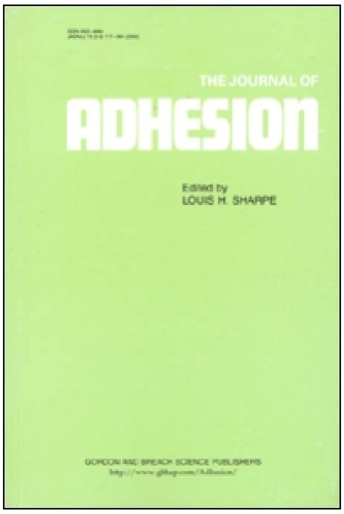

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Effect of Molecular Weight on Processing and Adhesive Properties of the Phenylethynyl-Terminated Polyimide LARC™-PETI-5

Roberto J. Cano[a]; Brian J. Jensen[a]
[a] NASA Langley Research Center, Hampton, VA, USA

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Effect of Molecular Weight on Processing and Adhesive Properties of the Phenylethynyl-Terminated Polyimide LARC^{TM}-PETI-5

ROBERTO J. CANO and BRIAN J. JENSEN
NASA Langley Research Center, Hampton, VA 23681-0001, USA

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Three different molecular weight versions of the phenylethynyl-terminated polyimide LARC^{TM}-PETI-5 were synthesized. The materials synthesized had theoretical number average molecular weights of 2500, 5000, and 10000 g/mol. Differential Scanning Calorimetry (DSC) was performed on the dry powder form of these materials to establish cure conditions which result in high glass transition temperatures. Lap shear specimens were prepared from adhesive tape made from each material and with the thermal cure conditions determined from the DSC data. The tensile shear data established which processing conditions provided the best adhesive strengths. Titanium tensile shear strengths as high as 52.6 MPa (7630 psi) at RT and 35.2 MPa (5100 psi) at 177° C were determined. Processing temperatures as low as 316° C and pressures as low as 0.17 MPa (25 psi) resulted in good adhesive properties. The tensile shear properties of these materials were unaffected by hydraulic fluid. The molecular weight of LARC^{TM}-PETI-5 has an important effect on the bonding pressures required to obtain good tensile shear strengths. The effect of molecular weight on the utility of PETI-5 to be used as a primer to maintain surface quality for bonding was also investigated.

KEY WORDS: Adhesives; polyimides; phenylethynyl; processing; molecular weight.

INTRODUCTION

Future civilian aircraft will require the use of advanced adhesive systems that can withstand exposure to high temperatures for extended periods of time over the lifetime of the aircraft. One such material has been developed at the NASA Langely Research Center, a phenylethynyl-terminated polyimide given the designation LARC^{TM}-PETI-5.[1,2] Recent work has shown the advantages of similar phenylethynyl-terminated polyimides as films, moldings, adhesives, and composite matrix resins.[3–10] Phenylethynyl-terminated oligomers provide greater processing windows than materials which incorporate simple ethynyl endcaps. Since these low molecular weight, low melt viscosity oligomers themally cure without the evolution of volatile by-products, they provide an excellent means of producing polymers with high glass transition temperatures, excellent solvent resistance, and high mechanical properties. The cure mechanism and cured products are currently under investigation.[11]

In an effort to assess the capabilities of PETI-5 as an adhesive as well as to determine the effect of molecular weight, three different versions of LARC™-PETI-5 with theoretical number average molecular weights (M_ns) of 2500, 5000, and 10000 g/mol were synthesized. Both poly(amide acid) solutions and imidized powders were produced. Differential Scanning Calorimetry (DSC) was performed on the dry powder form of these materials to establish cure conditions which resulted in high glass transition temperatures (T_gs). Lap shear specimens were prepared from adhesive tapes made of each material from its poly(amide acid) solution and with the thermal cure conditions determined from the DSC data. The tensile shear data established processing conditions which provided the best adhesive strengths. Further testing was performed to establish the properties of LARC™-PETI-5 as an adhesive material and to determine its solvent resistance. The ability of these materials to act as primers and maintain adherend surface quality after exposure to ambient conditions was also investigated.

EXPERIMENTAL

Polymer Synthesis

The three different molecular weight oligomers were prepared as previously reported[1,2] by offsetting the monomer ratio (Table I) in favor of the diamines and endcapping with the appropriate amount of 4-phenylethynyl phthalic anhydride (Equation (1)). Actual M_ns determined by Gel Permeation Chromatography/Differential Viscometry (GPC/DV) are also shown in Table I. In all three cases, the measured M_n was higher than the theoretical value.

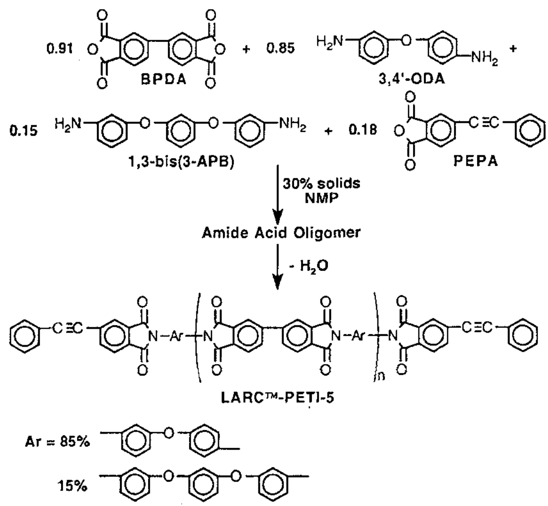
Characterization

Inherent viscosities were measured at 25°C on 0.5% solutions in *N*-methylpyrrolidinone (NMP). DSC was performed on a Shimadzu DSC-50 calorimeter at a heating rate of 20°C/min with the T_g taken at the inflection point in the heat flow *vs.* temperature curve.

TABLE I

Theoretical Molecular Weights, Experimentally Determined Molecular Weights, Inherent Viscosities, and Monomer Offset Ratios for Three Molecular Weight Versions of PETI-5

Theoretical Molecular Weight	Molecular Weight: Determined by GPC/DV	Inherent Viscosity, dL/g	Monomer Offset Ratio
2500 g/mole	5650 g/mole	0.22	0.8276
5000 g/mole	8050 g/mole	0.38	0.9098
10000 g/mole	12550 g/mole	0.44	0.9539



EQUATION 1 Polymer Synthesis of PETI-5.

Adhesive Specimens

Oligomer solutions (15-20% solids in NMP) were used to coat 112 E-glass (A-1100 finish). Each coat was dried in a circulating air oven for one hour each at 100 and 225° C to provide adhesive tapes with volatile contents of ~1 to 2%. Adhesive tape 0.30 to 0.38 mm (twelve to fifteen mil) thick was produced by applying several coats of the solution. Titanium (Ti-6Al-4v) treated with Pasa-Jell 107^{TM} surface treatment was bonded under varying conditions of temperature and pressure. Four tensile shear specimens of each material type for each condition were tested at either room temperature (RT) or 177°C according to ASTM-D1002. Four flatwise tension specimens were tested according to ASTM Standard C297.

RESULTS AND DISCUSSION

Glass Transition Temperature

Four initial cure conditions were chosen to evaluate the three versions of the LARC^{TM}-PETI-5 materials. The original standard practice for these types of materials at NASA Langley was a one-hour cure at 350°C. Slight variations to this temperature were initially investigated. Powdered versions of the 2500, 5000, and 10000 g/mol molecular weight materials cured for one hour at 300°C, 325°C, 350°C or 375°C were subjected to DSC analysis to determine T_g. The cure conditions evaluated and the corresponding T_gs are shown in Figure 1. All three materials showed the similar result of increasing T_gs with increasing cure temperature. With a 375°C cure, all three materials showed T_gs of 270°C or above. T_gs in the 255°C –265°C range were determined for cures of 325°C and 350°C. At a cure temperature of only 300°C, the T_gs were much lower for the 2500 and 5000 g/mol material. These

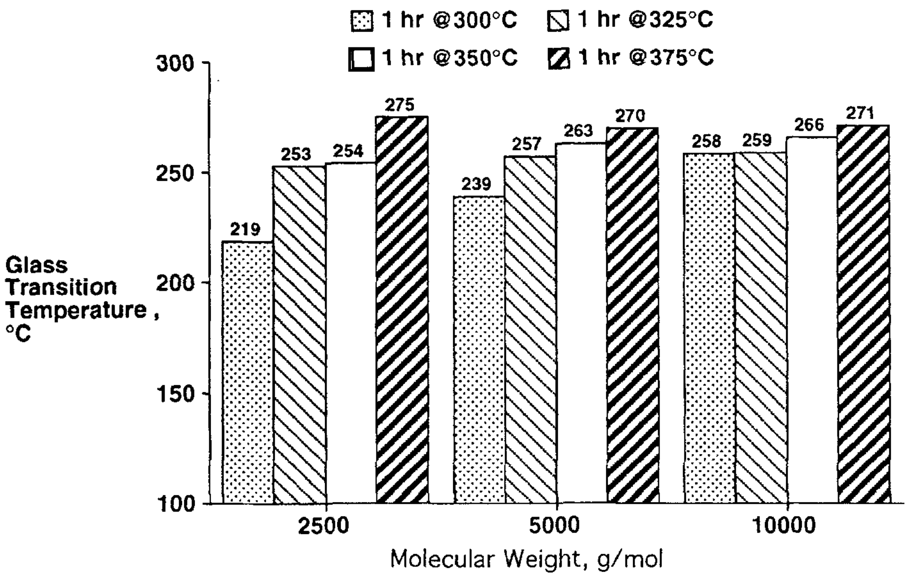


FIGURE 1 Glass transition temperatures of PETI-5.

results indicate that very little reaction occurs at temperatures near 300°C for times of about an hour.

Additional variations of the cure temperatures were performed using the 5000 g/mol material and are shown in Figure 2. As shown in the figure, a T_g as high as 274°C was determined for this material cured for 1/2 hr at 325°C and 1/2 hr at 375°C. The results also indicate that a hold at 375°C is required for significant reaction since the ramp to 375°C with no hold produced a T_g of only 234°C. A processing temperature as low as 316°C resulted in a T_g of 263°C when held for 2 hours. Several cure conditions produced T_gs in a similar range. Four cure conditions were then chosen to make Ti lap shear specimens in order to evaluate their adhesive properties. The four conditions chosen, the standard one hour at 350°C, one hour at 375°C, the combination hold at 325°C and 375°C, and the lower temperature hold of 316°C hold for two hours, provided adequate T_gs.

Lap Shear Strength

The results from the Ti tensile shear tests are presented in Figures 3 through 5. All bonding conditions except where noted utilize 0.517 MPa (75 psi) pressure. As shown in Figure 3, the highest tensile shear strengths at both RT and 177°C for the 2500 g/mol material were obtained by the two-hour hold at 316°C or the two temperature 325°C, 375°C hold. The holds at 350°C and 375°C produced very similar results but the resulting strengths were lower. All the RT failure modes were predominantly cohesive except the 375°C hold while all the failure modes at 177°C were predominantly adhesive in nature. The low molecular weight of this material

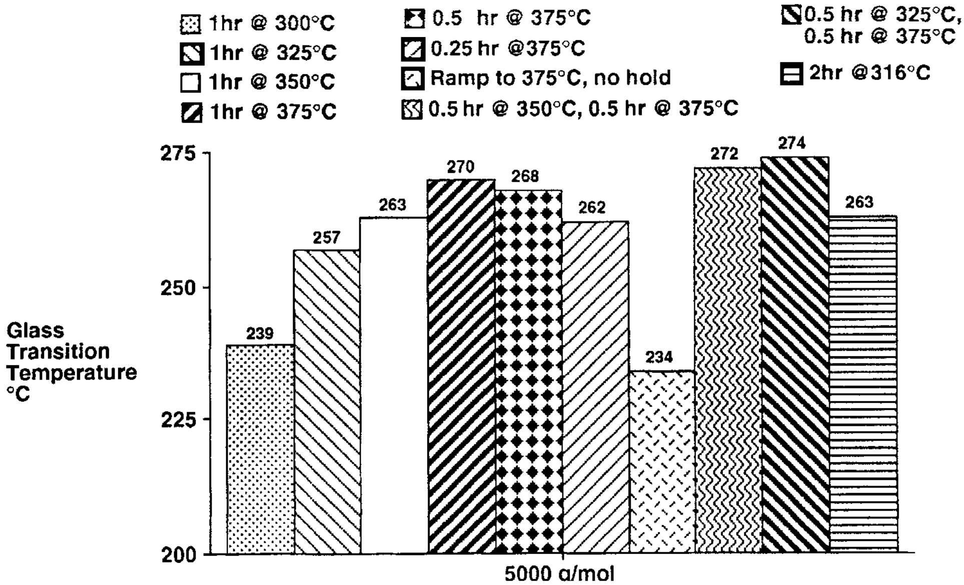


FIGURE 2 Glass transition temperatures for PETI-5, 5000 g/mol.

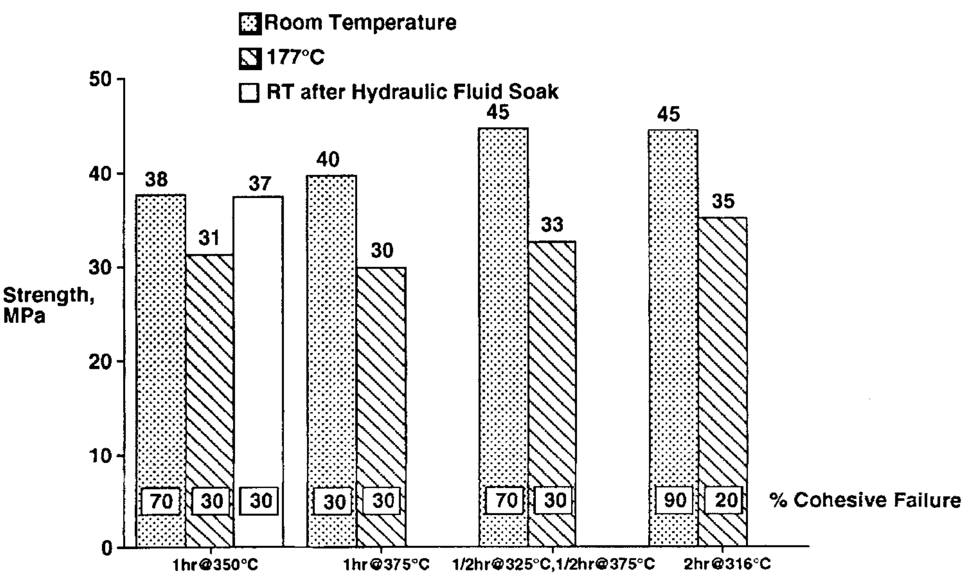


FIGURE 3 Lap shear values for PETI-5, 2500 g/mol.

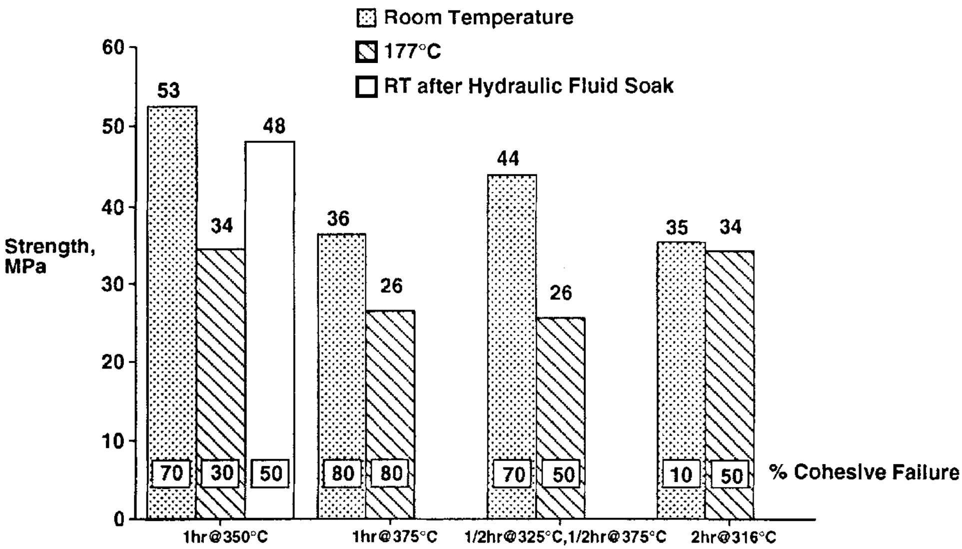


FIGURE 4 Lap shear values for PETI-5, 5000 g/mol.

appears to require a lower processing temperature, at least in the first step, to produce better strengths. Overall, bondline thicknesses for this material were somewhat low, ranging from 0.075 to 0.100 mm (3 to 4 mils), which would be indicative of excessive flow.

As shown in Figure 4, the highest tensile lap shear strengths for the 5000 g/mol version, 52.6 MPa (7630 psi) at RT and 34.5 MPa (5000 psi) at 177°C, were obtained for the one-hour cure at 350°C and 0.517 MPa (75 psi). The combination hold at 325°C and 375°C resulted in the next highest RT values. The holds at 375 and 316°C produced similar results at RT but with different failure modes. The 375°C cure produced an 80% cohesive failure while the 316°C cure produced a 90% adhesive failure. The bondline thicknesses for the 5000 g/mol material were close to the target value of 0.125 to 0.175 mm (5 to 7 mils) with thicknesses of 0.125 to 0.250 mm (5 to 10 mils).

As shown in Figure 5, the lap shear strengths obtained for the 10000 g/mol version were all very low. The RT values are less than those obtained with the 2500 g/mol version at elevated temperature. Such low values would indicate the necessity for an increased processing pressure. As shown in Figure 6, increasing the processing pressure greatly increased the lap shear strengths as well as the cohesive failure percentage. At a processing pressure of 0.689 MPa (100 psi), the strength increased to 43.8 MPa (6348 psi) with a 95% cohesive failure. Increasing the pressure beyond 0.689 MPa (100 psi) did not seem to provide any added benefit. The pressure dependence was also evidenced by the bondline thicknesses which decreased from 0.375 mm (15 mils) at 0.517 MPa (75 psi) to 0.325 mm (13 mils) at 0.689 MPa (100 psi) and 0.275 mm (11 mils) at 1.38 MPa (200 psi).

The effect of processing pressure was also investigated for the 2500 g/mol material. As shown in Figure 7, reducing the pressure from 0.517 MPa (75 psi) to 0.172

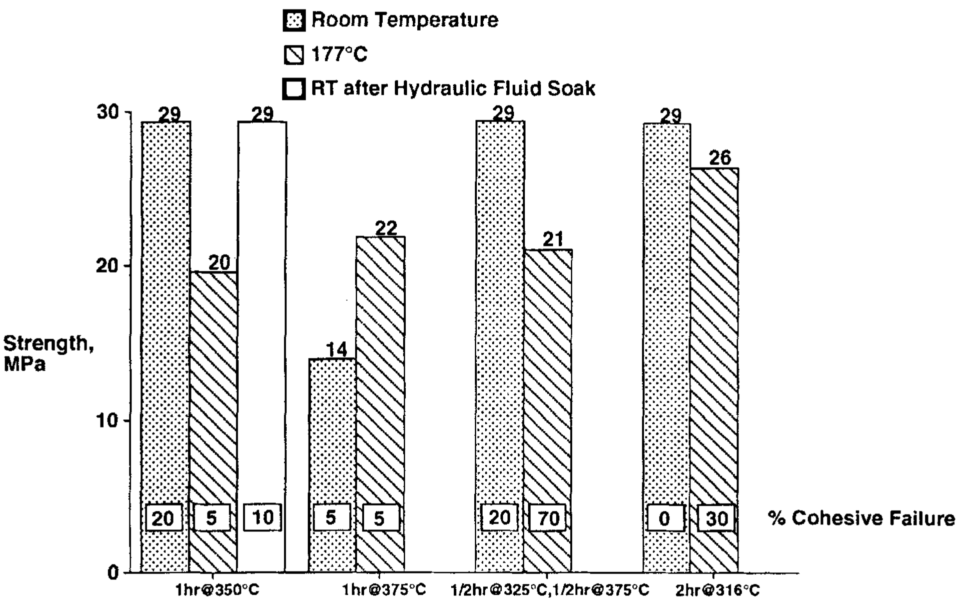


FIGURE 5 Lap shear values for PETI-5, 10000 g/mol.

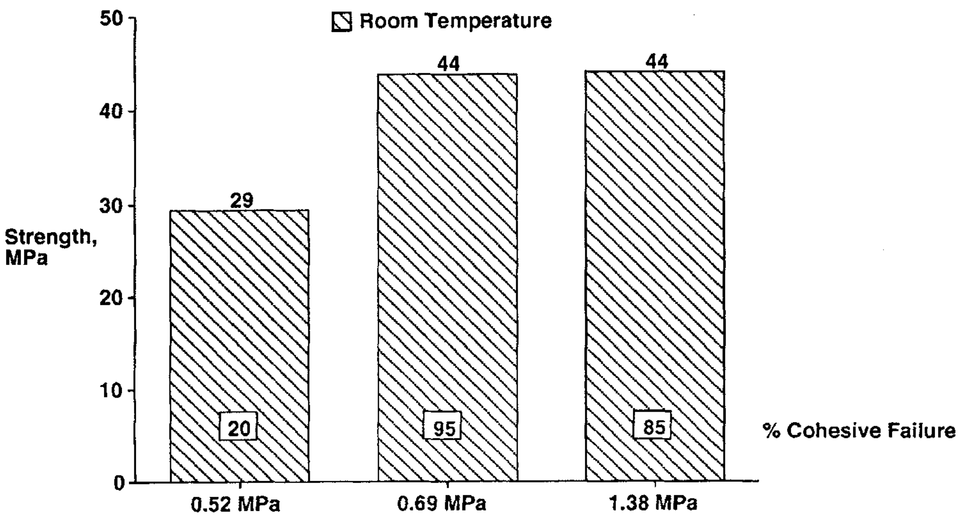


FIGURE 6 Lap shear values for PETI-5, 10000 g/mol under various processing pressures (Bonding Conditions: 1 hr at 350°C).

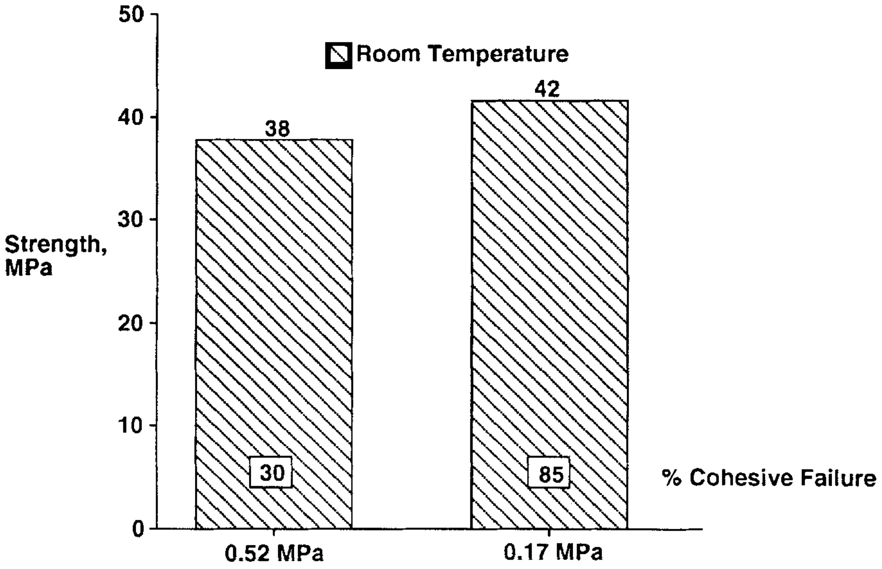


FIGURE 7 Lap shear values of PETI-5, 2500 g/mol, under various process pressures (Bonding Conditions: 1 hr at 350° C).

MPa (25 psi) produced an increase in lap shear strengths to over 41.4 MPa (6000 psi) with an 85% cohesive failure. Bondline thiknesses also increased from 0.075 to 0.100 mm (3 to 4 mils) to 0.125 to 0.150 mm (5 to 6 mils). Overall, excellent adhesive properties were obtained with each of these materials under relatively mild processing conditions.

Flatwise Tension

Flatwise tension results are presented in Figure 8. The 10000 g/mol material produced the highest values at both RT and 177°C. The preparation of these flatwise tension specimens involved surface treatment and priming of the Ti facesheets and honeycomb core and bonding with one layer of the adhesive tape. This method produced essentially no filleting around the honeycomb. A higher resin content adhesive tape and/or an adhesive paste applied directly to the honeycomb should produce much better strengths.

Primed Adherend Exposure

Figure 9 presents the lap shear strengths for the PETI-5, 2500 g/mol adhesive. The adherends were surface treated as previously described, primed, exposed to ambient conditions of 21°C (70°F) and 60% relative humidity for different lengths of time, then bonded. As indicated in Figure 9, the low molecular weight PETI-5 did not perform well as a primer after being exposed to ambient conditions. Lap shear

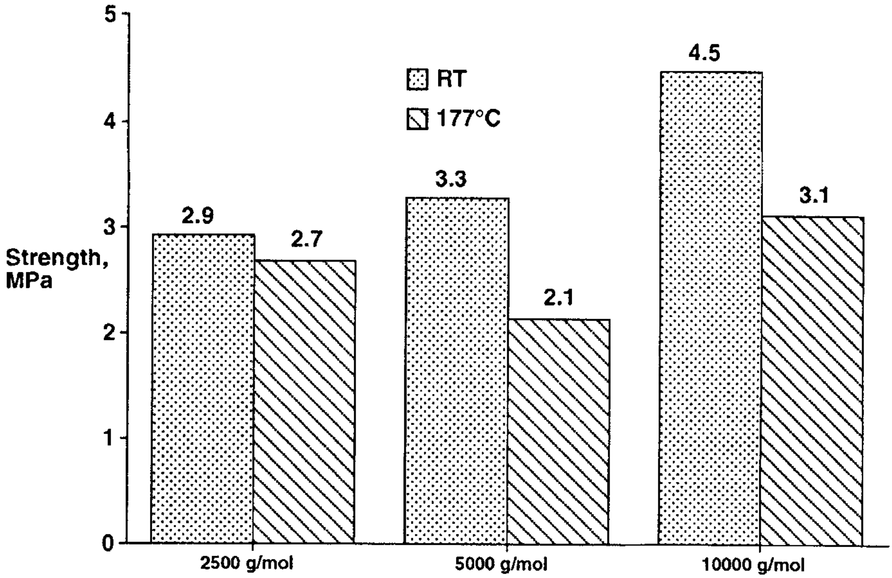


FIGURE 8 Flatwise tension values for PETI-5 (Bonding Conditions: 1 hr at 350° C).

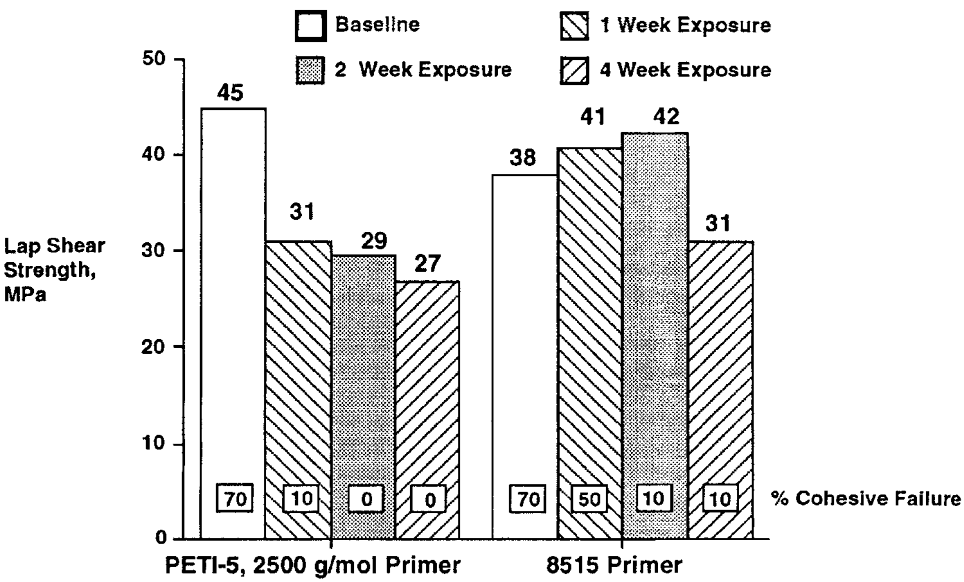


FIGURE 9 Lap shear values for PETI-5, 2500 g/mol adhesive after adherend exposure to ambient conditions (Bonding Conditions: 1/2 hr at 325° C, 1/2 hr at 375° C, 0.52 MPa).

strengths were reduced by up to 40% and failure modes became primarily adhesive. A thermoplastic polyimide primer, LaRC™-8515, 11600 g/mol (same polyimide backbone as PETI-5 but endcapped with phthalic anhydride), maintained the quality of the surface treatment as evidenced by maintaining the lap shear values close to the baseline value until an 18% decrease was observed after four weeks of exposure. Although the higher molecular weight PETI-5, 5000 g/mol adhesive produced mixed results with both the PETI-5, 5000 g/mol and 8515 primers at the exposure times studied, excellent strength retention was observed even after 8 weeks of exposure (Fig. 10). These results indicate the ability to use the 5000 g/mol version to prime adherend surfaces several weeks prior to actually bonding. From a manufacturing standpoint, this finding is important. In the real world, parts may sit around for relatively long periods awaiting bonding. The choice of the proper primer is critical. It appears that a molecular weight of 2500 g/mol does not provide adequate protection as a primer, possibly due to the fact that it was too low in molecular weight to form a film. The 10000 g/mol material was not evaluated in this part of the study.

Solvent Resistance

These materials also showed excellent solvent resistance. As shown in Figures 3, 4 and 5, all three materials were essentially unaffected (strength retentions between 92 and 100%) by a 48-hour hydraulic fluid soak.

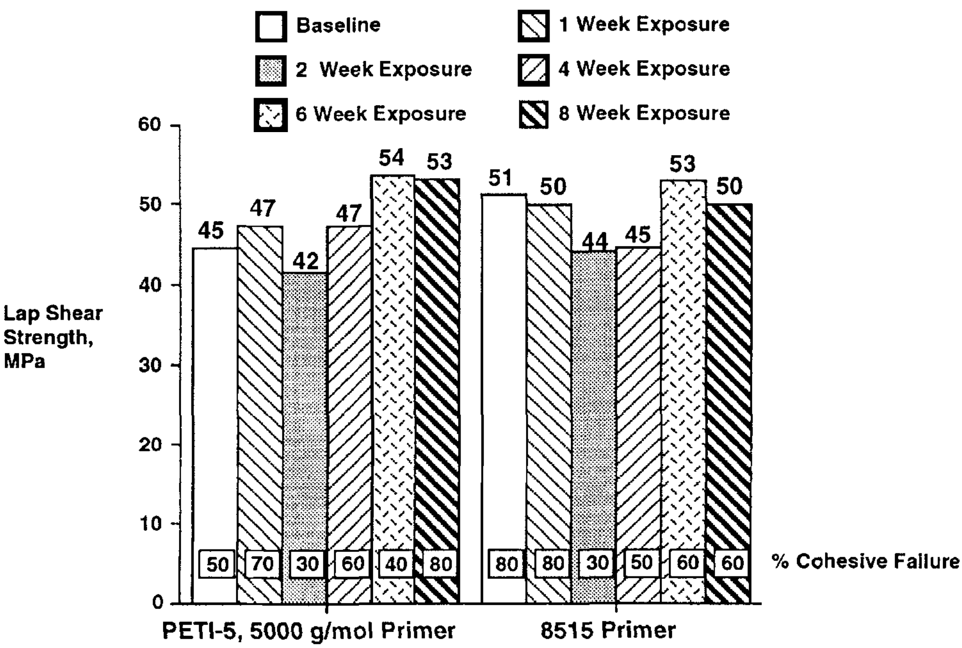


FIGURE 10 Lap shear values for PETI-5, 5000 g/mol adhesive after adherend exposure to ambient conditions (Bonding Conditions: 1 hr at 350° C, 0.52 MPa).

CONCLUSIONS

LARC^{TM}-PETI-5 displays excellent adhesive properties. Ti tensile shear strengths as high as 52.6 MPa (7630 psi) at RT and 35.2 MPa (5100 psi) at 177°C were obtained. Processing temperatures as low as 316°C and pressures as low as 0.172 MPa (25 psi) resulted in good adhesive properties. The tensile shear properties of these materials are also unaffected by hydraulic fluid. The molecular weight of LARC^{TM}-PETI-5 has an important effect on the bonding pressures required to obtain good tensile shear strengths. Priming the Ti adherend surfaces with a material that possesses a sufficiently high M_n or toughness is critical to maintaining the surface properties for proper bonding, especially if bonding is delayed for a significant period of time.

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