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ABSTRACT

Novel thermoplastic polyimides have been prepared and evaluated as adhesives. These materials are based on 4,4'-isophthaloyldiphthalic anhydride (IDPA) and either meta-phenylene diamine (MPD) or 3,3'-diaminobenzophenone (DBAP). Both polymers exhibit excellent adhesive properties; however, the IDPA-MPD is the more attractive system because of a combination of high mechanical and physical properties and because it is formulated from commercially attractive monomers. The IDPA-MPD is an isomeric form of the commercially available adhesive and matrix resin, LARC-TPI, and both systems have the same glass transition temperature and exhibit similiar adhesive properties.

1. INTRODUCTION

During the past decade, high temperature polymer research has been conducted in anticipation of the needs of the aerospace industry. One result of this research was the development of a thermoplastic linear polyimide, LARC-

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TPI (1-4), that exhibits exceptional adhesive properties and is presently commercially available in several forms: films, molding powder, varnish (30% solution) and prepreg. However, the 3,3'-diaminobenzophenone (DABP) component of LARC-TPI is expensive and gives a positive Ames test which makes commercialization difficult. The dianhydride used in preparing LARC-TPI is 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The development of an isomeric thermoplastic polyimide based on 4,4'-isophthaloyldiphthalic anhydride (IDPA) and meta-phenylene diamine (MPD), which retains the properties of LARC-TPI, would be very attractive because of the low cost of the IDPA. This IDPA-MPD composition and a phthalic anhydride (PA) endcapped version [IDPA-MPD (EC 4.00)] have been prepared for this study.

The object of this research was to investigate the adhesive properties of this potentially low cost isomer of LARC-TPI and a similar thermoplastic polyimide formed from IDPA and DABP, referred to as IDPA-DABP in this paper. Evaluation of the polymers' adhesive properties was based on lap shear strength (LSS) tests on bonded titanium alloy. Strength tests were performed at room temperature (RT), 204, and 232°C, before and after a 72-hour water boil and thermal exposure at 204°C for 1000 hrs in a forced-air oven. The results of these tests will be discussed. The chemical structures for the polymers studied are given in Figure 1.

2. EXPERIMENTAL

2.1 Materials and polymerizations

The synthesis of the 4,4'-isophthaloyldiphthalic anhydride has been reported (5). MPD was used as received from Fluka Chemical Corporation.*

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

The DABP was used as received from Mitsui Toatsu Chemicals, Incorporated. Poly(amic acid) solutions were prepared as 20 wt % solids solutions from the diamines in N,N-dimethylacetamide (DMAc), 2-methoxyethyl ether (diglyme) or mixtures of these solvents at 25°C. The following solutions were prepared for evaluation as adhesives and matrix resins.

2.1.1 IDPA-MPD Poly(amic acid), 20 wt % solution in DMAc, no endcap

IDPA (8.000 g, 0.01876 mol) was added to a solution of MPD (2.029 g, 0.01876 mol) in 40.116 g DMAc using a magnetic stirrer and allowed to stir at 25°C over the weekend. The inherent viscosity (η_{inh}) was 0.52 dl/g at 35°C in DMAc.

2.1.2 IDPA-MPD Poly(amic acid), 20 wt % solution in diglyme-DMAc, endcapped with 4.00 mol % PA

A solution of MPD (7.609 g, 0.07036 mol) was prepared in a mixture of 39.00 g diglyme and 111.4 g DMAc. The PA endcap (0.4169 g, 4 mol %) was added while stirring with a magnetic stirrer in a flamed out covered glass jar. After 0.5 hr, the IDPA (30.00 g, 0.07036 mol) was added and the stirring was continued for 3 hrs at ambient temperature. The solution had an η_{inh} of 0.43 dl/g at 35°C in DMAc and was stored in a refrigerator until used.

2.1.3 IDPA-MPD Poly(amic acid), 20 wt % solution in diglyme-DMAc, endcapped with 2.75 mol % PA

This solution was prepared identically as in 2.1.2 except that 0.2866 g (2.75 mol %) of PA was used as the endcap. The η_{inh} was 0.51 dl/g at 35°C in DMAc.

2.1.4 IDPA-DABP Poly(amic acid), 20 wt % solution in diglyme, no endcap

A slurry of IDPA (55.000 g, 0.1290 mol) and DABP (27.3807 g, 0.1290 mol) in 329.52 g diglyme was stirred for 0.75 hr with a magnetic stirrer in a flamed out glass jar. Solution was essentially complete, but stirring was continued with a mechanical stirrer under N_2 overnight to complete the process. The pale tan solution had an η_{inh} of 0.35 dl/g at 35°C in DMAc.

2.2 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 tables. The range of LSSs is indicated by dashed lines in the bar graph figures and is listed 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 except for the water boil tests which 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 0.024 cm for IDPA-MPD, 0.011 cm for IDPA-MPD (EC 4.00), 0.012 cm for IDPA-MPD (EC 2.75), 0.013 cm for IDPA-DABP and 0.009 cm for BTDA-DABP (LARC-TPI).

Glass transition temperatures (Tg) of the BTDA-DABP adhesive taken from the fractured area of the lap shear specimens were determined using a DuPont 990 Thermal Analyzer in conjunction with a DuPont Model 943 Thermal Mechanical Analyzer (TMA). 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. Tgs determined for IDPA-MPD, IDPA-MPD (EC 4.00) and IDPA-DABP were obtained on a DuPont 1090 Thermal Analyzer in conjunction with a Model 910 Differential Scanning Calorimeter (DSC) run at 20°C/min.

Inherent viscosity 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/vol % solids in DMAc was made and filtered. The average of five runs of the solution was reported.

The type of failure was determined visually using a 10X magnification and estimating the percent area of each type of failure, cohesive or adhesive.

2.3 Adhesive tape preparation

Adhesive tapes for IDPA-MPD, IDPA-MPD (EC 2.75) and IDPA-MPD (EC 4.00) were prepared by brush coating a primer solution of poly(amic acid), diluted to approximately 7.5 wt % solids in DMAc, onto 112 E-glass cloth with A-1100 finish (γ-aminopropylsilane). The glass cloth had been tightly mounted on a metal frame and dried in a forced-air oven for 30 min at 100°C prior to coating. The 0.01 cm thick glass cloth served as a carrier for the adhesive as well as for bondline control and an escape channel for solvent. The coated cloth was then air-dried for 1 hr at ambient temperature and heated for 30 min at each of three temperatures: 100, 150 and 175°C. Subsequently, each application of a 20 wt % solids solution [IDPA-MPD, ηinh 0.52 dl/g; IDPA-MPD (EC 2.75), 0.51 dl/g; IDPA-MPD (EC 4.00), 0.43 dl/g] was brush coated onto the cloth and exposed to the following schedule until a thickness of approximately 0.03 cm was obtained:

(1) Room temperature, held ~ 15 min; heated in a forced-air oven for 15 min at ~ 50°C

(2) RT → 100°C, held 30 min

(3) 100°C → 150°C, held 30 min

(4) 150°C → 175°C, held 30 min

The yellow colored adhesive tape produced possessed no tack or drape and was stiff and boardy.

The IDPA-DABP adhesive tape preparation was slightly different. A 20 wt % solids solution of IDPA-DABP poly(amic acid) in diglyme, η_{inh} 0.35 dl/g, was used to coat the glass cloth. After each of five applications of the 20 wt % solids solution, the tape was exposed to the following schedule:

(1) RT, held 30 min

(2) RT → 50°C, held 15 min

(3) Heat to 175°C in 25°C increments, each held 15 min

(4) 175°C, held 15 min

(5) 175°C → 275°C, held 2 hrs

The yellow colored tape produced was slightly foamy and possessed no tack or drape.

The involved procedure to prepare the tapes was necessary to drive-off solvent and reaction product volatiles when converting the poly(amic acid) resin to the polyimide. Imidization of poly(amic acids) to polyimides generally occurs above 160°C with the degree of conversion being a function of time and temperature.

2.4 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

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

20 wt % poly(amic 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 dried primer coating was < 0.013 cm thick. The primed adherends were placed in a polyethylene bag and stored in a desiccator until needed. Lap shear specimens were prepared by inserting the adhesive tape between the primed adherends using a 1.27 cm overlap (ASTM D-1002) and applying 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 were investigated for each adhesive during this study to determine a bonding process which would produce good strengths. The bonding pressure was varied from 0.34 MPa to 3.45 MPa, whereas the heating rate (8°C/min), bonding temperature and time-held-at bonding temperature (1 hr) were kept the same. Samples were cooled under pressure to ~ 150°C and removed from the bonding press. LSS tests were conducted at RT, 204 and 232°C.

Thermal exposures at 204°C for 1000 hrs were performed in a forced-air oven controlled to within ± 2°C. Lap shear tests were conducted at RT, 204 and 232°C before (initial or control) and after thermal exposure.

In order to determine the effects of humidity on an adhesive, a 72-hr water boil was performed in laboratory glassware containing distilled boiling water. The bonded area of the lap shear specimens was immersed during the 72-hr period. LSSs were subsequently determined at RT, 204 and 232°C.

These three adhesive systems, IDPA-MPD, IDPA-MPD (EC 4.00), and IDPA-DBAP, were compared with results previously reported for LARC-TPI (6,7). An IDPA-MPD system with less endcapping was dropped from our study in favor of the four percent system because of lower flow.

3. RESULTS AND DISCUSSION

3.1 Resin Chemistry

The synthesis of the IDPA is outlined in Figure 2 (5). O-xylene and isophthaloyldichloride were reacted in a Friedel-Crafts synthesis to produce the tetramethylaryldiketone. This intermediate was then oxidized in a pressure reactor by incrementally adding nitric acid, followed by chemically dehydrating the tetracarboxylic acid to the dianhydride. This three step reaction afforded a 69% yield of polymer grade IDPA. Polymerizations have been described in the Experimental section. End-capping, when used to control molecular weight, was conducted with PA.

3.2 Bonding conditions

The bonding conditions investigated for the IDPA-MPD adhesive are given in Table I and Figure 3 with the results of the lap shear tests. A heating rate of 8°C/min and a bonding temperature of 343°C for 1 hr were used together with a bonding pressure of either 2.07 MPa or 3.45 MPa. Also given in Table I are the number of specimens tested, the primary type of failure and the Tg, determined by DSC on the adhesive taken from "outside" the bond area. Results are expressed in graphical form for those interested in obtaining a quick pictorial summary of the results and in tabular form for those interested in more detailed information. No significant difference in LSS values was evident for the three test temperatures due to the two bonding pressures investigated. The strengths for any one test temperature were essentially the same - RT (18.5 and 18.8 MPa), 204°C (22.9 and 22.4 MPa) and 232°C (20.8 and 19.6 MPa). Past experience with these types of thermoplastic polyimides has shown a beneficial affect when heating the adhesive tape to higher temperatures for a period of time (8). Therefore, the adhesive tape was given an additional heat treatment of 1 hr at 250°C before bonding. In this case, the results indicate no improvement in strengths and actually provided slightly lower strengths. Ideally one would prefer cohesive type failures; however, as given in Table I, all failures at RT were adhesive. The failures were cohesive at 232°C. The color of the adhesive changed from yellow (before bonding) to dark brown (after bonding). Tg did not change significantly for these bonding conditions.

Since there were no significant differences in the results of bonding with either 2.07 MPa or 3.45 MPa, and 2.07 MPa had been used for the BTDA-DABP (LARC-TPI), 2.07 MPa was chosen for the IDPA-MPD adhesive to bond specimens for the thermal aging and water boil studies.

Test results are given in Table II and Figure 4 for IDPA-MPD (EC 4.00) bonded titanium. Bonding pressures investigated were 0.34, 0.69 and 2.07 MPa. The other bonding conditions were the same as used for IDPA-MPD. A general decrease in LSS was shown with increasing test temperature for each bonding condition. The high RT LSS values, 27.0 to 29.4 MPa, were within the scatter band of the test data and, therefore, show no effect due to the bonding pressure. A significant increase in LSSs at 204°C and 232°C was shown when pressure was increased from 0.34 MPa to 0.69 MPa (204°C, 17.1 MPa to 24.1 MPa; 232°C, 12.8 MPa to 17.5 MPa). The strengths of those bonded with 2.07 MPa were essentially the same as those bonded with 0.69 MPa pressure. All failures were cohesive but included small voids in the bondline. The color of the adhesive changed from yellow (before bonding) to dark brown (after bonding). Again, Tg did not change. The process using 2.07 MPa was selected because the results are basically the same as for the 0.69 MPa and a better comparison can be made with the IDPA-MPD results.

The results on the effect of the bonding pressures, 2.07 MPa and 3.45 MPa for the IDPA-DABP adhesive, are given in Table III and Figure 5. Excellent RT and 204°C LSSs were obtained; however, those bonded with 3.45 MPa were higher than those bonded with 2.07 MPa; RT, 34.4 MPa compared to 30.4 MPa; 204°C, 27.0 MPa compared to 21.2 MPa. Those tested at 232°C were tested above the measured Tg (~ 221°C) of the adhesive and failed thermoplastically with poor results. All failures were cohesive except for those that failed thermoplastically. Some small voids were found in the bondlines. Since those bonded at a pressure of 3.45 MPa produced the higher strengths at RT and 204°C, this was the pressure chosen to bond succeeding lap shear specimens.

3.3 Initial lap shear strengths

The initial LSS values for the three adhesives of the present study and those for BTDA-DABP reported in literature are given in Table IV and Figure 6. When comparing IDPA-MPD, a homopolymer, with the PA endcapped version IDPA-MPD (EC 4.00) which has a lower molecular weight than IDPA-MPD, the RT LSS was significantly higher for the IDPA-MPD (EC 4.00) than for the IDPA-MPD, 29.4 MPa compared to 18.5 MPa. No significant difference was found for the 204°C tests with both having a high LSS, 22.9 MPa and 24.5 MPa. The IDPA-MPD strengths are slightly higher at 232°C than the IDPA-MPD (EC 4.00), 20.8 MPa compared to 18.0 MPa. These results indicate that control of the molecular weight by endcapping improves the RT and 204°C strengths and slightly reduces the 232°C strength. The Tg was 11°C lower due to the endcapping, 258°C versus 269°C. Failures were cohesive at 204 and 232°C.

The IDPA-DABP LSSs were excellent at RT (34.4 MPa) and 204°C (27.0 MPa) but were greatly reduced at 232°C (5.3 MPa) due to the low Tg, ~ 221°C, which, in this case, caused a thermoplastic failure. The failures were cohesive at RT and 204°C.

Results for BTDA-DABP, produced in our laboratory and reported earlier (6,7), are reproduced here for comparison since the IDPA-MPD polymer is the isomer of this tough, flexible, thermooxidatively stable, solvent resistant, thermoplastic polyimide. A particular drawback, of course, is its relatively high cost, whereas IDPA-MPD is a potentially inexpensive polyimide. The LSS values for all three test temperatures were excellent: RT, 33.0 MPa; 204°C, 25.2 MPa; and 232°C, 17.5 MPa. The Tg determined by TMA and reported here for BTDA-DABP (225-236°C) is lower than that of an earlier reported Tg (260°C) determined by DSC on a film previously heated for 1 hr each at 100, 200 and 300°C (7). The LSSs for IDPA-MPD (EC 4.00) are similar to the initial LSSs of the BTDA-DABP adhesive.

3.4 Thermal exposure

Lap shear specimens of each adhesive were thermally exposed in a forced-air oven at 204°C for 1000 hrs. LSS tests were performed at RT, 204 and 232°C before and after exposure. Results are given in Table V and Figure 7 for the 1000 hr exposure. In the following, the results are compared with the initial LSSs found in Table IV and Figure 6.

LSSs for IDPA-MPD after exposure were slightly lower, retaining ~ 92% of the initial strength at RT, 86% at 204°C and 86% at 232°C. The type of failure at 204°C changed from cohesive to adhesive whereas failures at RT (adhesive) and 232°C (cohesive) remained the same. These percentages of strength retention are reasonably high and indicate promise for IDPA-MPD as an adhesive. However, IDPA-MPD (EC 4.00) shows even more promise since the initial strengths were as high or higher than IDPA-MPD and it retained 94% of its RT strength and even increased to 110% of its initial strength at 204°C and

112% at 232°C. All specimens failed cohesively for the three test temperatures both initially and after thermal exposure except for the initial RT test for IDPA-MPD which was an adhesive failure.

The IDPA-DABP specimens retained 91% and 86% of the initial RT and 204°C strengths, respectively, but still had poor strength at 232°C. Tgs were not determined after the thermal exposure, but, in some cases, they have been shown to increase due to the extended high temperatures which can result in an increase in LSSs. Apparently, this wasn't the case for this material since the strength remained the same as the initial strength. The failure changed from thermoplastic to an adhesive type failure.

The LSS for BTDA-DABP remained the same for the RT test but increased for the 204°C test (25.2 MPa to 27.8 MPa) and the 232°C test (17.5 MPa to 23.3 MPa). The data for the 232°C test was actually obtained on samples thermally exposed for 2260 hrs at 232°C, this being a more severe test than the 1000 hrs at 204°C and yet the strength increased.

The general results of the thermal exposure study indicates that the IDPA-MPD (EC 4.00) adhesive shows good adhesive performance. Because of its potential lower cost than BTDA-DABP, this new adhesive appears to be a candidate for future high temperature aerospace applications.

3.5 72-Hour water boil

The resistance of the three new adhesive systems to water (humidity) was assessed by immersing lap shear specimens in distilled boiling water for a 72-hr period and subsequently testing their LSS at RT, 204 and 232°C. Results of the present study of the three new materials along with earlier reported results of BTDA-DABP are given in Table VI and Figure 8. For comparison, initial strengths are given in Table IV and Figure 6. All adhesive systems showed greatly reduced LSSs after the 72-hr water boil with the percent of reduction increasing with increasing test temperature for each adhesive.

The RT LSS was retained for IDPA-MPD but only 46% of the 204°C strength and 11% of the 232°C strength was retained. The 10.5 MPa strength at 204°C is still usable; however, the 2.3 MPa value at 232°C is very low. The type of failure "after water boil" was all adhesive, whereas, they were initially cohesive for the 204°C and 232°C tests.

The LSS values after water boil were all significantly higher for the IDPA-MPD (EC 4.00) adhesive system than for the IDPA-MPD adhesive system. After water boil, IDPA-MPD (EC 4.00) retained 89% (26.2 MPa) of the initial RT strength, 67% (16.5 MPa) of the 204°C strength and 43% (7.8 MPa) of the 232°C strength. Failures were still cohesive except for the 232°C tests which were cohesive/adhesive failures.

The IDPA-DABP adhesive system retained 91% (31.2 MPa) of the initial RT strength but provided a greatly reduced strength for the 204°C test after water boil, 27.0 MPa to 4.9 MPa. The 232°C strength was poor both before water boil, 5.3 MPa and after water boil, 3.3 MPa. The failure was still cohesive at RT but changed from cohesive to thermoplastic type failure at 204°C. The failure at 232°C was the same as the initial test failure, thermoplastic.

The reported results for the water boil tests for BTDA-DABP followed that of the other adhesive systems - reduced strengths for each test temperature (6). The percent of strengths retained at RT, 204 and 232°C were 84, 40 and 30%, respectively. Though greatly reduced from the initial strength at 204°C, the 10.1 MPa is still a usable strength for some applications. Failures were cohesive at RT and 204°C but were thermoplastic at 232°C and probably due to plasticization of the polymer by the water.

The water boil test had a profound effect on the LSS of all the adhesive systems investigated and greatly reduced the strengths for the 204°C and 232°C tests. Also, in some cases, the failures were changed from cohesive to a thermoplastic type failure indicating plasticization of the polymer by water. After water boil, the highest LSS value at RT was 31.2 MPa for the IDPA-DABP adhesive system. IDPA-MPD (EC 4.00) had the highest LSS at 204°C, 16.5 MPa and at 232°C, 7.8 MPa. When comparing the results of the water boil test, the IDPA-MPD (EC 4.00) appears to provide better overall results than the BTDA-DABP adhesive system as well as the IPDA-MPD and IPDA-DABP adhesive systems.

4.0 SUMMARY

Two new polyimide adhesives have been synthesized and evaluated as adhesives on titanium adherends. Both exhibit potential for future aerospace applications; however, an endcapped version of one system, IDPA-MPD (EC 4.00), has overall properties that are slightly better than BTDA-DABP. In addition this material can be prepared from the relatively inexpensive MPD and a dianhydride that should have a reasonable price structure if prepared in large volumes.

The evaluation of the new polymers as adhesives, primarily based on the lap shear strength (LSS) tests, involved preparing adhesive tapes, conducting bonding studies and exposing lap shear specimens in air at 204°C for 1000 hrs and in boiling water for 72 hrs. LSS tests of bonded Ti-6Al-4V adherend specimens at RT, 204 and 232°C were performed before (initial or control) and after these exposures. The type of failure, as well as the glass transition temperature, Tg, was determined for the fractured specimens.

Of the three adhesive polymers, IDPA-MPD, IDPA-MPD (EC 4.00) and IDPA-DABP, the IDPA-MPD (EC 4.00) shows the best promise as a high temperature adhesive. The IPDA-MPD (EC 4.00) adhesive retained 94% (27.7 MPa) of its initial RT strength after thermal exposure and increased in strength for the 204°C test, 27.0 MPa and the 232°C test, 20.2 MPa. All specimens failed cohesively for the three test temperatures both initially and after thermal exposure.

The 72-hr water boil greatly reduced the 204°C and 232°C LSSs for all three new polymer adhesive systems. In some cases, the failures were thermoplastic, indicating the probable effect of water plasticization of the polymer. After water boil, the IDPA-DABP adhesive provided the highest RT LSS value, 31.2 MPa, whereas, IDPA-MPD (EC 4.00) produced the highest LSS at 204°C, 16.5 MPa and 232°C, 7.8 MPa.

The endcapping of the IDPA-MPD with 4 wt % PA, which controls the molecular weight and, therefore, its flow properties, also improved its adhesive performance at elevated temperatures to both thermal exposure in air at 204°C and to water boil for a 72-hr period.

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Table I. LSS results for IDPA-MPD bonded Ti-6Al-4V

Bonding[a] pressure [MPa (psi)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode[b]	Glass transition temperature, T_g[c] [°C (°F)]
2.07 (300)	4	RT (RT)	18.5 (2860)	15.5-20.8 (2260-3020)	Ad	269 (516)
	4	204 (400)	22.9 (3320)	21.2-24.8 (3080-3600)	Co	
	4	232 (450)	20.8 (3020)	18.8-21.8 (2720-3170)	Co	
3.45 (500)	4	RT (RT)	18.8 (2730)	15.8-20.5 (2300-2980)	Ad	270 (518)
	4	204 (400)	22.4 (3240)	20.9-24.8 (3030-3600)	Co/Ad	
	4	232 (450)	19.6 (2840)	17.4-21.5 (2520-3120)	Co	
3.45 (500)[d]	4	RT (RT)	16.4 (2370)	15.0-17.8 (2180-2580)	Ad	268 (514)
	4	204 (400)	18.7 (2710)	16.5-20.2 (2400-2920)	Co/Ad	

a Bonding conditions: "bonding pressure" from start, heating rate of 8°C/min (14°F/min) RT → 343°C (650°F), held 1 hr.

b Cohesive - Co, adhesive - Ad.

c Determined by DSC of the adhesive taken "outside" the bond area.

d Adhesive tape given an additional heat treatment of 1 hr at 250°C before bonding.

Table II. LSS results for IDPA-MPD (EC 4.00) bonded Ti-6Al-4V

Bonding [a] pressure [MPa (psi)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode [b]	Glass transition temperature, T_g [c] [°C (°F)]
0.34 (50)	4	RT (RT)	27.0 (3910)	25.2-28.8 (3660-4180)	Co	259 (498)
	4	204 (400)	17.1 (2480)	16.2-17.8 (2350-2580)	Co	
	4	232 (450)	12.8(1860)	11.4-14.1 (1650-2040)	Co	
0.69 (100)	4	RT (RT)	28.5 (4140)	28.0-29.6 (4070-4290)	Co	259 (498)
	4	204 (400)	24.1 (3490)	23.4-24.9 (3390-3610)	Co	
	4	232 (450)	17.5 (2540)	16.7-18.0 (2420-2610)	Co	
2.07 (300)	5	RT (RT)	29.4 (4260)	27.3-32.4 (3960-4700)	Co	258 (496)
	4	204 (400)	24.5 (3560)	23.1-25.5 (3350-3700)	Co	
	5	232 (450)	18.0 (2610)	14.3-19.6 (2070-2850)	Co	

a Bonding conditions: "bonding pressure" from start, heating rate of 8°C/min (14°F/min), RT → 343°C (650°F), held 1 hr.

b Cohesive - Co

c Determined by DSC of the adhesive taken "outside" the bond area.

Table III. LSS results for IDPA-DABP bonded Ti-6Al-4V

Bonding pressure [a] [MPa (psi)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode [b]	Glass transition temperature, T_g [c] [°C (°F)]
2.07 (300)	4	RT (RT)	30.4 (4410)	28.6-31.9 (4150-4630)	Co	222 (432)
	4	204 (400)	21.2 (3070)	18.8-24.6 (2720-3570)	Co	
	4	232 (450)	5.1 (740)	4.8-5.4 (700-780)	TP	
3.45 (500)	4	RT (RT)	34.4 (4490)	33.6-35.4 (4880-5130)	Co	221 (430)
	4	204 (400)	27.0 (3920)	26.0-28.3 (3780-4110)	Co	
	4	232 (450)	5.3 (770)	4.8-6.0 (700-870)	TP	

a Bonding conditions: "bonding pressure" from start, heating rate of 8°C/min (14°F/min), RT → 343°C (650°F), held 1 hr.

b Cohesive - Co, thermoplastic - TP.

c Determined by DSC of the adhesive taken "outside" the bond area.

Table IV. Initial lap shear strengths of polyimide adhesive bonded Ti-6Al-4V

Adhesive	Bonding pressure [a] [MPa (psi)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode [b]	Glass transition temperature, T_g [c] [°C (°F)]
IDPA-MPD	2.07 (300)	4	RT (RT)	18.5 (2680)	15.5-20.8 (2260-3020)	Ad	269 (516)
		4	204 (400)	22.9 (3320)	21.2-24.8 (3080-3600)	Co	
		4	232 (450)	20.8 (3020)	18.8-21.8 (2720-3170)	Co	
IDPA-MPD (EC 4.00)	2.07 (300)	5	RT (RT)	29.4 (4260)	27.3-32.4 (3960-4700)	Co	258 (496)
		4	204 (400)	24.5 (3560)	23.1-25.5 (3350-3700)	Co	
		5	232 (450)	18.0 (2610)	14.3-19.6 (2070-2850)	Co	
IDPA-DABP	3.45 (500)	4	RT (RT)	34.4 (4990)	33.6-35.4 (4880-5130)	Co	221 (430)
		4	204 (400)	27.0 (3920)	26.0-28.3 (3780-4110)	Co	
		4	232 (450)	5.3 (770)	4.8-6.0 (700-870)	TP	
BTDA-DABP (LARC-TPI)	2.07 (300)	4	RT (RT)	33.0 (4790)	32.3-33.5 (4680-4860)	Co	228 (442) [d]
		4	204 (400)	25.2 (3660)	25.0-25.4 (3620-3690)	Co	236 (457) [d]
		8	232 (450)	17.5 (2540)	14.8-19.7 (2150-2860)	Co	225 (437) [d]

a Bonding conditions: "bonding pressure" from start, heating rate of 8°C/min (14°F/min), RT → 343°C (650°F), held 1 hr.

b Cohesive - Co, adhesive - Ad, thermoplastic - TP.

c Determined by DSC of the adhesive taken "outside" the bond area.

d Determined by TMA.

Table V. LSS test results of thermal exposure in air at 204°C for bonded Ti-6Al-4V

Adhesive	Bonding pressure [a] [MPa (psi)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode [b]	Glass transition temperature, T_g [c] [°C (°F)]
IDPA-MPD	2.07 (300)	4	RT (RT)	17.0 (2460)	14.8-19.0 (2150-2750)	Ad	269 (516)
		4	204 (400)	19.8 (2880)	17.3-22.0 (2510-3190)	Ad	
		4	232 (450)	17.8 (2580)	16.5-19.1 (2390-2770)	Co	
IDPA-MPD (EC 4.00)	2.07 (300)	4	RT (RT)	27.7 (4010)	25.8-29.4 (3750-4270)	Co	258 (496)
		8	204 (400)	27.0 (3910)	25.3-27.9 (3670-4050)	Co	
		4	232 (450)	20.2 (2930)	19.8-20.7 (2880-3000)	Co	
IDPA-DABP	3.45 (500)	4	RT (RT)	31.2 (4520)	30.3-32.4 (4400-4700)	Co	221 (430)
		4	204 (400)	23.2 (3360)	21.5-24.5 (3120-3550)	Co	
		3	232 (450)	5.7 (830)	5.2-6.1 (760-890)	Ad	
BTDA-DABP (LARC-TPI)	2.07 (300)	4	RT (RT)	32.9 (4780)	32.3-34.4 (4690-4980)	Co	242 (468) [e]
		4	204 (400)	27.8 (4015) [d]	27.2-28.6 (3940-4160)	Co	246 (475)
		3	232 (450)	23.3 (3380)	21.8-24.5 (3160-3550)	Co	238 (460)

a Bonding conditions: "bonding pressure" from start, heating rate of 8°C/min (14°F/min), RT → 343°C (650°F), held 1 hr.

b Cohesive - Co, adhesive - Ad.

c Determined by DSC of the adhesive taken "outside" the bond area of specimens not thermally exposed.

d Thermally exposed in air at 232°C for 2260 hr.

e Determined by TMA on tested thermally exposed specimens.

Table VI. LSS test results of a 72-hour water boil for bonded Ti-6Al-4V

Adhesive	Bonding pressure [a] [MPa (psi)]	Number of specimens	Test temperature [°C (°F)]	Average LSS [MPa (psi)]	Range of LSS [MPa (psi)]	Primary failure mode [b]	Glass transition temperature, T_g [c] [°C (°F)]
IDPA-MPD	2.07 (300)	3	RT (RT)	19.0 (2760)	18.1-20.5 (2620-2980)	Ad	269 (516)
		4	204 (400)	10.5 (1530)	9.5-11.6 (1380-1680)	Ad	
		4	232 (450)	2.3 (330)	1.7-2.9 (250-420)	Ad	
IDPA-MPD (EC 4.00)	2.07 (300)	4	RT (RT)	26.2 (3800)	25.2-26.7 (3650-3870)	Co	258 (496)
		4	204 (400)	16.5 (2400)	12.6-21.1 (1830-3060)	Co	
		3	232 (450)	7.8 (1140)	6.9-9.0 (1000-1300)	Co/Ad	
IDPA-DABP	3.45 (500)	4	RT (RT)	31.2 (4520)	30.0-32.5 (4360-4720)	Co	221 (430)
		6	204 (400)	4.9 (710)	4.1-6.2 (590-900)	TP	
		2	232 (450)	3.3 (480)	3.2-3.4 (460-500)	TP	
BTDA-DABP (LARC-TPI)	2.07 (300)	4	RT (RT)	27.8 (4030)	26.7-28.8 (3870-4180)	Co	239 (462) [d]
		4	204 (400)	10.1 (1470)	9.4-11.0 (1360-1600)	Co	225 (437) [d]
		4	232 (450)	5.2 (720)	4.6-5.6 (670-810)	TP	--

a Bonding conditions: "bonding pressure" from start, heating rate of 8°C/min (14°F/min), RT → 343°C (650°F), held 1 hr.

b Cohesive - Co, adhesive - Ad, thermoplastic - TP.

c Determined by DSC of the adhesive taken "outside" the bond area on specimens not exposed.

d Determined by TMA on tested exposed specimens.

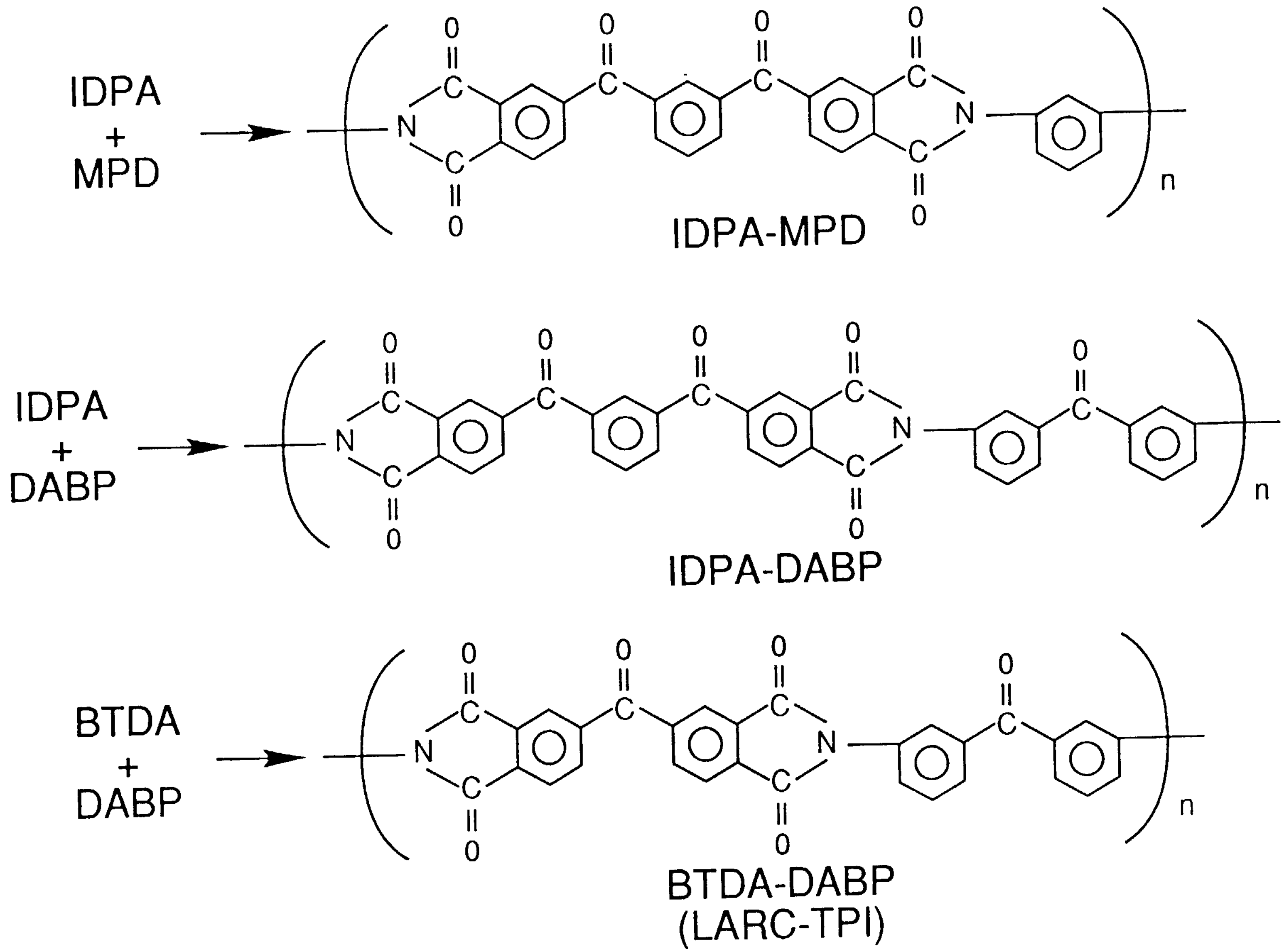


Figure 1. Chemical structure of polymers.

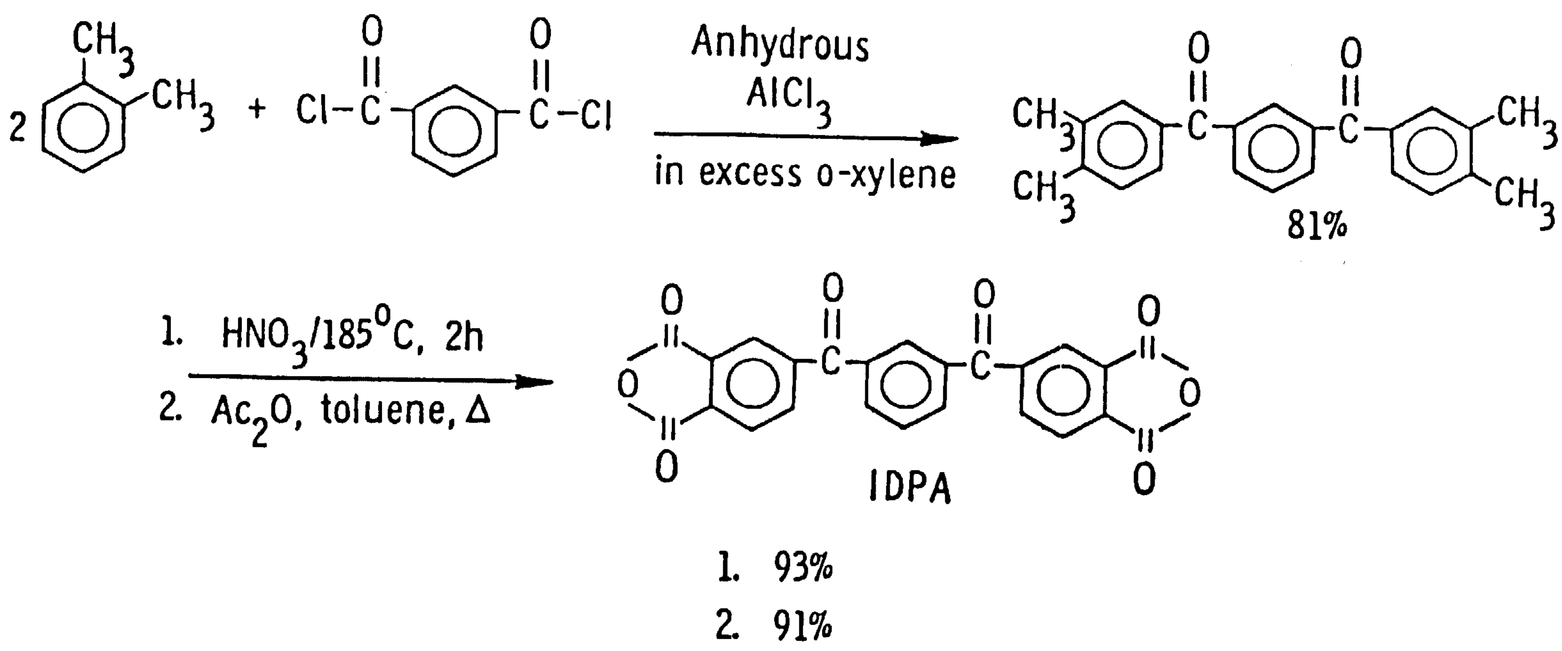
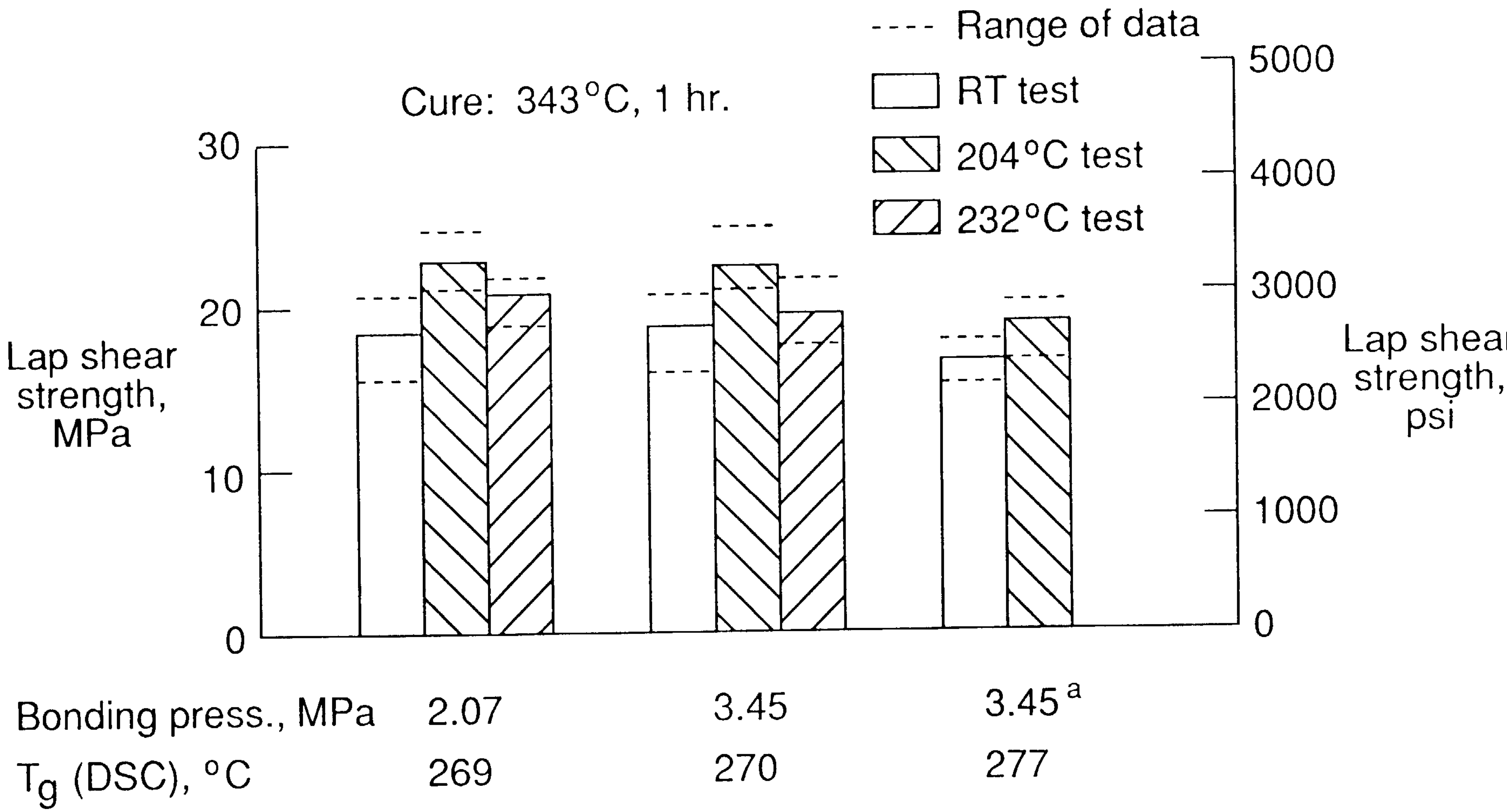


Figure 2. Preparation of the IDPA monomer.



[a] Adhesive tape given an additional heat treatment of 1 hr. at 250°C before bonding

Figure 3. The effect of bonding conditions on the lap shear strength for IDPA–MPD bonded Ti–6Al–4V.

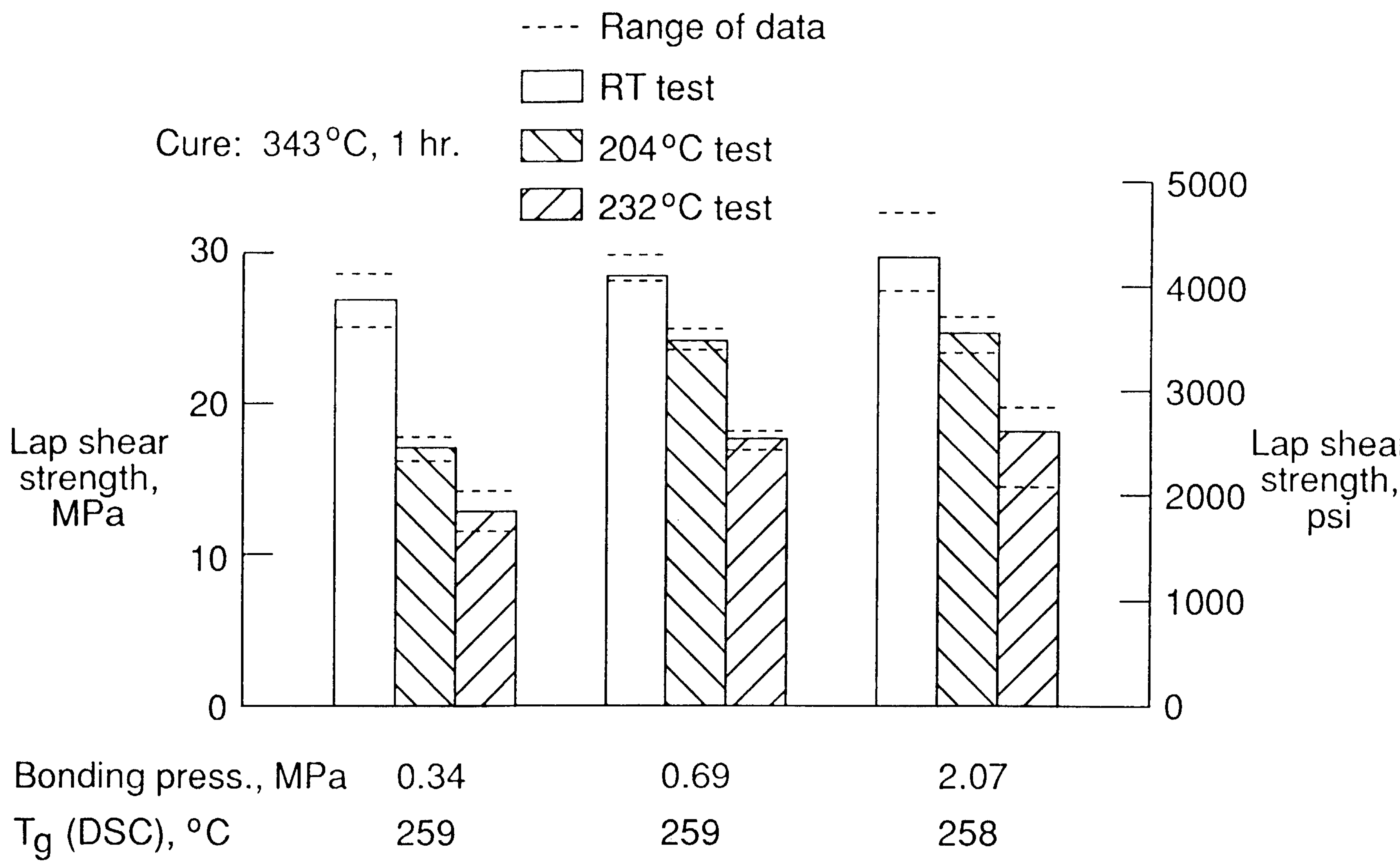


Figure 4. The effect of bonding pressure on the lap shear strength for IDPA-MPD(EC 4.00) bonded Ti-6Al-4V.

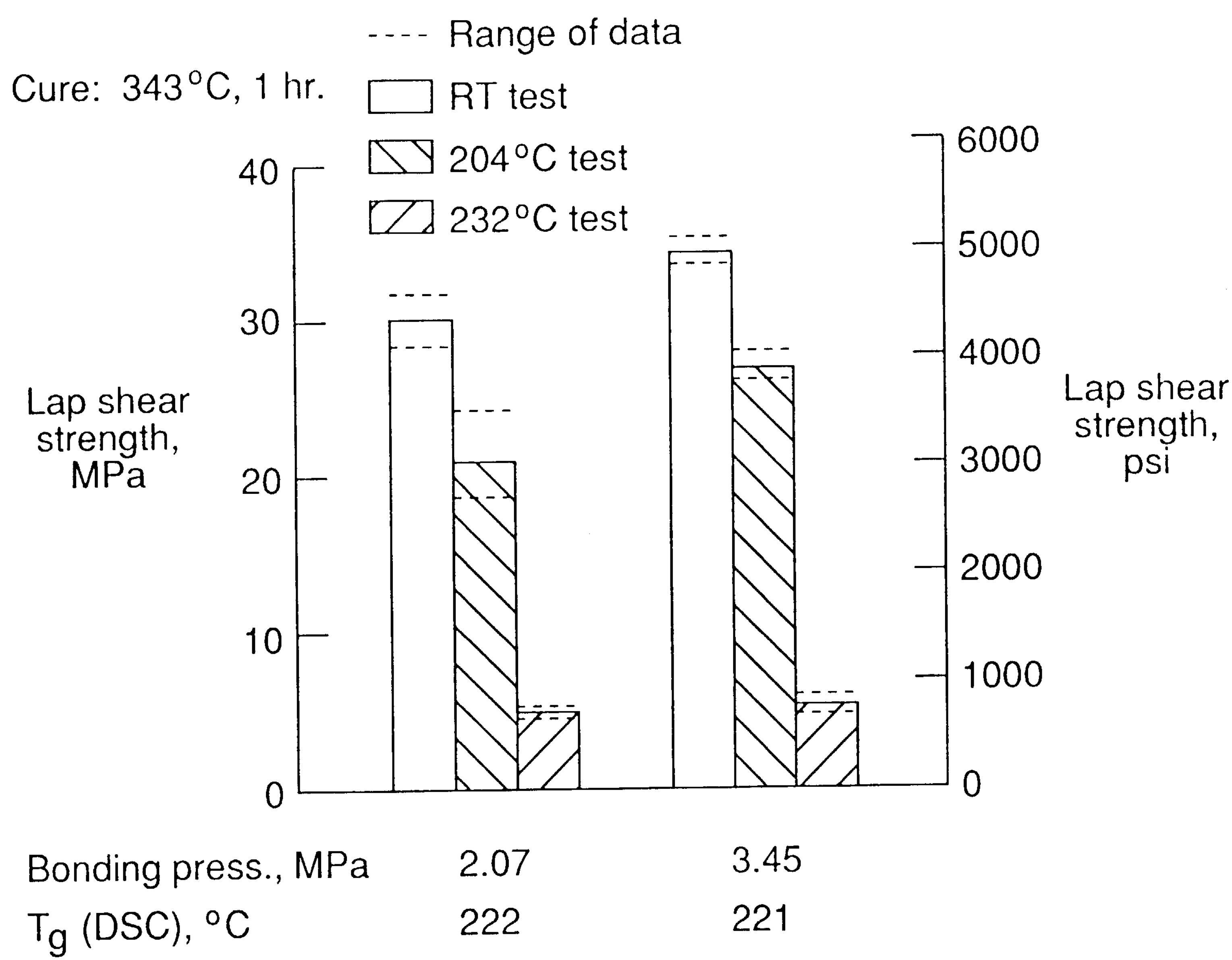


Figure 5. The effect of bonding pressure on the lap shear strength for IDPA-DABP bonded Ti-6Al-4V.

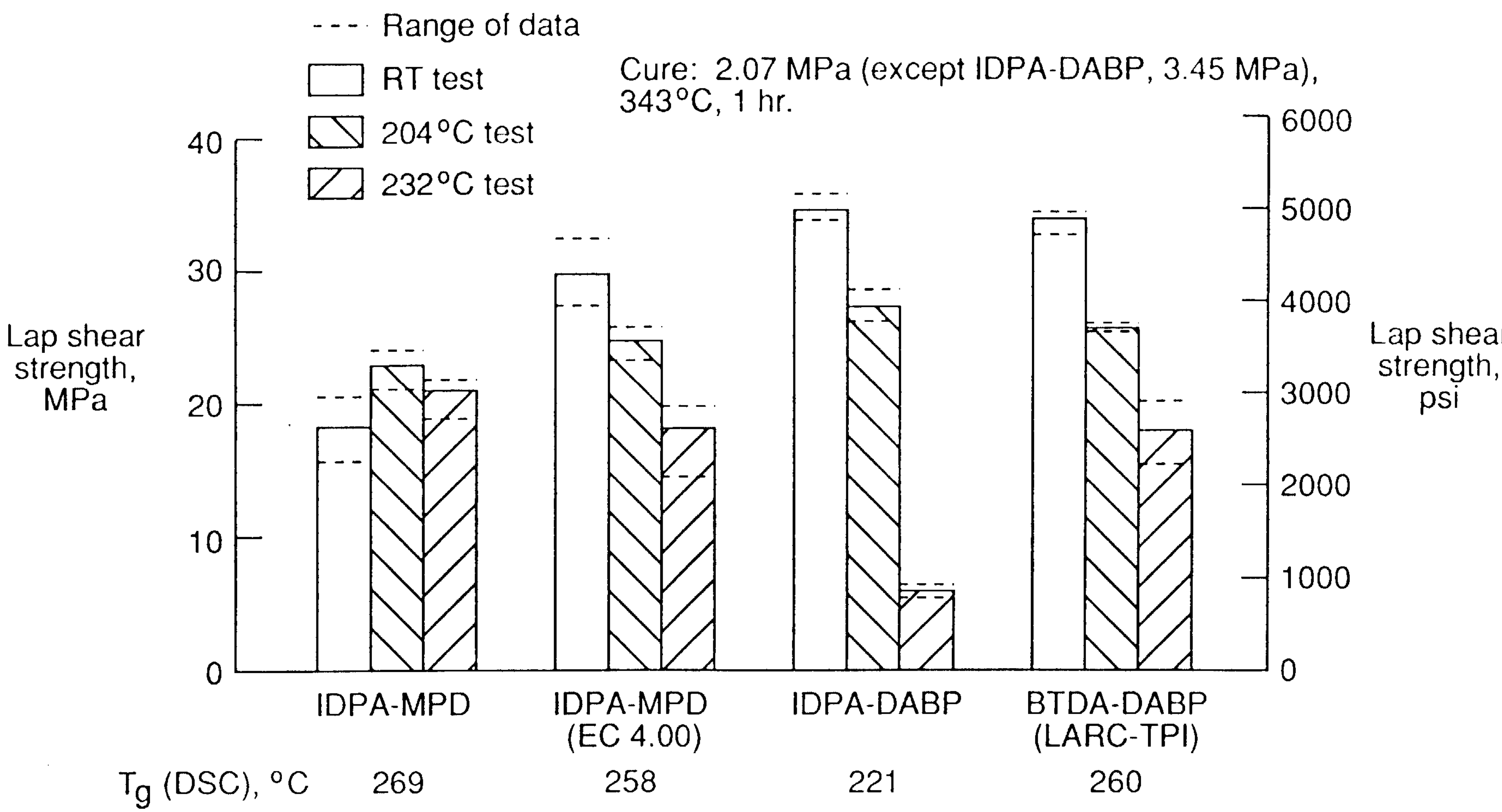
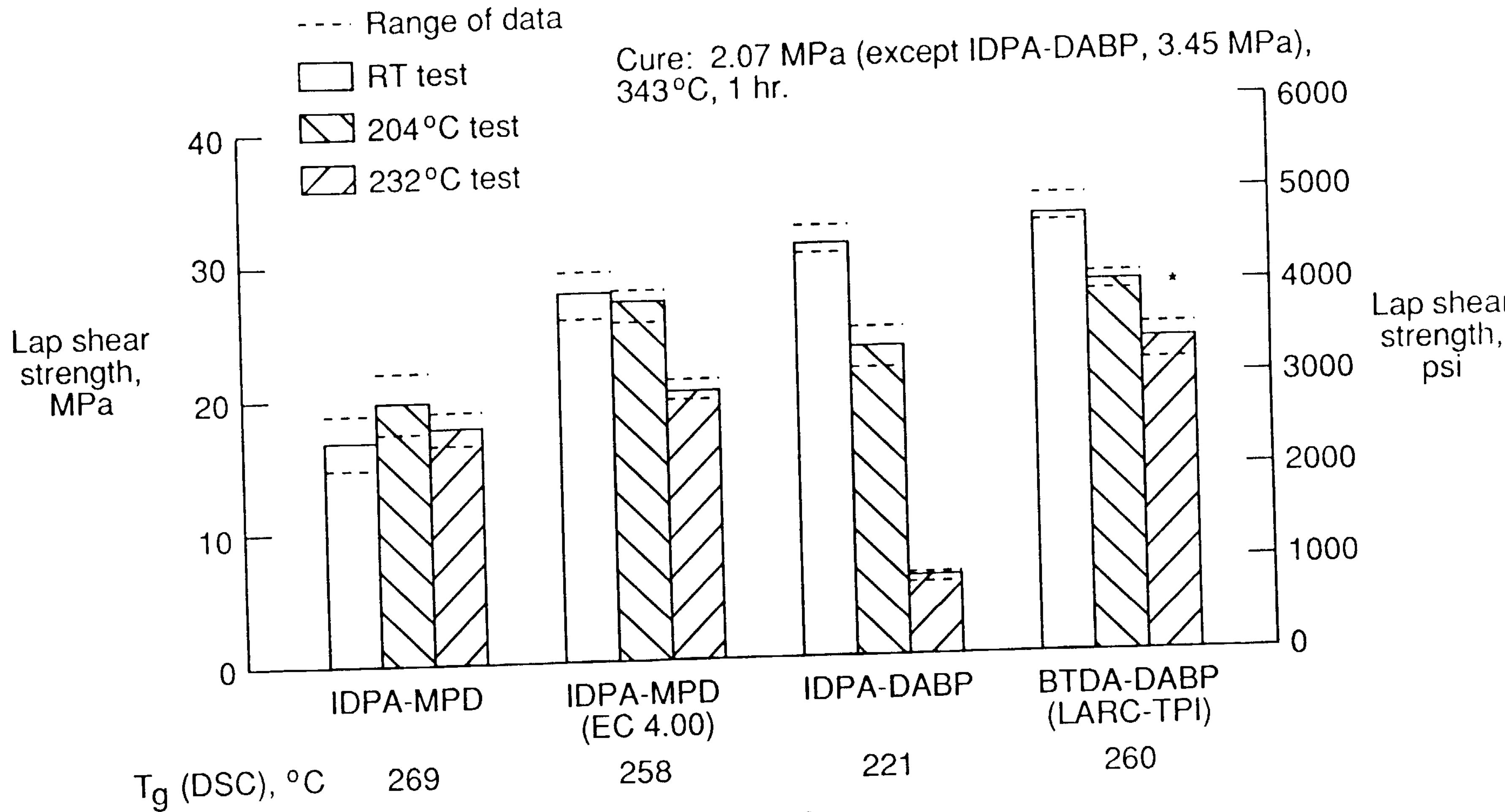


Figure 6. Initial lap shear strengths for IDPA–MPD, IDPA–MPD(EC 4.00), IDPA–DABP, and BTDA–DABP.



* Thermally exposed for 2260 hr. at 232°C

Figure 7. Lap shear strength results for bonded Ti−6Al−4V thermally exposed in air at 204°C for 1000 hrs.

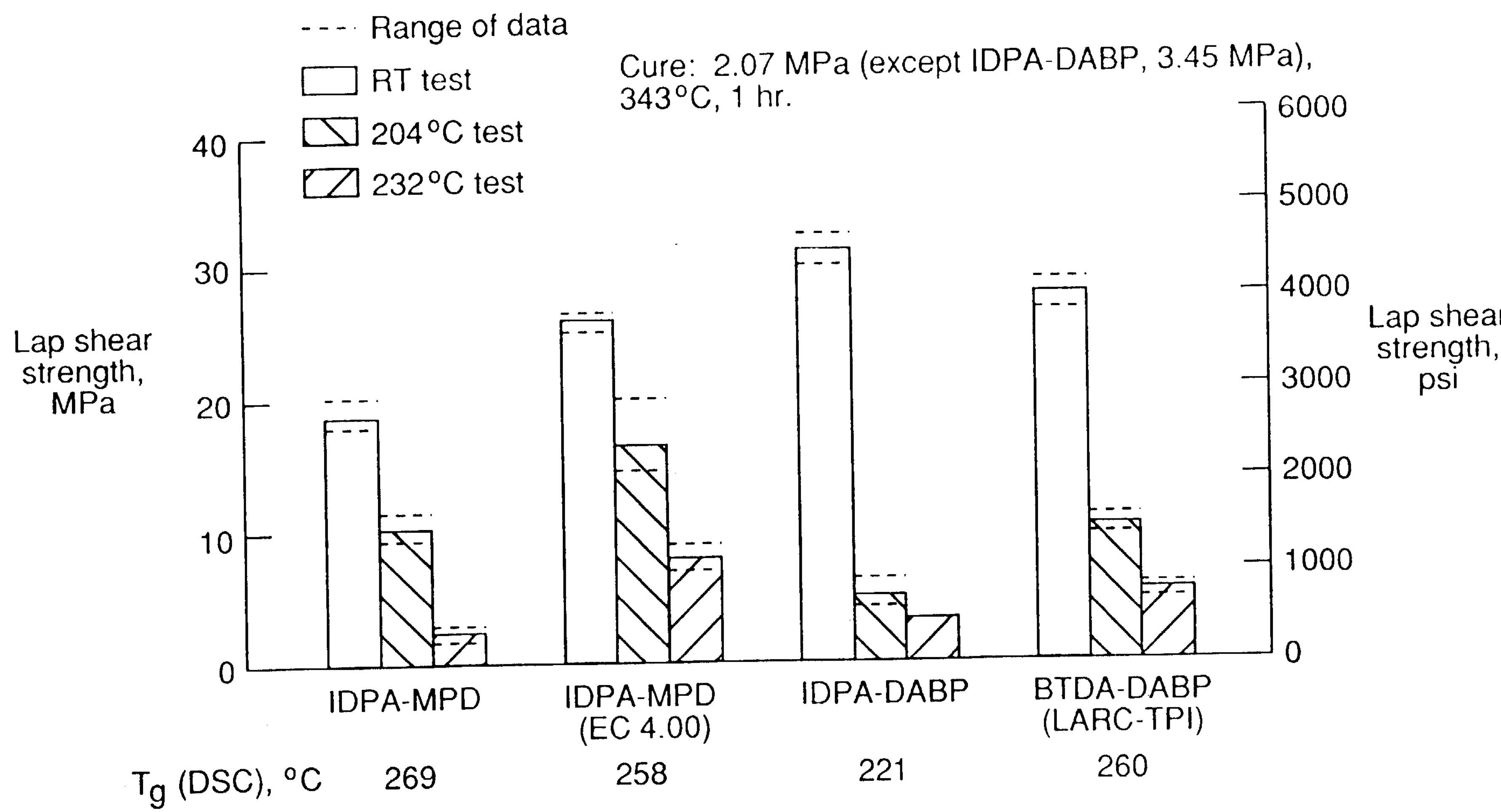


Figure 8. Lap shear strength results for bonded Ti−6Al−4V exposed to a 72−hr water boil.

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16. Abstract

Novel thermoplastic polyimides have been prepared and evaluated as adhesives. These materials are based on 4,4'-isophthaloyldiphthalic anhydride (IDPA) and either meta-phenylene diamine (MPD) or 3,3'-diaminobenzophenone (DBAP). Both polymers exhibit excellent adhesive properties; however, the IDPA-MPD is the more attractive system because of a combination of high mechanical and physical properties as well as being made from commercially attractive monomers. The IDPA-MPD is an isomeric form of the commercially available adhesive and matrix resin, LARC-TPI and both systems have the same glass transition temperature and exhibit similar adhesive properties.

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