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X-Ray Photoelectron Spectroscopy of the Fracture Surfaces of Iron/ Epoxy and Titanium/Epoxy Adhesive Joints

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The failure path of iron/epoxy and titanium/epoxy lap joints prepared from adherends pretreated with dilute aqueous solutions of Γ -aminopropyltriethoxysilane (Γ -APS) and then exposed to water at 60°C for varying times was determined using X-ray photoelectron spectroscopy (XPS). Iron/epoxy lap joints prepared using Γ -APS primers applied at pH 8.0 and tested without exposure to water failed near the oxide/primer interface with only a small amount of adhesive left on the substrate failure surface. Iron/epoxy joints that were primed with Γ -APS at pH 10.4 and tested without immersion in water failed partly within the adhesive and partly near the interface. All of the iron/epoxy joints failed in the primer near the primer/oxide interface when tested after exposure to water for seven days but very little corrosion of the substrates was observed. When titanium/epoxy lap joints were tested without exposure to water, failure was partly within the adhesive and partly near the primer/oxide interface regardless of the pH at which the primer was applied. However, the failure path shifted to near the primer/oxide interface after the joints were immersed in water for seven days. It was concluded that failure of the joints after exposure to water was associated with hydrolysis within the primer rather than with extensive corrosion of the substrate.

KEY WORDS Coupling agents; durability; iron/epoxy joints; locus of failure; silane primers; titanium/epoxy joints.

I INTRODUCTION

The use of silane coupling agents in primers to enhance the hydrothermal stability of adhesive bonds has been demonstrated.

Boerio and Williams¹ showed that thin films of Γ -aminopropyltriethoxysilane (Γ -APS) were very effective primers for iron/epoxy lap joints. Joints prepared from unprimed adherends retained only about 25% of their initial strength after immersion in water at 60°C for 60 days. However, iron/epoxy lap joints prepared from adherends that were pretreated in dilute aqueous solutions of Γ -APS at pH values of 10.4 and 8.0 retained about 50% and 75% of their initial strength after similar exposure to warm water. Boerio and Dillingham² showed that thin films of Γ -APS were also effective primers for titanium/epoxy lap joints. However, the pH at which the silane films were applied was not important for titanium substrates.

Kinloch³ showed that thin films of Γ -glycidoxypropyltrimethoxysilane (Γ -GPS) were also useful primers for enhancing the environmental stability of aluminum/epoxy adhesive bonds. They reported that the time to failure for aluminum/epoxy tapered double cantilever beams that were statically loaded and immersed in water at room temperature was increased about two orders of magnitude by the use of Γ -GPS primers. Very recently Boerio and Ho⁴ reported somewhat similar results using Γ -APS films as primers for aluminum/epoxy tapered double cantilever beams that were statically loaded and immersed in water at 60°C.

Relatively little fundamental information is available regarding the mechanisms by which silane coupling agents function to enhance the environmental stability of adhesive bonds to metals. However, Gettings⁵ used Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) to determine the locus of failure in iron/epoxy butt joints that were fractured after immersion in water for varying amounts of time. The failure path for joints that were not immersed in water was partly cohesive within the adhesive and partly cohesive within the substrate. After exposure to water, the failure of unprimed joints was very near the interface and there was evidence for considerable corrosion of the substrate. The failure path for joints that were prepared from adherends primed with Γ -GPS was within the silane after exposure to water and there was much less corrosion of the substrate.

Corrosion of the substrate was not considered as the reason for debonding in the unprimed joints. Gledhill and Kinloch⁶ had investigated the fracture surfaces of iron/epoxy butt joints that were

tested after immersion in distilled water at elevated temperatures for varying lengths of time. They showed that the failure path was nearly interfacial at the edges of samples that had been exposed to water for long times but was cohesive within the epoxy near the center of the samples. Corrosion had occurred near the edges of the samples but after debonding and was not a cause of failure. The principal cause of debonding was the displacement of the adhesive from the iron surface by water.

The primary purpose of this paper is to describe the use of XPS to determine the failure path for iron/epoxy and titanium/epoxy lap joints that were prepared from adherends pretreated with dilute aqueous solutions of Γ -APS, immersed in water at 60°C for long times, and then tested to determine their residual strength. The mechanical behavior of such joints has been described elsewhere^{1,2,7}

II EXPERIMENTAL

Lap joints were prepared according to ASTM standard D1002. Adherends ($1 \times 4 \times 0.063$ inches) were sheared from iron and titanium sheets and mechanically polished using a series of silicon carbide papers followed by wet polishing with alumina compounds. After final polishing with 0.3 micron alumina, the adherends were rinsed with distilled water and blown dry with nitrogen. In some cases the adherends were pretreated by immersion in dilute aqueous solutions of Γ -APS at pH 10.4 or at pH 8.0 for ten minutes and then blown dry using a strong stream of nitrogen. In other cases the adherends were left untreated as a control. The lap joints were assembled by bonding pairs of adherends together using an adhesive consisting of an epoxy resin (Epon 828, Shell Chemical Co.) and a tertiary amine curing agent (K-61B, Pacific Anchor Chemical Co.) and the adhesive was cured by heating the joints in an oven at 100°C for 1 hour.

After the adhesive was cured, the joints were allowed to cool to room temperature. Some of the joints were then tested in a mechanical testing instrument at a crosshead speed of 0.05 inches/minute to determine their dry strength. The remaining joints were immersed in a water bath at 60°C. At appropriate intervals, joints were removed from the water and tested to determine their residual

strength. Small samples were cut from the adhesive and adherend fracture surfaces for analysis using XPS.

Iron and titanium samples ($0.5 \times 0.5 \times 0.063$ inches) for surface analysis were sheared from large sheets and mechanically polished as described above. After final polishing, the samples were rinsed with distilled water and blown dry with nitrogen.

Neat films of Γ -APS and the adhesive were prepared for surface analysis by casting solutions onto clear glass slides. The primer films were dried in air at 100°C for thirty minutes and then outgassed in a vacuum oven at room temperature for twenty-four hours. The adhesive films were cured by heating in air at 100°C for one hour and then outgassed in the vacuum oven for twenty-four hours.

All of the XPS spectra were obtained with a Perkin-Elmer 5300 X-ray photoelectron spectrometer using Mg K_α X-rays. Most of the spectra were obtained using an exit angle of 45° but exit angles of 15° and 90° were used to obtain some of the high resolution spectra. The spectra were corrected for the effects of sample charging by referring the C(1s) band for hydrocarbons to a binding energy of 284.6 eV.

III RESULTS AND DISCUSSION

Iron, oxygen, carbon, and trace of copper, perhaps due to impurities, were observed in survey spectra of polished iron surfaces. Titanium, oxygen, carbon, and a small amount of aluminum due to an alloying element were detected on the titanium surfaces.

O(1s) spectra of both substrates consisted of bands near 529.7 eV and 531.1 eV that were characteristic of surface oxides and hydroxides, respectively.⁸ The relative intensities of the bands depended on the exit angle. At small exit angles, the shoulder near 531.1 eV became more intense than the band near 529.7 eV.

The $\text{Fe}(2p_{3/2})$ and $\text{Fe}(2p_{1/2})$ spectra of the iron substrates were observed near 711.1 and 724.7 eV and were typical of oxidized surfaces.⁹ However, a band characteristic of elemental iron was observed near 707.3 eV in $\text{Fe}(2p_{3/2})$ spectra obtained using large exit angles, indicating that the oxide was only about 50 Å in thickness. Similar results were obtained for the titanium substrates. The

Ti(2p_{3/2}) and Ti(2p_{1/2}) spectra were observed near 458.3 and 464.1 eV and were also typical of oxides.⁹ A band related to elemental titanium was observed near 453.2 eV in Ti(2p_{3/2}) spectra obtained using large exit angles, showing that the oxide on titanium was also only about 50 Å in thickness.

The Si(2p), C(1s), N(1s), and O(1s) spectra of the neat primer were observed near 102.3, and 284.6, 398.8, and 532.0 eV, respectively, in good agreement with results obtained previously for Γ-APS adsorbed onto copper.¹⁰ C(1s) spectra of the adhesive consisted of a band near 284.6 eV and a shoulder near 286.2 eV. The O(1s) spectra of the adhesive were observed near 533.0 eV.

XPS spectra obtained from the failure surfaces of iron/epoxy lap joints prepared from adherends primed with Γ-APS at pH 10.4 are shown in Figure 1. Strong bands characteristic of the adhesive and the oxide were observed near 532.9 and 529.6 eV in the adherend O(1s) spectra of joints that were tested without immersion in water (see Figure 1A). Only a weak band related to the primer was seen near 102.0 eV in the Si(2p) spectra, indicating that failure was mostly near the primer/oxide interface but with islands of adhesive left on the substrate. This conclusion was supported by the observation of strong bands characteristic of the primer near 532.3 and 102.1 eV in the O(1s) and Si(2p) spectra obtained from the corresponding adhesive failure surface (see Figure 1B).

The failure characteristics of iron/epoxy joints prepared from adherends primed with Γ-APS at pH 10.4 were considerably different after immersion in water at 60°C for 7 days. In that case the O(1s) spectra obtained from the adherend fracture surfaces consisted mostly of the band near 529.6 eV that was characteristic of the oxide and the Si(2p) spectra were very weak (see Figure 1C). The Si(2p) spectra from the adhesive failure surfaces were strong and the O(1s) spectra were observed near 532.0 eV (see Figure 1D) and were typical of the silane primer, demonstrating that failure after immersion in water was very near the oxide/primer interface.

XPS spectra from the failure surfaces of iron/epoxy lap joints prepared from adherends pretreated with dilute aqueous solutions of Γ-APS at pH 8.0 are shown in Figure 2. The spectra obtained from joints that were tested without immersion in water and after immersion in water at 60°C for 7 days were very similar. The O(1s) spectra from the substrate failure surfaces consisted mostly of the

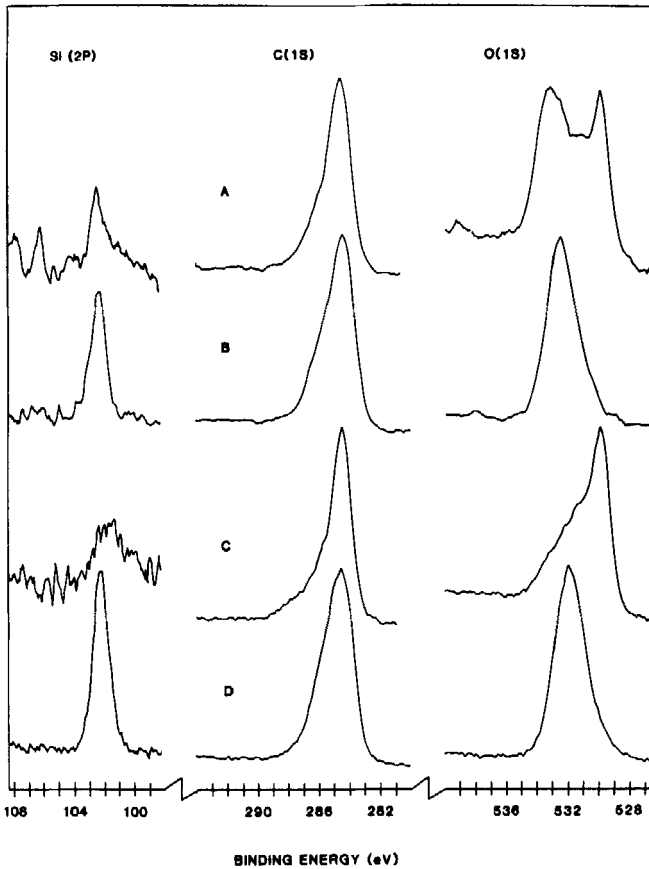


FIGURE 1 XPS spectra obtained from the failure surfaces of an iron/epoxy lap joint that was prepared from adherends that were pretreated with Γ -APS at pH 10.4: (A)—adherend surface, no immersion in water, (B)—adhesive surface, no immersion, (C)—adherend surface, after 7 days in water at 60°C, and (D)—adhesive surface after 7 days immersion.

bands typical of surface oxides and hydroxides and the Si(2p) spectra were very weak (see Figures 2A and 2C). The O(1s) spectra of the adhesive failure surfaces were near 532.0 eV and the Si(2p) spectra were strong (see Figures 2B and 2D). It was concluded that joints prepared from adherends primed with Γ -APS at pH 8.0 always failed very near the oxide/primer interface with very little adhesive left on the adherend failure surface.

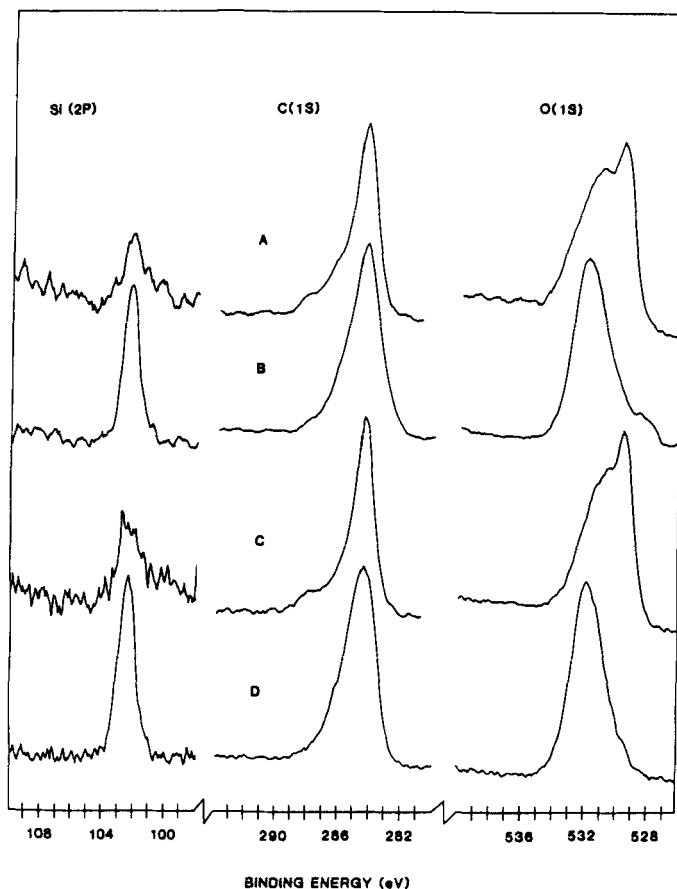


FIGURE 2 XPS spectra obtained from the failure surfaces of an iron/epoxy lap joint that was prepared from adherends that were pretreated with Γ -APS at pH 8.0: (A)—adherend surface, no immersion in water, (B)—adhesive surface, no immersion, (C)—adherend surface, after 7 days in water at 60°C, and (D)—adhesive surface after 7 days immersion.

Spectra from the failure surfaces of titanium/epoxy lap joints prepared from adherends pretreated with Γ -APS at pH 10.4 are shown in Figure 3. The Si(2p) spectra from the adherend failure surfaces of joints that were tested without immersion in water were weak and the C(1s) and O(1s) spectra were very similar to the corresponding spectra of the epoxy adhesive (see Figure 3A). Spectra of the adhesive failure surfaces were very similar (see

Figure 3B) and it was concluded that the locus of failure was mostly cohesive within the adhesive. Spectra obtained from the failure surfaces of joints that were prepared from adherends primed with Γ -APS at pH 10.4 and immersed in water for 7 days were quite different. Si(2p) spectra of the adherends were weak and the O(1s) spectra consisted of bands near 532.5 and 529.8 eV typical of the

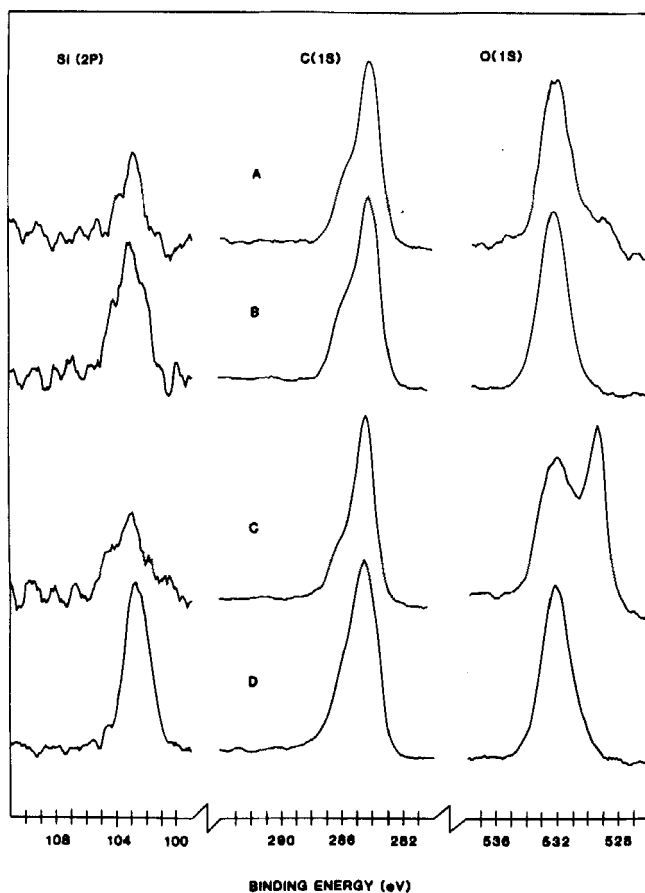


FIGURE 3 XPS spectra obtained from the failure surfaces of a titanium/epoxy lap joint that was prepared from adherends that were pretreated with Γ -APS at pH 10.4: (A)—adherend surface, no immersion in water, (B)—adhesive surface, no immersion, (C)—adherend surface, after 7 days in water at 60°C, and (D)—adhesive surface after 7 days immersion.

adhesive and the oxide, respectively (see Figure 3C). The Si(2p) spectra of the adhesive failure surfaces were strong and the O(1s) spectra consisted of a single band near 532.5 eV (see Figure 3D). Failure after exposure to water was near the oxide/primer interface but with islands of adhesive left on the substrate.

Spectra obtained from the failure surfaces of titanium/epoxy

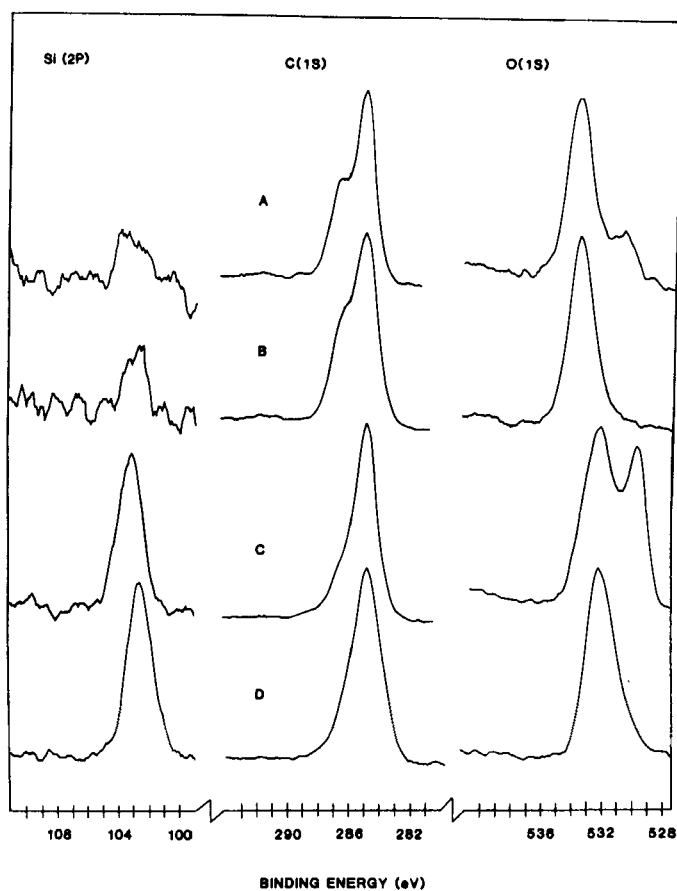


FIGURE 4 XPS spectra obtained from the failure surfaces of a titanium/epoxy lap joint that was prepared from adherends that were pretreated with Γ -APS at pH 8.0: (A)—adherend surface, no immersion in water, (B)—adhesive surface, no immersion, (C)—adherend surface, after 7 days in water at 60°C, and (D)—adhesive surface after 7 days immersion.

joints prepared from adherends pretreated with dilute aqueous solutions of Γ -APS at pH 8.0 are shown in Figure 4. The C(1s) and O(1s) spectra from adherend failure surfaces of joints that were tested without immersion in water were similar to the corresponding spectra of the epoxy and the Si(2p) spectra were weak. Very similar results were obtained for the adhesive fracture surfaces and it was concluded that failure in this case was mostly within the adhesive. The spectra obtained from the failure surfaces of joints tested after immersion in water for 7 days are shown in Figures 4C and 4D. The Si(2p) spectra from the adherends were strong and the O(1s) spectra contained bands near 532.0 and 529.7 eV that were characteristic of the primer and the oxide. Spectra from the adhesive failure surface were very similar to those of the primer. Failure in this case was mostly within the primer but close to the oxide/primer interface.

The results obtained in this investigation are summarized in Table I. Iron/epoxy lap joints that were prepared from adherends that were primed with Γ -APS at pH 10.4 and tested without immersion in water failed partly within the adhesive and partly near the primer/oxide interface. Joints that were prepared and tested in a similar manner except that the primer was applied at pH 8.0 failed near the primer/oxide interface. All of the iron/epoxy lap joints failed near the primer/oxide interface when they were tested after immersion in water at 60°C for seven days. Very little evidence for corrosion of the iron substrates was obtained.

The titanium/epoxy joints failed partly within the adhesive and partly near the primer/oxide interface regardless of the pH at which the primer was applied when they were tested without immersion in water. However, the failure path shifted to near the primer/oxide interface for joints that were tested after immersion in water for seven days.

These results are very similar to those obtained by Gettings⁵ for iron/epoxy butt joints using Γ -GPS primers and may indicate that failure within the primer after immersion in water for long times is a common feature for iron/epoxy and titanium/epoxy adhesive joints prepared using silane primers. The results obtained here also support the conclusion that large-scale corrosion of the substrate is not a factor in the failure of iron/epoxy and titanium/epoxy adhesive joints exposed to water at elevated temperatures. Hy-

TABLE I
Summary of Failure Characteristics of Iron/Epoxy and Titanium/Epoxy Lap Joints Prepared From Adherends Primed With Γ -Aminopropyltriethoxysilane (Γ -APS)

Adherend	Primer pH	Exposure Environment	Locus of Failure
Iron	10.4	none	Primer/oxide interface and within adhesive
Iron	10.4	7 days in water at 60°C	Primer/oxide interface
Iron	8.0	none	Primer/oxide interface
Iron	8.0	7 days in water at 60°C	Primer/oxide interface
Titanium	10.4	none	Primer/oxide interface and within adhesive
Titanium	10.4	7 days in water at 60°C	Primer/oxide interface
Titanium	8.0	none	Primer/oxide interface and within adhesive
Titanium	8.0	7 days in water at 60°C	Primer/oxide interface and within primer

drolysis near the interface but within the organic phase seems to be the principal cause of failure.

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