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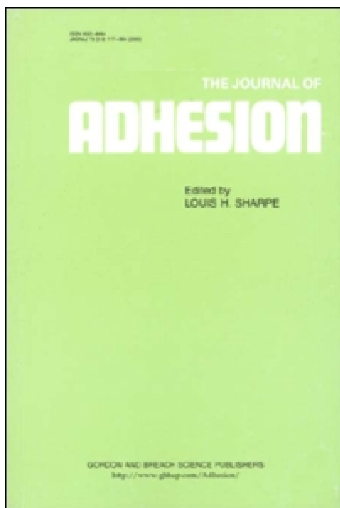

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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M. M. Ellison[a]; L. T. Taylor[a]
[a] Department of Chemistry, Virginia Polytechnic Institute and State Univeristy, Blacksburg, VA, USA

To cite this Article Ellison, M. M. and Taylor, L. T.(1997) 'Polyimide Adhesives and Aluminum', The Journal of Adhesion, 60: 1, 39 — 49
To link to this Article: DOI: 10.1080/00218469708014408
URL: http://dx.doi.org/10.1080/00218469708014408

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J. Adhesion, 1997, Vol. 60, pp. 39–49
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Polyimide Adhesives and Aluminum

M. M. ELLISON and L. T. TAYLOR*

Department of Chemistry, Virginia Polytechnic Institute and State Univeristy, Blacksburg, VA 24061-0212, USA

(Received July 19, 1995; in final form January 26, 1996)

This study examines the effect of thioether sulfur in the polyimide backbone, polyimide T_g, and adherend surface pre-treatment on aluminum bond strengths as determined with both peel and wedge specimens. Surface pretreatment and T_g had more of an effect on peel strength than the presence of sulfur in the polyimide backbone. NaOH etching and comparatively low T_g polyimides combined to produce the highest peel strengths. Together, these factors combined the removal of surface oxide from the adherend with a flexible polyimide which could better relieve stress during testing. Little difference was observed between the peel strengths of sulfur and non-sulfur containing polyimides, and no oxidation of sulfur was observed in the peel samples. NaOH etching also caused both wedge and peel specimens to fail more within the polyimide than in the oxide layer of the adherend. Thus, the NaOH etch appeared to increase interfacial adhesion between the aluminum and the polyimide. The low T_g polyimides performed better than the high T_g polyimides in the wedge test, with the polyimide derived from 4,4′-bis(3,4-dicarboxyphenoxy) diphenyl sulfide dianhydride and 4,4′-diaminodiphenyl ether (BDSDA/ODA) performing the best. This observation could be due to a metal-sulfur interaction since oxidized sulfur was surprisingly observed on the failed surfaces of these bonds regardless of the environment or surface pretreatment. A metal component in the aluminum alloy rather the aluminum is believed to promote the sulfur oxidation.

KEY WORDS: Aluminum; polyimide adhesives; peel test; wedge test; thioether sulfur; spectroscopy; XPS; surface pretreatment; synthesis.

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INTRODUCTION

Few studies have examined the adhesion of polyimides to aluminum substrates because the upper temperature limit on use is not very different from that for aluminum itself. Those that have used aluminum as an adherend were usually examining factors other than metal-polymer interactions. One example was the study by Driscoll and Walton which used aluminum 2024 alloy adherends to determine the lap shear strength of a variety of different commercial polyimides.[1]

Other polyimide-aluminum studies included attempts to create a graded interface region between an aluminum adherend and 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride with either 3,4-bis (aminophenoxy)benzene or 4,4′-diaminodiphenyl ether polyimide adhesive.[2,3] These studies used cobalt(II) chloride hexahydrate and tris(2,4-pentanedionato)aluminum(III) as modifers to create a concentration gradient of metal particles along the interface. The modified adhesives in

*Corresponding author.

these studies possessed lower peel strengths than the non-modified adhesive as determined by the floating roller peel test. None of these studies, however, examined the possibility of interaction between the metal adherend and the polymeric adhesive. This report will address in part the issue of polyimide-aluminum interaction.

Both sulfur and non-sulfur containing polyimides possessing either high or low T_g have been examined using aluminum adherends. Aluminum was studied first, as opposed to other more traditional adherends, because it was shown earlier not to catalyze the oxidation of the sulfur-containing polyimides.[4] Consequently, no metal catalyzed oxidation of the surface which would affect bond strength is likely. Surface analysis of failed bond specimens was used to determine the chemical state and composition of the interfacial regions. These data were then correlated with bond strength and the mechanism of bond failure. A study describing the interaction of polyimides and steel adherends will follow in a separate paper.

EXPERIMENTAL

Materials

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4,4′-Bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA) was obtained from NASA Langley Reserach Center (Hampton, VA), recrystallized twice from 2-butanone, and vacuum dried overnight at 120°C prior to use. 3,3′,4,4′-Benzophenonetetracarboxylic acid dianhydride (BTDA) was obtained from Allco Chemical Corp. (Galena, KS) and vacuum dried at 120°C. Zone refined 4,4′-diaminodiphenyl ether (ODA) was obtained from Aldrich Chemical Co. (Madison, WI) and was vacuum dried overnight at 70°C before use. Other diamines were 4,4′-diaminodiphenyl sulfide (ASD) and 3,4-bis(aminophenoxy) benzene (APB) obtained from Mitsui Toatsu (Tokyo, Japan), each vacuum dried at 80°C overnight. The molecular structures of these monomers are shown in Figure 1. *N*,*N*-Dimethylacetamide (DMAc) was also obtained from Aldrich Chemical Co. and was stored under nitrogen in Sure Seal® bottles. High purity aluminum foil (99.99%, 0.01 mm thick) and Al 6061 aluminum alloy coupons (15.2 cm × 2.54 cm × 0.64 cm) were used as adherends.

Synthesis

Poly(amide acid) solutions were made by reacting equal molar amounts of diamine and dianhydride in DMAc (11% solids for BDSDA solutions and 18% solids for BTDA solutions) under a nitrogen atmosphere at room temperature. The monomers were allowed to react for at least two hours in the stirred solution.

Bonding

The aluminum substrates were pretreated by either a quick acetone wipe or a chemical etch. The etching process consisted of immersing the aluminum in an aqueous 5% NaOH (w/w) bath for thirty seconds at room temperature followed by

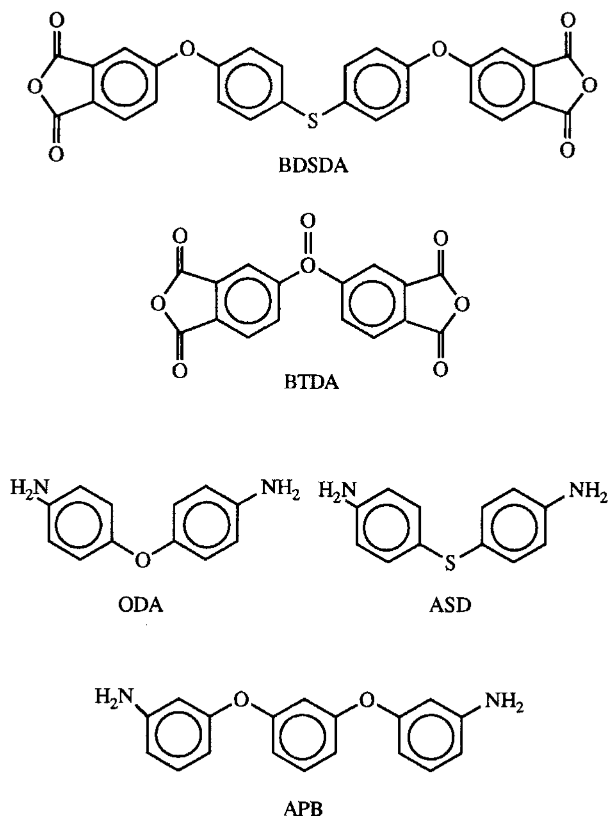

FIGURE 1 Molecular structure of monomers used in this study.

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a rinse with deionized water. The aluminum was then immersed in a 10% HNO_3 (w/w) solution for ten seconds, rinsed with deionized water, and air dried.

The peel samples were prepared by casting the poly(amide acid) solution using a doctor balde at a thickness of 0.5 mm for BDSDA solutions and 0.28 mm for BTDA solutions onto two pieces (17.8 cm × 15.2 cm) of the pretreated aluminum foil. These coated substrates were then cured under a dynamic air atmosphere at 80°C for 20 minutes and at 100° and 150°C for an hour each. Next, two trimmed pieces (15.2 cm × 12.7 cm) of the coated substrate were placed, adhesive sides together, in a Carver Hot Press. The specimen was heated to 200°C under contact pressure and then heated for an hour each at 200° and 300°C under 3.45 MPa. The press was then allowed to cool to room temperature under pressure. The bonded foil was cut into 0.5 cm strips for testing.

The wedge samples were prepared by casting the poly(amide acid) solution onto twelve coupons leaving 2.54 cm free along one end. The solution was cast at twice the thickness described for the peel specimens. The coated coupons were precured in a similar fashion to the peel samples. After the precure, the six sets of two coupons each were placed into the hot press and bonded as described above. After bonding,

the coupons were taken from the press and numbered one to six (left to right) with the odd-numbered bonds being stored in the dessicator and the even-numbered bonds being stored under water during testing.

Measurements

Peel strength was determined using the T-peel test on a Model 1123 Instron tensile tester with a 5 kN load cell at a cross-head rate of 100 mm/min. The wedge test was performed by inserting a 0.33 cm wedge into the bond to a distance of 0.64 cm. The initial crack was measured as was the subsequent crack growth as a function of time.

X-ray photoelectron spectroscopy data were obtained using a Perkin-Elmer Phi Model 500 ESCA system equipped with a magnesium anode ($K\alpha = 1253.6$ eV) operated at 400 W. The samples were attached to copper mounts using double-stick transparent tape. The binding energies obtained from XPS spectra were all corrected by positioning the C (1s) photopeak of the aromatic polyimide backbone at 284.6 eV.

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RESULTS AND DISCUSSION

Four polyimides were used to bond aluminum to aluminum in this study. Two were low T_g polyimides; one containing sulfur (BDSDA/ODA, 217 °C) and one not containing sulfur (BTDA/APB, 198°C). The other two were high T_g polyimides; sulfur-containing (BTDA/ASD, 285°C) and non-sulfur-containing (BTDA/ODA, 285°C). From previous work with metal-modified free standing films,[4] it was hypothesized that the aluminum from the substrates would not significantly catalyze the oxidation of thioether sulfur in the sulfur-containing polyimides.

Two tests were selected to examine the effects, if any, of high/low T_g and surface pretreatment. The T-peel test was chosen due to the simplicity of the test and its emphasis on interfacial strength, while the wedge test was chosen because of its emphasis on bond durability. While the stress situation in the peel test is difficult to assess, the peel test has often been used to compare the relative strengths of adhesives and the effects of surface pretreatment.[5,6]

Peel Tests

The T-peel results of several repetitions have been tabulated in Table I. The peel strength of the NaOH etched BTDA/APB bonds (5.21 ± 0.82 N/cm) corresponded well with that found by Horning (5.3 N/cm)[2] for the same polyimide and pretreatment even though he used the floating roller peel test. Comparisons with the other values were not found in the literature. Standard deviations for the peel strengths were good for most of the samples, especially the acetone wiped BTDA/ODA, BTDA/ASD, and BDSDA/ODA specimens.

For a given polyimide, the bonds made using etched aluminum adherends were significantly stronger than those using only acetone-wiped aluminum adherends. The enhanced strength of the etched aluminum bonds was most likely due to the

TABLE I
T-Peel Strength and Mode of Failure in the Polyimide/Aluminum Foil Bonds

			Wiped Bonds		Etched Bonds	
Polyimide	T_g	Sulfur	T-Peel Strength (N/cm)	Failure Mode	T-Peel Strength (N/cm)	Failure Mode
BTDA/APB	Low	No	3.85 ± 0.42	Oxide	5.21 ± 0.82	Adhesive
BDSDA/ODA	Low	Yes	2.88 ± 0.15	Oxide	6.64 ± 2.27	Adhesive
BTDA/ODA	High	No	0.38 ± 0.10	Oxide	3.40 ± 1.55	Mixed Mode
BTDA/ASD	High	Yes	1.04 ± 0.09	Oxide	1.63 ± 0.37	Mixed Mode

reduction or removal of a weak oxide layer at the surface prior to bonding. Surface analysis of the failed bonds corroborated this hypothesis. The atomic concentration of total aluminum (both oxide and metal) on the failed surfaces of the etched aluminum bonds was consistently lower within a given adhesive system than the acetone-wiped aluminum surfaces. The increased aluminum on the failed acetone-wiped surfaces seemed to indicate that these bonds failed within the oxide layer of the aluminum, thus leaving considerable amounts of aluminum on both surfaces. The etched substrates, on the other hand, have less of the oxide layer present. One failed surface of the etched bonds consistently had only a small (2–3%) amount of aluminum as opposed to the wiped failed surfaces. The presence of such a small amount of aluminum on one surface would seem to indicate that these bonds failed more within the polyimide portion of the interphase region as opposed to the oxide region.

It was also interesting to note that the low T_g polyimides possessed higher peel strengths than the high T_g polyimides for a given surface pretreatment. One possible explanation was that the processing conditions (*i.e.* the precure and press temperatures) were not high enough to allow sufficient intermingling of the two adhesive coats to produce a strong bond in the high T_g case. If there had been a strong bond, then the locus of failure would be expected to occur cohesively within the adhesive itself. Surface analysis of the failed surfaces, however, indicated that the locus of failure was primarily along the interface. The most likely answer, therefore, for this observation is that the stiff chains of the rigid polyimide backbone in the high T_g polyimides dissipate less energy by visocoelastic flow during the peeling process and are more likely to fail under lower stresses. No evidence could be detected for metal-sulfur interactions in the sulfur-containing polyimides which was as expected because aluminum had been shown earlier not to catalyze sulfur oxidation significantly.[4] The sulfur 2p photopeak from the failed surfaces had a binding energy of 163.2 eV which also indicated that the sulfur remained in the thioether form.[7]

Wedge tests were performed under wet and dry environments using the four polyimides with both surface pretreatments. The BTDA/ASD bonds failed upon insertion of the wedge no matter what pretreatment was used. Surface analysis (Fig. 2) indicated that the acetone-wiped Al 6061 bonds failed in mixed mode. Some aluminum (8.2 atomic % and 2.0 atomic %) was present on both failed surfaces in addition to the polyimide components. The NaOH-etched Al 6061 bonds failed

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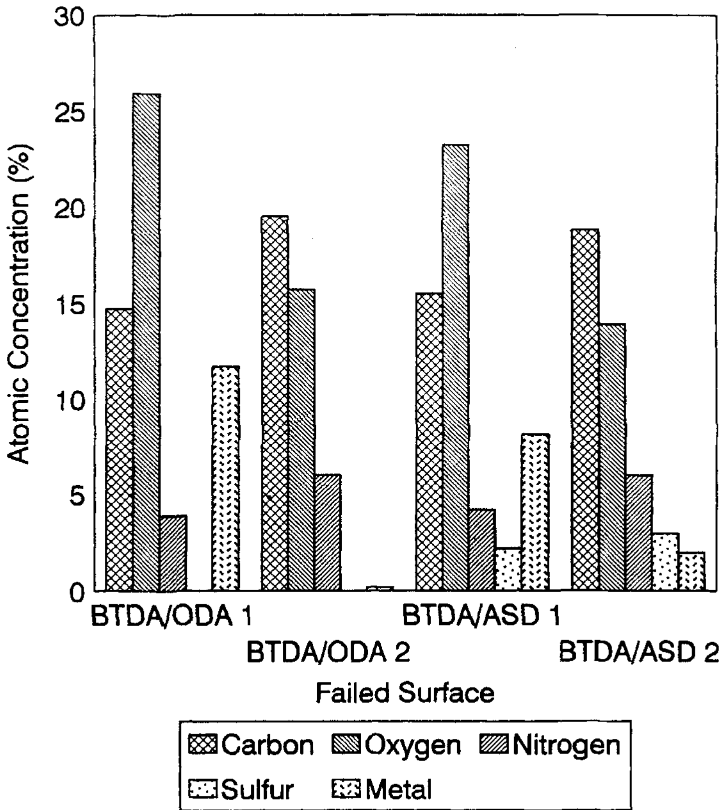

FIGURE 2 Surface atomic concentrations of failed acetone-wiped high T_g polyimide/aluminum wedge bonds tested in a dry environment.

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cohesively within the adhesive (Fig. 3). Less than 1% of aluminum was present on either surface.

The BTDA/ODA acetone-wiped bonds, both wet and dry, failed within ninety minutes, while the etched bonds failed within two hours. Again, the bonds seemed to fail too quickly for environmental conditions to have had much of an effect on crack growth, although environmental conditions did seem to affect how bonds failed. The dry acetone-wiped BTDA/ODA bonds failed adhesively (Fig. 2), as determined by XPS, since one side had a considerable amount of aluminum (11.7%), while the other side had practically none (0.2%). The dry NaOH-etched BTDA/ODA bonds appeared to fail in mixed mode (Fig. 3) since sizable amounts of both aluminum and polyimide were found on both surfaces. The wet acetone-wiped BTDA/ODA bonds were assumed to fail cohesively since only 1% of aluminum was found on either surface.

As in the peel tests, the low T_g polyimides generally performed better in the wedge tests than the high T_g polyimides. The acetone-wiped BTDA/APB bonds had an initial crack length of 51 mm $\pm$ 9 mm (Fig. 4). The wet acetone-wiped bonds failed after three hours, while the dry acetone-wiped bonds appeared to stop after a crack

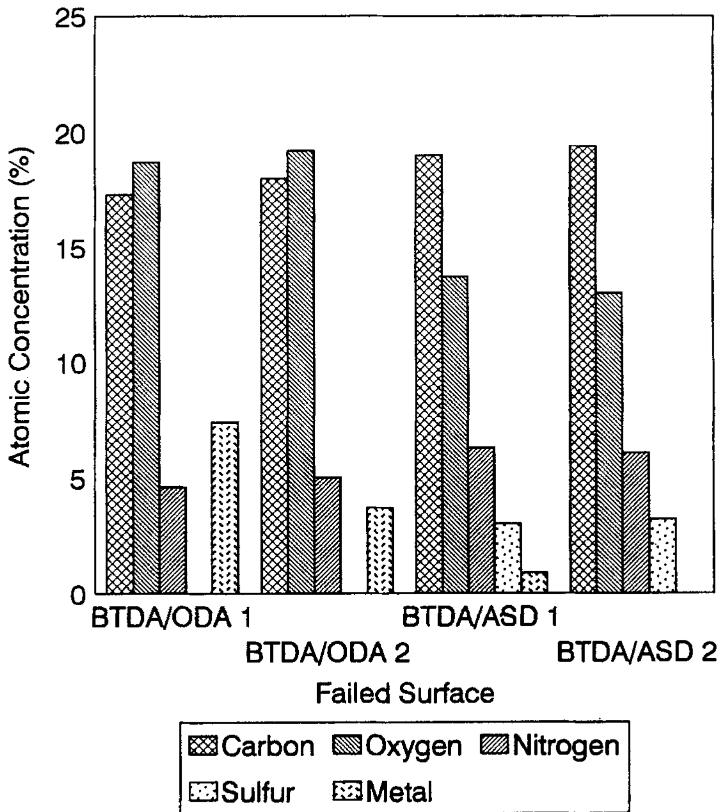

FIGURE 3 Surface atomic concentrations of failed NaOH-etched high T_g polyimide/aluminum wedge bonds tested in a dry environment.

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growth of 18 mm ± 7 mm in three hours. Surface analysis of both the wet and dry acetone-wiped BTDA/APB bonds indicated that they failed cohesively. The etched BTDA/APB bonds all failed within a few minutes (~2 min) of inserting the wedge and were determined to have failed cohesively *via* XPS (Fig. 5).

Overall, the BDSDA/ODA bonds performed the best in the wedge test. The bonds using acetone-wiped substrates had an initial crack growth of 48 mm ± 8 mm. After four hours, however, the average crack growth was only 5 mm ± 6 mm for the acetone-wiped BDSDA/ODA bonds tested in a dry environment. The acetone-wiped BDSDA/ODA bonds tested in a wet environment, however, had an average crack growth of 29 mm ± 11 mm after four hours. The NaOH-etched BDSDA/ODA bonds tested in a dry environment had an average crack growth of 38 mm ± 1 mm after eleven days. The NaOH-etched BDSDA/ODA bonds tested in a wet environment had an average crack growth of 42 mm ± 7 mm after eleven days, which was similar to the crack growth of 41 mm ± 16 mm after twenty-two days for the wet acetone-wiped BDSDA/ODA bonds.

The wet BDSDA/ODA bonds were determined to have failed within the substrate *via* XPS (Fig. 6) because very little polyimide (*i.e.* nitrogen and sulfur concentrations)

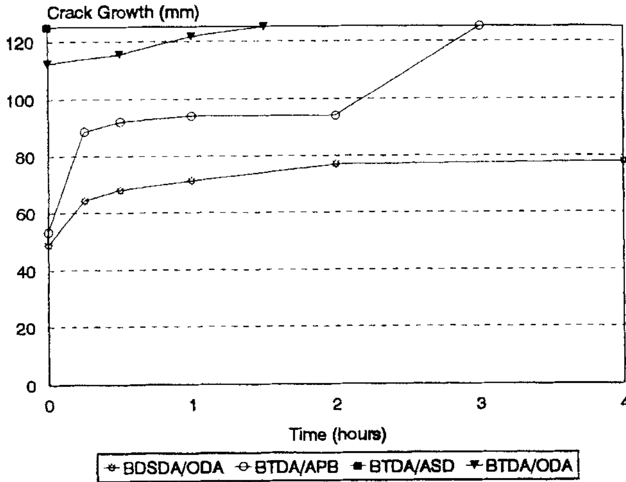

FIGURE 4 Crack growth in acetone-wiped polyimide/aluminum wedge bonds tested in a wet environment.

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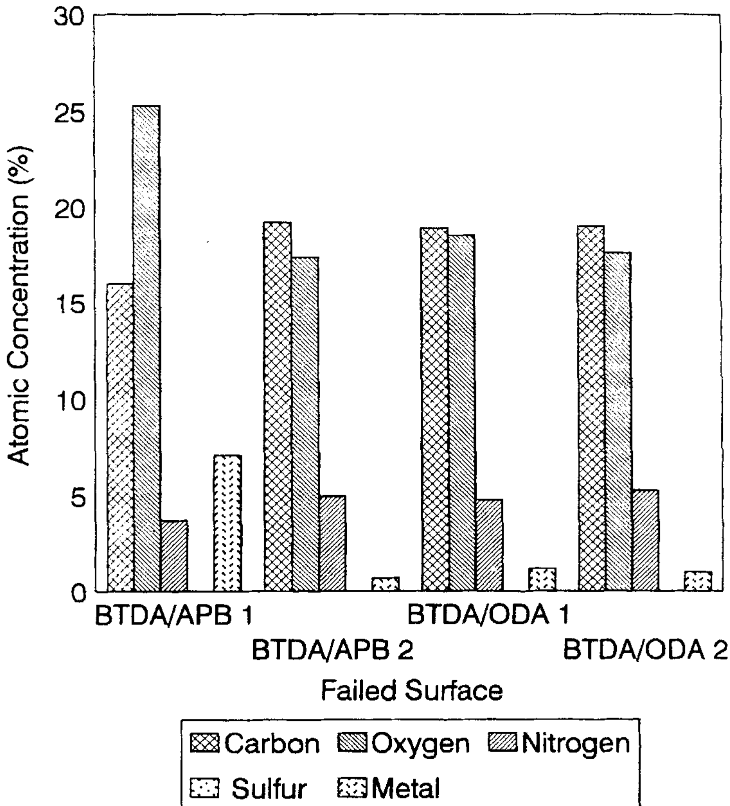

FIGURE 5 Surface atomic concentrations of failed acetone-wiped BTDA/ODA/aluminum and BTDA/APB/aluminum wedge bonds tested in a wet environment.

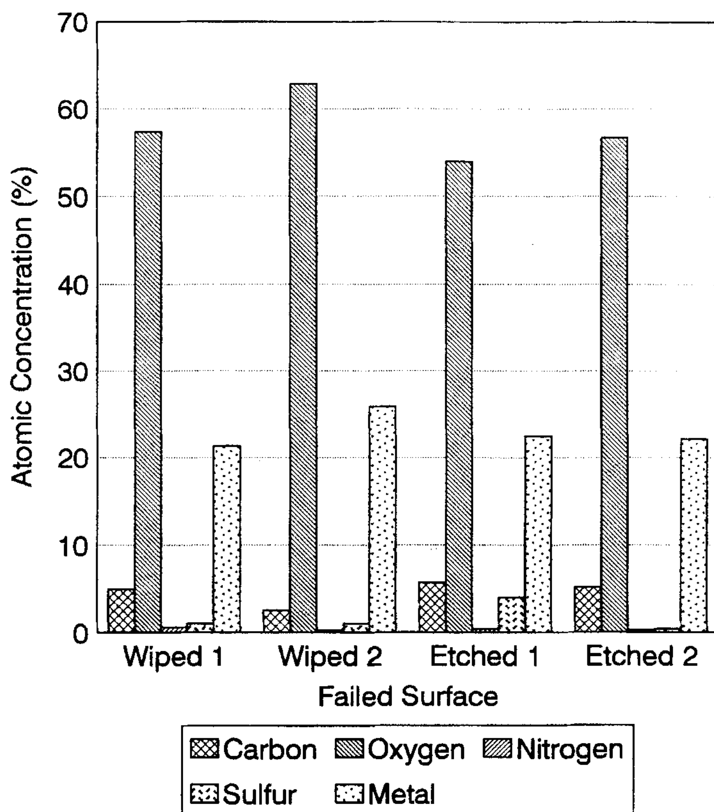

FIGURE 6 Surface atomic concentrations of failed acetone-wiped and NaOH-etched BDSDA/ODA/aluminum wedge bonds tested in a wet environment.

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was observed on either surface. The surface pretreatment did not seem to have an effect. Also, some sulfur had been oxidized along these surface (Fig. 7). The dry acetone-wiped BDSDA/ODA bonds failed interfacially since one side had some aluminum ($\sim$7.6 atomic %), while the other side had very little ($\sim$1 atomic %). Meanwhile, the dry NaOH-etched BDSDA/ODA bonds failed in mixed mode since aluminum and polyimide both were found on each surface in significant amounts.

The exposed surfaces of BTDA/ASD were not close enough to the interface to observe whether the sulfur was oxidized or not (Fig. 8). Oxidized sulfur was not observed, however, on the failed surfaces of the peeled samples. The substrates used in the wedge specimens were alloys, where as aluminum metal was used in the peel specimens. The peel specimens were also prepared from two pieces of 12.7 cm $\times$ 15.2 cm foil, while the wedge specimens were prepared using six sets of two 2.5 cm $\times$ 15.2 cm coupons. Thus, the smaller wedge specimens had more surface area around the edges for oxygen to diffuse into the polyimide to cause the oxidation but, as previously stated, with XPS we were unble to ascertain if sulfur had been oxidized. Obviously, from the data shown on BDSDA/ODA our assumption that sulfur is not oxidized in the presence of aluminum alloy is in error.

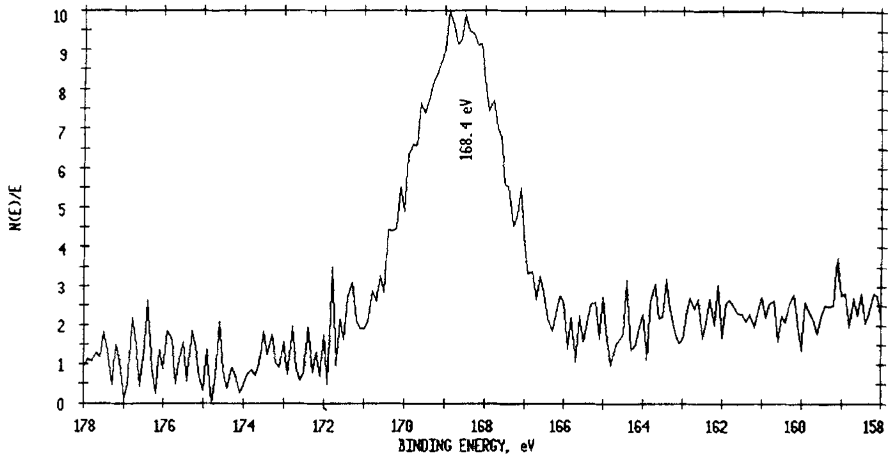

FIGURE 7 Sulfur 2p XPS photopeak of failed BDSDA/ODA wedge bonds surface tested in a wet environment (binding energy calibrated to C 1s = 284.6 eV).

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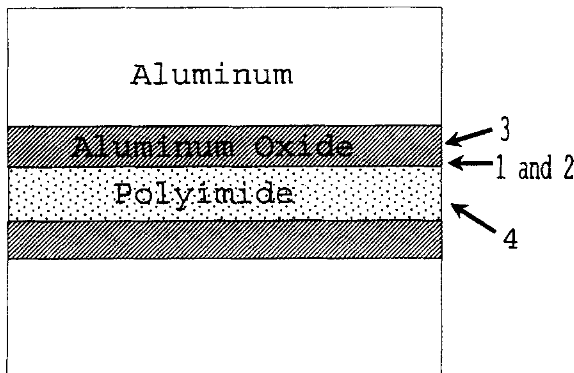

1 – Oxidized sulfur would be found here.
2 – Locus of failure for BDSDA/ODA bonds tested in a dry environment.
3 – Locus of failure for BDSDA/ODA bonds tested in a wet environment.
4 – Locus of failure for BTDA/ASD bonds.

FIGURE 8 Locus of failure and most probable location of oxidized sulfur.

CONCLUSIONS

Surface pretreatment and T_g had more of an effect on peel strength than the presence of sulfur in the polyimide backbone. NaOH etching of the adherend and compartively low polyimide T_g combined to produce the highest peel strengths. Little difference was observed between the peel strengths of sulfur and non-sulfur containing polyimides with similar T_gs. No oxidation of sulfur was observed in the peel samples. NaOH etching also caused peel specimens to fail more within the polyimide than in the oxide layer of the adherend. Thus, the NaOH etch appeared to increase interfacial adhesion between the aluminum and the polyimide due to the

removal of a weak oxide layer. The low T_g polyimides also performed better than the high T_g polyimides in the wedge test, with BDSDA/ODA performing the best. This observation could be due to the metal-sulfur interaction (BDSDA/ODA) since oxidized sulfur was observed on the failed surfaces of these aluminum alloy bonds regardless of the environment or surface pretreatment. Alternatively, the difference between high and lower T_g samples may be due to a difference in polymer viscous energy dissipation rather than to a difference in interphase strength.

Acknowledgements

Funding for this research was provided by the Center for Adhesive and Sealant Science at Virginia Tech and the Adhesive and Sealant Council, Inc. The advice and counsel of A. F. Rubira, T. L. St. Clair, J. Hollenhead, F. Cromer, S. McCartney and J. D. Rancourt are very much appreciated.

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