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ADHESIVE EVALUATION OF LARC-TPI AND A WATER-SOLUBLE VERSION OF LARC-TPI

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INTRODUCTION

Several years ago a linear thermoplastic polyimide, LARC-TPI, was developed at NASA Langley Research Center which showed promise as a high temperature adhesive for applications in aircraft and spacecraft. The material was of interest because of its toughness and flexibility, good thermal and thermo-oxidative stability and other desirable properties.[1-6] Boeing Aerospace Company had investigated the LARC-TPI as a high temperature adhesive for bonding titanium adherends and found it to retain its high strength for over 5000 hours at 232°C.[7] More recent data have shown the adhesive's excellent strength retention for 37,000 hours at 232°C.[8]

A water soluble version of the LARC-TPI, identified as TPI/H20 in this paper, was synthesized by United Technologies Research Center, East Hartford, Connecticut. A water solvent in the manufacturing and processing of an adhesive is very attractive because present polyimide adhesives, as well as matrix resins, use organic solvents which require strict safety requirements during manufacture and processing. Also, organic solvents cost more than water.

Mitsui Toatsu Chemicals, Incorporated (MTCI), Tokyo, Japan, was licensed by the U.S. Government in March 1984 to produce the LARC-TPI for subsequent sale in the U.S. MTCI made it commercially available the latter part of 1984. The adhesive manufactured by MTCI is identified as TPI/MTC in this paper. The material, supplied as a polyamic-acid solution, was prepared as an adhesive tape and used to bond titanium adherends. The material's lap shear strength properties were investigated with TPI/MTC and TPI/H20 as the primers.

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This report details the results of a study (1) on the adhesive bond strength of TPI/H20 up to 278°C, with and without fillers, using two bond cycles, (2) on the effects of thermal exposure for 500 and 1000 hrs at 204°C and a 72-hour water-boil on the lap shear strength for TPI/MTC adhesive with TPI/MTC and TPI/H20 as the primer. Lap shear strength data for TPI/MTC was also compared with that obtained from the literature.[1,7]

EXPERIMENTAL

Materials. A water-soluble polyamic-carboxylate solution, identified as TPI/H20 in this report, was supplied by United Technologies Research Center (UTRC), East Hartford, Connecticut. The material was received as a 10 wt% solids solution in water as the quaternary N,N-dimethylethanol amine salt.[9] R. A. Pike (UTRC) states that "there is the possibility that the degree of polymerization of the starting resin as well as the amine cation will influence adhesive performance". The resin solution was used as-received [inherent viscosity, η_{inh} 0.94 dl/g (35°C)] for preparing the adhesive tape as well as for use as a primer.

A 29.1 wt% solids polyamic-acid solution in bis(2-methoxyethyl)ether (diglyme) was manufactured and supplied by Mitsui Toatsu Chemicals, Incorporated (MTCI), Tokyo, Japan. The monomers used in the preparation of LARC-TPI were 3,3'-4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzophenone (3,3'-DABP).[2,7] The material supplied by MTCI is identified as TPI/MTC in this report. The solution, lot no. 26-001, had an η_{inh} of 0.54 dl/g (35°C) and a Brookfield viscosity of 24,600 cps (23°C).

Characterization

Lap shear strength (LSS) was obtained according to ASTM D-1002 using a Model TT Instron universal testing machine. The average LSS's reported represent at least four lap shear specimens tested for any one condition except as noted in the tables. 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. The range of LSS's 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 is given in Tables 1-5.

Glass transition temperatures (Tg) of the adhesive from the fractured lap shear specimens were determined by thermomechanical analysis (TMA) on a DuPont 943 Analyser in static air at a heating rate of 5°C/min using a hemispherical probe with a 15g mass.

Thermomechanical spectra of the polymers were obtained on a torsional braid analysis (TBA) system interfaced with an IBM PC. Individual glass braids were coated with a 7.5% solids TPI/MTC polyamic acid solution and a 10% solids TPI/H20 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 atmopshere to 400°C at 3°C/min. Tg was determined as the extrapolated maximum peak height of the damping versus temperature curve.

Inherent viscosity (η_{inh}) 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% solids in N,N-dimethylacetamide (DMAC) was made and filtered. The average of three runs of the solution was reported. Infrared spectra were obtained using a Nicolet Model 3600 Fourier Transform Infrared Spectrophotometer (FTIR) using a diffuse reflectance (DR) technique.

Adhesive Tape. Adhesive tape for the TPI/MTC was prepared by brush coating a 7.5 wt% solids polyamic-acid primer solution in diglyme onto 0.01 cm thick 112 E-glass cloth with A-1100 finish (γ-aminopropylsilane). The glass cloth served as a carrier for the adhesive as well as for bondline control and as an escape channel for solvent and volatile reaction products. After the primer was applied, the coating was air-dried for 1 hr and heated in a forced air oven for 1 hr at each of three temperatures: 100°C, 150°C, and 175°C. 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 brush application onto the glass cloth. Subsequent applications were exposed to the following schedule until a thickness of 0.02 - 0.025 cm was obtained:

(1) Room temperature for 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 rather involved procedure to prepare the tape was necessary 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 at temperature.

Adhesive tape for the TPI/H2O was prepared in a similar manner using a 10 wt% solids solution in water containing the N,N-dimethylethanol amine salt supplied by UTRC. This water soluble polyamic-carboxylate undergoes thermal conversion to the polyimide just as in the case of the polyamic-acid. After applying the 10 wt% solids solution on the glass cloth, the resin was air-dried for 0.5 hr with subsequent heating for 0.5 hr at 100°C and 0.5 hr at 150°C. DR-FTIR spectra were obtained to monitor imide formation after each step of a single cycle (i.e. air-dry, 0.5 hr; 100°C, 0.5 hr; 150°C, 0.5 hr).

In an attempt to increase the bond strength for the TPI/H2O adhesive, fillers were added to the adhesive in nominal amounts. Aluminum powder, Alcan's MD 105, was initially added to a solution of TPI/H2O, however due to the N,N-dimethylethanol amine salt, a chemical reaction occurred thus eliminating aluminum as a possible filler material. Mica and Cab-o-sil, 50 wt% and 5 wt% respectively, were added to the solution, applied to a glass cloth and cured in the same manner as the TPI/H2O adhesive tape. A final thickness of 0.027 to 0.029 cm was obtained.

Adhesive Bonding. The prepared adhesive tapes were used to bond titanium adherends (Ti 6AL-4V, per Mil-T-9046E, Type III Comp.) with a nominal thickness of 0.13 cm. The four-fingered Ti(6AL-4V) panels were grit blasted with 120 grit aluminum oxide, washed with methanol, and treated with a Pasa-Jell 107* treatment 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 respective adhesive solutions on

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

the surfaces to be bonded. They were air-dried under a fume hood for 0.5 hr then placed in a forced-air oven and heated for 15 to 30 min at 100°C and 15 to 30 min at 150°C. The primed adherends were stored in a polyethylene bag and placed 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 pressure in a hydraulic press. The bonding cycles used during this study were as follows:

<u>Cycle 1</u>

(1) Contact pressure, heating rate ≈ 8°C/min, RT → 200°C, apply 1.38 MPa at 200°C

(2) 200°C → 325°C, hold 0.5 hr

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

<u>Cycle 2</u>

(1) Apply 1.38 MPa pressure, heating rate ≈ 8°C/min, RT → 325°C, hold 0.5 hr

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

<u>Cycle 3</u>

(1) Apply 2.07 MPa pressure, heating rate ≈ 8°C/min, RT → 343°C, hold 1 hr

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

<u>Thermal and Water-boil Exposures</u>. TPI/MTC lap shear specimens were prepared with either TPI/MTC or TPI/H20 as the primer and thermally exposed in a forced-air oven for 500 and 1000 hrs at 204°C. The forced-air oven was controlled to within ±1% of the exposure temperature. Lap shear strength tests were conducted at RT, 177°C, and 204°C before (controls) and after exposure.

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

RESULTS AND DISCUSSION

Materials and Chemistry. The proposed reactions for the formation of the subject thermoplastic polyimides are shown in Figure 1. The monomers used in the preparation were BTDA and 3,3'-DABP. The water-soluble polyamic-carboxylate (I) (TPI/H2O) undergoes a thermal conversion with elimination of water and N,N-dimethylethanol amine to form the polyimide (III) whereas in the other scheme, the polyamic-acid (II) eliminates water to form the polyimide.

Indications of imide formation during preparation of the adhesive tape for TPI/H2O was determined by obtaining infrared spectra using the DR-FTIR technique.[10] Spectra are shown in Figure 2 after subsequent steps of a single cycle during tape preparation: (1) air-dry, 0.5 hr; (2) 100°C, 0.5 hr; and (3) 150°C, 0.5 hr.

Imide formation was evident as shown by increasing imide peak formations with heat treatment at 3485, 1780, 1732, 1384, 1109, and 724 cm^{-1}. Additional coatings were applied and heat treated until a thickness of 0.015 - 0.025 cm was obtained. Figure 3 shows the infrared spectra for the TPI/H2O adhesive of a fractured lap shear specimen which had been bonded at 325°C for 0.5 hr. Imidization is again evident as seen by the imide peaks observed at 3485, 1780, 1732, 1384, 1109, and 724 cm^{-1}.

TPI/H20 Adhesive Evaluation. The prepared TPI/H20 adhesive tape was used to bond titanium with Pasa-Jell acid surface treatment. Two bonding cycles were used as previously described: Cycle 1, in which the pressure was applied at 200°C, heated to 325°C and held for 0.5 hr, and Cycle 2, where the pressure was maintained throughout the cycle. Lap shear strength tests were conducted at RT, 232°C, and 278°C (Table 1 and Figure 4). The RT LSS was higher for Cycle 2 (30.3 MPa) than Cycle 1 (24.7 MPa), however the 232°C LSS results are about the same, 16.3 and 17.4 MPa. The 278°C LSS's are very low with the obvious reason being that the Tg of the adhesive was considerably lower (by 44°C) than the test temperature. Failure mode changed from cohesive at RT and 232°C to adhesive failure at 278°C.

The addition of fillers to the adhesive tape formulation, i.e. 50 wt% mica and 5 wt% Cab-o-sil, resulted in lower strengths for both Cycles 1 and 2 at RT and 232°C than the strengths of the adhesive without fillers. The very low LSS's at 278°C were the same for all cases.

The results of the tests for TPI/H20 without fillers were encouraging and therefore, the use of the TPI/H20 solution as a primer was investigated further with the TPI/MTC adhesive.

Thermal Exposure. The stability to long term thermal exposure was determined for the TPI/MTC adhesive system by exposing lap shear specimens for 500 and 1000 hrs at 204°C in a forced-air oven. Cycle 3 (2.07 MPa pressure; RT to 343°C, hold 1 hr) was used to bond the lap shear specimens for the thermal exposure study. Lap shear strength was determined at RT, 177°C, and 204°C before (controls) and after exposure.

Results are given in Table II and Figure 5 for TPI/MTC adhesive and primer. No significant difference was found in the LSS with time of thermal exposure for any one test 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 decreasing LSS with increasing test temperature, however the decrease is small, less than 24% for tests up to 204°C, when compared to most adhesive systems for this temperature range. All failures were 100% cohesive. There was a slight increase in Tg with thermal aging which is characteristic for these types of adhesives (polyimides).

Data are presented in Table III and Figure 6 for TPI/MTC adhesive with TPI/H2O primer. There appears to be a small inconsistency for the 500 hr exposure data for RT and 177°C tests. The RT LSS for the 500 hr test was higher, 31.3 MPa, than the RT LSS values for the controls, 27.4 MPa, and for the 1000 hr exposure, 28.8 MPa. Also the 177°C LSS was lower for the 500hr test than those of the controls and the 1000 hr exposure tests. The remaining data of LSS with time for thermal exposure for any one test temperature are about the same, i.e. RT, 27.4 - 28.8 MPa; 177°C, 27.5 - 29.7 MPa; and 204°C, 25.2 - 28.2 MPa. There appears to be less of a trend of decreasing LSS with test temperature than there was with the TPI/MTC adhesive and primer. Although the failure mode was primarily cohesive, there was a significant amount of adhesive failure. In contrast, those primed with TPI/MTC were 100% cohesive indicating that the primer does make a significant difference in the type of failure. The color was considerably darker for the TPI/H2O primed system compared to the TPI/MTC primed system. As for the TPI/MTC primed system, there was evidence of a postcuring effect on the adhesive as indicated by the increase in Tg with thermal exposure.

Other than the difference in failure modes between the two systems, i.e. 100% cohesive for the TPI/MTC primed system and combined cohesive/adhesive failure for the TPI/H2O primed system, the only other significant finding was the RT LSS was higher overall by approximately 16% for the system using the TPI/MTC as the primer.

72-Hour Water-boil. Results of the 72-hour water-boil test for lap shear specimens bonded with TPI/MTC adhesive and TPI/MTC primer are given in Table IV and Figure 7. LSS was determined at RT, 177°C, and 204°C. RT LSS decreased 16% from 33.0 MPa to 27.8 MPa. Significant LSS decreases were obtained at 177°C and 204°C with those at 177°C and 204°C being only 66% and 40% respectively that of the control's strength. All failures were 100% cohesive. Tgs are also given in the last column of Table IV and indicate a possible trend of decreasing Tg with increasing test temperature. Because only single measurements were made and because of the measurement technique, the trend is inconclusive.

Water-boil test results for TPI/MTC adhesive with TPI/H2O primer are given in Table V and shown in Figure 8. The control LSS values were quite similar for RT, 177°C, and 204°C. Again the LSS decreased significantly after the water-boil, especially those results of the 177°C and 204°C tests where the LSS's were 65% and 29% respectively of the control values. Failure modes for the controls were primarily cohesive, however the failure modes for the water-boil specimens were inconsistent, changing from 50/50 cohesive/adhesive at RT to cohesive at 177°C and to adhesive at 204°C. The above results indicate that the use of the TPI/H2O reduces the water resistance of the adhesive system compared to the use of TPI/MTC primer. In all cases the average LSS of specimens with TPI/MTC primer was slightly higher or, in one case, the same as those made with the TPI/H2O primer. Tg values for the TPI/MTC primed specimens were a little higher than those primed with TPI/H2O for the same conditions and test temperature.

Comparison with Literature Data for TPI Adhesives. Although variations in surface preparations, bonding conditions, starting adhesive solutions, etc. are evident, a cursory comparison of the present study's data with literature data is given in Table VI. Comparisons are made for the common test temperatures at RT and 232°C. LSS's range from 27.4 MPa to 41.4 MPa for the RT tests and from 14.8 MPa to 17.9 MPa for those at 232°C. The LSS data from the present study compare favorably with the reference 7 data, but it is lower than that reported in reference 1. The difference is probably due to variations in the resin preparation. Failure modes were not reported in Ref. 1 and Ref. 7.

Glass Transition Temperature. The technique used to determine the Tg generally is unique unto itself and the data obtained should not be compared directly with data from other techniques. Table VII gives the summary of Tg values determined by the TMA technique for TPI/H2O and TPI/MTC. The Tg gives an indication of the maximum possible use temperature for an adhesive. The Tg values determined ranged from 212°C to 242°C indicating a possible use temperature less than 212°C. The increase in Tg with thermal exposure at 204°C is indicative of a postcuring effect which is characteristic of this type of adhesive.

Tg values were also determined by the TBA technique for TPI/H2O and TPI/MTC using a 3°C/min heating rate from RT to 400°C in a nitrogen atmosphere. Prior to the measurements, the braids were precured by heating one hour at each of three temperatures: 100°C, 200°C, and 300°C. The values of

Tg for the TPI/H20 and TPI/MTC were 264°C and 258°C respectively. This is another indication that the materials formed from the two solutions are very similar.

SUMMARY

A commercially available version of LARC-TPI, originally developed at NASA Langley Research Center, from Mitsui Toatsu Chemicals, Incorporated, Tokyo, Japan, (TPI/MTC) and a water-soluble version from United Technologies Research Center, East Hartford, Connecticut (TPI/H2O) were evaluated as thermoplastic adhesives and primers for bonding titanium. This LARC-TPI polymer has shown promise as an adhesive for applications in aircraft and spacecraft because of its toughness, flexibility, good thermal and thermo-oxidative stability.

In the present study, lap shear strength was used to evaluate the material as an adhesive. The adhesives were characterized after fracture by determining their Tg. The mode of failure, cohesive and/or adhesive, was reported.

The TPI/H20 solution containing N,N-dimethylethanol amine salt with and without fillers was used to prepare an adhesive tape. The room temperature lap shear strength obtained with a bonding cycle wherein the bonding pressure was held throughout the cure was about 25% higher than that obtained using a cure cycle wherein the pressure was applied after the bond was heated to 200°C. The measured LSS's were 30.3 MPa and 24.7 MPa, respectively. LSS results at 232°C for the two different cycles were essentially the same (16.3 MPa and 17.4 MPa). The addition of fillers

resulted in lower LSS's than without fillers. The results of the LSS tests were encouraging and therefore the TPI/H2O was evaluated as a primer with the TPI/MTC adhesive. Imide formation was monitored using the DR-FTIR technique during adhesive tape preparation and after fracture of a lap shear specimen.

Long term thermal exposure at 204°C in a forced-air oven for up to 1000 hrs for TPI/MTC adhesive with either TPI/MTC or TPI/H2O as the primer produced promising results. This was shown by essentially no change in LSS with time of exposure for any one test temperature, i.e. RT, 177°C, and 204°C. The system with TPI/MTC as the primer produced higher RT strengths by approximately 16% than that with the TPI/H2O primer. The TPI/MTC primed system also resulted in 100% cohesive failure, whereas, the TPI/H2O primed system failed by a combination of cohesive/adhesive failure.

The 72-hour water-boil tests for lap shear specimens of TPI/MTC with either TPI/MTC or TPI/H2O as the primers showed significantly reduced LSS's after water-boil. The TPI/H2O primed system produced lower LSS's at 204°C than the TPI/MTC primed system (40% of the control value for the TPI/MTC primed system and 29% of the control value for the TPI/H2O primed system). Tg values for the TPI/MTC primed specimens were slightly higher than those primed with TPI/H2O for both the controls and the water-boil at all test temperatures. The LSS data generated at RT and 232°C in the present study were shown to compare favorably with the data obtained from literature.

Results of the study show the adhesive, prepared from either TPI/MTC or the TPI/H2O solutions, appears promising for potential structural applications for long term use, at least up to 1000 hrs, at about 200°C.

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TABLE I. - TEST RESULTS FOR TPI/H20 ADHESIVE[a]

Cycle	Adhesive filler	Test temperature, °C (°F)	Number of specimens	Avg. LSS, MPa (psi)	Range of LSS, MPa (psi)	Failure type,[b] percent Co/Ad	Avg. bondline thickness, mm (in.)	Glass transition temperature,[c] Tg °C (°F)
		RT (RT)	4	24.7 (3581)	23.8-25.2 (3450-3650)	80/20	0.09 (0.0037)	227 (442)
1	None	232 (450)	3	16.3 (2368)	15.1-17.4 (2390-2520)	90/10	0.10 (0.0039)	-- --
		278 (532)	4	2.7 (396)	2.5-3.0 (365-440)	5/95	0.11 (0.0042)	234 (453)
		RT (RT)	3	30.3 (4398)	30.1-30.7 (4365-4455)	100/0	0.10 (0.0039)	236 (457)
2	None	232 (450)	3	17.4 (2525)	16.5-18.1 (2400-2630)	100/0	0.10 (0.0039)	-- --
		278 (532)	2	3.2 (465)	3.1-3.3 (450-480)	0/100	0.10 (0.0039)	-- --
	50% Mica	RT (RT)	4	13.7 (1982)	12.8-14.6 (1850-2120)	93/0	0.18 (0.0073)	229 (444)
1	5% Cab-o-sil	232 (450)	4	10.3 (1492)	9.0-12.7 (1310-1840)	94/6	0.18 (0.0071)	-- --
		278 (532)	4	3.7 (541)	2.9-4.3 (420-630)	11/89	0.18 (0.0073)	-- --
	50% Mica	RT (RT)	3	13.9 (2015)	13.3-14.4 (1935-2095)	98/2	0.18 (0.0071)	238 (460)
2	5% Cab-o-sil	232 (450)	3	12.0 (1748)	10.2-13.6 (1480-1970)	100/0	0.18 (0.0069)	-- --
		278 (532)	2	3.6 (520)	3.0-4.2 (435-605)	85/15	0.18 (0.0070)	-- --

[a] TPI/H20 primer, titanium (6AL-4V) adherend.

[b] Cohesive-Co., adhesive-Ad, average for number of specimens tested.

[c] Single measurements.

TABLE II. - THERMAL EXPOSURE TEST RESULTS FOR TPI/MTC WITH TPI/MTC PRIMER[a]

Time of exposure, hr	Test temperature, °C (°F)	Avg. LSS,[b] MPa (psi)	Range of LSS, MPa (psi)	Failure type,[c] percent Co/Ad	Avg. bondline thickness, mm (in.)	Glass transition temperature,[d] Tg °C (°F)
0 (controls)	RT (RT)	33.0 (4791)	32.3-33.5 (4685-4860)	100/0	0.10 (0.0040)	228 (442)
	177 (350)	29.5 (4284)	28.8-30.7 (4180-4450)	100/0	0.09 (0.0035)	225 (437)
	204 (400)	25.2 (3660)	25.0-25.4 (3620-3690)	100/0	0.09 (0.0034)	236 (457)
500	RT (RT)	34.1 (4941)	32.7-35.3 (4740-5125)	100/0	0.09 (0.0035)	242 (468)
	177 (350)	29.0 (4200)	27.5-30.5 (3985-4420)	100/0	0.09 (0.0036)	242 (468)
	204 (400)	26.9 (3899)	26.6-27.1 (3855-3935)	100/0	0.09 (0.0036)	237 (459)
1000	RT (RT)	32.9 (4779)	32.3-34.4 (4690-4985)	100/0	0.09 (0.0036)	242 (468)
	177 (350)	29.9 (4336)	28.5-31.0 (4135-4490)	100/0	0.09 (0.0035)	246 (475)
	204 (400)	27.8 (4015)	27.2-28.6 (3940-4155)	100/0	0.09 (0.0036)	238 (460)

[a] Titanium (6AL-4V) adherends.

[b] Average of four test specimens.

[c] Cohesive failure-Co, adhesive-Ad.

[d] Single measurement.

TABLE III. - THERMAL EXPOSURE TEST RESULTS FOR TPI/MTC WITH TPI/H2O PRIMER[a]

Time of exposure, hr	Test temperature, °C (°F)	Avg. LSS,[b] MPa (psi)	Range of LSS, MPa (psi)	Failure type,[c] percent Co/Ad	Avg. bondline thickness, mm (in.)	Glass transition temperature,[d] Tg °C (°F)
0 (controls)	RT (RT)	27.4 (3969)	26.2-29.0 (3795-4215)	61/39	0.15 (0.0059)	221 (430)
	177 (350)	27.5 (3994)	27.1-27.9 (3930-4045)	76/24	0.15 (0.0061)	214 (417)
	204 (400)	25.2 (3660)	24.8-25.8 (3600-3740)	96/4	0.15 (0.0061)	215 (419)
500	RT (RT)	31.3 (4535)	29.8-32.8 (4320-4755)	90/10	0.18 (0.0071)	219 (426)
	177 (350)	24.5 (3549)	21.7-26.6 (3150-3860)	62/38	0.16 (0.0063)	238 (460)
	204 (400)	28.2 (4089)	27.6-28.8 (4000-4180)	94/6	0.16 (0.0065)	242 (468)
1000	RT (RT)	28.8 (4184)	26.4-30.9 (3835-4485)	51/49	0.16 (0.0065)	241 (466)
	177 (350)	29.7 (4308)	28.3-31.2 (4100-4525)	86/14	0.18 (0.0071)	240 (464)
	204 (400)	28.1 (4074)	26.9-29.8 (3900-4330)	84/16	0.16 (0.0064)	243 (469)

[a] Titanium (6AL-4V) adherends.

[b] Average of four test specimens.

[c] Cohesive-Co, adhesive-Ad; average of four specimens.

[d] Single measurements.

TABLE IV. - TEST RESULTS OF A 72-HOUR WATER-BOIL FOR TPI/MTC WITH TPI/MTC PRIMER[a]

	Test temperature, °C (°F)	Avg. LSS,[b] MPa (psi)	Range of LSS, MPa (psi)	Failure type,[c] percent Co/Ad	Avg. bondline thickness, mm (in.)	Glass transition temperature,[d] Tg °C (°F)
Controls	RT (RT)	33.0 (4791)	32.3-33.5 (4685-4860)	100/0	0.10 (0.0040)	228 (442)
	177 (350)	29.5 (4284)	28.8-30.7 (4180-4450)	100/0	0.09 (0.0035)	225 (437)
	204 (400)	25.2 (3660)	25.0-25.4 (3620-3690)	100/0	0.09 (0.0034)	236 (457)
72-Hour water-boil	RT (RT)	27.8 (4034)	26.7-28.8 (3870-4175)	100/0	0.09 (0.0036)	239 (462)
	177 (350)	19.7 (2856)	19.1-20.3 (2765-2950)	100/0	0.09 (0.0035)	230 (446)
	204 (400)	10.1 (1466)	9.4-11.0 (1360-1600)	100/0	0.08 (0.0033)	225 (437)

[a] Titanium (6AL-4V) adherends.

[b] Average of four test specimens.

[c] Cohesive-Co, Adhesive-Ad; average of four specimens.

[d] Single measurement.

TABLE V. - TEST RESULTS OF A 72-HOUR WATER-BOIL FOR TPI/MTC WITH TPI/H20 PRIMER[a]

	Test temperature, °C (°F)	Avg. LSS,[b] MPa (psi)	Range of LSS, MPa (psi)	Failure type,[c] percent Co/Ad	Avg. bondline thickness, mm (in.)	Glass transition temperature,[d] Tg °C (°F)
Controls	RT (RT)	27.4 (3969)	26.2-29.0 (3795-4215)	61/39	0.15 (0.0059)	221 (430)
	177 (350)	27.5 (3994)	27.1-27.9 (3930-4045)	76/24	0.15 (0.0061)	214 (417)
	204 (400)	25.2 (3660)	24.8-25.8 (3600-3740)	96/4	0.15 (0.0061)	215 (419)
72-Hour water-boil	RT (RT)	25.2 (3651)	23.5-27.3 (3405-3960)	50/50	0.15 (0.0060)	231 (448)[e]
	177 (350)	18.0 (2614)	15.5-19.2 (2250-2780)	91/9	0.16 (0.0063)	212 (414)[e]
	204 (400)	7.3 (1065)	6.7- 8.0 (975-1155)	30/70	0.16 (0.0065)	216 (421)

[a] Titanium (6AL-4V) adherends.

[b] Average of four test specimens.

[c] Cohesive-Co, Adhesive-Ad; average of four specimens.

[d] Single measurements.

[e] Average of two measurements.

TABLE VI. - LAP SHEAR STRENGTH COMPARISON OF TPI ADHESIVES[a]

Data source	Surface treatment	Bonding conditions	Test temperature, °C (°F)	Avg. LSS, MPa (psi)	Primary failure mode[b]
Present study TPI/MTC adh. TPI/MTC primer	Pasa-Jell 107	2.07 MPa; 8°C/min, RT → 343°C, hold 343°C for 1 hr	RT (RT) 177 (350) 204 (400) 232 (450)	33.0 (4791) 29.5 (4284) 25.2 (3660) 15.8 (2285)	Co Co Co Co
Present study TPI/MTC adh. TPI/H2O primer	Pasa-Jell 107	As above	RT (RT) 177 (350) 204 (400) 232 (450)	27.4 (3969) 27.5 (3994) 25.2 (3660) 14.8 (2144)	Co Co Co Co
Ref. 1	Pasa-Jell 107	7°C/min, RT → 325°C, apply 1.38 MPa at 280°C; hold 5 min at 325°C	RT (RT) 232 (450)	41.4 (6000) 17.9 (2600)	-- --
Ref. 7	Chromic acid anodize (CCA)	1.38 MPa; 2-3°C/min, RT → 343°C, hold 90 min; postcure 2 hrs at 316°C	RT (RT) 232 (450)	29.7 (4300) 14.8 (2150)	-- --

[a] Titanium (6AL-4V) adherends.

[b] Cohesive-Co.

TABLE VII. - GLASS TRANSITION TEMPERATURES FOR TPI/H2O AND TPI/MTC

Adhesive	Primer	Bond cycle	Exposure	Test temperature, °C (°F)	Glass transition temperature,[a] Tg, °C (°F)
TPI/H2O	TPI/H2O	1	--	RT (RT) 278 (532)	227 (442) 234 (453)
		2	--	RT (RT)	236 (457)
TPI/H2O 50% Mica 5% Cab-o-sil	TPI/H2O	1	--	RT (RT)	229 (444)
		2	--	RT (RT)	238 (460)
TPI/MTC	TPI/MTC	3	Controls	RT (RT) 177 (350) 204 (400)	228 (442) 225 (437) 236 (457)
			500 hrs at 204°C	RT (RT) 177 (350) 204 (400)	242 (468) 242 (468) 237 (459)
			1000 hrs at 204°C	RT (RT) 177 (350) 204 (400)	242 (468) 246 (475) 238 (460)
			72-hr water-boil	RT (RT) 177 (350) 204 (400)	239 (462) 230 (446) 225 (437)
TPI/MTC	TPI/H2O	3	Controls	RT (RT) 177 (350) 204 (400)	221 (430) 214 (417) 215 (419)
			500 hrs at 204°C	RT (RT) 177 (350) 204 (400)	219 (426) 238 (460) 242 (468)
			1000 hrs at 204°C	RT (RT) 177 (350) 204 (400)	241 (466) 240 (464) 243 (469)
			72-hr water-boil	RT (RT) 177 (350) 204 (400)	231 (448)[b] 212 (414)[b] 216 (421)

[a]Single measurements.
[b]Average of two measurements.

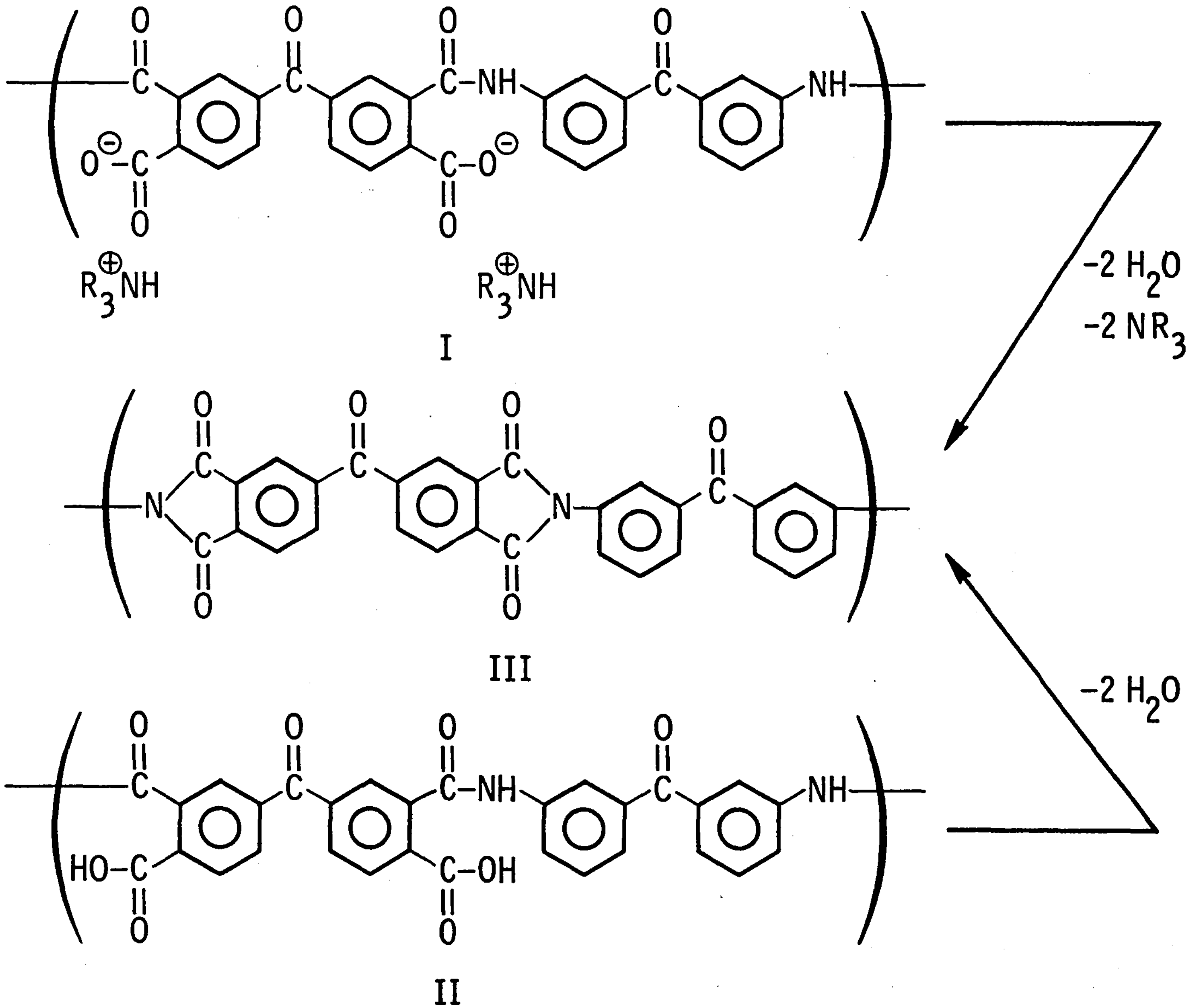

Figure 1. Chemistry for water-soluble version (TPI/H2O), I, and standard polyamic-acid version (TPI/MTC), II, which form LARC-TPI, III.

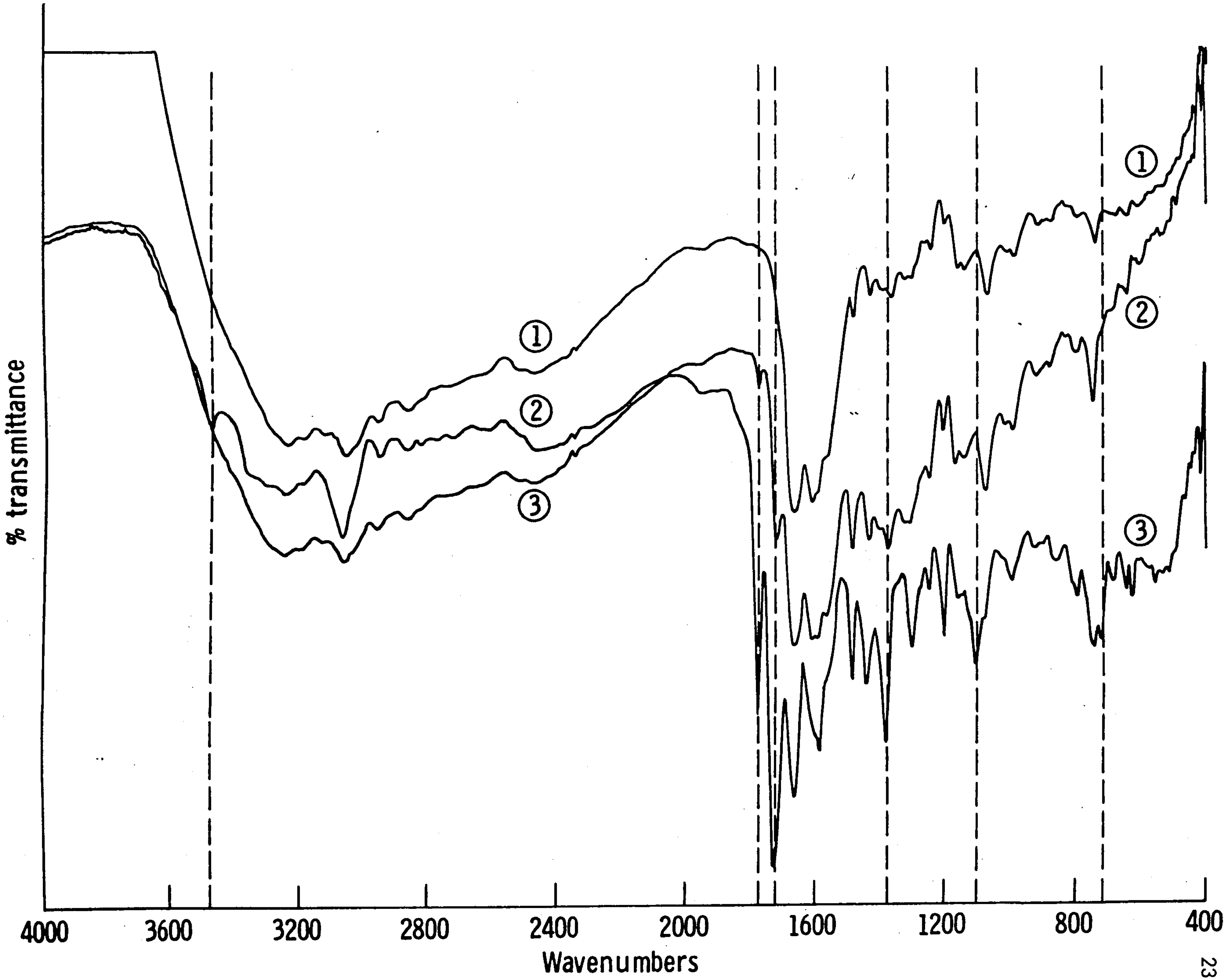

Figure 2. DR-FTIR spectra for TPI/H2O following (1) air-dry, 0.5 hr; (2) 100°C, 0.5 hr; and (3) 150°C, 0.5 hr.

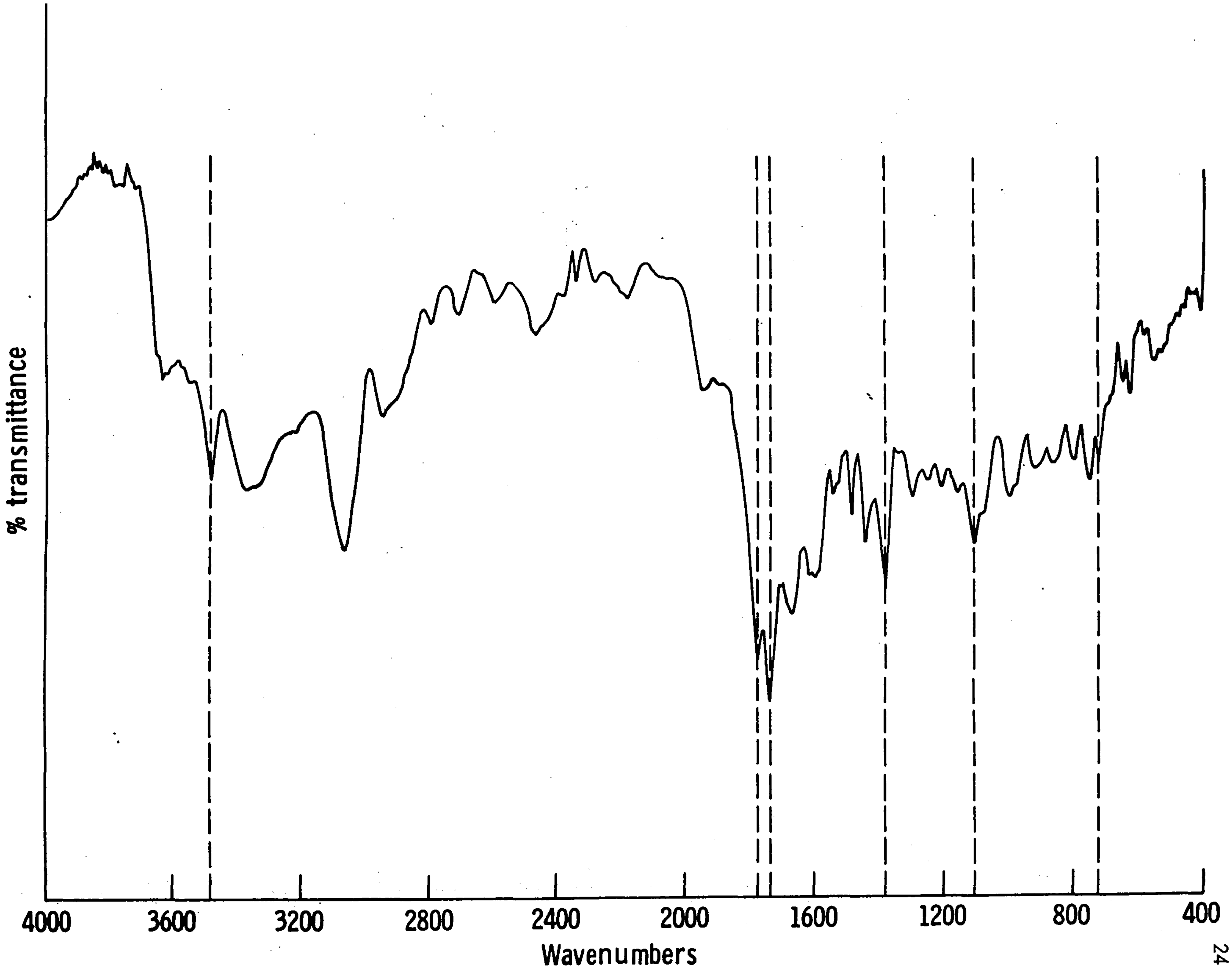

Figure 3. DR-FTIR spectra of fractured TPI/H20 specimen that was bonded for 0.5 hr at 325°C.

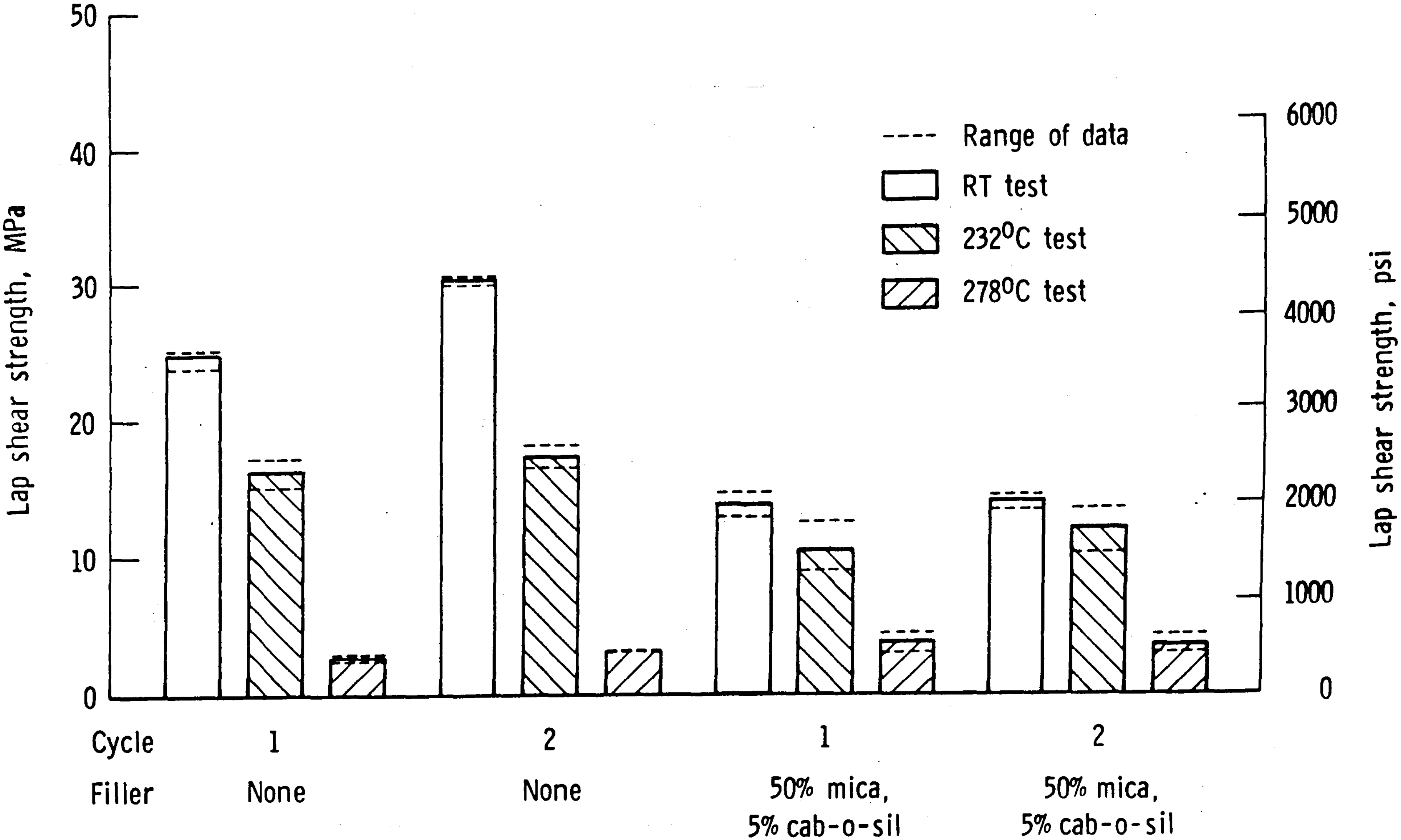

Figure 4. Comparison of lap shear strength at RT, 232°C, and 278°C for TPI/H2O bonded titanium with and without fillers for two bonding cycles.

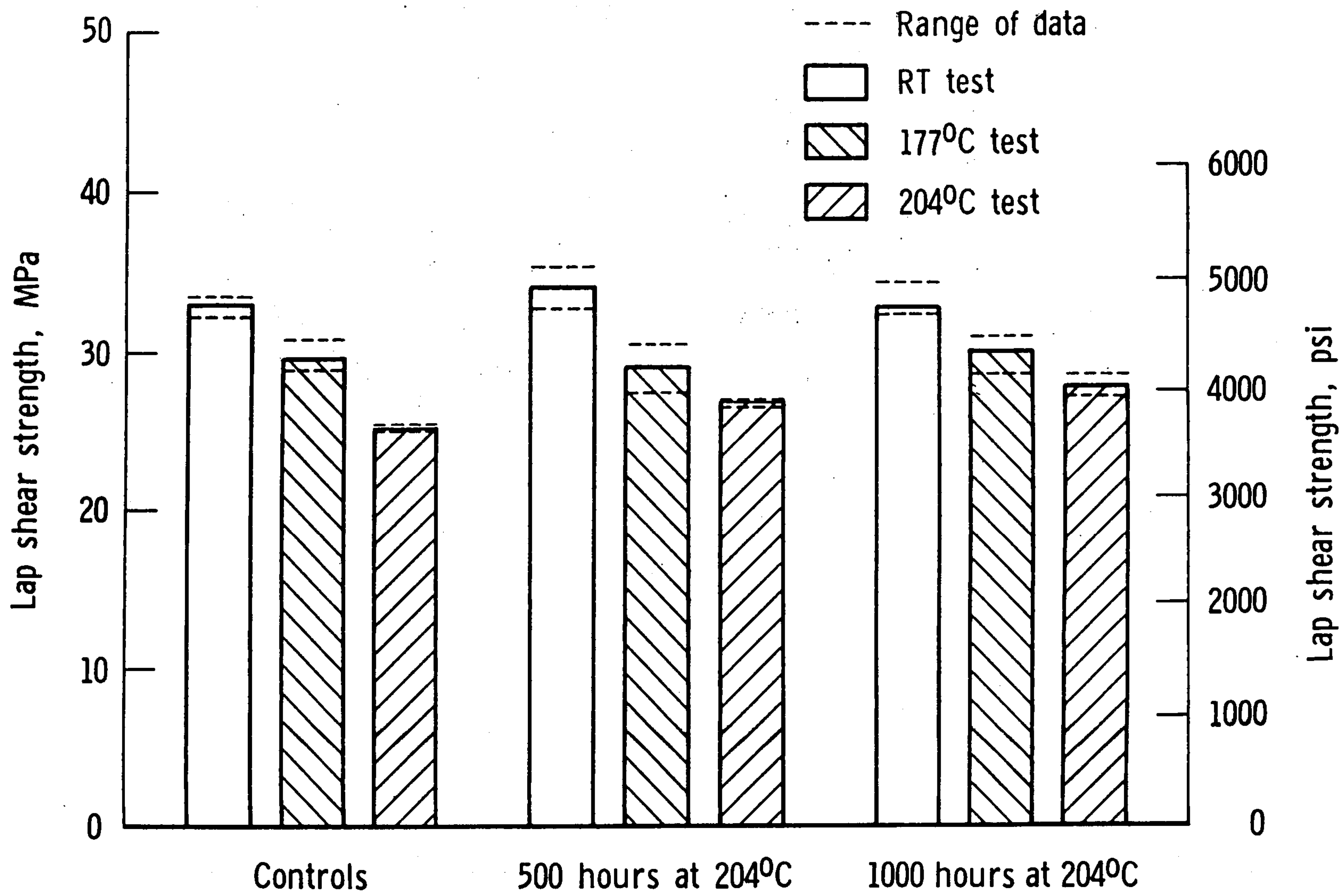

Figure 5. Effects of thermal exposure in air for 500 and 1000 hours at 204°C on lap shear strength for titanium bonded with TPI/MTC adhesive and primer.

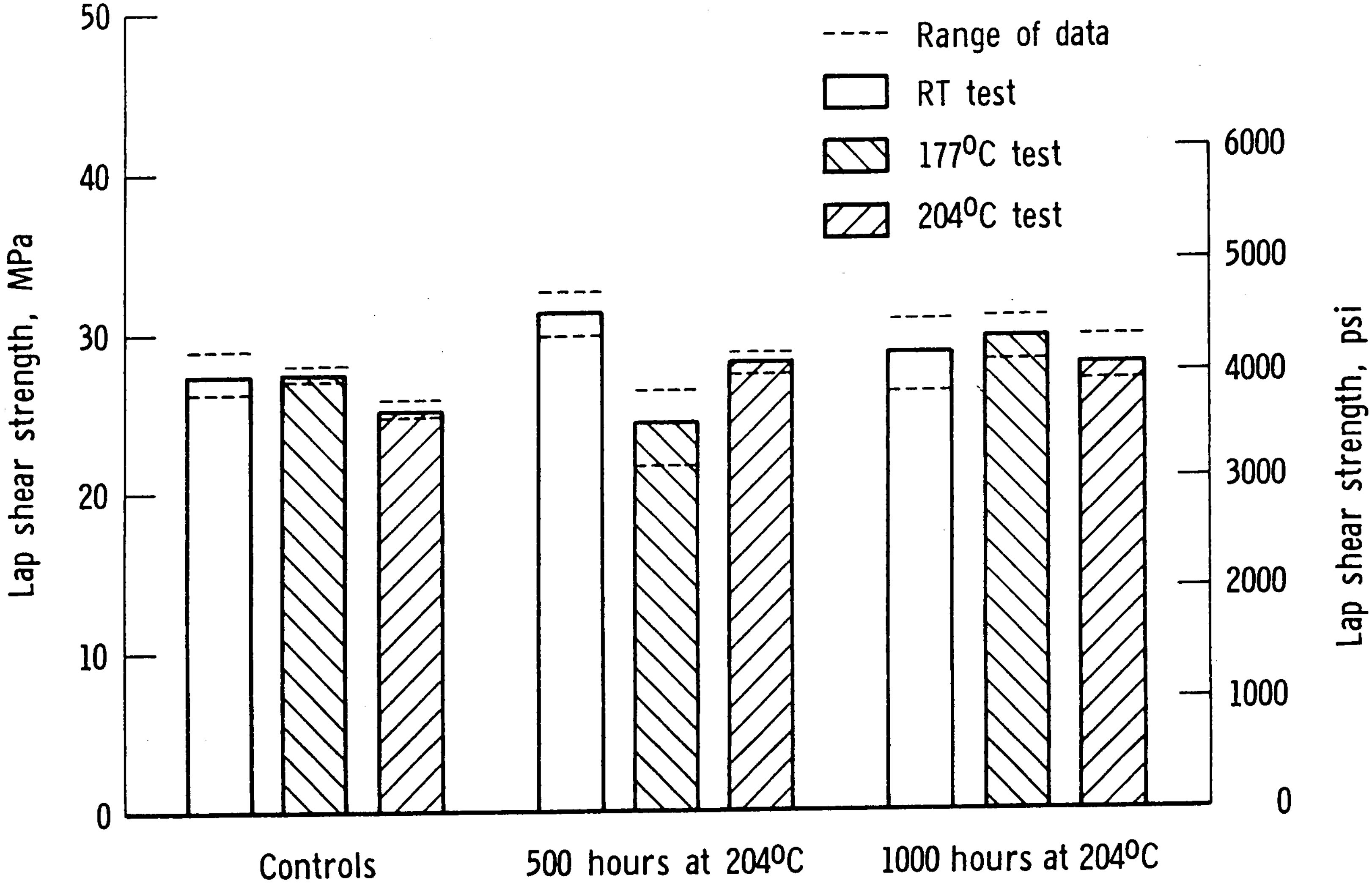

Figure 6. Effects of thermal exposure in air for 500 and 1000 hours at 204°C on lap shear strength for titanium bonded with TPI/MTC adhesive and TPI/H2O primer.

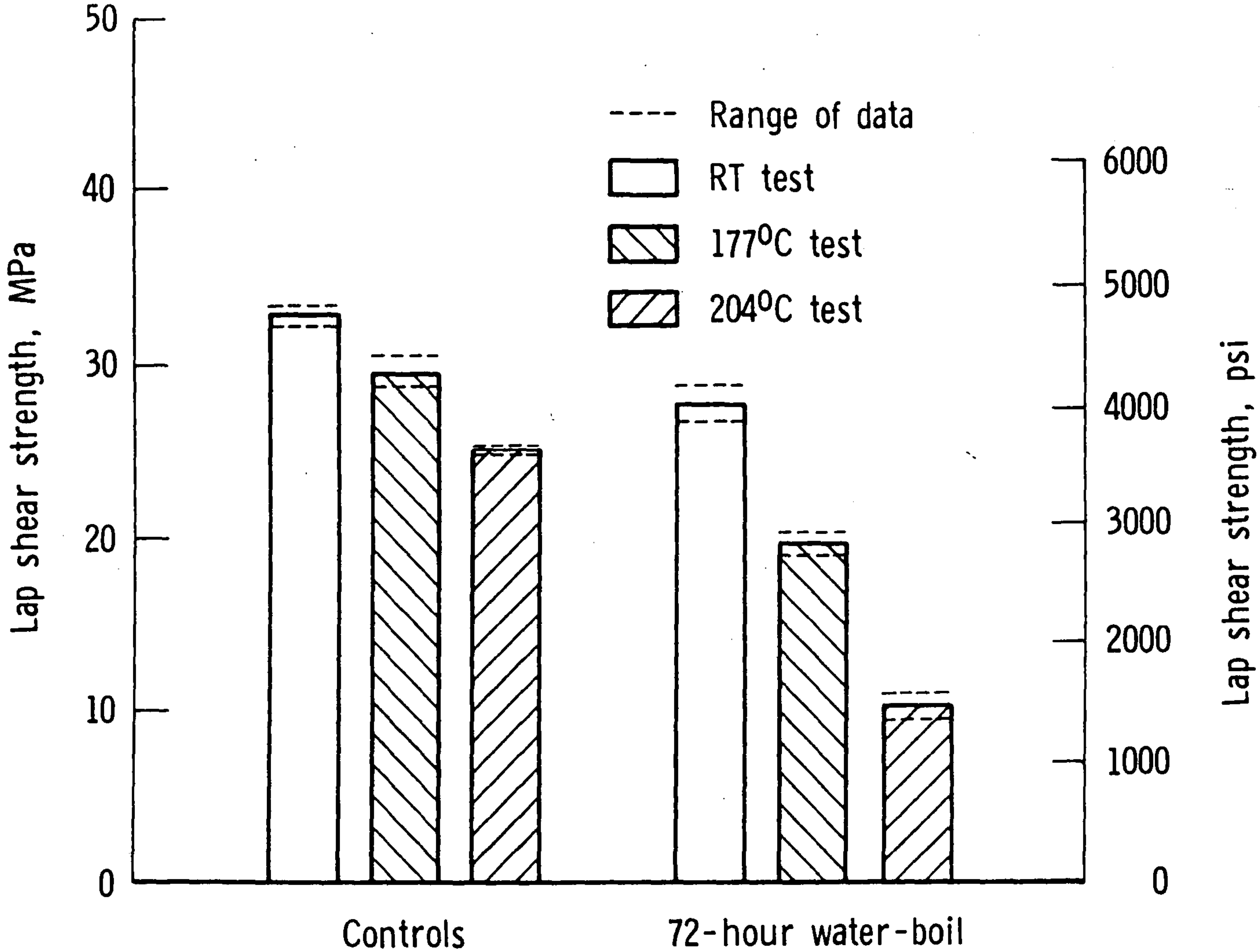

Figure 7. Effect of a 72-hour water-boil on lap shear strength for titanium bonded with TPI/MTC adhesive and primer.

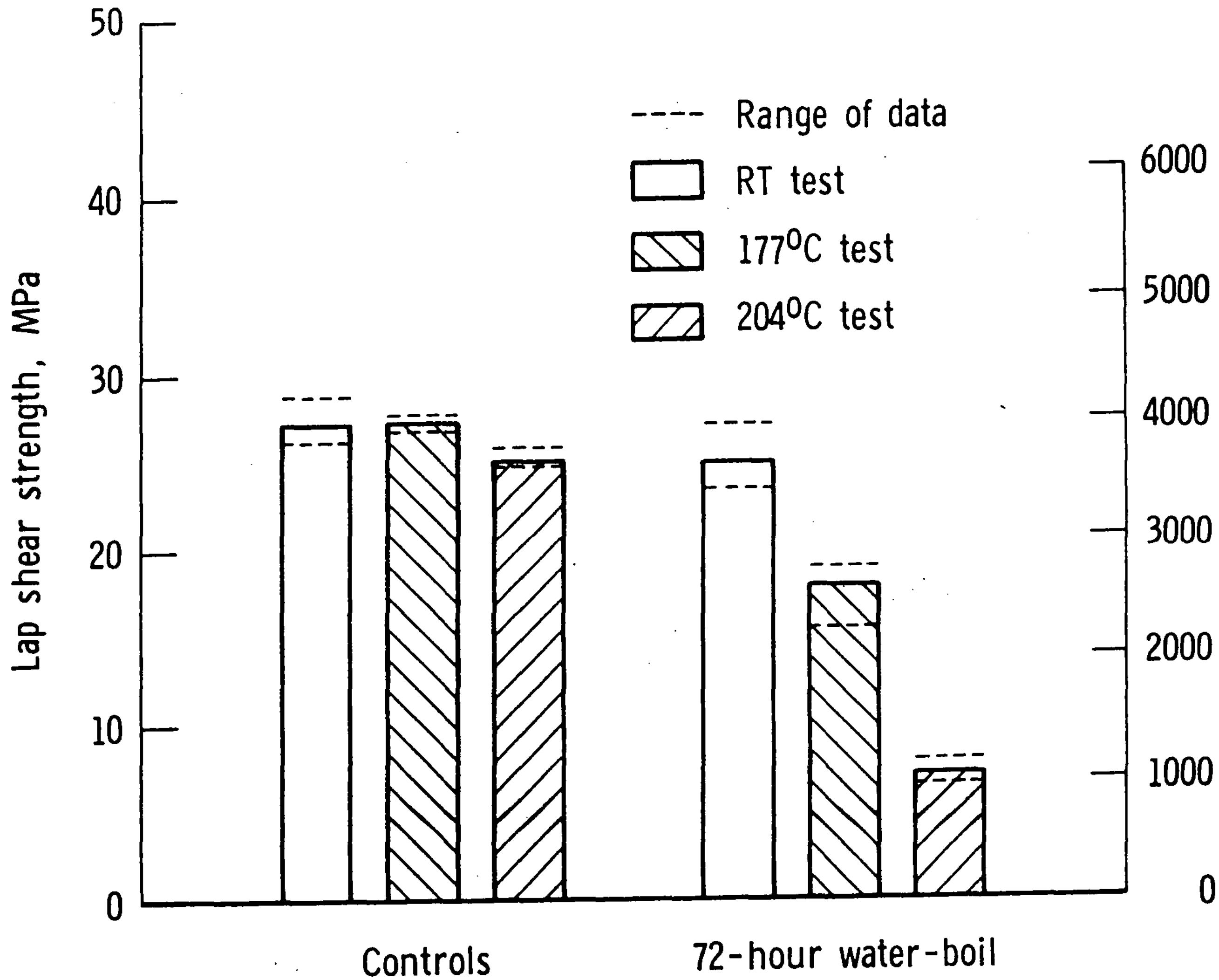

Figure 8. Effect of a 72-hour water-boil on lap shear strength for titanium bonded with TPI/MTC and TPI/H2O primer.

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16. Abstract

A linear thermoplastic polyimide, LARC-TPI, developed several years ago at NASA Langley Research Center showed promise as a high temperature adhesive for application in aircraft and spacecraft based on the material's toughness, flexibility, good thermal and thermo-oxidative stability, and other desirable properties. Since then, a commercial product manufactured and supplied by Mitsui Toatsu Chemicals, Inc., Tokyo, Japan has become available. In addition, a water-soluble version containing N,N-dimethylethanol amine salt was supplied by United Technologies Research Center (UTRC), East Hartford, Connecticut. The water-soluble version is highly attractive because of the safety requirements involved with organic solvents presently used for polyimide materials.

This report details the results of a study to evaluate the two LARC-TPI materials, identified as TPI/MTC for the material from Mitsui Toatsu Chemicals Inc. and TPI/H2O for the material from UTRC, as high temperature thermoplastic adhesives and primers for bonding titanium (6AL-4V) adherends. A limited characterization of the materials was performed using a Diffuse Reflectance-Fourier Transform Infrared Spectroscopy (DR-FTIR) technique. Thermomechanical Analysis (TMA) and torsional braid techniques were used to determine glass transition temperature. The adhesive's strength, as determined by simple lap shear tests, was used to evaluate the effects of long term thermal exposure (up to 1000 hrs) at 204°C and a 72-hour water-boil.

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