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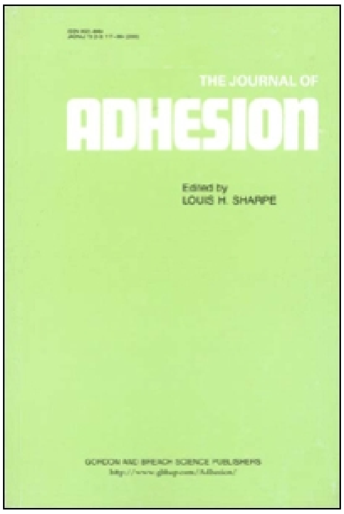

The Journal of Adhesion

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

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To cite this Article Ondrus, D. J. , Boerio, F. J. and Grannen, K. J.(1989) 'Molecular Structure of Polymer/Metal Interphases', The Journal of Adhesion, 29: 1, 27 — 42
To link to this Article: DOI: 10.1080/00218468908026475
URL: http://dx.doi.org/10.1080/00218468908026475

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J. Adhesion, 1989, Vol. 29, pp. 27–42
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Molecular Structure of Polymer/Metal Interphases†

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(Received August 19, 1988; in final form November 25, 1988)

The molecular structure of interphases in aluminum/epoxy and steel/epoxy adhesive joints was characterized using infrared spectroscopy. In one series of experiments, adhesive joints were prepared by curing beams of epoxy against aluminum or steel substrates. When the joints were cooled to room temperature, the residual stresses were sufficient for crack propagation along the interface. The adhesive and substrate failure surfaces were then analyzed with reflection-absorption infrared spectroscopy (RAIR), attenuated total reflection infrared spectroscopy (ATR) and X-ray photoelectron spectroscopy (XPS). When an epoxy/anhydride adhesive was cured against aluminum substrates primed with an aminosilane coupling agent, amide and imide groups were formed in the interphase. Chemical reaction between the primary amine of the primer and the anhydride of the curing agent precluded chemical bridge formation between the primer and adhesive. Metal cations from the 2024 aluminum substrate reacted with the anhydride to form carboxylate salts on the surface. When an epoxy/tertiary amine adhesive was cured against steel substrates, evidence of oxidation of the primary amine to imine was observed in the interphase.

KEY WORDS Aminosilane primer; polymer-metal interphases; epoxy-anhydride adhesive joints; infrared spectroscopy; fracture surface; coupling agent; interface; steel; aluminum.

INTRODUCTION

In all adhesive joints, the interface region between the adhesive and the substrate is primarily responsible for the transference of stress from one adherend to the other. The initial strength and stability of the joint depend on the molecular structure of the interface after processing and environmental exposure, respectively. Characterization of the molecular structure near the interface is essential in order to model and, subsequently, to maximize the performance of an adhesive system in a given environment.

A common technique for improving the hydrothermal stability of adhesive joints is the application of a silane primer to the adherend surface. These primers

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† Presented at the 35th Sagamore Army Materials Research Conference, Manchester, New Hampshire, U.S.A., June 26–30, 1988.

have been synthesized to bridge chemically the organic adhesive to the oxide on the adherend surface.

Silane primers used as coupling agents have the general monomeric structure

$$R—Si—(OR')_3$$

where (R) is an organofunctional group which is compatible with a particular polymer and (R') is a functional group that can be hydrolyzed to form a silanol group.

One model suggests that when an inorganic substrate is treated with a silane coupling agent applied from a dilute aqueous solution, the molecules are adsorbed through the silanol groups. During drying, the silanol groups polymerize and may react with the surface hydroxyl groups forming a polysiloxane network on the substrate, and the functional groups (R) can form a primary bond with an adhesive applied to the silanated substrate.[1]

These primers have a finite thickness and can be considered as separate phases. If an interaction between the primer and the adherend surface or adhesive occurs, a new "interphase" region is formed. This interphase has a molecular structure different from either molecular structure of the two primary phases from which it was formed. An interphase region may have mechanical or hydrothermal properties which can be different from either of the initial phases. Despite the importance of the need to characterize interphases, a limited amount of information regarding molecular structure, chemical resistance or mechanical properties exists about this region.

Chiang *et al.*[2] studied the reactions between individual components of an anhydride-cured adhesive and an aminosilane primer between salt plates with transmission infrared spectroscopy. They found that the anhydride curing agent reacted with the aminosilane at temperatures around 150°C to form an imide which would not chemically bond across an interface. This cyclic imide reduced the functionality of the amino group of the primer to zero, thereby eliminating the possibility of a chemical bridge. In addition, the curing accelerator, a tertiary amine, decreased the rate of reaction between the anhydride and the aminosilane. The results were based mostly on reactions in the bulk phase, which correlated with spectra taken on silica/silane/epoxy systems.

Culler *et al.*[3] investigated the effect of drying temperature on the properties of an aminosilane primer film formed on KBr plates. Amine bicarbonates were formed as a reaction product of the amino group of the primer with carbon dioxide and water from the atmosphere. They showed that temperatures above 95°C were required to dissociate the amine bicarbonates that were formed during the application process. They also showed that drying the films at temperatures exceeding 120°C resulted in oxidation of the amino groups to imine groups.

Culler[3] also investigated the reaction of an aminosilane primer with an epoxy resin between salt plates. Primer films were preheated for several minutes on salt plates at 120°C, then the epoxy resin was added. The reaction was followed with transmission infrared spectroscopy for 2 hours. They observed the formation of imine groups which appeared to inhibit the reaction between the amino group of the primer and the epoxy group of the adhesive. No vibrational frequencies related to secondary amines, the reaction products of the primer and the adhesive, were observed in the infrared spectra. These results were also based on reactions in the bulk phase.

Garton[4,5] used attenuated total reflection infrared spectroscopy (ATR) to characterize the molecular structure of an anhydride/epoxy adhesive cured at 150°C for 3 hours against an oxidized germanium crystal primed with an aminosilane coupling agent. It was shown that the amino group of the primer reacted with the anhydride to produce amides. There was no evidence of imide formation as suggested by Chiang[2]. He concluded that the water produced in an amide-to-imide reaction would not be able to escape, thus resulting in an unfavorable equilibrium for imide production.

Ondrus *et al.*[6] studied the effect of metal substrates on the molecular structure of aminosilane primers. It was shown that copper and copper-bearing alloys catalyzed the oxidation of the amino group of the primer. Aminosilane primer films applied to steel and titanium substrates oxidized to form imine groups when exposed to a temperature of 150°C for 1 hour in air atmospheres but did not oxidize when exposed to temperatures of 110°C. However, the amino groups oxidized to form imines when the primer was heated on copper-bearing substrates at 110°C. Commercially pure aluminum substrates inhibited the oxidation reaction. After 1 hour at 150°C very little imine formation was observed.

In a separate experiment,[6] epoxy films were shown to react with aminosilane primers on steel substrates when cured at 150°C, but the epoxy film did not react with the silane primer that was applied to a copper-bearing aluminum substrate. Steel and 2024 aluminum substrates primed with an aminosilane coupling agent were immersed in epoxy resin for 1 hour at 150°C. After cure, the substrates were rinsed with a solvent. Retained epoxy was observed on the steel substrates, but only the oxidized primer remained on the 2024 aluminum substrate as determined by infrared spectroscopy. No epoxy retention was observed on either primed metal substrate when the cure temperature was lowered to 75°C for 1 hour. The RAIR spectrum showed a low molecular weight polysiloxane network with amine bicarbonate formation which inhibited the primer/epoxy interaction.

We have also shown that the pH of the solution from which the primer was applied can affect the polymerization and reactivity of the film.[7] Aminosilane primers prepared from basic solutions of pH 10.4 contained amine bicarbonates and formed low molecular weight siloxane oligomers. Primer films prepared from solution, acidified with hydrochloric acid to pH 8.0, contained amine hydrochlorides and formed higher molecular weight polysiloxane networks.

Aminosilane primer films applied to steel substrates from basic solutions (pH 10.4) reacted with epoxy resins when heated at 110°C. However, films applied from acidified solutions (pH 8.0) did not chemically react with the epoxy resin at the same temperature. After the samples were rinsed with solvent, the infrared spectrum of the film applied from the basic solution showed evidence of retained epoxy, but the spectrum of the film applied from the acidified solution only showed the cured siloxane network and amine hydrochlorides.

In this investigation, the molecular structure of aminosilane primer interphases prepared on steel and copper-bearing aluminum substrates was characterized with infrared and X-ray photoelectron spectroscopy. Two adhesive systems, a tertiary amine-cured epoxy and an anhydride-cured epoxy, were considered.

EXPERIMENTAL

Adherend substrates for double cantilever beams (DCB) were machined from 2024-T3 aluminum (Alcoa) and 1018 steel barstock to a final size of 0.25" × 0.50" × 7.50" (Figure 1a). After machining, the samples were degreased with

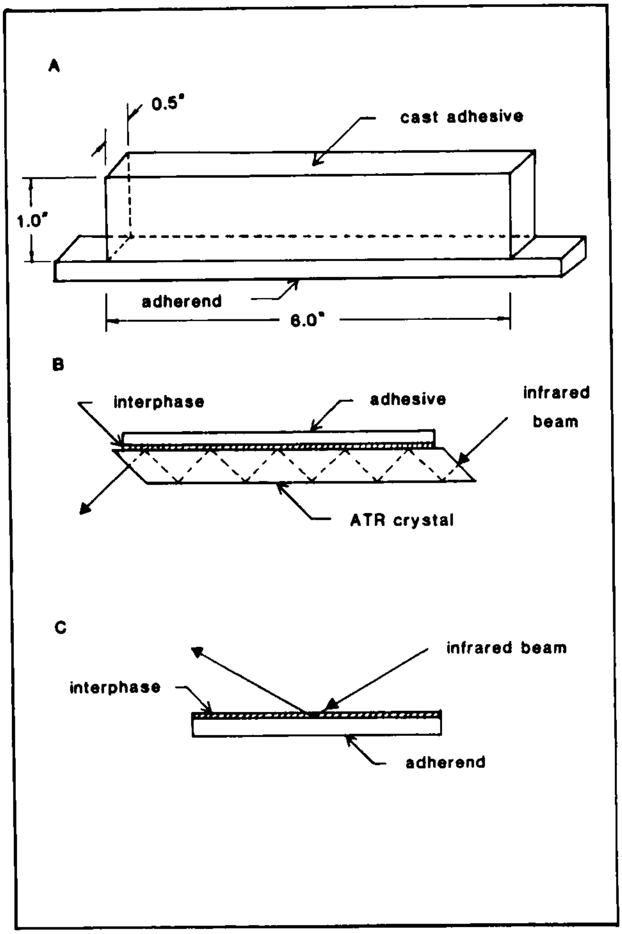


FIGURE 1 A) Geometric illustration of a double cantilever beam (DCB) sample. B) Schematic illustration of an infrared attenuated total reflection experiment on the adhesive side of a fracture surface. C) Schematic illustration of reflection-absorption infrared (RAIR) experiment on the adherend side of the fracture surface.

acetone and then metallographically polished to obtain a clean, specularly reflective surface.

The polishing sequence began on a series of dry silicon carbide abrasive papers (Carborundum) ranging from 240 to 600 grit. After the surface was ground, it was wet polished with a 14 μm alumina slurry followed by either a 0.3 μm alumina slurry for the steel samples or 3.0 μm magnesium oxide slurry for aluminum samples on Microcloths (Beuhler, Inc). Finally, the samples were rinsed in distilled deionized water and blown dry with a stream of nitrogen gas. The resulting surfaces were mirror-like and hydrophilic.

The first adhesive system analyzed consisted of an epoxy resin, (Epon 828, Shell Chemical Co.) cured with a tertiary amine (DMP-30, Miller Stephenson) in a 100:6 ratio by weight. The epoxy resin was preheated to 60°C prior to addition of the tertiary amine in order to achieve a more homogeneous mixture. The second adhesive system analyzed consisted of Epon 828 cured with Nadic methyl anhydride (NMA, Fisher) and an accelerator, benzyldimethylamine (BDMA, Fisher), in a 100:100:2 ratio by weight. The epoxy resin was preheated to 60°C prior to addition of the anhydride curing agent and tertiary amine accelerator.

Half of the adherend substrates were primed with a coupling agent, γ-aminopropyltriethoxysilane (γ-APS, Union Carbide). Metal substrates were immersed in a 1% aqueous solution at pH 10.4 for 1 minute and then withdrawn. Excess primer solution was blown off with a stream of nitrogen gas which left a film approximately 100A thick as measured by ellipsometry. The primer film was allowed to polymerize at room temperature for 30 minutes in the laboratory atmosphere before the adhesive was cast.

The DCB samples were produced by casting the warm adhesive into an aluminum mold, lined with a fluorocarbon, which was clamped around the polished adherend. The entire assembly was placed in an oven and cured at various temperatures and times. A chromel-alumel thermocouple was placed at the adherend/adhesive interface to monitor exotherms. After curing, the samples were removed from the mold and allowed to cool overnight. Due to differences between the thermal expansion coefficients of the adhesive and the adherend, residual stresses produced at the interface were sufficient to propagate cracks which caused failure very close to the interface. A section 2 inches long was cut from the adhesive failure surface on selected samples and analyzed with attenuated total reflection infrared spectroscopy (ATR) (Figure 1b). The adherend side of the fracture surface was sectioned into a 2-inch length and examined using reflection-absorption infrared spectroscopy (RAIR) (Figure 1c).

Some of the failure surfaces were analyzed with XPS in order to determine the locus of failure. Survey spectra were taken with a Perkin–Elmer ESCA 5300 spectrometer at 300 W using magnesium K_α radiation. The resolution was 0.5 eV at a pass energy of 44.0 eV.

Simulated polymer/metal interphases were created by reacting the epoxy/NMA adhesive without the BDMA accelerator with silane-treated metal substrates. The primed metal mirrors were immersed in dishes filled with the unactivated adhesive then placed in a pre-heated oven at various temperatures and times. Following cure, the mirrors were removed from the resin mixture, allowed to cool, then rinsed repeatedly with methylethylketone (MEK) to remove unreacted resin. The solvent-rinsed mirrors were examined using RAIR.

RAIR spectra were obtained using a Perkin–Elmer Model 1800 Fourier-transform infrared spectrophotometer and an external reflection accessory (Harrick Scientific). One reflection at an angle of 78° was used in all cases. Fifty scans at $4.0\,\mathrm{cm}^{-1}$ resolution were averaged to obtain the spectra. Unless otherwise stated, the spectra reported are actually difference spectra obtained by subtracting spectra of clean polished substrates from spectra of sample surfaces. ATR was used to analyze some of the adhesive fracture surfaces by clamping the 2 inch sections on an ATR crystal (see Figure 1b). A germanium parallelepiped crystal (50 mm × 20 mm × 3 mm) in an internal reflection accessory (Harrick Scientific) was used at an incidence angle of 45° to obtain ATR spectra.

RESULTS AND DISCUSSION

The RAIR spectrum of the fracture surface from a DCB made with the epoxy/tertiary amine adhesive cast on a primed 1018 steel substrate, and cured for 2 hours at 75°C, was dominated by a strong band near $1120\,\mathrm{cm}^{-1}$ and weaker bands near 1040, 1330, 1470, 1570 and $1640\,\mathrm{cm}^{-1}$ (Figure 2). The bands near 1040 and $1120\,\mathrm{cm}^{-1}$ have been assigned to SiOSi stretching frequencies. The bands near 1330, 1470, 1570, and $1640\,\mathrm{cm}^{-1}$ are related to the formation of amine bicarbonates.[8] These bicarbonates were formed when the primer was applied and did not dissociate during the cure. Therefore little, if any, reaction occurred between the primer and the adhesive. The interphase region consisted of a

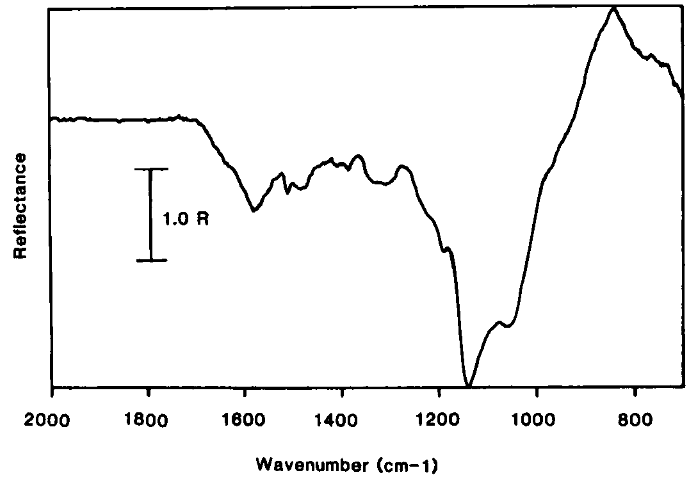


FIGURE 2 RAIR spectrum of a fracture surface from the adherend side of a 1018 steel/epoxy/tertiary amine DCB sample primed with γ-APS and cured for 2 hours at 75°C.

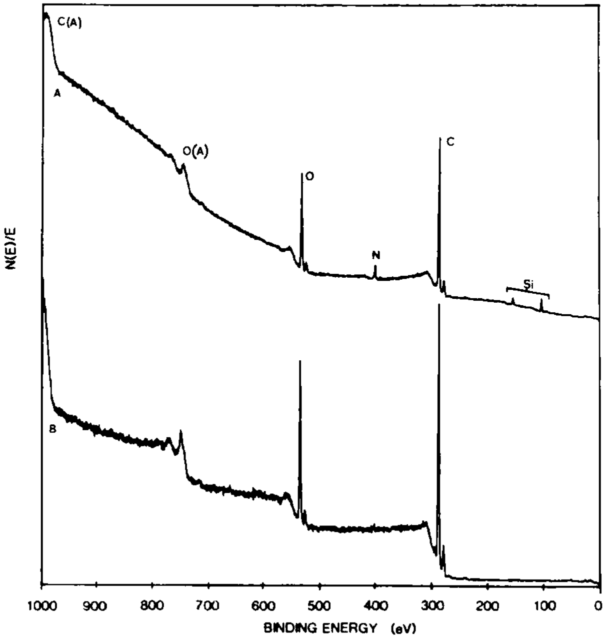


FIGURE 3 XPS survey spectra from A) adherend and B) adhesive failure surface of a 1018 steel/γ-APS/epoxy DCB that was was cured for 2 hours at 75°C.

polysiloxane network in which propylamine functional groups formed complexes with bicarbonates instead of forming secondary amine chemical bridges with the epoxy groups of the adhesive.

The XPS survey spectrum (Figure 3a) from the adherend failure surface shows photoelectron peaks near 285 eV (C1s), 530 eV (O1s), 400 eV (N1s), 150 eV (Si2s) and 100 eV (Si2p) indicative of the silane primer phase. The survey spectrum from the adhesive failure surface (Figure 3b) shows only two photoelectron peaks from carbon and oxygen which illustrates interfacial failure between the primer and adhesive.

When the curing temperature was raised to 150°C for 1 hour, the RAIR spectrum of the fracture surface (Figure 4a) was significantly different. Bands associated with the epoxy were seen near 1605, 1510, 1260, and 830 cm^{-1}. However, the intensity of these bands obscured the bands of the underlying primer interphase. In order to obtain a spectrum of the interphase, digital subtraction was used to eliminate absorption bands of the adhesive from the composite spectrum. The 1510 cm^{-1} phenyl absorption band was used to normalize the two spectra before subtraction.

Figure 4b is a spectrum of a film of epoxy resin with the tertiary amine curing agent cast from a 1% MEK solution onto a 1018 steel substrate and cured for 1 hour at 150°C. Normally, a fracture surface from an unprimed DCB sample would have been used to eliminate the absorption bands of the adhesive and substrate phases. However, complete interfacial failure occurred in the unprimed

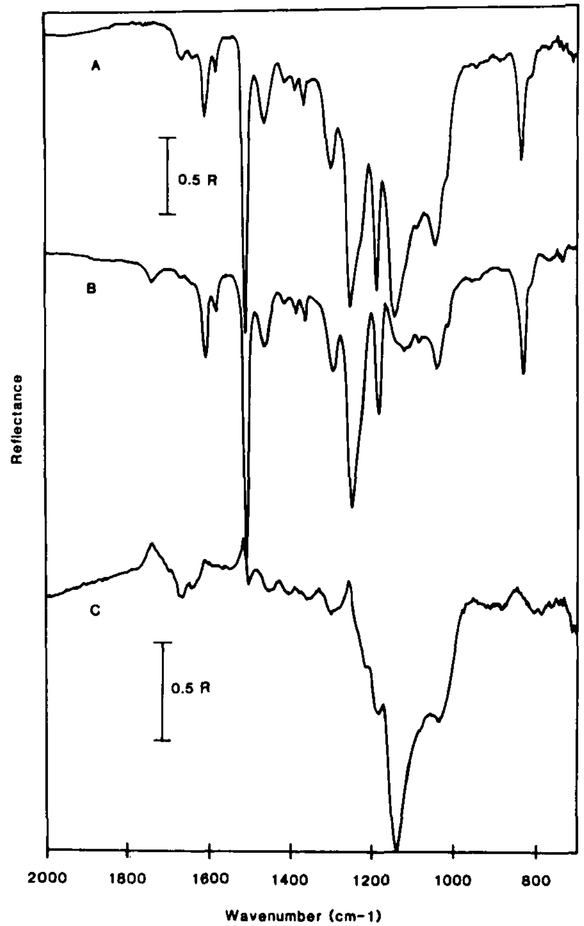


FIGURE 4 RAIR spectra of A) fracture surface from the adherend side of a 1018 steel/epoxy/tertiary amine DCB sample primed with γ-APS; B) unprimed 1018 steel covered with an epoxy/tertiary amine adhesive, both cured 1 hour 150°C: C) Difference spectrum.

DCB samples which left the adherend surfaces without an adhesive layer. Therefore, a fully cured adhesive phase had to be made as previously described.

Figure 4c is a difference spectrum of the fracture surface without the cured epoxy phase. The spectrum clearly shows the siloxane bands at 1040 and 1150 cm^{-1}. The latter siloxane absorption band is shifted up 30 cm^{-1} relative to the 1120 cm^{-1} peak in Figure 2, which corresponds to an increase in polymerization of the primer. The weaker band near 1660 cm^{-1} is due to a C=N stretching mode as a result of oxidation of the amino group in the primer. The negative peak near 1730 cm^{-1} is due to a C=O stretching vibration as a result of oxidation of the thin adhesive film cured against the steel substrate. The peak near 1730 cm^{-1} was not present in the spectrum of the uncured cast film. Therefore, it can be concluded that the peak is not due to residual ketonic solvent.

It is apparent that this interphase consisted of a highly-crosslinked siloxane network with some oxidized amine groups. No structural evidence of a primer/adhesive interaction could be concluded since most aliphatic secondary amines have no visible N–H bending vibrations above the 1470 cm^{-1} aliphatic bands. Secondary amine (CH—NH—C) vibrations give rise to a band near 1191–1171 cm^{-1} which could have been obscured by the strong siloxane stretching vibrations.[8]

Locus of failure, in primed DCB samples, occasionally occurred at the metal/primer interface. RAIR spectra from the adherend side of the fracture surface showed no retained organic phase. Therefore, in order to characterize the interphase, the adhesive fracture surface was analyzed. Figure 5a is an ATR

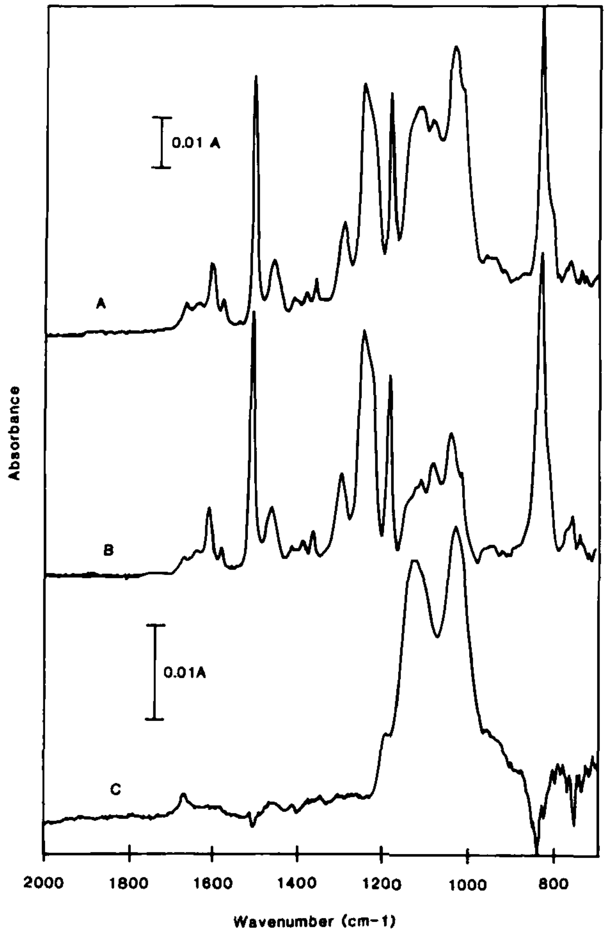


FIGURE 5 Infrared ATR spectra of fracture surfaces from adhesive side of a 1018 steel/epoxy/tertiary amine DCB samples; A) primed with γ-APS; B) unprimed, then cured for 1 hour at 150°C: C) Difference spectrum.

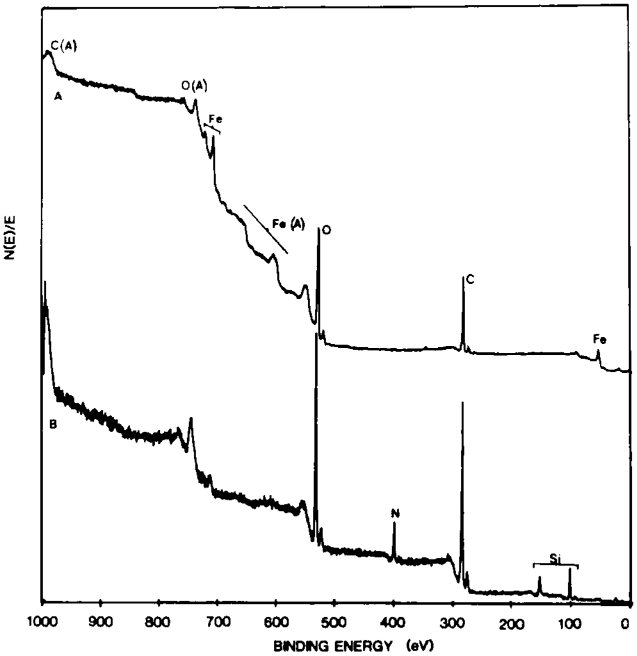


FIGURE 6 XPS survey spectra from A) adherend and B) adhesive failure surfaces of a 1018 steel/γ-APS/epoxy DCB that was cured for 1 hour at 150°C.

spectrum of the adhesive failure surface of a DCB made with the epoxy/tertiary amine adhesive cast on a primed 1018 steel substrate. The sample was cured at 150°C for 1 hour. The 1605, 1510, 1260, and 830 cm^{-1} bands associated with the epoxy phase again obscured the spectrum of the interphase. Figure 5c is the difference spectrum of the adhesive fracture surface from a primed DCB sample less a fracture surface from an unprimed DCB sample (Figure 5b). The 1510 cm^{-1} band was used to normalize the two spectra. The difference spectrum shows the siloxane bands near 1040 and 1150 cm^{-1} in addition to the imine band near 1660 cm^{-1}. This spectrum closely resembles the RAIR spectrum taken from the adherend side. Therefore, it is possible to characterize an interphase regardless of locus of failure.

The XPS survey spectrum (Figure 6a) from the adherend side of the failure surface shows photoelectron peaks near 710 eV (Fe2p) as well as peaks from oxygen and carbon indicative of the oxide phase and adventitious contamination, respectively. The survey spectrum from the adhesive failure surface shows photoelectron peaks from carbon, oxygen, nitrogen and silicon, illustrating failure at the metal oxide/primer interphase. It is clearly evident that there is very good chemical coupling between the primer and the adhesive since locus of failure occurs at either the oxide surface or in the adhesive phase when this adhesive is cured at high temperatures on primed steel surfaces.

The interphases characterized in the previous spectra were from a twocomponent adhesive system. The second adhesive is a more complex three-component system (Epon 828/NMA/BDMA). Several possible reactions can occur near the interface. First, the epoxy can react with the curing agent, primer or both. The curing agent can react with the primer or accelerator and the metal substrate may influence any of the reactions. Simulated polymer/metal interphases were created to investigate the reaction between the epoxy resin, anhydride curing agent and aminosilane primer. Actual interphases, which included the accelerator (BDMA), were characterized by using the fracture surfaces from the DCB samples.

Figure 7a is a RAIR spectrum of a simulated adhesive interphase illustrating the reaction between the epoxy/anhydride adhesive and the silane primer on an aluminum mirror. The system was cured at 75°C for 1 hour and rinsed in MEK. The spectrum clearly shows two peaks at 1040 and 1150 cm^{-1} associated with the siloxane stretching frequencies of the primer. The broad band near 1600 cm^{-1} could be an envelope of bands comprised of vibrations from amide groups and

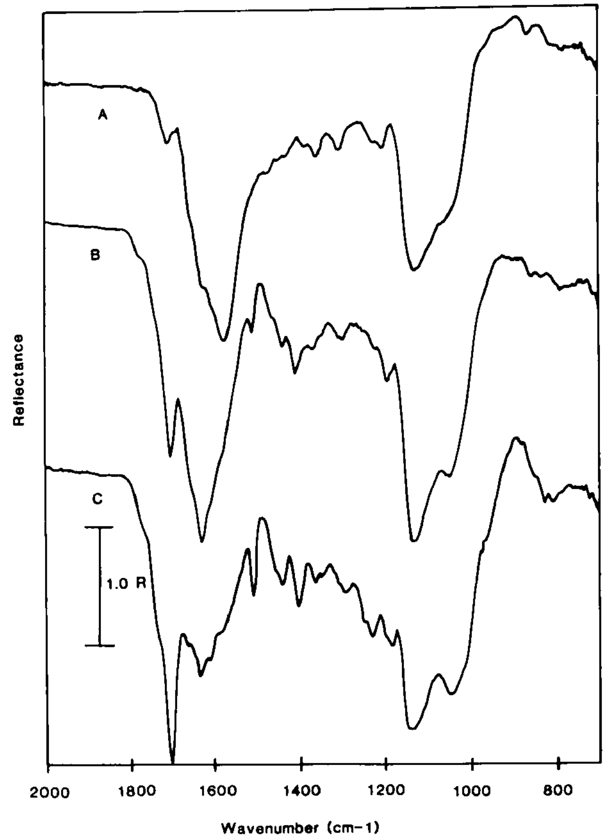


FIGURE 7 RAIR spectra obtained from 2024 aluminum mirrors primed with γ-APS then reacted with an epoxy resin/NMA 1:1 mixture at A) 75°C for 1 hour; B) 150°C for 1 hour; C) 150°C for 3 hours and rinsed with MEK.

carboxylate groups formed from interaction of the anhydride and either aluminum or copper ions. The peak could also be associated with an acid-amine carboxylate salt formation as observed by Linde.[9] No epoxy retention was observed, due to the absence of the sharp band near 1510 cm^{-1}.

When the cure temperature was raised to 150°C for 1 hour, the RAIR spectrum (Figure 7b) shows a sharp band near 1700 cm^{-1} in addition to the previous peaks at 1040, 1150, and 1600 cm^{-1}. The 1700 cm^{-1} peak and the high frequency shoulder near 1770 cm^{-1} are both associated with C=O stretching vibrations of a cyclic imide. The primary amine from the primer reacted with the anhydride group of the curing agent to form a cyclic imide. As a result, the functionality of the primer was reduced to zero and no chemical bridge was formed between the primer and the adhesive. Figure 5c shows that heating the system for 3 hours increased the intensity of the 1700 cm^{-1} band and reduced the intensity of the 1600 cm^{-1} band. This indicates that more cyclic imides were formed at the expense of the amide groups that were formed at lower temperatures. The previous two spectra have a small peak near 1510 cm^{-1} associated with the phenyl stretching vibration of the epoxy resin. It is possible that chemical bonding has occurred between the epoxy group of the adhesive and the amino group of the primer as suggested by Chaing for silane-treated silica/epoxy systems.[2]

These results correlate with spectra taken on silica[2] and germanium[5] substrates except for the carboxylate salt formation between metal cations and the anhydryde curing agent. This clearly illustrates the extra dimension that a metal surface contributes to the interphase region through dissolution of the oxide or cation transport to the oxide/polymer interface. These carboxylate/metal salts can diffuse into the adhesive and catalyze oxidation of the polymer matrix[10] or accelerate the curing reaction.[11]

Figure 8a is a RAIR spectrum taken from the adherend side of a fractured DCB sample made with a primed aluminum substrate and the epoxy/anhydride-cured adhesive. The spectrum contains bands near 1510 and 1740 cm^{-1} characteristic of the cured adhesive. The broad band near 1000 cm^{-1} may be associated with the aluminum substrate and the silane primer. Very little information can be taken directly from this spectrum. Therefore digital subtraction was used to eliminate the adhesive and adherend components from the composite spectrum.

Figure 8b is a RAIR spectrum of a thin film of the adhesive applied from an MEK solution and cured on an aluminum substrate. The band near 1740 cm^{-1} is due to the C=O stretching vibration and the shoulder near 1250 cm^{-1} is due to the C—O stretching vibration, both of the ester group. Esters were produced as a result of addition polymerization reaction between the anhydride and the epoxy.[12]

Figure 8c is the adherend side of a fracture surface from a DCB sample with an unprimed-aluminum substrate. The broad band near 1000 cm^{-1} is an envelope of bands due to oxidation products on the aluminum surface including Al_2O_3 (960 cm^{-1}) and a hydroxide species such as AlOOH (1100 cm^{-1}). The two bands near 1600 and 1450 cm^{-1} are from carboxylate anion vibrations due to salt formation between the curing agent and the aluminum or copper. A further

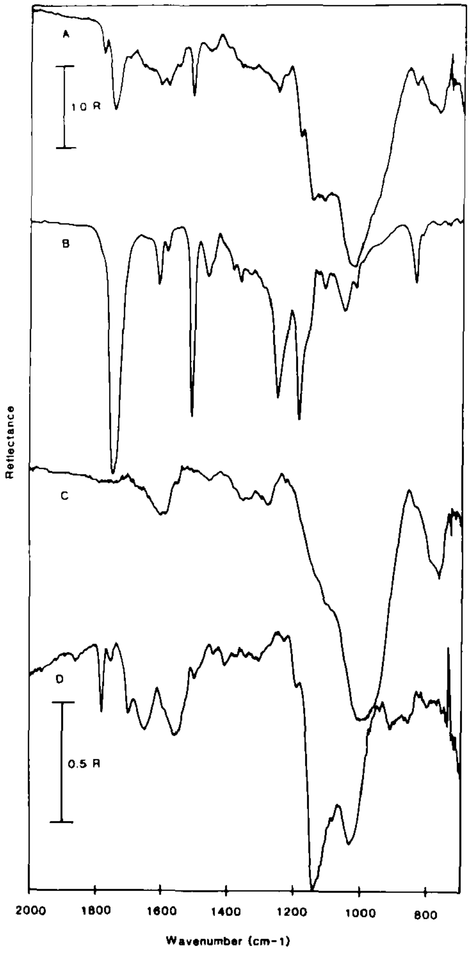
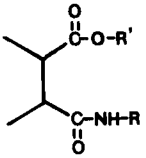


FIGURE 8 RAIR spectra of A) fracture surface from the adherend side of a 2024 aluminum/epoxy/anhydride DCB sample primed with γ-APS; B) unprimed 2024 aluminum coated with an epoxy/anhydride adhesive; C) fracture surface of unprimed DCB sample; all cured 2 hours 150°C: D) Difference spectrum.

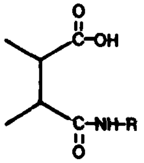
investigation of reactions involving the anhydride curing agent and metal substrates will be reported elsewhere.[13]

Figure 8d is the difference spectrum of the fracture surface without the adhesive phase and the oxidation products of the adherend surface. The adhesive spectrum was subtracted by normalizing the spectrum based on the 1740 cm^{-1} peak. The unprimed adherend surface phase was subtracted by normalizing the spectrum based on the 1000 cm^{-1} broad band. The difference spectrum shows bands near 1650 and 1550 cm^{-1} characteristic of amide formation. The small peaks near 1700 cm^{-1} and 1770 cm^{-1} are due to the C=O vibration of a cyclic imide as well as the 1400 cm^{-1} band due to the C—N vibration. The sharp peak near 1780 cm^{-1} is the C═O vibration from residual anhydride groups. The last two bands near 1150 and 1040 cm^{-1} are the SiOSi vibrations from the siloxane network. This interphase region contains amides, imides, residual unreacted curing agent, carboxylate salts, and a crosslinked siloxane network. The imide production is contrary to the results found by Garton[5] even though the curing temperatures and times were similar. However, it was noted that the adhesive layer in Garton's experiment was much thinner (100 μm) and the adhesive was capped with a Pyrex glass cover slide on the ATR crystal which could have inhibited water removal. Our system was large enough to allow diffusion of water away from the interface.

The previous spectrum does not clearly show that the amide group is part of a chemical bridge between the primer (R′) and adhesive (R) through the curing agent or part of the amic acid precursor of the imide.



(A)



(B)

In order to determine if the curing agent formed a chemical bridge between the epoxy and the primer, the three components were reacted in a step-wise procedure in the bulk and analyzed with transmission infrared spectroscopy. First, the curing agent was reacted with *n*-propylamine to form the the amic acid of NMA. Then the amic acid of NMA was mixed with the epoxy resin in order to determine whether ester or imide formation would occur indicating chemical bridge formation between primer/curing agent/adhesive or termination of reactivity of the primer, respectively. Figure 9a is a spectrum of a 1:1 molar mixture of *n*-propylamine and NMA reacted at room temperature, dissolved in 2-propanol and cast on a germanium window. The spectrum was taken after solvent evaporation. The band near 1730 cm^{-1} is due to the carbonyl-stretching vibration of the acid group of the amic acid product, and the two bands near 1650 and 1550 cm^{-1} are due to vibrations of the amide group. Figure 9b is a spectrum of a 2:1 molar mixture of the amic acid and the epoxy resin reacted for 1 hour at 50°C then dissolved in MEK and cast on a germanium window. The spectrum does not show a band near 1740 cm^{-1} associated with ester formation in the chemical bridge. After the amic acid of NMA/epoxy mixture was heated to 150°C for 1 hour, it was dissolved in MEK and cast on a germanium window. The spectrum of the product in Figure 9c shows a strong band near 1700 cm^{-1} and a weaker band near 1770 cm^{-1} associated with cyclic imide formation. Both spectra were

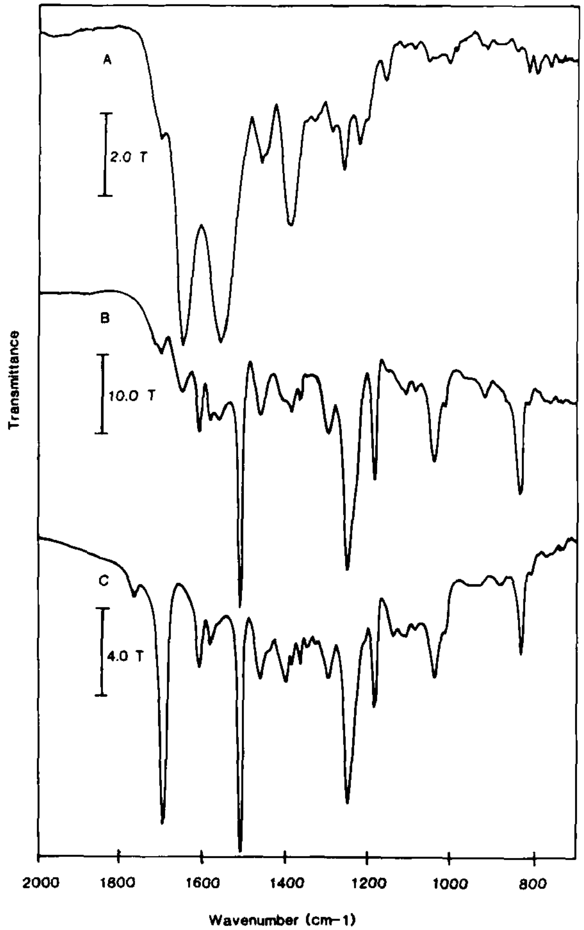


FIGURE 9 Transmission infrared spectra of A) The amic acid of NMA produced from a 1:1 molar mixture of NMA and *n*-propylamine; B) 2:1 molar mixture of the amic acid of NMA with an epoxy resin heated for 1 hour at 50°C; C) sample B heated for 1 hour at 150°C.

taken after solvent evaporation. Therefore, the imide formation is the favored reaction and no chemical bridging occurs between the aminofunctional primer and the epoxy adhesive through the anhydride curing agent in the bulk or at the interface.

CONCLUSIONS

The molecular structure of the interphase region in adhesive joints made with aminosilane primed adherends varied as a function of curing agent and temperature. Joints made with tertiary amine-cured epoxy adhesives contained an interphase region which consisted of low molecular weight siloxane oligomers and amine bicarbonates when cured at 75°C. There was no chemical reaction between the primer and adhesive, and failure occurred near the primer/adhesive interface.

The joints made with the same adhesive system cured at 150°C contained an interphase region that had a highly-crosslinked siloxane network and some oxidized amine species. There was no evidence of secondary amine formation which is indicative of chemical interaction between the aminosilane and the epoxy. However, the locus of failure either occurred at the primer/adherend interface or in the epoxy phase which indicates good bonding between primer and adhesive.

Adhesive joints made with the anhydride-cured epoxy system contained a more complex interphase region compared to the amine-cured system. The interphase consisted of a highly-crosslinked siloxane network with amide and imide functional groups in addition to residual anhydride curing agent, similar to results found in silica/epoxy and germanium/epoxy systems. However, carboxylate/metal salts and metal oxidation products from anhydride/adherend interactions were also found in this interphase region, clearly illustrating the differences in reactivity between metal oxide and silicon or germanium oxide substrates.

The imide formation was suppressed by the curing accelerator BDMA. The amide formation is part of the amic acid produced from reaction of the primer and the curing agent and not part of a chemical bridge between the primer and the adhesive through the curing agent. No imine formation occurred, even on copper-bearing aluminum substrates, which indicates that amide/imide formations are the favored reaction products of the amine at 150°C for the anhydride-cured epoxy adhesive system.

Acknowledgments

This work was supported in part by a contract from the Office of Naval Research. γ-APS primer and DMP-30 curing agent were donated by Union Carbide and Miller Stephenson respectively. The assistance of Kristen A. Boerio in preparing the figures is also acknowledged.

References

1. E. P. Plueddemann, *Siloxane Coupling Agents* (Plenum Press, New York, 1982).
2. C. H. Chiang and J. L. Koenig, *Polymer Composites* **1,** 88 (1980).
3. S. R. Culler, H. Ishida and J. L. Koenig, *ibid.* **7,** 231 (1986).
4. A. Garton, *ibid.* **5,** 258 (1984).
5. A. Garton, *J. Polym. Sci.: Polym. Chem. Ed.* **22,** 1495 (1984).
6. D. J. Ondrus and F. J. Boerio, *J. Colloid Interface Science* **124,** 349 (1988).
7. F. J. Boerio and D. J. Ondrus, in *Proc. Symp. Surf. Colloid Sci. Computer Tech.,* K. L. Mittal, Ed. (Plenum Press, New York, 1987).
8. N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic Press, New York, 1975).
9. H. G. Linde, *J. Polym. Sci.: Polym. Chem. Ed.* **20,** 1031 (1982).
10. D. L. Allara, *et al. ibid.* **14,** 93 (1976).
11. H. Matsuda, *J. Appl. Polym. Sci.* **23,** 2603 (1979).
12. H. Lee and K. Neville, *Handbook of Epoxy Resins* (McGraw-Hill, New York, 1972).
13. D. J. Ondrus and F. J. Boerio, to be published.