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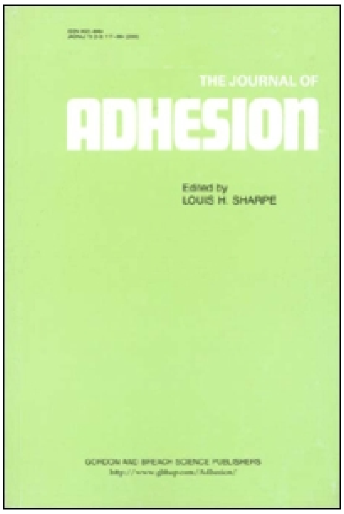

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LARC™TPI Containing Pendant Phenoxy Moieties*

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The poly(keto-imide), LARC™-TPI, was developed in the late 1970's and has proven to be remarkable stable as a high temperature adhesives. Thermal aging results that were generated at both NASA Langley Research Center and at Boeing Aerospace Company proved this material to be stable in adhesive bond form for at least 60,000 hours at 232°C. A commercial form of LARC™-TPI was made available in the mid-to-late 1980's by Mitsui Toatsu Chemicals, Inc. (MTC). Since that time, MTC has optimized the process for manufacturing LARC™-TPI with the major improvements being in molecular weight control. Most recently, MTC synthesized a derivatized version of LARC™-TPI which contains pendant phenoxy moieties. This material is soluble in a number of organic solvents and it exhibits outstanding melt-flow properties which make it attractive as a hot-melt-processable polyimide adhesive. The synthesis and characterization of this novel material is the subject of this research paper.

KEY WORDS Polyimide; polyimide adhesive; high temperature adhesive; hot-melt adhesive; thermoplastic adhesive; LARC™-TPI, LARC™-TPI-DPO.

INTRODUCTION

The need for high temperature adhesives for fabricating aircraft structural components continued to grow during the decade of the 1980's. This was driven primarily by the development of new military aircraft. During this same period, the world experienced a revolution in the development of advanced computers. As performance increased in hardware for both of these industries, so did the need for advanced materials, and adhesives in particular.

During this period of time, several advanced materials such as LARC™-TPI (Langley Research Center-Thermoplastic Polyimide) became important.[1-5] The chemical structure of LARC™-TPI is shown in Figure 1. As shown in the figure, LARC™-TPI is a poly(keto-imide) which contains two meta-linkages to benzene rings along the polymer chain backbone. Early researchers attributed the unique processability and adhesive properties of this polymer to these meta-linkages.[13]

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[*] One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

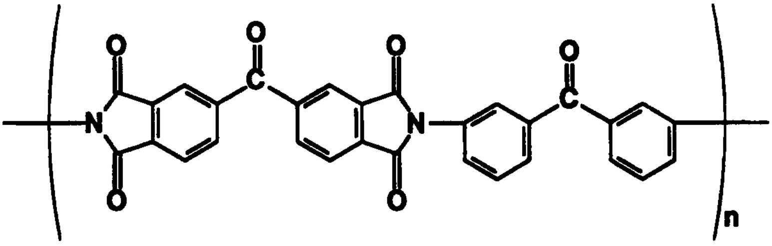

FIGURE 1 Structure of LARC™-TPI.

The presence of the two keto or carbonyl groups in the repeat unit of the polymer backbone is also important. Early polymer researchers reported on the difficulty in preparing linear, aromatic keto-containing polymers.[6] This was attributed to the lack of solubility of this class of polymers which often resulted in polymer precipitation or crystallization before high molecular weight could be attained. LARC™-TPI is only soluble in solvents such as chlorophenols. This is an advantage for the performance of this material as an adhesive; however, it is a limitation in the preparation of adhesive scrim cloths which have to be fabricated from the amide-acid precursor polymer which has poor shelf life in solution,[7] or from the polymer melt which limits wet-out of the scrim cloth.

A derivatized version of LARC™-TPI has been prepared which contains pendant phenoxy moieties which affords enhanced solubility to the polymer. The synthesis scheme for preparing the novel diamine monomer is shown in Figure 2 and the synthesis and structure of the novel polymer LARC™-TPI-DPO (Diphenyloxy) is shown in Figure 3. The melt-flow properties are equal to, or better than, the parent polymer and, as expected, the glass transition temperature is slightly higher because of the increased molecular weight of the repeat unit.

EXPERIMENTAL

Materials and Polymer Synthesis

All LARC™-TPI materials were supplied by Mitsui Toatsu Chemicals, Incorporated (MTC) of Japan either directly or through their American supplier, MTC America. Synthesis of LARC™-TPI has been reported previously.[4] The material identified as LARC™-TPI in this paper was supplied by MTC as an imidized medium-flow grade of the LARC™-TPI 1500 Series. The material, supplied as a film, was 0.18–0.22 mm thick and had an amber color. As given in Table I, the glass transition temperature, T_g was ~240 °C. T_g's were determined by differential scanning calorimetry (DSC) using a 16 °C/min. heating rate. The inherent viscosity, was η_{inh}, was 0.45–0.46 dL/g. All inherent viscosities were run at a concentration of 0.5% in a p-chlorophenol/phenol solvent at 35 °C. The number average molecular weight was ~26,200 and the weight average molecular weight was ~77,100.

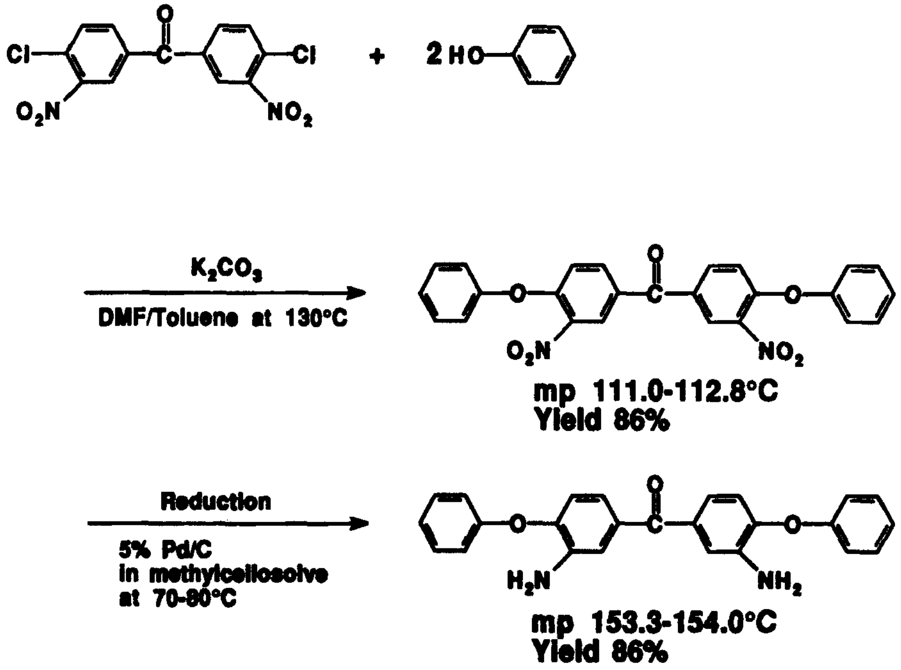

FIGURE 2 Scheme for formation of DABP-DPO.

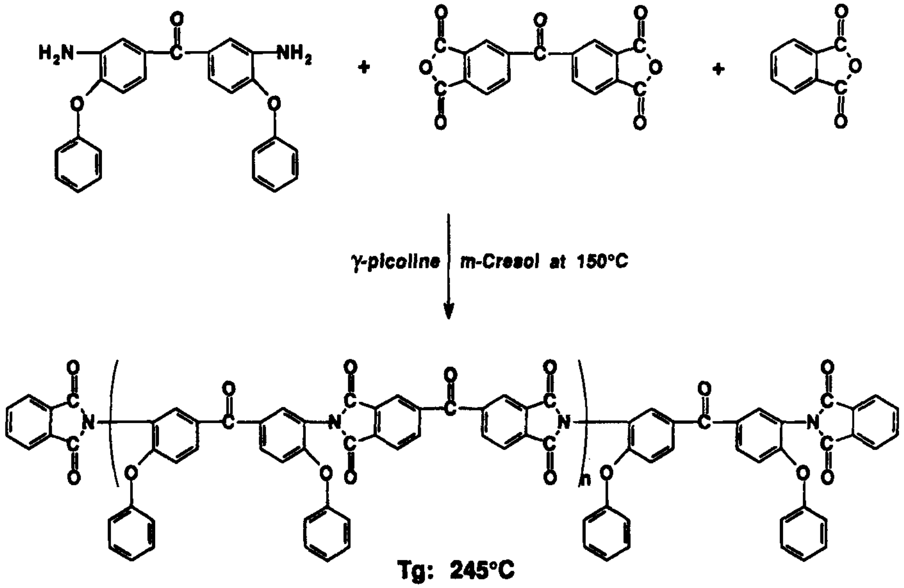

FIGURE 3 Scheme for formation of LARC™-TPI-DPO.

LARC™-TPI-DPO was supplied in a fine yellow powder form. Physical properties of the material are given in Table I. The synthesis and sources of the materials used for synthesis of the monomers and the LARC™-TPI-DPO are discussed below. N,N-Dimethylformamide (DMF), toluene, phenol and methylcellosolve were obtained from Kokusan Chemicals Co. and was used as received. 5%-Pd/C employed as a hydrogenation catalyst was obtained from N.E. Chem. Cat. Co. and was used as received.

3,3′-Dinitro-4,4′-dichlorobenzophenone was easily prepared by nitration of 4,4′-dichlorobenzophenone as follows. 50.2 g (0.2 mol) of 4,4′-dichlorobenzophenone was dissolved in 100 ml of 1,2-dichloroethane. 28.2 g of nitric acid (specific gravity 1.50) was added to the resultant mixture followed by the addition of 117 g of 98% sulfuric acid (30–40 °C) dropwise over a 30-minute period. After stirring for 8 hr at 70–80 °C, the mixture was cooled and separated into an organic layer and a mixed acid layer. The organic layer was washed with 100 ml of water and the solvent was removed by steam distillation. The precipitate was filtered, washed with water and dried to give slightly yellow prism-like crystals of 3,3′-dichlorobenzophenone (68.2 g). The yield was 99% and the purity, as determined by high performance liquid chromatography, was 99.7%. The melting point was 131–132.5 °C. Slightly yellow prism-like pure crystals were obtained by recrystallization from ethanol and had a melting point of 132.5 °C. Elemental analysis was calculated as C, 45.76%; H, 1.76%, N, 8.21% and Cl, 20.80%. Those determined from measurements were C, 45.80%; H, 1.78%; N, 8.25% and Cl, 20.82%.

The monomers used in the preparation of LARC™-TPI-DPO were 3,3′-diamino-4,4′-diphenoxybenzophenone (DABP-DPO) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA). Phthalic anhydride, used for the endcapper of polymer chains, and BTDA were obtained from commercial sources and were used as received. m-Cresol, γ-picoline and methylethylketone (MEK) were also obtained from commercial sources and were used as received.

The 3,3′-dinitro-4,4′-diphenoxybenzophenone (DNBP-DPO) synthesis was as follows. A 500 ml four-necked, round bottom flask containing 80 g (0.235 mol) of 3,3′-dinitro-4,4′-dichlorobenzophenone, 45.5 g (0.483 mol) of phenol, 39 g (0.282 mol) of K_2CO_3, 150 g of DMF and 20 g of toluene was fitted with a mechanical stirrer, condenser and thermometer. The contents were heated, with stirring, to 130 °C and maintained at that temperature for 5 hr. The reaction mixture was cooled to 80 °C and the inorganic salt was filtered off under hot conditions. Sixty grams of water were added to the filtrate and it was cooled to ambient temperature. Precipitated crystals were

TABLE I
Physical properties of LARC™-TPI-DPO and LARC™-TPI[a]

	TPI-DPO	TPI
Inherent viscosity[b] η_{inh}, dL/g	0.43	0.45–0.46
Glass transition temperature, °C (°F) (by DSC)	245 (473)	~ 240 (464)

[a] Data supplied by Mitsui Toatsu Chemicals, Inc.
[b] 0.5% p-Cl-phenol/phenol 90/10 wt.% at 35°C.

filtered and washed with methanol and dried at 60 °C under vacuum for 6 hr. The yield of DNBP-DPO was 92 g (86%): mp 111.0–112.8 °C; Proton-NMR δ (CDCL$_3$, ppm), 7.175 (d, 4H(1)), 7.19–7.69 (m, 6H(2)), 7.57 (d, 2H(3)), 8.06 (dd, 2H(4)), 8.52 (d, 2H(5)). The elemental analysis was calculated for $C_{25}H_{16}N_2O_7$ and determined to be C, 65.79%; H, 3.53% and N, 6.13%. Those determined from measurements were C, 65.81%; H, 3.43% and N, 6.01%.

The 3,3′-diamino-4,4′-diphenoxybenzophenone (DABP-DPO) synthesis was as follows. A mixture of 60 g (0.131 mol) of 3,3′-dinitro-4,4′-diphenoxybenzophenone; 150 g of methyl cellosolve and 3 g of 5% Pd/C was stirred under a hydrogen atmosphere at 70–80 °C for 4 hr. The resulting mixture was cooled to ambient temperature and then the catalyst was filtered off. After the removal of methyl cellosolve, pale yellow crystals were obtained and dried at 60 °C under vacuum for 6 hr. The yield of DABP-DPO was 45 g (86%): mp 153.3–154.0 °C; Proton-NMR (CDCL3, ppm), 4.17 (s, 4H(1)), 6.96 (d, 4H(2)), 7.12–7.63 (m, 6H(3)), 7.12–7.25 (m, 4H(4)), 7.43 (d, 2H(5)). Elemental analysis was calculated for $C_{25}H_{20}N_2O_3$ and determined to be C, 75.74%; H, 5.18% and N, 7.07%. Those determined from measurements were C, 75.62%; H, 5.20% and N, 7.01%.

The LARC™-TPI-DPO polyimide synthesis was as follows. A mixture of 39.65 g (0.100 mol) of DABP-DPO, 31.26 g (0.097 mol) of BTDA, 0.888 g (0.006 mol) of phthalic anhydride and 1.40 g of γ-picoline (catalyst) in 285 g of m-cresol was stirred at 150 °C under a nitrogen atmosphere. The polymerization was continued at 150 °C for 4 hr and, after cooling, the reaction mixture was poured into MEK. The precipitated polymer was collected by filtration, followed by thorough washing with MEK and drying at 230 °C for 4 hr under a nitrogen atmosphere. The yield of LARC™-TPI-DPO was 66.3 g (97.1%): IR(KBr) 1780, 1720 (-CO-) and 720 cm^{-1} (imide ring). The inherent viscosity of this polymer was 0.43 dL/g. The T_g of LARC™-TPI-DPO was 245 °C and the 5% weight loss temperature of this polymer in static air was 535 °C.

CHARACTERIZATION

Lap shear strength (LSS) was obtained according to ASTM D-1002 using a United Calibration Corporation Model No. SFM-10 testing machine. The LLSs reported generally represent an average of four single 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 temperature 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 bond line thickness for LARC™-TPI-DPO was 0.11 mm and for LARC™-TPI it was 0.12 mm.

Glass transition was determined using a Shimadzu DT-40 differential scanning calorimeter (DSC) with a 16 °C/min heating rate. The inherent viscosity of the polyimides was obtained at a concentration of 0.5% in a p-chlorophenol/phenol solvent at 35 °C. Proton-NMR spectra were obtained on a JEOL, EX-90 at 90 MHz frequency. Elemental analysis was performed by the Analysis Department of Mitsui Toatsu Chemicals, Inc. Thermogravimetric analysis (TGA) was performed on a Shimadzu DT-40 thermogravimetric analyzer with a 10 °C/min heating rate.

ADHESIVE TAPE PREPARATION

Due to the physical form of the materials received from MTC, a couple of techniques were used to prepare "adhesive" for bonding lap shear specimens. No LARC™-TPI adhesive tape was actually prepared. Instead, extruded films of the material totaling 0.18–0.22 mm in thickness were placed on both sides of the 112, A-1100 (γ-aminopropyltriethoxysilane) treated E-glass cloth between the titanium adherends to be bonded. This served as the "adhesive tape" for this technique.

LARC™-TPI-DPO was supplied as a pale yellow imidized fine powder which was melted onto 112, A-1100-treated E-glass cloth. The glass cloth was previously primed with a 7.5% solids solution of LARC™-TPI-DPO in N,N-dimethylacetamide (DMAc) and was heated for 15 min each at 100 °C, 150 °C and 175 °C. One-half of the powder charge (~ 5 g) was evenly spread on Upilex® (polyimide) film on the bottom part of a 75 mm × 175 mm 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 Upliex®. This was placed in a hydraulic press, contact pressure was applied and the temperature was increased to ~ 320 °C, at which time ~ 3.3 MPa pressure was applied. The 320 °C 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 thickness of the tape ranged from 0.3–0.4 mm.

ADHESIVE BONDING

The adhesives were used to bond titanium alloy adherends (Ti-6A1-4V, per Mil-T9046E, Type III Comp. C) with a nominal thickness of 1.3 mm. The Ti-6A1-4V 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. For LARC™-TPI-DPO, the treated adherends were primed within two hours of the surface treatment by applying a thin coat of a 7.5% solids solution of LARC™-TPI-DPO in DMAc on the surface to be bonded. They were then heated for 15 min each at 100 °C, 150 °C and 175 °C. The primed adherends were placed in a polyethylene bag and stored in a desiccator until needed. The adherends used for LARC™-TPI were not primed. Lap shear specimens were prepared by inserting the adhesive between the adherends using a 12.7 mm overlap and applying pressure in a hydraulic press during the heating

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

schedule. Bonding temperature was monitored using a type-K thermocouple spot-welded to the titanium adherend at the edge of the bondline.

Several bonding conditions for LARC™-TPI-DPO were investigated during this study to determine a bonding process which produced good strengths. Figure 4 and Table II give the bonding conditions investigated.

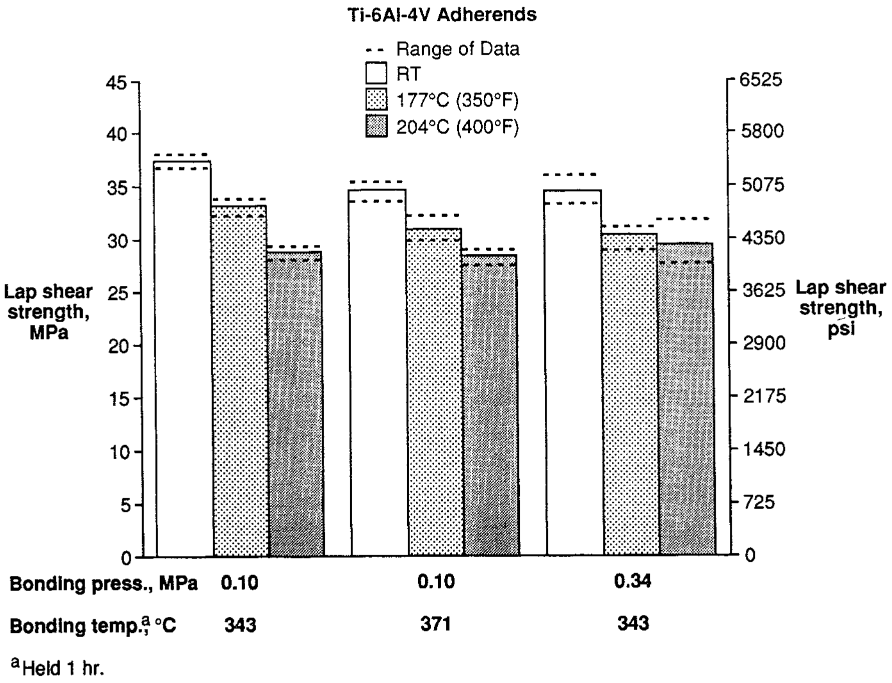


FIGURE 4 Effect of bonding conditions on the single lap shear strength for Ti-6Al-4V bonded with LARC™-TPI-DPO.

TABLE II
Lap shear strength for LARC™-TPI-DPO bonded Ti-6Al-4V

Bonding pressure[a] MPa (psi)	Bonding temperature[a] °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)	343 (650)	4				
		4				
		4				
0.10 (15)	371 (700)	4				
		4				
		4				
0.34 (50)	343 (650)	4				
		4				
		4				

[b]

Thermal exposures at 204 °C for 1000 hr 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 the adhesives, a 72-hr water boil was conducted in laboratory glassware containing demineralized boiling water. The bonded area of the lap shear specimens was immersed during the 72-hr period. LSSs were subsequently determined at RT, 177 °C and 204 °C.

RESULTS AND DISCUSSION

LARC™-TPI-DPO

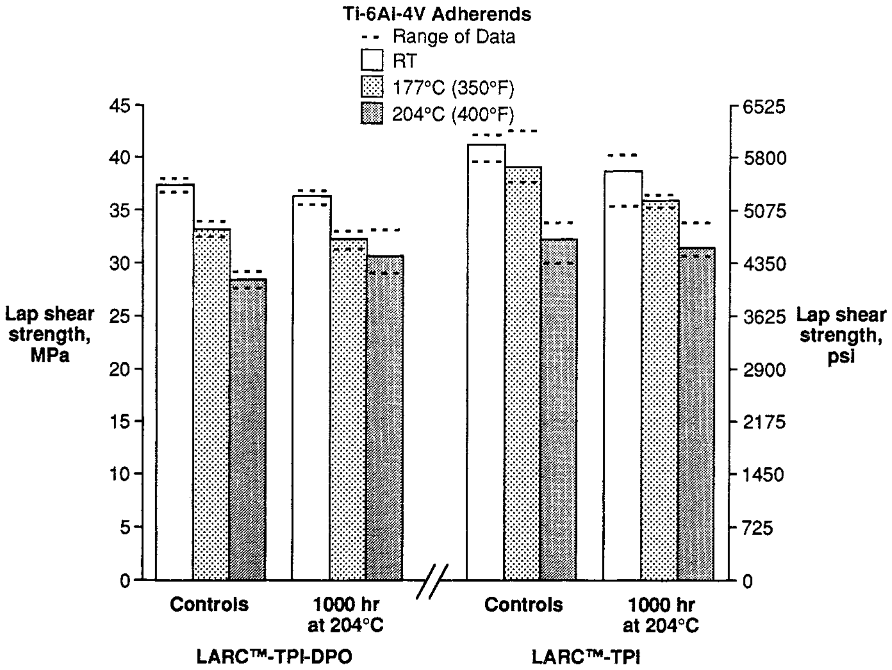
Selection of the appropriate bonding conditions for LARC™-TPI-DPO was based on results of LSS tests for three different bonding procedures as indicated in Figure 4 and Table II. The lower bonding pressure, 0.10 MPa, was of interest because this pressure can be obtained easily by vacuum-bagging techniques, whereas bonding pressures greater than this require the use of autoclaves or high-capacity presses when fabricating large parts. Large autoclaves are generally operable in the 1.38 MPa range. Obviously, the lower bonding temperatures place less temperature requirements on the equipment and allows for shorter processing schedules. Bonding pressures of 0.10 MPa and 0.34 MPa and temperatures of 343 °C and 371 °C were investigated. As seen in Figure 4, the LSS test results show insignificant differences in the three procedures studied. Therefore, the procedure selected for thermal aging and water-boil tests was that using 0.10 MPa bonding pressure and 343 °C bonding temperature held for 1 hr. The LSS values of joints prepared by this bonding procedure were excellent: 37.4 MPa at RT, 33.2 MPa at 177 °C and 28.9 MPa at 204 °C test temperatures. All joint failures were primarily cohesive.

TABLE III
Lap shear strength of thermally aged and water boil specimens of LARC™-TPI-DPO[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)	37.4 (5420)	37.0–38.0 (5360–5520)	Co
	4	177 (350)	33.2 (4820)	32.7–33.9 (4740–4920)	Co
	4	204 (400)	28.9 (4190)	28.3–29.4 (4110–4260)	Co
1000 hr at 204°C	4	RT (RT)	36.0 (5230)	35.4–36.7 (5140–5320)	Co
	4	177 (350)	32.3 (4680)	31.2–33.1 (4520–4800)	Co
	4	204 (400)	30.6 (4440)	29.1–31.3 (4220–4540)	Co
72-hr water boil	4	RT (RT)	29.4 (4260)	28.8–30.1 (4180–4370)	Co
	4	177 (350)	30.2 (4380)	29.2–31.0 (4240–4490)	Co
	4	204 (400)	26.9 (3900)	26.2–28.1 (3800–4080)	Co

[a] Bonded using 0.10 MPa (15 psi) and 343°C (650°F), held 1 hr.

[b] Co = cohesive.



Bonding conditions: 0.10 MPa (15 psi) and 343°C (650°F), held 1 hr for LARC™-TPI-DPO and 0.34 MPa (50 psi) and 343°C (650°F), held 1 hr for LARC™-TPI.

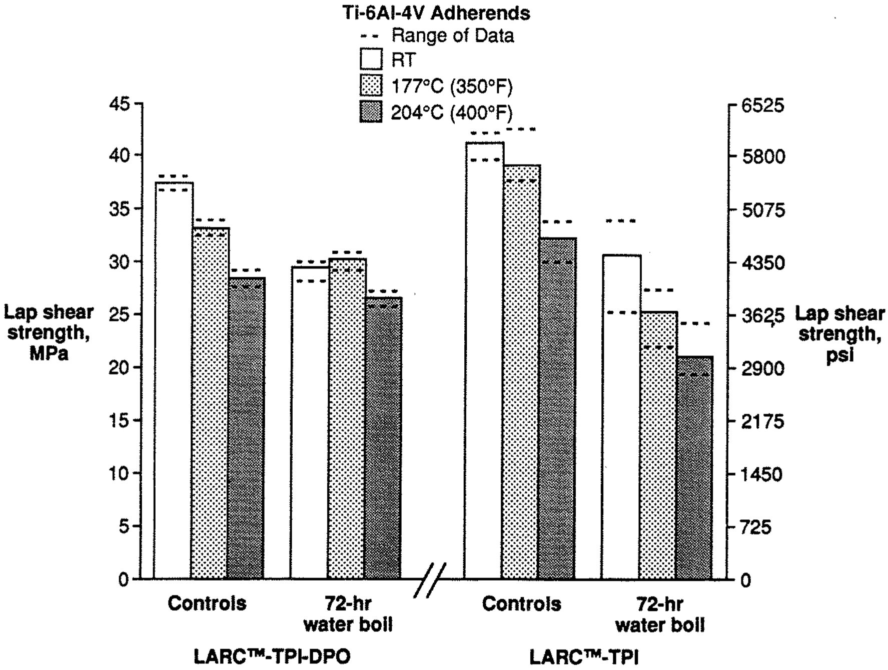
FIGURE 5 Single lap shear strengths on thermal aging in air at 204°C (400°F) for 1000 hr.

Results of thermal aging studies for LARC™-TPI-DPO are shown in Figure 5 and given in Table III. Unstressed lap shear specimens were thermally aged in a forced-air oven at 204 °C for 1000 hr. Essentially no changes in LSSs were observed after the aging period: 36.0 compared with the original 37.4 MPa at RT, 32.3 compared with 33.2 MPa at 177 °C and 30.6 compared with 28.9 MPa at 204 °C. All joint failures were cohesive in nature.

The resistance of the adhesive systems to humidity (moisture) was determined by immersing lap shear specimens in boiling water for a 72-hr period and subsequently obtaining the LSS at RT, 177 °C and 204 °C. The results of a 72-hr water boil test for specimens of LARC™-TPI-DPO are given in Figure 6 and Table III. Some decrease is noted, especially for the RT LSS test. LSS decreased from the original strength of 37.4 MPa to 29.4 MPa, a 21% reduction. The percent reduction in strength for tests at 177 °C and 204 °C compared with original strengths were 9% and 7%, respectively.

LARC™-TPI

Results of LSS tests for LARC™-TPI are given in Figures 5 and 6 and in Table IV for controls, thermally exposed specimens at 204 °C for 1000 hr, and water-boil tests.[4] Specimens were bonded using 0.34 MPa pressure and 343 °C bonding temperature and



Bonding conditions: 0.10 MPa (15 psi) and 343°C (650°F), held 1 hr for LARC™-TPI-DPO and 0.34 MPa (50 psi) and 343°C (650°F), held 1 hr for LARC™-TPI.

FIGURE 6 Single lap shear strengths on exposure to a 72-hr water boil.

TABLE IV
Lap shear strength of thermally aged and water boil specimens of LARC™-TPI[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
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
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

[a] Bonded using 0.34 MPa (50 psi) and 343°C (650°F), held 1 hr.
[b] Co = cohesive.

held for one hr. This pressure was determined to be the threshold pressure for obtaining good bonds.

Excellent initial LSSs were obtained for all test temperatures, from 41.1 MPa for RT to 32.3 MPa for 204 °C. Test failures were primarily cohesive. No voids were apparent in the bonded area when examined at the failed surfaces using 10X magnification.

After 1000 hr at 204 °C, strengths were essentially unchanged from the initial strengths for each test temperature (Figure 5).

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

After the 72 hr water boil, the LSSs were lower than the original strengths for all test temperatures (Figure 6). The specimens retained 74% for the RT tests, 64% for 177 °C, and 67% for 204 °C tests. The strengths retained were reasonably high for this severe test. The failures were primarily cohesive.

COMPARISON OF LARC™-TPI-DPO WITH LARC™-TPI

As shown in Figure 5 and Table III and IV, the LSSs of LARC™-TPI (controls) are higher than LARC™-TPI-DPO (controls): 10% for RT tests, 18% for 177 °C tests and 12% for 204 °C tests. A similar trend was determined for unstressed lap shear specimens thermally aged at 204 °C for 1000 hr. LARC™-TPI strengths were higher than LARC™-TPI-DPO LSSs: 8% at RT, 12% at 177 °C and 5% at 204 °C. However, both adhesives remained essentially unchanged from their original (control) strengths. The 72-hr water boil tests indicate that the LARC™-TPI-DPO retains more of its original strength than LARC™-TPI, especially for the 177 °C and 204 °C tests. LARC™-TPI-DPO retained 78% of its RT strength, 91% of its 177 °C strength and 93% of its 204 °C strength, whereas LARC™-TPI retained 74% of its RT strength, 64% of its 177 °C strength and 67% of its 204 °C strength. Remember, too, that the initial strengths were higher for LARC™-TPI.

SUMMARY

The incorporation of pendant phenoxy moieties in the diamine-derived portion of a linear aromatic polyimide has resulted in a soluble polyimide with a slight increase in glass transition temperature with only a slight overall decrease in adhesive properties. This novel material exhibited adequate meltflow properties which resulted in essentially void-free bondlines. There is no loss in overall adhesive properties after thermal aging at 204 °C for 1000 hrs. Adhesive strength retention after a 72 hr water boil is superior to the polymer that does not contain the pendant phenoxy moieties.

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