

## Aromatic Imide Polymers for High-Temperature Adhesives

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### Synopsis

During the past decade the aerospace industry has sought materials for bonding stainless-steel and titanium alloys that have a high degree of thermal and oxidative stability. The Air Force Materials Laboratory has anticipated these requirements and sponsored many development programs aimed at achieving these goals. This paper describes the results of one such program devoted to development of high-temperature adhesives from aromatic imide polymers. The family of polymeric materials known as aromatic polyimides possess excellent thermal and oxidative resistance at temperatures up to 650°F. Mechanical and electrical properties of glass-fiber-reinforced laminates prepared with these polymers have been reported. This work has been extended to the development of structural adhesives that will withstand long-time exposure in air at 600°F. Stainless steel and titanium have been successfully bonded with adhesives made from aromatic imide and benzimidazole imide polymers. Bonds made with stainless steel have retained approximately 80% of their original strength at 600°F. after 1000 hr. of aging at 600°F. Adhesives made with benzimidazole imide polymers are the preferred materials for bonding titanium. Initial bond strengths of 1300 psi have been measured at 600°F. After 1000 hr. at 600°F. the bond strengths drop to 800 psi. The processing conditions for making a bond are quite moderate, except that a high temperature is required. The preparation and processing conditions associated with these adhesives are described. A large number of aromatic imide and amide-imide polymers have been prepared and adhesives formulated. By comparing the bond strengths obtained with these adhesives it is possible to deduce the effect of molecular weight and various molecular components on bond strength.

### INTRODUCTION

Aromatic imide polymers are formed by reaction between aromatic diamines and aromatic polyacids or such derivatives as acyl halides and anhydrides.<sup>1,2</sup> The polymeric acid amide intermediates formed by these reactants are soluble in polar solvents such as dimethyl acetamide (DMAC), dimethylformamide, pyridine, *N*-methyl pyrrolidone, and dimethylsulfoxide. High solution viscosities are obtained at relatively low polymer concentrations.

The solution is a mixture of high molecular weight polyamic acids. The specific amic acid depends upon the reactants used. The polyamic acid is converted to the imide with heat. Normally either water or acetic acid

is a by-product of this reaction, depending on the choice of initial reactants. Because the polyamic acid solvents are of low volatility, the imidization reaction becomes almost complete when the solvent is removed from the polymer in the processing stage. At this point the polyimide formed is insoluble and infusible. Thus, to achieve the necessary flow required for wetting and subsequently bonding the substrate, it is necessary to heat the polymer above its glass transition temperature ( $T_g$ ) but below its decomposition point and apply pressure.

The polymer structure and molecular weight can be modified and controlled with a variety of difunctional and monofunctional anhydrides or amines or both. Difunctional molecules provide polymers of maximum molecular weight. Monofunctional molecules limit the polymer's molecular weight by providing a nonfunctional component (endblocker) at the ends of the polymer molecule. Crosslinking and chain-stopping (endblocking) can be achieved with latent difunctional amines, one of the amido groups participating in the original reaction and so terminating the polymer and the second amido group reacting with another functional group on another molecule at a higher temperature.

Theoretically, at least, aromatic polyimides are high molecular weight (up to 500,000) linear polymers without any crosslinks. No melting point has been observed for any of these polymers below the decomposition temperature even in the absence of crosslinking induced by latent functionality monomers.

## EXPERIMENTAL

### Adhesive Protection

The adhesives consisted of the polymer and in some cases fillers coated onto a woven glass-cloth substrate. The viscous polymer mixture was manually coated on the glass cloth and heated to drive off solvent. Three to five coats of polymer mixture were required for the desired 40-45% resin content when style 181 E-glass cloth was used. Less dense glass cloth, such as style 112, required about 80% resin by weight and eight to ten coats of polymer mixture. After each coat the polymers were cured for 1 hr. at 212°F. and then at successive 15 min. intervals at 302, 392, and 482°F. and for 5 min. at 572°F.

### Sample Preparation

Lap-shear tensile specimens 1 in. wide by 7.5 in. long with 0.5 in. overlap were used exclusively throughout this program.

### Bonding Mold

The mold comprised a top and bottom die. Each die consisted of a molding surface made of a piece of hardened tool steel  $7 \times 3 \times \frac{3}{8}$  in. thick, that had been chrome-plated. The molding surface of the bottom die had a groove  $1 \times \frac{7}{64}$  in. deep extending along its length. The mold-

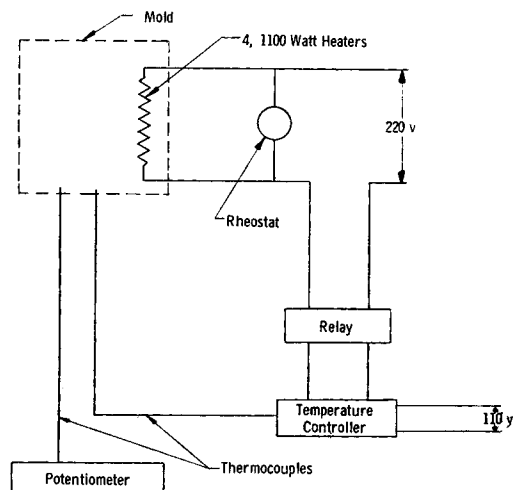


Fig. 1. Schematic diagram of heating and temperature-control circuits.

ing surface was bolted to a piece of SAE 4140 steel,  $7 \times 3 \times 1\frac{1}{2}$  in. thick, which was cored to receive two 1100-watt Chromolox, Red Head heating cartridges.

The four Chromolox heating cartridges were connected to a 220 v. ac. power source through a mercury relay. A temperature controller was used for operating the relay. The voltage was controlled by a rheostat. Two iron-constantan thermocouples were placed in the center of the bottom die immediately beneath the molding surface. One thermocouple was connected to the temperature controller and the other to a potentiometer. The potentiometer served to determine the mold temperature, while the temperature controller adjusted and maintained the temperature within  $\pm 4^\circ\text{F}$ . A schematic diagram of the circuitry is shown in Figure 1.

### Modification of the Preco Laboratory Press

A Preco Laboratory Press was modified to permit accurate pressure measurement. The high-pressure gage was removed and a 0-100 lb. Ashcraft hydraulic test gage installed. A 0-400 lb. Permaga gage was available for measuring higher pressures. This combination of gages permits measurement of bond line pressure between 0 and 800 psi. The Ashcraft gage can be read to 1 psi and the Permaga to 10 psi. In order to eliminate pressure variation and provide positive pressure control it was necessary to replace the  $\frac{3}{32}$  in. hydraulic line to the pressure gage with a line  $\frac{1}{4}$  in. in diameter. A photograph of the modified press with the mold installed is shown in Figure 2.

### Metal Preparation

Stainless steel AM350SCT and Titanium 8A1-1Mo-1V (811) were used in this program. Stainless steel AM350 was obtained from the supplier in

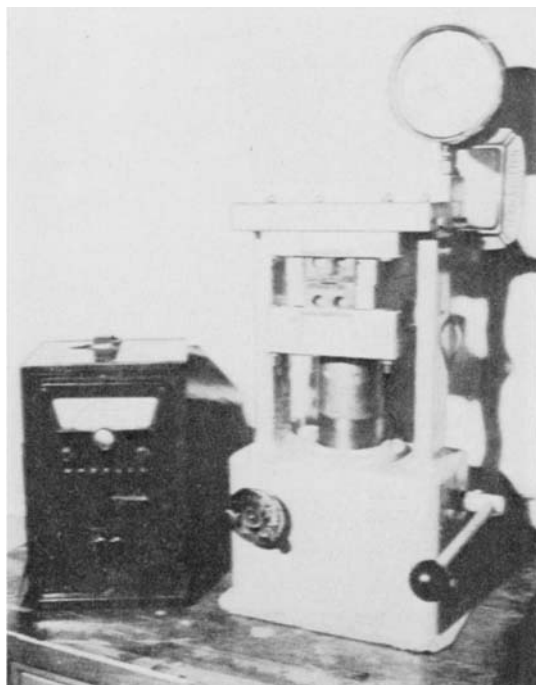


Fig. 2. Modified Preco press, the mold installed.

the anneal temper condition. The metal was then cut into  $1 \times 4$  in. strips and hardened by subzero cooling and tempering (SCT). Groups of the samples were clamped together with C clamps and cooled to  $-110 \pm 5^\circ\text{F}$ . in a mixture of solid carbon dioxide and acetone. Samples were maintained at this temperature for 3 hr. After being removed and warmed to room temperature the samples were tempered at  $850^\circ\text{F}$ . for a minimum of 3 hr. At the conclusion of the tempering process the samples conform to stainless-steel specification AM350SCT.

The AM350SCT panels were dipped in a concentrated solution of hydrochloric acid, so as to remove the scale formed during the tempering process. After a few seconds immersion in the acid the panels were washed in running tap water.

The surface preparation procedure was as follows.

The panels were degreased by being wiped with trichlorethylene, scrubbed with Comet (a chlorinated cleanser) and warm water, washed in tap water, dried at  $200^\circ\text{F}$ . for 15 min., and etched in an acid mixture of 35% hydrochloric acid (84 ml.), 85% *o*-phosphoric acid (80 ml.), and 60% hydrofluoric acid (43 ml.). The acid mixture was heated in a water bath maintained at  $185$ – $190^\circ\text{F}$ . When the temperature of the acid mixture reached  $185$  to  $190^\circ\text{F}$ ., the bonding edges of the panels were immersed for 2 min. and then thoroughly rinsed in running distilled water. Panels were dried at  $200^\circ\text{F}$ . for 15 min. then cooled and stored in a desiccator.

Titanium 811 was received in the duplex annealed condition, and no further annealing or tempering was required. Initially all of the titanium samples were degreased in trichlorethylene and scrubbed with Comet. On the advice of Air Force Materials Laboratory this portion of the procedure was modified to eliminate halogenated cleaning agents. The samples were scrubbed with methyl ethyl ketone. Then the scrubbed samples were thoroughly rinsed in tap water and dried at 200°F. for 15 min. The ends of the panels to be bonded were etched in the following solution: distilled water (270 ml.), sodium fluoride (9 g.), chromium trioxide (4 g.), and concentrated sulfuric acid (30 ml.). The panels were etched for 8 min. at room temperature, washed with running distilled water for 1 min., dried at 200°F. for 15 min., cooled, and stored in a desiccator.

### Testing

All tests were performed according to MIL-A-00509OE (Wep), which requires that lap-shear tensile specimens be made by bonding two large sheets of metal together and then cutting the 1-in. wide samples from the sheets. This procedure was not followed because of the high heat generated when titanium 811 and stainless steel AM350SCT are cut and the problems associated with maintaining uniform temperature along a large molding surface. Consequently, all the test samples were made by bonding 1 × 4 in. precut panels. A lap-shear joint with a nominal 1/2 in. overlap was used exclusively. The samples were allowed to soak at the test temperature 10 min. before being tested.

### Thermal Aging Studies

The thermal aging studies were performed in Norman kilns and a forced-air oven. The Norman kilns were made of firebrick with Nichrome wire heating elements embedded in the walls. The kilns were 11 in. square and 7 in. high on the inside. Three iron-constantan thermocouples were fastened to the center sample. One of the thermocouples was used for periodically checking the temperature with a potentiometer, the second was used in conjunction with a Minneapolis-Honeywell Elektronik Controller, and the third was the sensor for a multipoint temperature recorder. The center sample was not tested during the thermal aging program. Samples were loosely mounted on edge, about 1/4 in. apart, in a metal frame. There were no provisions for forced-air circulation. The Norman kiln was chosen because the temperature gradient in any plane, i.e., on the floor, was within  $\pm 5^\circ\text{F.}$ , provided a metal barrier was placed between the heating elements and the first sample.

The forced-air oven was a Model CW-7712F manufactured by the Blue M Electric Co. The sample racks and spacing were the same as used with the Norman kilns. A single thermocouple was placed on the center sample so as to monitor the temperature continuously with a multipoint temperature controller.

## DATA AND DISCUSSION

### Bonding Stainless Steel

Stainless steel AM350SCT was successfully bonded with three polymers, I-8, I-40, and I-66. Polymer I-8 is the reaction product of equimolar parts of *m*-phenylenediamine and benzophenonetetracarboxylic dianhydride. I-40 resin is an endblocked version of I-8; the endblockers are *p*-aminoacetanilide and phthalic anhydride. I-66 differs from I-40 only in that the phthalic anhydride is omitted.

A series of experiments was performed to determine the optimum bonding temperature for each adhesive at 200 psi bond-line pressure and a 5 min. bonding time. Early in the program it was established that bonding temperature was the most significant variable. Bond-line pressures above 200 psi improved the consistency of test results but did not significantly improve the bond strength. Five minutes was chosen as the minimum practical bonding time. The bonding temperature must be above the second-order transition temperature ( $T_g$ ) but below the decomposition temperature. The temperature difference between  $T_g$  and the decomposition temperature is rather limited in many of the polymers investigated; hence, relatively short bonding times are preferred. The optimum bonding temperatures for I-8, I-40, and I-66 polymers were 752, 842, and 797°F., respectively, although good bonds could be obtained over a range of about 50°F. both above and below these values. The maximum strength in the adhesive joints was obtained at the temperatures indicated.

### Shelf Life of Polyimide Adhesives

When polyimide polymers are coated on glass cloth they can completely react chemically and be rendered essentially free from volatiles. In this condition they possess almost indefinite shelf life. We have successfully prepared laminates of such materials after many months of storage of the prepreg cloth at room temperature. To test this characteristic with respect to adhesive materials and to ensure that the introduction of latent reactive endgroups and lower molecular weight would not result in undue loss of shelf life, appropriate tests were performed on two adhesive compositions. Samples of 181-A1100 E-glass cloth impregnated with polymers I-66 and I-40 were used for bonding AM350SCT steel specimens after they had been stored on the shelf for periods of 4 and 6 months at ambient conditions. The samples were bonded under the appropriate conditions for each specimen, and lap-shear tensile strength measurements were made at 550°F. The results were excellent (average strength exceeded 3300 psi at 550°F.). There was no detectable loss in strength of any specimen compared to that of bonds made with newly prepared material.

### Thermal Aging of Unfilled Polymers or 181-A1100 E-Glass Cloth

A series of thermal aging experiments were performed with these polymers on 181-A1100 E-glass cloth. Adhesives made with polymers I-8 and

I-40 were aged at 550, 625, and 700°F. and tested both at 70°F. and at the aging temperature. The results obtained with I-8 and I-40 are shown in Figures 3 and 4. The points plotted on all of the graphs are an average

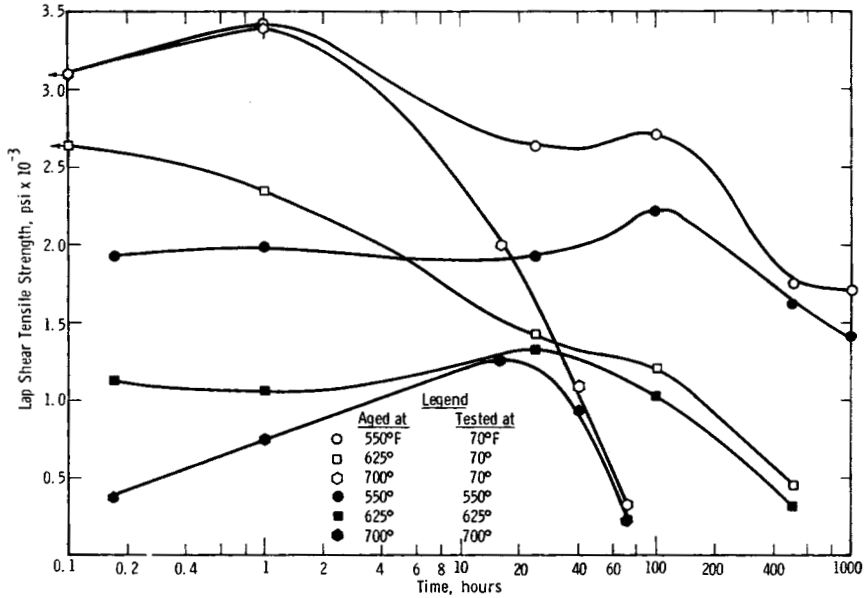


Fig. 3. Thermal aging of I-8 polymer on 181-A1100 E-glass cloth; adherends, stainless steel, AM350SCT 0.063 in. thick.

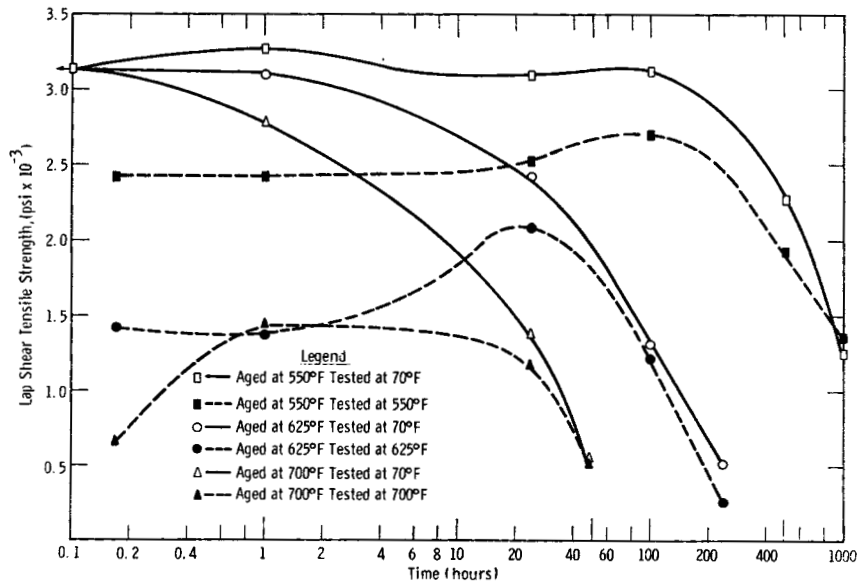


Fig. 4. Aging of adhesive I-40 on 181-A1100 E-glass cloth in air at three temperatures; adherends, AM350SCT 0.063 in. thick.

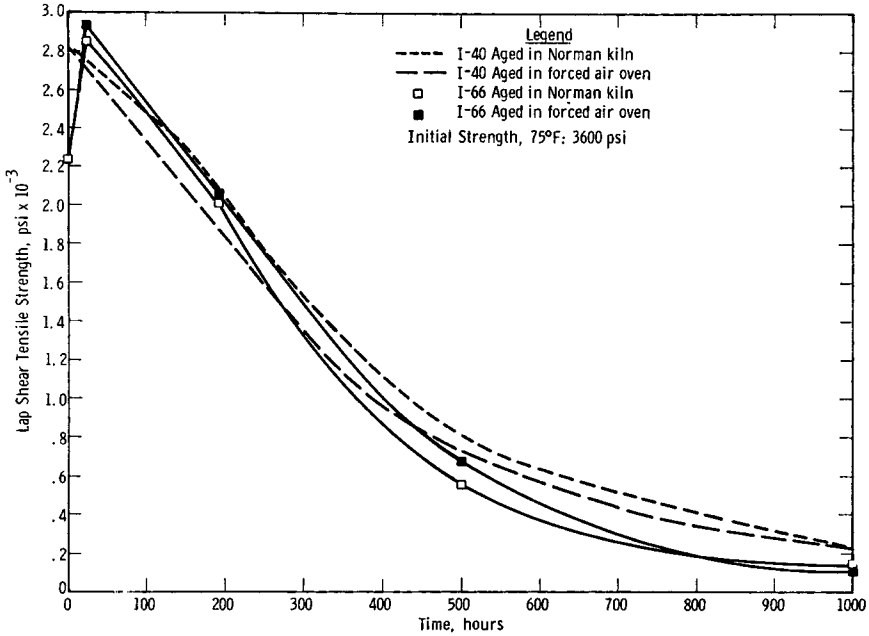


Fig. 5. Comparison of bond strength of I-40 and I-66 resins on 181-A1100 E-glass cloth after thermal aging at 600°F. in a forced-air oven and Normal kiln: adherends, AM305SCT 0.063 in. thick; tested at 600°F.

of three test values. A comparison of the thermal aging characteristics at 600°F. of adhesives made with polymer I-40 and I-66 is shown in Figure 5. The samples were tested at 600°F. Aging was done both in Norman kilns and in a forced-air oven, in order to assess the effect of stagnant air versus circulating air. Circulating air had little apparent effect on the aging results, as long as good temperature control was maintained.

At a lap-shear tensile strength of 1000 psi the thermal lives of I-8 and I-40 adhesives are as shown in Table I. The life values at 550°F. were obtained by extrapolating curves in Figures 3 and 4. Both I-8 and I-40 have about the same properties except at 550°F. where I-8 appears to have

TABLE I  
Thermal Life of I-8 and I-40 Adhesives with Lap-Shear  
Tensile Strength of 1000 psi as Endpoint

Adhesive	Aging temp. °F.	Time required to decrease to 1000 psi lap-shear tensile strength, hr.
I-8	550	4,000
I-40	550	2,000
I-8	625	100
I-40	625	135
I-8	700	35
I-40	700	35



a longer life. However, up to 500 hr. at 550°F. the I-40 adhesive has higher strength values.

Figure 5 indicates that adhesives made from I-40 and I-66 behave similarly at 600°F., the I-40 being slightly inferior initially but somewhat superior after 400 hr. of aging. Thermal life from both adhesives is 400 to 425 hr. when 1000 psi lap-shear tensile strength at temperature is the criterion. In addition, these data show only a slight difference between samples aged in stagnant air and those aged in circulating air.

### Thermal Cycling of Polyimide Adhesive Samples

Since a metal-nonmetal interface is involved, it was thought desirable to appraise the possible effect of thermal cycling compared with aging at constant temperature. A series of tests were carried out on stainless-steel specimens (AM350SCT) bonded with I-8 polymer on 181-A1100 E-glass cloth. The bonds were made at 752°F. and 200 psi for 5 min. The samples were aged in air at 550°F., cooled rapidly to 40°F. for 1 hr. out of each working day, and then returned to the aging oven (this constitutes one cycle). The samples were tested after 100 hr. and four such cycles, after 500 hr. and 14 cycles, and after 1000 hr. and 27 cycles. Lap-shear tensile tests were performed at 550°F. The results of these experiments were not significantly different from the results shown on the curve for constant-temperature aging at 550°F., shown in Figure 3, allowing the tentative conclusion that cycles of repeated heating and cooling within these temperature limits is not appreciably more deleterious than constant-temperature aging at the high-temperature condition. A like set of experiments with the higher-strength I-40 adhesive showed similar results, except that a slight deterioration in hot strength ( $\approx 15\%$ ), attributable to the effect of thermal cycling, was observed.

### Thermal Aging of Filled Adhesives

Other investigators have reported that arsenic pentoxide ( $\text{As}_2\text{O}_5$ ) and arsenic thioarsenate ( $\text{AsSAsS}_3$  or  $\text{As}_2\text{S}_4$ ) appreciably improve the thermal aging characteristics of high-temperature adhesives on stainless steel.<sup>3</sup> Presumably, the  $\text{As}_2\text{O}_5$  and  $\text{As}_2\text{S}_4$  scavenge iron oxide that would otherwise catalyze and accelerate the degradation rate of the polymer. These experiments were designed to determine whether oxides of other group V elements would perform the same function as the  $\text{As}_2\text{O}_5$  and  $\text{As}_2\text{S}_4$ . In addition, experiments were performed to determine the effect of aluminum powder (type MD101 used exclusively in this program) by itself and in conjunction with several of the oxides. Titanium dioxide ( $\text{TiO}_2$ ) was used as a control, since the effect achieved with the group V elements would not be present. Polymer I-40 was used throughout these experiments, and the adhesive mixtures were on 181-A1100 E-glass cloth.

The compositions of the filled I-40 adhesive formulations are shown in Table II. The results of thermal aging experiments with the formulations are shown in Figures 6 and 7. The effect of fillers with I-40 is very specific.

TABLE II  
Compositions of Filled I-40 Resin on 181-A1100 E-Glass Cloth

Filler	Tot. amt. filler, parts filler per 100 parts I-40 resin solids	Solids of I-40 resin in DMAC, %	Resin content (tot. resin and filler) of 181-A1100 E-glass cloth, %
Vanadium pentoxide ( $V_2O_5$ )	5	25.69	47.1
Arsenic trioxide ( $As_2O_3$ )	5	25.69	46.9
Antimony trioxide ( $Sb_2O_3$ )	5	25.69	46.0
Bismuth trioxide ( $Bi_2O_3$ )	5	26.15	43.5
Arsenic pentoxide ( $As_2O_5$ )	5	26.15	40.6
Tantalum pentoxide ( $Ta_2O_5$ )	5	26.15	41.4
Titanium dioxide ( $TiO_2$ )	5	26.15	43.1
Aluminum powder	40	26.15	44.7
Arsenic thioarsenate ( $As_2S_4$ )	5	30.00	46.3
Aluminum powder-35 + Vanadium pentoxide ( $V_2O_5$ )-5	40	26.15	46.9
Aluminum powder-35 + Antimony trioxide ( $Sb_2O_3$ )-5	40	26.15	45.4

Initially, all fillers degrade the bond strength of the I-40 adhesives. However, after aging the I-40 adhesives containing 5% of such fillers as  $V_2O_5$ ,  $Sb_2O_3$ ,  $As_2O_3$ ,  $Bi_2O_3$ ,  $As_2S_4$ , and  $As_2O_5$  have better bond strengths than the

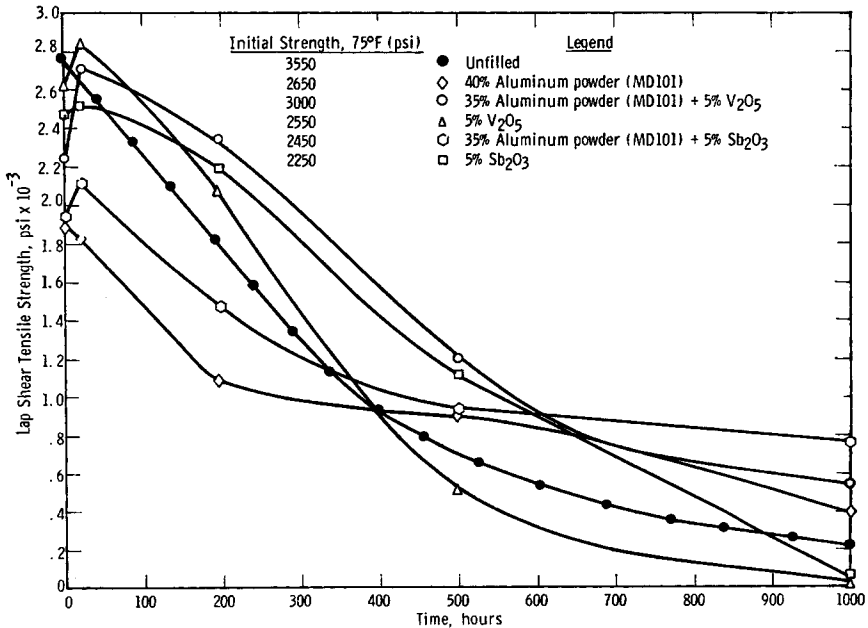


Fig. 6. Comparison of filled and unfilled I-40 resin on 181-A1100 E-glass cloth; adherends, AM350SCT 0.063 in. thick; aged in forced-air oven at 600°F.; tested at 600°F.

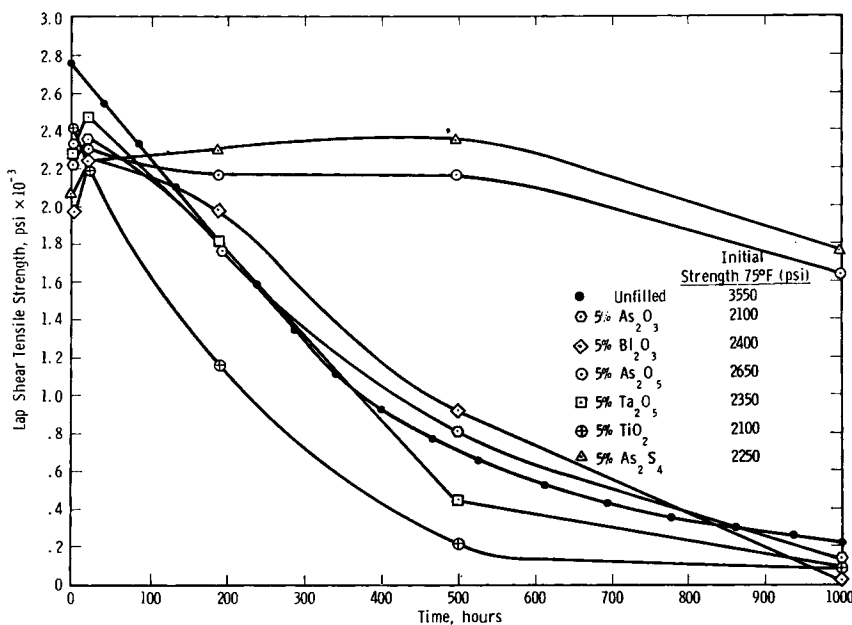


Fig. 7. Comparison of filled and unfilled I-40 resin on 181-A1100 E-glass cloth; adherends, AM350SCT 0.063 in. thick; aged in forced-air oven at 600°F.; tested at 600°F.

unfilled I-40. A substantial improvement was obtained with  $As_2O_5$  and  $As_2S_4$  over the complete aging period. After 1000 hr. of aging the I-40 adhesives filled with  $As_2O_5$  and  $As_2S_4$  are eight times better than the unfilled I-40 adhesive. The addition of 5%  $TiO_2$  in the I-40 adhesive provides inferior bond strength over the entire 1000 hr. aging period. The filled adhesives with improved bond strength during the initial portion of the aging program degrade below the strength of unfilled I-40 during the latter stages;  $As_2O_5$  and  $As_2S_4$  are the exceptions to this phenomena. The increase above, and subsequent decrease below, the bond strengths of unfilled I-40 adhesives indicate that the filler is scavenging materials that contribute to the degradation rate of the polymer, such as oxygen, iron oxide, or both. When the bond strengths decrease below those of unfilled I-40, the filler is apparently completely consumed by the reaction. Since the bond strengths of the adhesives filled with  $As_2O_5$  and  $As_2S_4$  do not decrease below the bond strength of the unfilled material, it may be concluded that these fillers are the most efficient scavengers. It may be concluded further that additional amounts of the fillers that show an improvement and then a loss would cause the aging characteristics of the I-40 adhesives to approach those of  $As_2O_5$  and  $As_2S_4$ . It is of interest that the fillers that improve the aging characteristics of I-40 adhesives ( $As_2O_5$ ,  $As_2S_4$ ,  $As_2O_3$ ,  $Bi_2O_3$ , and  $Sb_2O_3$ ) are compounds of group V elements with a primary valence of 3 and a secondary valence of 5.

The contribution of aluminum powder in the I-40 adhesives is selective and subtle. When used with  $V_2O_5$ , aluminum powder improves the thermal aging properties of I-40 adhesives; however, when used with  $Sb_2O_3$ , it substantially degrades the bond strength initially, but eventually the bond strengths are higher than both the unfilled I-40 adhesive or the I-40 adhesive with 5%  $Sb_2O_3$ . Adhesive I-40 filled with 40% aluminum powder behaves like the adhesive containing 5%  $Sb_2O_3$  and 35% aluminum powder. In fact, after 500 hr. of aging at 600°F. the average bond strengths are about equal.

A major function of metallic fillers in adhesives is matching the coefficients of thermal expansion of the adhesive and adherends, reducing residual thermal stress. The aluminum powder is apparently performing this function well while negating the beneficial effects of the  $Sb_2O_3$ . A possible explanation of this is that the  $Sb_2O_3$  is scavenging aluminum oxides, which are quite abundant compared with iron oxides, and the net result is an adhesive with 40% of inert filler. The less active  $V_2O_5$  is less receptive to the aluminum oxides; hence it performs the scavenging function which, along with reduced residual stress provided by the aluminum powder, results in an improved adhesive.

### Experiments With Style 112 E-Glass Cloth

The type 181 E-glass cloth provides a weight penalty when used as an adhesive carrier in airborne structures; consequently, experiments were performed with I-8 resin on style 112 E-glass cloth, which is thinner and less dense. Both 112 (heat-cleaned) and A1100 finishes were utilized.

An optimum resin content was established for the 112 E-glass cloth

TABLE III  
Effect of Resin Content: I-8 Resin on 112 E-Glass Cloth  
with 112 Finish, Adherends, AM350SCT, 0.063 in. Thick<sup>a</sup>

Resin content, <sup>b</sup> %	Bonding conditions		Bond-line thickness, in.	Test temp., °F.	Lap-shear tensile strength, psi	Cohesive failure, %
	Temp., °F.	Time, min.				
42.9	752	10	Did not bond			
64.8	752	5	0.0041	550	1,150	95
64.8	752	5	0.0051	550	750	100
72.3	752	5	0.0067	550	1,150	95
72.3	752	5	0.0064	550	750	100
70.2	752	5	0.0057	550	1,050	90
70.2	752	5	0.0057	550	1,050	98
79.0	752	5	0.0086	550	1,390	100
78.5	752	5	0.0082	550	1,370	75
78.5	752	5	0.0081	550	1,450	100
78.5	752	5	0.0087	550	1,450	95

<sup>a</sup> All samples pressed at 200 psi; all tests after 10 min. at temperature.

<sup>b</sup> No bonds were obtained with a resin content of 27% under any conditions of time (5 to 60 min.) or temperature (697 to 752°F.).

TABLE IV  
 Bonds with I-8 Resin on 112-A1100 E-Glass Cloth,  
 Adherends AM350SCT 0.063 in. Thick, Tested at 550°F. after 10 min.

Bond-line thickness, in.	Lap-shear tensile strength, psi	Cohesive failure, %
0.0063	1675	60
0.0068	1350	25
0.0052	2075	20
0.0056	1200	20
0.0063	1725	75
0.0065	1375	20

coated with I-8 resin. Adhesive bonds were made with these materials of differing resin content. The samples were bonded under a variety of conditions. Results of the experiments are shown in Table III. The best and most consistent bond strengths are obtained with 79 wt.-% resin. The higher resin content (percentage) is necessary to compensate for the lower glass density in the fabrics. However, these strength values are well below those obtained when 181-A1100 E-glass cloth was the carrier.

The 112-112 E-glass cloth was also treated with an A1100 finish prior to impregnation. This cloth was hand-dipped in a solution of ethyl alcohol (125 g.), water (125 g.), and A1100 (25 g.). Then the saturated cloth was dried in an oven at 302°F. for 1 hr. The 112-A1100 E-glass cloth was then coated with I-8 resin. The final resin content was 73%. Stainless steel AM350SCT, 0.063 in. thick, was bonded with this adhesive combination for 5 min. at 752°F. and 200 psi. Lap-shear tensile tests were performed at 550°F. Results of these experiments are given in Table IV.

The best bonds were obtained with the preferred polymers impregnated on style 181-A1100 E-glass cloth. The bond lines were about 0.010–0.013 in. thick. Bonds made with other substrates, such as 112-112 and 112-A1100 E-glass cloth, were inferior. The bond lines with these materials were about 0.007 in. thick. This contradicts generally accepted adhesive theory, which states that the thinner the bond line, the better the bond.

To explain this apparent contradiction it must be recognized that the best bonds were obtained with adhesives that had little flow and, consequently, no distortion in the glass cloth. The glass-cloth fibers were well oriented in the same manner as in glass-cloth laminates. Thus, the glass cloth in the adhesives was functioning as a stress-supporting member of a composite. This is not so with high-flow adhesives, in which the fiber bundles are separated from each other and frequently squeezed from the bonding area forming a thin bond line. In this case the structural integrity of the glass cloth is lost and serves little purpose beyond supporting the adhesive prior to and during bonding.

From a mechanical point of view the adhesive made of style 181 glass cloth will have a higher shear, Young modulus, and strength than the ad-

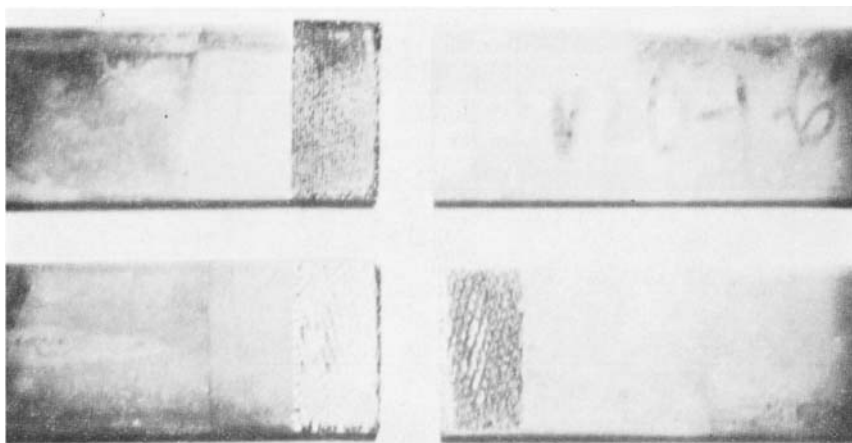


Fig. 8. Lap-shear failure interface. Top sample illustrates an adhesive failure; bottom, a cohesive failure. Note glass fibers in right side of bottom sample.

hesive made with style 112 glass cloth, simply because more high-strength high-modulus glass fibers are present in the style 181 cloth, and certainly the resin-glass composite will have a higher strength and moduli than the resin alone. The best bond strengths were obtained when failure occurred within the glass-cloth-resin composite, so that a layer of resin and some glass cloth remained on each adherend. This is a 100% cohesive failure (see Fig. 8).

Bonding with a high-modulus high-strength glass-cloth composite results in two bonds, both of which are between structural materials with a thin, organic, adhesive layer between. The bonds are between each metallic adherend and the glass-cloth-resin composite. This sort of construction results in two bond lines that are much thinner than 0.004 in. considered optimum for most adhesives. The thickness of style 181 glass cloth is 0.0085 in. So that a nominal bond line thickness of 0.011 in. obtained with the resin-glass composite results in a total resin or adhesive thickness of 0.0025 in. and a bond line thickness for each bond to the glass-cloth composite of 0.00125 in. This is about one-third the optimum bond-line thickness established for most other adhesives. To approach the generally accepted optimum of 0.004 in. bond-line thickness for each bond to the glass-cloth composite, a total bond-line thickness of 0.0145 to 0.0165 in. is required. Our experience has been that when the bond-line thickness exceeds about 0.014 in., the bond strengths are inferior, and predominantly adhesive-type failures occur.

The very thin bond lines between the metal adherends and the glass-fiber composite support greater loads, because statistically there are fewer flaws at which failure may be initiated. This is the reason why thin metal wires and glass fibers usually have higher strengths than similar materials with larger sections.

### BONDING TITANIUM

Early in the bonding program many aromatic imide polymers were evaluated for the ability to bond titanium 811. A few of these had fairly good bond strengths at room temperature and 550°F., but most polymers provided poor bond strengths. Consequently, a polymer was sought for bonding titanium alloys that would provide good bond strength and strength retention between 550 and 700°F.

Benzimidazole polymers were reported to provide good bond strengths and strength retention when used for bonding titanium metal. However, processing difficulties have been associated with imidazole structures in polymeric form, primarily because they have no soluble intermediate stage. Aromatic polyimides possess an intermediate soluble amic acid stage, and techniques for handling these polymers in solution have been well established.

An imidazole-imide copolymer designated BI-1 was synthesized, which possessed the desired imidazole structures along with the processing convenience of aromatic imides. BI-1 is the reaction product of benzophenone tetracarboxylic dianhydride and 5,4'-diamino-2-phenylbenzimidazole. The bonding conditions for BI-1 on 181-A1100 E-glass cloth were 797°F. and 200 psi for 5 min.

The results obtained with polymers that form good bonds with stainless steel are compared with BI-1 in Table V. BI-1 has the best strength retention at 700°F. of any of the polymers tested, besides having comparable bond strengths at lower temperatures.

TABLE V  
Bond Strengths Obtained With Titanium Adherends And Several Polymers

Polymer on 181-A1100 E-Glass Cloth	Average Lap Shear Tensile Strength at Test Temp. (°F.), psi			
	70	550	625	700
BI-1	1250	1420	1290	1130
I-8		600		
I-40		1760	1020	390
I-66		1520	870	250

#### Thermal Aging BI-1 Adhesives

Excellent bond strengths obtained with the BI-1 adhesive and titanium 811 prompted an investigation of the thermal aging characteristics of this system. The BI-1 on 181-A1100 E-glass cloth adhesive was used for bonding titanium 811, 0.063 in. thick, at 797°F. and 200 psi for 5 min. Aging studies were performed in Norman kilns at 550, 600, and 650°F. and in a forced-air oven at 600°F. Results of these experiments are presented graphically in Figure 9.

Aluminum powder and vanadium pentoxide were added to the BI-1 and this mixture coated on 181-A1100 E-glass cloth. The proportions were as follows:

Component	Resin solids, pph
BI-1 (15% solids in DMAC)	100
Aluminum powder	35
V <sub>2</sub> O <sub>5</sub>	5

After each coat the resin was cured in the manner described for the unfilled resins. The resin content was 46%.

This adhesive was used for bonding titanium 811, 0.063 in. thick, at 797°F. and 200 psi for 5 min. The samples were aged in a forced-air oven at 600°F. The results of these experiments are shown in Figure 9.

At 550 and 600°F. about 75% of the original hot strength is retained after 1000 hr. at temperature. At 650°F. degradation is much more rapid. At 600°F. the strengths are above those obtained at 550°F. This suggests that a postcure above 550°F. is required for maximum thermal-aging performance and bond strength. The presence of the powdered metal and oxide filler in the formulated sample appears to have little effect on this resin-metal combination.

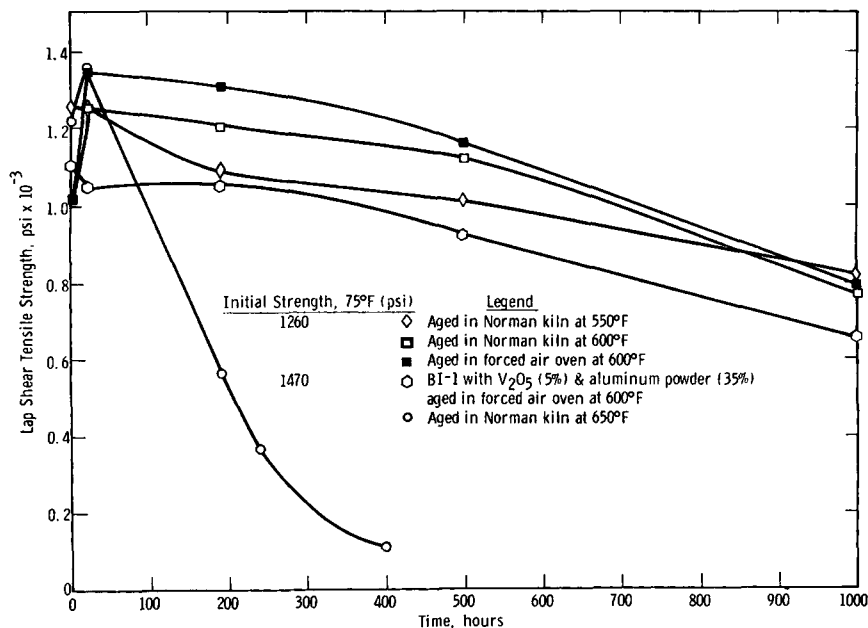


Fig. 9. Thermal aging; filled and unfilled BI-1 on 181-A1100 E-glass cloth; tested at aging temperature; adherends, titanium 811, 0.063 in. thick.

### EFFECT OF MOLECULAR STRUCTURE ON BOND STRENGTH

In order to illustrate clearly the structure of the aromatic imide copolymers it is convenient to consider four classes of unit structures. Class A structures are divalent radicals derived from diamines, Class B structures are divalent radicals derived from dianhydrides, Class C structures are


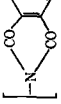



TABLE VI  
Structure and Adhesive Properties of I-8, I-40, and I-66

Polymer	Reactants (monomers)		Structure of polymer units				Lap-shear tensile strength at 550° F., <sup>a</sup> psi
	Chemical name	Structure	A	B	C	D	
I-8	<i>m</i> -Phenylenediamine (MPD), 100 parts						
	3,4,3',4'-Benzophenonetetracarboxylic dianhydride (BTDA), 100 parts					1930	
I-40	MPD, 98 parts BTDA 99.5 parts						2400
	<i>p</i> -Aminoacetanilide (PAA), 4 parts						
	Phthalic anhydride, 1 part						
I-66	MPD, 96 parts BTDA, 100 parts PAA, 4 parts						3300



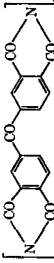


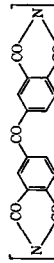

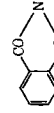
<sup>a</sup> Stainless steel AM350SCT, adherends; tested after 10 min. at 550°F.; lap-shear tensile strength is an average of three tests.

TABLE VII  
Structure and Adhesive Properties of I-54, I-55, and I-65

Polymer	Reactants (monomers)		Structure of polymer units				Lap-shear tensile strength at 550°F. <sup>a</sup> psi
	Chemical name	Structure	A	B	C	D	
I-54	MPD, 100 parts BTDA, 99 parts Phthalic anhydride, 2 parts	— — —			—		1650
I-55	MPD, 100 parts BTDA, 98 parts Phthalic anhydride, 4 parts	— — —	Same as I-54 but lower molecular weight (one-half molecular weight of I-54)				1600
I-65	MPD, 100 parts BTDA, 97.5 parts Phthalic anhydride 5 parts	— — —	Same as I-54 & I-55 but the lowest molecular weight of the series				1930

<sup>a</sup> Stainless steel AM350SCT, adherends; tested after 10 min. at 550°F.; lap-shear tensile strength is an average of three tests.

TABLE VIII  
Structure and Adhesive Properties of I-51, I-59, I-60, and I-61

Polymer	Reactants (monomers)		Structure of polymer units				Lap-shear tensile strength at 550°F., <sup>a</sup> psi
	Chemical name	Structure	A	B	C	D	
I-51	MPD, 98 parts BTDA, 100 parts Aniline, 4 parts						2180
I-59	MPD, 95 parts BTDA, 100 parts Aniline, 10 parts	—	Same as I-51 but lower molecular weight				1690
I-60	MPD, 99 parts BTDA, 99 parts Aniline, 2 parts Phthalic anhydride, 2 parts	—					2130
I-61	MPD, 97.5 parts BTDA, 97.5 parts Aniline, 5 parts Phthalic anhydride, 5 parts	—	Same as I-60 but lower molecular weight				1730

<sup>a</sup> Stainless steel AM350SCT, adherends, tested after 10 min. at 550°F.; lap-shear tensile strength is an average of three tests.

monovalent radicals derived from monoamines, and Class D structures are monovalent radicals derived from monoanhydrides. The polymer chains may consist of a sequence of A-B-A-B units, or, when terminating monofunctional reactants are used, the polymer chain sequence may be D-A-B-A- or A-B-A-B-C or D-A-B-A-B-C. In some cases several different A units are used, so that a typical chain would be A-B-A'-B. Regardless of the combinations and degree of functionality, amine-derived radicals link to anhydride-derived radicals.

The following experiments form several correlating and interlocking series of structural variations. For each series the reactants and various structures are provided in the appropriate table with the bond strength. To provide a basis for comparison, the structural varieties of I-8, I-40, and I-66 are shown in Table VI.

The following polymer series illustrates the effect of endblocking with phthalic anhydride. Polymers I-54, I-55, and I-65 are progressively lower molecular weight versions of I-8, and I-55 is one half the molecular weight of I-54. The structures and bond strengths are shown in Table VII. This method of endblocking has little effect on bond strength compared with the parent polymer I-8. In addition, lower molecular weight has little effect on bond strength.

The following group of experiments further demonstrates the effect of decreasing molecular weight through endblocking. This series of experiments (Table VIII) also indicates the effect which the method of endblocking (i.e., through the diamine or both the diamine and anhydride) has on bond strength. Comparison with other experiments will indicate the effect of the various components. The polymers were endblocked versions of polymer I-8. The chain stops used were aniline and phthalic anhydride, both monofunctional reagents in imide polymerizations. Polymers I-51 and I-60 have the same calculated molecular weight. In I-51 was used 4 molar parts of aniline per 100 moles of BTDA; in I-60, 2 molar parts of aniline and phthalic anhydride, for a total of 4 molar parts of endblockers. Polymers I-59 and I-61 are of lower molecular weight than I-51 and I-60. In I-59 and I-61 10 molar parts of endblockers was used. Ten molar parts of aniline in I-59 and 5 molar parts each of aniline and phthalic anhydride was used in I-61.

This series of experiments demonstrates that lower bond strengths are obtained as molecular weight is decreased. Moreover, the method of endblocking (i.e., through the diamine or through both the diamine and dianhydride) has little effect on bond strength, probably because either supplies a phenyl ring to terminate the chain. A comparison of polymers I-51 and I-60 with polymer I-55, all of which have the same theoretical molecular weight in Table VIII, indicates that endblocking with an anhydride alone is deleterious for the bond strength.

Bonds were also made with several polymers to determine the effect of the various diamine components on bond strength. Polymers I-57 and I-67 are similar in that each has 2 molar parts of *p*-aminoacetanilide and phthalic

TABLE IX  
Structure and Adhesive Properties of I-7, I-57, I-67, I-79, and I-69

Polymer	Reactants (monomers)		Structure of Polymer units				Lap-shear tensile strength at 550°F. <sup>a</sup> , psi
	Chemical name	Structure	A	B	C	D	
I-7	BTDA, 100 parts <i>p,p'</i> -Diaminodiphenyl ether, 100 parts						210
I-57	MPD, 49 parts BTDA, 98 parts PAA, 2 parts <i>p,p'</i> -Methylene-dianiline (MDA), 49 parts						2270
I-67	Phthalic anhydride, 2 parts MDA, 98 parts BTDA, 98 parts PAA, 2 parts Phthalic anhydride, 2 parts						1820
I-69	BTDA, 98 parts Phthalic anhydride, 2 parts <i>p,p'</i> -Diaminodiphenyl ether (DAPE), 100 parts						890
I-79	MDA, 96 parts BTDA, 100 parts PAA, 4 parts						2230

<sup>a</sup> Stainless steel AM350SCT, adherends, tested after 10 min. at 550°F.; lap-shear tensile strength is an average of three tests.

TABLE X. Structure and Adhesive Properties of I-43, I-44, I-45, and I-80

Polymer	Chemical name	Reactant (monomers)	Structure	A	B	C	D	Lap-shear tensile strength at 550°F., <sup>a</sup> psi.
I-43	MPD, 50 parts	=	=					900
	BTDA, 100 parts							
	3,5-Diaminobenzoic acid, DAB, 25 parts							
	2,4-Diamino acetanilide (DAA), 25 parts							
I-44	MPD, 70 parts	$C_2H_4-O-C_2H_4OH$	=					110
	BTDA, 100 parts							
	DAA, 20 parts							
	2-Ethoxyethanol, 20 parts							
I-45	DAB, 25 parts	=	=					180
	BTDA, 100 parts							
	DAA, 25 parts							
	DAPE, 50 parts							
I-80	MPD, 90 parts	=	=					2140
	DAA, 6 parts							
	PAA, 4 parts							
	BTDA, 100 parts							

<sup>a</sup> Stainless steel AM350SCT adherends; tested after 10 min. at 550°F.; lap-shear tensile strength is an average of three tests.

anhydride and 98 molar parts of BTDA. Polymer I-67 has 98 molar parts of methylenedianiline, while I-57 has 49 molar parts each of methylenedianiline and *m*-phenylenediamine. Polymer I-79 is similar to I-66 but contains methylenedianiline rather than *m*-phenylenediamine. A comparison is provided between polymers I-7 and I-8, the difference being that I-7 contains diaminophenyl ether rather than *m*-phenylenediamine.

The structures and strengths of the polymers are shown in Table IX. A comparison of the data (shown in Table VIII) obtained with polymers I-79, I-66 (see Table VI), I-57, and I-67 shows that methylenedianiline used as a whole or part of the diamine portion of the molecule degrades the properties from those obtained with *m*-phenylenediamine. The data obtained with I-69 and I-54 also indicate that linked two-ring diamines (diaminophenyl ether) provide inferior adhesives. This observation is further substantiated by the good bonds provided by I-8 (see Table VI) and the inferior bonds made with I-7.

A series of experiments was conducted in an effort to determine whether reacting free acetamido with free carboxylic acid groups, to increase molecular weight during the bonding process, would improve the bond strength (Table X). The presence of additional side chain acetamido groups (unreacted during bonding) was also examined, to learn whether a wetting effect (similar to I-66) would improve the adhesive strength. Diaminoacetanilide and diaminobenzoic acid were the reagents used for introducing the desired acetamido and carboxyl groups. The polymers chosen were I-80 (a polymer similar to I-66 with 6 molar parts of diaminoacetanilide and no diaminobenzoic acid), I-43 (which is similar to I-8, but half the *m*-phenylenediamine being replaced by equimolar parts of diaminoacetanilide and diaminobenzoic acid), and I-44 (another polymer similar to I-8, but containing 20 molar parts of diaminoacetanilide and employing an excess of BTDA partly esterified with 2-ethoxyethanol as a temporary endblocker). During the cure of polymer I-44 some condensation occurs with the elimination of 2-ethoxyethanol and acetic acid, giving amide crosslinks.

Polymers I-43, I-44, and I-45 did not provide acceptable bonds, and the bonds formed with I-80 were degraded somewhat compared with I-40 and I-66. However, all of these polymers flowed considerably, and the glass fibers were displaced in all of the bonds. Displacement occurred to a greater extent in the bonds with lower lap-shear tensile strengths. The high flow and good bond strengths obtained with I-80 indicate that this may be a good polymer for making high-temperature adhesives that will bond satisfactorily at lower temperatures and pressures. The diaminoacetanilide and diaminobenzoic acid do not improve strength but rather degrade bond strength considerably. Apparently, the expected reaction between the free acetamido and carboxyl groups did not occur to any appreciable extent, and unreacted side chains tended to plasticize the adhesive. If the reaction did occur to any appreciable extent, it is probable that the reaction by-products (water and acetic acid in the case of I-43, I-45, and I-80, and 2-ethoxyethanol and acetic acid in the case of I-44) provided a barrier between the metal and adhesive that prevented adhesion.

## CONCLUSIONS

Two polymers have emerged from this program as excellent high-temperature adhesives. Polymers I-40 and I-66, when used in conjunction with 181-A1100 E-glass cloth, provide bonds of high strength and high thermal and oxidative resistance with stainless steel AM350SCT.

When these adhesives are used for bonding properly cleaned stainless-steel adherends, lap-shear tensile strengths in excess of 3000 psi are observed at room temperature. Strength values well in excess of 2000 psi are consistently obtained at 550°F. More than 50% of this original value is retained at temperature after 1000 hr. in air at 550°F.

This family of resins also provides useful adhesive strength at temperatures up to 700°F. The life expectancy for bond strengths of 800–1000 psi at the higher exposure temperatures is about 40 hr. at 700°F., about 100 hr. at 650°F., and 400–450 hr. at 600°F. Repeated temperature-cycling between 40 and 550°F. causes little reduction in elevated temperature strength during the early stages of the aging period but has some effect on the long-term aging values.

The addition of powdered metal or oxide fillers generally does not provide any advantage to the optimum polyimide adhesive in terms of improved bond strength. An exception is the use of 5% of either arsenic pentoxide or arsenic thioarsenate, where considerably improved thermal life is observed with steel adherends ( $\approx$ 1600 psi at 600°F. after 1000 hr. at temperature).

Benzimidazole-imide copolymer BI-1 on 181-A1100 E-glass cloth is the preferred adhesive for bonding titanium 811. The BI-1 polymer provides the best strength retention at elevated temperatures, although the initial strengths are about half those obtained with other imide polymers. After 100 hr. of aging at 550 and 600°F. the bond strengths of BI-1 adhesives is three to four times better than other imide polymers used for bonding titanium. With polymer BI-1 and titanium 811 alloy, lap-shear tensile strengths of 1500 psi at 550°F. and 1100 psi at 700°F. have been achieved. After 1000 hr. in air at 600°F. the average strength at temperature was still in excess of 800 psi. Fillers and antioxidants do not improve the properties of BI-1 adhesives. Further investigation may lead to polymers showing even higher-strength bonds for titanium, since this is the parent structure of a family of materials.

Experiments performed to determine the effect of the various polymer components indicate the following conclusions.

(1) Endblocking with *p*-aminoacetanilide (I-40 and I-66) provides a substantial improvement in bond strength when compared with the parent polymer I-8.

(2) Phthalic anhydride in I-40 offers only a marginal improvement in thermal aging properties compared with I-8.

(3) Reducing the molecular weight through chain stops alone has little beneficial effect on adhesive strength of aromatic imide polymers, although greater solubility and more concentrated treating solutions can be obtained.



Solution viscosity also is stabilized by this means. Bond strengths are degraded when molecular weight is reduced by endblocking with phthalic anhydride (I-54, I-55, and I-65).

(4) Metaphenylenediamine is the preferred diamine. Other diamines, such as diaminoacetanilide, methylene dianiline, diaminobenzanilide, and diaminophenyl ether, form polymers with high flow and poor adhesion.

Adhesives made with aromatic imide and benzimidazole-imide copolymers require relatively moderate processing conditions, i.e., 750–850°F. and 200 psi for 5 min. The relatively high bonding temperature is severe compared with conventional adhesives. However, such a requirement is not unrealistic when the adhesives are expected to retain strength at 700°F. Generally, both metals and plastics must be processed at temperatures higher than they may expect to encounter in service.

Adhesives made with imide and benzimidazole-imide polymers have excellent shelf life, since the processing conditions associated with the polymers do not depend upon either residual volatiles or partially complete reaction stages.

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