Adhesive Bonding of Poly Aryl Phosphine-oxide Polyimide Polymers to Surface Treated Aluminum

An Honors Thesis (HONRS 499)

by

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signature

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Abstract

The durability of adhesively bonded aluminum using poly aryl phosphine-oxide polyimide polymers as adhesives has been investigated. The aluminum surface was prepared for bonding via reaction in acid and base solutions and by a neutralization process. The wedge geometry test was adopted for the durability studies. Crack propagation was followed for the bonded samples in order to determine the time-to-failure of the bond. The failure rate as a function of surface treatment varied in the manner: acid > base > neutral. The failure mode was determined by surface analytical spectroscopic methods including x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDX), and the mode of failure was found to be independent of the surface treatment. The mode of failure for all samples was found to be primarily cohesive with some adhesive failure near the edges of the samples. Overall, the poly aryl phosphine-oxide polyimide polymer was found to make a good bond with aluminum.
Introduction and Background Information

A primary concern in using adhesives is durability. The significant question is, "How long will the bonded structure last under stressful conditions?" Additional questions concern the specific role of environmental conditions and other factors on bond degradation. In tests using laboratory specimens and in tests of model components, it is well recognized (1,2) that environmental conditions, including water vapor and other liquids and vapors, accelerate adhesive bond failure. The combination of environmental conditions and applied stress accelerate failure to an even greater extent than either condition alone (3). The search for high temperature, durable adhesives has become increasingly important for the aerospace and electronic industries. Applications include use in supersonic transports, use as insulative and conductive materials for electronic chip boards, and use as lightweight, thermally stable structural materials for automobiles and aircraft (4-6). However, the aerospace and electronic industries are not the only places these high performance polymers and adhesives are being used. As a matter of fact, these polymers affect our everyday lives. They are used in binding systems in brake shoes, fire-resistant clothing, non-stick surfaces for cookware, lightweight electric irons, copying machines gears and picks, etc... (7).

The electronics industry utilizes adhesives in a variety of ways. Some forms of adhesives act as sealants and can be used to protect electrical devices from
environmental conditions. Adhesives that act as insulators, can be used for battery construction, pressure-sensitive tapes, flexible printed wiring boards, and other laminations (6). On the other hand, adhesives that act as conductors can be applied to attaching lead wires, hybrid circuits, light-emitting diodes, or in general, anywhere the bonds formed require the flow of electrostatic charges (6).

As mentioned previously, high temperature structural adhesives play a major role in the aerospace industry. In recent years, the U.S. government has been pushing for the development of high temperature polymers and adhesives because the development of such adhesives is behind the development of structural aerospace materials. Without adhesives that can withstand the temperatures and loads that the materials can withstand, the materials themselves can not be used to their potential. Typical service lives for these materials can be expected to range from the single flight of a missile at 500°C to the use of a supersonic transport at temperatures between 177-232°C for 50,000 hours (5).

The use of aluminum as the adherend in studies presents an easily altered surface since aluminum readily forms an oxide layer. The strength of the bond made is primarily dependent upon the interaction that occurs at the adhesive/adherend interface even for cohesive failure. It is therefore especially important to analyze the interface when bonding is preceded by a prebonding surface treatment (8). It has been found that in general, bond durability is increased when the prebonding treatment produces a slightly rough yet uniform surface (9). Understanding these issues, the use of a prebonding surface treatment
was used in the following studies.

Of course, the main concern of these studies is whether or not the poly aryl phosphine-oxide polyimide could be used as a high temperature adhesive. The worldwide market for high temperature adhesives in 1988 was estimated to be at 90 million kg with a value of $23 billion and of that 22% was polyimides (10). There are both advantages and disadvantages to the production and use of polyimides. Most polyimides are thermally stable and can now be manipulated easily to control molecular weight, add different functional groups, and alter many physical properties such as \( T_g \), \( T_m \), dielectric constant, toughness, etc... However, it is the chemical structure of the polyimides that makes them thermally stable; that same chemical structure makes many polyimides insoluble and difficult to use (7). The poly aryl phosphine-oxide polyimide being investigated shows "exceptional thermal and oxidative stability and solvent resistance (but not insoluble) and is complemented by excellent mechanical and electrical performance and dimensional stability over a wide temperature range (11-13)." Also, by adding the phosphorus group to the polyimide, the polymer demonstrates even better thermal stability and acts as a flame retardant (14).

From samples that have been bonded and failed, a significant amount of information can be determined. Not only can the mode and rate of failure be determined, but also such things as the elastic energy due to the deformation of the metal plates, the thermodynamic energy of adhesion (15), energy dissipation (16), and the surface free energy (16). All of these examples come from mechanical
tests such as the wedge geometry test (15), cantilever beam tests (15), lap shear tests, etc. Also, the internal stresses of a system can be studied. When a bond is made, a surface layer forms at the adherend/adhesive interface whose properties are different from the bulk of the adhesive. This difference is described as being due to internal stresses (8). By comparing the relaxation properties of the surface layer to those of the bulk of the material, one can determine the variation in mechanical properties throughout the transition layers of the polymer. For the purpose of durability studies in the following experiments, the wedge test will be used as a tool for debonding samples, but not, however, as a means of determining the energy stored in the bond. Eventually the aforementioned tests will be done with the poly aryl phosphine-oxide polyimide/aluminum system in order to complete the studies. Also, the mode of failure will be studied using surface spectroscopic techniques.

**Experimental**

Aluminum specimens, 1" X 4" X 1/16" were prepared for bonding via reactions in aqueous solutions (see procedure below). Following the treatment of the aluminum, the adherends were dried in a desiccator.

The aryl phosphine-oxide polyimide polymer, whose preparation is shown in scheme 1, was applied to the aluminum adherend from a 10-15% (w/w) solution in DMAC and then the specimen was heated at 170°C in a vacuum oven in order
to remove all solvent. This specimen was subsequently heated to 340°C in air and the second adherend bonded to the adhesive-coated aluminum by maintaining the sample in a press at 15,000 psi. for 10 minutes.

A crack was initiated in the bonded specimen by inserting a wedge. The cracked sample was then placed in a container containing room temperature air. Time to failure for the specimens was measured. The mode of failure was determined using surface analytical spectroscopic techniques.

Preparation of Neutral, NaOH, NH₄OH, HNO₃, and H₃PO₄ treated aluminum

Aluminum panels were first cleaned in methylene chloride to remove surface oil and lubricants-submerge panels at room temperature several times (3-4). Between each submersion the panels were allowed dry in air. The new oxide surface was prepared by submerging the panels in a 5% (w/w) NaOH solution at 50°C for 5 min. (the solution will evolve hydrogen gas). Panels were then removed from the caustic solution and submerged in 50% (v/v) conc. HNO₃ solution at room temperature for 2 min. The panels were removed from the acid solution and submerged in distilled (deionized) water for 2-3 min. Then the panels were rinsed in flowing distilled (deionized) water. Finally, the panels were submerged in appropriate solution:
a) 5% (w/w) NaOH solution (not solution from above) at room temp. for 3 min.

b) conc. NH₄OH at room temp. for 5 min.

c) 50% (v/v) HNO₃ at room temp. for 3 min.

d) 15% (v/v) H₃PO₄ at room temp for 3 min.

e) for neutral aluminum no further treatment necessary

Samples were stored in a desiccator until ready for bonding.

Preparation of modified FPL etch aluminum

To make solution, 122.5 g/L Fe₂(SO₄)₃·4H₂O in .185L of H₂SO₄ was diluted to 1L with water. Panels were submerged for 8 min. at 63°C then rinsed with DI water and stored in desiccator (17).
Preparation of the poly aryl phosphine-oxide polyimide was done by Dr. James McGrath's group at Virginia Tech. (18)
Preliminary Results

X-ray photoelectron spectroscopy (XPS) proved to be a valuable analytical technique for determining the mode of failure for samples; especially when the two components to be bonded had different compositions that could be used to distinguish between failure at the adhesive/metal interface (adhesive failure) or failure within the bulk of the adhesive (cohesive failure). See picture below for example of cohesive and adhesive failure. Such was the case with a poly aryl phosphine-oxide polyimide polymer bonded to aluminum. The polymer had a representative 2:1 nitrogen to phosphorus ratio which was observed on both sides of the adherends when cohesive failure was observed. On the other hand, aluminum was detected on at least one of the adherends when adhesive failure was observed. (See representative XPS data in Tables 1 & 2 for treated Al and polymer before bonding). Also to be noted was the increase in the concentration of carbon when polymer was detected on the surface, and the increase in the oxygen concentration that usually coincided with adhesive failure due to the Al$_2$O$_3$.
### XPS for Phosphine Oxide Polyimide Before Bonding

**Table 1**

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Cl</th>
<th>N</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-polyimide</td>
<td>79.23</td>
<td>15.08</td>
<td>0.15</td>
<td>1.32</td>
<td>0.61</td>
<td>3.62</td>
</tr>
<tr>
<td>2-polyimide</td>
<td>76.36</td>
<td>15.49</td>
<td>0.00</td>
<td>1.82</td>
<td>0.98</td>
<td>5.35</td>
</tr>
</tbody>
</table>

### XPS for Treated Al Before Bonding

**Table 2**

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>N</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$OH</td>
<td>10.7</td>
<td>59.8</td>
<td>22.1</td>
<td>1.5</td>
<td>0.00</td>
<td>5.9</td>
</tr>
<tr>
<td>FPL/Fe(III)</td>
<td>14.2</td>
<td>56.2</td>
<td>26.2</td>
<td>1.4</td>
<td>0.00</td>
<td>1.4</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>14.9</td>
<td>58.3</td>
<td>14.5</td>
<td>7.00</td>
<td>0.00</td>
<td>5.4</td>
</tr>
<tr>
<td>H$_3$PO$_4$</td>
<td>15.0</td>
<td>59.6</td>
<td>6.7</td>
<td>1.4</td>
<td>15.1</td>
<td>2.1</td>
</tr>
<tr>
<td>NaOH (Na made up 17.26%)</td>
<td>7.28</td>
<td>54.53</td>
<td>8.40</td>
<td>12.38</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Neutral</td>
<td>17.02</td>
<td>53.20</td>
<td>26.57</td>
<td>0.84</td>
<td>1.06</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Upon failure and analysis of the samples that were treated with the original five surface treatments- Neutral, NaOH, H$_3$PO$_4$, HNO$_3$, and NH$_4$OH, it was found that those surface treatments that produced relatively smooth oxide layers (ie. H$_3$PO$_4$, NH$_4$OH, and Neutral) produced the best bonds; whereas, the NaOH and the HNO$_3$ samples, which showed large residual oxide layers, did not bond well. Criterion used to determine a "good" bond was the mode of failure, whether it be cohesive (good) or adhesive (bad), and the time to failure. (See Appendix A for SEM photographs of treated Al before bonding.)

It appeared as though all samples except the H$_3$PO$_4$ and the neutral samples had failed mostly adhesively with a few spots of cohesive failure upon visual inspection. (See Figures 1-4). However, XPS data shown in Table 3 showed more cohesive failure than originally expected. Such was represented by the various spots tested where high concentrations of carbon, nitrogen, and phosphorus were detected. As seen in the XPS data the 2:1 nitrogen to phosphorus ratio was askewed; but the nitrogen and phosphorus presence was still contributed to the polymer because the treated Al before bonding had little or no phosphorus and nitrogen. The preliminary results were primarily used as a determining factor for the next step and were not relied on heavily in making conclusions. From these results, it was decided to continue the use of the neutral and NH$_4$OH treatments and to begin using the modified FPL etch, which also produced a relatively smooth oxide layer (See Appendix A).
## XPS Data for Failed Samples

### Table 3

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>N</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-H₃PO₄ (dull spot)</td>
<td>80.60</td>
<td>14.14</td>
<td>0.00</td>
<td>3.56</td>
<td>1.70</td>
<td>0.00</td>
</tr>
<tr>
<td>2-H₃PO₄ (dull spot)</td>
<td>80.64</td>
<td>13.90</td>
<td>0.00</td>
<td>3.76</td>
<td>1.70</td>
<td>0.00</td>
</tr>
<tr>
<td>1-H₃PO₄ (shiny spot)</td>
<td>76.60</td>
<td>16.51</td>
<td>1.46</td>
<td>3.72</td>
<td>1.71</td>
<td>0.00</td>
</tr>
<tr>
<td>2-H₃PO₄ (silver spot)</td>
<td>19.49</td>
<td>57.34</td>
<td>19.58</td>
<td>1.11</td>
<td>0.49</td>
<td>1.02</td>
</tr>
<tr>
<td>1-HNO₃ (black spot)</td>
<td>80.28</td>
<td>13.19</td>
<td>0.95</td>
<td>3.55</td>
<td>2.03</td>
<td>0.00</td>
</tr>
<tr>
<td>2-HNO₃ (black spot)</td>
<td>79.68</td>
<td>14.28</td>
<td>0.98</td>
<td>2.93</td>
<td>2.14</td>
<td>0.00</td>
</tr>
<tr>
<td>1-HNO₃ (silver spot)</td>
<td>30.03</td>
<td>46.68</td>
<td>19.56</td>
<td>2.96</td>
<td>0.48</td>
<td>0.00</td>
</tr>
<tr>
<td>2-HNO₃ (yellow spot)</td>
<td>54.72</td>
<td>30.86</td>
<td>11.08</td>
<td>2.24</td>
<td>0.93</td>
<td>0.00</td>
</tr>
<tr>
<td>1-NH₂OH (shiny spot)</td>
<td>80.38</td>
<td>11.35</td>
<td>0.48</td>
<td>4.97</td>
<td>2.66</td>
<td>0.00</td>
</tr>
<tr>
<td>2-NH₂OH (silver spot)</td>
<td>46.74</td>
<td>37.12</td>
<td>3.64</td>
<td>2.31</td>
<td>9.52</td>
<td>0.66</td>
</tr>
<tr>
<td>1-NH₂OH (dull spot)</td>
<td>70.30</td>
<td>20.43</td>
<td>1.67</td>
<td>3.11</td>
<td>4.08</td>
<td>0.41</td>
</tr>
<tr>
<td>2-NH₂OH (dull spot)</td>
<td>65.76</td>
<td>23.56</td>
<td>1.72</td>
<td>2.99</td>
<td>5.30</td>
<td>0.68</td>
</tr>
<tr>
<td>1-NEUTRAL (silver spot)</td>
<td>30.34</td>
<td>49.67</td>
<td>19.99</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2-NEUTRAL (shiny spot)</td>
<td>74.94</td>
<td>16.56</td>
<td>1.38</td>
<td>3.56</td>
<td>1.61</td>
<td>1.86</td>
</tr>
</tbody>
</table>

**NOTE:** Figures 1-4 coincide with Table 3 with the exception that there was no neutral sample picture. There was a picture but no data for the NaOH sample.
Durability studies or time to failure studies were done by the wedge geometry test (19). The wedge geometry test could be further used to determine the energy stored in a bond, but for our purposes, it was used only as a device to break the bonds and roughly determine which bonds had the greatest durability. The main disadvantage to the wedge test was that the force being applied to insert the wedge (see diagram below) was not controlled.
Time to failure results are recorded in Table 4.

Wedge Specimens - Time to Failure

Table 4

Preliminary tests

<table>
<thead>
<tr>
<th>surface treatment</th>
<th>time to failure (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>I</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>I</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>2</td>
</tr>
<tr>
<td>HNO₃</td>
<td>I</td>
</tr>
<tr>
<td>Neutral</td>
<td>FF-26</td>
</tr>
</tbody>
</table>

FF = force failed (crack propagation stopped)
I = immediate (upon entering wedge)

The randomness of the preliminary data caused us to once again use it merely as a deciding factor for the next step and not as a source for drawing conclusions.
Final Results

For the final tests, six samples of each of the three surface treatments (Neutral, NH$_2$OH, and modified FPL) were bonded, debonded, and analyzed. The samples all showed failure similar to that of the picture below with primarily cohesive failure and a some adhesive failure near the edges.

![Picture of failure sample](image)

The XPS data in Table 5 also coincided with the visual analysis. The data showed that for the failed samples, independent of the surface treatment, the two failure sides were equivalent and that the results were similar to those for the pure adhesive including the 2:1 nitrogen to phosphorus ratio.

In this case, the wedge geometry tests were a little more conclusive. Table 6 shows that the rate to failure did seem to be dependent upon surface treatment in order of acid > base > neutral.
**XPS Data for Failed Samples**

Table 5

Element: Percent Concentration

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>N</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-FPL B</td>
<td>61.63</td>
<td>26.77</td>
<td>4.61</td>
<td>2.66</td>
<td>1.36</td>
<td>2.98</td>
</tr>
<tr>
<td>2-FPL B</td>
<td>75.63</td>
<td>16.79</td>
<td>0.00</td>
<td>2.96</td>
<td>1.69</td>
<td>2.92</td>
</tr>
<tr>
<td>1-FPL D</td>
<td>74.55</td>
<td>16.14</td>
<td>0.00</td>
<td>2.65</td>
<td>1.47</td>
<td>5.20</td>
</tr>
<tr>
<td>2-FPL D</td>
<td>76.05</td>
<td>15.61</td>
<td>0.00</td>
<td>3.14</td>
<td>1.59</td>
<td>3.62</td>
</tr>
<tr>
<td>1-NH₄OH B</td>
<td>76.64</td>
<td>15.30</td>
<td>0.00</td>
<td>2.61</td>
<td>1.71</td>
<td>3.74</td>
</tr>
<tr>
<td>2-NH₄OH B</td>
<td>75.72</td>
<td>15.60</td>
<td>0.00</td>
<td>2.96</td>
<td>1.60</td>
<td>4.12</td>
</tr>
<tr>
<td>1-NH₄OH D</td>
<td>76.25</td>
<td>15.38</td>
<td>0.00</td>
<td>3.01</td>
<td>1.60</td>
<td>3.76</td>
</tr>
<tr>
<td>2-NH₄OH D</td>
<td>76.57</td>
<td>15.16</td>
<td>0.00</td>
<td>2.95</td>
<td>1.61</td>
<td>3.72</td>
</tr>
<tr>
<td>1-NEUT. A</td>
<td>70.38</td>
<td>18.90</td>
<td>0.00</td>
<td>2.34</td>
<td>1.36</td>
<td>7.02</td>
</tr>
<tr>
<td>2-NEUT. A</td>
<td>67.41</td>
<td>20.75</td>
<td>0.00</td>
<td>2.25</td>
<td>1.18</td>
<td>8.41</td>
</tr>
<tr>
<td>1-NEUT. B</td>
<td>69.45</td>
<td>18.38</td>
<td>0.00</td>
<td>3.28</td>
<td>1.51</td>
<td>7.37</td>
</tr>
<tr>
<td>2-NEUT. B</td>
<td>69.92</td>
<td>18.22</td>
<td>0.00</td>
<td>2.99</td>
<td>1.53</td>
<td>7.34</td>
</tr>
</tbody>
</table>
Final tests

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Time to Failure for four samples (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>FF,FF,FF,FF</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>10,1,6,FF</td>
</tr>
<tr>
<td>Modified FPL etch</td>
<td>FF,16,I,I</td>
</tr>
</tbody>
</table>

One explanation for the failure results could be that if the SEM's of the Al treated before bonding were analyzed, it appeared as though the FPL and the NH₄OH oxide layers contained pits, whereas, the neutral sample had a relatively smooth, uniform oxide layer. Should the polymer fill these pits and create anti-parallel layers or possibly even pockets throughout the bulk of the material, it would allow for rapid progression of the crack when it reached one of these pits.

Scanning electron microscope/energy dispersive x-ray analysis (SEM/EDX) was used to verify the modes of failure for both preliminary and final tests. SEM imaged the surface while EDX was another way besides XPS to do elemental analysis. Figures 5-8 show the different modes of failure and what a representative photo and elemental analysis of the pictured area would look like. Light dots are used to represent the patterns of elemental distribution on the samples. One must note when doing EDX that the per cent concentration of each element was not evaluated with respect to the other elements but was evaluated with respect to its own abundance throughout the surface being analyzed. Figure 5 is an example of
adhesive failure with only the aluminum surface being exposed and analyzed. As mentioned before, even though there were light spots in the regions of carbon, oxygen, and phosphorus, that only means that no difference in concentration was detected, whether that concentration be 0% or 50%. Another example of adhesive failure is Figure 6. However, in this case small pieces of polymer had pulled onto the Al surface. The EDX map showed high concentrations of Al with a piece cut out around the polymer, in which case the presence of phosphorus was observed. Figure 7 is an example of cohesive failure with only the polymer showing with the exception of a small concentration of Al along the edge of the scanned area. Due to the presence of the polymer the EDX scan primarily showed the presence of phosphorus. Figure 8 is an example of mixed mode failure but is mostly cohesive failure which could be noted by the overall high concentration of phosphorus. There are areas were the polymer had pulled onto to the opposite adherend and left the Al surface exposed. The SEM/EDX system approved to be quite valuable in determining the mode of failure for the samples and to what degree each mode was prevalent.
SEM/EDX of Aluminum after Adhesive Failure

Figure 5

Carbon

Oxygen

Aluminum

Phosphorus
SEM/EDX of Adhesive Failure

Figure 6

Carbon

Oxygen

Aluminum

Phosphorus
SEM/EDX of Polymer after Cohesive Failure

Figure 7

Carbon

Oxygen

Aluminum

Phosphorus
SEM/EDX of Mixed Mode Failure

Figure 8
Conclusions

The poly aryl phosphine-oxide polyimide was found to make a good bond with aluminum, which was represented by the cohesive failure. It was found that the mode of failure was independent of the surface treatment, but the rate of failure was dependent on the surface treatment and varied in the manner acid > base > neutral. From these tests come many new unanswered questions and new areas to be investigated. Among these areas include trying to determine which functional groups of the polymer are doing the bonding to the Al, what effect solvents will have on the rate of failure, and how much energy is stored in the bond. Also not discussed was the presence of silicon in many of the failed samples and how the silicon may have affected the bond made and broken.
References


Appendix A
neutralized

modified FPL etch
NaOH

HNO₃