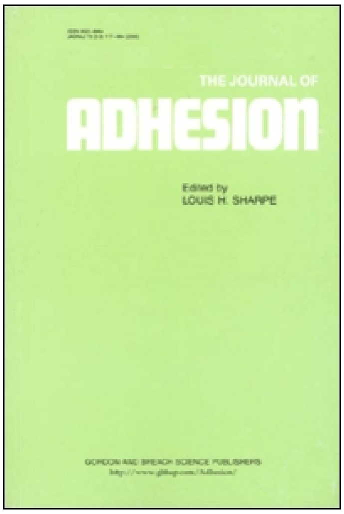

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The Modification of Epoxy/Metal Interphases by Adsorbed Contaminants

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The Modification of Epoxy/Metal Interphases by Adsorbed Contaminants

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The interfacial region formed between an epoxy/polyamide adhesive and three metallic substrates has been investigated using x-ray photoelectron spectroscopy. The effect of adsorbed contaminants on the interfacial region has also been studied. The substrates studied were cold-rolled steel, electrogalvanized steel and 2024 aluminum. A "ship-out" oil was used to contaminate the cold-rolled steel and electrogalvanized steel whereas an aerospace hydraulic fluid was used to contaminate the 2024 aluminum. Preferential adsorption of the curing agent by the substrates was observed, the effect being most marked in the case of the electrogalvanized steel substrates. The interaction between the galvanized steel and the 2024 aluminum and the curing agent was primarily *via* the free amines in the polyamide curing agent. In the case of cold-rolled steel the interaction occurred *via* the amide component. Cold-rolled steel and 2024 aluminum protonated the curing agents. No protonation was detected in the case of the electrogalvanized steel substrates due to the formation of a zinc/amine coordination compound involving the lone pairs of electrons on the nitrogen atoms. When the contaminated cold-rolled steel substrates were studied, the adhesive displaced the majority of the ship-out oil, but no protonation of the curing agent was observed. This indicated that some residual contaminant remained associated with the cold-rolled steel substrate. The majority of the ship-out oil was not displaced from the electrogalvanized steel because the strong preferential adsorption of the curing agent by the substrates created an adhesive layer enriched in epoxy. As the epoxy resin was incompatible with the oil, this epoxy-rich layer acted as a barrier, preventing the absorption of the oil by the bulk adhesive. In the case of the 2024 aluminum substrate, the level of preferential adsorption of the curing agent was decreased, but protonation of the nitrogen groups was still observed. These results indicated that the hydraulic fluid was displaced from the 2024 aluminum in some areas.

KEY WORDS epoxy; polyamide; contaminant; metals; interphase; preferential adsorption.

1.0 INTRODUCTION

Structural adhesives are being increasingly used in industrial manufacturing and assembly operations for replacing spot-welding and other mechanical fastening methods. This is because adhesive bonding offers advantages such as high fatigue resistance, a reduction in stress concentration and good corrosion resistance which

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traditional fixing methods, such as spot-welding, can not provide.[1] Field repair of damaged equipment is another example of an area where adhesive bonding has particular applications. However, field repair and general manufacturing applications require the adhesive systems to be capable of bonding to contaminated metal surfaces. Substrates within a production environment are normally contaminated either with the various oils used during the fabrication of the substrate (*i.e.* drawing, stamping or milling operations) or with oils and greases usually present in a factory environment. Thus, a major disadvantage of adhesives to date has been the necessity for a separate cleaning procedure in order to remove these contaminants. Clearly, an adhesive capable of forming strong and durable adhesive joints on contaminated substrates would offer considerable savings in terms of both time and equipment.

In order to form a strong adhesive bond with an oil-contaminated metal surface, the adhesive must be capable of performing two separate tasks. Firstly, the adhesive should be capable of absorbing the majority of the oil and diffusing to the metal surface. Secondly, having absorbed the bulk of the contaminant, the adhesive should be capable of displacing the oil adsorbed directly onto the metal surface. Debski *et al.*[2] have shown that it is thermodynamically possible for a model epoxy resin based on the diglycidyl ether of bisphenol A (DGEBA) to displace an apolar standard ASTM 3 mineral oil from the metal surface. They also showed that an epoxy resin cured with 6% dicyandiamide could absorb the oil from the metal surface but that the oil could inhibit crosslinking reactions and also plasticize the adhesive.

Bowen and Volkmann[3] tested the performance of epoxy adhesives cured using aliphatic amines and polyamidoamines (hereafter referred to as polyamides) at bonding oil-coated cold-rolled steel. They found that epoxy systems cured with polyamide curing agents were superior in tensile shear strength to those cured with aliphatic amines. They suggested that epoxies cured with polyamide curing agents had a greater affinity for the oily metal surface than those cured with simple amines. This was due to the oleophilic character of the aliphatic fatty acid moieties found in the polyamide curing agents. Rosty *et al.*[4] used a model epoxy/polyamide adhesive to study the adhesive bonding of oil-contaminated cold-rolled steel joints. They used the lap shear test to determine the effects of both fillers and curing temperature on the performance of the adhesive system. Increased lap shear joint strengths were obtained when the joints were cured at higher temperatures. The increased strengths were attributed to increased absorption of the oil by the bulk adhesive and also to a higher crosslink density. The addition of fillers also improved the bond strength of the epoxy system on the oily steel surface. In a second study, Rosty *et al.*[5] reported that the lap shear strength of the joints decreased as the viscosity of the oil increased.

Epoxy/polyamide adhesives appear capable of displacing oil-based contaminants from the surface of metallic substrates and so these adhesives may have industrial applications. However, the above researchers did not investigate how the interaction between the adhesive and the metal was affected by the presence of the adsorbed contaminants. This aspect of the bonding of contaminated substrates has been addressed in the current research.

The effect that adsorbed contaminants have on the interphase region formed by the interaction of epoxy/polyamide adhesives and metallic substrates has been investigated. In view of the results obtained by previous researchers, a model epoxy adhesive based on a DGEBA epoxy resin cured with a polyamide was used throughout the current work. The aim of the work was to investigate the interphase region formed at the adhesive/substrate interface and to determine how the presence of a contaminant adsorbed onto the substrate changed the interphase. The substrates studied were cold-rolled steel (CRS), electrogalvanized steel (EGS) and 2024 aluminum. CRS and EGS substrates were contaminated with a typical ship-out oil. 2024 aluminum, in view of its extensive use in the aerospace industry, was contaminated with an aerospace grade hydraulic fluid.

2.0 EXPERIMENTAL

2.1 Substrate Preparation

Cold-rolled steel (CRS) substrates were cleaned by immersion in a 3% w/w solution of Parco 338 (Parker Chemical Co.) at 60°C for 30 minutes. This was followed by ultrasonic cleaning in the same solution for 15 minutes. The etched substrates were rinsed using deionized water and dried using a stream of dry nitrogen. Electrogalvanized steel (EGS) substrates were cleaned using a 2% w/w solution of Parco 1500 at 40°C for 3 minutes, followed by ultrasonic cleaning in the same solution for 3 minutes. The cleaned substrates were then rinsed and dried in the same way as the CRS substrates. The 2024 aluminum substrates were prepared by mechanical polishing using varying grades of alumina powders. Final polishing was performed using 2 μm magnesia. The substrates were then rinsed and dried as described above. The above cleaning procedures produced surfaces that were fully wetted out by water indicating the formation of clean, hydrophilic surfaces. The substrates were then contaminated by wiping a tissue saturated with either the ship-out oil (Ferrocote FC-61; Quaker Chemical Co.) or the hydraulic fluid (MIL-H-83282; an aerospace hydraulic fluid) along the surface of the substrate. This procedure left a clearly visible contaminant film on the substrate. Transmission infra-red analysis of the two contaminants revealed that the ship-out oil and the hydraulic fluid were both basically hydrocarbons, but the hydraulic fluid also contained a high proportion of an ester.

2.2 Preparation of the Fracture Surfaces

1 × 2 cm metallic substrates were cleaned and contaminated as described above and a thick (1–2 mm) film of adhesive applied. In order to investigate the intrinsic ability of the adhesive to displace the contaminant no pressure was applied to the substrate. The model adhesive was a DGEBA epoxy resin, Epon 828 (Shell Chemical Co.), which was cured overnight at room temperature using 120 phr of the polyamide curing agent, Versamid V15 (Shell Chemical Co.). The adhesive was then post-cured for five hours at 50°C. The cured joints were fractured by immersion in liquid nitrogen and the adherend and adhesive fracture surfaces analyzed using x-ray

photoelectron spectroscopy. The bulk adhesive was prepared by scraping away the outermost layers using a clean knife and then analyzing the freshly exposed adhesive. A Perkin-Elmer 5300 x-ray photoelectron spectrometer equipped with a MgKα x-ray source (20mA, 15kV, 300W) was used to acquire the spectra at an electron take-off angle of 45°. Survey spectra were acquired using a pass energy of 45 eV at 0.5 eV/step and a dwell time of 25 ms/step. The high resolution spectra were acquired using a pass energy of 18 eV at 0.05 eV/step and a dwell time of 50 ms/step. The chamber pressure was maintained at 10^{-8} to 10^{-9} Torr. All the XPS spectra were corrected for charging by referencing the hydrocarbon component of the carbon 1s peak to 284.6 eV. The peak shape (90/10% gaussian/lorentzian) and the positions of the various components were determined by analyzing the bulk adhesive and the analysis parameters were then held constant during the analysis of the various fracture surfaces. This procedure allowed the results obtained from the various fracture surfaces to be compared and the differences analyzed.

3.0 RESULTS AND DISCUSSION

The atomic concentrations obtained from the adherend and adhesive fracture surfaces of specimens prepared using clean and contaminated substrates are summarized in Tables I and II, respectively. Significant levels of metallic elements on the adherend fracture surfaces were detected (see Table I), together with the presence of high levels of carbon and nitrogen. While some carbon was present on the surfaces of the cleaned substrates, no significant levels of nitrogen were detected. This result indicated that the residual carbon and nitrogen detected on the fracture surfaces was associated with the adhesive and so it was concluded that the joints failed within the adhesive, close to the metal/adhesive interface. This conclusion was supported in the case of the EGS and 2024 aluminum substrates by the detection of low levels of the zinc and aluminum on the polymer fracture surfaces. Metals would not have been present on the adhesive fracture surface if the adhesives had failed within the bulk adhesive.

When the nitrogen to carbon ratios (N/C%) were calculated for the clean joints, marked differences were observed (see Table I). The N/C ratio obtained from the

TABLE I
Summary of the elemental concentrations and the calculated nitrogen to carbon ratios obtained from the bulk adhesive and adherend and adhesive fracture surfaces from the uncontaminated joints

Substrate	Surface	Fe	Zn	Al	C	O	N	N/C%
Bulk Adhesive		n/a	n/a	n/a	84.5	9.9	5.6	6.6
CRS	Adherend	5.1	n/a	n/a	58.5	31.1	3.7	6.3
	Adhesive	n/d	n/a	n/a	79	14	5.7	7.2
EGS	Adherend	n/a	9.2	n/a	41.4	36.5	8.8	21.3
	Adhesive	n/a	0.2	n/a	82.7	11	5.6	6.8
2024 Al	Adherend	n/a	n/a	14.8	47.5	31.8	4.3	9.1
	Adhesive	n/a	n/a	0.8	82.9	10.4	5.5	6.6

(N.B. n/a means not applicable; n/d means not detected.)

TABLE II
Summary of the elemental concentrations and the calculated nitrogen to carbon ratios obtained from the bulk adhesive and the adherend and adhesive fracture surfaces from the contaminated joints

Substrate	Surface	Fe	Zn	Al	C	O	N	N/C%
Bulk Adhesive		n/a	n/a	n/a	84.5	9.9	5.6	6.6
CRS	Adherend	9.5	n/a	n/a	43.5	40.7	3.6	8.3
	Adhesive	n/d	n/a	n/a	82.2	12	5.9	7.2
EGS	Adherend	n/a	1.8	n/a	87.9	8.6	1.5	1.7
	Adhesive	n/a	n/d	n/a	88.4	7.4	3.4	3.8
2024 Al	Adherend	n/a	n/a	20.6	39.9	34.8	1.6	4
	Adhesive	n/a	n/a	0.6	84.1	10	5.3	6.3

(N.B. n/a means not applicable; n/d means not detected. The CRS and EGS joints were contaminated with a ship-out oil. The 2024 aluminum joints were contaminated with a hydraulic fluid.)

bulk polymer was 6.6%. In the case of the clean CRS joints the N/C ratios for both the adherend and adhesive fracture surfaces were similar to that obtained from the bulk adhesive. This indicated that the adhesive at the metal surface was similar in composition to the bulk adhesive. In the cases of the 2024 aluminum and especially the EGS adherend fracture surfaces, the N/C ratios were greater than the ratio obtained from the bulk polymer. These results suggested that increased concentrations of curing agent were present at the EGS/adhesive and Al/adhesive interfaces. This effect was particularly large in the case of the EGS substrate. When the adhesive fracture surfaces were investigated the nitrogen to carbon ratios were all similar to that of the bulk adhesive. These results suggested that the enrichment of the curing agent was confined to a thin adhesive layer adjacent to the EGS and 2024 aluminum substrates.The above results, therefore, indicated that the nature of the interphase region at the metal/adhesive interface was strongly dependent on the substrate.

The atomic concentrations and N/C ratios from the adherend and adhesive fracture surfaces obtained from specimens prepared using contaminated substrates are presented in Table II. In the case of the CRS substrates contaminated with the ship-out oil, the N/C ratio obtained from the adherend fracture surface increased compared with the ratio obtained from the clean CRS adherend fracture surface. This observation suggested that an increased concentration of the curing agent was present at the metal/adhesive interface. The adhesive fracture surface once more possessed a similar N/C ratio to the bulk adhesive resin. Thus, the increased concentration of curing agent appeared to be associated with the substrate. In the case of the joints prepared using EGS substrates contaminated with the ship-out oil, the N/C ratios for both the adherend and adhesive fracture surfaces were much lower than the N/C ratio obtained from the bulk adhesive. This result, therefore, suggested that the adhesive did not displace the contaminant from the EGS surface. The N/C ratio obtained from the adherend fracture surface of 2024 aluminum joints contaminated with the hydraulic fluid was lower than that of the bulk adhesive. The ratio from the adhesive fracture surface was once more similar to that of the bulk adhesive. These results implied that the hydraulic fluid was not fully displaced from the 2024 aluminum surface.

In the case of the CRS and aluminum joints, the intensities of the iron and aluminum peaks from the adherend fracture surfaces prepared using contaminated substrates were higher than the intensities obtained from the uncontaminated joints. These results suggested that the contaminant caused the loci of failure to move closer to the adherend surface and implied that the contaminant was not completely displaced from the substrate. In order to investigate the reasons for the above observations, the carbon and nitrogen 1s peaks were analyzed and these results are discussed in detail in the subsequent sections. The oxygen 1s peaks were also analyzed, but interference from the metal oxide and hydroxide peaks prevented any precise analysis.

3.1 Cold-rolled Steel Substrates

In order to study the interfacial region in greater detail the carbon and nitrogen 1s spectra from the bulk adhesive were analyzed. The carbon and nitrogen 1s spectra obtained from the bulk adhesive are presented in Figures 1a and b, respectively.

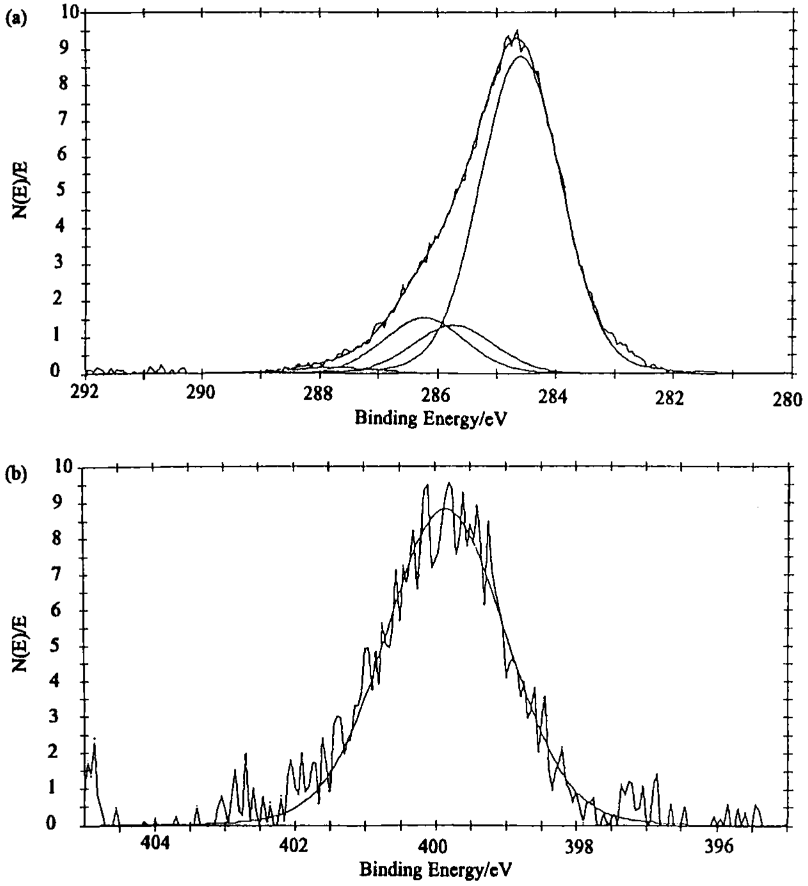

FIGURE 1 (a) Carbon 1s and (b) nitrogen 1s XPS spectra obtained from the bulk epoxy/polyamide adhesive resin.

The C1s region for the bulk adhesive exhibited four peaks. The main peak at 284.6 eV was due to carbon bonded to carbon or hydrogen. The smaller peaks with separations of +1.1, 1.6 and 3.2 eV from the main hydrocarbon peak at 284.6 eV were assigned to carbon bonded to nitrogen, carbon bonded to oxygen and the amide carbonyl groups, respectively. The nitrogen 1s peak was a single peak centered at 399.8 eV due to the amine and amide groups in the curing agent.

The results obtained from the carbon 1s and nitrogen 1s spectra (see Figure 2) of the CRS adherend and adhesive fracture surfaces prepared using a clean substrate are summarized in Table III. The adhesive fracture surface was very similar in composition to the bulk adhesive which was consistent with the conclusion drawn from the comparison of the N/C ratios. Surprisingly, the adherend fracture surface was different in composition compared with the bulk adhesive, in spite of the similarity in the N/C ratios.

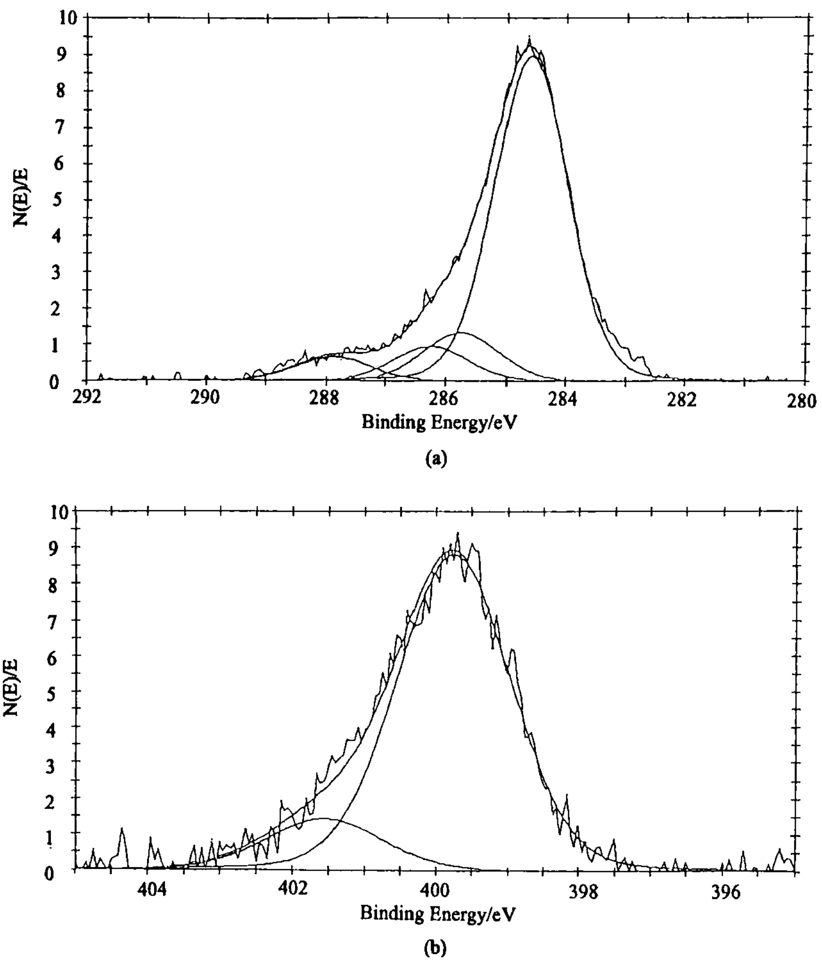

FIGURE 2 (a) Carbon 1s and (b) nitrogen 1s XPS spectra obtained from the adherend fracture surface of uncontaminated cold-rolled steel joints.

TABLE III
Summary of the C1s and N1s XPS results obtained from the adherend and adhesive fracture surfaces from uncontaminated joints

Substrate	Surface	C—C/H	C—N	C—O	N—C=O	O—C=O	N—H	N—H+
Bulk	Adhesive	69.3	13.1	14.7	2.9	0	100	0
CRS	Adherend	74	11.7	8.4	6	0	85	15
	Adhesive	69.3	12.5	15.5	2.7	0	100	0
EGS	Adherend	50.5	28.7	12	4.4	4.4	100	0
	Adhesive	67.1	15.3	13.8	3.8	0	100	0
2024 Al	Adherend	66.3	16.9	10.8	3.4	2	82	18
	Adhesive	68	15.4	13.1	3.4	0	84	16

The carbon 1s spectrum obtained from the CRS adherend fracture surface revealed a decrease in the intensity of C—O peak and an increase in the N—C=O intensity relative to the C—O peak (see Figure 2a) when compared with the bulk adhesive. The C—O peak was associated with the epoxy resin, whereas the N—C=O peak was due to the polyamide curing agent. These observations suggested that a higher concentration of curing agent was associated with the CRS surface than was expected from the analysis of the bulk adhesive. It was expected that the increase in intensity of the N—C=O peak was associated with a similar increase in the intensity of the C—N peak. However, the C—N peak actually decreased slightly in intensity.

The nitrogen peak (see Figure 2b) contained two components, one at 399.8 eV due to the amine and amide nitrogens and one 1.5 eV upfield from the peak at 399.8 eV. Dillingham and Boerio[6] studied the curing reaction between a DGEBA epoxy resin and a primary amine at a 2024 aluminum interface and detected an upfield peak in the nitrogen spectrum which was assigned to a protonated amine. These researchers also detected an increase in the intensity of the C—N peak *versus* the C—O peak compared with the bulk resin, but found no evidence for preferential adsorption of the curing agent. The changes in the C1s spectrum were attributed to an increase in the crosslink density at the aluminum surface caused by the protonated amine catalyzing the curing reaction. This process was not thought to be occurring at the CRS/adhesive interface in the current research, as a reduction in the C—N intensity and the C—O intensity was detected. In addition, an increase in the N—C=O peak was observed. No increase in the N—C=O peak would have been expected if increased crosslinking was occurring at the interface as the amide carbonyl group does not participate in the curing reaction.

The increase in the intensity of the N—C=O could be explained by the presence of surface contaminants which adsorbed onto the adherend fracture surface prior to analysis. Peaks associated with C—C/H, C—O, C=O and O—C=O were detected on the CRS fracture surface after cleaning. While the C=O and the N—C=O species possessed similar binding energies, it should be noted that no O—C=O peak was detected on the adherend fracture surface obtained from the clean CRS joints. As both the C=O and O—C=O species were detected on the CRS surface after cleaning, it is unlikely that the increase in the N—C=O peak on the CRS substrates can be explained by the presence of an adsorbed contaminant.

Supporting this observation is the fact that the C—O peak decreased in intensity compared with the bulk adhesive. If the increase in the N—C=O peak was due to the presence of a contaminant, an increase in the C—O intensity would have been expected.

A possible explanation for the increase in the N—C=O levels is linked to the fact that the curing agent does not solely consist of the polyamide, but also contains triethylenetetramine.[7] The increase in the N—C=O levels, therefore, suggested that the CRS substrate preferentially adsorbed the amide component of the curing agent, rather than the epoxy or the free amine. The preferential adsorption of the polyamide also explains why no increase in the N/C ratio was observed for the adherend fracture surface relative to the bulk adhesive. The increase in the concentration of the polyamide adsorbed onto the CRS substrate was offset by the reduction in the amine concentration.

The protonation of the amine groups in the curing agent adjacent to the CRS surface can be explained by considering the isoelectric point of the surface. Cold-rolled steel possesses an isoelectric point of 10.[8] The pK_a of primary amines is also approximately 10. Thus, the amine groups adjacent to the CRS substrate were protonated by the surface hydroxyl groups.

When the polymer fracture surface was studied, no protonation of the nitrogen peak was observed and the carbon 1s region was similar to that obtained from the bulk adhesive. This result indicated that the interphase region at the CRS/adhesive interface was very thin, being confined to the adhesive adjacent to the metal substrate. This conclusion was supported by the work of Horner and Boerio[9] who studied thin films of γ-aminopropyltrimethoxysilane adsorbed onto a range of metals using angle-resolved XPS. These researchers found that mild steel substrates protonated the aminosilane, but that the protonation appeared to be confined to the silane/steel interface.

When the CRS substrates were contaminated using the ship-out oil, several interesting observations were made. In the case of the adherend fracture surface the nitrogen to carbon ratio increased to 8.3% (see Table II). The C1s spectrum (see Table IV) obtained from the contaminated adherend fracture surface compound with the bulk adhesive exhibited an increase in both the C—N and the N—C=O

TABLE IV
Summary of the C1s and N1s XPS results obtained from the adherend and adhesive fracture surfaces from contaminated joints

Substrate	Surface	C—C/H	C—N	C—O	N—C=O	O—C=O	N—H	N—H+
Bulk Adhesive		69.3	13.1	14.7	2.9	0	100	0
CRS	Adherend	64.9	16.4	10.5	8.3	0	100	0
	Adhesive	71.6	15.6	10.7	2.1	0	100	0
EGS	Adherend	90.8	9.2	0	0	0	100	0
	Adhesive	87	6.5	6.5	0	0	100	0
2024 Al	Adherend	81.7	3.7	9	2.8	2.8	84	16
	Adhesive	73.7	11.8	11	3.5	0	84	16

(N.B. The CRS and EGS were contaminated with ship-out oil and the 2024 aluminum joints were contaminated with the hydraulic fluid.)

peaks. The increase in the N—C═O peak was particularly large. These results indicated that an increased concentration of the polyamide curing agent was present on the adherend fracture surface. Initial compatibility studies revealed that the ship-out oil, while being compatible with the polyamide curing agent, was incompatible with the epoxy resin. Thus, presence of the ship-out oil on the CRS substrate may have caused the adhesive to phase separate slightly during cure, thus explaining the increased levels of polyamide on the adherend fracture surface. When the adhesive fracture surface was analyzed, an increase in the C—N peak and a decrease in the C—O peak was observed. As the N—C═O peak exhibited a reduction in intensity, these results implied that the adhesive fracture surface was depleted of polyamide and also epoxy resin. This observation was consistent with the observation of higher levels of N—C═O on the adherend fracture surface compared with the bulk adhesive.

Analysis of the nitrogen 1s region revealed the presence of only one peak centered at 399.8 eV and so no protonation of the curing agent by the substrate occurred. The lack of protonation of the curing agent by the CRS substrate can only be explained if the contaminant was not fully displaced and that a thin layer of the oil remained associated with the CRS surface. This would have, therefore, prevented the amine groups from interacting with the surface hydroxyl groups and being protonated. The presence of the contaminant would have increased the C—C/H intensity and so the calculated nitrogen to carbon ratio of 8.3% may have underestimated the levels of curing agent present in the residual adhesive on the adherend fracture surface.

3.2 Electrogalvanized Steel Substrates

Tables III and IV summarize the results obtained from the analysis of the carbon 1s and nitrogen 1s regions obtained from the clean and contaminated EGS joints. Firstly, as discussed previously, the nitrogen to carbon ratio of 21.3% obtained from the adherend fracture surface of clean EGS joints was extremely high. This implied that a high degree of preferential adsorption of the curing agent occurred during cure. The carbon 1s spectrum obtained from the clean surface exhibited several changes from the spectra obtained from the bulk adhesive (see Figure 3). The C1s spectrum exhibited an extremely intense C—N peak, but this peak was accompanied by only a small increase in the amide N—C═O peak, compared with the bulk adhesive. Thus, the increase in the C—N peak was not solely associated with the polyamide curing agent. As discussed in the previous section, the curing agent contains some free amine. The results, therefore, suggested that the amine preferentially adsorbed onto the zinc surface. The C—O peak was less intense than expected from the bulk adhesive resin indicating the presence of decreased levels of epoxy resin. A peak assigned to O—C═O was also observed. If the O—C═O peak was due to the presence of an air-borne contaminant, increases in both the C—O and C═O peaks would be expected. A decrease in the C—O peak was detected and so contamination is not believed to be the reason for the observed O—C═O peak. One possibility is that zinc can form carbonates upon exposure to the atmosphere which could explain the detection of the O—C═O peak.

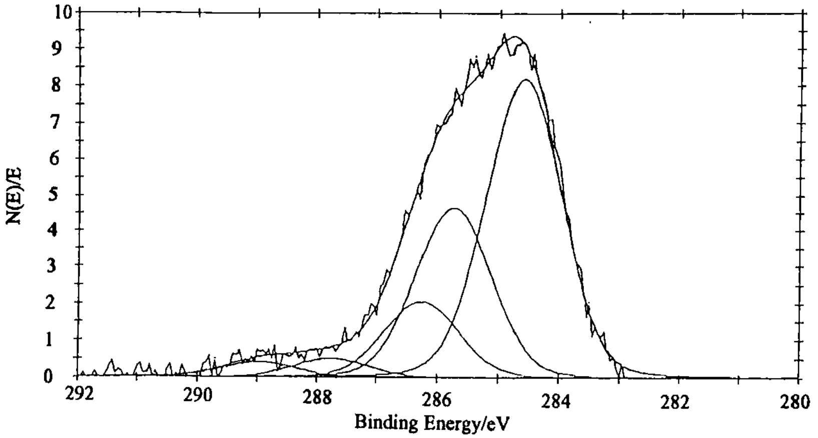

FIGURE 3 Carbon 1s XPS spectra obtained from the adherend fracture surface of an uncontaminated electrogalvanized steel joint.

The adhesive fracture surface was similar in composition to the bulk adhesive resin. However, small increases in the C—N and N—C=O peaks and a small decrease in the C—O peak were observed compared with the bulk adhesive. These observations indicated a slight enrichment in the curing agent components. Thus, it appeared that the interphase region in the case of the EGS/adhesive joints was more extensive than that observed for the CRS/adhesive joints. The high concentration of curing agent at the interface was a cause for concern as it implied that a weakened interphase was formed, which could act as a weak boundary layer.

The nitrogen peak consisted of only one component, centered at 399.8 eV. The isoelectric point for a zinc surface is expected to be approximately 9.[8] As this value was similar to that of CRS, the failure to observe protonation of the nitrogen atoms was surprising. This implied that the amine groups were not available for reaction and so the zinc and amine groups may have reacted to form a zinc/amine coordination compound. If this occurred, the lone-pair of electrons on the nitrogen groups would be used to coordinate to the zinc and so would not be available to react with the epoxy resin, preventing protonation of the curing agent.

In the case of the EGS joints contaminated with the ship-out oil, a marked change in the composition of the interphase was observed. The nitrogen to carbon ratios for the adherend and adhesive fracture surfaces dropped to 1.7% and 3.8% respectively. Analysis of the carbon 1s spectra (see Figure 4) obtained from the adherend fracture surface revealed that the surface consisted of mostly hydrocarbon with a small shoulder in the position associated with the C—N peak. No additional peaks associated with the C—O or the N—C=O components were detected. When the adhesive fracture surface was analyzed, a large hydrocarbon peak was once more detected, together with small C—N and C—O peaks. Analysis of the nitrogen once more found no evidence of protonation.

The above results indicated that the adhesive was not capable of displacing the ship-out oil from the EGS substrate. This was a surprising result as the same adhesive successfully displaced the oil from the cold-rolled steel surface. The observed behavior was associated with the strong preferential adsorption of the amine by the

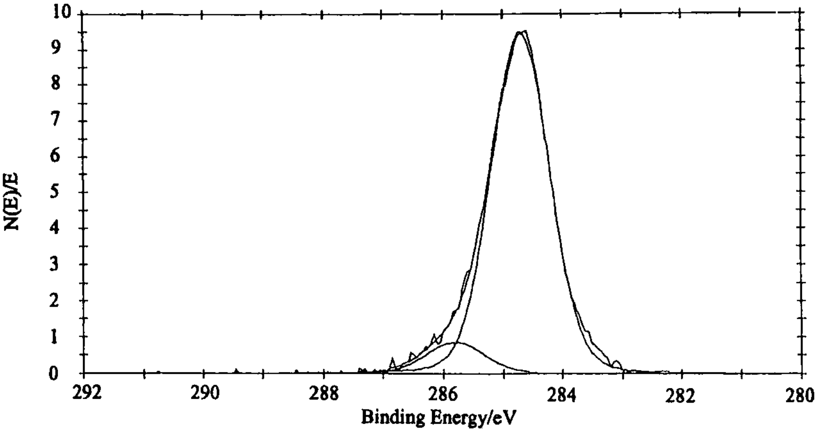

FIGURE 4 Carbon 1s XPS spectra obtained from the adherend fracture surface of electrogalvanized steel joint contaminated with Ferrocote FC-61.

zinc surface and also by the incompatibility of the oil with the epoxy resin. The strong adsorption of the amine by the zinc surface would leave an adhesive layer rich in epoxy. This epoxy-rich adhesive layer would then be incompatible with the oil and so the oil could not be absorbed into the bulk adhesive. This hypothesis explains why the adhesive was unable to displace completely the oil from galvanized steel, but was efficient at displacing the same contaminant from cold-rolled steel substrates.

3.3 2024 Aluminum Substrates

The results obtained from the analysis of the C1s and N1s regions of the fracture surfaces from the uncontaminated and contaminated 2024 aluminum joints are presented in Tables III and IV. In the case of the uncontaminated joints the N/C ratio obtained from the adherend fracture surface suggested that preferential adsorption of the curing agent by the substrate occurred. The carbon 1s spectra (see Figure 5) of the adherend fracture surface exhibited an increase in the C—N and a decrease in the C—O levels. This was consistent with the presence of higher levels of curing agent at the interface than was expected from the analysis of the bulk adhesive. However, the increase in the C—N levels was not associated with a similar increase in the N—C═O peak and so it appears than the aluminum substrate preferentially adsorbed the free amine. The increase in the N/C ratios means that the increase in the C—N peak relative to the C—O peak is unlikely to be due to increased crosslinking of the adhesive resin as found by Dillingham and Boerio.[6]

The carbon 1s spectrum obtained from the adhesive fracture surface exhibited larger C—N and N—C═O peaks when compared to the bulk adhesive, indicating the presence of the amide. This observation was consistent with the preferential adsorption of the amine by the aluminum surface. The presence of a peak associated with a carboxylic acid or ester (O—C═O) on the adherend fracture surface was unexpected. In the case of the adherend fracture surfaces obtained from the 2024 Al substrates, a O—C═O peak was detected. The C—O peak did not increase in

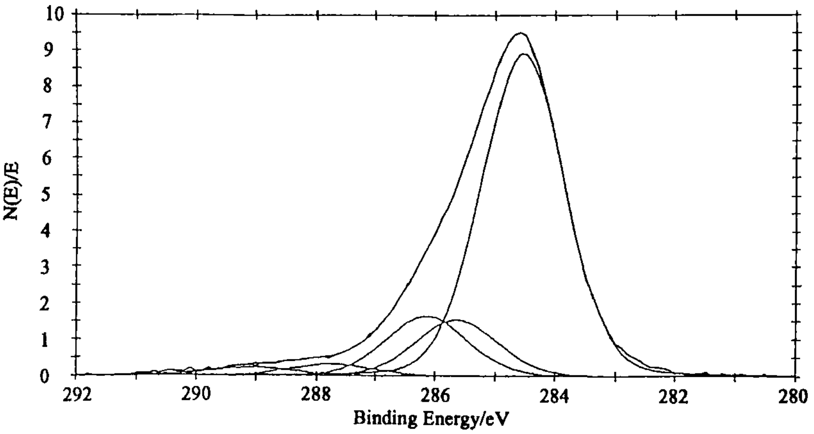

FIGURE 5 Carbon 1s XPS spectra obtained from the adherend fracture surface of an uncontaminated 2024 aluminum joint.

intensity as would be expected if the O—C=O peak was due to a contaminant. The reason for the presence of the O—C=O peak is, therefore, surprising and no plausible explanation can be proposed at present.

Analysis of the nitrogen 1s region from the adherend fracture surface revealed that protonation of the amine groups had occurred. The isoelectric point of aluminum is approximately 9[8] and so protonation of the basic amine groups would be expected. When the adhesive fracture surface was analyzed, the levels of protonation were similar to those obtained from the adherend fracture surface.

The analysis of the adherend and adhesive fracture surfaces implied that the interphase region for the aluminum/adhesive joints was much deeper in extent than for either cold-rolled steel or electrogalvanized steel. Horner and Boerio[9] studied the adsorption of γ-aminopropyltrimethoxysilane from aqueous solutions onto aluminum. These researchers detected high levels of protonation, which were not strongly dependent on the electron take-off angle. In addition, the aluminum signal did not decrease as the take-off angle decreased which implied that aluminum was present in the silane film. They concluded that the aminosilane had etched the aluminum oxide. 0.8% aluminum (see Table I) was detected on the adhesive fracture surface in the current work. Recent electron microscopy and EDS studies detected aluminum oxide particles on the adhesive fracture surface.[10] Therefore, oxide failure during fracture was the probable reason for the presence of the aluminum on the adhesive fracture surface in this work.

When the adherend and adhesive fracture surfaces from the aluminum joints contaminated with the hydraulic fluid were investigated, a marked increase in the C—C/H level was observed when compared with the uncontaminated joints. In addition, both the C—N and C—O peak intensities dropped, although the drop for the C—O peak was smaller than that observed for the C—N peak. These results are consistent with the presence of some undisplaced contaminant. The presence of the C—O bonds in the ester may explain the much smaller reduction in the C—O peak compared with the C—N peak. This indicated that some undisplaced ester was present on the adherend substrate. The presence of the ester would also explain the observed increase in the intensity of the O—C=O peak. Care must be taken in the interpretation of this increase as a O—C=O peak was also detected on the adherend fracture surface of the uncontaminated joint.

Analysis of the adhesive fracture surface revealed deficiencies in both the C—O and C—N peaks. As no evidence for the presence of a O—C=O peak was obtained, the reduction in the C—O and C—N peaks indicated that the hydrocarbon component of the hydraulic fluid was displaced into the bulk adhesive, whereas the ester may have remained associated with the aluminum surface, assuming that the hydrocarbon and the ester are separate components. The detection of 0.6% aluminum on the adhesive fracture surface indicated that some oxide failure occurred during fracture.

Analysis of the nitrogen 1s region obtained from both fracture surfaces obtained from the contaminated aluminum/polyamide joints revealed that protonation of the curing agent occurred. This observation is in contrast to the behavior of the cold-rolled steel joints prepared using contaminated substrates, which exhibited no protonation of the curing agent. This result indicated that the contaminant was displaced in some areas, but not others. This would explain the observed protonation, the increased intensity of the C—C/H peak and finally the detection of aluminum on the adhesive fracture surface.

4.0 CONCLUSIONS

The chemistry of the interphase region of uncontaminated metal/polyamide adhesive joints was very dependent on the substrate. A high level of perferential adsorption of an amine component in the curing agent occurred on electrogalvanized steel. The free amine also appeared to be adsorbed onto the 2024 aluminum. In contrast, the amide groups adsorbed onto the cold-rolled steel surface. The adsorption of the curing agent components was, however, much lower in the case of the aluminum and cold-rolled steel joints than for galvanized steel. The strong adsorption observed in the case of galvanized steel indicated that a strong reaction occurred between the amine and the zinc which may have formed a zinc/amine coordination compound. Protonation of the curing agent occurred in the case of 2024 aluminum and cold-rolled steel joints. No protonation of the curing agent was detected in the case of electrogalvanized steel joints as the lone pair of electrons on the nitrogen atoms were coordinated to the zinc metal and so were unable to accept the protons.

The interphase regions of the joints were markedly affected by the presence of any adsorbed contaminants. The model polyamide adhesive proved capable of largely displacing a mineral oil and a hydraulic fluid from cold-rolled steel and 2024 aluminum substrates, respectively. Surprisingly, the same adhesive proved incapable of displacing the mineral oil from an electrogalvanized steel substrate, resulting in joint failure within the adsorbed contaminant film. This was due to the strong interaction of the curing agent with the zinc to form an epoxy-rich adhesive layer adjacent to the substrate. As the oil was incompatible with the epoxy resin, the oil was not absorbed into the bulk adhesive. The results obtained in the current study indicate that substrate/adhesive interaction combined with the nature of the adsorbed contaminant will have a marked effect on both the initial strength and durability performance of an adhesive joint.

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