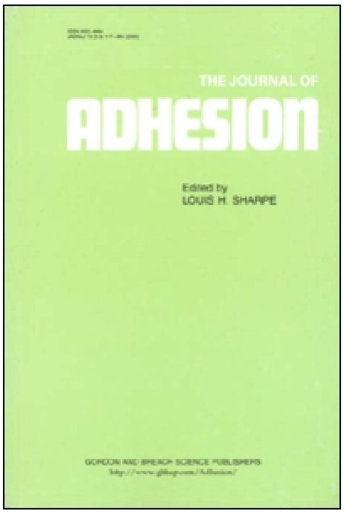

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Comparison of the Degradation Mechanisms of Zinc-Coated Steel, Cold-Rolled Steel, and Aluminium/Epoxy Bonded Joints

M. Brémont[a][b]; W. Brockmann[a]
[a] Arbeitsgruppe Werkstoff und Oberflächentechnik (AWOK), Fachbereich Maschinenwesen, Universität Kaiserslautern, Kaiserslautern, Germany [b] A. RAYMOND GmbH, Spezialbefestigungssysteme Weltweit, Lörrach, Germany

To cite this Article Brémont, M. and Brockmann, W.(1996) 'Comparison of the Degradation Mechanisms of Zinc-Coated Steel, Cold-Rolled Steel, and Aluminium/Epoxy Bonded Joints', The Journal of Adhesion, 58: 1, 69 — 99
To link to this Article: DOI: 10.1080/00218469608014400
URL: http://dx.doi.org/10.1080/00218469608014400

J. Adhesion, 1996, Vol. 58, pp. 69–99
Reprints available directly from the publisher
Photocopying permitted by license only

Comparison of the Degradation Mechanisms of Zinc-Coated Steel, Cold-Rolled Steel, and Aluminium/Epoxy Bonded Joints*

M. BRÉMONT** and W. BROCKMANN

Arbeitsgruppe Werkstoff und Oberflächentechnik (AWOK), Fachbereich Maschinenwesen, Universität Kaiserslautern, Postfach 3049, 67663 Kaiserslautern, Germany

(Received May 30, 1995; in final form October 31, 1995)

The durability properties of bonded lap shear joints made from an epoxy/dicyandiamide adhesive and zinc, zinc-coated steel, two different aluminium alloys or cold-rolled steel metal coupons have been investigated. The influence of the dicyandiamide content of the adhesive on the durability properties has been assessed by salt spray testing or by storing the joints in water at 70°C or 90°C for periods of time up to five weeks. The degradation products formed during ageing of the epoxy adhesive in water have been investigated using high performance liquid chromatography (HPLC) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). The degradation mechanisms of aluminium/epoxy bonded joints have been thoroughly studied using X-ray photoelectron spectroscopy.

The performances of the bonded joints under a pure corrosive environment have been found to be little influenced by the quantity of dicyandiamide in the adhesive. When the bonded joints were aged in hot water, the stability of the interface toward an excess of dicyandiamide directly followed the sensitivity of the oxide layer at high pH values. Optimal durability properties without peel strength losses of the adhesive were achieved both with zinc and aluminium-coated substrates by reducing the quantity of dicyandiamide in the epoxy adhesive by 20% (the initial dicyandiamide content in the commercial adhesive being *ca.* 9%, with respect to the epoxy resin).

KEY WORDS: Adhesion; aluminium; aluminium alloys; cold-rolled steel; DRIFT, durability; epoxy adhesive; HPLC; infrared spectroscopy; interphase; morphology; X-ray photoelectron spectroscopy; zinc; zinc-coated steel.

1. INTRODUCTION

For the past thirty years, scientists dealing with adhesion problems have emphasized the great influence of the adherend surface on the reactions taking place in the interphase region of a bonded joint. As a result, the structure of the adhesive layers located within the first nanometers close to the metal surface have been found to differ from that of the bulk adhesive. However, it is still not clear today to what extent such

---

* One of a Collection of papers honoring Jacques Schultz, the recipient in February 1995 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

** Corresponding author. New address: A. RAYMOND GmbH, Spezialbefestigungssysteme Weltweit, Teichstrasse 57, 79539 Lörrach, Germany.

effects as the modification of the polymer structure, cross-linking density, segregation of adhesive components at the metal/adhesive interface, affect the long term properties of the bonded joints. For instance, a bad curing of the adhesive resulting in a segregation of highly polar amino-residues at the interface of a dicyandiamide-cured epoxy/metal interface can jeopardize the hydrolytic stability of the bonded joints. On the other hand, too high a level of cross-linking in the interphase region is likely to render the adhesive brittle and lead to premature failure during mechanical testing of the joints.

The curing mechanisms of dicyandiamide/epoxy resin systems have been investigated by many research groups.[1–3] Due to its insolubility in the adhesive at room temperature, dicyandiamide is latent and only reacts with the epoxy resin when heated (above 80°C). At the present time, the common analytical tools make it difficult to follow the polymerization reactions occuring between multifunctional epoxy resins and dicyandiamide so that most of the results available from the literature deal with investigations on model systems. Reference 1 is recommended for a recent review of the currently accepted curing mechanisms.

The three main products stemming from the reaction of diglycidylether of Bisphenol A and dicyandiamide are presented in Figure 1. The main reaction product (pathway 1) is formed by addition of the primary amino groups of dicyandiamide to the epoxy

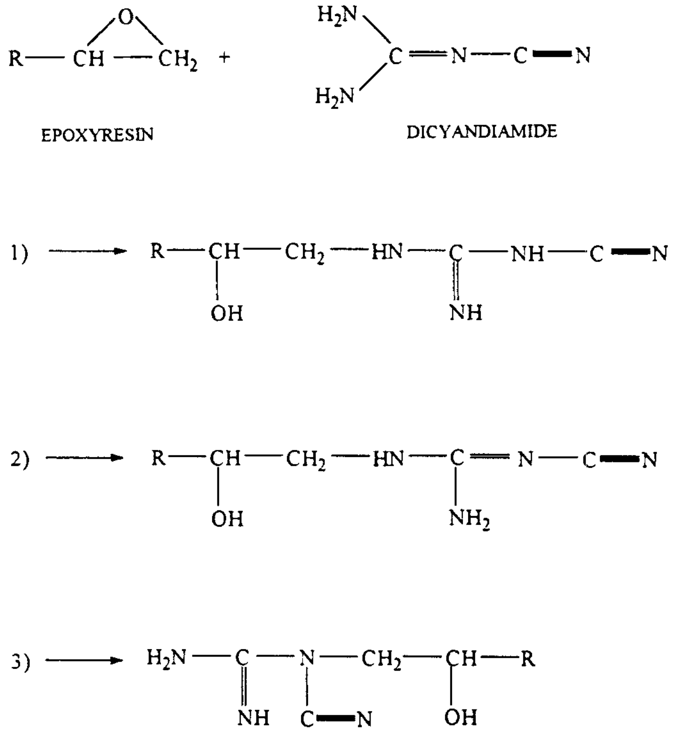

FIGURE 1 Main reaction pathways between dicyandiamide and an epoxy resin.

group of the resin. Two other products (pathways 2 and 3) stemming from side reactions involving the nitrile or the C=NH group can also be formed.[1] Zukas *et al.* showed, using mixtures of diglycidylether of bisphenol A and 3,3′- or 4,4′-diaminodiphenyl sulfone curing agents, that the presence of finely-divided aluminium oxides (used as high surface area models of aluminium adherend surfaces) resulted in a catalysis of the adhesive curing as well as the homopolymerization of the epoxy resin.[4-5] The model adhesive used by the authors did not contain any accelerator, thus allowing one to pinpoint directly the catalytic effects of the aluminium oxides using DSC. While the presence of aluminium oxides resulted in a much faster initial rate of reaction, the cured, filled adhesives had lower glass transition temperatures, showing that the aluminium oxides lowered the cross-linking density of the model adhesives.

At about 210°C, the melting of dicyandiamide is accompanied with an endothermal peak with a minimum at 216°C (Fig. 2a). The exothermal peak between 220°C and *ca.* 292°C gives evidence that a reaction is taking place in this temperature range. Bente *et al.* carried out similar experiments and showed that the product most likely to be formed is melamine.[1] A study was carried out to determine the influence of the metal or metal oxide on the transformation of dicyandiamide into melamine. At (powder), Al_2O_3 (corundum, activated, neutral or basic), and Fe_2O_3, each mixed at a 1:1 weight ratio with dicyandiamide, did not bring any change in the main features of the DSC spectra (Fig. 2b). But the spectrum obtained from the zinc metal/dicyandiamide mixture was greatly modified (Fig. 2c). The minimum of the endothermal peak associated with the melting stage of dicyandiamide was shifted toward lower temperatures, around 202°C (−15°C). The effects were the same for zinc oxide. The transformation of dicyandiamide was completed at 213°C, as against 290°C for the other metal oxides/dicyandiamide systems. The much faster reaction rates for these systems clearly show that zinc or zinc oxide is likely to catalyze the transformation of dicyandiamide into melamine. The effects were similar when reducing the zinc oxide/dicyandiamide ratio to 1/10 and 1/20 and were still significant with a 1/100 ratio.

Gaillard *et al.* showed that, whereas dicyandiamide readily reacts with pure zinc, it reacts far less with galvanized and not at all with cold-rolled steel.[6] The formation of a urea complex between zinc-coated steel and products stemming from the hydrolysis of dicyandiamide has been investigated in detail by Holubka *et al.*[7-9] Carter *et al.* also demonstrated that a zinc-coated surface has a greater tendency to form a complex with dicyandiamide than a surface covered with iron oxide, but the influence of a zinc-dicyandiamide complex at the metal/adhesive interface remains unclear.[10]

While the presence of side products stemming from the polymerization reaction can influence the quality of the metal/adhesive interface in the unaged state, the products used in the formulation of the adhesive and, in particular, their presence in the vicinity of a hydrated oxide layer can also affect the long-term properties of the bonded joints. Under the influence of heat and moisture, dicyandiamide can be transformed mainly into three products (Fig. 3). Guanylurea is the hydrolysis product of dicyandiamide obtained under acidic conditions and cyanurea can be obtained in significant amounts when dicyandiamide is heated up in a concentrated sodium hydroxide solution.[11] The cyclization reaction leading to melamine is only possible at higher temperatures.[1]

It is not possible to solve the durability problems by replacing dicyandiamide with an acid anhydride curing agent. The curing times of acid anhydride/epoxy systems are

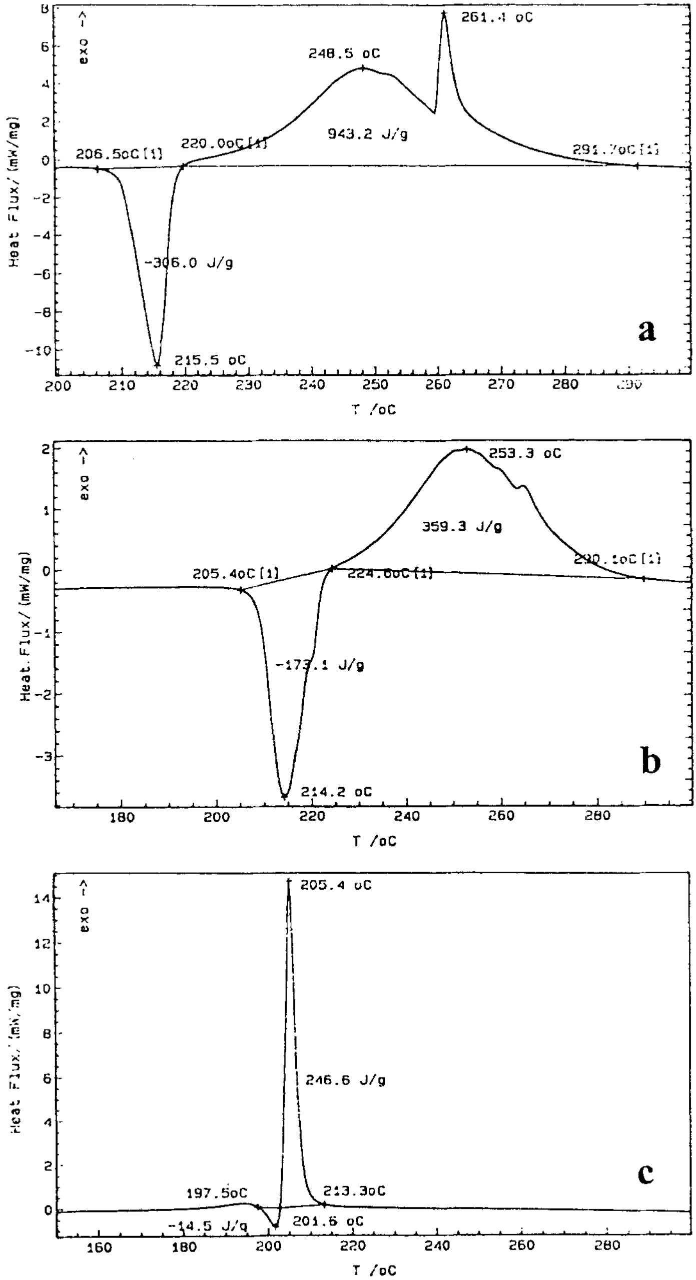

FIGURE 2 Influence of the metal oxide on the transformation of dicyandiamide (a) Dicyandiamide; (b) Dicyandiamide/neutral aluminium oxide (1:1) (c) Dicyandiamide/Zinc oxide (1:1).

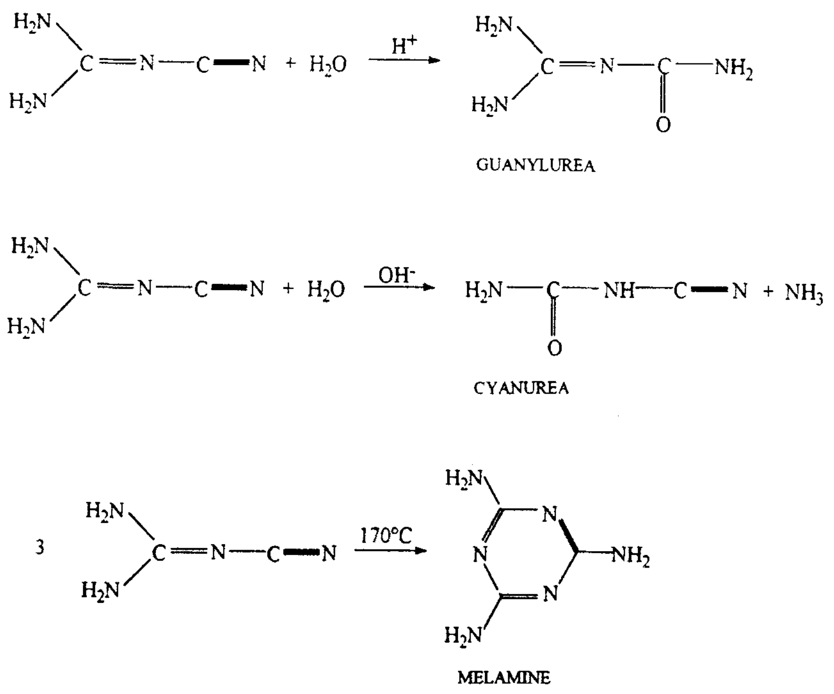

FIGURE 3 Possible pathways for the degradation of dicyandiamide.

too long and acid anhydrides do not enable the formulation of one-component (1K) systems.[12] Our efforts to find new methods leading to an improvement of the hydrolytic stability of bonded joints have focused in the past three years on the study of well-known adhesion promoters such as the silane coupling agents, the development of zinc-specific coupling agents as well as methods aiming to generate stable oxide layers at the surface of zinc-coated substrates.[12–13]

The present study describes an investigation of the durability and fracture surfaces of bonded joints made from a commercial hot-curing epoxy adhesive and zinc, zinc-coated steel, cold-rolled steel or two aluminium alloys.

As is the case for most commercial hot-curing epoxy adhesives, the level of dicyandiamide in the epoxy adhesive used in this study (1K-A) is significantly above the stochiometric level necessary to ensure full curing of the adhesive (*ca.* 9%, with respect to the epoxy resin). In the first part of this study (Sections 3–4), an investigation of the formulation of the adhesive has been carried out in order to determine to what extent excess dicyandiamide in the epoxy adhesive can influence the durability performance of the bonded joints. Such an investigation had to stay within realistic limits so that the improved formulation could be used later in the automotive industry. The influence of the dicyandiamide content of the adhesive on the durability properties of the joints has been assessed by salt-spray testing or by storing the joints in water at 70°C or 90°C for periods of time up to 5 weeks. The degradation products formed during ageing of the epoxy adhesive in water have been investigated using high performance liquid chromatography (HPLC) and diffuse reflectance infrared fourier transform spectroscopy (DRIFT).

The degradation mechanisms of zinc-coated steel/epoxy bonded joints were thoroughly investigated by Dickie *et al.* in Refs. 7, 10 and 14, Foister *et al.* in Refs. 15–16 and Brémont *et al.* in Refs. 9, 13 and 17. In contrast, as structurally bonded aluminium has only found a few applications in the automotive industry, fewer XPS analyses dealing with aluminium/epoxy interfaces are available. The second part of this study (Section 5) presents an investigation of the degradation mechanisms of aluminium/epoxy bonded joints. The metal/adhesive interfaces were investigated by XPS after immersion and salt-spray tests to determine the mechanisms responsible for debonding.

2. EXPERIMENTAL METHODS

2.1 Preparation of the Bonded Joints

The zinc substrate used in this study consisted of Zn99 (1.5 mm, DIN 17770). The cold-rolled substrate is referred to as XES (0.7 mm). The zinc-coated substrates referred to as G2F and EZ2 correspond, respectively, to a 0.7 mm ultrasmooth, hot-dipped galvanized steel (Ra = 1.5 μm) supplied by SOLLAC (France) and a 0.7 mm electroplated-phosphated steel. The surfaces of XES, EZ2, and G2F were thoroughly investigated in Ref. 17.

The two aluminium alloys investigated in Section 5 consist of:

1) The crack-resistant aluminium forging alloy QQ-A-250/4 T3 (2024 T3 clad alloy) which is used as a sheet metal in civil aeroplane construction in clad-AlCuMg2. This 1.5 mm thick material is cladded on both sides with a *ca.* 50 μm thick layer of pure aluminium, QQ-A-250/1 1100, which acts as a sacrificial anode during corrosion.[11]
2) The 1.5 mm thick aluminium alloy AlMg3 (alloy 5252). The characteristics of this alloy make it ideal for car and ship building. Although not as well-performing as the alloy containing a higher level of magnesium, its corrosion resistance is very good and makes it ideally suited for structural use in agressive conditions.

The metal coupons were degreased in an ultrasonic bath for 15 min prior to bonding and subsequently bonded with a one-component, dicyandiamide-cured adhesive supplied by CECA/Elf Atochem (curing conditions: 1 hour, 200°C) and referred to as "1K-A" in the text. Lap shear and T-peel samples were made, respectively, with a 12.5 mm × 25 mm and a 100 mm × 25 mm bond overlap and a 0.2 mm bondline thickness (DIN 53281). The bonded joints were tested on a Frank UPM 81804 universal testing machine (DIN 53283).

The glass transition temperatures of the cured adhesives were determined by Differential Scanning Calorimetry (DSC) with a Netzsch DSC 200 Calorimeter (DIN 51005).

2.2 Durability Tests

The durability properties of the bonded joints were assessed using two accelerated ageing tests: "total immersion" test in water (I.T.) in air-tight containers at 70°C or 90°C ("I.T.") (DIN 53 287) or the salt spray test ("S.S.T.") (35°C, 5% NaCl) (DIN 50 021-SS).

2.3 Surface Analysis

XPS analyses were performed with an SSI model 301 spectrometer using focused (diameter of the irradiated area: 600μm) monochromatic AlKα radiation (10 kV, 10 mA). The residual pressure in the chamber was approximately 5×10^{-8} Pa. The sample charging effects were minimized with a low energy flood gun (5 eV). The calibration of the spectra was done with the C(ls) (284.8 eV) from the carbonaceous contaminant overlayer. The spectra were recorded in the constant pass energy (50 eV) mode. XPS peaks were decomposed into subcomponents using a Gaussian (80%)-Lorentzian (20%) curve-fitting program with a nonlinear (Shirley)[18] background. Quantitative analyses were performed with the sensitivity factors given by Scofield.[19]

3. INFLUENCE OF THE DICYANDIAMIDE CONTENT OF 1K-A ON THE DEGRADATION OF THE BONDED JOINTS

The epoxy adhesive 1K-A is a typical one-component epoxy adhesive used in the production line of automotive manufacturers to bond cold-rolled or zinc-coated steels. An investigation of the formulation of the adhesive was carried out in order to determine to what extent excess dicyandiamide in the epoxy adhesive could influence the durability performance of the bonded joints.

Apart from requirements concerning the durability performance, the two most important values influencing the choice of an automotive manufacturer for a particular adhesive are the peel and the shear strengths. As the quantity of dicyandiamide directly influences the extent of polymerization of the adhesive, the peel strength of unaged bonded joints is much more sensitive to the dicyandiamide content than the shear strength.

The modified adhesives were prepared from a formulation of 1K-A free of any dicyandiamide. The required quantity of dicyandiamide was added to 100 g of resin and the resulting adhesive was thoroughly mixed for 30 minutes and then degassed under vacuum (10^{-5} Bar) for an additional 30 minutes.

The choice of cold-rolled steel for the assessment of the peel strength of unaged specimens was dictated by the cohesive nature of the failure for this steel. The bad bonding properties of the zinc coating for G2F (peeling within the zinc coating during mechanical testing) makes it difficult to measure the peel strength of the adhesive.[17] The curing cycle used in this investigation was satisfactory to ensure the full curing of the adhesive (1 hour, 200°C).

Figure 4 illustrates the great influence of the dicyandiamide content of the adhesive on the initial T-peel strength of XES/1K-A bonded joints. The adhesive 1K-A is already optimized with respect to the peel strength, with a value of 39.9 ± 3.1 N/cm. Variations within the range ± 20% dicyandiamide (relative to the initial formulation) do not modify the peel strength significantly. An excess of dicyandiamide in the adhesive increases the cross-linking density and makes the cured adhesive more brittle. Hence,

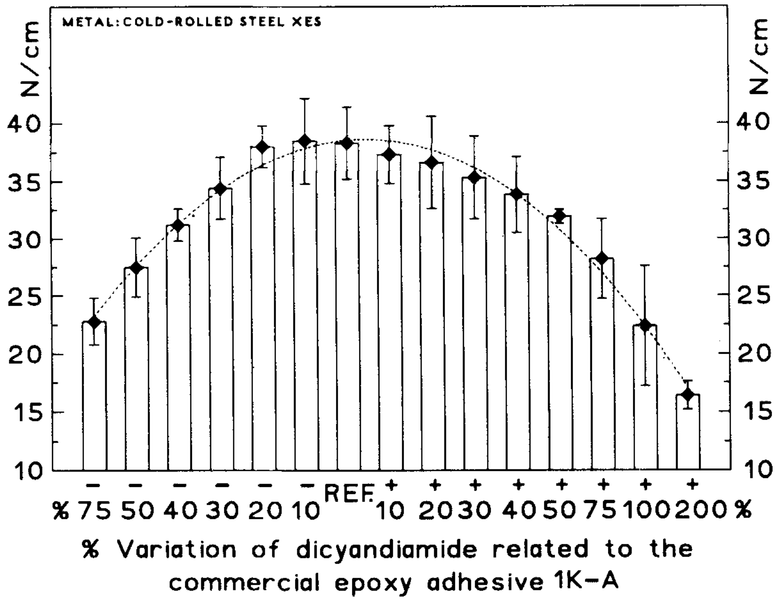

FIGURE 4 Influence of the dicyandiamide content of 1K-A adhesive on the peel strength of XES/1K-A bonded joints.

the adhesive loses its "rubbery" character and the stress exerted during mechanical testing cannot relax to the same extent as for the adhesive containing less dicyandiamide. Therefore, the fracture, which was cohesive well inside the adhesive layer for 1K-A, takes place at the metal/adhesive interface for the adhesive containing an excess of 200% dicyandiamide. The glass transition temperature of 1K-A is not significantly influenced by a dicyandiamide content variation within the range −20%/+200% ($Tg_{-20\%/+200\%} = 106 \pm 3$°C), giving evidence of satisfactory curing of the adhesive for a dicyandiamide level 20% lower than that of the commercial adhesive. However, the Tg of 1K-A −30% and 1K-A −40% are significantly lower, at 94 and 75°C, respectively. When the quantity of dicyandiamide is far too low to ensure a full curing of the adhesive, as is the case for −75%, the adhesive displays, as expected, a very high rubbery or flexible character.

Zn99 was then chosen as a model substrate to study the influence of the dicyandiamide content on the degradation of zinc/epoxy single lap shear joints. The investigations in Ref. 13 have shown that the surface of this substrate consists of 65.5% ZnO and 34.5% $Zn(OH)_2$.

Figure 5 presents the evolution of the shear strengths of Zn99/1K-A (+/− % dicyandiamide) bonded joints after 3 and 5 weeks of immersion in water at 70°C. The initial shear strength does not vary significantly for adhesives containing −40% to +100% dicyandiamide and stays within the range 15 ± 1.7 MPa. Both a big excess (> 100%) or a too low level (−50%) of dicyandiamide are detrimental to the initial adhesion.

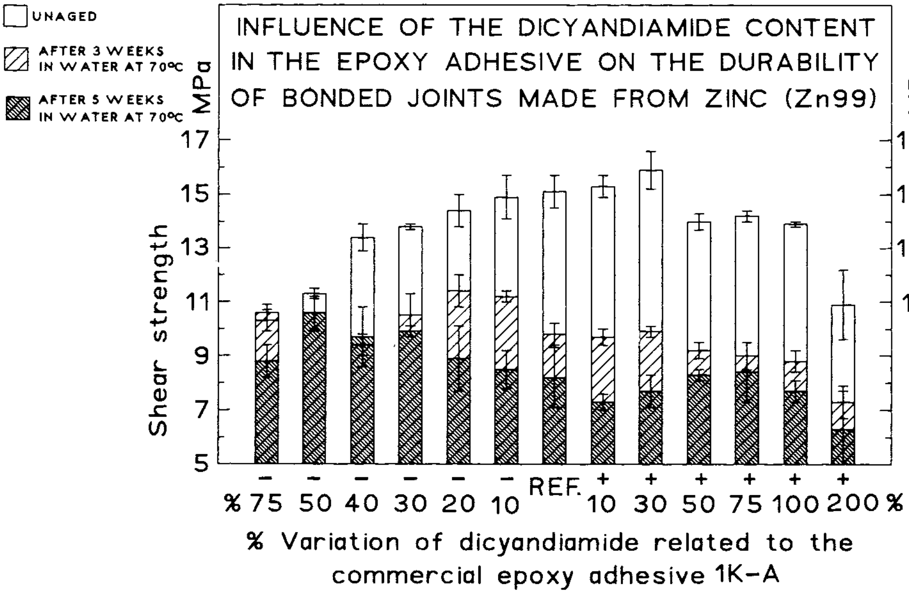

FIGURE 5 Influence of the dicyandiamide content of 1K-A adhesive on the hydrolytic stability of Zn99/1K-A bonded joints.

After 3 and 5 weeks of durability testing in water, the shear strengths stay within the ranges 8.8–11.4 MPa and 7.3–10.6 MPa, respectively. It is particularly interesting to see that an excess of up to 100% of dicyandiamide with respect to the initial formulation does not speed up the degradation process. The shear strengths stay within the small range of 7.3–8.2 MPa which is not a significant variation if one considers the experimental error (*ca.* 0.6 MPa). Although Figure 5 clearly demonstrates that the durability problems cannot be solved by simply reducing the amount of dicyandiamide in the adhesive, the trend observed for adhesives containing less dicyandiamide than the original adhesive is interesting. A progressive increase is observed after 5 weeks of testing for adhesives containing – 10% (8.5 MPa) to – 50% (10.6 MPa) dicyandiamide, as against 8.2 MPa for the reference specimens. When the residual shear strengths are expressed with respect to the initial shear strength, the improvement is more significant: 57% for 1K-A – 10, and 72 and 94%, respectively, for 1K-A – 30 and – 50.

A further study was then carried out on EZ2 (0.7 mm electroplated-phosphated steel, see Ref. 17) and G2F (0.7 mm hot-dipped galvanized steel) for adhesives containing up to 50% less dicyandiamide than the original adhesive.

As can be seen in Figure 6, the amount of dicyandiamide in the adhesive does not significantly influence the durability after the immersion test, and not at all after the salt-spray test. In agreement with what was mentioned above for 99% pure zinc, the results show a trend of improvement for adhesives containing less dicyandiamide. Considering the scattering of the values, this improvement is more pronounced for G2F than for EZ2 after the immersion test. Shear strengths 1.8, 3.2 and 2.8 MPa higher

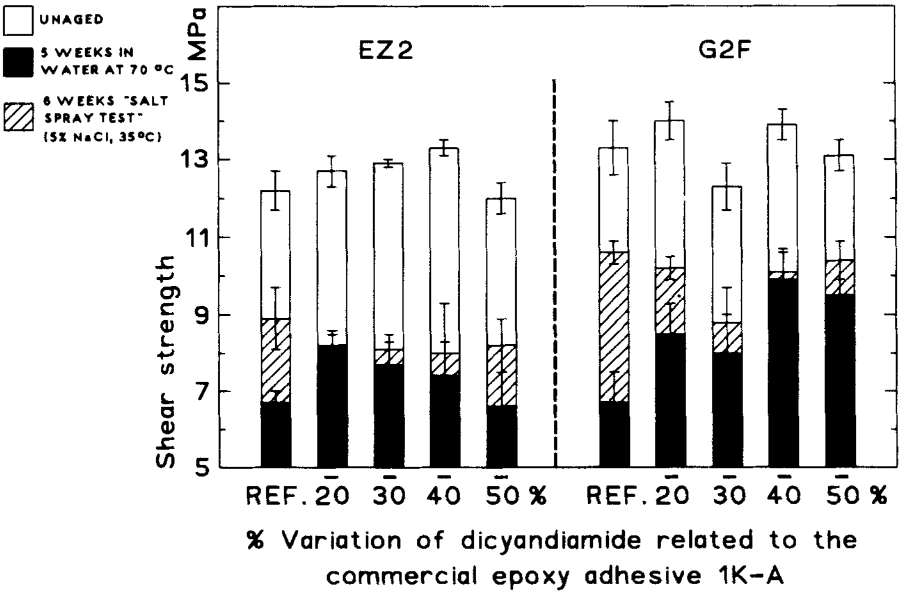

FIGURE 6 Influence of the dicyandiamide content of 1K-A adhesive on the durability of EZ2 and G2F/1K-A bonded joints.

than the reference specimens are measured on G2F for the adhesives containing −20%, −40% and −50% dicyandiamide, respectively, as against 1.5, 0.7 and −0.1 MPa for the bonded joints made from EZ2.

Small discrepancies in experimental values can be explained by the difficulty in obtaining a homogeneous dispersion of dicyandiamide in the adhesive without industrial mixers. High localized concentrations of dicyandiamide, which is very soluble in water, are likely to increase greatly the hydrophilicity of the metal/adhesive interface.

The quantity of dicyandiamide in the adhesive has a much more drastic effect on the fracture surfaces of the bonded joints than on the residual strengths. In Figure 7, the decrease in size of the corroded area near the edges of the bonded joints nicely follows the decrease in the dicyandiamide content of the adhesive. One would normally expect a rise in joint performance for the non-corroded joints made from EZ2. But it is likely that a decrease in the quantity of dicyandiamide is accompanied by a decrease in the density of polymerization near the boundary layer. This side effect could explain why the amount of adhesive left on the metal side gradually decreases when the quantity of dicyandiamide is reduced.

The particularly strong improvement observed for the hot-dipped galvanized substrate, the surface of which contains about two thirds of aluminium oxides and one third of zinc oxide,[17] led us to study the influence of the dicyandiamide content on the hydrolytic stability of bonded joints made from clad-AlCuMg2. According to XPS results which will be presented later in Section 5, the surface of clad-AlCuMg2 mainly consists of $Al_2O_3 \cdot xH_2O$. In order to reduce the number of parameters to a minimum, the tests were carried out for the +50%, REF, −20%, and −40% modified adhesives.

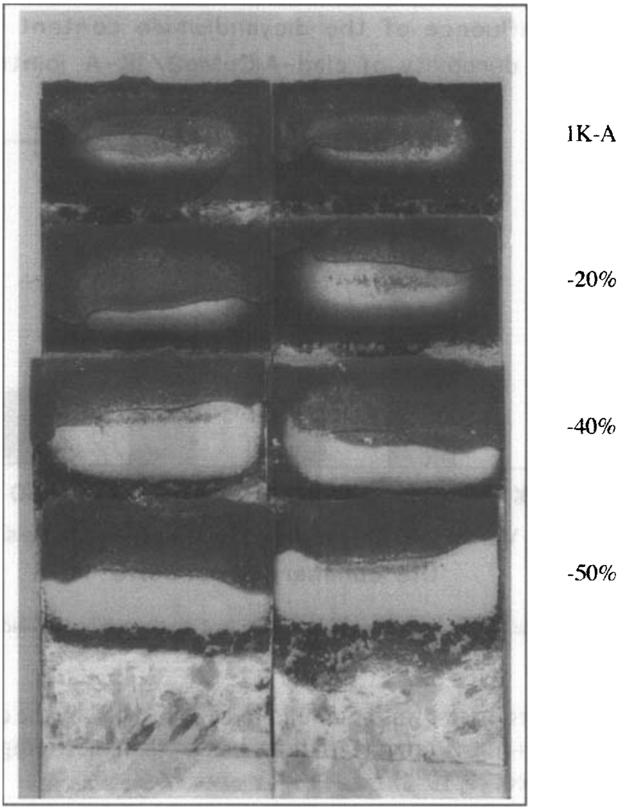

FIGURE 7 Fracture surfaces of EZ2/1K-A (top), 1K-A – 20%, 1K-A – 40%, and 1K-A – 50% (bottom) bonded joints after 5 weeks water immersion test (I.T.) at 70°C. (See Color Plate IV).

After 5 weeks of testing in water at 70°C, the residual strength of the reference specimens was still 77% of the initial strength so that the test was prolonged for an additional 3 weeks. The results presented in Figure 8 show that the influence of the quantity of dicyandiamide is far greater on aluminium oxides than on zinc oxides. While an increase of the dicyandiamide content of 50% results in a 27% decrease of the shear strength, a 20% reduction results in a 44% improvement of the shear strength, from 12.5 to 18 MPa after testing in water. The extent of delamination could also be directly related to the dicyandiamide content of the adhesive. The failure, which was 100% cohesive for all the unaged specimens, was around 30% and 55% cohesive for the reference and – 20% specimens, respectively.

Specimens were also aged following the salt-spray test but the results are not presented here. The results presented in Section 5 demonstrate that the scattering of the values for clad-aluminium samples simply degreased before bonding is too high to allow a reliable comparison of the values.

To complement this study, the long-term properties of bonded joints made from cold rolled steel and the modified adhesives were also investigated. The durability after the

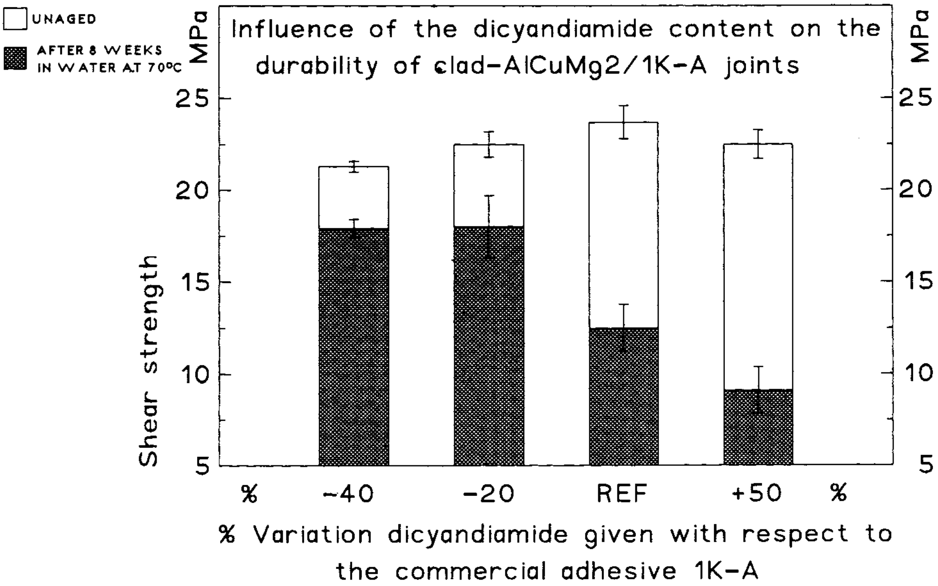

FIGURE 8 Influence of the dicyandiamide content on the hydrolytic stability of clad-AlCuMg2/1K-A bonded joints.

salt-spray or the immersion test was not found to be influenced by the dicyandiamide content in the − 50 to + 100% range (variations smaller than the average scattering of the values were observed, *ca.* 10%).

3.1 Conclusion

The performance of the bonded joints under a corrosive environment (e.g. salt-spray testing) are not influenced by the quantity of dicyandiamide, within the range − 50 to + 100% dicyandiamide, with respect to the commercial adhesive 1K-A.

When the bonded joints are aged in hot water, the stability of an interface toward an excess of dicyandiamide directly follows the sensitivity of the oxide layer at high pH values. The classification presented in Figure 9 is given along with the main components present on the surface of the substrates.

In order to reach optimal durability properties both on zinc and aluminium-coated substrates, without affecting the peel strength of the adhesive, it is advisable to reduce the quantity of dicyandiamide by 20% in 1K-A.

4. STUDY OF THE DEGRADATION OF THE EPOXY ADHESIVE 1K-A

4.1 Introduction

Brockmann *et al.* observed the formation of guanylurea on aluminium substrates anodized in phosphoric acid.[11] In their experiments, dicyandiamide was adsorbed on a

XES ($Fe_2O_3.xH_2O$)
↓
EZ2 ($Zn_3(PO_4)_2.xH_2O$)
↓
Zn99 ($ZnO.xH_2O$)
↓
G2F (60% $Al_2O_3.xH_2O$, 40% $ZnO.xH_2O$)
↓
clad-AlCuMg2 ($Al_2O_3.xH_2O$)

Increasing sensitivity of the bonded joints toward an excess of dicyandiamide
↓

FIGURE 9 Influence of the metal substrate on the hydrolytic stability of the bonded joints.

freshly anodized substrate and heated at 120°C for 30 minutes. A comparison of the infrared spectrum of pure dicyandiamide with the surface of the treated anodized substrate made it possible to pinpoint a decrease in the $C \equiv N$ intensity and the presence of some extra peaks in the $C{=}O$ region of the spectrum of the heat-treated, dicy-coated aluminium substrates. This is what is expected if the nitrile group of dicyandiamide is hydrolyzed to a carbonyl group.

4.2 HPLC Results

In the present work, the role of the metal substrate in the degradation of dicyandiamide (some of which may remain unreacted in fully-cured adhesive) was investigated by ageing 6 metal coupons (surface: 10 cm^2/coupon) of XES, A199 , $AlMg_3$, and Zn99 in 500 ml of water containing 10 grams of dicyandiamide.

In order to identify the products stemming from the degradation of dicyandiamide, a reference HPLC spectrum of a mixture consisting of dicyandiamide, cyanurea, guanylurea, and melamine was recorded (experimental method: see Ref. 12) and is presented in Figure 10a. If the polar compounds observed in this spectrum are products stemming from a degradation of dicyandiamide, they could be detrimental to the durability of the bonded joints by creating a high pH in the vicinity of the metal surface and destroying the aluminium or zinc oxides which are soluble for pH values higher than 8 and 11, respectively.

The spectrum obtained from the water extract of the zinc/dicyandiamide solution after 1 month of ageing at 70°C displays similar features and shows that both cyanurea and guanylurea, giving retention times of *ca.* 3.7 and 5.3 min respectively, are likely to be formed when dicyandiamide is aged in the presence of a zinc substrate (Fig. 10b).

By adding a small amount of guanylurea to the aged zinc/dicyandiamide solution, the intensity of the guanylurea peak increases and the presence of this latter is confirmed. The two compounds detectable at *ca.* 4 and 5.8 min. could not be identified. It is, however, possible to state that they do not originate from the possible formation of the zinc complexes of guanylurea and cyanurea. These latter compounds are not UV-active and, therefore, cannot be detected in Figure 10. Although the peak observed at 5.5 min is in very good agreement with the position recorded for melamine, it is important to emphasize that the formation of melamine normally requires much higher

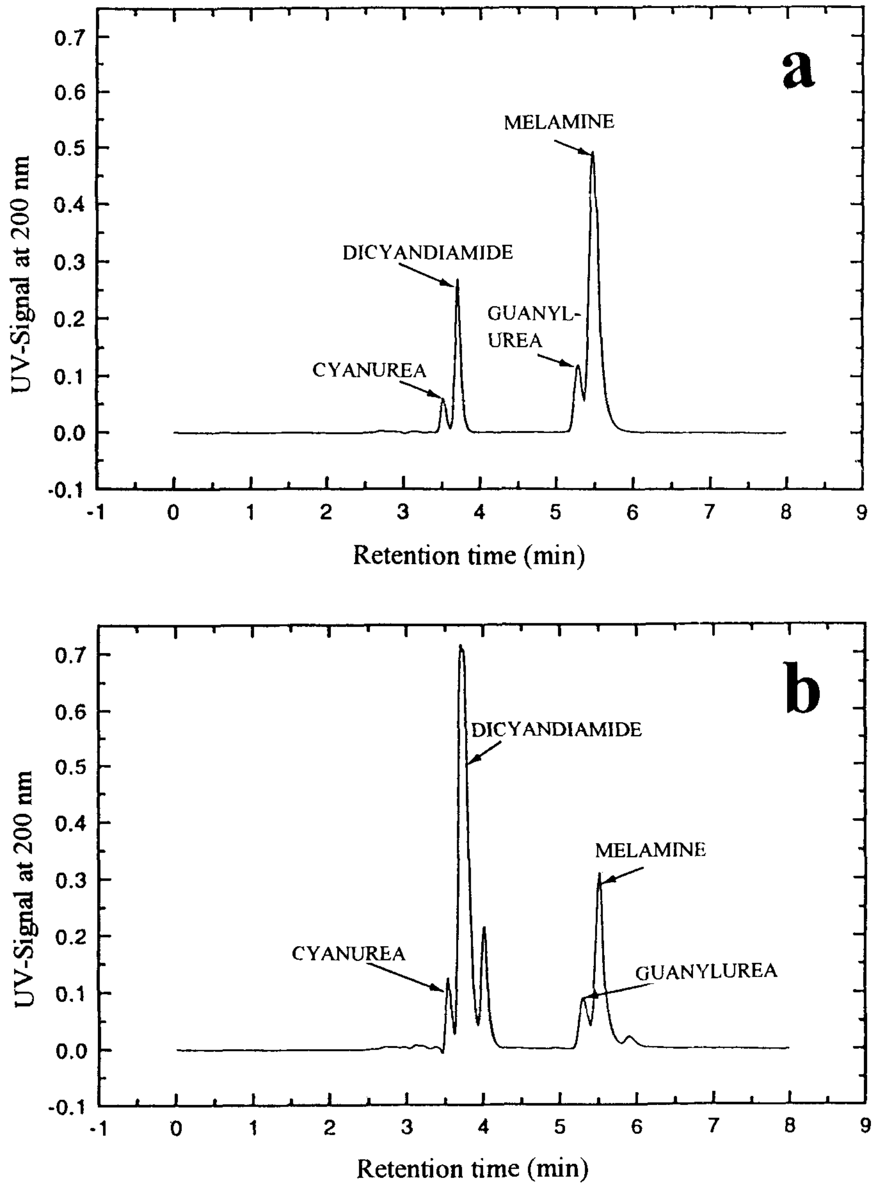

FIGURE 10 (a) Reference chromatogram of a mixture of dicyandiamide, cyanurea, guanylurea, and melamine; (b) Chromatogram of a dicyandiamide solution containing zinc metal coupons after 1 month at 70°C.

temperatures than 70°C.[1] Other amino residues stemming from the degradation of dicyandiamide with similar retention times could be formed and these results must be interpreted with great caution.

The spectra obtained from the solutions of dicyandiamide containing aluminium or steel specimens displayed the same peaks with lower intensity after ageing at 70°C for 1 month so that the degradation of dicyandiamide in hot water is largely independent of the metal substrate.

The relative intensities of the characteristic HPLC chromatograms of the acetonitrile extracts of 1K-A as well as the modified adhesives are presented in Table I. Gaps are formed between the macromolecules of the polymeric network after curing the adhesive. The impurities in the adhesive components that do not take part in the polymerization process, as well as the product in stochiometric excess and some low molecular reaction products, will fill up some of these gaps. As a result of the extraction in acetonitrile, the adhesive swells and the possibility of the substances to diffuse out of the adhesive increases. If acetonitrile makes it possible to reduce the interactions between these substances and the polymeric network to a minimum, the low molecular weight reaction/degradation products will stop diffusing only when an equilibrium with the solution is established.

While a high excess of dicyandiamide is logically detectable at 2.2 min (other recording parameters than those used in Fig. 10) in the adhesive containing + 100% dicyandiamide (about 16 times the amount measured in 1K-A), the − 30% spectrum gives the best chromatogram with the smallest amount of dicyandiamide and other reaction products or residues. The adhesive obtained by lowering the dicyandiamide content further is not satisfactorily cured, as bisphenol A and some non-polar compounds associated with the epoxy resin are clearly detectable in the − 50% spectrum.

For retention times between 2.2 and 9.6 min, the reduction of the peak areas associated with the degradation products (Table I) clearly demonstrates the lower level of polar compounds obtained by reducing the amount of dicyandiamide in the adhesive. After ageing in water, the position of the peaks in the chromatogram of 1K-A are not modified (Table II). In this range of retention time, the formation of new compounds due to the ageing of the adhesive is not observed. The higher amounts of products detected in the aged adhesive samples can be explained by the better ability of water than acetonitrile alone to break the polar interactions between the macromolecules and the smaller monomers. In addition, the aged polymer molecules are likely to be destroyed at certain locations, making it possible for monomers originally trapped in the polymeric network to diffuse out of the adhesive.

The quantity of polar products after the ageing test gradually decreases with a decreasing amount of dicyandiamide and the best result with respect to the stability of

TABLE I
Relative peak areas measured in the chromatograms of the unaged modified adhesive

Adhesive/t_R =	2.2 min	3.7 min	5.3 min	5.9 min	8.5 min	9.6 min
XEP + 100%	272.9	29.9	46.0	21.3	38.7	25.6
XEP + 50%	149.4	34.0	36.3	18.9	19.3	10.9
XEP 1K-A	16.5	38.5	16.2	16.4	0	0
XEP − 10%	4.9	18.2	9.1	9.1	0	0
XEP − 20%	0	8.1	0	0	0	0
XEP − 30%	0	0	0	0	0	0
XEP − 40%	0	0	0	0	0	0

TABLE II
Relative peak areas measured in the chromatograms of the aged modified adhesive

Adhesive/t_R =	2.2 min	3.7 min	5.3 min	5.9 min	8.5 min	9.6 min
XEP + 100%	234.4	45.0	73.5	41.7	78.2	36.7
XEP + 50%	184.2	103.4	103.5	30.0	62.5	27.3
XEP 1K-A	65.2	76.7	45.5	25.9	18.3	0
XEP − 10%	18.3	45.1	31.5	20.1	10.8	0
XEP − 20%	6.2	26.1	15.6	9.0	0	0
XEP − 30%	0	22.7	8.3	9.8	0	0
XEP − 40%	0	21.6	0	0	0	0

the adhesive is observed for the −40% sample (the high polarity of water makes it possible only to detect products with retention times smaller than 15 minutes).

Conclusions

Dicyandiamide is not stable in hot water in the presence of zinc or aluminium oxides. Several degradation products are formed and it was possible in the course of this study to identify guanylurea and cyanurea.

By reducing the quantity of dicyandiamide in the adhesive, the amount of side products or low molecular weight oligomers formed while curing the adhesive and after the immersion in water is reduced.

4.3 Investigation of the Degradation of Dicyandiamide with Infrared Spectroscopy

DRIFT (Diffuse Reflectance Infrared Fourier Transform) measurements were also carried out to analyze the chemical transformations of dicyandiamide during the ageing test in water (standard Nicolet I.R. spectrometer equipped with a diffuse reflectance accessory). This technique allows one to record an infrared spectrum directly from a metal surface.[20]

After a series of preliminary tests, 10 µl of a 10^{-2} mol·l^{-1} dicyandiamide solution prepared in isopropanol were applied on a zinc metal sample degreased in acetone. This procedure allows the deposition of a film of even thickness. The same procedure was repeated to obtain reference spectra of cyanurea and guanylurea (Fig. 11). The assignment of the main bands is summarized in Table III.[10] The spectrum of dicyandiamide exhibits a band of high intensity around 2215/2174 cm^{-1} which is assigned to the C ≡ N group. The N—C=O group in guanylurea can easily be detected through a sharp band at 1753 cm^{-1}. This band is not detectable in the spectrum of cyanurea and the conjugation of the C ≡ N bond with the C=O bond in guanylurea is likely to be responsible for a shift of this band toward lower frequencies.

After 2 months of ageing at 70°C, the spectra obtained from the solutions of dicyandiamide containing the XES, Zn99 or clad-AlCuMg2 samples exhibit important differences. In each case, after the ageing test, 1 gram of the solution was mixed with

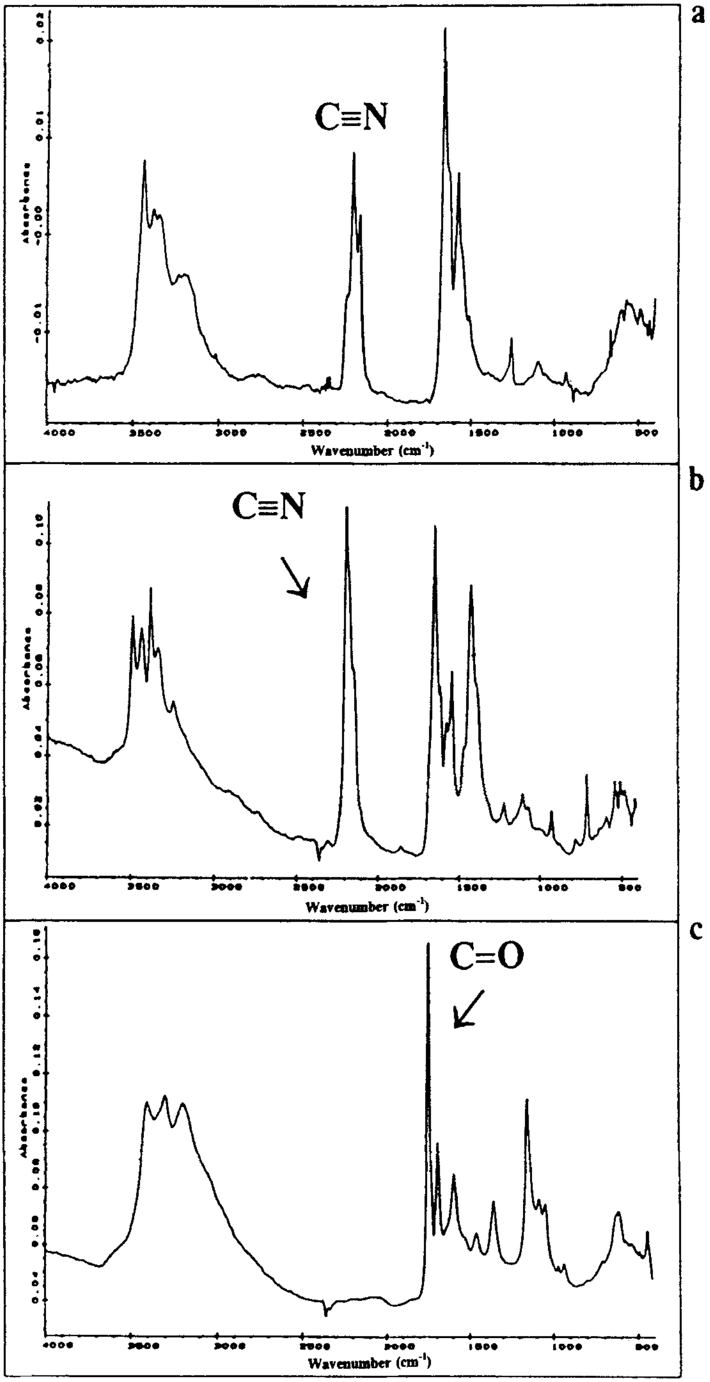

FIGURE 11 DRIFT. Spectra of thin films of dicyandiamide (a), cyanurea (b), and guanylurea (c) deposited on Zn99.

TABLE III
Position of the main bands of dicyandiamide, cyanurea, and guanylurea.[10]

Dicyandiamide	Cyanurea	Guanylurea	Vibrational Assignment
3434 s	3494 m	3409 m	
3381 s	3438 m	3304 m	NH_2
3352 s	3388 s		asym. stretch
	3339 m		
3235 m	3248 m	3200 m	NH_2
3177 m			sym. stretch
2215 s	2203 s		$N—C \equiv N$ asym.
2174 s	2170 m		stretch ($C \equiv N$)
		1753 s	C=O stretch
		1693 m	
1670 s	1659 s	1601 m	C=O stretch
	1619 m		NH_2 deform.
1586 s	1581 m		N—C—N
	1546 m		asym. stretch
1504 m			N=C—N asym.
			stretch (C=N)
	1431 s		
		1356 m	
1259 m	1224 w		N=C—N sym.
			stretch (C—N)
		1159 m	
1096 w	1107 w	1089 w	
			NH_2 rock
	1074 w	1047 w	
930 w	930 w		N—C—N sym.
			stretch (C—N)

9 grams of methanol. 10 μl of the mixture were deposited on a zinc specimen which was allowed to dry for 30 minutes before recording of the spectrum.

As shown in Figure 12, the nitrile band is not detectable in the spectrum obtained from the solution containing the zinc specimens, whereas this band is still present in the spectra obtained from the two other solutions. In addition, Figure 12a is very similar to the spectrum of guanylurea. The strong peak at 1720 cm^{-1} gives evidence of the presence of carbonyl groups. Zn^{2+} is usually considered to be an acid of intermediate strength.[21] The high concentration of zinc ions generated by the rapid dissolution of the zinc metal coupons in hot water is, therefore, likely to catalyze the transformation of dicyandiamide into guanylurea. Figures 12b/12c are very similar and the degradation of dicyandiamide in the presence of aluminium or iron metal coupons is substantially slower. There is no decrease in the relative intensity of the $C \equiv N$ group after the ageing test and the main features of the dicyandiamide spectrum are retained. The shift of the NH_2 band to lower frequencies around 1600 cm^{-1} as against 1670 cm^{-1} for dicyandiamide may indicate the presence of a small amount of guanylurea.

Therefore, this set of spectra clearly demonstrates that the degradation of dicyandiamide is faster in the presence of zinc oxides than in the presence of aluminium or iron oxides.

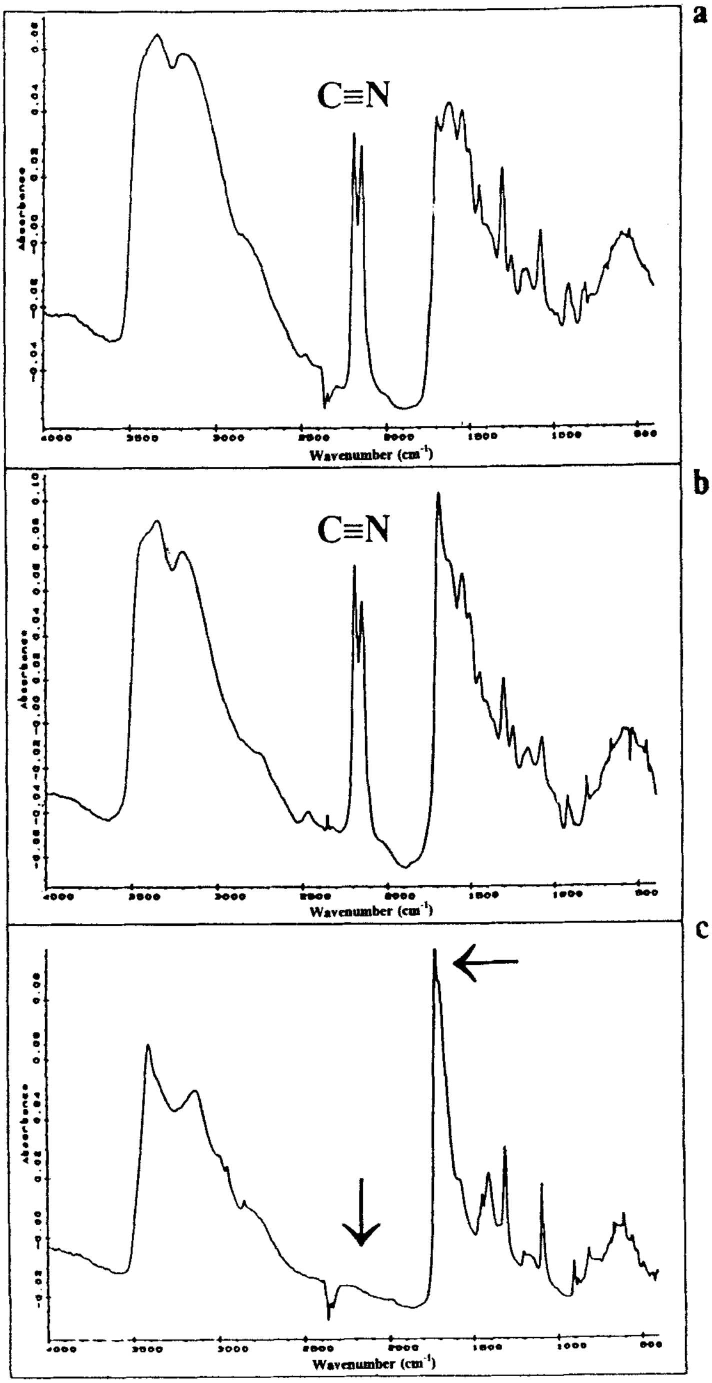

FIGURE 12 DRIFT. Spectra of dicyandiamide solutions containing XES (a), clad-AlCuMg2 (b), or Zn99 (c) metal coupons after ageing for 2 months at 70°C.

5. DEGRADATION MECHANISMS OF ALUMINIUM/EPOXY BONDED JOINTS

5.1 Introduction

Aluminium alloys have been used extensively in the past 50 years in the aircraft industry. High durability bonded structures are now obtained by using adhesives based on phenolic or epoxy resins.

New concepts for the development and manufacturing of a car body fully made of aluminium were presented by Audi in 1993 ("Space frame ASF").[22–23] While a great deal of experience gained on bonded aluminium structures in airplanes can also be applied for the bonding of car bodies, the prediction of the life service of bonded joints made from aluminium alloys used for the construction of a car frame is still not satisfactory and it is not planned in the near future to bond such frames. Some car manufacturers have begun to study thoroughly the durability of bonded joints made from standard epoxy adhesives and various aluminium alloys. In the following work, the durability properties of bonded joints made from two aluminium alloys and the epoxy adhesive 1K-A were investigated.

While a great deal of work has been done to assess the influence of the surface treatment of the substrate on the durability of adhesively-bonded aluminium joints, progress has still to be made to understand the role of the aluminium alloy, and of the surface chemistry, on the long-term properties of the joints.

Therefore, an XPS study was carried out to assess the role of the surface state of the aluminium substrate on the degradation of clad-AlCuMg2 and AlMg3/1K-A bonded joints.

5.2 Surface Composition of the Metal Substrates

Table IV presents the atomic compositions of the degreased and gritblasted AlMg3 and clad-AlCuMg2 substrates.

12.7% of magnesium and 10.6% of aluminium are detectable on the surface of the clean, degreased AlMg3 substrate. This very high concentration of Mg, compared with measurements made on the surface of a gritblasted specimen, of *ca.* 2.5% Mg and 24% Al, respectively, is due to the diffusion of magnesium to the surface during the cooling of the alloy. The maximum solubility of magnesium in aluminium is about 2% at room temperature.[32] About 9.4% of the overall aluminium was found to be in the metallic state (Al2p *ca.* 71.5 eV) for the degreased substrate, as against *ca.* 19% for the gritblasted specimen. Taking into account the small penetration depth of XPS, the

TABLE IV
Atomic composition of the metal substrates

Element (atom.%)	C	O	O/C	Al	Mg	Al/Mg
AlMg3 degreased	39.1	37.6	0.96	10.6	12.7	0.83
AlMg3 gritblasted	21.5	51.9	2.41	24.0	2.5	9.6
Clad-AlCuMg2 degreased	36.4	43.7	1.2	19.3	0.8	24.1
Clad-AlCuMg2 gritblasted	27.6	48.3	1.75	23.6	0.5	47.2

oxide layer on untreated AlMg3 can be estimated to be only around 5 to 10 nm thick, in agreement with earlier studies.[24]

The surface of the degreased clad-AlCuMg2 substrate consists mainly of hydrated aluminium oxides (24% Al) and a very small amount of magnesium hydroxide (0.8%). While the position of the Mg Auger lines enables a clear distinction between MgO (303.9 and 308.5 eV) and $Mg(OH)_2$ (305.7 and 310.5 eV),[25] it remains much more difficult to determine with precision, using the position of the Al2p energy, the degree of hydration of aluminium on the surface of the alloy. Mullins *et al.* reported Al2p energies of 74.9, 74.4, and 74.5 eV for Al_2O_3 (Sapphire), γ-AlOOH (Boehmite$\Leftrightarrow Al_2O_3 \cdot H_2O$), and $Al(OH)_3$ (Gibbsite$\Leftrightarrow Al_2O_3 \cdot 2H_2O$), respectively.[26] The O/Al ratio is probably the best means for obtaining an approximate idea of the degree of the surface hydration. The layer of nearly pure aluminium oxide on clad-AlCuMg2 is over 50 µm thick so that gritblasted specimens used in this study have a surface composition which is about the same as that of the degreased specimen. About 14.8% of the aluminium detected on the surface is in the metallic state.

5.3 Hydrolytic Stability of the Bonded Joints

5.3.1 Introduction

The microscopic investigation of the unaged bonded joints indicated that the failure of all bonded joints (degreased or gritblasted prior to bonding) was cohesive well inside the adhesive layer.

The effect of moisture on the long-term properties of the joints was assessed by measuring the residual shear strength (rss) after storage in water at 70°C for periods of time up to 12 weeks. The results presented in Figure 13 show that the ingress of water had an overall more detrimental effect on bonded joints made from clad-AlCuMg2 than from AlMg3.

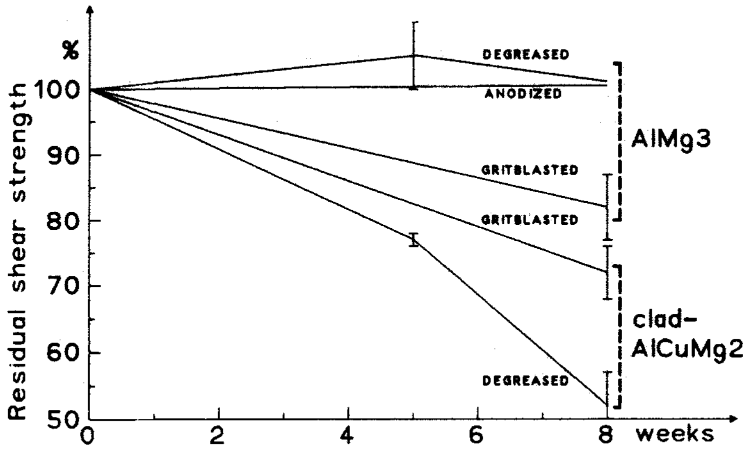

FIGURE 13 Residual shear strengths of aluminium/1K-A bonded joints stored in water (I.T.) at 70°C.

While degreased clad-AlCuMg2/1K-A specimens retained only 52% of their initial strength after 8 weeks in water, bonded joints made from degreased AlMg3 hardly showed any sign of strength loss, even after 12 weeks of testing (*ca.* 96% rss). In this latter case, the failure was *ca.* 95% cohesive and around 5% of the fracture surfaces was corroded near the edges of the bonded joints (Fig. 14). The anodized specimens also performed very well (101% rss after 12 weeks). Surprisingly, gritblasting the metal substrates prior to bonding had the normally expected beneficial effect for clad-AlCuMg2 but was detrimental as far as AlMg3 is concerned (resp., 82 and 72% rss after 8 weeks in water).

Therefore, the morphology of the metal substrate seems to play a less important role than the surface composition and, in particular, the Al/Mg ratio, on the hydrolytic stability of the bonded joints. At first sight, the increase in the Al/Mg ratios on the surface of degreased AlMg3 (0.83), gritblasted AlMg3 (9.6), and degreased clad-AlCuMg2 (24.1) correlates well with the increase in sensitivity of the metal/adhesive interface in relation to the ingress of water. Local corrosion cells originating from the different electrochemical behaviours of aluminium and magnesium, as well as a higher sensitivity of aluminium oxides than magnesium oxides at high pH values, are likely to explain this difference in performance. An apparent discrepancy is observed for gritblasted clad-AlCuMg2 specimens (Al/Mg ratio *ca.* 47.2). The gritblasted joints performed slightly better than degreased specimens (72% rss, as against 52%). But the difference in magnesium content between the two surfaces of these substrates (degreased: 0.8%; gritblasted: 0.5%) is not significant so that the beneficial effect of the surface treatment is sensible.

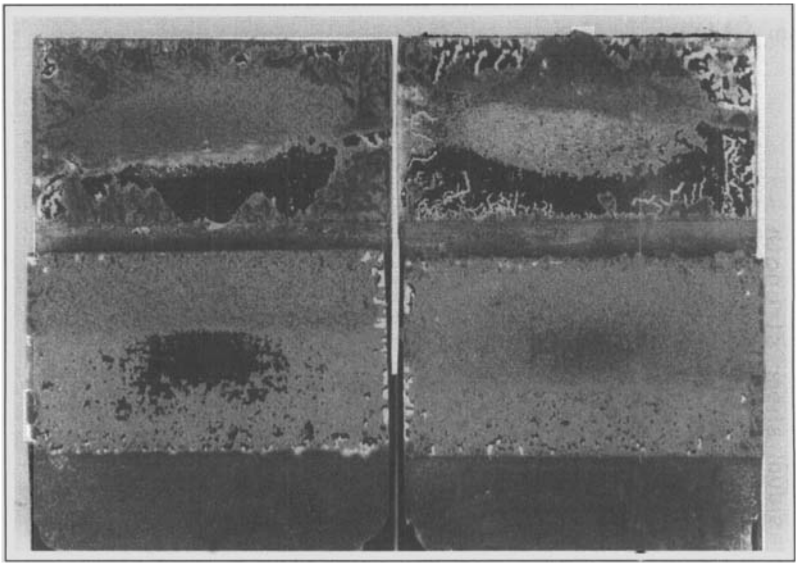

FIGURE 14 Fracture surfaces of clad-AlCuMg2 (top, 8 weeks I.T.) and AlMg3/1K-A (bottom, 12 weeks I.T.) bonded joints. The metal substrates were degreased prior to bonding. (See Color Plate V).

The extremely high durability of bonded joints made from anodized AlMg3 substrates (30 sec., 1 A/dm^2, 20% H_2SO_4) can be explained by the presence of a thick, insulating, poorly soluble aluminium oxide layer which prevents most processes associated with electrochemical corrosion. Due to the high porosity of the oxide layer, mechanical interlocking effects are also often mentioned in the literature to explain the good durability properties of anodized substrates.[27]

XPS was used to analyze the fracture surfaces of bonded joints made from degreased AlMg3 and clad-AlCuMg2 substrates after ageing in water at 70°C (Table V).

5.3.2 Bonded joints made from degreased AlMg3

The white, dull zone close to the edges of the bonded joints was analyzed (Fig. 14, Table V). Both the surface of the unaged metal substrate and the corroded area had similar atomic compositions. The high resolution Al2p spectrum allows one to distinguish between Al (*ca.* 71 eV) and Al_2O_3 but the small difference in binding energies, *ca.* 1 eV, makes it difficult to separate Al_2O_3 from $Al(OH)_3$. Al which was initially present at 1 and 9.6% levels in the metallic and oxidized states, respectively, on the reference substrate (the 10.6% Al concentration given in Table IV includes all Al species), was detectable at *ca.* a 7% level in the form of Al_2O_3 and *ca.* 2.6% in the form of $Al(OH)_3$ near the edges of the aged specimen.

The 3.6% of Si probably arises from the segregation of fumed silica during the curing of the adhesive.[12] The absence of N in the layer of corrosion products suggests that the degradation of the adhesive plays a minor role in the overall process.

The Al/Mg ratio is not significantly modified in this zone (*ca.* 0.97, as against 0.83 for the degreased substrate) and the effect of corrosion remained limited for this alloy.

TABLE V
Analysis of the various zones of the fracture surfaces after immersion test at 70°C

Element (atom.%)	C	O	O/C	N	Si	Al	O/Al	Mg	Cl	Ca	Na
	AlMg3 (degreased)/1K-A aged for 12 weeks at 70°C										
Metal, dull white zone near the edges	30.8	44.4	1.44		3.6	9.6		9.9	1.8		
	Clad-AlCuMg2 (degreased)/1K-A aged for 8 weeks at 70°C										
Metal, bright zone in the center	23.2	47.5	2.05	3.4	9.6	14.4	3.3	0.5		0.7	0.8
Adhesive, light red in the center	58.7	29.0	0.49	3.2	6.2			2.9			
Metal, dull white zone near the edges	22.0	57.1	2.6	1.6	2.8	16.4	3.48				
Adhesive, deep red near the edges	33.5	48.2	1.44	1.6	1.5	15.2	3.17				
	Adhesive 1K-A unaged										
Bulk cross-section	63.4	25.1	0.4	3.3	7.2			0.9			

5.3.3 Bonded joints made from degreased clad-AlCuMg2

Four zones were investigated to study the progress of corrosion responsible for the destruction of around 50% of the fracture surface after 8 weeks of ageing in water (Fig. 14).

Inside the bonded joint, the light red zone of the interfacial adhesive side had the same composition as the bulk adhesive. Al was not detectable and the failure in this zone was cohesive well inside the adhesive layer.

The bright metallic zone, which had a similar macroscopic aspect to the clean metal substrate, had a very different atomic composition from the latter. The Al concentration decreased from 19.3 to 14.4%. The high O/C ratio, *ca.* 2.05 against 0.4 and 1.2 for the bulk adhesive and reference metal substrate, respectively, show that the failure occured in a layer of corrosion products (aluminium hydroxide).

In the layer of corrosion products, two components characteristic of the adhesive were present at a high level for N (3.4%) and a very high level for Si (9.6%), as against 3.3 and 7.2% for the bulk adhesive, respectively. These amino and fumed silica residues are likely to stem from a partial hydrolysis of the adhesive during the ageing test. The low molecular weight amino residues are likely to diffuse to the metal oxide/polymer interface and react with water, following the reaction: $NR_3 + H_2O \rightarrow NR_3H^+ + OH^-$.[12,28] The aluminium oxides are then hydrolyzed following: $Al_2O_3 + 3H_2O + 2OH^- \rightarrow 2(Al(OH)_4)^-$.

The atomic composition of the dull white metallic zone close to the edges of the bonded joints displays some interesting differences. Mg, which was present at a 0.8% level on the reference substrate, was not detectable after the ageing test. The O/Al ratios in sapphire (Al_2O_3), Boehmite (γ-AlOOH), and Gibbsite (γ-$Al(OH)_3$) are 1.5, 2, and 3, respectively. The drastic increase in O/Al ratio, from 2.26 for the metal substrate (2.05 in the bright metallic zone) to 3.48 in this zone accounts for an increase in the degree of hydration of the aluminium oxides. Lower quantities of characteristic components of the adhesive were detectable (*ca.* 1.6 and 2.8% of N and Si, respectively). As the effect of water is more pronounced close to the edges of the bonded joints, the failure was less dominated by the degradation of the adhesive and occured in a layer of fully-hydrated aluminium oxides. MacDonald *et al.* reported, from thermodynamic calculations, that the domain of stability of aluminium hydroxide was markedly reduced at a temperature as low as 60°C. The transformation of $Al(OH)_3$ into AlO_2^- would occur at $pH = 8$ at 60°C, as against 10 at room temperature.[29]

The nearly identical atomic composition of the deep red zone of the interfacial adhesive side which was in contact with the dull white metallic zone confirms this interpretation. It is also important to emphasize that the repartition of aluminium detected on the delaminated interfacial adhesive side (15.2%, see Table V) is very heterogeneous: up to 50% variations were observed by changing the location of the X-Ray beam during the surface analysis.

5.3.4 Conclusion

Durability performance and results obtained from the XPS surface analysis demonstrate the outstanding hydrolytic stability of AlMg3/1K-A joints. In contrast, the degradation of bonded joints made from clad-AlCuMg2 is dominated by a full hydration of the aluminium oxides accompanied by a partial degradation of the adhesive.

5.4 Results Obtained After the Salt Spray Test

5.4.1 *Introduction*

As far as aluminium/epoxy bonded joints are concerned, a test simulating a corrosive environment has a much more detrimental influence than an accelerated ageing procedure simulating the influence of moisture. After 6 weeks in the salt-spray chamber, degreased, cladded aluminium samples retained only 6% of their initial strength, as against 49% for bonded joints made from degreased AlMg3 (Figs. 15–16, Table VI).

The scattering of the values shows a poorer reproducibility of the results. This can readily be understood. During immersion in water, failure at the metal/adhesive interface is a direct consequence of the diffusion of water. It starts from the edges of the bonded joints and its ingress follows more or less the application of Fickian laws.[30] In contrast, the bondline failure mechanism has been shown many times to depend strongly on the quality of the preparation of the edges of the bonded joints before storage in the salt-spray chamber. Chlorine ions accumulate at the weak points of the metal/polymer system and prevent the metal from passivating itself with an aluminium oxide layer.[31] Once initiated, the corrosion front can progress extremely quickly and the small variations of time needed to initiate corrosion from one sample to another explain the lower reproducibility of the salt-spray test.

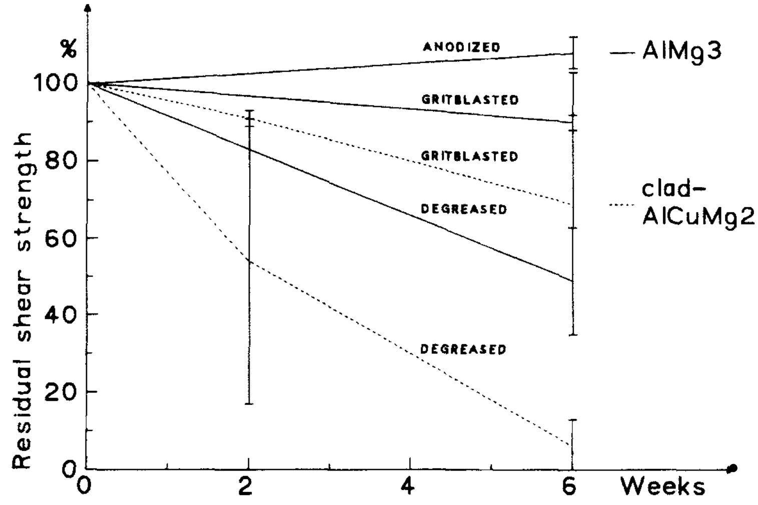

FIGURE 15 Residual shear strengths of aluminium/1K-A bonded joints after salt-spray test (S.S.T.).

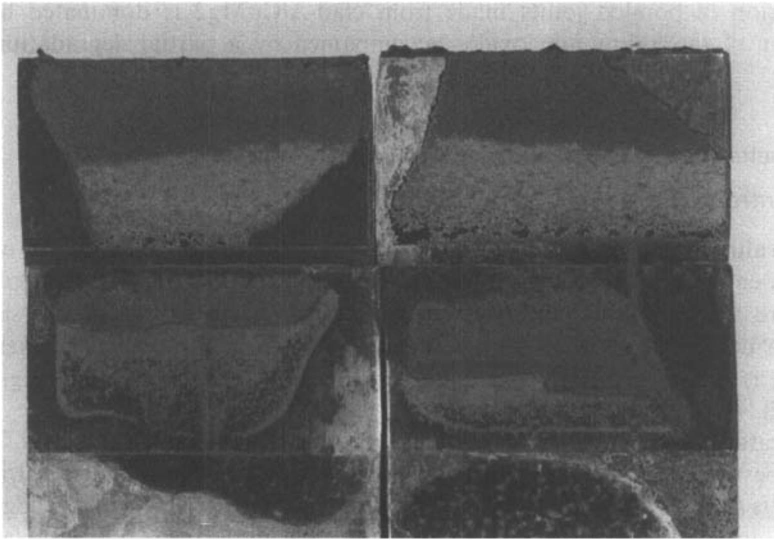

FIGURE 16 Fracture surfaces of clad-AlCuMg2 (2 weeks "S.S.T.", top) and AlMg3 (6 weeks S.S.T., bottom)/1K-A bonded joints. The metal substrates were degreased prior to bonding. (See Color Plate VI).

TABLE VI
Analysis of the various zones of the fracture surfaces after salt-spray test

Element (atom.%)	C	O	O/C	N	Si	Al	O/Al	Mg	Cl	Ca
AlMg3 (degreased)/1K-A after 6 weeks of salt-spray test										
Adhesive, deep red near the edges	21.1	57.1	2.71			20.4	2.8		1.4	
Metal, dull white zone near the edges	26.4	53.6	2.03			18.3	2.92		1.3	
Adhesive, light red in the center	56.9	28.9	0.51	3.2	5.8			3.8	0.4	1.1
Metal, bright zone in the center	32.6	44.6	1.37			11.4		7.8	3.6	
Clad-AlCuMg2 (degreased)/1K-A after 2 weeks of salt-spray test										
Adhesive, deep red near the edges	57.8	28.6	0.49	3.2	0.5	6.9	4.14		3.0	
Metal, dull white zone near the edges	27.2	51.1	1.88			19.2	2.66		2.5	
Adhesive, light red in the center	54.7	28.4	0.52	2.9	6.9	1.2		4.1	0.4	1.3
Metal, bright zone in the center	34.8	41.6	1.2	0.9	1.7	19.9	2.09		1.1	

The fracture surfaces of the specimens after 6 weeks of the ageing test can be divided into three distinct zones which were also observed by Brockmann *et al.* for anodized clad-AlCuMg2 specimens bonded with an epoxy adhesive.[11]

1) A zone where heavy corrosion starting from the edges of the bonded joints diminishes with increasing distance from the edges
2) Further inside the bonded joint, a bright metallic zone where the adhesive is delaminated and the metal substrate is practically not corroded
3) Adjacent to the previous zone, a zone where there is no visible sign of the detrimental effects of corrosion. The failure was cohesive inside the adhesive layer.

The XPS analysis of the various zones of the fracture surfaces are summarized in Table VI.

5.4.2 Bonded joints made from degreased AlMg3

1) There were 26.4% C, 53.6% O, 18.3% Al, and 1.3% Cl on the interfacial metal side near the edges of the fracture surface after the ageing test (Fig. 16, Table VI). The progress of corrosion was also less superficial than observed during the ageing in water. No trace of adhesive was found and the failure occured in a mixed layer of aluminium hydroxide and aluminium chloride. Taking into account the low percentage of Cl, aluminium chloride would account for a maximum of 2% of the corrosion products. The energy of hydration of aluminium ions is very high and these are likely to be spontaneously hydrolyzed in aluminium hydroxide.[31]

   It is also very interesting to observe the nearly identical composition of the corresponding interfacial adhesive side. Neither N nor Si were detectable at significant levels and the failure clearly occured within a layer of corrosion products in the bulk metal.

   The heavy corrosion of the metal substrate was also accompanied by a preferential dissolution of magnesium which was not present on the adhesive and metal interfacial sides. As a result of the segregation of magnesium during manufacturing of the alloy, a Mg_2Al_3 phase is likely to be formed near the surface of the metal.[32] The latter is less noble than the bulk metal and is more susceptible to electrochemical corrosion. After the ageing test, the "magnesium-rich islands" are, accordingly, entirely dissolved away from the surface near the edges of the bonded joints.
2) In the corrosionless adhesive delaminated zone, there were 32.6% C, 44.6% O, 11.4% Al, 7.8% Mg, and 3.6% Cl. This is essentially the same composition as for the clean metal substrate. The slight increase in the Al/Mg ratio, *ca.* 1.46, as against 0.83 for the clean metal substrate, may indicate a partial dissolution of the top layers of the interfacial metal side. No characteristic component of the adhesive was detectable and the failure essentially occured at the metal adhesive interface.
3) The interfacial adhesive side adjacent to the previous zone showed a very similar composition to the bulk adhesive. The 3.8% of magnesium is attributable to the presence of a mixed calcium and magnesium carbonate filler in the adhesive. No

aluminium stemming from the metal substrate was detectable and the failure was cohesive well inside the adhesive layer.

5.4.3 Bonded joints made from degreased clad-AlCuMg2

After 2 weeks in the salt-spray chamber, the joints retained only 54% of their initial strength, with a corrosion covering over 50% of the surface (Figs. 15–16). The joints did not have any significant strength after 6 weeks of testing and it was necessary to carry out the XPS analysis on the specimens aged for only 2 weeks so as to follow the ingress of corrosion inside the joint.

There were 27.2% C, 51.1% O, 19.2% Al, and 2.5% Cl on the interfacial metal side near the edges of the fracture surface after the ageing test (Table VI). The failure thus occurred in a layer of aluminium hydroxide. In addition to 6.9% Al, 3.2% N and 0.5% Si were detectable on the corresponding area of the interfacial adhesive side, giving evidence of a failure closer to the adhesive layer than was observed for AlMg3.

There were 34.8% C, 41.6% O, and 19.9% Al in the bright metallic zone (center). This is essentially the same composition as for the clean metal substrate. The aluminium oxides were not modified and the 0.9 of N and 1.7% of Si demonstrate that the failure was at the metal/adhesive interface.

After 6 weeks of salt-spray test, the specimens which were gritblasted prior to bonding retained 90 and 69% of their initial strength, for AlMg3 and clad-AlCuMg2, respectively (Fig. 15). The very high scattering of the values observed for clad-AlCuMg2 (34%) indicates that the surface treatment simply delays the initial attach of corrosion. This is understandable when considering the identical compositions of both gritblasted and degreased specimens. The much higher corrosion resistance of joints made from gritblasted AlMg3, the surface of which contains only 2.5% magnesium, is likely to stem partially from a suppression of intergranular corrosion at the Al_2Mg_3/Al grain boundaries.

5.5 Conclusion

The main conclusions to be drawn from this study are:

1) The type of aluminium alloy drastically influences the long-term properties of the bonded joints. It is particularly important to consider the surface composition if good durability properties are to be attained.

   The aluminium oxides present on the surface of clad-AlCuMg2 are not stable against hydration and bonded joints exposed to water ultimately fail in a layer of hydrated aluminium oxides. The limited increase in durability observed by gritblasting the surface prior to bonding shows that this surface treatment is inadequate to ensure the generation of stable oxide layers.

   AlMg3 contains approximately equal amounts of aluminium and magnesium hydroxides on its surface. When it is gritblasted, the Al/Mg ratio increases by a factor of 10. In direct contrast to the observation of Kinloch *et al.*, the lower durability of bonded joints made from gritblasted samples would indicate that a high magnesium content in the oxide layer leads to a better hydrolytic stability of the bonded joints.[24] Poole *et al.* did not find any evidence of a correlation between Mg concentration and the durability of wedge specimens.[33] However, in both of these studies the concentration of aluminium always far exceeded that of magnesium and the range of variation in the Al/Mg ratio (*ca.* 4 to 110 in Refs. 24 & 33, as against 0.8 to 4.7 in the present study) makes any direct comparison difficult. In agreement with the results presented in this paper, Critchlow *et al.* recently demonstrated that bonded joints made from a degreased 5251 aluminium alloy (Al/Mg ratio *ca.* 2) and Araldite 2007 (AV 119, single part, 120°C-curing, toughened epoxy) had a higher durability in hot water (60°C) than grit blasted specimens (Al/Mg ratio $\gg 10$).[34]

2) The corrosion resistance of both alloys bonded with the epoxy adhesive is much more critical than their hydrolytic stability.

While the sensitivity of clad-AlCuMg2 to corrosion is extremely high, the segregation of Mg makes the surface of AlMg3 particularly prone to intercrystalline corrosion. Gritblasting the specimens prior to bonding does not significantly reduce the sensitivity to bondline corrosion. The oxide layer generated by a short anodizing treatment offers both outstanding hydrolytic stability and corrosion resistance (Figs. 13 and 15). The performances are very good for anodizing times as short as 30 seconds. In a study not reported here, excellent stability was also obtained when polyethylene was used as a model polymer instead of the epoxy adhesive. This demonstrates that the polymer plays a negligible role in the degradation process, the kinetics of which are above all influenced by the intrinsic stability of the oxide layers.

SUMMARY

The durability properties of bonded lap shear joints made from an epoxy/dicyandiamide adhesive and zinc, cold-rolled steel, or aluminium metal coupons have been investigated. The influence of the dicyandiamide content of the adhesive on the durability properties has been assessed by salf-spray testing or by storing the joints in water at 70°C or 90°C for periods of up to 12 weeks. The degradation products formed during the ageing of the epoxy adhesive in water have been investigated using high performance liquid chromatography (HPLC) and Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. The degradation mechanisms of aluminium/epoxy bonded joints have been thoroughly studied using X-ray photoelectron spectroscopy.

The performance of the bonded joints faced with a corrosive environment (salt-spray) have been found to be little influenced by the quantity of dicyandiamide in the adhesive. When the bonded joints were aged in hot water, the stability of an interface toward an excess of dicyandiamide directly followed the sensitivity of the oxide layer at high pH values. Optimal durability properties without peel strength losses of the adhesive were achieved both on zinc and aluminium-coated substrates by reducing the quantity of dicyandiamide by 20% in the epoxy adhesive.

In the course of a model investigation, the degradation of dicyandiamide was found to occur more quickly when put in contact with zinc oxides than with aluminium oxides. By reducing the quantitiy of dicyandiamide in the adhesive, the amount of side products or low molecular weight oligomers formed during the curing of the adhesive and after the immersion in water (cyanurea, guanylurea) was shown to be substantially reduced.

A detailed investigation of several aluminium alloy/epoxy systems demonstrated the superior hydrolytic stability of bonded joints made from simply degreased AlMg3. This very good performance was attributed to the high surface concentration of magnesium oxides and their high stability in alkaline media.

Acknowledgements

The authors gratefully acknowledge the support of this work by CECA/ELF ATOCHEM (France) and the technical advice of Dr. Jean-Yves Chenard of the research group of Lacq (ELF AQUITAINE) as well as Dr. Marie-Francoise Guimon for the XPS analyses carried out at Pau. The authors are also grateful to Dr. Werner Dellsperger (Institut für Wissenschaftsförderung (ELF AQUITAINE) and Mr. Erhard Mohr (CECA KLEBSTOFFE).

References

1. M. P. Bente, Ph.D. Thesis, University of Pau, France, 1992.
2. J. Barwich, Ph.D. Thesis, University of Bielefeld, Germany, 1989.
3. A. Gross, Ph.D. Thesis, University of Bielefeld, Germany, 1987.
4. W. X. Zukas, K. J. Craven and S. E. Wentworth, *J. Adhesion*, **33**, 89 (1990).
5. W. X. Zukas, S. E. Wentworth and M. S. Sennett, *Proceedings, The Adhesion Society*, p. 187 (1993).
6. F. Gaillard, H. Hocquaux, M. Romand and D. Verchere, *Proceedings of the European Adhesion Congress*, Dechema, Adhecom and DVS, in Karlsruhe, Bundesrep. Deutschland, p. 122, September 1992.
7. R. A. Dickie, J. W. Holubka and J. E. Devries, *J. Adhesion Sci. Technol.*, **4**, 57 (1990).
8. J. W. Holubka and J. C. Ball, *J. Adhesion Sci. Technol.*, **4**, 443 (1990).
9. H. Kollek, in *Handbuch Fertigungstechnologie Kleben, Forschungsergebnisse aus dem BMFT-Verbundprojekt*, O. D. Hennemann, W. Brockmann and H. Kollek, Eds. (Carl Hanser Verlag, München, 1992), p. 209.
10. R. O. Carter, R. A. Dickie, J. W. Holubka and N. E. Lindsay, *Ind. Eng. Chem. Res.*, **28**, 48 (1989).
11. W. Brockmann, O. D. Hennemann, H. Kollek and C. Matz, *Int. J. Adhesion and Adhesives*, **6**, 115 (1986).
12. M. Brémont, in "Verbesserung der Beständigkeit von Klebverbindungen aus Verzinktem Stahl und einem warmhärtenden Epoxidharzklebstoff", Ph.D. Thesis, University of Kaiserslautern, Germany (Hinterwaldner-Verlag, Munich, 1994).
13. M. Brémont and W. Brockmann, *J. Adhesion*, to be published.
14. J. E. Devries, L. P. Haack, J. W. Holubka and R. A. Dickie, *J. Adhesion Sci. Technol.*, **3**, 203 (1989).
15. R. T. Foister and K. J. Schroeder, *J. Adhesion*, **24**, 259 (1987).
16. R. T. Foister, *J. Adhesion*, **24**, 279 (1987).
17. M. Bremont, W. Brockmann, M. F. Guimon and G. Pfister-Guillouzo, *J. Adhesion*, **41**, 147 (1993).
18. D. A. Shirley, *Phys. Rev. B*, **5**, 4709 (1972).
19. J. H. Scofield, *J. El. Spect.*, **8**, 129 (1976).
20. G. Körtum, *Reflexionsspektroskopie* (Springer-Verlag, Heidelberg, 1969).
21. R. G. Pearson, *Chemistry in Britain*, **3**, 103 (1967) and *Science*, **151**, 172 (1966).
22. M. J. Wheeler, P. G. Sheasby and D. Kewley, SAE Technical Paper Series 870146 (1987).
23. P. G. Sheasby, Aluminium 2000, 2nd World Congress, Florenz, Italien, 29 March–4 April 1993.
24. A. J. Kinloch, H. E. Bishop and N. R. Smart, *J. Adhesion*, **14**, 105 (1982).
25. M. F. Guimon, private communication.
26. W. M. Mullins and B. L. Averbach, *Surf. Sci.*, **206**, 52 (1988).
27. J. S. Ahearn, G. D. Davis, T. S. Sun and J. D. Venables, in *Adhesion Aspects of Polymeric Coatings*, K. L. Mittal, Ed. (Plenum Press, New York, 1983), p. 281.
28. O. D. Hennemann, E. Preußner, J. Bischoff and R. Lüschen in *Dechema Monographie*, **119**, 73 (VCH-Verlag, Frankfurt am Main, 1990).
29. D. D. MacDonald and P. Butler, *Corros. Sci.*, **13**, 259 (1973).

30. A. J. Kinloch and W. Abbey, in *Haftung als Basis für Stoffverbunde und Verbundwerkstoffe*, W. Brockmann, Ed. (Deutsche Gesellschaft für Metallkunde, 1982), p. 181.
31. W. H. Slabaugh, W. Dejager, S. E. Hoover and L. L. Hutchinson, *J. Paint Technol.*, **44**, 76 (1972).
32. L. F. Mondolfo, in *Aluminium Alloys, Structure and Properties*, Part 4-2 (Butterworth, London, 1976).
33. P. Poole and J. F. Watts, *Int. J. Adhesion and Adhesives*, **5**, 33 (1985).
34. G. W. Critchlow and D. M. Brewis, *Int. J. Adhesion and Adhesives*, **15**, 173 (1995).