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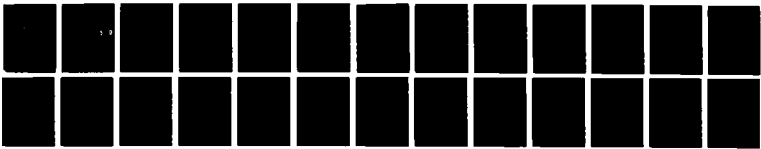
STRUCTURE AND PROPERTIES OF POLYMER INTERPHASES(U)  
CINCINNATI UNIV OH DEPT OF MATERIALS SCIENCE AND  
ENGINEERING F J BOERIO 81 AUG 87 N00014-85-R-8459

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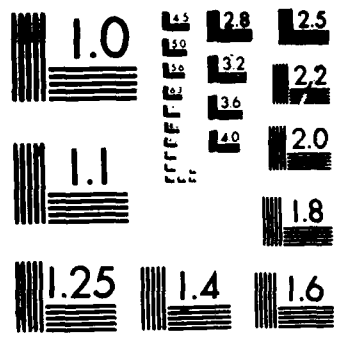
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Structure and Properties of Polymer Interphases

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FIELD	GROUP	SUB-GROUP	
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significantly. After drying at 150°C, the films formed on titanium, steel, and 2024 aluminum were all oxidized to the imine but the oxide on 1100-series aluminum inhibited the free radical oxidation reaction. Dissociation of the bicarbonates and oxidation of the amino groups were important factors in the reaction of the primers with epoxy resins. Reaction of primer films on steel and 2024 aluminum with epoxy resins at 50 or 75°C was slow because the temperature was too low for dissociation of the bicarbonates to occur. At 110 or 150°C, epoxies reacted readily with  $\gamma$ -APS films on steel but not with those on 2024 aluminum. For primer films on 2024 aluminum, the preferred reaction was oxidation of the amino groups.

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## I. Introduction

A great deal of progress has been made in recent years in understanding the importance of the surface properties of the substrate in obtaining strong, durable adhesive bonds to metals. Adhesive bonds to aluminum provide an interesting case in point. Hydration of the oxide to pseudoboehmite is responsible for the failure of most adhesive bonds to aluminum during exposure to warm, moist environments (1). Anodizing aluminum in phosphoric acid provides a porous oxide that is very resistant to hydration in warm water (2). The resistance of the anodic oxide to hydration is due to the formation of a thin film of  $\text{AlPO}_4$  on the outer surface and is essential for durability (3). The porosity of the oxide is important in determining the strength of the joint since it facilitates mechanical interlocking between the adhesive and the substrate. Somewhat similar results have been obtained for titanium anodized in chromic acid (4).

One aspect of the surface properties of the substrate that is not very well understood concerns the structure and properties of polymer interphases. Interphases represent the transition regions between polymer/substrate interfaces and the bulk of the polymer. As a first approximation, it is usually assumed that the properties of the interphase are the same as those of the bulk polymer. However, chemical and physical processes are influenced by interfaces and there may be a gradation of properties as the interface is approached but the extent of those structural gradations and

their depth away from the interface and into the polymer are not well known.

Polymer interphases were discussed some time ago by Kumins and Kwei. Kumins (5) suggested that the mobility of a polymer in contact with a solid was different from that of the bulk polymer due to the adsorption of polymer segments onto the surface of the solid. Kwei (6) subsequently suggested that the effects of adsorption onto a filler particle could extend as far as 1500 A into a polymer.

There has been little experimental evidence provided for the existence of such polymer "interphases." However, Racich and Koutsky used transmission electron microscopy to show that the morphology of epoxy resins cured with polyamine curing agents was different in the bulk and near an interface (7). The morphology of the resin generally consisted of small nodules about 100 to 400 A in diameter. Immediately adjacent to the adherend, there was a layer of closely packed smaller nodules while somewhat farther away (about 1000 A) there was a layer in which the nodules were considerably larger. The high density of small nodules near the adherend surface was attributed to segregation of the curing agent. Similarly, the layer of large nodules somewhat farther away from the surface was attributed to depletion of the curing agent in that region.

Despite their importance, there have been few other investigations of interphases in adhesive joints, perhaps due to the difficulty in gaining access to them for

analysis. Recently, we have begun an investigation of the effects that metal substrates have on the structure of adhesive systems cured against them. In one type of experiment, we have prepared double cantilever beam (DCB) specimens by curing beams of epoxy resins against polished metal beams. After cooling from the post-cure, the residual stresses in these specimens are usually sufficient to enable starter cracks to be propagated along the interface, providing easy access to the adhesive and substrate fracture surfaces for analysis by x-ray photoelectron spectroscopy (XPS), reflection-absorption infrared spectroscopy (RAIR), and internal reflection infrared spectroscopy (ATR). We have used these techniques to determine the effect that metal substrates have on the structure of epoxy adhesives and to determine the structure of the silane/epoxy interphase. Some results of those investigations have been reported previously (8, 9). The purpose of this report is to describe additional results we have obtained concerning the effects that metal substrates have on the structure of silane primer films, the reactivity of those films with epoxy resins, and the structure of the silane/epoxy interphase.

Several previous investigations of the structure of silane primer films adsorbed onto metals from aqueous solutions have been reported. Boerio et al (10, 11) showed that as-formed  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS) films deposited onto polished steel mirrors from solutions at pH

10.4 were composed of low molecular weight polysiloxane films containing absorbed carbon dioxide that formed bicarbonate salts with the primary amino groups. The as-formed films were stable in a dry environment but slowly polymerized during exposure to atmospheric moisture. When films were deposited on steel from solutions acidified to pH 8.0 by the addition of HCl, the as-formed films had greater degrees of polymerization than those deposited from solutions at pH 10.4 and the amino groups were protonated to form hydrochlorides.

When the as-formed films deposited from solutions at pH 10.4 were dried at elevated temperatures, the extent of polymerization increased and the amount of bicarbonate decreased. However, when those prepared at pH 8.0 were heated, there was little additional polymerization and the hydrochlorides were not dissociated. Films formed at pH 10.4 and dried at room temperature reacted readily with epoxy resins but films dried at elevated temperatures did not react to any great extent. Films formed at pH 8.0 also showed little tendency to react with epoxies.

Sung et al (12) used infrared spectroscopy (ATR) and x-ray photoelectron spectroscopy (XPS) to investigate the effect of drying temperature on the structure of  $\gamma$ -APS films adsorbed onto KRS-5 and sapphire internal reflection elements from aqueous solutions at pH 10.4. They found that the bicarbonates were easily dissociated when the films were dried under vacuum at 110°C but were not dissociated during

drying at 25°C for one hour. Slow oxidation of the amino groups to imine groups was also observed during drying at 110°C. The O(1s) binding energy in the XPS spectra shifted upward by about 0.4 eV after drying under vacuum for 90 hours at 25°C. However, few other changes were observed in the XPS spectra.

Sung (13) also investigated the effect of  $\gamma$ -APS primers on the peel strength of adhesive bonds between polyethylene and sapphire and found that drying the primer films at 110°C before the polyethylene was laminated onto the sapphire resulted in decreased joint strength. It was suggested that the decreased strength was due to increased polymerization in the primer films, which limited interdiffusion between polyethylene and the primer.

Culler et al (14) recently investigated the effect of drying temperature on the properties of  $\gamma$ -APS films formed on KBr plates. They showed that temperatures above about 95°C were required to dissociate the amine bicarbonates but that drying the films at temperatures exceeding about 120°C resulted in the oxidation of the amino groups to imine groups. Drying the films at 150°C resulted in similar oxidation but at a much greater rate. Culler (14) also investigated the reaction of  $\gamma$ -APS films with epoxy resins between salt plates at 120°C and showed that the principle reaction occurring was oxidation of the amino groups. Little reaction of the silane with the epoxy was observed. It was suggested that  $\gamma$ -APS be reacted with epoxy resins at

temperatures between 95 and 120°C. Within that temperature range, the bicarbonates would be dissociated but oxidation of the amino groups would be minimized.

Culler (14) reported mostly bulk oxidation of  $\gamma$ -APS and did not consider the effect of substrates. Although there have been several investigations into the structure of  $\gamma$ -APS adsorbed onto metals, the effects that metallic substrates have on the structure of films dried at elevated temperatures has not been investigated previously.

## II. Experimental

Sheets of titanium-6 Al, 4V, oxygen-free, high conductivity (OFHC) copper, and low carbon steel were obtained from Timet, Inc., AMAX Copper, Inc., and Armco, Inc., respectively. 1100 and 2024 aluminum were purchased from commercial suppliers. Coupons (1/8 x 2 x 3") were cut from the sheets and mechanically polished to a mirror finish using standard metallographic techniques. The coupons were ground on a series of dry corundum papers with grit sizes ranging from 350 through 600 and then polished on cloths with 15  $\mu\text{m}$  alumina abrasive slurries. Aluminum coupons were given a final polish to a mirror finish using 3.0  $\mu\text{m}$  MgO slurries. Titanium, steel, and copper substrates were polished to a mirror finish using a series of alumina slurries with particle sizes ranging from 0.3 to 0.05  $\mu\text{m}$ . After the polishing was completed, the mirrors were rinsed several times in distilled, deionized water, blown dry in a

stream of nitrogen, and examined using reflection-absorption infrared spectroscopy (RAIR).

Primer films were applied by immersing the mirrors into 1 or 2% aqueous solutions of  $\gamma$ -APS (A-1100, Union Carbide) at pH 10.4 for one minute, blowing the excess solution off the mirrors using a strong stream of nitrogen, and allowing the films to dry at room temperature. After drying for thirty minutes, the primer films on the mirrors were examined using RAIR. The mirrors were then placed into an oven and the films were dried in air at an elevated temperature for an additional hour before being re-examined using RAIR.

Reactivity of silane primer films with respect to epoxy resins (Epon 828, Shell Chemical Co.) was determined by applying  $\gamma$ -APS films to polished metal mirrors as described above and allowing the films to dry at room temperature for thirty minutes. The mirrors were then placed in a shallow container filled with epoxy resin, and the container was placed into an oven which had been pre-heated to the desired temperature. After one hour, the mirrors were removed from the oven, rinsed repeatedly with methylethylketone (MEK) to remove unreacted epoxy, and examined using RAIR.

Double cantilever beam (DCB) specimens were prepared by casting beams of adhesive (epoxy mixed with tertiary amine curing agent) onto polished, primed metal beams as shown in Figure 3 and then curing the adhesive either by heating at 50°C for one hour and then at 75°C for an additional hour or

else by heating at 110°C for two hours. After curing, the specimens were cooled to room temperature and a crack was propagated along the interface to separate the adhesive and the substrate.

All infrared spectra were obtained using a Perkin-Elmer 1800 Fourier transform infrared spectrophotometer. RAIR spectra were obtained using one reflection at an angle of 78° with an external reflection accessory from Harrick Scientific. ATR spectra were obtained using an internal reflection accessory provided by Harrick, germanium or KRS-5 internal reflection crystals, and an angle of incidence of 45°. In most cases, 50 scans at 4.0 cm<sup>-1</sup> resolution were averaged together to obtain the spectra.

XPS spectra were obtained using a Perkin-Elmer Model 5300 ESCA System. K<sub>α</sub> radiation from a magnesium anode at a power of 300 watts was used to excite the spectra. Pass energy was 44.74 eV for survey spectra and 17.89 eV for multiplex spectra.

### III. Results and Discussion

The RAIR spectrum obtained from a steel mirror that was immersed in a 2% aqueous solution of γ-APS at pH 10.4 for one minute, dried in a stream of nitrogen, and then dried in air at room temperature for thirty minutes was dominated by a strong band near 1120 cm<sup>-1</sup> and by weaker bands near 920, 1040, 1330, 1470, 1570, and 1640 cm<sup>-1</sup> (see Figure 2A). The band near 920 cm<sup>-1</sup> has previously been assigned to SiOH groups while those near 1040 and 1120 cm<sup>-1</sup> have been

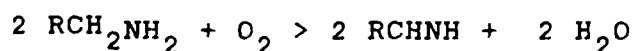
assigned to SiOSi bonds (10, 11). These results show that the silane was hydrolyzed in solution and polymerized during drying on the surface to form siloxane polymers. The bands near 1330, 1470, 1570, and 1640  $\text{cm}^{-1}$  have been the subject of considerable discussion in the past but it is now firmly established that they are related to the absorption of carbon dioxide from the atmosphere and the formation of amine bicarbonates (10, 11).

When the as-formed films were dried in air at 110 $^{\circ}$ C for one hour, several changes were observed in the spectra (see Figure 2B). The band near 1120  $\text{cm}^{-1}$  shifted upward to about 1150  $\text{cm}^{-1}$ , the shoulder near 1040  $\text{cm}^{-1}$  became well resolved, and the band near 920  $\text{cm}^{-1}$  decreased in intensity, all due to increased polymerization in the films (10, 11). In addition, the bands near 1330, 1470, 1570, and 1640  $\text{cm}^{-1}$  all decreased in intensity, indicating either that some of the amine bicarbonates were dissociated by heating the films at 110 $^{\circ}$ C or that most were dissociated and some reformed.

Essentially identical results were obtained when  $\gamma$ -APS films were formed on titanium and 1100-series aluminum substrates and then dried at 110 $^{\circ}$ C. However, the results obtained for 2024 aluminum substrates were somewhat different. As-formed films were characterized by a strong, broad band near 1100  $\text{cm}^{-1}$  and by weaker bands near 890, 1330, 1470, 1570, and 1640  $\text{cm}^{-1}$  (see Figure 3A). The bands near 890 and 1100  $\text{cm}^{-1}$  were attributed to SiOH and SiOSi groups, respectively, while those near 1330, 1470, 1570, and

1640  $\text{cm}^{-1}$  were again related to amine bicarbonates. The frequencies of the bands due to SiOH and SiOSi groups were both lower for aluminum substrates than for steel and titanium substrates, indicating less polymerization of the silane on 2024 aluminum, perhaps due to hydrogen bonding between silanol groups and hydroxyl groups on the oxidized surface of the aluminum.

After the as-formed films on 2024 aluminum were dried at 110°C for one hour, the spectrum shown in Figure 3B was obtained. The shape of the band near 1100  $\text{cm}^{-1}$  changed very little, showing that little additional polymerization occurred. More interesting, however, was the observation that the bands due to the bicarbonate had all disappeared and been replaced by bands near 1600 and 1660  $\text{cm}^{-1}$ . The band near 1660  $\text{cm}^{-1}$  was related to the CN stretching mode of an imine formed by the oxidation of the amine as shown below:



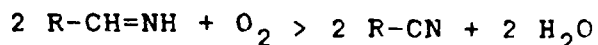
The origin of the band near 1600  $\text{cm}^{-1}$  is not known with certainty at this time but it may be related to the  $\text{NH}_2$  deformation mode of residual primary amino groups as suggested by Culler (14). However, it is interesting to note that bicarbonates did not reform after the films on 2024 aluminum were dried at 110°C for an hour, perhaps implying that the band observed near 1600  $\text{cm}^{-1}$  after drying is not due to primary amino groups.

The results obtained for copper substrates were very similar to those for 2024 aluminum. When as-formed  $\gamma$ -APS films were dried at 110°C for one hour, the bands due to bicarbonates disappeared and the band due to imines appeared near 1660  $\text{cm}^{-1}$ . The band near 1600  $\text{cm}^{-1}$  also appeared but it was somewhat more intense for films formed on copper than for those formed on 2024 aluminum (see Figure 4).

When the experiments described above were repeated but the as-formed  $\gamma$ -APS films were dried at 150°C for one hour after drying at room temperature for thirty minutes, some extremely interesting results were obtained. The infrared spectra of the films formed on steel, titanium, and 1100-series aluminum were very similar and consisted of bands near 1040 and 1150  $\text{cm}^{-1}$  due to SiOSi groups and near 1660  $\text{cm}^{-1}$  due to imines (see, for example, Figure 5). The bands near 1330, 1470, 1570, and 1640  $\text{cm}^{-1}$  due to bicarbonates were not observed and neither was the band near 1600  $\text{cm}^{-1}$ . However, the bands due to bicarbonates were definitely observed in spectra of  $\gamma$ -APS films that were formed on 1100-series aluminum and then dried at 150°C for one hour but the band near 1660  $\text{cm}^{-1}$  was relatively weak (see Figure 6).

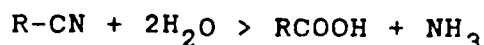
The spectrum shown in Figure 7A was obtained after films formed on copper were dried at 150°C for one hour. A broad, medium intensity band having components near 1660 and 1571  $\text{cm}^{-1}$  and a weak band near 2189  $\text{cm}^{-1}$  were observed. When films formed on copper were dried at 175°C, the bands near 2189 and 1571  $\text{cm}^{-1}$  became stronger, implying that they

are related to oxidation of the primer films (see Figure 7B). The band near  $2189\text{ cm}^{-1}$  may be related to a nitrile formed from the oxidation of the imines (15) as shown below:



However, the band near  $2189\text{ cm}^{-1}$  is somewhat lower than is usually observed for alkyl nitriles (16) and is very close in frequency to the CN absorption in copper cyanide. Some nitrile groups may have been cleaved from the oxidized propylamine groups but more work will be required before the origin of the band near  $2189\text{ cm}^{-1}$  can be substantiated.

The band near  $1571\text{ cm}^{-1}$  in the spectra shown in Figure 7 is not related to bicarbonates since other bands characteristic of bicarbonates, such as those near  $1330$  and  $1470\text{ cm}^{-1}$ , are not observed. Instead, it is considered that the band observed near  $1571\text{ cm}^{-1}$  after  $\gamma$ -APS films have been dried over copper at  $150$  or  $175^\circ\text{C}$  for one hour is related to carboxylate species, perhaps resulting from additional oxidation of the nitrile groups (15) as shown below:



There was some question as to whether the oxygen required for the oxidation of amines to the imine and to the nitrile was from the atmosphere or from reduction of the oxide. However, when as-formed films on steel and copper were heated in an oven at  $150^\circ\text{C}$  for one hour under nitrogen, most of the bicarbonates were dissociated but little oxidation was observed, showing that the required oxygen was from the atmosphere (see Figure 8).

These results show that oxidation of the amine to the imine is favored when  $\gamma$ -APS films formed on 2024 aluminum are dried at 110°C but not when films formed on iron, titanium, or 1100-series aluminum are. The difference between the behavior of  $\gamma$ -APS films on 2024 aluminum and the other substrates is attributed to catalysis of the oxidation reaction by copper, which is present in 2024 aluminum as an alloying element at a concentration of about 4.5%.

When the as-formed films were dried at 150°C for one hour, extensive oxidation of the amine to the imine was observed on iron, titanium, and 2024 aluminum substrates but very little imine formation was observed for  $\gamma$ -APS films formed on 1100-series aluminum. These results may indicate that iron and titanium catalyze the oxidation of the amino groups at 150°C as well as does copper. However, they may also show that the oxidation proceeds quickly at 150°C without catalysis and that the lack of oxidation for the  $\gamma$ -APS films formed on 1100-series aluminum during drying at 150°C is related to the ability of the oxidized surface of that substrate to inhibit the oxidation.

We consider that the latter explanation is correct. Iron and titanium may catalyze the oxidation of amino groups in  $\gamma$ -APS at 150°C to some extent. However, Culler has shown that almost complete conversion of the amino groups to imines occurs when  $\gamma$ -APS films on KBr are heated at 150°C for fifteen minutes (14) and it is unlikely that KBr has any catalytic effect. Moreover, evidence that the oxidized

surfaces of some metals, notably aluminum, inhibit free radical reactions has been presented previously. For example, Plueddemann (16) investigated the polymerization of styrene with benzoyl peroxide and showed that the polymer formed in the presence of fillers such as aluminum trihydrate had a much larger low molecular weight fraction than that formed in the absence of fillers. Plueddemann (17) also correlated the lowering of exotherms in polyester resins with the relative electron donor activities of filler particles and concluded that filler surfaces inhibit free radical polymerization by terminating growing chains. Oxidation of the amino groups in  $\gamma$ -APS is also a free radical reaction and the oxidized surface of 1100-series aluminum may inhibit the reaction to a greater extent than the oxidized surfaces of the other metal substrates considered here.

Several investigations have been carried out to determine if the oxidation of the amino groups to imine groups was likely to occur during curing of adhesive joints and to determine if such oxidation would inhibit the reaction between a silane primer and an adhesive, say an epoxy, cured against a primed substrate. In one series of experiments,  $\gamma$ -APS primers were applied to steel and 2024 aluminum mirrors as described above. The mirrors were immersed in shallow containers filled with epoxy resin and the containers were placed in an oven that was preheated to either 75 or 150°C. After one hour, the mirrors were

removed from the containers, rinsed several times with MEK to remove unreacted epoxy, and then examined using infrared spectroscopy.

When the reaction between the epoxy and the silane film formed on steel was carried out at 75°C, the bicarbonates were not dissociated and there was little reaction between the epoxy and the silane. Infrared spectra obtained from the mirrors after rinsing in MEK clearly showed the bands near 1330, 1470, 1570, and 1640  $\text{cm}^{-1}$  that were related to the bicarbonates but only a weak band characteristic of epoxies was observed near 1510  $\text{cm}^{-1}$ , showing that little epoxy was retained on the mirrors (see Figure 9). Very similar results were obtained for 2024 aluminum substrates.

When the reaction between the epoxy and  $\gamma$ -APS films formed on steel was carried out at 150°C, the results were much different. Little evidence of the bands near 1330, 1470, 1570, and 1640  $\text{cm}^{-1}$  was observed in the infrared spectra from the mirrors after rinsing, showing that the bicarbonates had dissociated and only a very weak band due to the imine was observed near 1660  $\text{cm}^{-1}$ . At the same time, several bands characteristic of the epoxy, including those near 1605, 1510, and 1260  $\text{cm}^{-1}$  were seen, demonstrating that there was considerable reaction between the silane and the epoxy and that a significant amount of epoxy was retained on the mirrors after rinsing (see Figure 10).

However, when the infrared spectra were obtained from the primer films on 2024 aluminum after reaction with the

epoxy at 150°C for one hour and rinsing, much different results were found (see Figure 11). The band near 1660 cm<sup>-1</sup> was observed but those near 1330, 1470, 1570, and 1640 cm<sup>-1</sup> were not, showing that the bicarbonates were dissociated. Considering the intensity of the band near 1660 cm<sup>-1</sup>, it was evident that significant oxidation of the amine to the imine had occurred. The band near 1510 cm<sup>-1</sup> was relatively weak, implying that there was little reaction between the silane and the epoxy and that there was little retained epoxy on the 2024 aluminum mirrors after rinsing. At 150°C,  $\gamma$ -APS films on iron reacted readily with epoxy resins but films on 2024 aluminum underwent oxidation of the amino groups.

Some preliminary results have been obtained from another series of experiments in which double cantilever beam (DCB) specimens were prepared by casting beams of adhesive (epoxy mixed with tertiary amine curing agent) onto polished and primed steel beams as shown in Figure 1 and then curing the adhesive either by heating at 50°C for one hour and then at 75°C for an additional hour or else by heating at 110°C for two hours. After curing, the specimens were cooled to room temperature, a crack was propagated along the interface to separate the adhesive and the substrate, and ATR, RAIR, and XPS were used to examine the failure surfaces.

Failure was near the silane/epoxy interface when the adhesive was cured at the lower temperatures. As shown in Figure 12, RAIR spectra obtained from the adherend failure

surface of steel/epoxy DCB specimens were very similar to spectra of as-formed  $\gamma$ -APS primer films (see Figure 2A), indicating that curing temperatures of 50 or 75°C were not sufficient to dissociate the bicarbonates and that there was little reaction between the silane primer and the epoxy adhesive. Those conclusions were supported by results obtained from XPS. Survey spectra obtained from the adherend failure surface (see Figure 13A) were very similar to those obtained from neat primer films and were characterized by bands near 102 and 153 eV that were attributed to Si. Spectra from the adhesive failure surface were very similar to those of the neat adhesive (see Figure 13B) and showed little evidence for silicon.

However, when the higher curing temperature was used, the locus of failure was considerably different. As shown in Figure 14A, survey spectra from the adherend failure surface were characterized by bands near 711 and 724 eV that were related to iron but there were only very weak bands near 102 and 153 eV. XPS survey spectra obtained from the adhesive failure surface were characterized by bands near 100 and 154 eV that were related to silicon from the primer (see Figure 14B). It is evident that the amine bicarbonates were dissociated when the higher curing temperature was used and that a cohesively strong interphase was formed between the adhesive and primer. Failure in that case was near the primer/oxide interface.

Results obtained thus far using DCB specimens are consistent with those obtained when primed metals were simply reacted with epoxy resins at various temperatures. Work on DCB specimens is being extended to other substrates, such as 2024 aluminum and copper, and to higher curing temperatures so that the effects of primer oxidation on interphases in actual adhesive joints can be determined.

#### IV. Conclusions

Considering these results, it is evident that metal surfaces can have a significant effect on the structure, and thus the properties, of adhesive systems cured against them and that interphases with different properties can be obtained by curing the same adhesive system against different metal substrates. Such differences in interphases may result from acceleration or retardation of the curing reaction or degradation reactions within the adhesive system by the oxidized surface of the metal substrate or by certain alloying metals, such as copper, within the substrate. Regardless of their origin, differences in the properties of interphases must be considered when the results of mechanical or durability tests of adhesive joints are interpreted. The surface composition of the substrate must be known and the possibility that catalytically active metals, and in particular copper, are present on the surface must be considered before the properties of adhesive joints can be related to the molecular structure of the adhesive system.

In the specific case of  $\gamma$ -APS primers, the bicarbonates must be dissociated and the oxidation of the amino groups suppressed in order to obtain significant interaction between the silane and an adhesive or matrix resin. That can be accomplished by carrying out curing reactions under an inert atmosphere such as nitrogen. If that is not practical, then the curing reactions should be carried out at a temperature that is high enough to dissociate the bicarbonates but low enough that oxidation of the amino groups is not dominant.

The oxidized surfaces of certain metals, such as aluminum and perhaps zinc (17), can inhibit free radical reactions. That has obvious implications for the use of free radical curing systems on such substrates.

## VI. References

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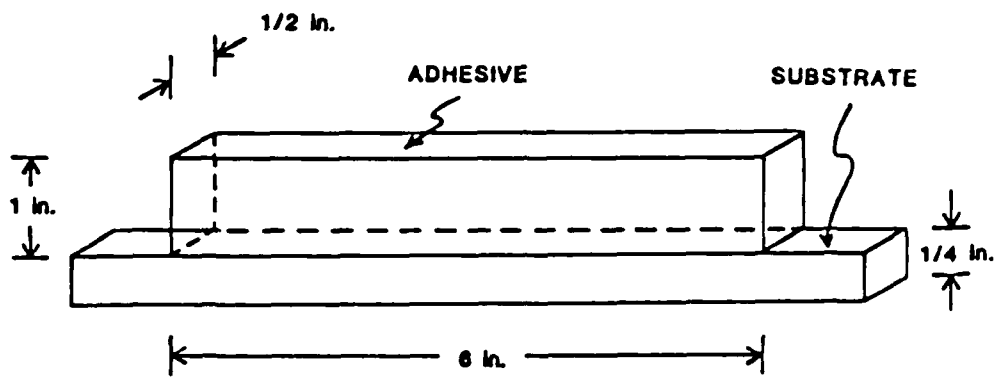
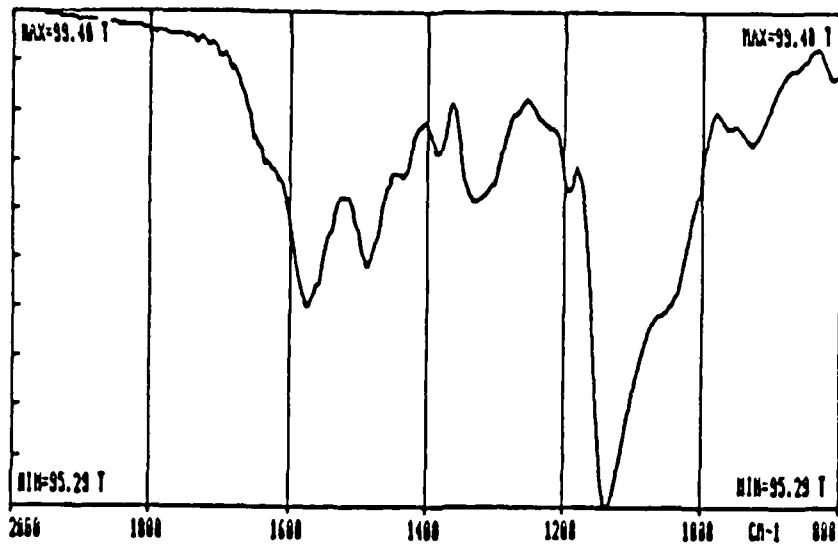
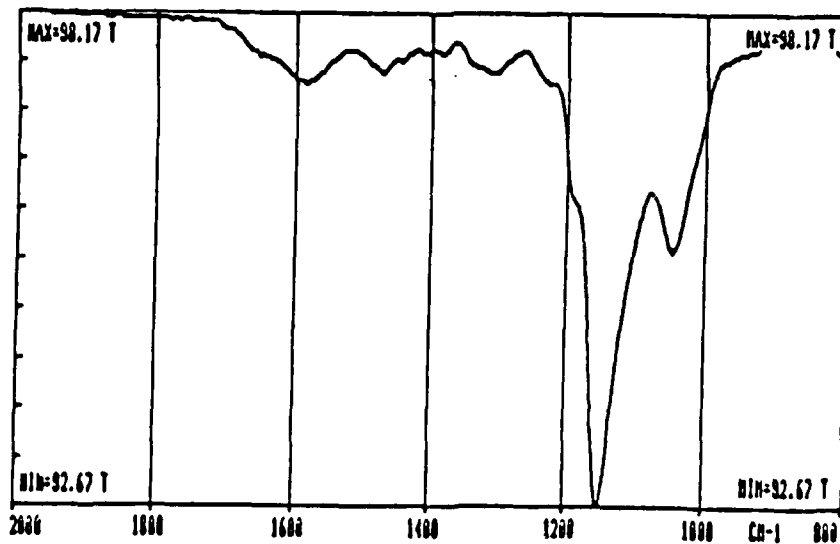


Figure 1. Double cantilever beam test specimen.

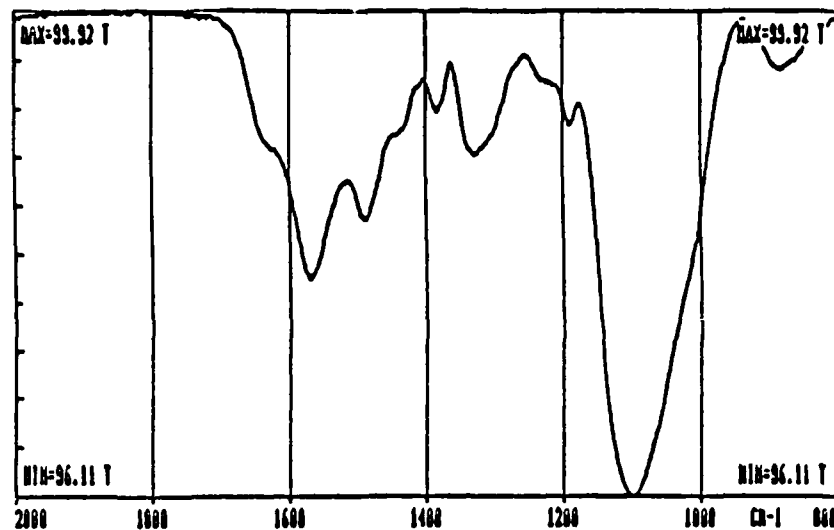


(A)

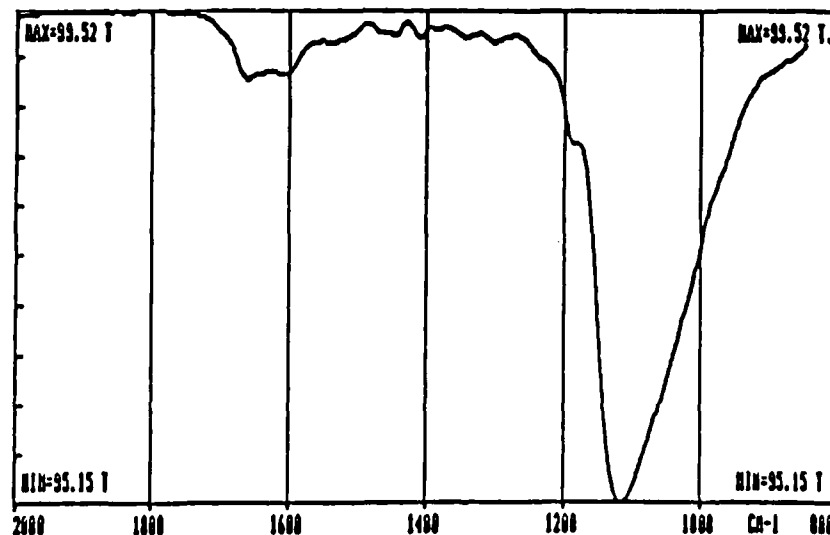


(B)

Figure 2. RAIR infrared spectra obtained from polished steel dipped into a 2% aqueous solution of  $\gamma$ -APS for 1 minute and then blown dry with  $N_2$ : (A) - after curing for 30 minutes at room temperature and (B) - after post curing for 1 hour at  $110^\circ C$ .



(A)



(B)

Figure 3. RAIR infrared spectra obtained from polished 2024 aluminum dipped into a 2% aqueous solution of  $\gamma$ -APS for 1 minute and then blown dry with  $N_2$ : (A) - after curing for 30 minutes at room temperature and (B) - after post curing for 1 hour at  $110^\circ C$ .

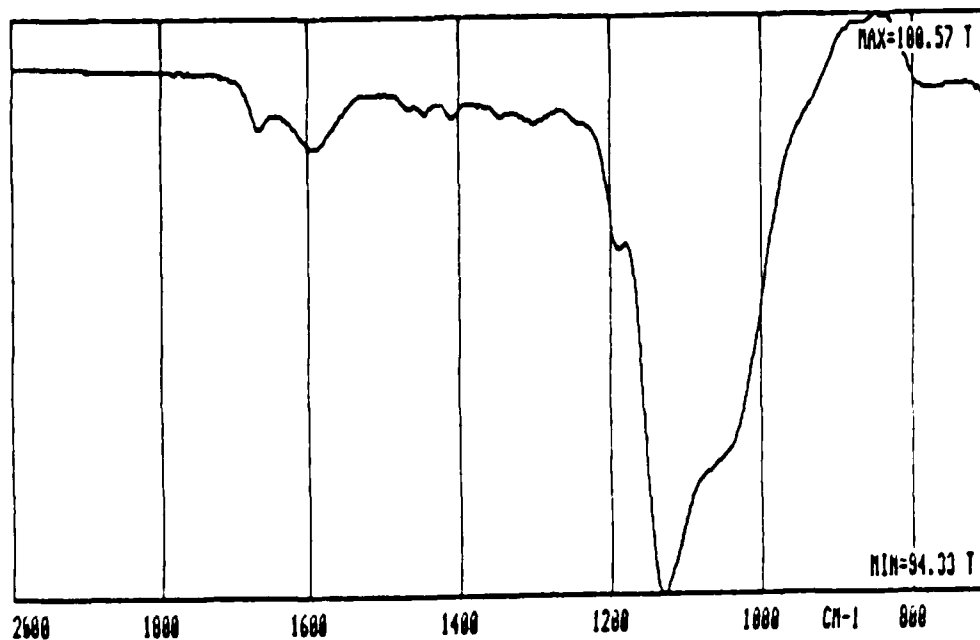


Figure 4. RAIR infrared spectra obtained from polished OFHC copper mirror dipped into a 2% aqueous solution of  $\gamma$ -APS for 1 minute, blown dry with  $N_2$ , cured at room temperature for 30 minutes, and post-cured at  $110^\circ C$  for 1 hour.

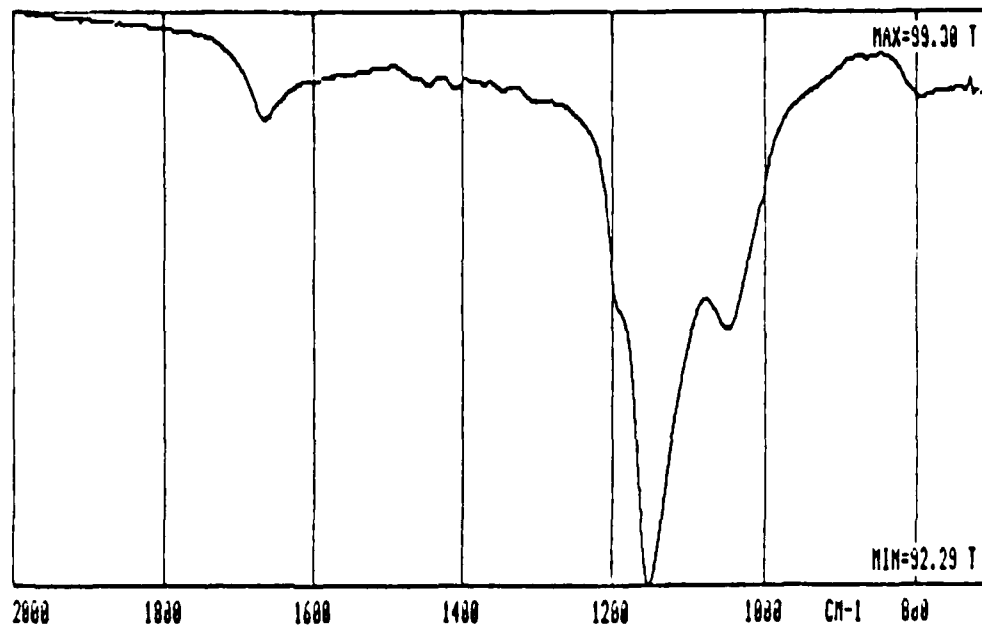


Figure 5. RAIR infrared spectra from a polished steel mirror dipped into a 2% aqueous solution of  $\gamma$ -APS for 1 minute, blown dry with  $N_2$ , cured at room temperature for 30 minutes, and post-cured at  $150^\circ C$  for 1 hour.

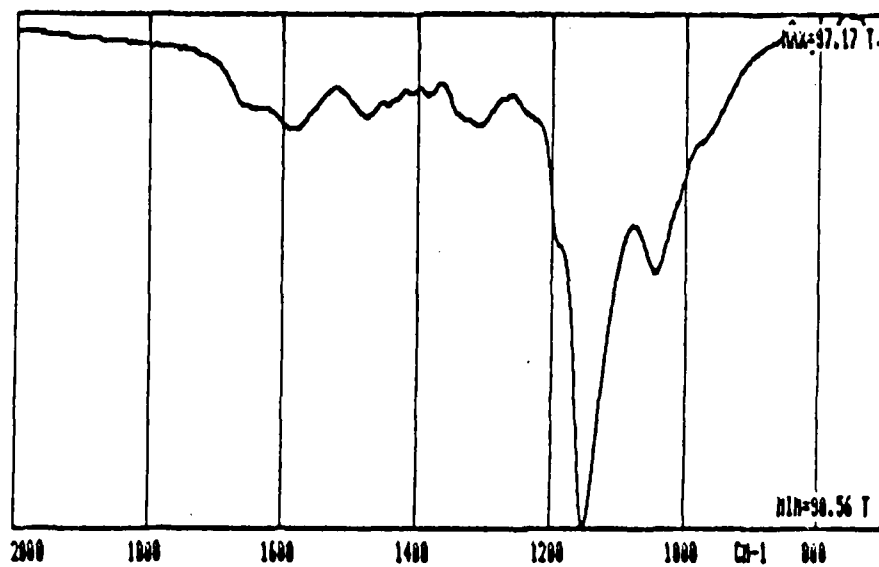


Figure 6. RAIR infrared spectra obtained from polished 1100 series aluminum mirror dipped into a 2% aqueous solution of  $\gamma$ -APS for 1 minute, blown dry with  $N_2$ , cured at room temperature for 30 minutes, and post-cured at 150°C for 1 hour.

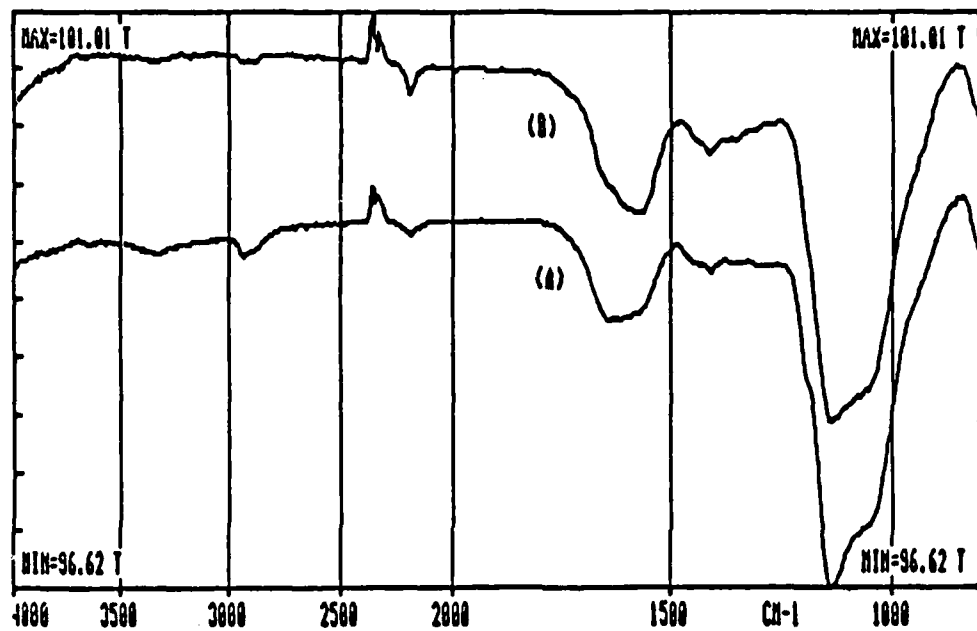
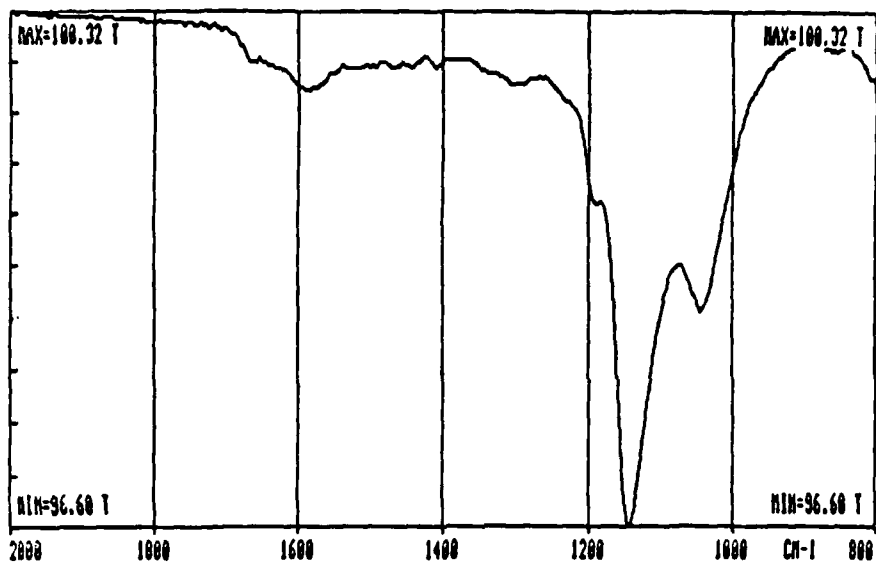
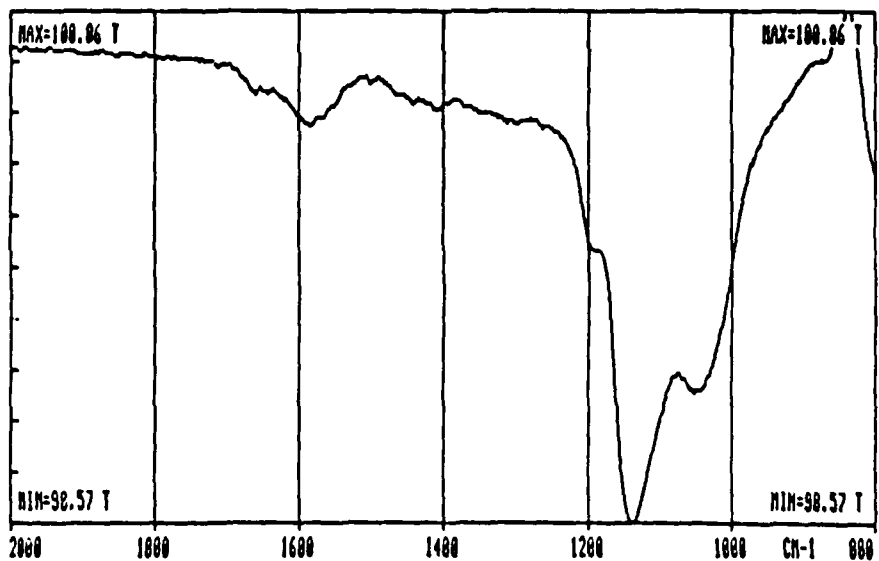


Figure 7. Infrared spectra of  $\gamma$ -APS films on OFHC copper after drying at (A) - 150°C and (B) - 175°C for one hour.



(A)



(B)

Figure 8. Infrared spectra obtained from (A) - steel and (B) - copper mirrors that were dipped in 1%  $\gamma$ -APS solutions at pH 10.4 for 1 minute, dried in air at room temperature for 30 minutes, and then dried under  $N_2$  at  $150^\circ C$  for 1 hour.

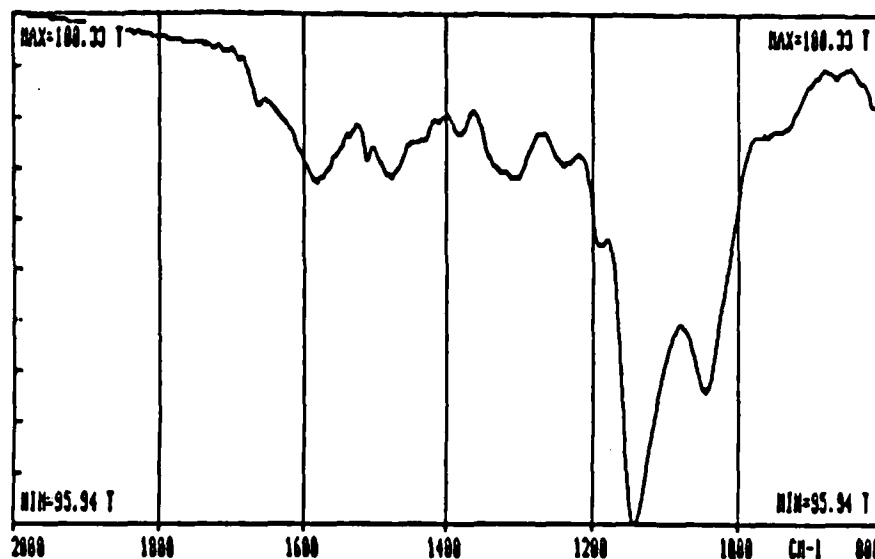


Figure 9. Infrared spectrum obtained from a polished steel mirror that was immersed in an aqueous solution of  $\gamma$ -APS at pH 10.4 for 1 minute, dried at room temperature for 30 minutes, reacted with epoxy resin at 75°C for 1 hour, and rinsed with MEK.

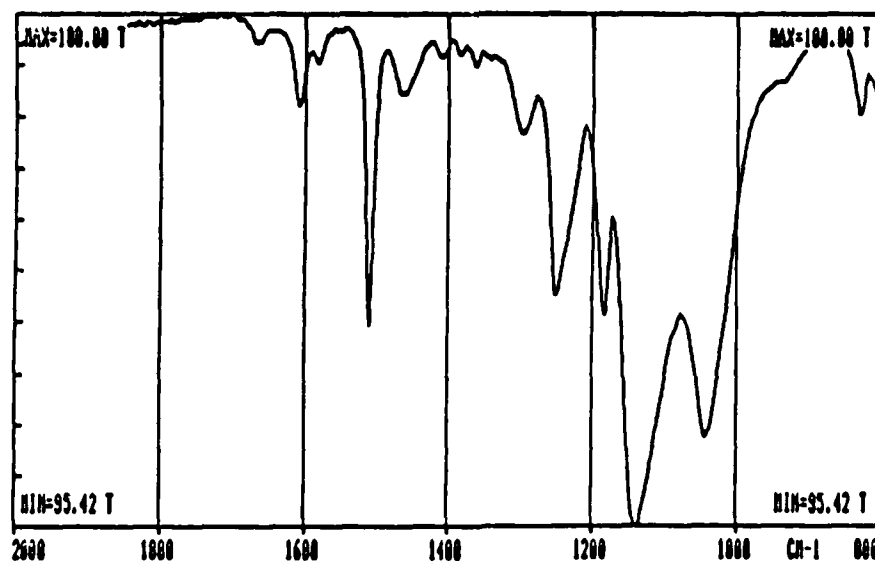


Figure 10. Infrared spectrum obtained from a polished steel mirror that was immersed in an aqueous solution of  $\gamma$ -APS at pH 10.4 for 1 minute, dried at room temperature for 30 minutes, reacted with epoxy resin at 150°C for 1 hour, and rinsed with MEK.

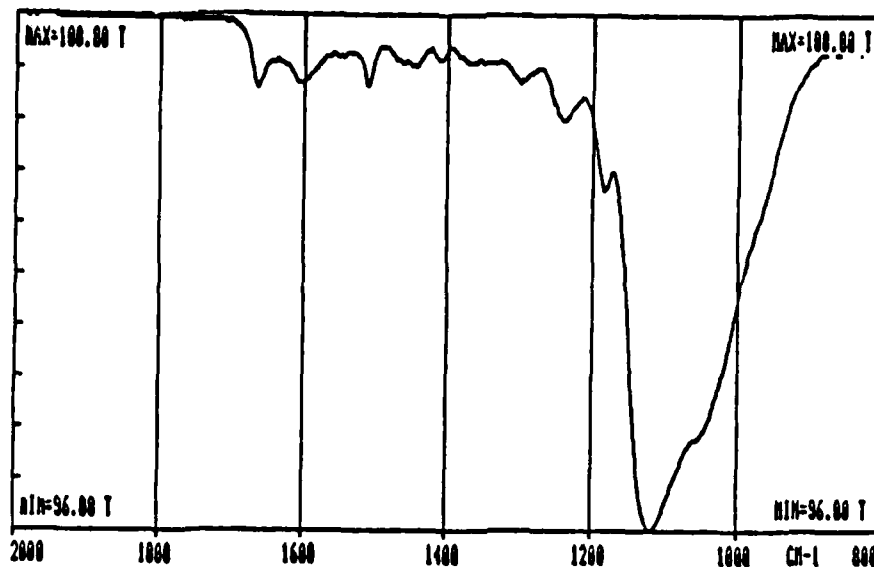


Figure 11. Infrared spectrum obtained from a polished 2024 aluminum mirror that was immersed in an aqueous solution of  $\gamma$ -APS at pH 10.4 for 1 minute, dried at room temperature for 30 minutes, and then reacted with epoxy resin at 150°C for 1 hour and rinsed with MEK.

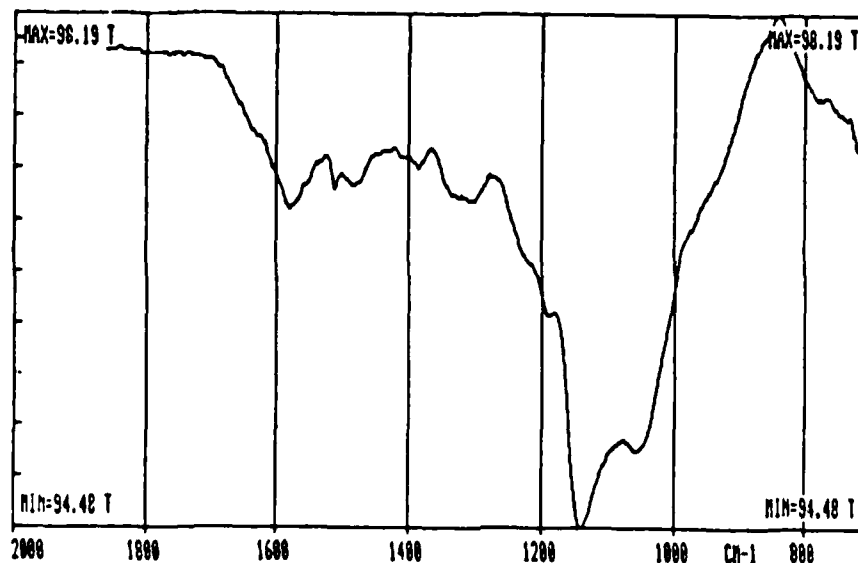
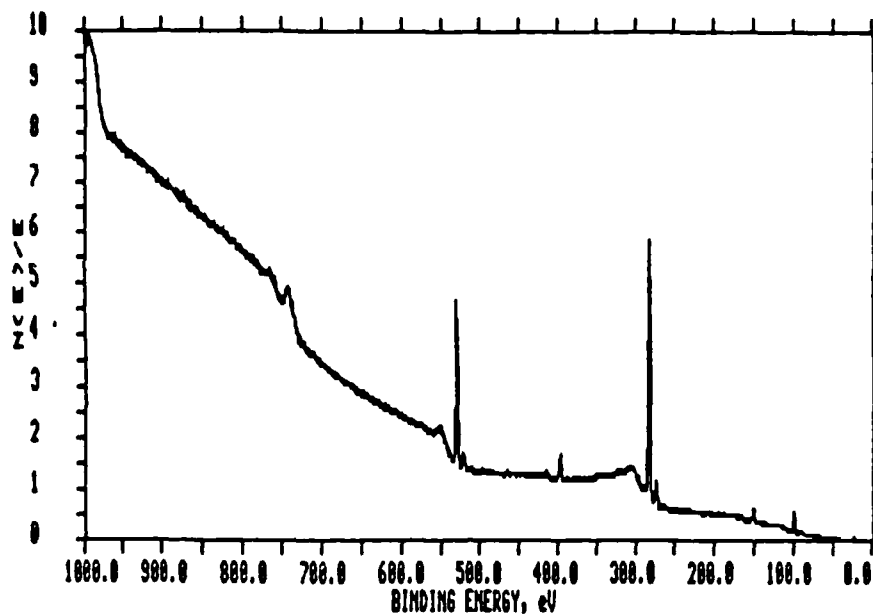
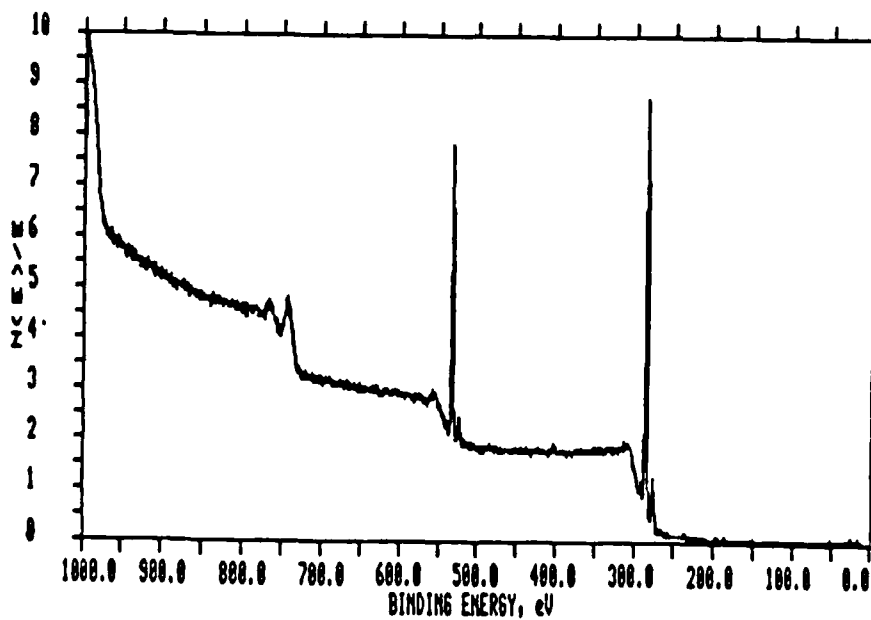


Figure 12. RAIR spectrum obtained from the adherend failure surface of a steel/epoxy double cantilever beam that was cured for 1 hour at 50°C and 1 hour at 75°C.

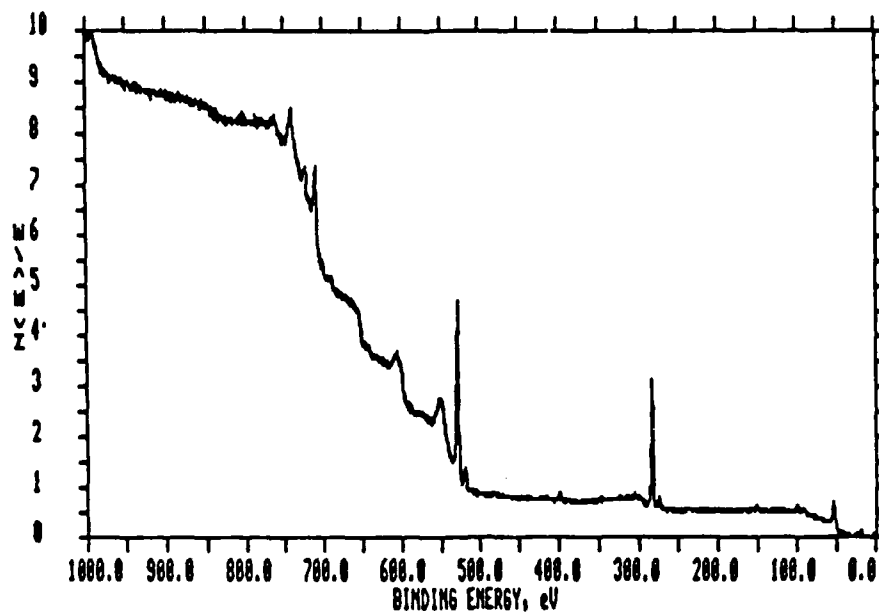


(A)

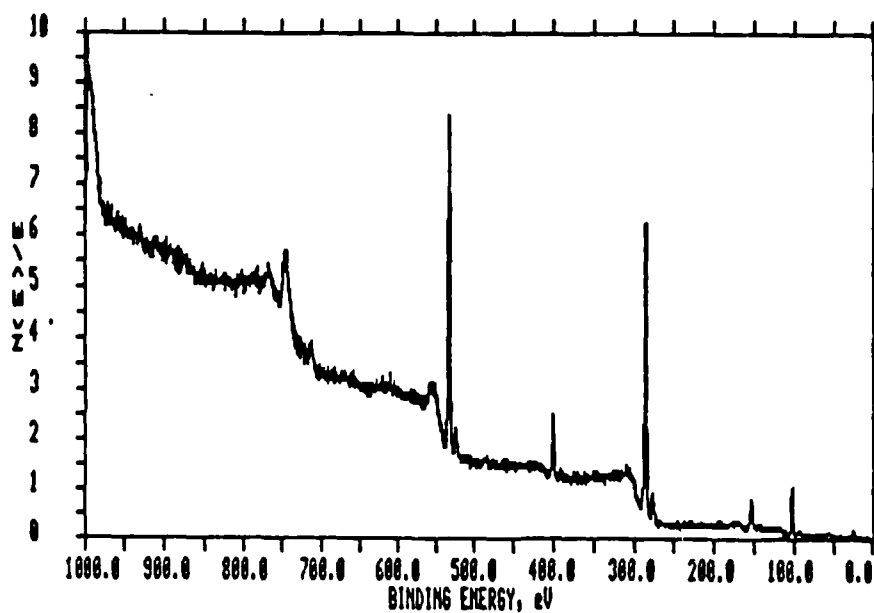


(B)

Figure 13. XPS survey spectra from (A) - adherend and (B) - adhesive failure surfaces of a steel/epoxy DCB that was cured for 1 hour at 50°C and 1 hour at 75°C.



(A)



(B)

Figure 14. XPS survey spectra from (A) - adherend and (B) - adhesive failure surfaces of a steel/epoxy DCB that was cured for 2 hours at 110°C.

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