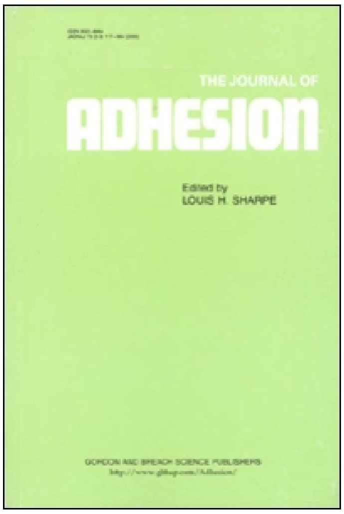

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Sulfur Versus Non-Sulfur Containing Polyimide Adhesives for Bonding Steel

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Due to their superior thermal and chemical stability, polyimides are often used as adhesives in harsh environments. This study examines the effect on bond strength of thioether sulfur in the polyimide backbone. Bonds were made using steel that was believed to catalyze the oxidation of sulfur. In addition, non-sulfur containing polyimides with similar T_g were also studied for comparison. The polymer/metal interface was studied using both the *T*-peel and wedge tests. No apparent effect was observed in the *T*-peel test with steel where the *T*-peel strengths of non-sulfur and sulfur containing polyimides were similar. In the wedge test, however, the sulfur-containing BDSDA/ODA bonded to steel had the smallest initial crack length of 34 mm. However, the BTDA/APB bonds tested in a dry environment had the smallest crack growth. The sulfur-containing BTDA/ASD performed best of the bonds tested in a wet environment. Metal-catalyzed oxidation of sulfur was observed to take place in the steel case, but not to an extent to have a noticeable effect on peel strength.

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

INTRODUCTION

While most reports have examined the adhesion of polyimides to titanium alloys or composites[1–3] only a few studies have examined the bonding of polyimides to steel. One study[4] used the polyimide NR-150, developed by DuPont Co., either to bond Type 17-7 PH stainless steel (used in airframe parts) with itself or to bond Type 430 stainless steel (used in automobile trim) with SP-22 composite.[5] The surface pretreatment used in this study was not identified. Lap shear strengths, which had been corrected for the percent of area bonded, of 29.6 MPa for Type 17-7 and 8.97 MPa for Type 430 were reported for bonds tested at room temperature. The lower value for the steel/composite samples was believed to be due to failure within the composite.

Another adhesive study used stainless steel adherends in an effort to determine the effects of high temperature aging on bonded joints. The polyimides studied were (a) P4A/A5FA, a copolymeric blend of TRW A-type polyimide and Amoco AI1137 amide-imide resins, and (b) BR34/FM34, an American Cyanamid condensation

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polyimide.[6] The P4A/A5FA polyimide contained arsenic pentoxide as an oxidation scavenger which was believed to be necessary for bonding stainless steel. One of the key components of the A-type polyimide was thiodianiline, a sulfur-containing diamine. No mention of the possibility of oxidized sulfur could be found in this report. Both polyimides exhibited similar lap shear strengths for bonding stainless steel when tested at room temperature, 19.3 MPa (P4A/A5FA) and 22.1 MPa (BR34/FM34).

A study by Burgman and co-workers[7] examined the bonding of stainless steel AM350SCT with one of three polyimides. The polyimides examined were I-8 (synthesized from *m*-phenylenediamine and BTDA), I-40 (I-8 endcapped with *p*-aminoacetanilide and phthalic anhydride), and I-66 (I-8 endcapped with only *p*-aminoacetanilide). Polyimdes I-40 and I-66 when used with 181-A1100 E-glass cloth produced the best bonds with lap shear strengths in excess of 20.7 MPa when tested at room temperature. Both polyimides also performed well at elevated temperatures, having lap shear strengths in excess of 13.8 MPa at 550°C. Over 50% of this strength was retained after 1000 hours in air at 550°C.

More recently, Tamai and co-workers reported, in a patent, the development and use of polyimides that contain an indane structure in the diamine portion of the polymer to bond cold-rolled steel panels.[8] Bonds possessed lap shear strengths of 26.0 MPa when tested at room temperature and 19.2 MPa when tested at 200°–240°C. No other reports of polyimides with steel adherends could be found.

Metal-catalyzed oxidation of thioether sulfur may have ramifications for thioether-containing polymeric adhesives. The peel strength of polyethylene bonded to cold-rolled mild steel containing an antioxidant was 0 kg/cm, while the peel strength of the polyethylene/steel specimen without the antioxidant was 6.5 kg/cm.[9] The nature of the reactive groups at the polymer/steel interface was not investigated. In studies with polyethylene bonded to copper and aluminum,[10] IR analysis detected the formation of carbonyl groups which were believed to be interacting (*e.g.* chemisorption) with the metal surface. Adhesion, on the other hand, may suffer if the polymer undergoes extensive catalytic oxidative degradation[11] wherein the integrity of the polymer is damaged and a weak boundary layer between polymer and adherend forms, thus weakening the bond.

Beneficial metal-sulfur adhesive interactions have been suggested to take place in bonds composed of polyphenylene sulfide and steel where the thioether sulfur was stated to be oxidized to SO_2 and SO_3 when the bonds were prepared in an O_2 atmosphere.[12] These sulfur oxidation products reacted with the Fe_2O_3 on the steel surface to produce $Fe_2(SO_4)_3$ and $FeSO_4$ as determined by XPS of the failed surfaces. The 1010 cold-rolled steel and the AISI 304 stainless steel substrates were subjected to an acetone wipe prior to coating with the polyphenylene sulfide. The bonds made using a 99.5% O_2 cure atmosphere showed a 50% increase in lap shear strength compared with those made using a 99.9% N_2 cure atmosphere. Sugama and Carciello concluded that the formation of $Fe_2(SO_4)_3$ and $FeSO_4$ was responsible for the increased lap shear strength, but no speculation as to the manner in which these reaction products enhanced bond strength was provided. The relative brittleness of iron oxide and iron sulfate was not addressed. The study reported here examines the possibility of metal-sulfur interactions in bonded specimens of steel adherends and sulfur-containing polyimide adhesives where the percentage of sulfur is much less than in polyphenylene sulfide. 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.

EXPERIMENTAL

Materials

4,4′-Bis (3,4-dicarboxyphenoxy) diphenyl sulfide dianhydride (BDSDA) was obtained from NASA Langley Research Center (Hampton, VA), recrystallized twice from 2-butanone, and vacuum dried overnight at 120°C prior to used. 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 (aminophenoxyl) benzene (APB) obtained from Mitsui Toatsu (Tokyo, Japan), each vacuum dried at 80°C overnight. The molecular structures of these monomers are showin in Figure 1. *N,N*-Dimethylacetamide (DMAc) was also obtained from Aldrich Chemical Co. and was stored under nitrogen in Sure Seal® bottles. 1010 cold-rolled steel foil (0.04 mm thick) and 1010 cold-rolled steel coupons (15.2 cm × 2.5 cm × 0.3 cm) were used as adherends. The steel substrates were approximately one-half as thick as the aluminum substrates used in the previous study[14] in order to reduced the effects of different adherend moduli.

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 while the solution was continuously stirred.

Bonding

The steel substrates were pretreated by either an acetone wipe or a chemical etch. The etching process, which was similar to the one used by Hollenhead and Wightman,[13] consisted of immersing the steel in an aqueous 6M HCl bath for five minutes at room temperature followed by a rinse with deionized water and then acetone. The etched substrates were then air dried.

The peel samples were prepared by casting the poly(amide acid) solution at a thickness of 0.5 mm for BDSDA solutions and 0.3 mm for BTDA solutions onto two pieces (17.8 cm × 15.2 cm) of the pretreated steel 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

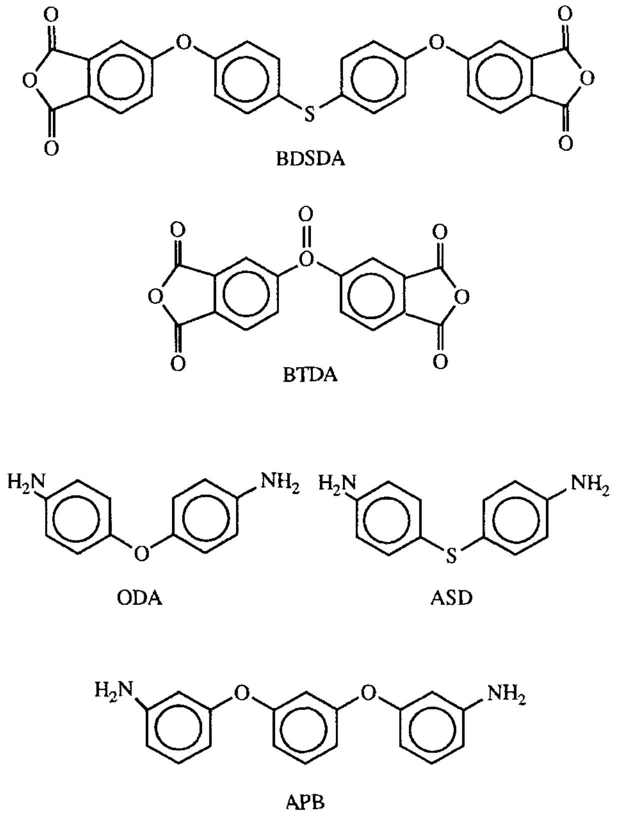


FIGURE 1 Molecular structures of monomers used in this study.

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 with the specimen 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 3.3 mm wedge into the bond to a distance of 6.4 mm. The initial crack was measured as was the subsequenct 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.

RESULTS AND DISCUSSION

The same four polyimides used in our earlier aluminum bonding study were used in this study to bond steel to steel.[14] 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[15] with iron-modified free standing films, it was hypothesized that the iron from the steel substrates would significantly interact with and catalyze the oxidation of thioether sulfur in the sulfur-containing polyimides. Such a mechanism of interaction obviously would not exist for the non-sulfur-containing polyimides. The surface pretreatments were chosen to examine the interaction of thioether sulfur with both a hydrated "as is" steel surface and one in which the oxide layer had been partially removed. 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. The peel test has often been used to compare the relative strengths of adhesives and the effects to surface pretreatment.[16,17]

Characterization of Steel Foil and Coupon Substrates

Surface analysis was performed on both the HCl-acid-etched and acetone-wiped steel surfaces to characterize the chemistry at the surface prior to casting the poly(amide acid) solution. Multiplet splitting of the iron 3d electrons, excess surface oxygen, and non-stoichiometry can cause shake-up satellite peaks to occur quite readily. Often these satellite peaks have the same relative intensity as the parent Fe 2p photopeak, thereby resulting in broad signals with a half-width of 3.8 to 4.4 eV.[18,19] It is also known that iron oxides dissociatively chemisorb water and oxygen.[20] This chemisorption process produces a surface rich in hydroxyl groups which, in turn, broadens the high binding energy side of the oxygen 1s photopeak.

Analysis of the surface of the acetone-wiped steel *foil* revealed $Fe2p_{3/2}$ and Fe $2p_{1/2}$ photopeaks with binding energies of 710.7 ± 0.2 eV and 724.2 ± 0.2 eV, respectively. These photopeaks indicated that the iron on the surface was in the form of Fe(III). Unfortunately, the binding energies for the Fe 2p photopeaks in the various iron(III) oxides (*e.g.* Fe_2O_3, FeOOH, and Fe_3O_4) are all within a range of 1 eV, thus making it difficult to identify the exact forms of iron oxide or oxyhydroxide present. The position of the O 1s photopeak was indicative of the oxide oxygen found in Fe_2O_3. It was evident, however, that the surface also contained chemisorbed water due to the high binding energy shoulder that appeared on the O 1s photopeak at 531.6 ± 0.1 eV. This photopeak position is typical of the oxygen signal found in species that contain Fe—O—H bonds.[24-26] Analysis of the 6M HCl-etched steel foil surface was similar to that of the acetone-wiped surface.

The acetone wiped *coupon* surface appeared to be primarily FeOOH, rather than a mixture of Fe_2O_3 and FeOOH, with Fe $2p_{3/2}$ and Fe $2p_{1/2}$ binding energies at 711.0 ± 2 eV and 724.7 ± 0.2 eV, respectively. The signals observed here for the hydroxide oxygen with a binding energy of 531.8 ± 0.1 eV and the oxide oxygen at 530.2 ± 0.1 eV were nearly equal, as would have been predicted from the compound formula (Fig. 2).

The acid-etched coupon surface was quite different from the acetone-wiped coupon surface. Over twice as much iron was observed on the etched surface (13.9 At-% *versus* 6.1 At-%) as compared with the wiped surface, but no iron was visible in the metallic state in contrast to the etched steel foil case. The binding energies for Fe $2p_{3/2}$ and Fe $2p_{1/2}$ were 711.6 ± 0.2 and 725.2 ± 0.2 eV, respectively. Also, a strong oxide oxygen photopeak was observed at 530.2 eV. These assignments indicated that the iron was present as Fe_2O_3. The presence of the high binding energy shoulder on the oxygen photopeak, however, indicated that chemisorbed oxygen/water was also present. The main non-iron components of the steel used here are carbon and possibly manganese. Manganese was not observed in significant amount on the surface of either the foil or coupon.

Peel Tests-Wiped Substrates

The *T*-peel results of several repetitions have been tabulated in Table I. The low T_g BTDA/APB/acetone-wiped steel bonds had a peel strength of 2.84 ± 0.60 N/cm.

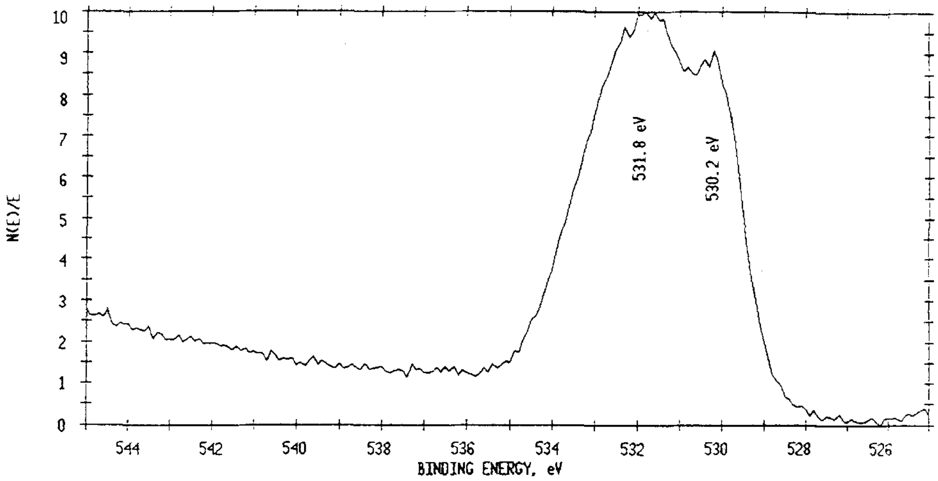


FIGURE 2 Oxygen 1s XPS photopeak of acetone-wiped 1010 low carbon steel coupon (binding energy calibrated to C 1s = 284.6 eV).

These bonds appeared to fail in mixed mode as judged by the fact that both failed surfaces contained primarily polyimide as indicated by the atomic concentration of surface nitrogen (*e.g.* one failed surface had 4.5 At-% nitrogen and the other had 3.5 At-% (Fig. 3), close to the expected value of 4.5 At-% nitrogen calculated for BTDA/APB). Some iron, nevertheless, was observed on both surfaces (*e.g.* 1.4 At-% iron on one side and 2.5 At-% on the other), and the Fe 2p binding energy indicated that it was primarily in the form of Fe_2O_3.

Wiped steel bonds with the low T_g sulfur-containing polyimide (BDSDA/ODA) exhibited a peel strength of 2.83 ± 0.84 N/cm, similar to BTDA/APB. By just examining peel strengths, it would appear that the presence of thioether sulfur in the backbone had no beneficial effect on bonding. Analysis of the failed BDSDA/ODA surfaces, however, provided an interesting difference. Less than 0.2 At-% iron was observed on either surface in contrast to the 1–3 At-% iron on the failed BTDA/APB surfaces, Figure 4. The sulfur 2p photopeaks from the two failed surfaces had binding energies of 163.2 ± 0.1 eV, which was characteristic of the thioether sulfur found in this polyimide. Had the sulfur been oxidized, the S 2p photopeak would have had a binding energy of 168.3 ± 0.1 ev.[27] Since only trace amounts of iron were observed, it was assumed that these bonds failed cohesively (*i.e.* within the adhesive itself). Thus, it was not surprising that the observed sulfur was not oxidized because it was obviously not close enough to the interphase to have interacted with the iron.

The peel strength, 0.78 ± 0.27 N/cm, of the wiped steel bonds made using the high T_g sulfur-containing polyimide (BTDA/ASD) was quite similar to that of the high T_g BTDA/ODA/acetone-wiped steel bonds. Even though the peel strengths for both high T_g polyimides were similar, the BTDA/ASD/wiped steel bonds failed more cohesively. Little iron, for example, was observed on either failed surface (1.0 At-% ± 0.2 At-%). While the concentration of iron on BTDA/ASD/wiped steel bonds was more than had been seen on the failed BDSDA/ODA/wiped steel bonds, it was, nevertheless, much less than what was observed in the case of the high T_g BTDA/ODA/wiped steel bonds.

Peel Tests-Etched Substrates

While the *T*-peel strengths of the BTDA/APB bonds with wiped and etched steel were similar, the results were much different in the case of BDSDA/ODA bonds. The

TABLE I
T-peel Strength and Mode of Failure in the Polyimide/1010 Steel Foil Bonds

Polyimide	T_g	Sulfur	Wiped Bonds		Etched Bonds	
			T-peel Strength (N/cm)	Failure Mode	*T*-peel Strength (N/cm)	Failure Mode
BTDA/APB	Low	No	2.84 ± 0.60	Mixed Mode	2.75 ± 0.44	Mixed Mode
BDSDA/ODA	Low	Yes	2.83 ± 0.84	Cohesive	0.78 ± 0.33	Cohesive
BTDA/ODA	High	No	0.53 ± 0.09	Mixed Mode	0.36 ± 0.11	Mixed Mode
BTDA/ASD	High	Yes	0.78 ± 0.27	Mixed Mode	0.39 ± 0.04	Mixed Mode

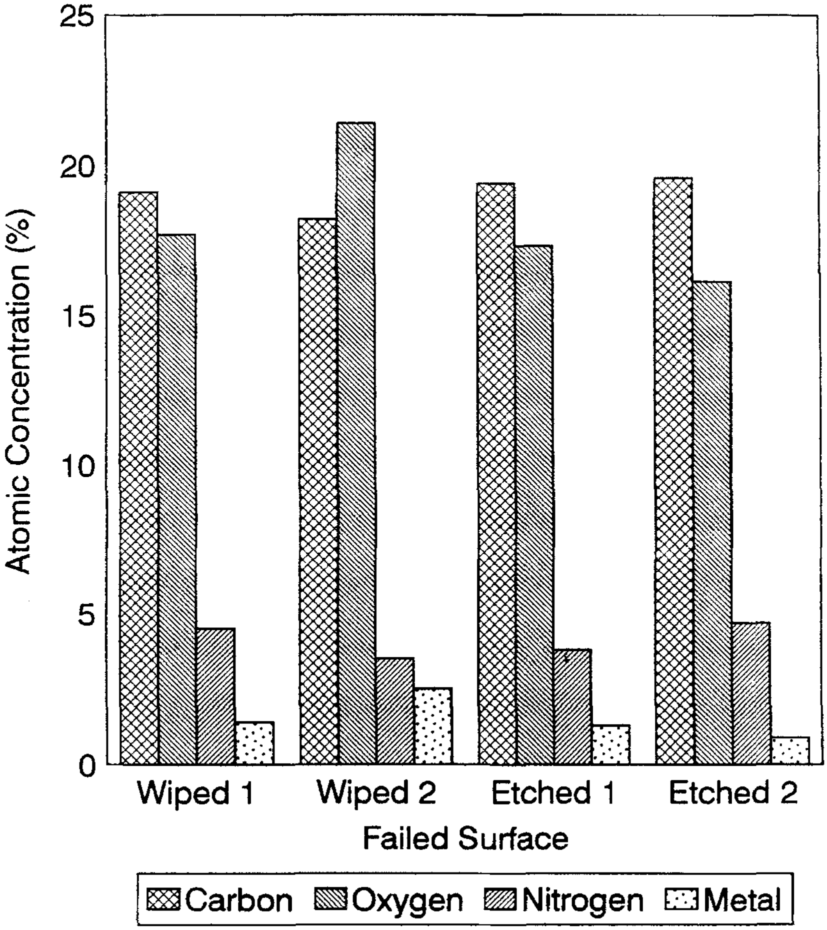


FIGURE 3 Atomic concentrations of failed BTDA/APB/1010 steel peel bond surfaces (carbon concentration/4).

etched steel bonds of BDSDA/ODA had a *T*-peel strength of only 0.78 ± 0.33 N/cm, less than 30% of the strength of wiped steel bonds. While this drop in peel strength could be due to the oxidation of thioether sulfur, the XPS results did not corroborate that theory. The nitrogen and sulfur concentrations on both failed surfaces (Fig. 4) were similar to that of the polyimide itself, 4.0 At-% and 2.0 At-%, respectively. Again, hardly any iron was observed, ~0.2 At-%. Not surprisingly, no oxidized sulfur was observed. The mode of failure, therefore, was the same as discovered with the wiped steel substrates (*i.e.* cohesive failure). If thioether oxidation was the cause of the decreased peel strength, then the bonds should have failed at the interface where the oxidation would have occurred. Since the mode of failure was cohesive, this result was most likely due to poor mixing of the two polyimide layers during the bonding process.

Etched steel bonds using BTDA/ODA had a very poor *T*-peel strength (0.36 ± 0.11 N/cm). Also, like the acetone-wiped steel bonds, the etched bonds failed

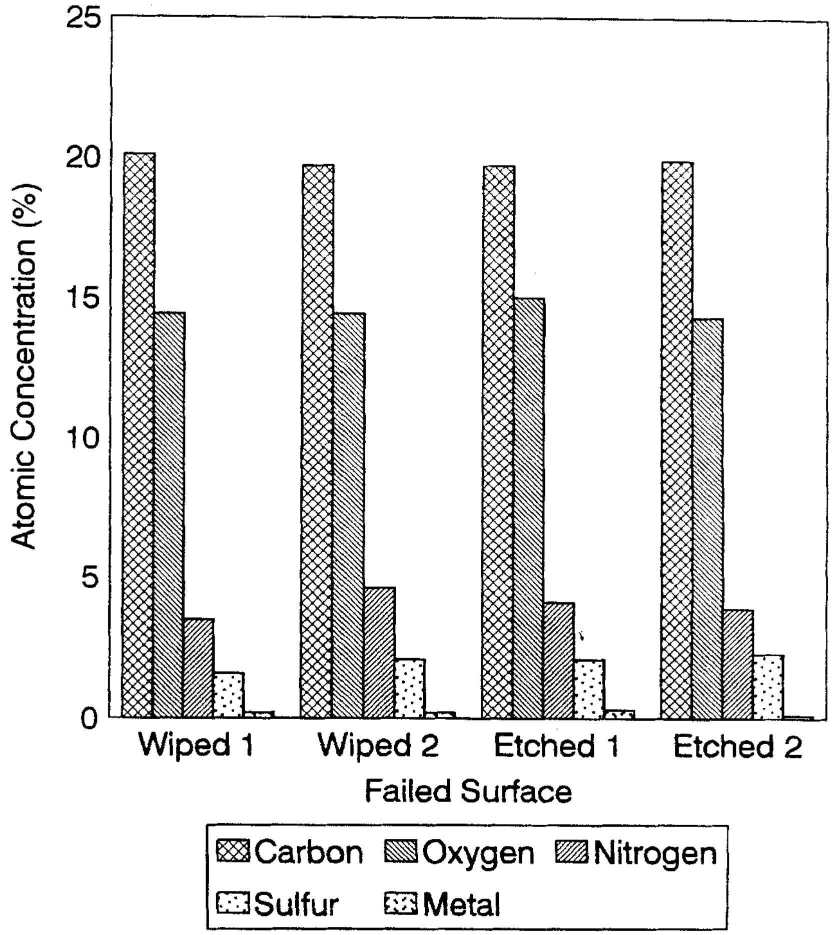


FIGURE 4 Atomic concentrations of failed BDSDA/ODA/1010 steel peel bond surfaces (carbon concentration/4).

in mixed mode. The iron concentrations on the failed surfaces were not as high with the etched steel bonds (3.5 At-% and 1.3 At-%) as with the acetone-wiped specimens. The iron appeared to be Fe_2O_3.

As was the case with BDSDA/ODA, the etched steel bonds of BTDA/ASD had a much lower *T*-peel strength than the wiped steel bonds using the same polyimide. The *T*-peel strength, 0.39 ± 0.04 N/cm, dropped 50% compared with the wiped steel bonds. Slightly more iron was observed on the failed surfaces (1.9 At-% and 1.2 At-%) compared with the wiped steel bonds, but it was still in the form of iron oxide. Again, no oxidized sulfur was observed.

Of all the steel bonds, both wiped and etched, only the BDSDA/ODA bonds failed cohesively; all of the others failed in a mixed mode. It is also interesting to note that for a given set of parameters (*i.e.* similar T_g and surface pretreatment) the sulfur-containing polyimides consistently showed less iron on the failed surfaces than the non-sulfur-containing polyimides. Bonds synthesized using etched steel and sulfur-containing polyimides were considerably weaker than the wiped steel bonds, whereas the surface pretreatment did not have a noticeable effect on the peel strength of the non-sulfur-containing polyimides.

Comparison of the *T*-peel strengths (Table II) of these polyimide/steel bonds with the polyimide/aluminum bonds studied previously revealed several interesting observations. One is the close agreement in *T*-peel strengths between the acetone-wiped steel and acetone-wiped aluminum bonds[14] for a given polyimide. Since the modulus of steel is approximately twice that of aluminum, the thickness of the steel adherend was chosen to be half that of the aluminum adherends to compensate for this factor. Even though *T*-peel strengths were very similar, bond failure in the aluminum and steel cases occurred in different locations. The study with aluminum substrates reported[14] that bonds (*i.e.* both wiped and etched substrates) failed in the aluminum oxide layer, since large amounts of aluminum (5–15 At-%) were found on both failed surfaces. This mode of failure was not observed with the steel bonds. When etched aluminum substrates were used, the *T*-peel strength of all the polyimides increased relative to the wiped aluminum bonds. This increase is most likely due to the removal of a weak surface oxide layer in the NaOH etch. With etched steel, however, the non-sulfur-containing polyimides had *T*-peel strengths that were essentially the same as the acetone-wiped steel bonds. For the sulfur-containing polyimides, the etched steel bonds were actually worse than the acetone-wiped steel bonds. This seems to indicate that the original native oxide layer provides a bonding surface equal to or better than the etched steel.

Wedge Tests

Wedge tests on steel substrates were performed under dry (Table III) and wet (Table IV) environments with both surface pretreatments (*i.e.* wiped and etched). The initial crack lengths of the BTDA/APB/steel bonds were similar to each other regardless of surface pretreatment: 49 ± 4 mm for the acetone wipe and 47 ± 7 mm for the HCl etch. Both bonds showed excellent resistance to crack growth. After

TABLE II
T-peel Strength of the Acetone-Wiped Polyimide/Aluminum and Polyimide/1010 Stell Foil Bonds

Polyimide	Adherend	Peel Stength* (N/cm)
BDSDA/ODA	Aluminum	2.88 ± 0.15
BDSDA/ODA	1010 Steel	2.83 ± 0.84
BTDA/APB	Aluminum	3.85 ± 0.42
BTDA/APB	1010 Steel	2.84 ± 0.60
BTDA/ASD	Aluminum	1.04 ± 0.09
BTDA/ASD	1010 Steel	0.78 ± 0.27
BTDA/ODA	Aluminum	0.38 ± 0.10
BTDA/ODA	1010 Steel	0.53 ± 0.09

*Values for Aluminum from previous study (see Ref. 14) twelve days, the acetone-wiped bonds had a crack growth of 7 ± 4 mm and the HCl-etched bonds had a crack growth of 5 ± 1 mm (Figs. 5 and 6, respectively). In both cases, the bonds failed cohesively, since practically no iron (<0.5 At-%) was observed on either failed surface.

In the BTDA/APB bonds tested in a wet environment, the extent of crack growth was much worse. The crack growth in the wet/wiped bond case was quite large, 36 mm, after twelve days (Fig. 7). Analysis of the failed surfaces of this bond indicated that it failed predominantly within the iron oxide layer. Sizable amounts of iron (9–12 At-%) and reduced amounts of nitrogen (2–3.5 At-%) were observed on both surfaces. The wet/etched BTDA/APB bonds had a smaller total crack growth of 28 ± 1 mm after twelve days (Fig. 8). These bonds failed almost completely within the oxide layer. Only about 1 At-% nitrogen and more than 10 At-% iron was observed on each surface.

BDSDA/ODA bonds with steel proved to have the best resistance to crack growth of the four polyimides, regardless of surface pretreatment or testing environment. While the initial crack lengths (Figs. 5 and 6), 34 ± 7 mm for the acetone wipe and 32 ± 3 mm for the HCl etch, were virtually the same, they were significantly lower than for the other three polyimides. The extent of crack growth for the dry bonds was twice that of the BTDA/ODA bonds: 13 ± 5 mm for the acetone wipe after twelve days and 14 ± 5 mm for the HCl etch after eleven days. Thus, while the original crack was less than that of BTDA/ODA bonds, they were worse at controlling crack growth. The dry BDSDA/ODA steel bonds seemed to fail similarly

TABLE III
Crack Growth and Mode of Failure in the Polyimide/1010 Steel Wedge Bonds Tested in a Dry Environment

Polyimide	T_g	Sulfur	Wiped Bonds		Etched Bonds	
			Crack Growth (mm)	Failure Mode	Crack Growth (mm)	Failure Mode
BTDA/APB	Low	No	7 ± 4	Cohesive	5 ± 1	Cohesive
BDSDA/ODA	Low	Yes	13 ± 5	Mixed Mode	14 ± 5	Mixed Mode
BTDA/ODA	High	No	11 ± 1	Cohesive	7 ± 3	Mixed Mode
BTDA/ASD	High	Yes	13 ± 5	Mixed Mode	15 ± 8	Mixed Mode

TABLE IV
Crack Growth and Mode of Failure in the Polyimide/1010 Steel Wedge Bonds Tested in a Wet Environment

Polyimide	T_g	Sulfur	Wiped Bonds		Etched Bonds	
			Crack Growth (mm)	Failure Mode	Crack Growth (mm)	Failure Mode
BTDA/APB	Low	No	36	Oxide	28 ± 1	Oxide
BDSDA/ODA	Low	Yes	26 ± 12	Oxide	31 ± 6	Oxide
BTDA/ODA	High	No	17 ± 10	Oxide	23 ± 19	Oxide
BTDA/ASD	High	Yes	10	Mixed Mode	18 ± 15	Oxide

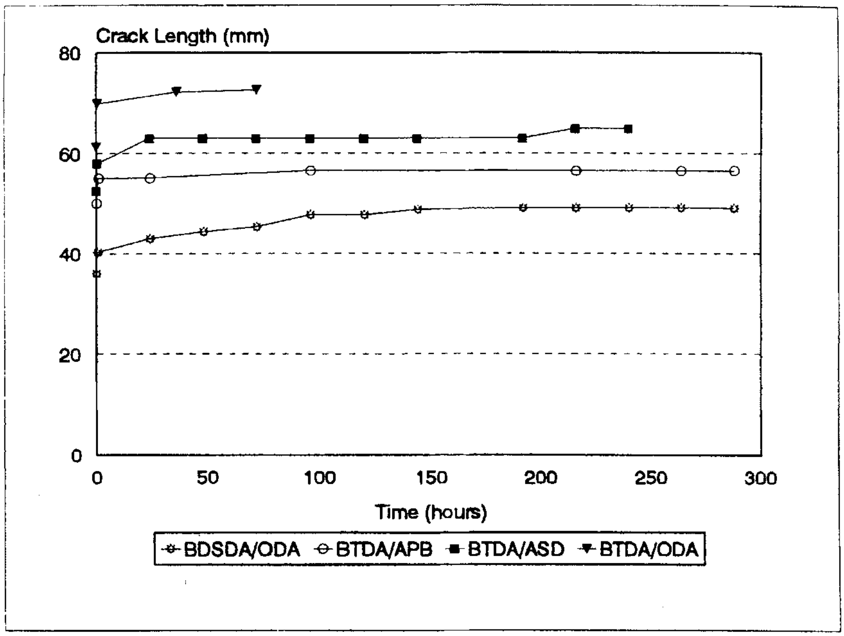


FIGURE 5 Crack growth in acetone-wiped polyimide/1010 steel wedge bonds tested in a dry environment.

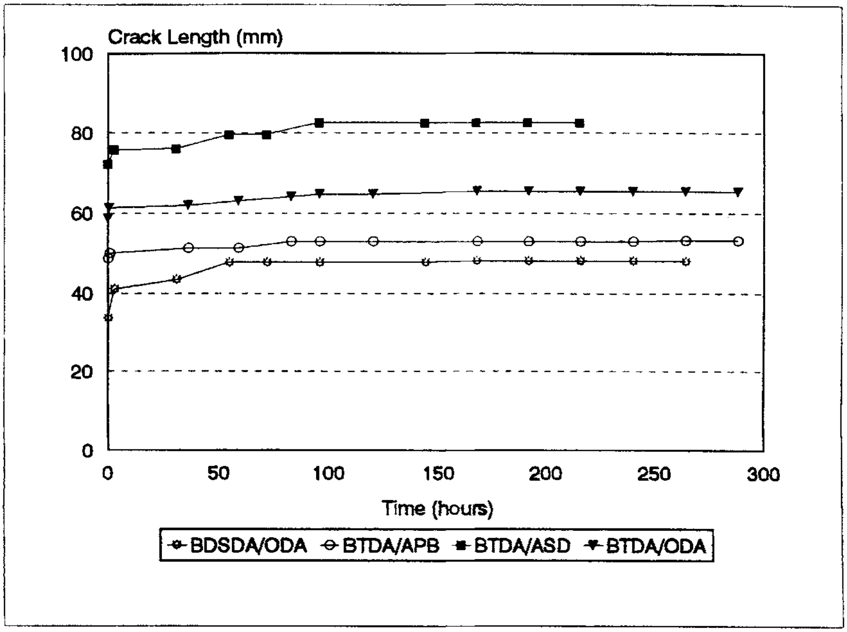


FIGURE 6 Crack growth in HCl-etched polyimide/1010 steel wedge bonds tested in a dry environment.

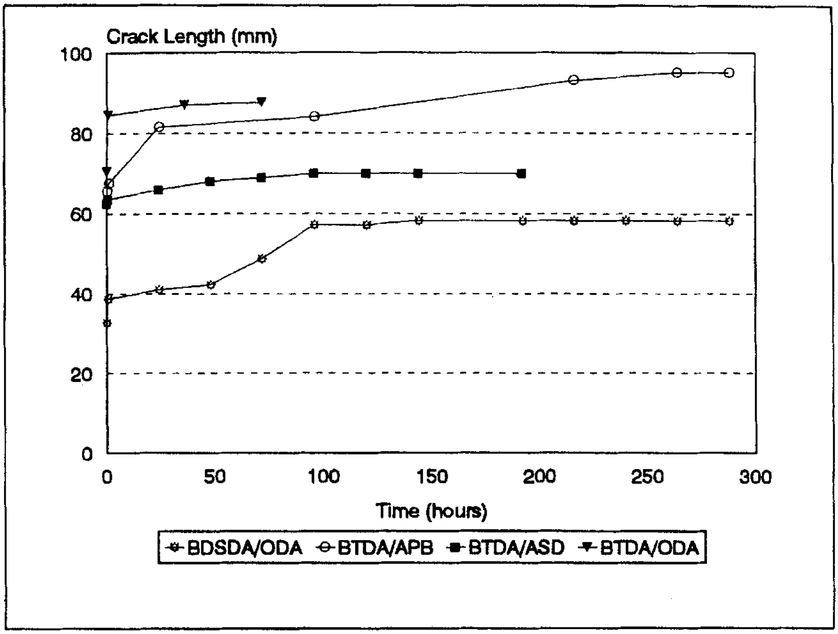


FIGURE 7 Crack growth in acetone-wiped polyimide/1010 steel wedge bonds tested in a wet environment.

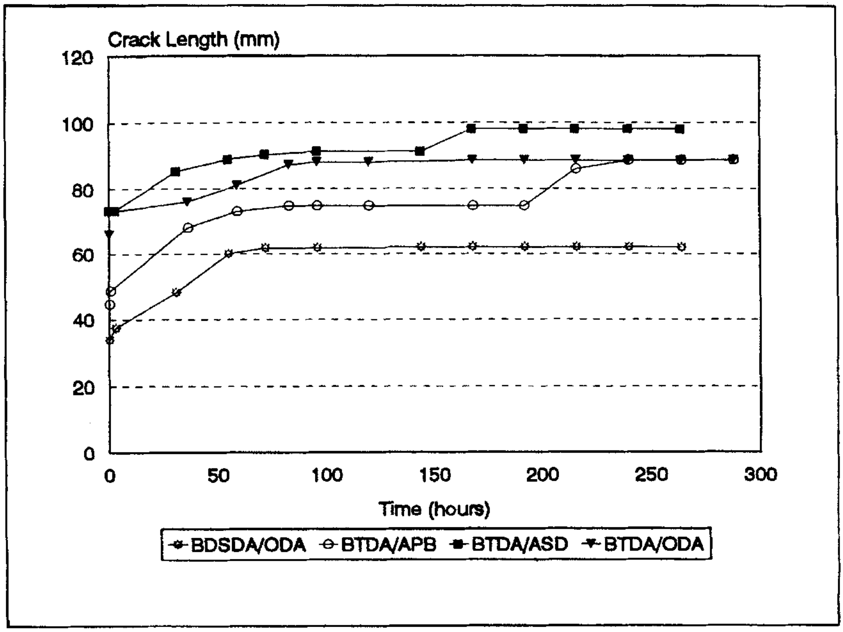


FIGURE 8 Crack growth in HCl-etched polyimide/1010 steel wedge bonds tested in a wet environment.

regardless of surface pretreatment, according to XPS. Both bonds showed some iron (~2 At-%) and some polyimide (~2 At-% sulfur and 3.5–4 At-% nitrogen) indicating mixed mode failure. No oxidized sulfur was observed on these surfaces. Again, these bonds probably did not fail close enough to the interface for oxidized sulfur to be observed.

The wet BDSDA/ODA/steel bonds had somewhat worse crack growths, 26 ± 12 mm for the acetone wipe after twelve days and 31 ± 6 mm for the HCl etch after eleven days (Figs. 7 and 8) than the bonds tested in a dry environment. These bonds both failed within the oxide layer of the steel. Practically no sulfur was observed on either the acetone wiped or HCl-etched failure surfaces, so it could not be determined if the sulfur had been oxidized at the interface.

As in the case of the *T*-peel tests, the BTDA/ODA bonds had the worst initial crack length: 65 ± 17 mm for the acetone wipe and 62 ± 13 mm for the HCl etch (Figs. 4 and 5). The extent of crack growth in the dry BTDA/ODA/steel bond case was similar regardless of pretreatment and very close to that of the BTDA/APB bonds: 11 ± 15 mm for the acetone wipe after three days and 7 ± 3 mm after twelve days for the HCl etch. The dry and wet BTDA/ODA/steel bonds did have different failure modes. The dry/wiped bonds failed entirely cohesively; no iron was detected on either surface. The dry/etched BTDA/ODA bond failed in mixed mode since some iron (1.4 At-% and 4.1 At-%) was found on both surfaces.

The crack growth in the wet BTDA/ODA/steel bond case (Figs. 7 and 8) was similar to that found with BDSDA/ODA, regardless of surface pretreatment: 17 ± 10 mm for the acetone wipe after three days and 23 ± 19 mm for the HCl etch after twelve days. The wet/wiped BTDA/ODA/steel bond failed deep into the oxide layer since large amounts of iron (8–10 At-%) were found on both failed surfaces. Also, very little nitrogen (2–3 At-%) was observed on these surfaces. The wet/etched BTDA/ODA/steel bonds, on the other hand, failed completely within the oxide layer of the steel as was the case with the wet/etched BTDA/ASD. Large amounts of iron (11–13 At-%) and practically no nitrogen (~0.5 At-%) were observed on either surface.

The initial crack length for BTDA/ASD was 52 ± 4 mm for the acetone-wiped bonds (Fig. 5). The HCl etch pretreatment produced a significantly larger crack length of 71 ± 11 mm (Fig. 6). The extent of crack growth, however, was essentially the same for both types of pretreated BTDA/ASD bonds tested in a dry atmosphere, 13 ± 5 mm for the acetone wipe after nine days and 15 ± 8 mm for the HCl etch after ten days. These values are similar to our results using BDSDA/ODA. Surface analysis of the failed BTDA/ASD bonds tested in a dry environment revealed similar atomic concentrations regardless of the surface pretreatment. The bonds failed in mixed mode, since a small amount of iron (~ 1.5 At-%) was found on both surfaces. Since this amount of iron was very similar to that found on the failed peel surfaces of BTDA/ASD bonds, it was not surprising that no oxidized sulfur was observed.

The acetone-wiped BTDA/ASD/steel bond tested in a wet environment had a crack growth of 10 mm after eight days, while the HCl-etched BTDA/ASD/steel bonds had a crack growth of 18 ± 15 mm after ten days (Figs. 7 and 8). The small crack growths are superior to those seen in the other polyimides. Surface analysis of the failed surfaces of these bonds indicated different modes of failure from the dry bonds and from each other. The wet/wiped bonds failed in mixed mode with approximately 5 At-% iron on either surface. The sulfur peak from these surfaces was significantly broadened compared with the photopeak found in the XPS analysis of the dry surfaces (Figs. 9 and 10). This broadening indicated that some oxidation of sulfur had occurred at the interface. The wet/etched bonds failed within the oxide layer of the steel since little nitrogen (0.4–1.6 At-%) or sulfur (0.6 At-%) was

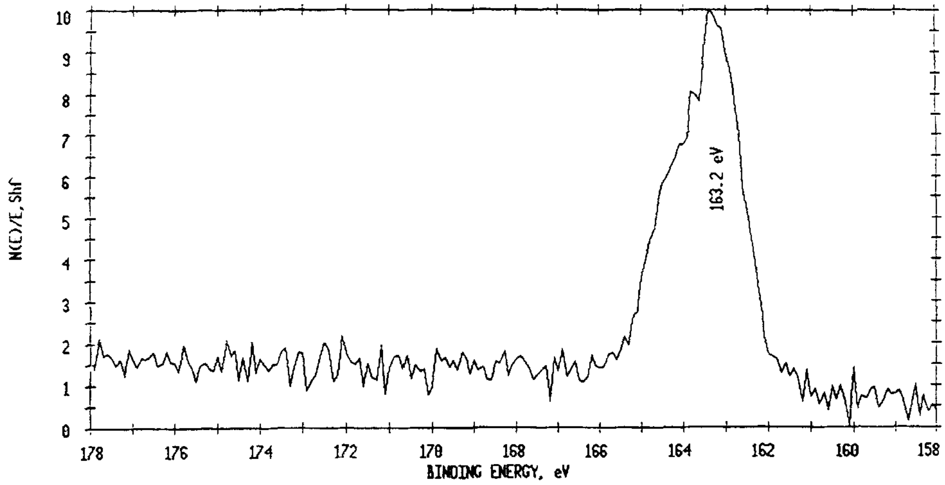


FIGURE 9 Sulfur 2p XPS photopeak of failed acetone-wiped BTDA/ASD wedge bond surface tested in a dry environment (binding energy calibrated to C 1s = 284.6 eV).

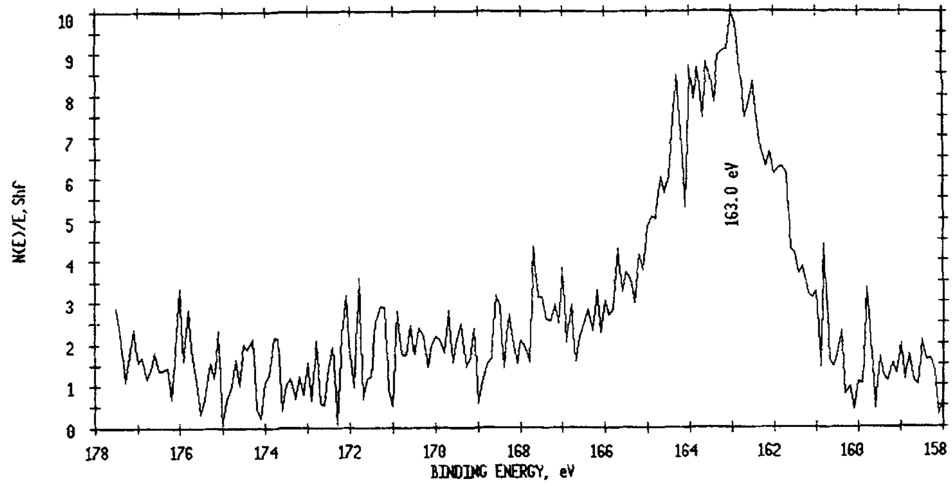
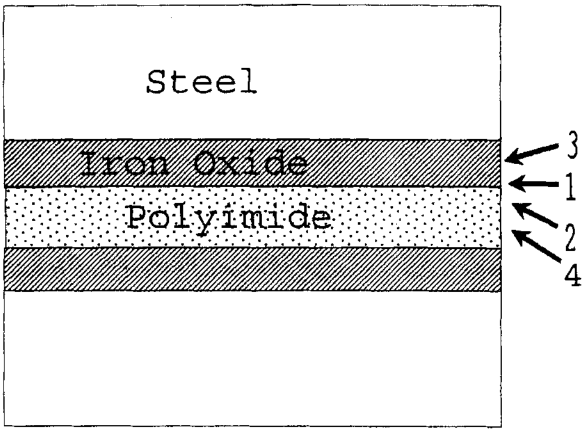


FIGURE 10 Sulfur 2p XPS photopeak of failed acetone-wiped BTDA/ASD wedge bond surface tested in a wet environment (binding energy calibrated to C 1s = 284.6 eV).



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

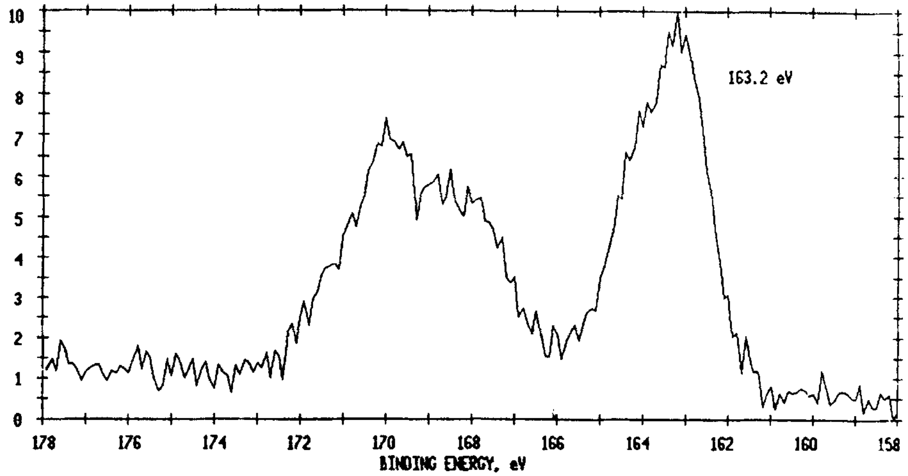
FIGURE 11 Locus of failure and probable location of oxidized sulfur in steel bonds.

observed in contrast to large amounts of iron (12–14 At-%). Too little sulfur was observed, however, to determine if any oxidized species were present.

Steel Versus Aluminum

While the etching pretreatment seemed to have a detrimental effect on the bond strength of the aluminum bonds in the previous study,[14] it did not seem to have much of an effect on the steel bonds. In fact, the initial crack lengths and subsequent crack growth were usually very similar regardless of whether the steel was etched or just wiped with acetone prior to casting. Most of the failed steel surfaces for a given polyimide were also similar within the same test environment. If the failed surfaces were different between the etched and the wiped bonds (as in the case of the dry BTDA/ODA bonds), then more iron was observable on the failed etched surfaces which was also counter to the findings with aluminum.

Oxidized sulfur had been observed on the failed surfaces of the wet BDSDA/ODA/aluminum bonds in the previous study. No oxidized sulfur was observed on the failed surfaces of the wet BDSDA/ODA/steel bonds, although very little sulfur (<0.5 At-%) was present. Thus, it was quite possible that the sulfur had been oxidized, but was not at the locus of failure (Fig. 11). This hypothesis is supported by the noticeable broadening of the sulfur peak on the failed surfaces of the wet/wiped BTDA/ASD/steel bonds which indicated that some oxidation had taken place (Figs. 9 and 10). In an attempt to clarify this situation, further a BDSDA/ODA solution was cast on a steel coupon and fully cured to 300°C in the oven. The film was then peeled off the coupon using a razor blade, and the surface that had been cured against the



IGURE 12 Sulfur 2p XPS photopeak of BDSDA/ODA film cured on steel coupon (binding energy librated to C 1s = 284.6 eV.

eel was analyzed *via* XPS. The sulfur in this film did show oxidized sulfur in addition) thioether sulfur (Fig. 12) indicating that sulfur oxidation can take place along the terface between the polyimide and the metal substrate. One reason that oxidized ilfur was observed in this experiment was probably due to the fact that the polyimide as completely exposed to the atmosphere except for the surface against the coupon. hus, the surface area through which oxygen could diffuse into the polyimide was reatly increased, which should enhance oxidation.

UMMARY

Vith the wiped steel bonds, low T_g polyimides had significantly higher T-peel strengths ian the high T_g polyimides as was the case with aluminum in the previous study. The wered T-peel strengths of the sulfur-containing etched bonds cannot be attributed to xidation of the thioether sulfur since no oxidized sulfur was observed at the point of ilure. It is possible that the surface area around the edges of the peel specimens was ot enough to permit significant amounts of oxygen to diffuse into the polyimide and d in the oxidation of thioether sulfur. In contrast with the aluminum substrates, the eel surface pretreatment by chemical etching only affected the T-peel strength of ilfur-containing polyimides, and that effect was a detrimental one.

For the most part, the initial cracks in the wedge specimens parallelled the results om the T-peel test. The stronger polyimides in the T-peel test (BTDA/APB and DSDA/ODA) also had the smallest initial crack lengths in the wedge test. This is iost likely due to the difference in the ability to dissipate viscoelastic energy. The ifferences that do exist between the two tests can most likely be attributed to the ifferent testing geometries and the different adherend thicknesses.

In the wedge test specimens tested in a dry environment, the non-sulfur-containing polyimides showed the least crack growth. In the wet environment, however, the sulfur-containing BTDA/ASD performed the best. The BDSDA/ODA and BTDA/ODA bonds also performed well. Even though no oxidized sulfur was observed on the failed surfaces, it can be assumed that thioether sulfur along the interface was oxidized, because of the XPS photopeak broadening that was noticed in the wiped steel BTDA/ASD bond tested in a wet environment (Fig. 9) and the oxidized sulfur observed in the BDSDA/ODA film cast on the steel coupon (Fig. 11). These results would seem to indicate that the oxidation of sulfur may aid bond durability since BTDA/ASD performed the best in the wet environment. At worst, the oxidation of sulfur did not appear to reduce bond performance. If this had been the case, the oxidized sulfur should have been observed on the failed surfaces of the bond since that would have been the cause to bond failure. One reason that the oxidation of sulfur seems to have only a minimal effect could be due to the amount of sulfur present. For the polyimides in this study, sulfur only comprised 5–6 wt% of the polymer. In the polyphenylene sulfide used by Sugama and Carciello,[12] sulfur was present at 30 wt%. The effect of oxidized sulfur may become more noticeable as the sulfur content is increased.

Acknowledgements

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