI and

TABLE VI
Effect of 72-hour water-boil on LSS for LARC-STPI bonded Ti 6-4

	Number of specimens	Test temperature, °C	Average LSS, MPa	Range of LSS, MPa	Primary failure mode†	T_g , ‡ °C
Controls	4	RT	26.6	24.2–29.6	CO	267
	4	177	27.0	23.6–30.0	CO	—
	4	204	25.0	24.1–26.0	CO	—
72-hour water-boil	4	RT	23.3	20.8–25.2	CO	265
	4	177	16.9	14.8–18.1	CO	264
	4	204	17.0	16.7–17.5	CO	257

† AD—adhesive.

CO—cohesive (through glass cloth).

‡ Glass transition temperature, single measurement.

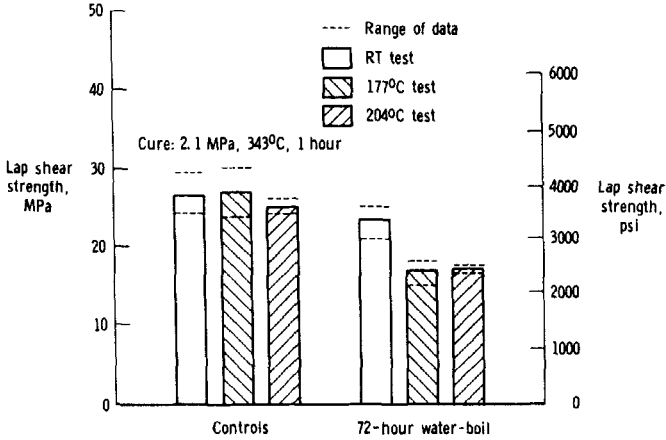


FIGURE 9 Effect of a 72-hour water-boil on lap shear strength for titanium bonded with LARC-STPI adhesive.

LARC-TPI adhesive systems retain a high percentage of the original RT strength. The LARC-STPI also retained the highest percentage, 68%, of the original strength for the 204°C test temperature. Failures were primarily cohesive for the LARC-STPI and LARC-TPI adhesive systems whereas they were cohesive/adhesive after water-boil for the STPI-LARC-2 adhesive system.

TABLE VII
Effect of 72-hour water-boil on LSS for STPI-LARC-2 bonded Ti 6-4

	Number of specimens	Test temperature, °C	Average LSS, MPa	Range of LSS, MPa	Primary failure mode†	T_g , ‡ °C
Controls	4	RT	34.3	31.2-38.2	CO	266
	—	177	—	—	—	—
	3	204	25.3	22.6-28.0	CO	261
72-hour water-boil	3	RT	18.0	15.8-20.0	AD	260
	4	177	15.2	13.4-18.8	CO/AD	260
	4	204	12.7	11.4-14.2	CO/AD	260

† AD—adhesive.

CO—cohesive.

‡ Glass transition temperature, single measurement.

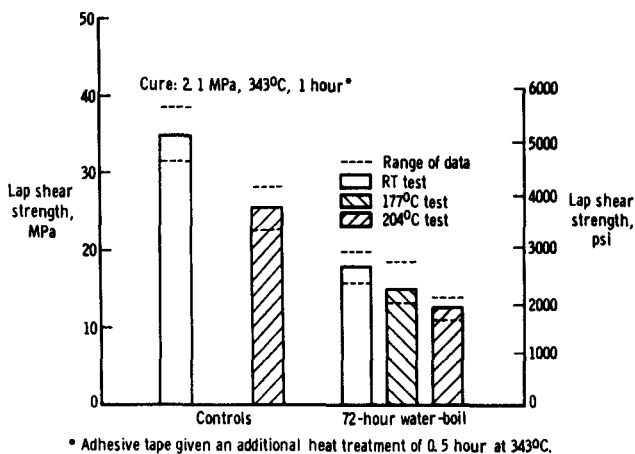


FIGURE 10 Effect of a 72-hour water-boil on lap shear strength for titanium bonded with STPI-LARC-2 adhesive.

Essentially no changes were measured for the T_g 's after the water-boil for the LARC-STPI and LARC-TPI, or the STPI-LARC-2 adhesive systems.

The LARC-TPI provided the highest lap shear strengths after water-boil for the RT and 177°C tests, whereas LARC-STPI retained the highest strength at 204°C after water-boil, 17.0 MPa

TABLE VIII
Effect of 72-hour water-boil on LSS for LARC-TPI bonded Ti 6-4

	Number of specimens	Test temperature, °C	Average LSS, MPa	Range of LSS, MPa	Primary failure mode†	T_g , ‡ °C
Controls	4	RT	33.0	32.3-33.5	CO	228
	4	177	29.5	28.8-30.7	CO	225
	4	204	25.2	25.0-25.4	CO	236
72-hour water-boil	4	RT	27.8	26.7-28.8	CO	239
	4	177	19.7	19.1-20.3	CO	230
	4	204	10.1	9.4-11.0	CO	225

† AD—adhesive.

CO—cohesive.

‡ Glass transition temperature, single measurement.

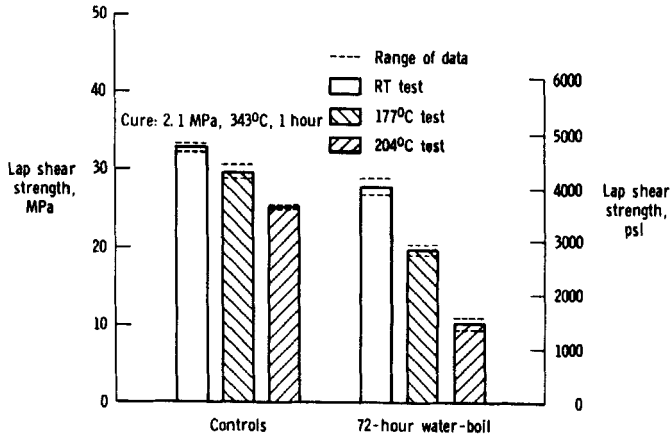


FIGURE 11 Effect of a 72-hour water-boil on lap shear strength for titanium bonded with LARC-TPI adhesive.

compared to 10.1 MPa for LARC-TPI and 12.7 MPa for STPI-LARC-2.

CONCLUSIONS

A thermoplastic polyimide, LARC-TPI, has previously been shown to be an excellent adhesive for several applications. The reason for the thermoplastic nature of this polymer has been attributed to the flexibility of the backbone caused by the use of the meta-linked diamine—3,3'-diaminobenzophenone.

In this work the use of a combination of two flexibilizing diamines in the polymers, LARC-STPI and STPI-LARC-2, has resulted in copolyimides with adhesive performances that are very similar to LARC-TPI. The experimental data on a commercially available LARC-TPI and on the experimental LARC-STPI and STPI-LARC-2 shows all three systems to possess exceptional lap shear strengths at room and elevated temperatures up to 204°C both before and after aging at 204°C. The LARC-STPI, because of its high T_g , provided high lap shear strengths up to 260°C. In general, the LARC-TPI and STPI-LARC-2 adhesive systems had approximately the same range of lap shear strengths, which were higher overall

than the LARC-STPI system. The LARC-STPI system had a higher T_g than LARC-TPI and STPI-LARC-2 which generally indicates a higher potential use temperature. After a 72-hour water-boil exposure, LARC-TPI bonded specimens exhibited the highest lap shear strengths for room temperature and 177°C tests, whereas the LARC-STPI retained a higher percentage of its original strength when tested at 204°C after the water-boil exposure [68% versus 50% (STPI-LARC-2), 40% (LARC-TPI) retention].

An attractive feature of the LARC-STPI and STPI-LARC-2 is that they were prepared from relatively inexpensive, commercially available chemicals. Therefore, these flexible, thermoplastic copolyimides show considerable potential as adhesives based on this initial study.

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