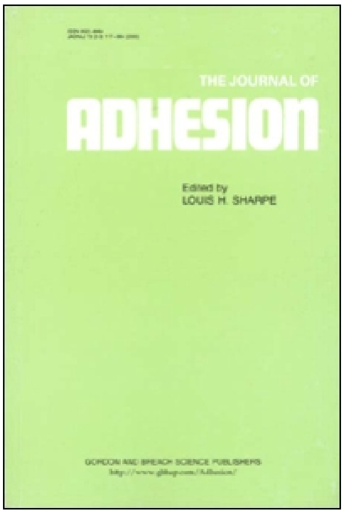

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Zinc Coated Steel/Epoxy Adhesive Systems: Investigation of the Interfacial Zone by FTIR Spectroscopy*

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The present study takes advantage of the ability of Fourier Transform Infrared Spectroscopy (FTIR) for the analysis of ultrathin organic films on metals. FTIR in the reflection mode (IRRAS) is used in order to study the interaction of ultrathin films of dicyandiamide (hardener of most one-pack epoxy resins) with various substrates, model ones such as gold or zinc and industrial ones such as steel and zinc-coated steels.

Pure zinc surfaces and, to a lesser extent, zinc-coated steels are shown to react with dicyandiamide after heating at 180°C, as evidenced by the frequency shift of the absorption band (at about 2200 cm^{-1}) characteristic for nitrile groups. As real systems consist of thick layers of a fully formulated adhesive cured onto a metallic substrate, the direct investigation of such a buried interphase is no longer possible by FTIR and by most of the known spectroscopies. Some mechanically tested specimens are then analysed, after failure, by FTIR microspectrometry. The spectra obtained, corresponding to the fracture initiation zone which is about 100 μm in diameter, advocate for the presence of an ultrathin layer of modified polymer still covering the substrate.

KEY WORDS epoxy/dicyandiamide adhesive; galvanised steel; adhesion; interphase; infrared spectrometry and microspectrometry; FTIR; IRRAS; thin films; surface analysis.

INTRODUCTION

For corrosion-protection purposes, the automotive industry uses more and more zinc-coated steels for the elaboration of car bodies. Some recently manufactured ones consist of more than 30%of such steels. Adhesive bonding of such materials appears as a valuable process and is generally performed with epoxy resins. From a chemical point of view, the surface of a hot-dip galvanised steel is quite complicated.[1] It has been shown that some elements, such as aluminium, which are added to the galvanisation bath, can be found at high concentration at the surface of the coated steel and play a detrimental

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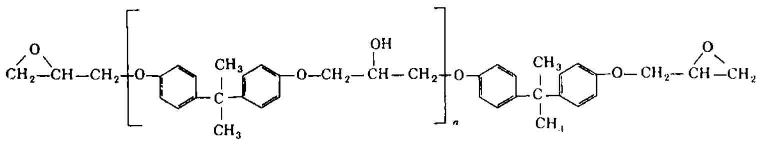
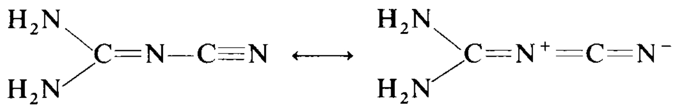
role with respect to adhesion properties.[2] Segregations of lead (another component of the galvanisation bath) and aluminium, particularly at grain boundaries, have also been shown to be responsible for adhesion strength decrease upon exposure to wet atmosphere.[3] The one-pack adhesives mainly used are mixtures of DGEBA (diglycidyl ether of bisphenol A, $M_w = 340$ g.mol^{-1}) and dicyandiamide (dicy: $(NH_2)_2C{=}N{-}C{\equiv}N$) with some accelerators (benzylamines or imidazoles). The chemical formula of DGEBA is recalled here:



From an infrared point of view, this molecule is clearly identified by its main absorption bands at about 1509 cm^{-1} (ν(C—C) in aromatic rings) and 1248 cm^{-1} (ν_{as}(C—O) in aromatic ether). Curing of epoxy resins with dicy is quite a complicated phenomenon, account being taken of its high functionality, its low solubility in epoxy resins and of its various chemical forms.[4-7] It is generally taken as granted that the two following chemical forms, refered to as A and B, can be distinguished by distinct infrared absorption bands for C≡N groups, the B form corresponding to a weakening of the C≡N bond by a resonance effect:



$$(H_2N)_2C{=}N{-}C{\equiv}N \longleftrightarrow (H_2N)_2C{=}N^+{=}C{=}N^-$$

Previous results[8,9] suggest that dicy can readily react with zinc surfaces. Such a reaction is known to modify interfacial properties, for example by displacing some organic contaminants.[10] The purpose of this study is to determine if such a chemical reaction can lead to the formation of an interphase between the substrate and the bulk adhesive, the presence of which could give explanations for the results provided by adhesion mechanical tests.

As a first step, gold-dicy and pure zinc-dicy systems are studied by FTIR and compared. Industrial systems such as cold-rolled steel and various zinc-coated steels are considered also. Then, three-point flexure test[11] specimens are prepared with an industrial system which consists of galvanised steel and of an epoxy adhesive. After fracture under test, the delamination zone is analysed by FTIR microspectrometry at grazing angle (GAMFTIR), in order to determine if a thin film of adhesive remains or not on the substrate and if this layer originates from an interphase, the chemical composition of which differs from the bulk adhesive.

EXPERIMENTAL

The model substrates are obtained by evaporation from tungsten wires of pure gold or zinc onto glass slides in a 10^{-4} Torr vacuum. The industrial substrates, provided by

SOLLAC (Montataire, France), are cold rolled steel (CRS), hot-dip galvanised steel (HDGS) and electrogalvanised steel (EGS).

The dicy thin films are deposited by spreading a 10^{-3} mol.l^{-1} solution, in methanol or dimethylformamide, on the substrates and then spin-coating them at 2000 rpm for 2 min. The samples are placed for 30 min in the spectrometer atmosphere (dry air) and analysed. Then samples are heated for 5 min at 180°C, which is the temperature at the beginning of adhesive curing, allowed to cool in air, rinsed with methanol in order to remove unreacted organic material, placed in the spectrometer for 30 min, and analysed again.

The three-point flexure test specimens are obtained according to the standard (NFT 76143) procedure described elsewhere.[11] The adhesive was provided by SHELL (Louvain la Neuve, Belgium) and consists of Epikote 828 with Epikure DX191 hardener. As this model mixture does not contain any accelerator (such as an imidazole) curing at 180°C is not possible. In order to avoid a strong exothermic effect, curing is achieved by four steps of 30 min at 180, 185, 190, and 195°C, respectively, Before testing, the bonded samples are maintained 3 days in a chamber at 95% R.H., 70°C. The test is carried out at a displacement speed of 0.5 mm min^{-1}.

The XPS data are recorded on an RIBER SIA200 multitechnique (XPS, AES, ISS) spectrometer, equipped with a MAC2 analyser. Non monochromatised MgKα radiation is used for XPS analysis and the take-off angle of analysed photoelectrons is 45 degrees.

The FTIR spectra are recorded on a NICOLET 710 spectrometer fitted with a liquid nitrogen-cooled MCT detector, and a SPECAC reflection accessory. This accessory allows one to work at variable incidence angle. In order to obtain a good sensitivity to ultrathin layers, an angle of 80° is chosen and the infrared radiation is polarised with the electric field vector within the incidence plane (p mode) by means of a SPECAC ZnSe grid polariser. As this device uses a single beam technique, a background is collected on each substrate prior to organic coating. Microspectrometry is performed with a NIC-PLAN device, fitted to the 710 bench, and equipped with both conventional (40°, x15) and grazing incidence (84°, x32) objectives. Such a device allows one to select visually and then to analyse by FTIR (in reflection or transmission mode) areas ranging from 20 to 250 μm in diameter. Diffuse reflectance (DRIFTS) experiments are carried out with the Collector accessory from SPECTRATECH. Heating cell experiments are performed with the multimode device #2000 from AABSPEC.[12] This cell enables one to perform FTIR analysis in transmission and reflection modes with controlled sample temperature (up to about 500°C) and cell atmosphere.

RESULTS

Surface Treatment of Hot-dip Galvanised Steel

In order to choose a specimen preparation procedure, the effects of surface treatments of HDGS are evaluated by AES as shown in Figure 1. We consider the apparent peak-to-peak height ratios for samples as-received (a), after acetone (b), trichloroethylene (c), and ethyl acetate (d) degreasing in an ultrasonic bath. Degreasing with ethyl acetate is

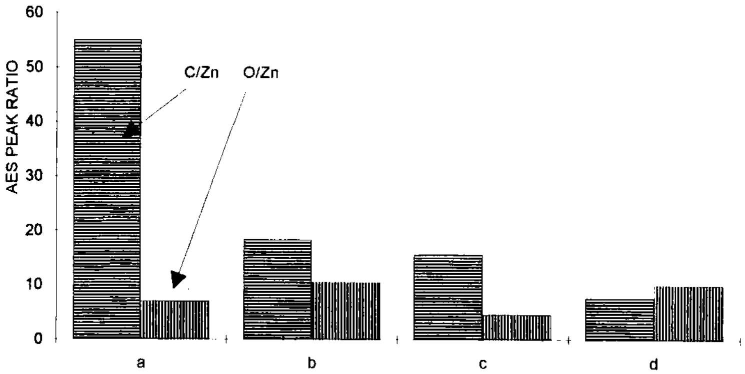


FIGURE 1 AES analysis of HDGS as-received (a), after acetone (b), trichloroethylene (c), and ethyl acetate (d) degreasing (apparent peak-to-peak height ratios).

chosen for the remainder of this study because it is efficient for removing organic contaminants (lower C/Zn peak ratio) and it avoids the contamination by chlorine carried by solvents such as trichloroethylene. Spectra shown in Figure 2 are characteristic of ethyl acetate-degreased samples (a) submitted, under industrial conditions, respectively to alkaline etching (b) and chromic rinsing (c). These treatments are shown, respectively, to remove most of the aluminium contamination (disappearance of Al2s and Al2p peaks) and to create a chromate-like layer covering the HDGS surface (appearance of Cr2p and Cr3p peaks and decrease of Zn-related features) and are then expected to modify the reactivity of the substrate surface with respect to some organic compounds.

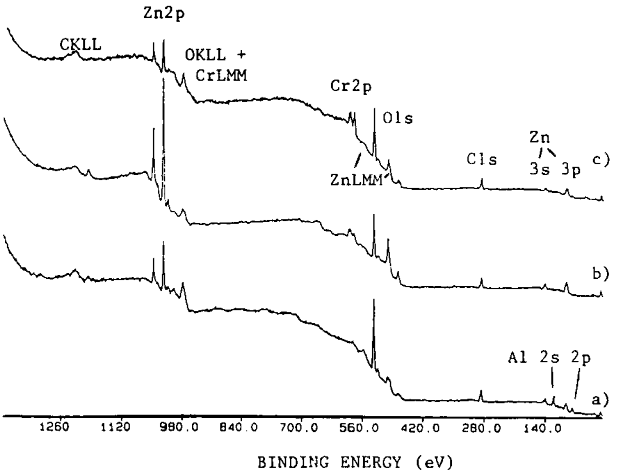


FIGURE 2 XPS spectra of HDGS degreased with ethyl acetate (a) and then submitted to alkaline etching (b) and chromic treatment (c).

TABLE I
Assignment of the main IR absorption bands of dicy
(from Ref. 13)

wavenumber (cm^{-1})	assignment
2208	$\nu(C\equiv N)$
2165	$\nu(C\equiv N)$
1658	$\delta(NH_2)$
1639	$\delta(NH_2)$
1587	$\nu_{as}(N-C-N)$
1506	$\nu_{as}(N=C-N)$

Reaction Between Dicyandiamide and Metallic Substrates

The results shown in Figure 3 are relative to dicy thin layers deposited onto gold and zinc prior to (a) and after (b) heating at 180°C and methanol rinsing. The main IR absorption bands of dicy are listed in Table I, according to data from the literature.[13] Before heating, the dicy thin layers deposited onto gold and zinc both exhibit the main absorption bands characteristic of bulk dicy.

After heating and methanol rinsing, no trace of organic compound is detected on the gold substrate. Here gold is considered as an inert metal, for instance not exhibiting oxidation-reduction catalytic properties, and is used as a "zero-reaction" surface to take into account the possible formation of dicy degradation products. Conversely, the spectrum recorded on zinc shows the main bands remaining after heating, which

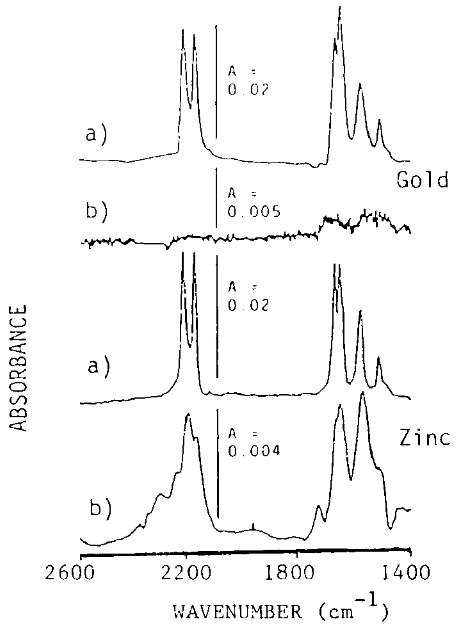


FIGURE 3 IRRAS spectra of dicy deposits on gold and zinc prior to (a) and after (b) heating at 180°C for 5 min and methanol rinsing.

indicates that no degradation reaction of dicy occurs, although the amount of material is drastically decreased. Although quantification is not easy in such an analytical case, the low values of absorbance recorded on the corresponding spectrum are consistent with 2 nm thick films as reported by Holubka *et al.*[14] The difference of behaviour between the two substrates investigated here advocates the formation of a definite zinc-dicy compound. Such a reaction is observed neither with aluminium [15,16] nor with iron.[17]

As evident from Figure 3, the most interesting modification of dicy when heated onto zinc concerns nitrile bands in the spectral range 2100–2300 cm^{-1}. Figure 4 is relative to industrial substrates, ethyl acetate degreased and then covered with thin dicy layers, heated for 5 min at 180°C and methanol rinsed. Spectra plotted in Figure 4 are characteristic of dicy deposits heated onto CRS (b), HDGS (c) and EGS (d) substrates and of the original uncured deposit (a). No reaction product can be detected on CRS. Conversely, nitrile bands shifted towards lower frequencies clearly appear in the spectrum of EGS and, to a lesser extent, in that of HDGS. As shown in previous work on model substrates,[16] the presence of aluminium at the top surface of HDGS partially inhibits the zinc-dicy reaction compared with what is observed on pure zinc.

Epoxy Resin—Metal Interface and Adhesion

The aforementioned results only deal with the behaviour of dicy alone on various substrates. As the main purpose of this compound is to act as a hardener of epoxy resins, similar experiments are to be carried out with complete systems in order to know if such a dicy-zinc reaction remains possible. Very thin layers of DGEBA/dicy stoichiometric mixture are spread by spin-coating onto a HDGS surface, then mounted in the reflection FTIR heating cell, heated at 180°C and *in-situ* analysed *versus* curing time. In these conditions of continuous, *in-situ* analysis, organic material removing by solvent is, of course, impossible and the totality of the adhesive layer is investigated. The spectral changes shown in Figure 5 (bathochromic shift of the nitrile band) clearly

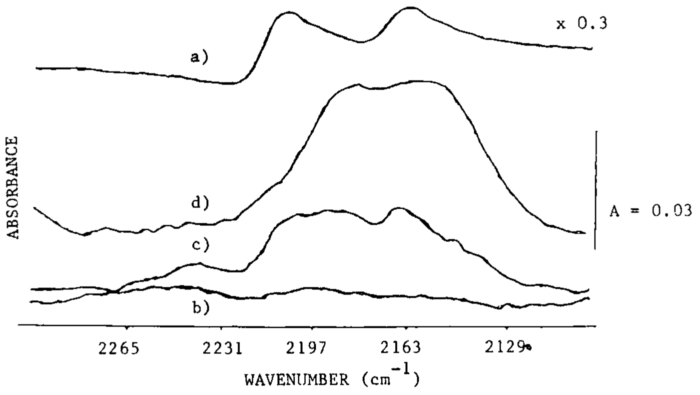


FIGURE 4 IRRAS spectra of nitrile bands for dicy deposits on CRS (b), degreased HDGS (c), and EGS (d) after heating at 180°C for 5 min and methanol rinsing. Unheated deposit spectrum is drawn as reference (a).

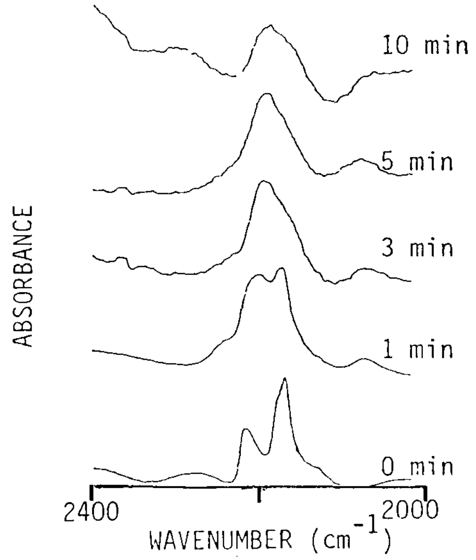


FIGURE 5 Change in FTIR spectrum (nitrile bands region) during curing at 180°C of a thin layer of DGEBA/dicy mixture deposited onto HDGS surface (*in-situ* analysis in reflection heating cell).

advocate the reaction between the HDGS surface and dicy, even in presence of epoxy resin. Such an observation is in full agreement with the results of Carter *et al.*[8] As zinc and iron are shown to behave in different ways with respect to dicy, it seems interesting to compare the curing of ultrathin adhesive films on both of these substrates. The experiments are carried out in a heating cell and Figure 6 shows, for the two substrates, the change of the parameter $r = 1 - (h(t)/h(t = 0))$, where h is the height of the peak at

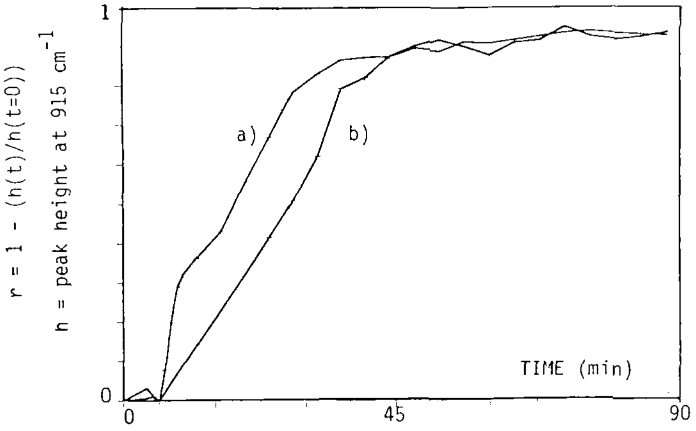


FIGURE 6 Curing of a thin layer of DGEBA/dicy mixture on zinc (a) and iron (b) surfaces (*in-situ* analysis in reflection heating cell).

915 cm^{-1} characteristic of epoxy groups. These curves show a quite marked difference in curing kinetics. Although no explanation is given, for the time being, for such a phenomenon, other examples of curing activation of an adhesive on a zinc surface have been reported elsewhere in the literature.[18] In fact, FTIR spectroscopy alone is not able to elucidate the change in curing mechanism with respect to the nature of the substrate and we can only observe the consequences of it. In the particular case of DGEBA-dicy systems, the curing mechanism is so complex[4-7] that it is not fully understood, even in the case of bulk adhesive where a lot a powerful techniques (calorimetry, chromatography, etc.) are available which cannot be used in surface science.

From the pioneering work of Greenler,[19] it is well-known that the sensitivity of IRRAS for the detection of ultrathin films on metals can greatly be improved by using grazing incidence (about 80° or more) of the infrared beam. As far as microspectrometry is concerned one could not take advantage of such an enhancement before the very recent development of grazing incidence objectives. An example is shown in Figure 7, relative to the surface of a HDGS sample exposed some hours to the laboratory atmosphere. Both of the spectra are recorded on the same area (100 μm in diameter) at near-normal (a) and grazing (b) incidences. The value of 100 μm corresponds to the sample area which is actually irradiated after partially masking the original IR beam of about 250 μm in diameter. Only GAMFTIR allows the detection of ν(C—H) absorption bands representative of the organic contamination of the substrates by oil residues and by exposure to ambient atmosphere. This result justifies the use of GAMFTIR for the remainder of the study. Such a sensitivity enhancement is very useful in adhesion studies where one could erroneously conclude from a conventional micro-FTIR spectrum that interfacial failure had occurred, while the GAMFTIR spectrum gives evidence for cohesive failure within the polymer.

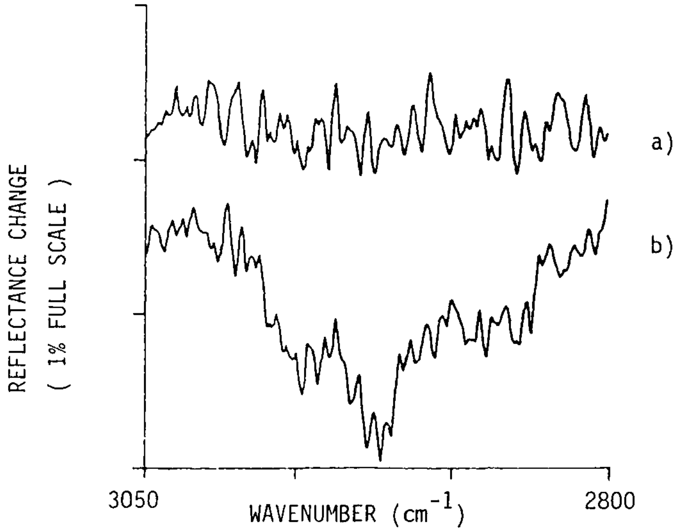


FIGURE 7 Micro-FTIR spectra (ν(C—H) zone) of the surface of a HDGS sample submitted to alkaline etching, recorded on the same area (100 μm in diameter) at near-normal (a) and grazing (b) incidences.

In order to know if a dicy-substrate reaction, which occurs in a model system, can play a significant role between galvanised steel and epoxy adhesive, three-point flexure specimens were prepared and tested. As fracture initiation is the main phenomenon influencing the results of this test, the corresponding zone is investigated by GAM-FTIR, using a spot of about 100 μm in diameter. The corresponding spectrum is shown in Figure 8a. The analysis is carried out directly on an industrial sample and, therefore, the spectrum is not of high quality. However, it clearly appears that a thin layer of polymer remains at the sample surface after fracture. Though the main bands characteristic of DGEBA and dicy can be seen, this spectrum is quite different from what one can expect from bulk adhesive (Fig 8b). Particularly, a high concentration of C≡N groups is to be noted. This observation is in full agreement with some XPS and EPMA results indicating a huge nitrogen enrichment near the galvanised steel / epoxy interface.[20] As the C≡N band undergoes a large modification when the zinc/dicy reaction takes place, it seems interesting to focus on the spectral range 2300–2100 cm^{-1}, as reported in Figure 9, for bulk adhesive deposited on gold, before curing (a), bulk adhesive deposited on gold, after curing (b), reaction product of dicy with pure zinc (c), and for a delaminated sample (d). The comparison of spectra (a) and (b) confirms that the C≡N groups take an active part to curing, as has been largely reported in the literature. Spectrum (c) shows that the considered absorption bands undergo a shift of about 10–20 cm^{-1} towards low frequencies. Finally, the spectrum of the polymer remaining after failure (Fig. 9d) exhibits features quite different from those of the bulk adhesive and closer to the spectrum 9c.

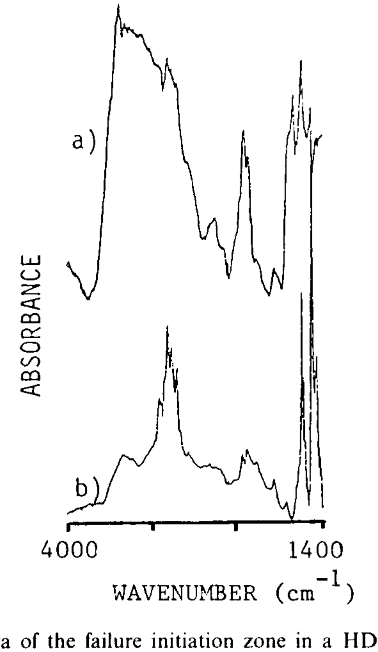


FIGURE 8 GAMFTIR spectra of the failure initiation zone in a HDGS/epoxy adhesive three-point flexure test sample (a) and of epoxy adhesive before curing (b).

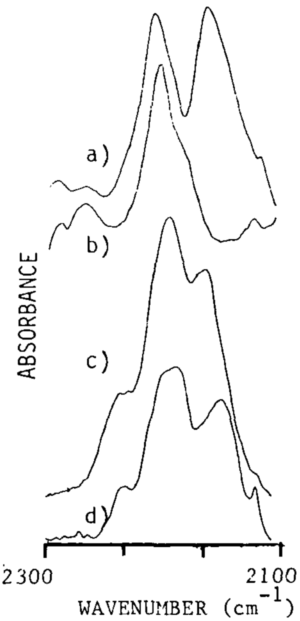


FIGURE 9 FTIR spectra of C≡N band for bulk adhesive (deposited on gold) before curing (a), bulk adhesive (deposited on gold) after curing (b), reaction product of dicy with pure zinc (c), and for a delaminated sample (d).

As alkaline treatment of HDGS has been shown by XPS to be responsible for removal of most of the top surface aluminium contamination, the comparison of the fracture initiation zone composition prior to and after this treatment is of interest. The relevant spectra are drawn in Figure 10, respectively after sample degreasing with ethyl acetate (a), and etching in an alkaline bath (b). In the first case very little polymer can be detected at the failed sample surface. This observation suggests a near-interface delamination. After alkaline etching (followed or not by chromic rinsing) a thin adhesive layer still covers the failed surface, advocating a cohesive fracture in a weak boundary layer of the adhesive. This displacement of failure locus is correlated to an improvement of adherence (chromic rinsing $\geq$ alkaline etching $\gg$ degreasing) as shown by the three point flexure test results presented in Figure 11.

Although a quantitative evaluation is difficult, the amount of modified polymer remaining after failure of etched samples is much larger than a few molecular monolayers and originates from a real interfacial zone. Its extent is investigated by studying a failed single lap shear specimen. This sample is made from two etched HDGS sheets bonded with a 300 μm thick adhesive layer. After cohesive disbonding, the remaining adhesive is gradually abraded using SiC discs (13 mm in diameter) which are analysed by DRIFTS. The so-obtained spectra are ratioed against a background recorded on a virgin SiC disc. Although this technique, which is largely employed for characterisation of paint layers, appears to be crude, about 1–2 μm can be removed at each step. In Figure 12 is plotted the variation of the apparent nitrile (about 2200

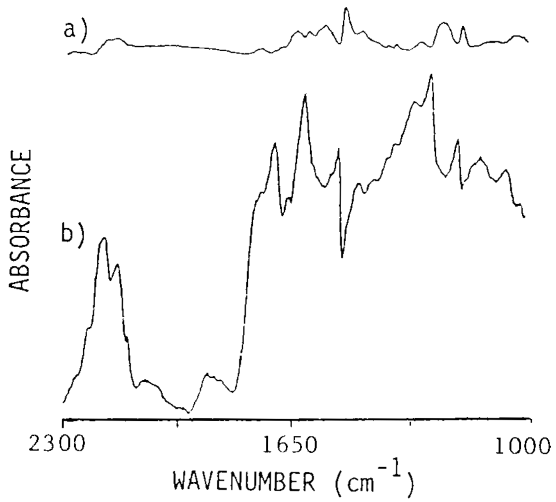


FIGURE 10 GAMFTIR spectra of the failure initiation zone in a HDGS/epoxy adhesive three-point flexure test specimen. Samples degreased (a) and submitted to alkaline etching (b).

cm^{-1})/aromatic(1509 cm^{-1}) band ratio with mechanical abrading. A marked tendency to nitrile enrichment close to the zinc-coated surface is evidenced. The augmentation of the nitrile/aromatic ratio near the substrate surface cannot be attributed to an increase of the extinction coefficient of the nitrile band upon reaction with zinc because such an increase does not appear in the case of pure dicy reaction product on zinc (see Fig. 3) where the nitrile/N—H band ratio remains quite constant after heating. Under these

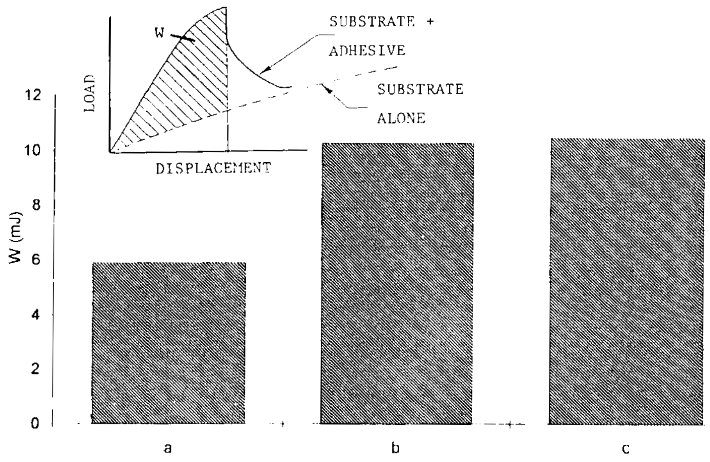


FIGURE 11 Three-point flexure test results for HGDS/epoxy adhesive systems. HDGS treatment is: ethyl acetate degreasing (a), degreasing followed by alkaline etching (b), and alkaline etching followed by chromic rinsing (c).

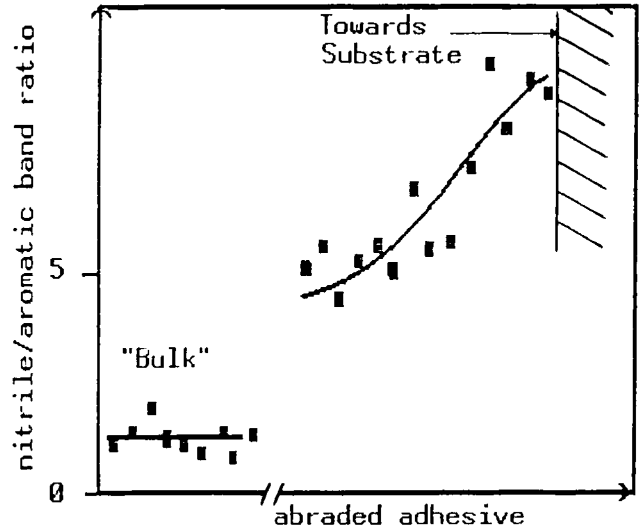


FIGURE 12 Variation of nitrile/aromatic band ratio (DRIFTS), *versus* mechanical abrading, for the adhesive remaining after the failure of an etched HDGS/epoxy single lap shear test specimen.

conditions, one could expect a change in nitrile band spectra recorded at various stages of the abrading process; the closer to the substrate, the more it is governed by the zinc-dicy reaction. This is fully confirmed by the spectra plotted in Figure 13 which undergo such a change. The spectra of the adhesive layers which are closer to the substrate exhibit nitrile bands with the bathochromic shift characteristic of the zinc-

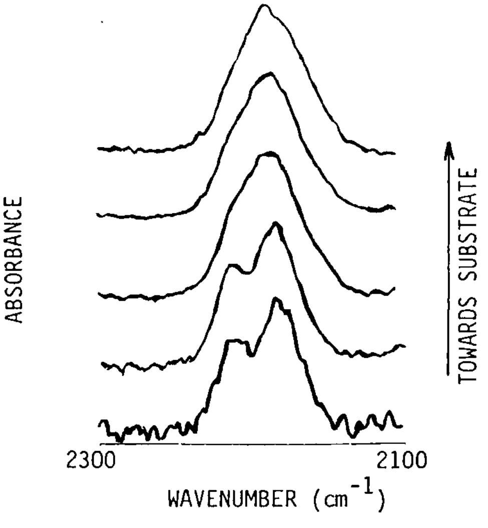


FIGURE 13 DRIFTS spectra (nitrile bands region) at various stages of mechanical abrading (see also Fig. 12).

dicy reaction product (see Fig. 9c). The results presented (Figs. 12 and 13) give evidence for the diffusion of such compounds creating an interphase between the substrate and the bulk adhesive.

DISCUSSION AND CONCLUSION

By means of model systems, dicy is shown to react readily when heated in contact with zinc substrates. A theoretical study carried out by Holubka and Ball,[21] and supported by previous experimental work of Carter *et al.*,[8] suggests that the reduction of dicy by metallic zinc is likely to occur. The FTIR spectral changes observed after heating the dicy on zinc show the formation of a definite compound. The major changes are relative to the nitrile band. Upon end-on coordination to a metal, through the nitrogen lone-pair orbital, this band is known to shift generally towards higher frequencies.[22] The shift towards low frequencies that we observe suggest that the dicy acts as a π acceptor.[23] As the amine groups of dicy seem unaffected by the reaction with the zinc-coated surface, our results advocate the formation of a radical anion reduction product which leads to the formation of a carbodiimide (proposed from $(NH_2)_2CH—N{=}C{=}N—Zn\ldots$) at the zinc-coated surface, as previously stated by Holubka and Ball.[21] In this context, such a reaction should be governed by the electron donor (basic) properties of the substrate surface and is, therefore, very dependent on the nature of the metal (no reaction occurs with iron or aluminium) and surface treatment. Some further experiements are being carried out in our laboratory to correlate acid-base properties of the surfaces to their reactivity with organic materials in the fields of adhesion science. The purpose of this paper is not to elucidate fully the mechanism of dicy reaction with metallic surfaces but to show that such reactions can exist, that they depend upon the nature and treatment of the metallic surface and that they can influence adhesion properties. As far as real systems are concerned, the analysis of the adhesive/zinc interphase is not possible directly. Therefore, we investigate the fracture initiation zone of three-point flexure test specimens, made from hot dip galvanised steel and a fully formulated one-pack epoxy adhesive. The analysis, performed by grazing incidence FTIR microspectrometry with a spot 100 μm in diameter, clearly indicates that a thin layer of polymer remains on the metal after fracture occurs. This polymer layer is quite different from the bulk adhesive. In fact, it is a modified zone of adhesive near the coated steel surface, greatly enriched in $C{\equiv}N$ groups. Such a nitrogen enrichment has also been reported by Hong and Boerio[10] in the case of oil-contaminated steel substrates bonded with epoxide adhesives cured with amidoamine agents having low amine number. These authors give evidence, using XPS, that such adhesives could displace oil from the steel surface. Dickie *et al.*,[24] studied by XPS the interfacial chemistry of epoxy/dicy adhesive bonded to cold-rolled and galvanised steels. They drew the conclusion that the failure between zinc and adhesive is not mainly governed by the original contamination layer, which is partially displaced during adhesive curing. This is supported by our previous FTIR results[16] which indicate that the zinc/dicy reaction occurs on pure zinc even when it is covered with ASTM #3 oil, and by the work of Debski *et al.*,[25] which shows that an epoxy resin can displace a non-polar mineral oil from a metal surface. These authors also demonstrate that oil from metal surfaces can be absorbed by a dicy-cured epoxy resin, which is then plasticised and undergoes a low crosslinking. The present work gives evidence for the presence of an interphase, originating from the affinity between zinc and dicy and from contaminant displacement by the zinc/dicy interaction. Boerio *et al.*[26] have also shown such a preferential dicy adsorption on silver, leading to an interphase that was relatively rich in curing agent. The extent of the modified polymer layer is far larger than some molecular layers, which could indicate a diffusion of the dicy-zinc reaction products within the bulk adhesive. Such an explanation is largely supported by recent results of Kinzler, Grunze *et al.*,[27,28] obtained by XPS "microscopy". This interfacial zone exhibits chemical (and obviously mechanical) properties which are very different from the ones of the bulk polymer. The formation of such a weak boundary layer can, therefore, lead to a cohesive failure within the adhesive.

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