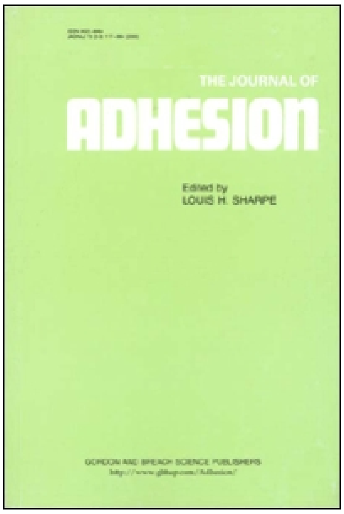

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Flexible Backbone Aromatic Polyimide Adhesives†

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Continuing research at Langley Research Center on the synthesis and development of new inexpensive flexible aromatic polyimides as adhesives has resulted in a material identified as LARC-F-SO_2 with similarities to polyimidesulfone ($PISO_2$) and other flexible backbone polyimides recently reported by Progar and St. Clair. Also prepared and evaluated was an endcapped version of $PISO_2$. These two polymers were compared with LARC-TPI and LARC-STPI, polyimides researched in our laboratory and reported in the literature.

The adhesive evaluation, primarily based on lap shear strength (LSS) tests, involved preparing adhesive tapes, conducting bonding studies and exposing lap shear specimens to 204°C air for up to 1000 hrs and to a 72-hour water boil. LSS tests at RT, 177°C and 204°C were performed before (controls) and after these exposures. The type of adhesive failure as well as the Tg was determined for the fractured specimens.

The results indicate that LARC-TPI provides the highest LSSs, 33 MPa at RT, 30 MPa at 177°C, and 26 MPa at 204°C. LARC-F-SO_2, LARC-TPI and LARC-STPI all retain their strengths after thermal exposure for 1000 hrs and $PISO_2$ retains greater than 80% of its control strengths.

Most of the four adhesive systems showed reduced strengths for all test temperatures although they still retained a high percentage of their original strength (>60%) except for one case.

The predominant failure mode was cohesive with no significant change in the Tgs.

Although the LARC-F-SO_2 could not be prepared in diglyme alone as the solvent, the properties of the resulting adhesive were notable. The darkening of the adhesive during bonding was typical of systems which utilize amide solvents.

KEY WORDS Polyimide adhesives; flexible aromatic polyimides; thermoplastic; copolyimide; high temperature adhesives.

INTRODUCTION

During the past decade, considerable research at NASA Langley Research Center has been directed towards the synthesis of flexible aromatic polyimides.[1–7] Two notable polyimides that are now commercially available resulted from this work. They are LARC-TPI and polyimidesulfone ($PISO_2$).[5,7] Both of these

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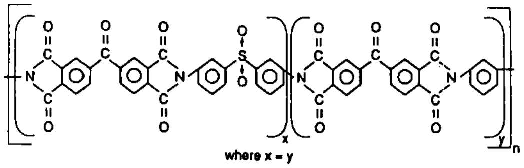
polyimides contain bridged aromatic diamines with *meta* catenation as described by Bell *et al.*[1] Recently Progar and St. Clair reported on two flexible backbone copolyimides that were synthesized in an effort to develop a relatively-inexpensive, high-temperature adhesive.[6,8] These polymers contained the diamines 4,4'-diaminodiphenylether (commonly referred to as oxydianiline or ODA) and *meta* phenlenediamine (MPD). The combined use of these two compounds afforded adhesives with attractive properties. Research of a similar nature continues in our laboratory with the development of a new copolyimide with structural similarities to PISO$_2$. This material, designated as LARC-F-SO$_2$, is shown below.

This paper compares the novel LARC-F-SO$_2$ to its progenitors, PISO$_2$, LARC-STPI flexible copolyimide and LARC-TPI polymer.



where x = y

LARC-F-SO$_2$

EXPERIMENTAL

Materials and Polymer Synthesis

The experimental procedures for the synthesis of the polyimides, LARC-F-SO$_2$ and endcapped PISO$_2$, are reported in this paper. Synthesis of LARC-TPI,[5] LARC-STPI[6] and PISO$_2$[7] have been reported previously. The procedure for the synthesis of LARC-F-SO$_2$ involved the use of reagent grade monomers and solvents that are commercially available. The list of chemicals, abbreviations, their source and m.p. or b.p. follows: benzophenonetetracarboxylic acid dianhydride (BTDA), Allco Company, Pittsburg, KS, U.S.A., m.p. 224–226°C; *meta*-phenylenediamine (MPD), purissimus grade from Fluka Chemical Company, Hauppauge, NY, U.S.A., m.p. 61–63°C; 3,3'-diaminodiphenylsulfone (3,3'-DDSO$_2$), FIC Corporation, San Francisco, CA, U.S.A., m.p. 165–167°C; bis-2-methoxyethylether (diglyme), Fluka Chemical Company, b.p. 160–162°C; N,N-dimethylacetamide (DMAc), Fluka Chemical Company, b.p. 165–167°C.

The preparation of the polymers was carried out at room temperature in a 1000 ml cylindrical flask with a removable, four-neck 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 (16.273 g, 0.0505 M) was slurried in 135 g of diglyme at ambient temperature (~20°C). Next the 3,3'-DDSO$_2$ (6.20 g, 0.0250 M) was added and the mixture was allowed to stir for approximately one hour. At this point the materials were all in solution as the 3,3'-DDSO$_2$ and the BTDA had reacted as evidenced by a slight increase in temperature. The MPD (2.704 g, 0.0250 M) was added to the reaction vessel, the polymerization reaction continued rapidly and a precipitation of the polyamide-acid copolymer occurred within 15 min. In order to redissolve the polymer, 55 g of DMAc was added and stirring continued overnight. The polymer redissolved and was used as a 11.6 wt% solid solution to prepare the adhesive scrim cloth and for priming. The inherent viscosity (η_{inh}) of the polymer, as determined at 0.5 wt% solids in DMAc at 35°c, was 0.724 dl/g.

The monomers used in the preparation of endcapped $PISO_2$ were BTDA, 3,3′-$DDSO_2$, and phthalic anhydride (PA) obtained from Eastman Kodak Company, Rochester, NY, U.S.A., m.p. 131°C w/3°C range. The polymer was prepared as a 20 wt% solids solution in a mixed solvent of diglyme and tetrahydrofuran (THF). The THF was obtained from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin, U.S.A., Gold label (99.9%), b.p. 67°C.

The BTDA (193.2 g, 0.6 M) and 3,3′-$DDSO_2$ (148.8 g, 0.6 M) were dissolved at ambient conditions in the diglyme/THF (1410 g/90 g) mixed solvent and stirred for 16 hours. Most of the solids, approximately 90 percent, dissolved initially with the rest of the BTDA dissolving over the remaining reaction time. The solution was amber-orange in color. The PA (1.2 g, 0.008 M) was dissolved in 8 ml of DMAc and added to the polyamic-acid solution. Some precipitation occurred initially but cleared up within one minute. The inherent viscosity was determined to be 0.589 dl/g.

Characterization

Lap shear strength (LSS) was obtained according to ASTM D-1002 using a Model TT Instron Universal Testing Machine. The LSSs reported represent an average of four lap shear specimens per test condition except as noted in the table. The range of LSSs is indicated by dashed lines in the bar graph figures. Elevated temperature tests were conducted in a clam-shell, quartz-lamp oven with temperatures controlled to within ±3°C for all tests. Specimens were held 10 min at temperature prior to testing except for the water-boil test specimens for which the tests were conducted as soon as the test temperature was reached (approximately 1–2 min).

Bondline thickness 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 0.025 cm for $PISO_2$, 0.015 cm for LARC-F-SO_2, 0.009 cm for LARC-TPI, and 0.017 cm for LARC-STPI.

Glass transition temperatures (Tg) of the adhesive from the fractured lap shear specimens were determined by thermomechanical analysis (TMA) on a DuPont 943 Analyzer.† TMAs were run on the fractured lap shear specimens in static air at a heating rate of 5°C/min using a hemispherical probe with a 15 g load. Thermomechanical spectra of the polymers were obtained on a torsional braid

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

analysis (TBA) system interfaced with an IBM PC. Individual glass braids were coated with 11.6 wt% solids LARC-F-SO_2 polyamic acid solution and a 5 wt% solids $PISO_2$ solution and precured in air for one hour at each of three temperatures: 100°C, 200°C and 300°C. Tests were conducted by heating in a nitrogen atmosphere to 400°C at 3°C/min. Tg was determined as the extrapolated maximum peak height of the damping *versus* temperature curve.

Inherent vicosity 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% solids in N,N-dimethylacetamide (DMAc) was made and filtered. The average of three runs of the solution was reported.

Adhesive Tape Preparation

Adhesive tape for the $PISO_2$ was prepared by brush-coating a primer solution of polyamic acid, diluted to approximately 5 wt% solids in diglyme/THF, 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 at ambient temperature and heated for 1 hr at each of three temperatures: 100°C, 150°C and 175°C. Subsequently, each application of a 20 wt% solids solution, η_{inh} 0.589 dl/g, was brush-coated onto the cloth and exposed to the following schedule until a thickness of 0.025–0.027 cm was obtained:

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

Adhesive tape for LARC-F-SO_2 was prepared in a similar manner in an attempt to standardize the tape preparations. An approximately 5 wt% solids solution of polyamic acid in diglyme/DMAc was used to prime coat the oven-dried glass cloth. The prime-coated cloth was air-dried for 1 hr at ambient temperature and heated for 1 hr at each of three temperatures: 100°C, 150°C and 175°C. Subsequently, after each application of an 11.6 wt% solids solution onto the cloth, the tape was exposed to the following schedule until a thickness of 0.018–0.023 cm was obtained:

(1) RT, held 1 hr
(2) RT→100°C, held 1 hr
(3) 100°C→150°C, held 2 hrs
(4) 150°C→175°C, held 3 hrs

The involved procedure to prepare the tapes was required 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.

Adhesive Bonding

The prepared adhesive tapes were used to bond titanium alloy adherends (Ti-6Al-4V, per Mil-T-9046E, Type III Comp. C) with a nominal thickness of 0.13 cm. 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 hours of the surface treatment by applying a thin coat of the polyamic acid solution of the respective adhesive 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-10002) and applying 2.07 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.

Several bonding cycles for the LARC-F-SO_2 adhesives were investigated during this study to determine a bonding process which produced good strengths. The cycle selected was as follows:

(1) 2.07 MPa pressure, heating rate ≈8.2°C/min, RT→343°C

(2) Held 1 hr at 343°C

(3) Cool under pressure to ≈150°C and remove from bonding press

Past experience with these types of thermoplastic polyimides had shown a beneficial affect when the adhesive tape was heated to higher temperatures for a period of time.[9] The adhesive tape heat treatment selected was that which gave the best lap shear strengths and involved an additional heat treatment of 1 hr each at 200°C, 225°C and 250°C. The color of the tape changed from straw-yellow to amber. The heat-treated LARC-F-SO_2 adhesive tape which was stiff and "boardy" was used to prepare lap shear specimens for thermal exposure and water-boil tests. LSS tests were conducted at RT, 177°C and 204°C.

A similar procedure was used to determine the best heat treatment for the $PISO_2$ adhesive tape. The same bonding cycle that was used for LARC-F-SO_2 was used for $PISO_2$. The heat treatment chosen for the $PISO_2$ included additional heating for 1 hr at each temperature from 200°C to 275°C in 25°C increments. Some foaming of the tape resulted due to the heat treatment and the adhesive was stiff and "boardy" with no tack or drape. Specimens were prepared with this tape for thermal exposure and water boil.

Thermal exposures at 204°C for 500 hrs and 1000 hrs were performed in a forced-air oven controlled to within ±2°C. Lap shear tests were conducted at RT, 177°C and 204°C before (controls) and after thermal exposure.

In order to determine the effects of humidity (moisture) on an adhesive, a 72-hr water boil was conducted in laboratory glassware containing distilled boiling

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

water. The bonded area of the lap shear specimens was immersed during a 72-hr period. LSSs were subsequently determined at RT, 177°C and 204°C.

These two adhesive systems, LARC-F-SO_2 and $PSIO_2$ were compared with results previously reported for LARC-TPI and LARC-STPI.[10]

RESULTS AND DISCUSSION

Resin Chemistry

The proposed general reaction scheme for the formation of the polyimide polymers to be evaluated is shown in Figure 1. A discussion of the reactions to form LARC-F-SO_2 and $PISO_2$, in this case a PA-endcapped version, is given since the reaction scheme of LARC-TPI and the random copolymer, LARC-STPI, is reported in the literature.[5,6,10]

The structure of LARC-F-SO_2 formed from the monomer BTDA, 3,3′-$DDSO_2$ and MPD is shown in Figure 2. The copolymer contains bridged, aromatic diamines with *meta* catenation. *Meta*-oriented diamines were shown to have improved processability and improved adhesive strength when compared to *para*-oriented diamines.[7] The *meta* linkages, as in both amine-derived moieties,

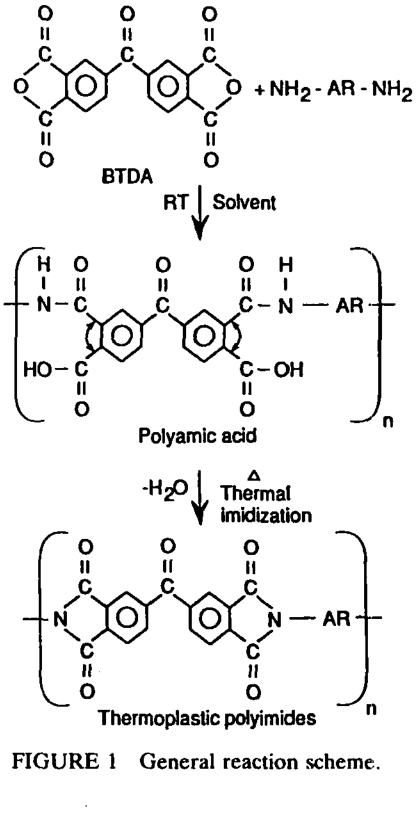

FIGURE 1 General reaction scheme.

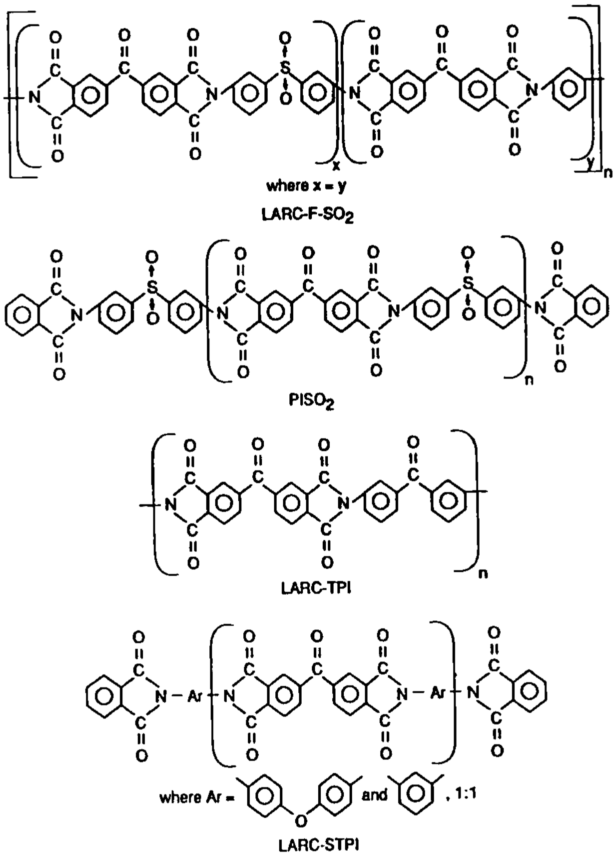

FIGURE 2 Thermoplastic polyimide structures.

should introduce thermoplasticity because of the inherent flexibility of these units of the polymer chain. The use of mixed solvents, as in the preparation of LARC-F-SO_2, is not preferred. Data from our laboratory have shown that the use of diglyme is preferred over amide solvents such as DMAc.[4] However, in the present study the use of a mixed solvent system was necessitated by the insolubility of the polyamic acid of LARC-F-SO_2 in diglyme. We feel that the ultimate adhesive properties of this copolymer are lower than would be expected if only diglyme were the solvent. Some of the darkening of the adhesive during bonding might be attributable to the presence of DMAc since this phenomenon was noted in adhesives reported in Reference 4.

The structure of $PISO_2$ formed from BTDA and 3,3'-$DDSO_2$ with PA end caps is shown in Figure 2. The formation of $PISO_2$ without endcapping had been discussed in References 7 and 9. The purpose of endcapping this polymer was to control the molecular weight of the polymer chains allowing greater flow during processing and to prevent chain extension during cure which creates volatiles and foaming. Again, the *meta*-oriented diamine, 3,3′-DDSO$_2$, allows flexibility in the polymer chain and is partially responsible for some of the thermoplasticity of the polymer. Also shown in Figure 2 are the structures of LARC-TPI and LARC-STPI.

LSS and Durability Comparison

Test results from this study for LARC-F-SO$_2$ and PISO$_2$ are compared with data reported for PISO$_2$ in Table I and Figure 3. Figure 3 shows the LSSs for

TABLE I
Comparative LSS data for PISO$_2$ and LARC-F-SO$_2$

Adhesive	Bonding conditions	Test temperature, °C(°F)	Exposure time at 204°C, hr	LSS, MPa(psi)
LARC-F-SO$_2$ (present study)	8°C/min, 2.07 MPa (300 psi), RT to 343°C (650°F), hold 1 hr	RT (RT)	0	17.9 (2600)
		177 (350)	0	18.8 (2720)
		204 (400)	0	19.6 (2840)
		RT (RT)	500	17.0 (2460)
		177 (350)	500	19.3 (2800)
		204 (400)	500	19.8 (2870)
		RT (RT)	1000	18.0 (2620)
		177 (350)	1000	20.1 (2920)
		204 (400)	1000	20.4 (2950)
PISO$_2$ (present study)	8°C/min, 2.07 MPa (300 psi), RT to 343°C (650°F), hold 1 hr	RT (RT)	0	27.5 (4000)
		177 (350)	0	27.5 (4000)
		204 (400)	0	24.0 (3490)
		232 (450)	0	23.1 (3340)
		RT (RT)	500	22.8 (3310)
		177 (350)	500	20.2 (2930)
		204 (400)	500	21.7 (3140)
		232 (450)	500	20.2 (2940)
		RT (RT)	1000	24.8(3590)
		177 (350)	1000	22.0 (3190)
		204 (400)	1000	20.8 (3020)
		232 (450)	1000	19.8 (2870)
PSIO$_2$ Ref. 7	7°C/min, RT to 325°C (617°F), apply 1.38 MPa (200 psi) at 280°C (536°F), hold 325°C for 15 min	RT (RT)	0	32.0 (4650)
		177 (350)	0	22.1 (3210)
		204 (400)	0	20.1 (2920)
		232 (450)	0	18.1 (2620)
		RT (RT)	5000	20.5 (2980)
		204 (400)	2500	21.9 (3180)
		204 (400)	5000	20.5 (2980)
PISO$_2$ Ref. 9	Vacuum, contact pressure, 4°C/min, RT to 343°C (650°F), apply 0.34 MPa (50 psi) at 250°C (482°F), after 5 min at 343°F, apply 1.38 (200 psi), hold 343°C for 5 min	RT (RT)	0	25.2 (3650)
		232 (450)	0	19.8 (2870)

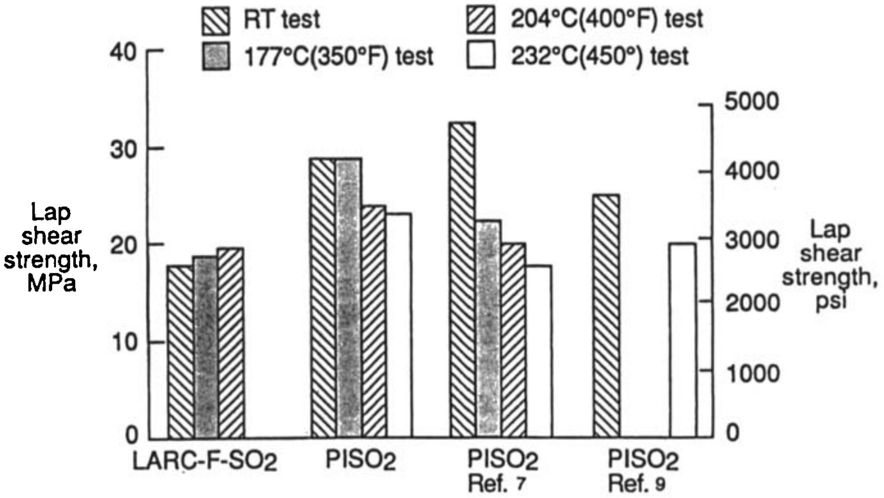

FIGURE 3 Comparative LSS data for LARC-F-SO_2 and $PISO_2$.

non-exposed specimens for tests conducted at RT, 177°C, 204°C and 232°C where Table I includes processing information and thermal aging data. LARC-F-SO_2 and $PISO_2$ each have BTDA and the diamine, 3,3′-$DDSO_2$, in common. The strength test results of the present study indicate the $PISO_2$ adhesive system provides significantly higher strengths at RT, 177°C and 204°C than the LARC-F-SO_2 adhesive system: RT, 27.5 MPa compared with 17.9 MPa; 177°C, 27.5 MPa compared with 18.8 MPa; and 204°C, 20.4 MPa compared with 19.6 MPa. $PISO_2$ also had a LSS of 23.1 MPa at 232°C. Slight differences in the bonding process, the adhesive resin, the preparation of the adhesive tape, and surface treatment may account for the small differences in the strength values for $PISO_2$ reported in References 7 and 9, although they are still comparable with those of the present study. Note the good strengths retained for those thermally aged up to 5000 hrs at 204°C in Reference 7, *i.e.* 20.5 MPa for RT and 204°C tests.

Figure 4 presents the LSS results of thermal exposure in air at 204°C for LARC-F-SO_2 and $PISO_2$ (present study). Results are expressed in graphical form to provide a quick pictorial summary of the results. No change in LSS at RT, 177°C and 204°C was observed for LARC-F-SO_2 thermally aged for up to 1000 hrs. A slight increase in strength with test temperature was indicated although the range of strengths tend to overlap in most cases. Failures were primarily cohesive except for the RT tests for the 500 hrs and 1000 hrs exposure which were primarily adhesive failure. The darkening of the adhesive in the fractured area (almost black) is typical of systems which use the amide solvents. A significant increase in Tg from 255°C to 273°C was determined after the 1000 hr exposure. This increase is not unusual for polyimides and has been noticed in past studies. Tg, measured by the TBA technique, of LARC-F-SO_2 pretreated for 1 hr

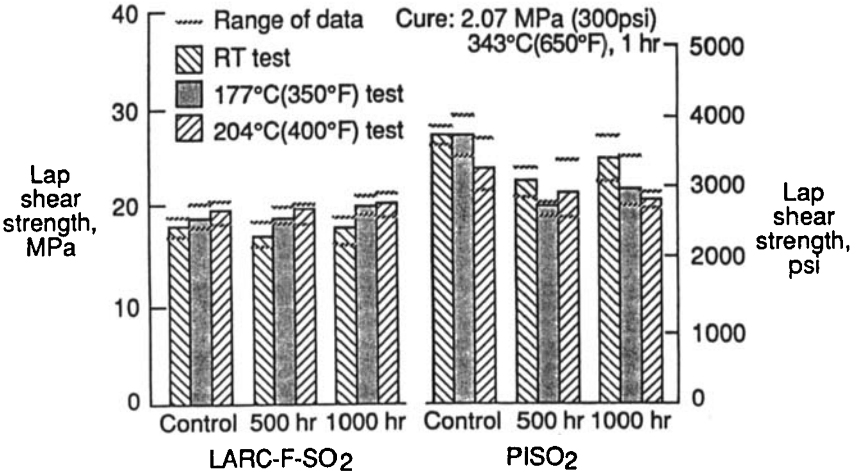

FIGURE 4 Effects of thermal exposure in air at 204°C on LSS for LARC-F-SO_2 and $PISO_2$ bonded Ti-6Al-4V.

each at 100°C, 200°C and 300°C was 282°C compared with the Tg determined by TMA (penetration technique) in the fractured area, 255°C.

A slight decrease in LSS was found for $PISO_2$ specimens exposed for 500 hrs and 1000 hrs at 204°C. Those exposed for 1000 hrs were 90% of the control's value at RT, 80% at 177°C, 87% at 204°C and 86% at 232°C. Joint failures were primarily cohesive for all tests except for the RT control test which was cohesive/adhesive. The color of the adhesive in the failed bond area was almost black. A slight general increase in Tg with increasing time of thermal exposure was observed, increasing from an average 256°C for the controls to 268°C for those exposed for 1000 hrs. As with LARC-F-SO_2, this phenomenon is typical of polyimides. The Tg determined by TBA for $PISO_2$ pretreated for 1 hr each at 100°C, 200°C and 300°C was 272°C.

LSS results of thermal exposure in air at 204°C for LARC-TPI and LARC-STPI are given in Figure 5. Data are shown for LSS tests conducted at RT, 177°C and 204°C after thermal exposures of 500 hrs and 1000 hrs.

LARC-TPI provides excellent strength for all three test temperatures with no change in strength due to the thermal exposure. Previous work reported has shown the polymer to have excellent thermooxidative resistance.[5] There is a general decrease in strength with increasing test temperature; however, the decrease is small: less than 24% for the worst case, *i.e.* 33.0 MPa to 25.2 MPa. All failure were 100% cohesive. Tgs ranged from 225°C to 246°C. The Tg of a film treated for 1 hr each at 100°C, 200°C and 300°C, determined by DSC, was 260°C.[10]

The copolymer, LARC-STPI, which has the *meta*-linked phenylenediamine structure in common with LARC-F-SO_2, showed a slight decrease in strength with thermal exposure. The strengths of those exposed for 500 hrs and 1000 hrs,

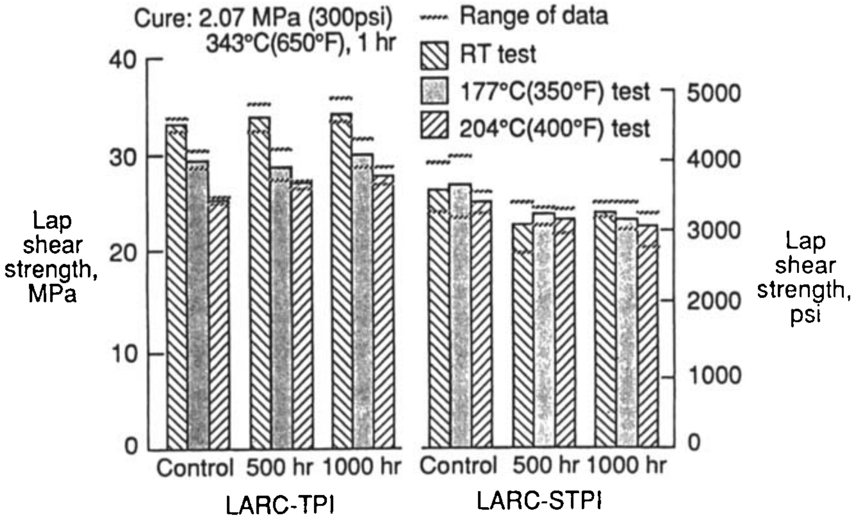

FIGURE 5 Effects of thermal exposure in air at 204°C on LSS for LARC-TPI and LARC-STPI bonded Ti-6Al-4V.

approximately 23 MPa, are the same, but slightly lower than the control's strengths, approximately 26 MPa. The primary failure mode was cohesive except for the 500 and 1000 hr exposure specimens tested at RT which were cohesive/adhesive and adhesive, respectively. The Tgs determined for LARC-STPI fractured specimens were between 260°C and 267°C. A Tg of 283°C, determined by TBA, was reported earlier for LARC-STPI pretreated for 1 hr each at 100°C, 200°C and 300°C.

An overall comparison of the four adhesive systems shows LARC-TPI to provide the highest LSSs, approximately 33 MPa at RT, 30 MPa at 177°C and 26 MPa at 204°C. LARC-F-SO_2, LARC-TPI and LARC-STPI all retain their strengths after thermal exposure up to 1000 hrs at 204°C and $PISO_2$ retains greater than 80% of the control's strength at each test temperature after exposure. LARC-TPI had the lowest range of Tgs, 228°C to 246°C, of the four adhesives. All the others ranged from 251°C to 273°C. The predominant failure mode was cohesive.

72-Hour Water Boil

The resistance of the four adhesive systems to water (humidity) was determined by immersing lap shear specimens in boiling distilled water for a 72-hr period and subsequently testing their LSS at RT, 177°C and 204°C. Results of the present study for LARC-F-SO_2 and $PISO_2$ are given along with results reported for LARC-TPI and LARC-STPI[10] in Figure 6.

LARC-F-SO_2, which has the lowest control strengths of the four adhesive systems for all three test temperatures, shows a slight increase in strengths at RT and 177°C (112% and 102% of the controls' values, respectively). However, at

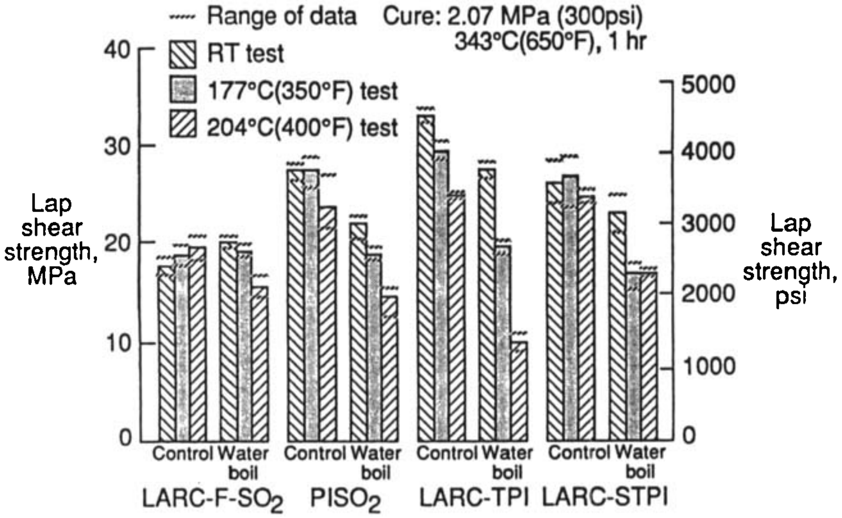

FIGURE 6 Effects of a 72-hour water boil on LSS for bonded Ti-6Al-4V.

204°C the strength was 80% of the control's strength. This percentage retention was excellent when compared with other polyimide systems including those reported here. The primary failure mode after water boil was cohesive whereas the control's failures were a combination of cohesive/adhesive at RT and 177°C. There was essentially no change in Tg due to the water boil.

A decrease in LSS with increasing test temperature was determined for the $PISO_2$ system. The LSS values after water boil were 79% of the control's RT strength, 68% for the 177°C test, and 61% for the 204°C test. The control strengths for $PISO_2$ were significantly higher than those for LARC-F-SO_2; therefore, even though the percent of strength retention was lower for $PISO_2$, the absolute LSS values after water boil were still about the same as those for LARC-F-SO_2. Specimens examined after the water boil tests were found to be primarily cohesive failures as were those of the controls. No significant change in Tg was noted after the water boil tests.

LARC-TPI, of the four adhesive systems, initially provided the highest control LSSs at RT and 177°C and about the same strength at 204°C as $PISO_2$ and LARC-STPI (24 to 25 MPa). After water boil, LARC-TPI retained 84% of the control's RT strength, 67% of the control's 177°C strength, and only 40% of the control's 204°C strength, the poorest percent retention and the lowest strength value, 10.1 MPa, of the four adhesives tested. Failures were all primarily cohesive before and after water boil. No significant changes in Tg were found.

Water boil also produced reduced strengths for LARC-STPI. The LSSs of LARC-STPI specimens tested 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. LARC-STPI had the highest strength at 204°C of the four adhesive systems, an average of 17.0 MPa; slightly higher than LARC-F-SO_2, 15.7 MPa and $PISO_2$, 14.7 MPa and significantly higher than LARC-TPI, 10.1 MPa. The failure mode for the tested LARC-STPI was primarily cohesive. No change in Tg was determined after water boil.

SUMMARY

Research continues at Langley Research Center on synthesis and development of new, inexpensive, flexible, aromatic polyimides as adhesives which contain bridged aromatic diamines with *meta* catenation. The present work resulted in a material identified as LARC-F-SO_2 with similarities to polyimidesulfone, $PISO_2$, and other flexible backbone polyimides recently reported by Progar and St. Clair. Also prepared in our laboratory and evaluated was a phthalic anhydride endcapped version of $PISO_2$. These two polymers were synthesized and evaluated as adhesives and compared with LARC-TPI and LARC-STPI, polyimides researched in our laboratory and reported in the literature.

The adhesive evaluation, primarily based on lap shear strength (LSS) tests, involved preparing adhesive tapes, conducting bonding studies, and exposing lap shear specimens to a thermal exposure in air at 204°C for up to 1000 hrs and a 72-hr water boil exposure. LSS tests at RT, 177°C and 204°C were performed before (controls) and after these exposures. The type of adhesive failure as well as the glass transition temperature, Tg, was determined for the fractured specimens.

When comparing all four adhesive systems, the results indicate that LARC-TPI provides the highest LSSs, 33 MPa at RT, 30 MPa at 177°C and 26 MPa at 204°C. LARC-F-SO_2, LARC-TPI and LARC-STPI all retain their strengths after thermal exposure at 204°C in air for up to 1000 hrs, the maximum time considered in this study. $PISO_2$ retained greater than 80% of its control strengths. The predominant failure mode was cohesive.

After a 72-hr water boil exposure, most of the four adhesive systems showed reduced strengths for all elevated test temperatures. All adhesive systems exhibited a high percentage of strength retention for the three test temperatures (>60%) except for LARC-TPI tested at 204°C which had a 40% retention. LARC-STPI retained the highest strength at 204°C, approximately 17.0 MPa; slightly higher than LARC-F-SO_2, 15.7 MPa and $PISO_2$, 14.7 MPa; and significantly higher than LARC-TPI, 10.1 MPa. Failure modes were primarily cohesive for all adhesive systems. No significant changes in Tgs were found.

Although the LARC-F-SO_2 could not be prepared in diglyme alone as the solvent, the properties of the resulting adhesive were notable. The darkening of the adhesive during bonding was typical of systems which utilize amide solvents.

References

1. V. L. Bell, B. L. Stump and H. Gager, *J. Polym. Sci.: Polym. Chem. Ed.* **14,** 2275 (1976).
2. V. L. Bell, "Process for Preparing Thermoplastic Aromatic Polyimides," U.S. Patent 4,094,862 (1968).

3. D. J. Progar, V. L. Bell and T. L. St. Clair, "Polyimide Adhesives," U.S. Patent 4,065,345 (Dec. 1977).
4. T. L. St. Clair and D. J. Progar, in *Adhesive Sci. and Tech.* **9A,** (Plenum Press, New York, 1975), p. 187.
5. A. K. St. Clair and T. L. St. Clair, "A Multipurpose Thermoplastic Polyimide", *26th Nat. SAMPE Symp.* **26,** 165 (1981).
6. D. J. Progar and T. L. St. Clair, *J. Adhesion* **21,** 35 (1987).
7. T. L. St. Clair and D. A. Yamaki, "A Thermoplastic Polyimidesulfone," *NASA TM-84574* (1984).
8. T. L. St. Clair and D. J. Progar, "Adhesive Evaluation of New Polyimides," *Proc. Fifth International Joint Military/Goverment-Industry Symp. on Structural Adhesive Bonding* (Nov. 1987), p. 37.
9. D. J. Progar, *Int. J. of Adhesion and Adhesives* **4,** 79 (1984).
10. D. J. Progar and T. L. St. Clair, "A Thermoplastic Copolyimide," *2nd Int. Conf. on Polyimides,* in *SPE Proceedings, Recent Advances in Polyimide Sci. and Tech.* (1987), p. 139 or *NASA TM-86447* (July 1985).