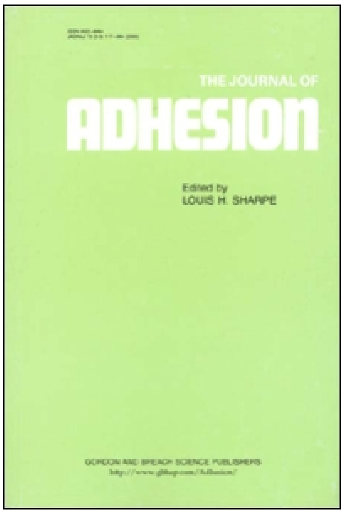

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Adhesive Evaluation for New Forms of LARC™-TPI*

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LARC™-TPI is a linear aromatic polyimide that was developed at NASA Langley Research Center in the 1970's and subsequently licensed to Mitsui Toatsu Chemicals, Inc., (MTC) in Japan. This company has made it easier to process for use in application as a structural adhesive or as a composite matrix resin. The present forms that exist are (1) high melt viscosity or Low Flow Grade (LFG); (2) medium melt viscosity or Medium Flow Grade (MFG); and (3) low melt viscosity or High Flow Grade (HFG). As expected, the low melt viscosity material is the easiest to process but has poor toughness; the high melt viscosity material is very tough but is more difficult to process. Because of these two extreme situations we have worked closely with MTC to develop an optimized system. This work has resulted in the medium melt viscosity material as well as two other modified or blended medium-flow variations.

These novel forms of LARC™-TPI have resulted in adhesives that can be melt processed at pressures as low as 0.01 MPa (15 psi) at temperatures between 343–371°C (650–700°F). Evaluation of adhesive performance has been accomplished using lap shear specimens and evaluating flow, wet out and shear strength. Initial strengths for these optimized materials range from 20.7–41.4 MPa (3000–6000 psi) at room temperature and 13.8–20.7 MPa (2000–3000 psi) at elevated test temperatures.

KEY WORDS polyimide adhesives; linear aromatic polyimides; high temperature adhesives; hot-melt adhesive; LARC™-TPI polyimide; processing; flow properties.

INTRODUCTION

There is a growing need for high temperature adhesives in both the aerospace and electronic industries. The class of material that has exhibited the best overall combination of properties for both industries has been the linear aromatic polyimide.

In particular the polyketoimide, LARC™-TPI, has become commercially available in several forms over the past decade. This material is sold as a polyamide-acid in diglyme for bonding polyimide film to copper.[1-5] It is also marketed as a molding powder which can be used as a hot-melt adhesive. During this same period of time, several versions of LARC™-TPI have been made commercially available and this has caused some confusion among users. The technical details presented in this paper should help to clarify some of this confusion. Several forms of LARC™-TPI

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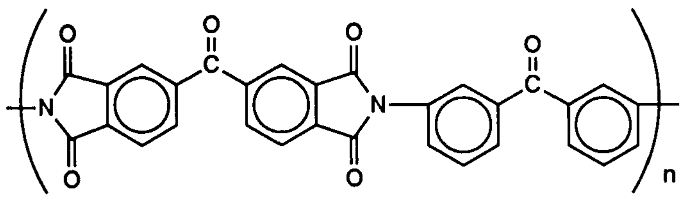
have been investigated for use as melt processable, high temperature, high performance adhesives and are discussed in this paper.



LARC™-TPI

EXPERIMENTAL

Materials

All LARC™-TPI materials were supplied by Mitsui Toatsu Chemicals, Incorporated (MTC) of Japan either directly or through their American supplier, MTC America (Tables I and II). The High Flow Grade (HFG) LARC™-TPI 1500 series (Lot no. 2941) was obtained as a fully-imidized fine powder form with a glass transition temperature (T_g) of ~236°C (457°F).[6] The inherent viscosity (η_{inh}) of the material was 0.37–0.38 dl/g. The weight average molecular weight (M_w) determined by two methods, Low Angle Laser Light Scattering and Gel Permeation Chromatog-

TABLE I
History of LARC™-TPI supplied by Mitsui Toatsu Chemicals, Inc.

First Generation—Lacked Adequate Molecular Weight Control
1000—High Molecular Weight
2000—Limited Molecular Weight Control
Second Generation—Controlled Molecular Weight, LARC™-TPI 1500 series
HFG—High Flow Grade, Low Molecular Weight
MFG—Medium Flow Grade, Intermediate Molecular Weight
LFG—Low Flow Grade, High Molecular Weight

TABLE II
Physical properties of LARC™-TPI 1500 HFG, MFG and LFG*

	HFG	MFG	LFG
Inherent Viscosity of Polyimide, η_{inh}, dl/g (0.5% p-Cl-phenol/phenol 95/5 wt%)	0.37–0.38	0.45–0.46	0.61–0.62
Glass Transition Temperature, °C (by DSC)	~236	~240	~245
M_w (by LALLS)	~21,700	~26,200	—
M_w (by GPC)**	~66,400	~77,100	—
Relative Flow at 380°C	1.0	0.2	0.06

*Data supplied by Mitsui Toatsu Chemicals, Inc.
**Data relative to polystyrene standards [runs made at 80°C in p-chlorophenol/toluene (1:1)].

raphy, were ~21,700 and ~66,400, respectively. These data were supplied by MTC.

The Medium Flow Grade (MFG) LARC™-TPI 1500 series was supplied as an imidized film 0.18–0.22 mm (7–9 mil) thick and had an amber color. The T_g of the material was ~240°C (464°F). η_{inh} was 0.45–0.46 dl/g, M_n was ~26,200 and M_w was ~77,100. This information was supplied by MTC.

As shown in Figure 1, the relative flow at 380°C (716°F) gives the order of magnitude for flow between the two materials.

Although only limited data are reported for the Low Flow Grade (LFG), information on some of its properties is also given in Table II.

A 1:1 blend of imidized HFG and MFG, designated as HFG/MFG 50/50 (Lot no. 57-701 PL), was supplied in pellet form. It had a melt viscosity similar to HFG and provided good flow.

High flow grade LARC™-TPI with a 6% additive flow enhancer, (HFG/B6), Lot no. 910617, <1% volatiles, was obtained as a prepared adhesive tape 0.25 mm (10 mil) thick containing two plies of glass fabric (W_f 28.3 wt %).

Another form of material identified as MFG/B6, which had a 6% additive of a low molecular weight imide, was supplied in pellets (Lot no. 57-702 PL) and also provided a flow similar to HFG. The η_{inh} of MFG/B6 was 0.426 dl/g.

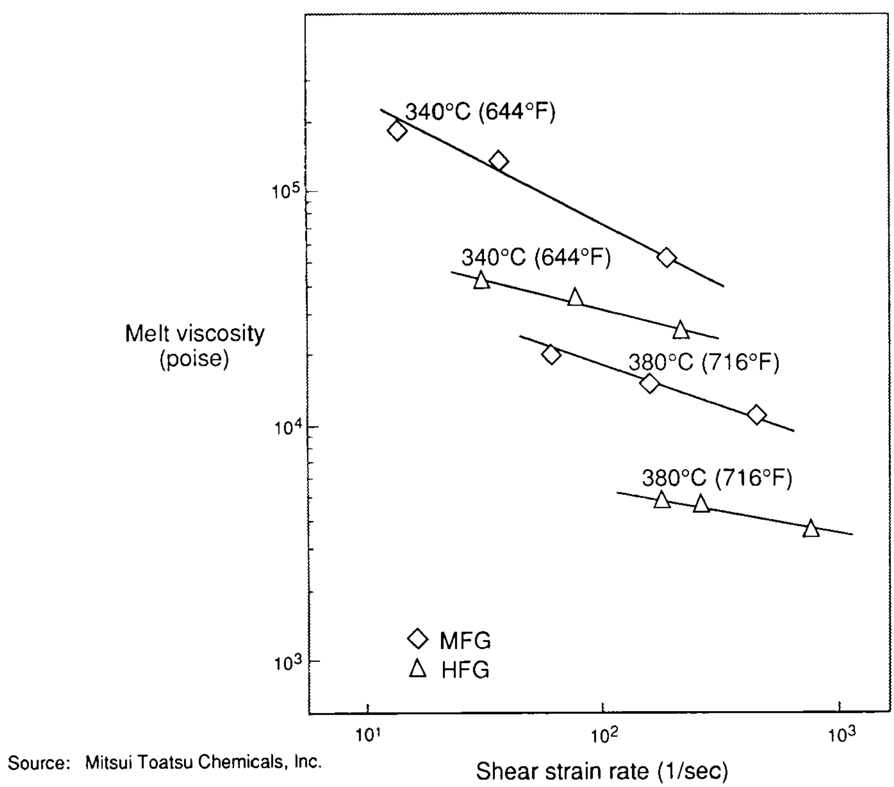


FIGURE 1 Relationship between shear rate and the melt viscosity at 340°C and 380°C for LARC™-TPI 1500 HFG and MFG (Data supplied by Mitsui Toatsu Chemicals, Inc.).

Characterization

Lap shear strength (LSS) was obtained according to ASTM D-1002 using a United Calibration Corporation Model No. SFM-10 testing machine. The LSSs reported generally represent an average of four lap shear specimens per test condition. The range of LSSs is indicated by dashed lines in the bar graph figures. Elevated temperature tests were conducted in a Parabolic Clamshell Radiant (quartz lamps) Heating Chamber, Model 4068-12-10, manufactured by R•I Controls. Chamber temperatures were 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 which were tested 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 each material is given in Table III.

The physical properties given in Table II were supplied by MTC and, therefore, details of the measurements, other than those given in the table, were not available.* The abbreviated designations given in Table II are DSC, Differential Scanning Calorimetry; LALLS, Low Angle Laser Light Scattering; and GPC, Gel Permeation Chromatography.

Adhesive Tape Preparation

Due to the physical form of the materials received from MTC, a couple of techniques were used to prepare adhesive tapes for those not in an "as-received" usable form. Information on the tape preparation is given in Table III and discussed in the following paragraphs.

HFG

HFG was supplied as an imidized powder which was melted on to 112, A-1100 (γ-aminopropyltriethoxysilane)-treated, E-glass cloth. One-half of the powder charge (~5 g) was evenly spread on Upilex (polyimide) film on the bottom of a 75 mm × 175 mm (3 in. × 7 in.) steel matched-die mold. The glass cloth was placed on top of the powder and the other half of the powder charge was spread evenly over the cloth. A film of Upilex was placed on top of the powder and the top (male part) of the mold was placed on the Upilex. This was placed in a hydraulic press, contact pressure was applied and the temperature was increased to ~300°C (572°F), at which time ~3.3 MPa (475 psi) pressure was applied. The 300°C (572°F) temperature and pressure were maintained for ~15 min after which the pressure was released and the tape removed from the mold. The Upilex films were stripped off, leaving the adhesive tape. The average thickness of the tape was 0.25 mm (10 mils).

*Private communication with Mitsui Toatsu Chemicals, Incorporated (Mr. Y. Sugita).

TABLE III
Information on the LARC™-TPI 1500 series adhesives

	Tape preparation	Bonding conditions[a]
HFG	Powder on primed 112, A-1100 E-glass cloth molded at 300°C (572°F) using ~3.3 MPa (~475 psi) pressure for 15 min	0.10 MPa (15 psi) pressure, RT→343°C (650°F), held 1 hr
MFG	112, A-1100 E-glass cloth (not primed) sandwiched between 0.18–0.22 mm (7–9 mil) films	0.34 MPa (50 psi) pressure, RT→343°C (650°F), held 1 hr
HFG/MFG 50/50	Pellets molded on primed 112, A-1100 E-glass cloth at 305°C (580°F)-313°C (595°F) using 3.3 MPa (475 psi) for ~5 min	0.10 MPa (15 psi) pressure, RT→343°C (650°F), held 1 hr
HFG/B6	Tape prepared by Mitsui Toatsu Chemicals, Inc., 0.25 mm (~10 mil) thick, contains 2 plies of glass fabric (W_f 28.3 wt%)	Either 0.10 MPa (15 psi) or 1.38 MPa (200 psi) pressure, RT→either 350°C (662°F) or 371°C (700°F), held 1 hr
MFG/B6	Pellets molded on (primed and not primed) 112, A-1100 E-glass cloth at 305°C (580°F)-313°C (595°F) using 3.3 MPa (475 psi) for ~5 min	0.10 MPa (15 psi) pressure, RT→either 343°C (650°F) or 371°C (700°F), held 1 hr

[a]Heating rate—8°C/min (14°F/min).

TABLE III (concluded)
Information on the LARC™-TPI 1500 series adhesives

	Comments	W/WO voids	Color after tested	Avg. bondline, mm (mils)
HFG	Has highest degree of melt flow, possibly too much flow (voids between cloth's weave)	W	Medium Amber	0.11 (4.3)
MFG	Higher degree of toughness, flexible films, good flow	WO	Light Amber	0.12 (4.8)
HFG/MFG 50/50	Melt viscosity approximates HFG, good flow	W	Dark Amber	0.11 (4.3)
HFG/B6	High flow grade with a 6% additive, less flow than expected—tape possibly heated too high during preparation	W	Medium Amber	0.20 (7.8) for 0.10 MPa (15 psi) bonds 0.14 (5.6) for 1.38 MPa (200 psi) bonds
MFG/B6	Medium flow grade with a 6% additive of a low molecular weight imide, similar flow to HFG	W	Medium Amber	0.14 (5.6)

MFG

No MFG adhesive tape was actually prepared. Instead, extruded films of the material totaling 0.18–0.22 mm (7–9 mils) were placed on both sides of the 112, A-1100-treated, E-glass cloth between the titanium adherends to be bonded. This served as the "adhesive tape" for this technique.

HFG/MFG 50/50

The adhesive tape for HFG/MFG 50/50 was prepared in a similar manner to the HFG preparation except that pellets of the material were used instead of the powder form. A 6 g charge of pellets was placed in the bottom (female part) of the mold. The 112, A-1100-treated, E-glass cloth was primed with a 7.5 wt% of LARC™-TPI amic-acid solution in diglyme ($\eta_{inh} = 0.49$ dl/g) prior to use. The primed glass cloth was heat-staged for 15 min each at 100°C (212°F) and 165°C (329°F) prior to processing the adhesive tape. The assembled mold was placed in the press and contact pressure was applied. The temperature was increased from RT to ~305°C (581°F), at which time ~3.3 MPa (475 psi) was applied. The temperature was increased to ~313°C (595°F) and held for 5 min after which the pressure was released and the tape removed from the mold. The Upilex films were removed, leaving the adhesive tape ready for use. The average thickness of the tape was 0.30 mm (12 mil).

HFG/B6

This adhesive tape was prepared by MTC and supplied to us as a 0.25 mm (10 mil) thick tape containing two plies of glass fabric ($W_f = 28.3$ wt%). The conditions used to prepare the tape are unknown; however, indications were that it was processed at reasonably high temperatures since the material did not flow well during the bonding process.

MFG/B6

The adhesive tape was prepared in the same manner as the HFG/MFG 50/50 except that a 5 g charge was used and the maximum temperature, 313°C (595°F), was held for 15 min. The average thickness of the tape was 0.38 mm (10.5 mil). Both primed and unprimed glass cloth was used with no significant difference noticed between the two prepared adhesive tapes. When primed, a 7.5 wt% solution of LARC™-TPI amic-acid in diglyme was applied by brush to the glass cloth. The primer was partially imidized by heat treating for 15 min each at 100°C (212°F) and 150°C (302°F) prior to use.

All of the adhesive tapes prepared, except for the thin film adhesive (MFG), were stiff and "boardy" and had an amber color.

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 1.3 mm (0.05 in.). 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 (212°F) for 5 min. The treated adherends were primed within two hours of the surface treatment by applying a thin coat of polyamic acid solution on the surfaces to be bonded. After air drying in a forced-air hood for 30 min, they were heated for 15 min at 100°C (212°F) and 15 min at either 150°C (302°F) or 165°C (329°F). The primed adherends were placed in a polyethylene bag and stored in a desiccator until needed. The adherends used for MFG were not primed. Lap shear specimens were prepared by inserting the adhesive tape between the adherends using a 12.7 mm (0.50 in.) overlap (ASTM D-1002) and applying 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 adhesives were investigated during this study to determine a bonding process which produced good strengths. Table III gives the bonding conditions used for each adhesive material. The cycles selected were as follows:

(1) Either 0.10 MPa (15 psi) or 0.34 MPa (50 psi) pressure, heating rate ~8°C/min (14°F/min), RT→either 343°C (650°F) or 371°C (700°F)
(2) Hold at temperature for 1 hr
(3) Cool under pressure to ~150°C (302°F) and remove from bonding press

Thermal exposures at 204°C (400°F) for up to 30,000 hr were performed in a forced-air oven controlled to within ±2°C (±4°F). Lap shear tests were conducted at RT, 177°C (350°F), 204°C (400°F) and 232°C (450°F) before (controls) and after thermal exposure for the HFG, MFG and HFG/MFG 50/50 adhesives.

In order to determine the effects of humidity (moisture) on an adhesive, a 72-hr water boil was conducted in laboratory glassware containing boiling distilled water. The bonded area of the lap shear specimens was immersed during the 72-hr period. This water exposure was conducted for HFG and MFG adhesives only. LSSs were subsequently determined at RT, 177°C (350°F), 204°C (400°F) and 232°C (450°F).

RESULTS AND DISCUSSION

LFG

Almost seven years ago a program was initiated to evaluate one of the early forms of LARC™-TPI. A total of 32 lap shear specimens was bonded and placed in a convection oven for long-term thermal aging. Aging data for LFG (LARC™-TPI 1000), the high molecular weight material that lacked molecular weight control, was obtained for up to 60,000 hr (6.85 years) exposure in air at 232°C (450°F) (Fig. 2). The

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

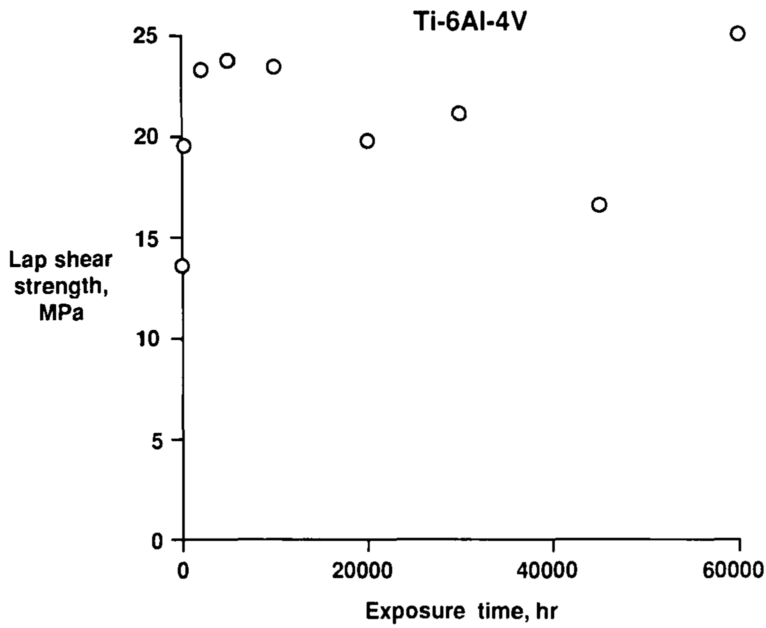


FIGURE 2 Lap shear strength of LFG adhesive tested at 232°C (450°F) after thermal exposure in air at 232°C for up to 60,000 hr.

lap shear specimens were bonded at 343°C (650°F) for 1 hr using a 2.07 MPa (300 psi) bonding pressure. This adhesive system provided excellent strength retention for such a long exposure at elevated temperature [232°C (450°F) LSSs of 24.8 MPa (3600 psi) for the 60,000 hr exposure tests].

HFG

A preliminary study to determine the temperature necessary to provide sufficient flow for good wetting and bond strengths using a low bonding pressure, *i.e.* 0.10 MPa (15 psi), indicated that a temperature of approximately 343°C (650°F) was needed. This is also evident from Figure 1 which gives the relationship between shear rate and melt viscosity for HFG. Higher temperatures, *i.e.* 380°C (716°F), decrease the melt viscosity with increased shear rate.

Figure 3 and Table IV show the LSSs for the HFG controls, thermally-exposed and water-boil specimens. Initial strengths are excellent with a RT strength of 32.8 MPa (4760 psi). Strength decreases with increasing test temperature. For a 232°C (450°F) test temperature, the strength is 14.4 MPa (2090 psi), an excellent value. After 1000 hr at 204°C (400°F), there is essentially no change for the RT strengths. Data for specimens aged at 204°C (400°F) for 5000 and 10,000 hr and tested at 204°C (400°F) were 14.3 MPa (2080 psi) and 13.9 MPa (2020 psi), respectively, compared with the original 22.8 MPa (3000 psi). Results of the 72-hr water boil test indicate a decrease in strength for all test temperatures which is typical of most high-temperature adhesives. The water-boil specimens retained 83.6% (RT), 79.4%

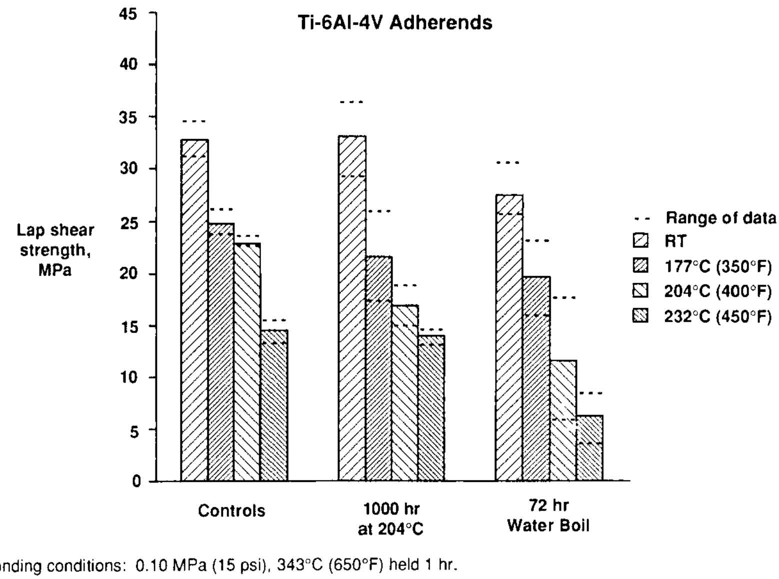


FIGURE 3 Lap shear strength of HFG—controls, thermally-aged and water-boil specimens.

TABLE IV
Lap shear strength of Ti-6Al-4V bonded with HFG—controls, thermally aged and water boil specimens[a]

Exposure	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[b]
None (Controls)	4	RT (RT)	32.8 (4760)	31.7–34.8 (4600–5050)	Co
	4	177 (350)	24.7 (3590)	23.2–26.2 (3360–3800)	Co
	4	204 (400)	22.8 (3000)	22.5–23.1 (3270–3350)	Co
	4	232 (450)	14.4 (2090)	13.5–15.2 (1960–2200)	Co
1000 hr at 204°C	4	RT (RT)	33.1 (4800)	29.3–36.5 (4250–5300)	Co
	4	177 (350)	21.6 (3140)	17.2–26.2 (2500–3820)	Co
	4	204 (400)	16.8 (2430)	15.0–18.4 (2180–2670)	Co
	4	232 (450)	13.9 (2020)	13.0–14.8 (1880–2140)	Co
72-hr water boil	4	RT (RT)	27.4 (3980)	25.4–30.7 (3680–4450)	Co
	4	177 (350)	19.6 (2850)	15.9–22.7 (2310–3290)	Co
	4	204 (400)	11.6 (1690)	5.9–17.5 (860–2540)	Co/I[c]
	4	232 (450)	6.3 (920)	3.9–8.3 (560–1200)	Co

[a]Bonded using 0.10 MPa (15 psi) and 343°C (650°F), held 1 hr.
[b]Co = cohesive; I = interfacial.
[c]2 specimens failed interfacially and 2 failed cohesively.

[177°C (350°F)], 56.3% [204°C (400°F)] and 44.0% [232°C (450°F)] of their control strengths. The failures of all test specimens were primarily cohesive except for the water-boil specimens tested at 204°C (400°F) which were (visually) cohesive/interfacial. The failed specimens all contained some voids in the bond area possibly due to the excessive flow of the adhesive. The adhesive tape contained less than 1%

volatiles as determined by exposing a 6.25 cm^2 piece of the tape in a forced-air oven at 371°C (700°F) for 30 min.

MFG

Results of LSS tests for MFG are given in Figure 4 and in Table V for controls, thermally-exposed specimens at 204°C (400°F) for 1000 and 30,000 hr and water-

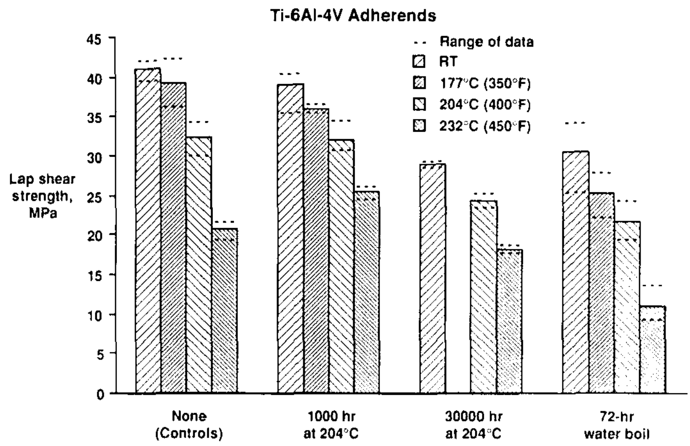


FIGURE 4 Lap shear strength of MFG—controls, thermally-aged and water-boil specimens.

TABLE V
Lap shear strength of Ti-6Al-4V bonded with MFG—controls, thermally aged and water boil specimens[a]

Exposure	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[b]
None (Controls)	4	RT (RT)	41.1 (5960)	39.5–42.1 (5730–6110)	Co
	4	177 (350)	39.2 (5690)	37.2–42.4 (5400–6150)	Co
	4	204 (400)	32.3 (4690)	30.0–34.0 (4350–4940)	Co
	4	232 (450)	20.8 (3010)	19.4–21.7 (2810–3150)	I
1000 hr at 204°C	4	RT (RT)	39.1 (5670)	35.3–40.4 (5200–5860)	Co
	4	177 (350)	36.0 (5220)	35.3–36.5 (5120–5300)	Co
	4	204 (400)	32.0 (4650)	31.0–34.3 (4500–4980)	Co
	3	232 (450)	25.4 (3680)	24.8–26.0 (3600–3770)	Co
30000 hr at 240°C	3	RT (RT)	29.0 (4210)	28.9–29.2 (4190–4230)	Co
	—	177 (350)	—	—	—
	3	204 (400)	24.7 (3590)	24.2–25.2 (3510–3650)	Co
	2	232 (450)	18.5 (2680)	18.3–18.8 (2650–2720)	Co
72-hr water boil	4	RT (RT)	30.5 (4430)	25.4–34.1 (3690–4950)	Co
	6	177 (350)	25.3 (3670)	22.2–27.7 (3220–4340)	Co
	3	204 (400)	21.6 (3130)	19.6–24.3 (2840–3520)	Co
	6	232 (450)	11.1 (1610)	9.6–13.4 (1400–1940)	TP

[a]Bonded using 0.34 MPa (50 psi) and 343°C (650°F), held 1 hr.
[b]Co = cohesive; I = interfacial; TP = thermoplastic (adhesive softening).

boil tests. Specimens were bonded using 0.34 MPa (50 psi) pressure and 343°C (650°F) bonding temperatre and held for one hour. This pressure was determined to be the threshold pressure for obtaining quality bonds.

Excellent LSSs were obtained for all test temperatures, from 41.1 MPa (5960 psi) for RT to 20.8 MPa (3010 psi) for 232°C (450°F). Test failures were primarily cohesive except for those tested at 232°C (450°F) which failed (visually) interfacially. No voids were apparent in the bond area when the failure surfaces were examined using 10× magnification.

After 1000 hr at 204°C (400°F), strengths were essentially unchanged except for a possible increase for those tested at 232°C (450°F), *i.e.* 25.4 MPa (3680 psi) compared with the control strength of 20.8 MPa (3010 psi). This increase after aging at elevated temperatures is not uncommon for high temperature polyimides.

After 30,000 hr at 204°C (400°F), the LSS decreases for all test temperatures. After the thermal exposure, 70% (RT), 76% [204°C (400°F)] and 89% [232°C (400°F)] of the original strengths were retained. These are considered excellent strength retention percentages for such a long period of thermal exposure at elevated temperature. The failures were all primarily cohesive.

The resistance of the adhesive systems to water (humidity) was determined by immersing lap shear specimens in boiling water for a 72-hr period and subsequently obtaining the LSS at RT, 177°C (350°F), 204°C (400°F) and 232°C (450°F). After the 72-hr water boil, the LSSs were lower than the original strengths for all test temperatures. The specimens retained 74% for the RT tests, 64% for 177°C (350°F), 67% for 204°C (400°F) and 53% for the 232°C (450°F) tests. The strengths retained are reasonably high for this severe of a test. The failures were cohesive except for those at 232°C (450°F) which failed thermoplastically (adhesive softening due to water plasticization).

HFG/MFG 50/50

Figure 5 and Table VI show the LSS results for titanium alloy bonded with HFG/MFG 50/50 adhesive. A preliminary study to determine reasonable bonding conditions indicated that a bonding pressure of 0.10 MPa (15 psi) at 343°C (650°F) held for one hour provided excellent bond strengths. The LSSs for specimens bonded using those conditions are shown in Figure 5 and given in Table VI. RT strengths over 41.3 MPa (6000 psi) were obtained and are the highest of those reported in this paper. The strengths at 204°C (400°F) and 232°C (450°F) are also very good, 27.4 MPa (3980 psi) and 20.5 MPa (2970 psi), respectively. All failures were cohesive.

LSSs after 1000 hr at 204°C (400°F) were slightly lower than the controls. Approximately 80% of the original strengths were retained for all the tests and the failures were all 85% or better cohesive.

HFG/B6

HFG containing 6 wt% of a flow-increasing additive did not produce the flow expected, possibly due to the processing of the adhesive tape by MTC. The authors feel that it was processed at an excessively high temperature.

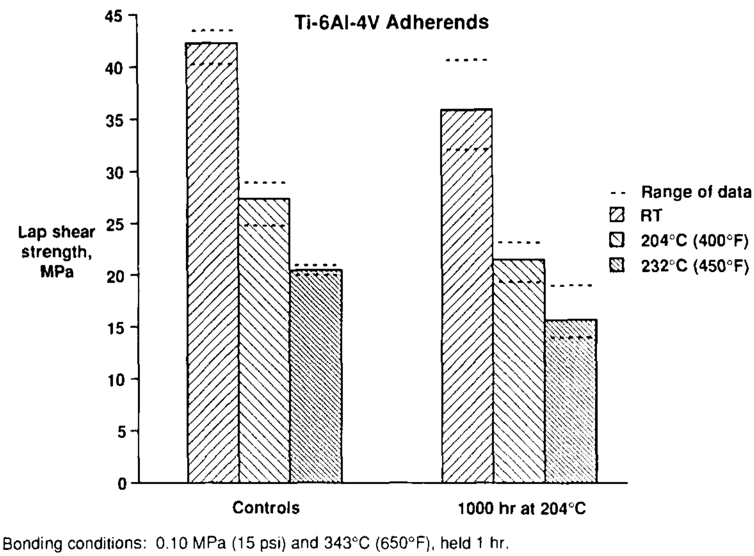


FIGURE 5 Lap shear strength of Ti-6Al-4V bonded with HFG/MFG 50/50—controls and thermally-aged specimens.

TABLE VI
Lap shear strength of Ti-6Al-4V bonded with HFG/MFG 50/50[a]

Exposure	Bonding temperature °C (°F)	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[b]
None	343 (650)	4	RT (RT)	42.3 (6140)	40.3–43.6 (5850–6320)	Co
		4	204 (400)	27.4 (3980)	24.9–28.7 (3610–4160)	Co
		4	232 (450)	20.5 (2970)	20.0–21.1 (2900–3060)	Co
1000 hr at 204°C	343 (650)	4	RT (RT)	35.8 (5190)	32.0–40.7 (4650–5900)	Co
		4	204 (400)	21.4 (3110)	19.2–22.8 (2790–3310)	Co
		4	232 (450)	15.7 (2280)	13.8–19.0 (2000–2760)	Co

[a]Bonded using 0.10 MPa (15 psi), temperature held 1 hr.
[b]Co = cohesive.

Results of a bonding process study using the HFG/B6 adhesive tape are shown in Figure 6 and Table VII. Those bonded at 350°C (662°F) using 0.10 MPa (15 psi) did not flow sufficiently to fill the bond area and produced voids in the adhesive due to the poor contact. Similar results were obtained when the bonding temperature was increased to 370°C (698°F). Increasing the bonding pressure to 1.38 MPa (200 psi) increased the RT LSS from ~20.5 MPa (2980 psi) to 28.0 MPa (4070 psi), but only increased the strength at 232°C (450°F) from 9.2 MPa (1340 psi) to 11.5 MPa (1670 psi). No further work was performed with this system due to the poor results.

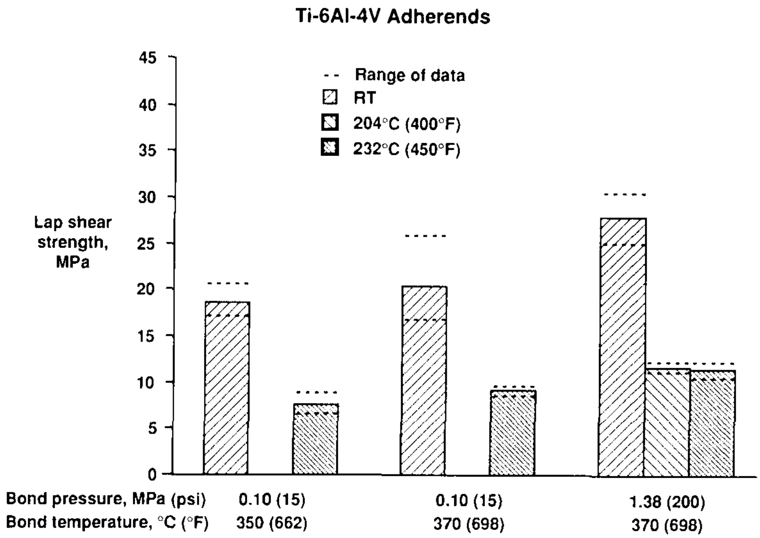


FIGURE 6 Lap shear strength of HFG/B6 adhesive.

TABLE VII
Lap shear strength of Ti-6Al-4V bonded with HFG/B6 adhesive[a]

Bonding Conditions						
Pressure MPa (psi)	Temperature °C (°F)	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[b]
0.10 (15)	350 (662)	4	RT (RT)	18.7 (2710)	17.3–20.5 (2510–2970)	X
		4	232 (450)	7.6 (1110)	6.8–8.8 (980–1280)	Co/X
	370 (698)	4	RT (RT)	20.5 (2980)	17.0–26.2 (2460–3800)	Co
		4	232 (450)	9.2 (1340)	8.6–9.6 (1250–1400)	Co
1.38 (200)	370 (698)	4	RT (RT)	28.0 (4070)	25.2–30.7 (3650–4450)	Co
		4	204 (400)	11.7 (1700)	11.4–12.3 (1660–1780)	Co
		4	232 (450)	11.5 (1670)	10.6–12.3 (1540–1790)	Co

[a]Adhesive tape supplied by MTC.
[b]Co = cohesive; X = poor contact and/or no contact.

MFG/B6

MFG/B6 is a medium flow grade with a 6 wt% additive of a low molecular weight imide that provides a flow similar to HFG. Results of LSS tests to determine a bonding process for the adhesive are shown in Figure 7 and Table VIII. Using a 0.10 MPa (15 psi) bonding pressure, two bonding temperatures were tried, 343°C (650°F) and 371°C (700°F). Neither of the temperatures produced good adhesive strengths. The fractured bonds had voids and the polymer was brittle. The low

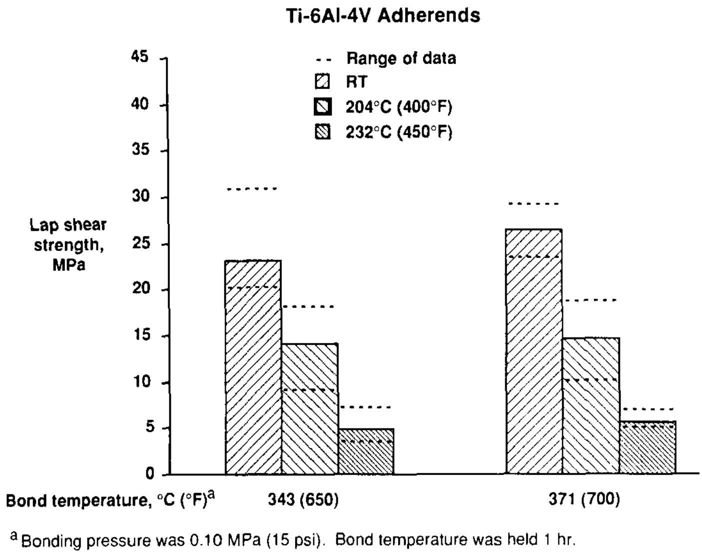


FIGURE 7 Lap shear strength of MFG/B6 adhesive.

TABLE VIII
Lap shear strength of Ti-6Al-4V bonded with MFG/B6 adhesive

Bond temperature[a] °C (°F)	Number of specimens	Test temperature °C (°F)	Average LSS MPa (psi)	Range of LSS MPa (psi)	Primary failure mode[b]
343 (650)	8	RT (RT)	23.1 (3350)	20.1–30.9 (2910–4480)	Co
	8	204 (400)	14.1 (2040)	9.6–18.1 (1390–2630)	Co
	4	232 (450)	4.9 (710)	3.4–7.8 (500–1140)	Co
371 (700)	8	RT (RT)	26.3 (3820)	23.2–29.0 (3370–4200)	Co
	8	204 (400)	14.6 (2120)	10.1–18.8 (1460–2730)	Co
	4	232 (450)	5.6 (820)	5.0–7.0 (720–1010)	Co

[a]Bonding pressure was 0.10 MPa (15 psi). Bonding temperature was held 1 hr.
[b]Co = cohesive.

molecular weight imide increases flow but also seemed to increase the brittleness of the adhesive. Because of the poor results of the preliminary study, thermal-exposure and water-boil tests were not performed.

Comparison of LARC™-TPI 1500 Series of Adhesives

Figure 8 shows a comparison of the LSSs for the five adhesive materials investigated for this report. The two systems that provided the highest LSSs were the MFG and the HFG/MFG 50/50. The toughness of the MFG apparently gives the material its

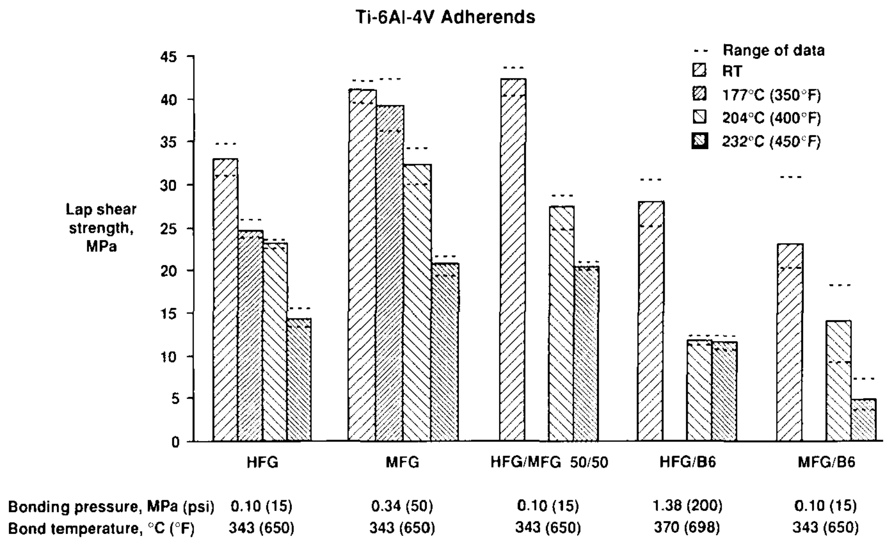


FIGURE 8 Lap shear strength comparison for the LARC™-TPI 1500 series of adhesives evaluated.

excellent strength properties. The good strength of the 1:1 blend of HFG and MFG is a result of the toughness of the MFG and the improved flow due to the HFG. Although the addition of low molecular weight imide had been shown to improve the processing of polyimide/fiber composites, that improvement does not translate to its adhesive strength properties. Direct comparison of the adhesive properties is very difficult because, in addition to the material changes, there were also changes in the approach used in the film preparation (*e.g.*, scrim cloth surface preparation), the surface treatment of the adherends, and the process conditions.

SUMMARY

The various forms of LARC™-TPI that are commercially available have been identified and discussed. This product line has been evolutionary in nature as a result of the manufacturer trying to meet the needs of the users. The trade-offs that have occurred have involved a lowering of molecular weight in the polymer in order to afford more melt flow. This has resulted in a considerable improvement in processability. The melt viscosity and adhesive data for some of these controlled molecular weight forms are very impressive.

Present research at NASA involves studies of what effect this lowering of molecular weight has had on thermooxidative stability, toughness and solvent sensitivity. Ongoing research by the manufacturer of LARC™-TPI is concentrating on narrowing the molecular weight distribution for each version in order to maximize performance.

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