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Interaction of Epoxy/Dicyandiamide Adhesives with Metal Substrates

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The molecular structure of the interphase formed by curing a model adhesive system consisting of the diglycidyl ether of bisphenol-A (DGEBA) and dicyandiamide (DDA) against mechanically polished aluminum and electrogalvanized steel (EGS) substrates was determined using reflection–absorption infrared spectroscopy (RAIR) and X-ray photoelectron spectroscopy (XPS). RAIR analysis suggested that DGEBA/DDA mixtures created an interphase with a different molecular structure from the bulk of the adhesive when cured in contact with aluminum. The formation of this unique interphase was mainly due to interactions between DDA and the Al surface. XPS analysis indicated that aluminum ions exposed by heating the substrate surface were necessary for this interaction. DDA was found to adsorb onto the aluminum surface via the lone pair of electrons on the nitrogen atoms of the nitrile groups. A slight decrease in the nitrile stretching frequency suggested an additional back-bonding interaction between aluminum ions and the nitrile groups. Slight back donation of electrons from the metal to DDA resulted in a reduction product that led to the formation of the carbodiimide form of DDA. This specific reaction caused a decrease in the concentration of nitrile groups in the interphase and changed the extent of the reaction between DDA and DGEBA by inhibiting the formation of oxazolidine structures. The interaction of DDA with EGS surfaces followed a similar trend. However, the effects were much more pronounced with EGS and the extent of the curing reaction and the cross-linking rate near the metal surface were strongly affected by EGS/DDA interactions.

Keywords: Aluminum; Dicyandiamide; Diglycidyl ether of bisphenol-A; Electrogalvanized steel; Interphase; Reflection–absorption infrared spectroscopy; X-ray photoelectron spectroscopy

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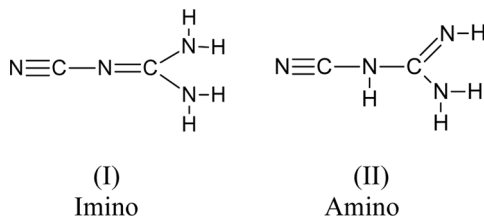
1. INTRODUCTION

Knowledge of the adhesive/substrate interphase is very important for both fundamental and practical aspects of adhesion. Indeed, the interphase and its properties can significantly influence the final overall properties of composite systems (practical adhesion, corrosion resistance, and durability) consisting of a substrate and a polymeric coating. Different studies have analyzed the interfacial reactions of different epoxy/metal systems and found that the interphase usually shows distinct chemical composition and has properties different from those of bulk resins [1–9].

Nigro and Ishida [1] characterized the curing reaction of BF_3 -ethylamine catalyzed epoxy films on steel surfaces using reflection-absorption infrared (RAIR) spectroscopy and found that the extent of epoxide conversion increased with decreasing thickness of the epoxy films. The high degree of conversion observed near the steel surface was attributed to a surface-affected reaction. A similar reaction was also found on copper surfaces [2]. Dillingham and Boerio examined the failure surfaces of epoxy-triethylenetetramine/aluminum adhesive joints using X-ray photoelectron spectroscopy (XPS) and showed that amine protonation occurred at the epoxy/aluminum interface but not in the bulk of the epoxy [3]. They attributed the amine protonation to acidic sites on the surface of the aluminum substrate. Bolouri *et al.* [4] used XPS to examine the interaction of oxidized aluminum surfaces with adducts of an amine and an epoxy. On the basis of the N(1s) binding energies, they suggested that amine protonation occurred for both phosphoric acid-anodized and air-oxidized aluminum. Gaillard and co-workers used XPS [5] and FTIR [6] to show that the reaction rate of an epoxy and dicyandiamide (DDA) was faster on the zinc surfaces of galvanized or electrogalvanized steel (EGS) than on polished steel. They concluded that the catalytic effect of zinc ions leads to a higher extent of cross-linking. Carter *et al.* [7] studied the reactions of an epoxy/DDA system with cold-rolled steel (CRS) and EGS surfaces and found that a new compound was formed through specific chemical reactions between DDA and EGS. DDA was chemically reduced when heated with metallic zinc at 170°C for a short time, whereas no reaction was observed when DDA was heated against steel or zinc oxide [8,9]. In contrast, DDA formed guanylurea upon heating on an anodic aluminum oxide surface [9].

Epoxies cured with DDA are used in high-temperature adhesive and coating systems. The cured products exhibit excellent adhesion, flexibility, and impact resistance [10]. Epoxy/DDA systems are extensively used as coatings or bonding materials for metallic substrates. Several investigators have considered the chemical interactions that

may occur between epoxy/DDA systems and metallic surfaces [5–9]; however, these processes are still not fully understood. This is mainly due to the complex structure of DDA, which exists in two tautomeric forms, the imino (I) and amino (II) forms [11], and



the difficulty of characterizing buried interfaces at a molecular scale. Furthermore, curing epoxy resins with DDA is quite a complicated phenomenon, considering the high functionality of DDA, its low solubility in epoxy resins, and its various chemical forms [12–14].

The goal of the research described in this article was to determine the nature of chemical reactions occurring at the interface between DDA-cured epoxy adhesives and metal substrates. A model adhesive system consisting of the diglycidyl ether of bisphenol-A (DGEBA) and DDA was used to simulate the reactions occurring between an actual adhesive system and a metal substrate. RAIR and XPS were used to determine the interfacial reactions.

2. EXPERIMENTAL

The substrates used in this study were 16-mm by 16-mm coupons of aluminum alloy 6111 and EGS. Aluminum substrates were rough polished with 800- and 1200-grit silicon carbide paper and then polished to a mirror finish using 2 μm of MgO powder. After final polishing, the substrates were rinsed with high-performance liquid chromatography (HPLC)-grade water several times and blown dry with nitrogen. EGS substrates were cleaned ultrasonically in acetone for 15 min, rinsed with acetone, and blown dry with nitrogen.

The model adhesive consisted of the DGEBA epoxy resin DER 332 (provided by Dow Chemical Company, Midland, MI) and the curing agent DDA (Aldrich Chemical Company, Milwaukee, WI). Thin films of the model adhesive were deposited on the substrates by spin-coating dilute solutions of the adhesive in N,N-dimethyl formamide (DMF, Aldrich Chemical Company) onto the substrates at 30 rpm for 30 s. RAIR spectra were obtained from the as-prepared samples and from samples that were heated in a vacuum oven at 150°C under nitrogen

for different times, cooled to room temperature in air, rinsed with DMF for 30 min. to remove compounds that were not tenaciously bonded to the substrates, and blown dry with nitrogen. Samples of the neat model adhesive were prepared by mixing DGEBA with DDA in a 7:1 mol ratio and curing for 6 h at 150°C.

A Nicolet Magna 760 Fourier-transform infrared spectrometer (Thermo Electron Corp., Madison, WI) was used to obtain all infrared spectra. RAIR spectra were obtained using a Nicolet FTS-85 accessory that provided one reflection at an angle of incidence equal to 85°. All RAIR spectra were recorded at 4-cm⁻¹ resolution by averaging 512 scans. Transmission spectra of the neat adhesive were obtained at a resolution of 4 cm⁻¹ by averaging 256 scans.

XPS spectra were obtained using a Perkin-Elmer Model 5300 spectrometer (Perkin-Elmer Corp., Eden Prairie, MN). Mg K_α radiation was used to obtain the spectra. Survey and high-resolution spectra were acquired using a take-off angle of 45° and pass energies of 89.45 eV and 37.35 eV, respectively. The effect of sample charging

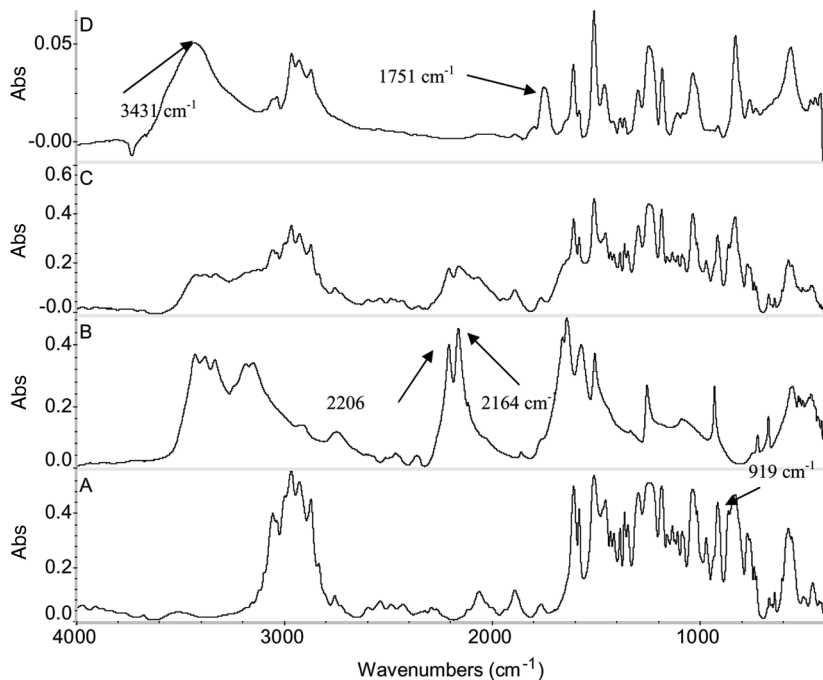


FIGURE 1 Transmission infrared spectra of (A) DGEBA, (B) DDA, (C) model adhesive consisting of DGEBA and DDA in a 7:1 molar ratio before curing, and (D) model adhesive after curing at 150°C for 6 h.

was eliminated by referring the C(1s) binding energy of saturated hydrocarbons to a value of 284.6 eV.

3. RESULTS AND DISCUSSION

3.1. Model Adhesive System

Transmission infrared spectra of DGEBA and DDA are shown in Figures 1(A) and 1(B), respectively. The spectrum of DGEBA was characterized by a sharp band at 915 cm^{-1} that was related to the epoxy groups whereas the spectrum of DDA was characterized by a doublet at 2206 and 2165 cm^{-1} that was related to the tautomeric imino (I) and amino (II) forms of the compound. Assignments of the other bands in the infrared spectra of DGEBA and DDA are given in Table 1. Figure 1 also shows the transmission infrared spectra of the bulk adhesive before (C) and after (D) curing for 6 h at 150°C . Significant changes in the spectra as a result of the curing reaction were easily observed. As curing proceeded, the intensities of the nitrile bands at 2206 and 2165 cm^{-1} and the epoxy ring band at 915 cm^{-1} decreased significantly, and new absorption bands appeared at 3431 and 1751 cm^{-1} . Figure 2 shows the intensities of some absorption bands of the neat epoxy adhesive relative to the intensity of the phenyl absorption at 1517 cm^{-1} as a function of curing time. The consumption of amine and epoxy groups throughout curing can be explained by the well-known amine-to-epoxy addition reaction [15]. The amino

TABLE 1 Band Assignments in the Infrared Spectra of DDA and DGEBA

DDA	Assignments ^a	DGEBA	Assignments ^a
3430, 3382, 3328	NH ₂ asym. stretch	2961, 2872,	CH ₃ asym. stretch
3189, 3148	sym. stretch	2925	CH ₂ asym. stretch
2206	C≡N (II)	2872	CH ₃ sym. stretch
2165	C≡N (I)	2834	CH ₂ sym. stretch
1661	C=N	1607, 1582,	p-disubstituted benzene
1642	NH ₂ scissor vib.	1517, 1184	
1571	N-C-N asym. stretch	1455	CH ₃ asym. def. + CH ₂ def
1501	N=C-N asym. stretch	1246	C-O-C asym stretch
1254	NH ₂ rocking	1035	O-CH ₂
1096	C-N in NH ₂	919	Epoxy ring
928	N-C-N sym. stretch		
723	NH wagging		
670	NH out of plane bending		

^aColthup, N. B., Daly, L. H., and Wiberley, S. E., *Introduction to Infrared and Raman Spectroscopy*, 3rd ed. (Academic Press CA, 1990), Chap. 5, pp. 215-233; Chap. 6, pp. 240-241; Chap. 8, pp. 261; Chap. 10, pp. 327; Chap. 11, pp. 339-341.

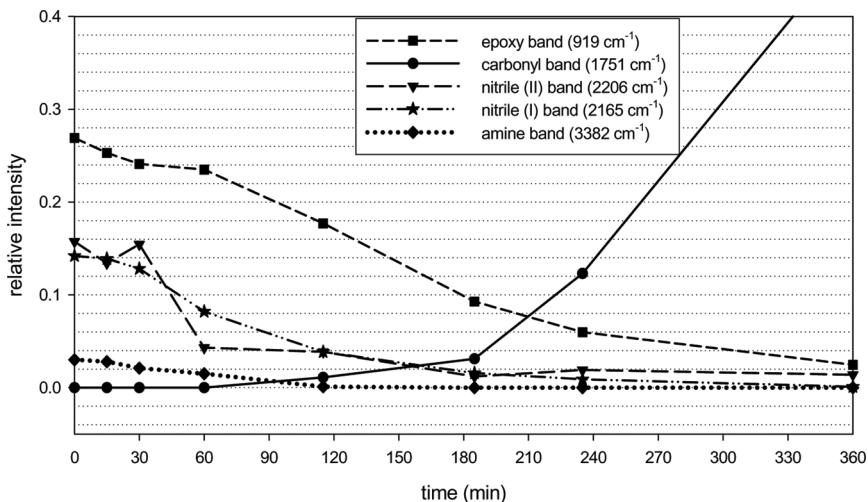


FIGURE 2 Relative intensity *versus* cure time for selected absorption bands of the model adhesive prepared by mixing DGEBA and DDA in a 7:1 molar ratio. The intensity of the phenyl ring absorption band at 1515 cm^{-1} was taken as a reference because the intensity of that band was not expected to change during curing reactions.

groups react with epoxy rings to form linkages containing secondary hydroxyl groups that give rise to an absorption band at 3431 cm^{-1} . Secondary hydroxyl groups can further react with epoxy rings to form ether linkages. In the second stage of curing, hydroxyl groups added across the $\text{C}=\text{N}$ bond of the DDA moieties with the loss of ammonia to form five-membered iminoxazolodine rings [16]. The imino groups were then hydrolyzed by water to produce five-membered cyclic urethane (2-oxazolidinone) rings that gave rise to an absorption band at 1751 cm^{-1} [16–18].

3.2. Model Adhesive on Aluminum

Significant spectral differences were observed when the RAIR spectra of a thin film of the model epoxy adhesive that was spin-coated onto Al 6111 from a 1% solution in DMF and cured under nitrogen at 150°C for 6 h were compared with the transmission spectra of the neat adhesive that was cured similarly (see Figure 3). The most noticeable difference between the RAIR and transmission spectra was the relatively low intensity of the carbonyl band at 1751 cm^{-1} in the RAIR spectra of the model adhesive. A small shift in the nitrile absorption to lower wavenumbers was also recognized. A new peak that was related

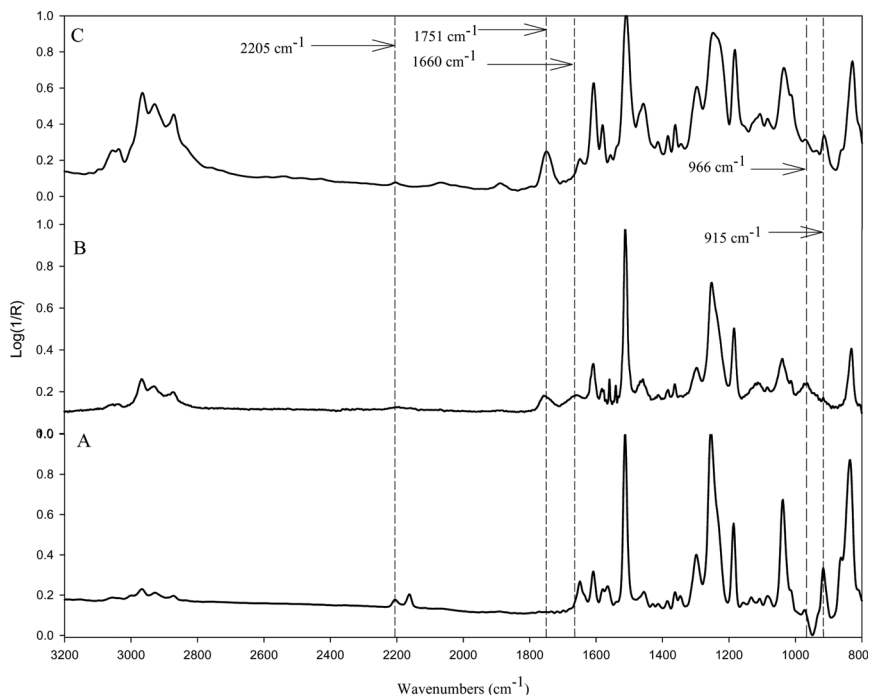


FIGURE 3 RAIR spectra obtained from thin films of the model adhesive that were spin-coated onto polished aluminum substrates from 1% solutions in DMF: (A) before curing and (B) after curing at 150°C for 6 h under nitrogen and rinsing with DMF.

to imine or amide functional groups appeared near 1660 cm^{-1} in the RAIR spectra. Moreover, a band appeared near 966 cm^{-1} in the RAIR spectra and was attributed to an increase in the thickness of the oxide layer on aluminum during curing.

To explain these differences, thin films of DDA and DGEBA were spin-coated onto polished Al 6111 substrates, heated under nitrogen at 150°C for 15 minutes, and then rinsed with DMF. RAIR spectra were then obtained from the substrates to determine if any DDA or DGEBA was retained. Figure 4 shows that there was little evidence for retained DGEBA after rinsing. However, the nitrile bands of DDA were clearly observed (see Figure 5), although they did shift to lower wavenumbers by approximately 15 cm^{-1} . These results showed that some DDA but little DGEBA was chemisorbed onto the aluminum substrates.

To determine if the shift in the nitrile absorption bands that was observed when DDA was spin-coated onto aluminum and then heated

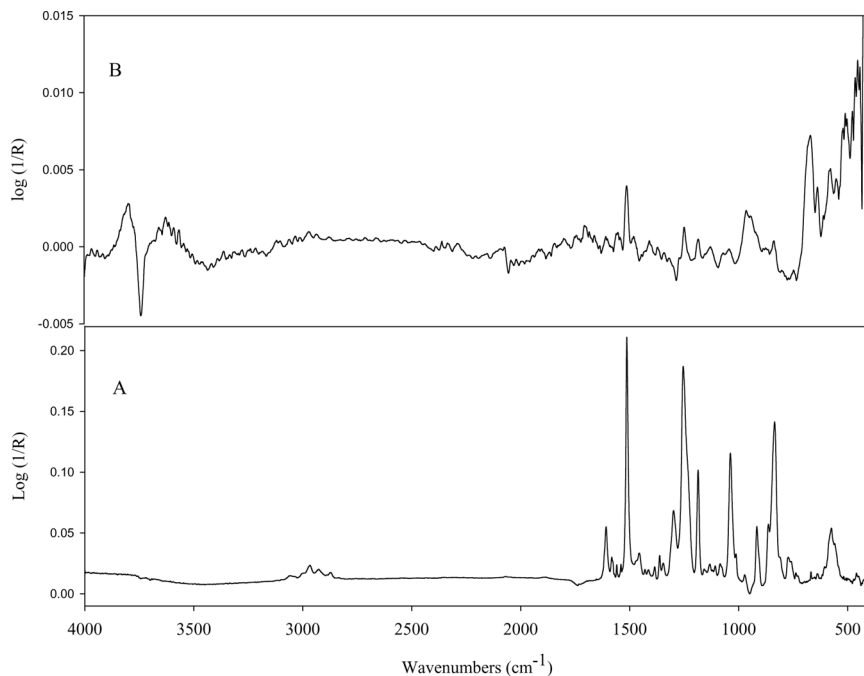


FIGURE 4 RAIR spectra of a film formed by spin-coating a 1% solution of DGEBA in DMF onto Al: (A) before and (B) after heating for 15 min at 150°C under nitrogen and rinsing in DMF.

in nitrogen at 150°C was related to thermal degradation, thin films of DDA were spin-coated onto gold substrates, heated under nitrogen at 150°C for 15 min, and then rinsed in DMF. No evidence for retained DDA was observed in RAIR spectra obtained from these samples (see Figure 6), indicating that thermal degradation of DDA did not occur under these conditions and that the shift toward lower frequencies that was observed for $\nu(\text{C}\equiv\text{N})$ when thin films of DDA were heated against aluminum was related to chemisorption.

Nitrile-containing molecules can interact with metals through several mechanisms. End-on ($\eta^1\text{-NCR}$) coordination occurs by σ -bonding through the lone pair of electrons on the nitrogen atom and is often accompanied by an increase in the $\nu(\text{C}\equiv\text{N})$ stretching frequency [19]. However, in several transition-metal/nitrile complexes, the $\nu(\text{C}\equiv\text{N})$ stretching frequency remains virtually unchanged or even shifts to lower frequencies by 20–100 cm^{-1} . This has been attributed to significant back bonding between the d orbitals of the transition metals and the π^* orbitals of the nitriles in these compounds [20]. A side-on

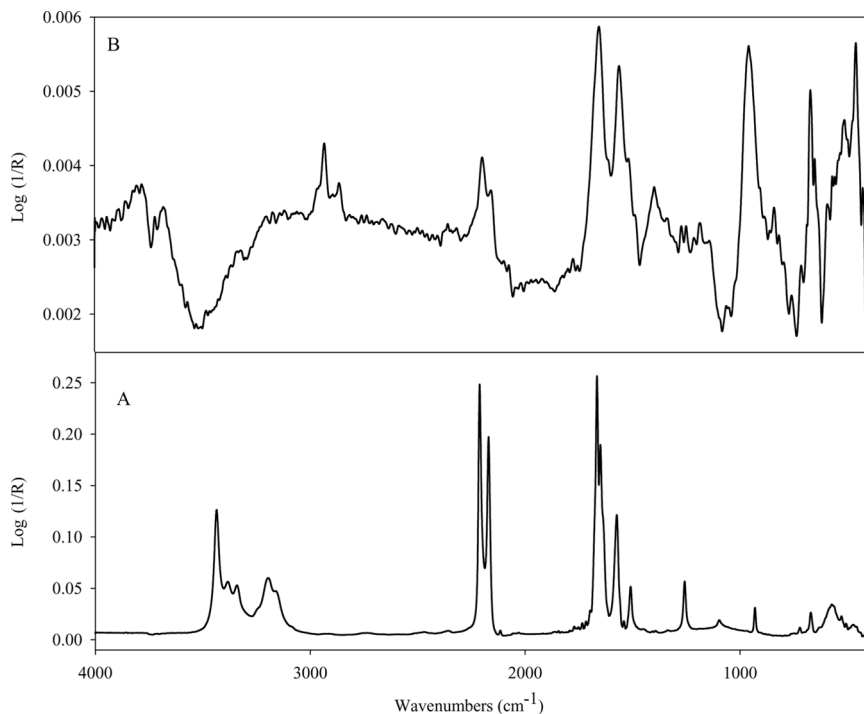
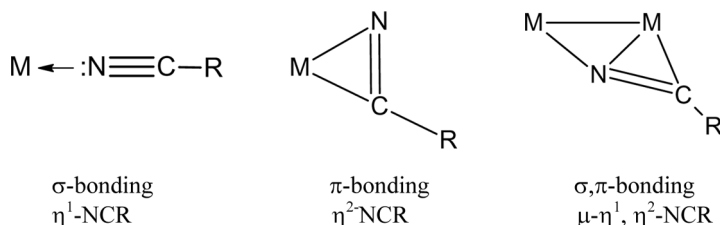


FIGURE 5 RAIR spectra of thin films formed by spin-coating a 1% solution of DDA in DMF onto Al: (A) before and (B) after heating for 15 min at 150°C under nitrogen and rinsing in DMF.

(η^2 -NCR) [21–23] coordination that occurs through the π system of the C \equiv N bond generally results in a large decrease in the C \equiv N stretching frequency (up to 500 cm^{-1}). In bridging (μ - η^1, η^2 -NCR) [24,25], the nitrile ligand is σ -coordinated *via* the nitrogen atom to one metal center that is π -coordinated to the other. This type is not very common and is encountered on interaction of nitrile with di- or poly-nuclear systems.



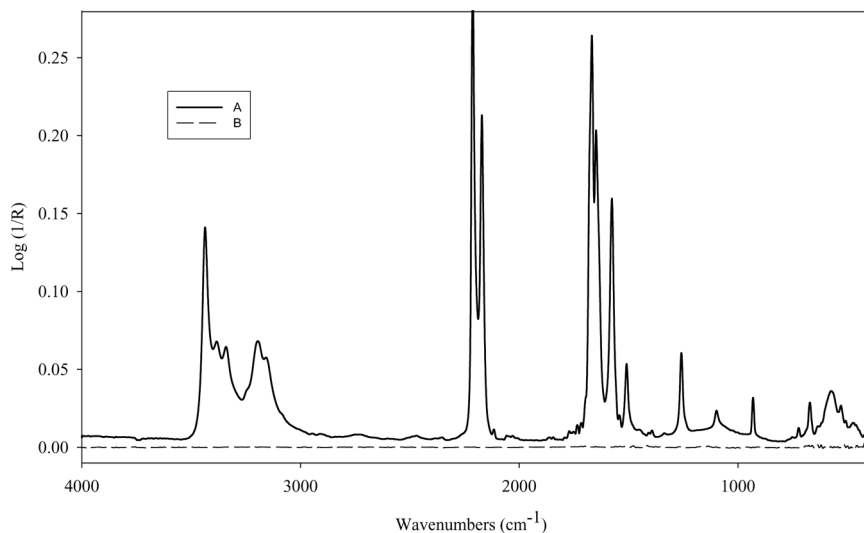


FIGURE 6 RAIR spectra of a film formed by spin-coating a 1% solution of DDA in DMF onto gold: (A) before and (B) after heating for 15 min at 150°C under nitrogen and rinsing in DMF.

The observed decrease in the $\nu(\text{C}\equiv\text{N})$ frequency in Figure 5 was relatively small for side-on coordinated nitriles. As pointed out in the previous discussion, this small shift can be explained by end coordination of the nitrile to the aluminum substrate and slight back donation of electrons from aluminum to nitrile-containing molecules. Although aluminum atoms do not present any d orbitals, π^* bonding between a vacant p-orbital of aluminum and phenyl rings has been reported [26,27].

Hydroxyl groups on the oxidized aluminum surface are not the only active sites for the adsorption of basic molecules. Aluminum ions can act as Lewis acids and may bind basic molecules. Although these aluminum ions are not found in the top layer, they may be exposed by vacancies in the surface layer consisting of oxygen and hydroxyl ions [28]. Vacancies in the top layer are formed due to surface dehydroxylation as the temperature is increased [29]. Upon heating, the number of hydroxyl groups decreases and the number of Lewis sites increases, with increasing activation energy.

Figure 7(A) shows the high-resolution Al(2p) XPS spectrum that was obtained from a mechanically polished substrate. Curve fitting of the Al(2p) signal required two components, a Gaussian peak due to the oxide and a non-Gaussian peak due to metallic aluminum

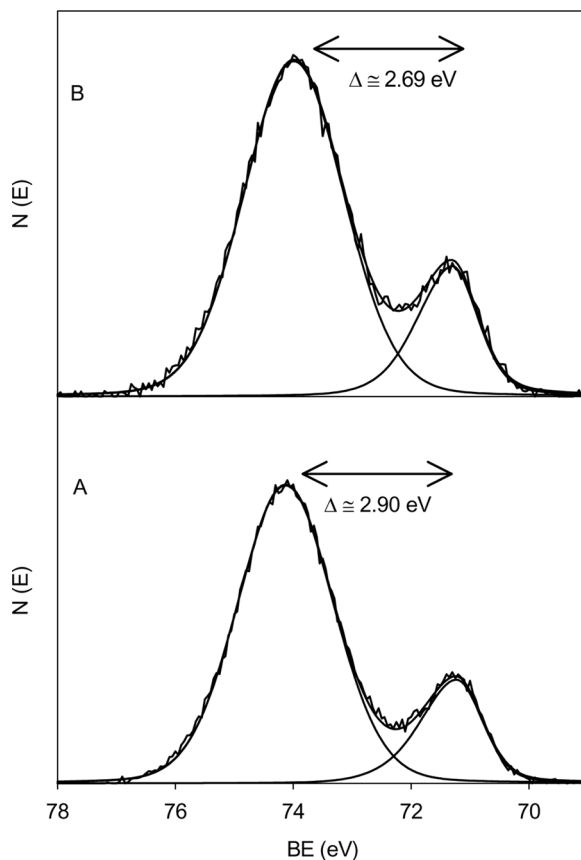


FIGURE 7 High-resolution Al(2p) XPS spectra of mechanically polished Al (A) before and (B) after heating for 15 min at 150°C under nitrogen.

located at 74.13 eV and 71.23 eV, respectively. The separation between these two peaks was calculated as 2.9 eV. As shown in Figure (7B), the separation between these peaks decreased to 2.69 eV after heating the substrate for 15 min at 150°C. Similar shifts were explained in the literature by oxygen vacancies occurring at the surface that exposed Al ions by dehydroxylation [30]. Dehydroxylation of oxidized aluminum occurs upon condensation of two nearby OH groups to form H₂O. This process leaves behind coordinatively unsaturated Al⁺³ and oxide ions on the surface [31]. Al₂O₃ surfaces exhibit a high population of diverse surface Al-OH groups [32]. Removal of -OH groups will modify the chemical state of the aluminum, which would lead to the binding energy shifts observed by XPS. However, it must be kept in mind that

the Al(2p) spectra of the oxidized aluminum compounds (oxide, oxyhydroxide, and hydroxide) show very small differences [33]; the resulting changes in binding energy and peak positions in the XPS spectra after removal of the hydroxyl groups were expected to be small.

Figure 8 shows the XPS survey spectra obtained from DDA films that were spin-coated onto Al substrates from 1% solutions in DMF. The spectra of the as-deposited film and the as-deposited film after heating in nitrogen at 150°C for 15 min and rinsing in DMF are shown in Figures 8(A) and 8(B), respectively. Figure 8(C) shows the XPS survey spectrum of a film that was spin-coated onto Al from a 1% solution in DMF, air-dried for 15 min, and rinsed in DMF. The surface composition of all three films is summarized in Table 2, where it is shown that the as-deposited film spectra consisted of 9% nitrogen, 19% carbon, 50% oxygen, and 19% aluminum. Because the XPS analysis depth (~ 100 Å) was greater than the thickness of the films, peaks due to Al atoms in the substrate were also observed in the spectra.

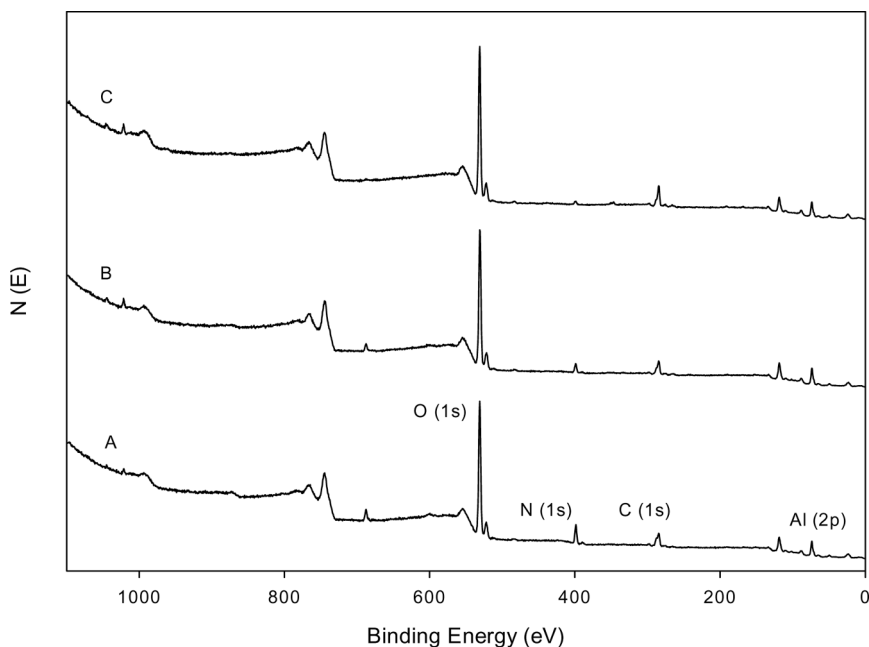


FIGURE 8 XPS survey spectra of thin films formed by spin-coating DDA onto aluminum substrates from 1% solutions in DMF: (A) as deposited, (B) after heating at 150°C for 15 min and rinsing in DMF, and (C) after air drying for 15 min and rinsing in DMF.

TABLE 2 Surface Composition of Samples Prepared by Spin-Coating DDA onto Polished Aluminum Mirrors from a 1% Solution in DMF

Sample description	C (%)	O (%)	N (%)	Al (%)
As-deposited film	19	50	9	19
As-deposited film after heating at 150°C for 15 min and rinsing with DMF	19	52	5	22
As-deposited film after drying at room temperature for 15 min and rinsing with DMF	23	55	1	20

The film that was heated at 150°C had similar surface composition except that the concentration of N decreased to 5%. However, only a very small amount of N (~1%) was detected for the film that was dried in air and then rinsed with DMF. Furthermore, curve fitting of the high-resolution Al(2p) spectra for the as-deposited film revealed that the separation between the peaks due to the oxide and metallic aluminum was 2.95 eV, whereas it was 2.69 eV for the film that was heated at 150°C (see Figure 9). It was concluded that aluminum ions exposed by heating were necessary for chemisorption of DDA to the aluminum surface.

RAIR spectra obtained from films of the model adhesive that were spin-coated onto aluminum substrates, cured at 150°C for different times, and then rinsed with DMF are shown in Figure 10. The spectrum of an as-deposited film is also shown in Figure 10 for reference. For curing times less than about 3 min, only the characteristic bands of DDA were observed in the RAIR spectra, indicating that DDA was preferentially adsorbed onto the surface. The shift in the nitrile absorption bands to lower frequencies was also observed, confirming the chemisorption of DDA onto aluminum. As the curing time increased, the intensity of bands characteristics of the epoxy resin, including the band near 1515 cm⁻¹, increased, indicating that cross-linking had begun.

Figure 11 represents the effect of thickness on the RAIR spectra of films of the model adhesive that were spin-coated onto aluminum substrates, cured at 150°C in nitrogen for 6 h, and then rinsed in DMF. The thickness of the adhesive films on the aluminum substrates was varied by increasing the concentration of the solutions from which the films were spin-coated and/or by decreasing the spin-coating rate. Film thickness was determined by weighing substrates before and after coating and assuming that the density of the epoxy adhesive was 1.16 g/mL. At least three samples were measured per condition. As the film thickness of the model adhesive increased from 40 Å

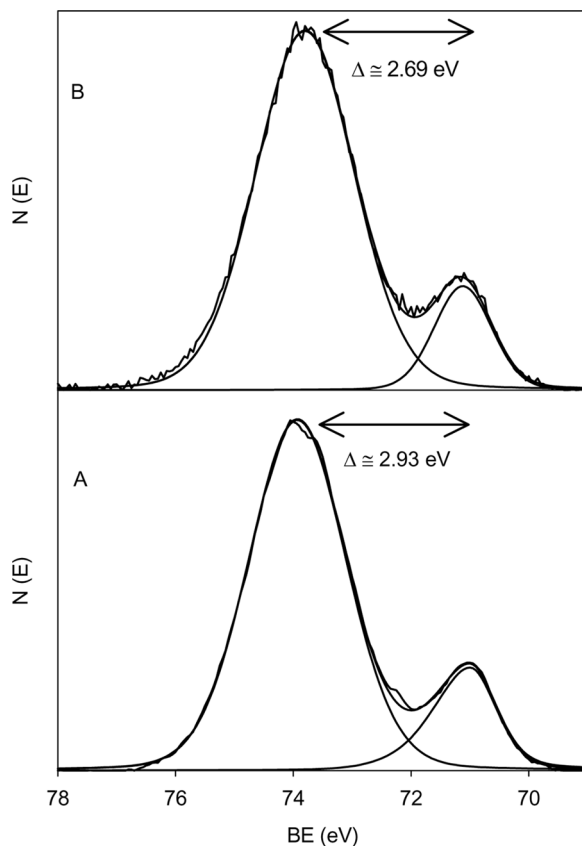


FIGURE 9 High-resolution Al(2p) XPS spectra of thin film of DDA spin-coated onto aluminum from a 1% solution in DMF: (A) as deposited and (B) after heating at 150°C for 15 min and rinsing in DMF.

to 1300 Å, the intensity of the carbonyl band around 1751 cm⁻¹ increased considerably and the RAIR spectrum became very similar to the transmission spectrum of the model adhesive.

To obtain complementary information, XPS survey spectra of the thin films of the model epoxy adhesive that were spin-coated onto Al 6111 from a 1% solution in DMF, cured at 150°C under nitrogen for 15 min or 6 h, and then rinsed with DMF were compared with the XPS survey spectra of the neat adhesive that was cured for 6 h at 150°C. The surface composition of all three samples is summarized in Table 3, which shows that the bulk adhesive consisted of 78.8% C, 18.6% O, and 2.5% N. The film that was cured for 6 h on Al had

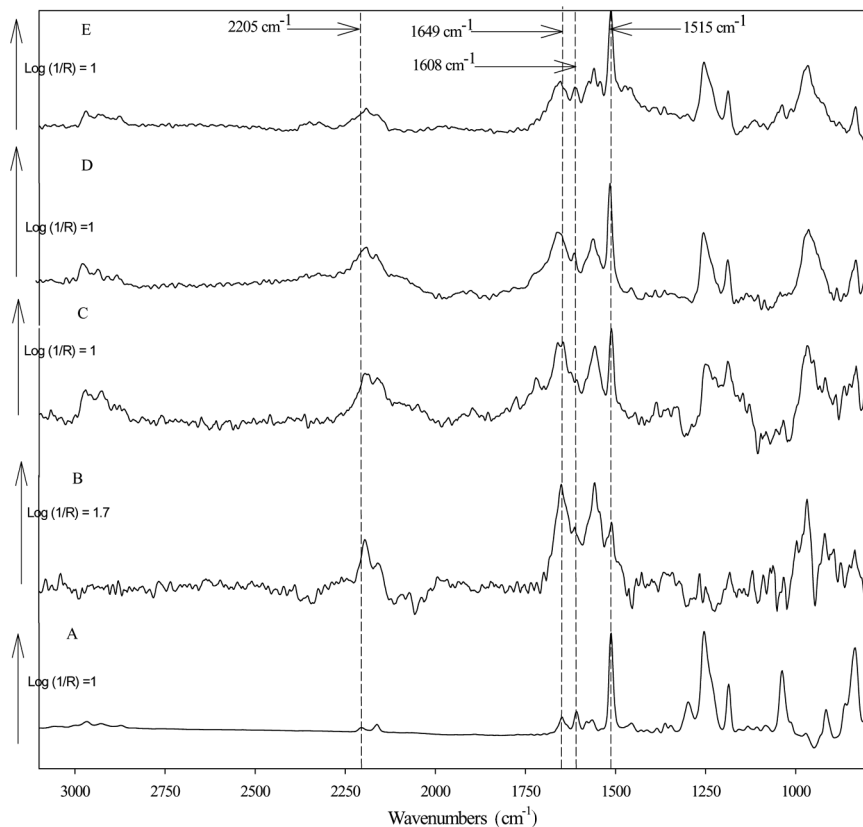


FIGURE 10 RAIR spectra obtained from a thin film of the model adhesive that was spin-coated onto an aluminum substrate from a 1% solution in DMF: (A) as deposited and after curing for (B) 2.5, (C) 5, (D) 10, and (E) 15 min at 150°C under nitrogen and rinsing with DMF.

similar surface composition (79.6% C, 17.5% O, 2.9% N) to the bulk. In the case of the 15-min. cured sample (53.5% C, 29.7% O, 5.1% N, and 11.3% Al), which presented some aluminum in the spectrum indicating that the film thickness was less than the 6-h cured sample, there was a significant increase in the N concentration in contrast to the bulk and the 6-h cured sample, suggesting that adjacent to the metal surface the adhesive had a composition enriched in DDA. The observed decrease in the C concentration pointed out that the degree of cross-linking at this region was less than that in material located far away from the interphase and in the bulk.

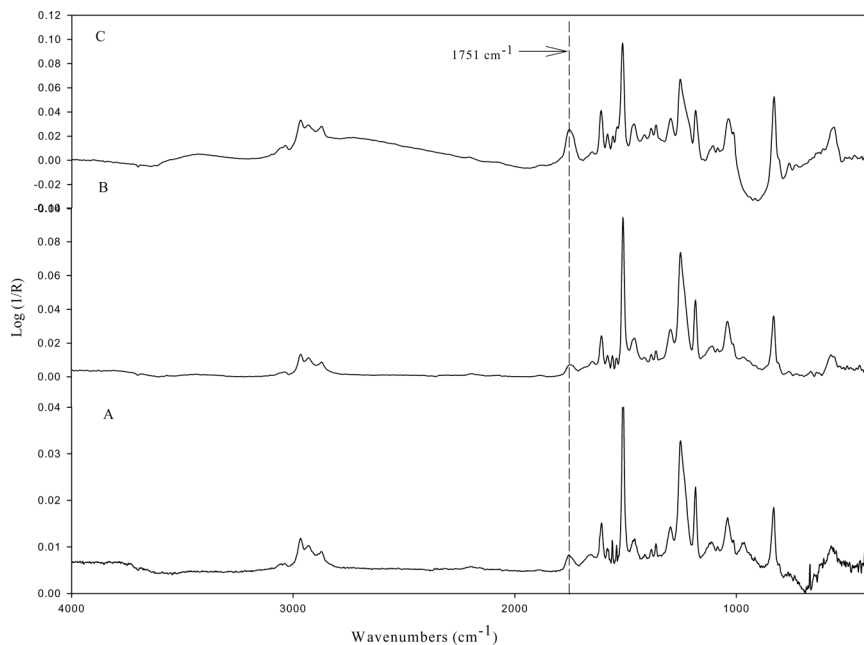


FIGURE 11 RAIR spectra of thin films formed by spin coating the model adhesive onto polished aluminum substrates from (A) 1%, (B) 5%, and (C) 5% solutions in DMF, curing for 6 h at 150°C under nitrogen, and rinsing with DMF. The film thicknesses and spin coating rates were 40 Å, 30 rpm; 500 Å, 30 rpm; and 1300 Å, 20 rpm, respectively.

To characterize the interfacial region in greater detail, the N(1s) spectra of the samples were analyzed. Curve fitting of the N(1s) spectra usually required a single component located near 399.5 eV for the bulk adhesive cured at 150°C for 6 h and for the thin films cured at 150°C for 15 min and 6 h. However, the shape of the N(1s) spectrum

TABLE 3 Surface Composition of the Bulk Adhesive and the Samples Prepared by Spin-Coating Model Adhesive onto Polished Aluminum Mirrors from a 1% Solution in DMF

Sample description	C (%)	O (%)	N (%)	Al (%)
Bulk adhesive	78.8	17.6	2.5	—
As-deposited model adhesive after curing at 150°C for 15 min and rinsing with DMF	53.5	29.7	5.1	11.3
As-deposited model adhesive after curing at 150°C for 6 h and rinsing with DMF	79.6	17.5	2.9	—

for the thin film cured for 15 min was somewhat different from the spectra of the bulk adhesive and the thin film cured for 6 h (see Figure 12). To determine the origin of this difference, the high-resolution N(1s) spectrum of the thin film that was cured for 6 h was subtracted from that of the sample cured for 15 min (see Figure 12). A small peak located near 398.3 eV was observed and assigned to $C\equiv N$ groups [34], indicating that there was a higher concentration of nitrile groups close to the substrate surface for thin films cured for 15 min than for films cured for 6 h. These results were consistent with those obtained from RAIR.

These results indicated that there was a unique interphase in the model adhesive adjacent to the aluminum substrate and that the structure of the interphase was different from that of the bulk of the model adhesive. These differences were mainly due to the interaction between the curing agent and aluminum that caused a lack of nitrile groups during curing and changed the extent of reaction. It is

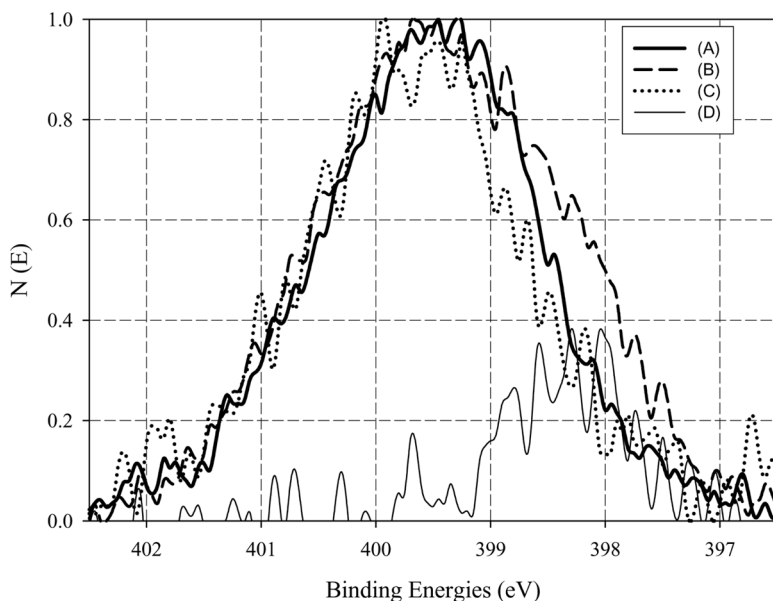


FIGURE 12 High-resolution N(1s) spectra obtained at a 45° take-off angle from (A) the model adhesive consisting of DGEBA and DDA in a 7:1 molar ratio, after curing at 150°C for 6 h, (B) a thin film of the model adhesive that was spin-coated onto an aluminum substrate from a 1% solution in DMF and cured for 15 min and (C) 6 h at 150°C under nitrogen and rinsed with DMF. Curve (D) shows the difference spectrum, B minus C.

likely that the main stage of curing (epoxy–amine and epoxy–hydroxyl reactions) was not affected by this interaction. However, the second stage of curing that corresponds to the growth of a strong carbonyl peak at 1751 cm^{-1} was inhibited.

3.3. Model Adhesive on Electrogalvanized Steel (EGS)

Adsorption of the model adhesive system onto EGS was also studied for comparison. RAIR spectra of the model adhesive system spin-coated onto EGS from 1% solutions in DMF are shown in Figure 13. The spectrum of the as-deposited film is shown in Figure 13(A), whereas the spectrum of a film that was heated at 150°C in nitrogen for 6 h and then rinsed with DMF is shown in Figure 13(B); the

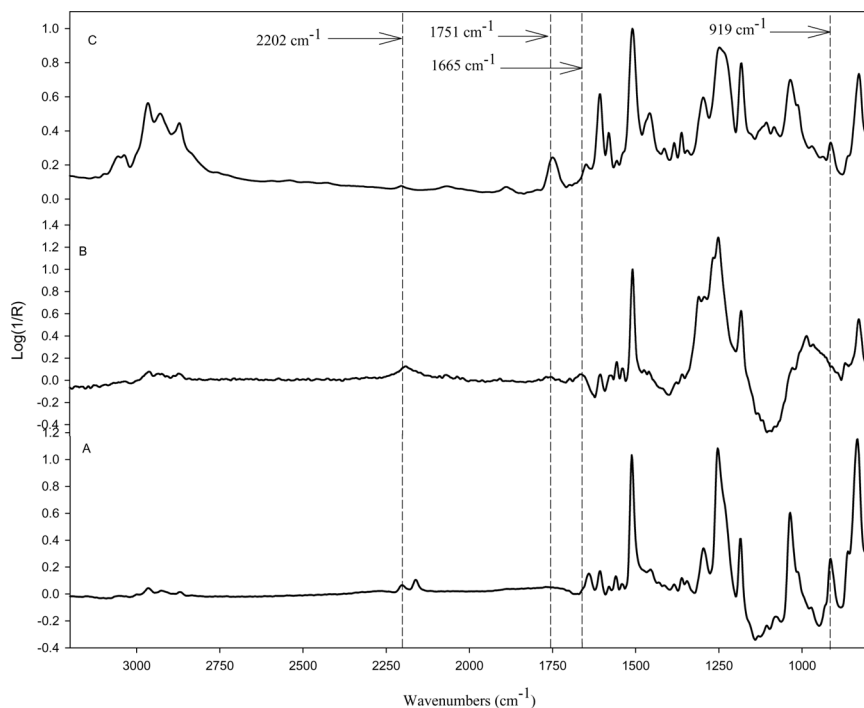


FIGURE 13 RAIR spectra obtained from thin films of the model adhesive that were spin-coated onto EGS substrates from 1% solutions in DMF: (A) before and (B) after curing at 150°C for 6 h under nitrogen and rinsing with DMF. The transmission infrared spectrum of the model adhesive obtained by mixing DGEBA and DDA in a 7:1 molar ratio and curing at 150°C for 6 h is shown in (C).

transmission spectrum of the model adhesive system after curing at 150°C for 6 h is shown for reference in Figure 13(C). The RAIR spectra of the films formed on EGS substrates were quite similar to the spectra of films formed on aluminum (see Figure 3). The intensity of the epoxy and nitrile bands decreased throughout the reaction, new bands appeared at 1665 cm^{-1} and 1751 cm^{-1} , and the bands due to the nitrile groups shifted to lower wavenumbers. However, it was observed that the band near 1751 cm^{-1} was much weaker and the band near 1665 cm^{-1} was much stronger for films cured against EGS than for films cured against aluminum. These findings suggested that the degree of curing on EGS was lower than on aluminum. When thin films of DDA in contact with EGS were heated for 15 min and rinsed with DMF, the bands due to $\text{C}\equiv\text{N}$ bonds of DDA remained after heating, and a significant shift ($\sim 25\text{ cm}^{-1}$) in the nitrile peaks to lower wavenumbers was recognized, as on aluminum (see Figure 14).

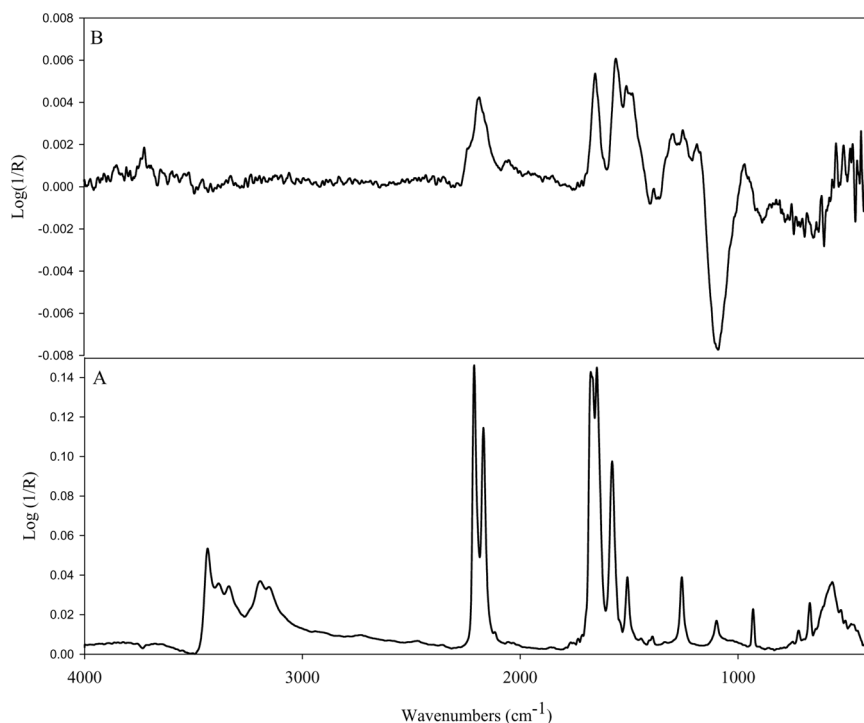


FIGURE 14 RAIR spectra of films formed by spin-coating DDA from a 1% solution in DMF onto EGS: (A) before and (B) after heating for 15 min at 150°C under nitrogen and rinsing in DMF.

These results are consistent with those obtained by Carter *et al.* [7] in previous infrared studies using RAIR. They suggested that DDA was reduced to a carbodiimide compound when heated with metallic zinc at 170°C for 5 min. Holubka and Ball [35] obtained results from a molecular modeling approach that supported the findings of Carter *et al.* They showed that the most stable tautomer of DDA as well as the structure of the most likely zinc/DDA reduction product was consistent with the results from infrared spectroscopy, *i.e.*, with a carbodiimide intermediate.

Although the curing agent presented similar behavior on EGS as on aluminum, it was observed that, in the first 15 min of curing, the IR

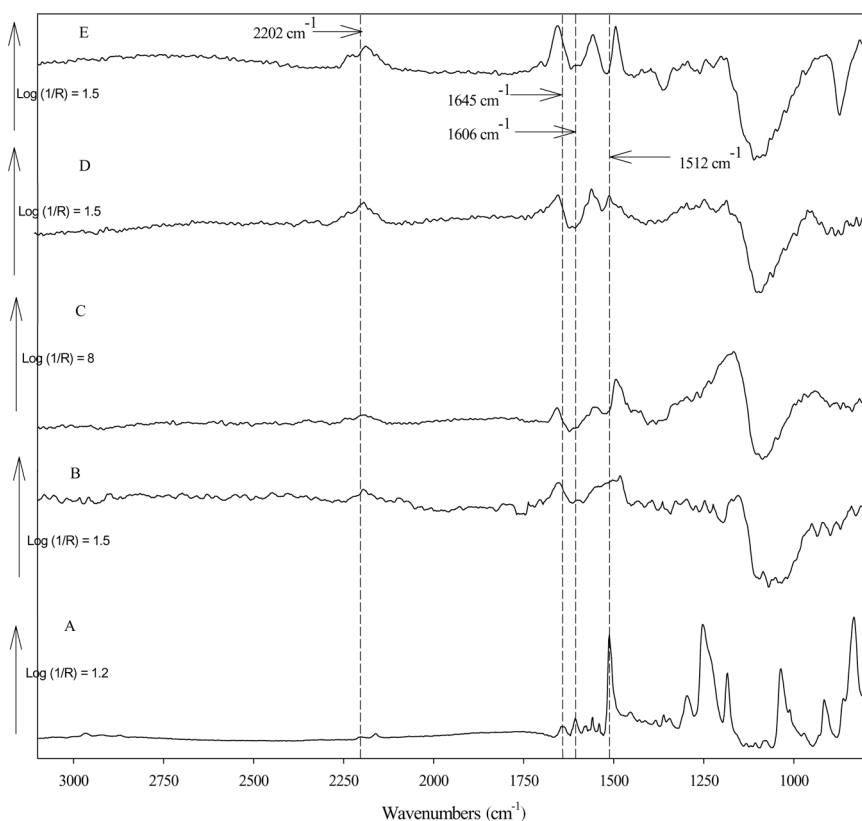


FIGURE 15 RAIR spectra obtained from films formed by spin-coating a 1% solution of the model adhesive in DMF onto EGS substrates: (A) before and after curing at 150°C under nitrogen for (B) 2.5, (C) 5, (D) 10, and (E) 15 min and rinsing with DMF.

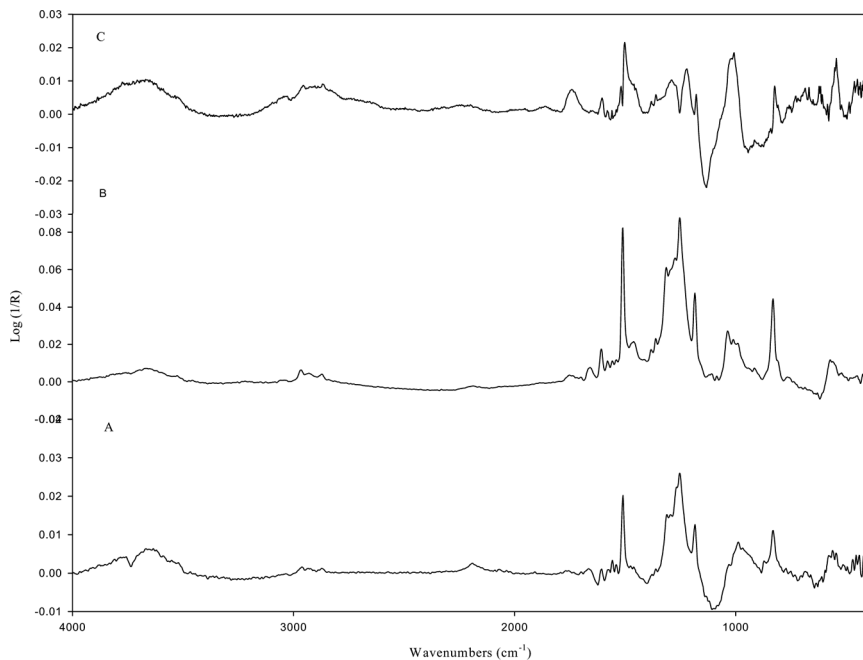


FIGURE 16 RAIR spectra obtained from thin films formed by spin-coating the model adhesive onto EGS substrates from (A) 1%, (B) 5%, and (C) 5% solutions in DMF, curing for 6 h at 150°C under nitrogen, and rinsing with DMF. The film thickness and spin-coating rates were 27, 30 rpm; 425, 30 rpm; and 1048 Å, 20 rpm, respectively.

spectrum presented only main bands of DDA when the epoxy adhesive was cured in contact with the surface of EGS (see Figure 15), which indicated that the curing rate was strongly affected by the zinc/DDA interaction.

The effect of film thickness on curing properties on EGS gave somewhat similar results to those on aluminum surfaces. As the film thickness of the adhesive was increased on the substrate surface, the intensity of the carbonyl band near 1751 cm^{-1} increased and the spectrum became similar to that of the bulk of the adhesive (see Figure 16). However, the amount of adhesive adsorbed on the EGS surface was less than that on Al.

4. CONCLUSIONS

RAIR analysis suggested that a model adhesive consisting of DGEBA and DDA formed an interphase with a unique molecular structure

when cured in contact with aluminum substrates. The differences in molecular structure were mainly due to the interaction between DDA and the metallic substrate. DDA was found to adsorb on the surface *via* the lone pair of electrons on the nitrogen atoms of nitrile groups. A slight decrease in the stretching frequency of the nitrile bond suggested an additional back-bonding interaction between aluminum ions and the nitrile groups. Slight back donation of electrons from the metal to the curing agent resulted in a reduction product that led to the formation of the carbodiimide form of DDA. These reactions between DDA and the aluminum surface caused a lack of nitrile groups during curing and changed the extent of reaction by inhibiting the formation of oxazolidine structures. These effects were much more pronounced when the model adhesive was cured against EGS; EGS was found to react with DDA and was also reduced to a carbodiimide compound. However, the EGS/DDA interaction not only changed the extent of curing close to the metal surface but also retarded the polymerization rate.

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