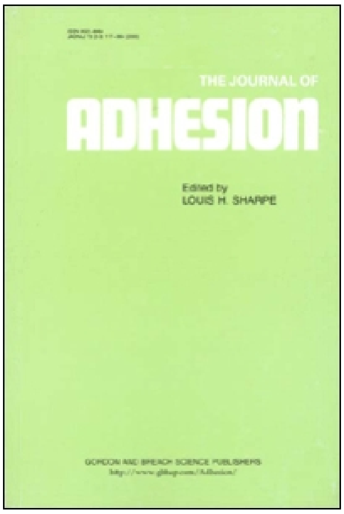

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Water-Resistant Oxide Layers at the Interface of Zinc/Epoxy Bonded Joints*

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The durability properties of bonded lap shear joints made from an epoxy/dicyandiamide adhesive and zinc metal coupons have been investigated. The metal coupons were anodized in sodium hydroxide solutions before bonding. The influence of the anodizing conditions on the morphology and composition of the oxide layers has been studied using SEM and TEM imaging analyses as well as X-ray photoelectron spectroscopy. The hydrolytic stability of the bonded joints has been assessed by storing the joints in water at 70 °C or 90 °C for periods of time up to 5 weeks. Polypropylene has been used as a model adhesive to study the influence of mechanical interlocking effects on the performance of the bonded joints. Depending on the anodizing conditions, the improved durability properties have been attributed either to "mechanical interlocking effects" or to the higher hydrolytic stability of the oxide layers generated during the anodizing treatment.

Some of the results gained from the anodization of zinc have been extrapolated to hot-dipped galvanized steel. Bonded joints made from hot-dipped galvanized coupons anodized under smooth conditions (2% NaOH) displayed residual shear strengths of up to 70% higher than specimens simply degreased after immersion test. The generation of stable oxide layers as well as the suppression of intergranular corrosion phenomena at the metal/adhesive interface can explain the improved durability properties.

KEY WORDS Adhesion; zinc; zinc-coated steel; galvanized steel; epoxy adhesives; durability; anodization; interphase; zinc oxide; morphology; X-ray photoelectron spectroscopy.

INTRODUCTION

We reported in a previous paper some aspects concerning the improvement of the durability of zinc-coated steel/epoxy bonded joints.[1] The hydrolytic stability of the joints is jeopardized by the ability of zinc to corrode in hot water.[2] During immersion in water at 70 °C or an accelerated ageing test such as the "Cataplasme Humide" test (used in the automotive industry), the zinc coating is dissolved and the failure ultimately occurs in a layer of corrosion products consisting of ZnO and $Zn(OH)_2$.[1]

In principle, the degradation effects caused by the progress of corrosion at the interface of zinc/epoxy or zinc-coated steel/epoxy bonded joints during immersion in hot water are the same. These are illustrated in Figure 1 which presents two TEM-pictures of a cross-section at the interface of a bonded joint made from Zn99 (zinc pure

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* One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

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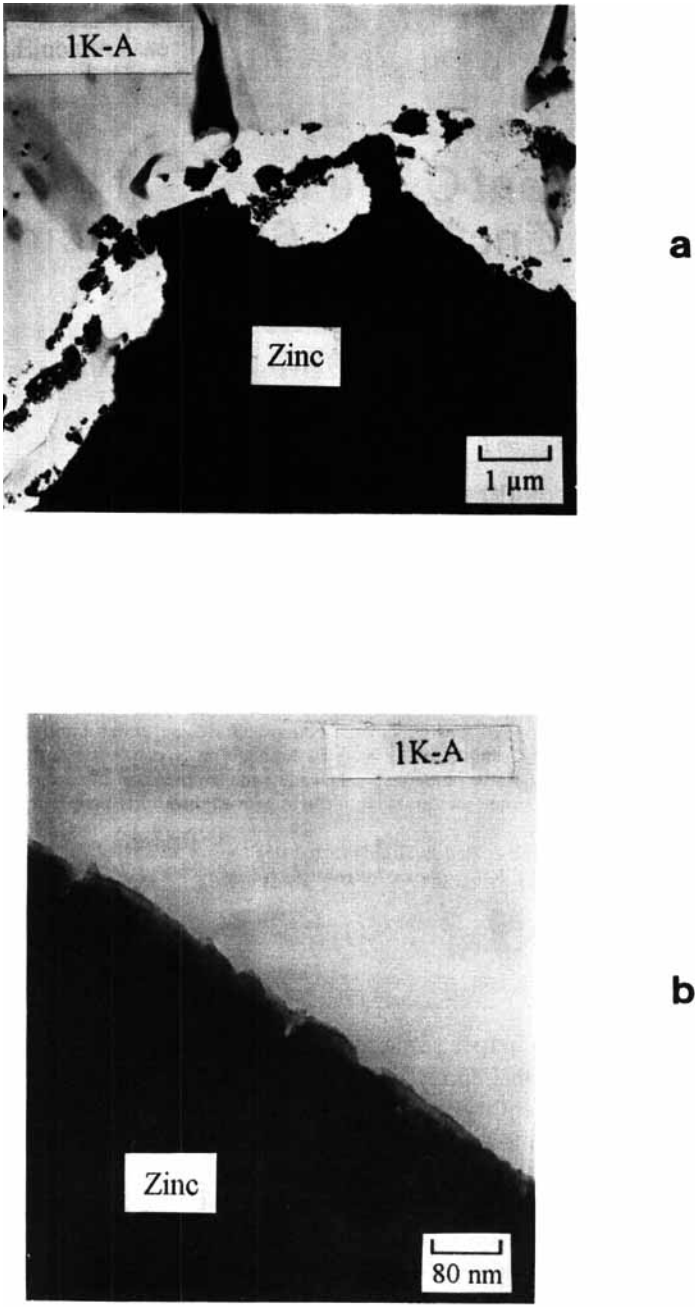

FIGURE 1 TEM image of the interface of a zinc (degreased)/1K-A bonded joint aged for 2 weeks in water at 90°C (a) image showing the transition between delaminated and corroded areas (10200 *x*), (b) delaminated area (120000 *x*).

at a 99% level) and the commercial hot-curing epoxy adhesive 1K-A (see experimental part below) after ageing in water for 2 weeks at 90 °C.

In the adhesive/metal interphase region, Figure 1a (10200 x) presents several zones consisting of corroded and delaminated areas. The effects of the dissolution of zinc are drastic on the left and right hand sides of the picture. The pits where zinc was removed are up to several micrometers deep. The large quantity of zinc removed from the surface during the corrosion process is likely to involve concentrations of zinc derivatives exceeding several moles per liter at the interface. In the particular case of a zinc/epoxy interface, this would only be achievable in a very alkaline medium for zinc oxide. More likely, as a result of their high energy of hydration, zinc ions are probably immediately hydrated and transported away from the interface (the hydration energy of most zinc salt derivatives is around 70 kcal/mole for every complexed mole of water).[3]

In Figure 1b (120000 x) which corresponds to a zone where the interfacial metal side was delaminated but did not show any sign of corrosion (bright metallic zone), the 20 to 40 nm thick oxide layer remained largely unattacked by the ingress of water. Due to the very small thickness of the oxide, the metal is at some places practically in direct contact with the adhesive.

As is the case for most hot-curing epoxy adhesives, the level of dicyandiamide in 1K-A is significantly above the stochiometric level necessary to ensure full curing of the adhesive. It is not possible, however, to solve the durability problems satisfactorily by lowering the dicyandiamide/epoxy resin ratio in the adhesive (the optimization of the dicyandiamide content in 1K-A led to a mere 20% improvement of the residual shear strength of Zn99/1K-A bonded joints after immersion test) or by using an anhydride acid as a curing agent.[4]

Our efforts to find new methods leading to an improvement of the hydrolytic stability of the bonded joints have focused in the past two years on the development of zinc-specific coupling agents as well as on methods aiming to generate stable oxide layers at the surface of zinc-coated substrates.[4]

The anodization of aluminium as a surface pretreatment before bonding has been used in the airplane industry for more than fifty years. The aluminium oxide layer which is created during the anodizing process has a high stability in the 4 to 9 PH range and provides an insulating layer for the base metal. The possibility that electrochemical corrosion occurs at the aluminium/adhesive interface is reduced accordingly as compared with what usually occurs with bonded joints made from simply degreased aluminium substrates. Moreover, the porosity of the oxide layer created during the anodizing process enables the adhesive to wet a surface sometimes exceeding 500 times the geometrical area of the anodized sample. A convoluted interface and mechanical interlocking effects prevent interfacial crack propagation. The final microstructure of the anodized layer mainly depends on the choice of the anodizing solution.

American aircraft manufacturers preferably anodize aluminium in phosphoric acid (lower oxide layer thickness, higher porosity), whereas in Europe one currently tends to favour anodization in chromic-acid solutions (higher oxide layer thickness, lower porosity).[5,6]

Due to the more restricted use of zinc, suface treatments of this metal have not been studied to the same extent. Certain electrolytes are used sometimes to polish zinc chemically to create a bright surface. The anodization of zinc is applied commonly to produce coatings that provide a good support for painting. The Batelle Institute in America has shown that zinc anodized under conditions favouring the formation of thick coatings (up to 50 μm) has a corrosion resistance even higher than that obtained with anodized aluminium.[7] To our knowledge, the anodizing of zinc as a surface treatment prior to bonding applications is not yet applied in the industry.

The anodization of zinc was investigated as early as 1943 by K. Huber. He studied, in great detail, the structure of anodized layers deposited on zinc from sodium hydroxide solutions as a function of the electrolyte concentration and the applied voltage.[8-12] Evans *et al.* found that it was possible to improve the adhesion of polyethylene to zinc by treating zinc coupons in an electrolyte consisting of 100 g/l potassium hydroxide and 0.5 g/l zinc oxide. They showed that the growth of a surface consisting of zinc dendrites was responsible for the improved adhesion strength to polyethylene.[13,14]

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 or zinc-coated steel. The metal substrates were anodized in sodium hydroxide solutions prior to bonding. The morphology of the oxide layers and the metal/adhesive interfaces were investigated with SEM and TEM imaging analyses and their composition with X-ray photoelectron spectroscopy (XPS). A study was carried out with polypropylene as a model adhesive to study the influence of mechanical interlocking effects on the performances of the bonded joints.

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). Before anodization, the zinc coupons (100 mm × 25 mm) were degreased in an ultrasonic bath in acetone for 10 minutes, etched in hydrochloric acid (18.5% vol.) for 10 seconds, and thoroughly washed with deionized water to eliminate traces of acid. The zinc coupons (each time 6 specimens) were then anodized in a sodium hydroxide solution with a zinc cathode in order to avoid any contamination. The anodization was carried out at 20 °C under constant stirring of the solution. The distance between the cathode and the 6 samples was always 8 cm and the overall surface of the anode 100 cm^2.

Under these experimental conditions, Figure 2 presents, for various sodium hydroxide concentrations, the evolution of the measured voltage between the zinc cathode and the zinc anode as a function of the current density applied on zinc coupons. Although our intention was not to study these curves in detail, it proved to be particularly interesting in the course of the investigations to correlate the properties of the bonded joints with the presence (or not), of a passive oxide layer at the metal/adhesive interface.

The Current/Voltage curves can typically be divided into three regions. In region O to B, zinc, which is in an "active state", dissolves in the sodium hydroxide solution. Although such conditions do not allow for the growth of an oxide layer, the morphology of the oxides is greatly modified in comparison with what is observed, for example, after etching in hydrochloric acid. At B, the anode becomes passive. The region B-C can

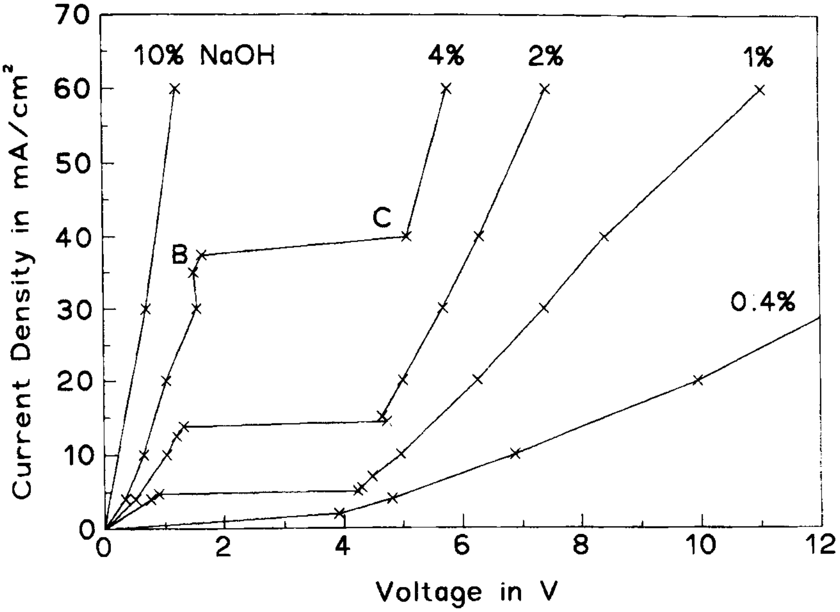

FIGURE 2 Variation of the potential between the zinc cathode and the zinc metal coupons during anodization in sodium hydroxide solutions (for applied current densities ranging from 0 to 60 mA/cm^2).

be used successfully to polish the zinc surface which passivates itself with a bright and even layer of zinc oxide. From C onwards, the surface, still in a passive state, covers itself with a black layer of zinc oxide under oxygen evolution.[8]

After anodization, the metal samples were washed with de-ionized water to get rid of the last traces of sodium hydroxide, dried in an oven for 1 hour (2 drying temperatures were tested: 70 °C and 150 °C), and bonded with a one-component dicyandiamide-cured adhesive supplied by CECA (curing conditions: 1 hour, 200 °C) and referred to as "1K-A" in the text. Lap shear samples were made with a 12.5 mm × 25 mm bond overlap and a 0.2 mm bondline thickness (DIN 53281).

In Section 6, the zinc-coated substrate referred to as G2F is a 0.7 mm ultrasmooth hot-dipped galvanized steel (*Ra* = 1.5 μm) supplied by SOLLAC (France). The surface of G2F was thoroughly investigated in Ref. 1.

2.2 Durability Tests

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

2.3 Surface Analysis

XPS analyses were performed with a SSI model 301 spectrometer using a focused (diameter of the irradiated area: 600 μm) monochromatic AlKα radiation (10 kV, 10 mA). The residual pressure in the chamber was about 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(1s) (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)[8] background. Quantitative analyses were performed with the sensitivity factors given by Scofield.[9] The micro-characterization of the anodized specimens was carried out using a Scanning (SEM) (JEOL JSMT 300 electron microscope) or a Transmission Electron Microscope (TEM) (Zeiss EM 10 or Phillips 420). For the TEM analyses of the samples displayed in Figures 1, 6, 10 and 12, a suitable preparation technique had to be developed. The production of thin sections was carried out with the aid of an ultra-microtome (Ultracut, Reichert-Jung). Cross-sections about 30 to 60 nm thick were cut from the transition zone using a diamond knife and investigated without further preparation.

3 INFLUENCE OF THE ANODIZATION CONDITIONS ON THE BONDING PROPERTIES OF ZINC

Following a series of preliminary tests, an anodizing current of 30 mA/cm^2 was used for this study. In order to assess the improvement brought about by the anodizing treatment, the results obtained with 2 conventional surface treatments, namely degreasing or gritblasting the zinc coupons prior to bonding, are presented in Figure 3,

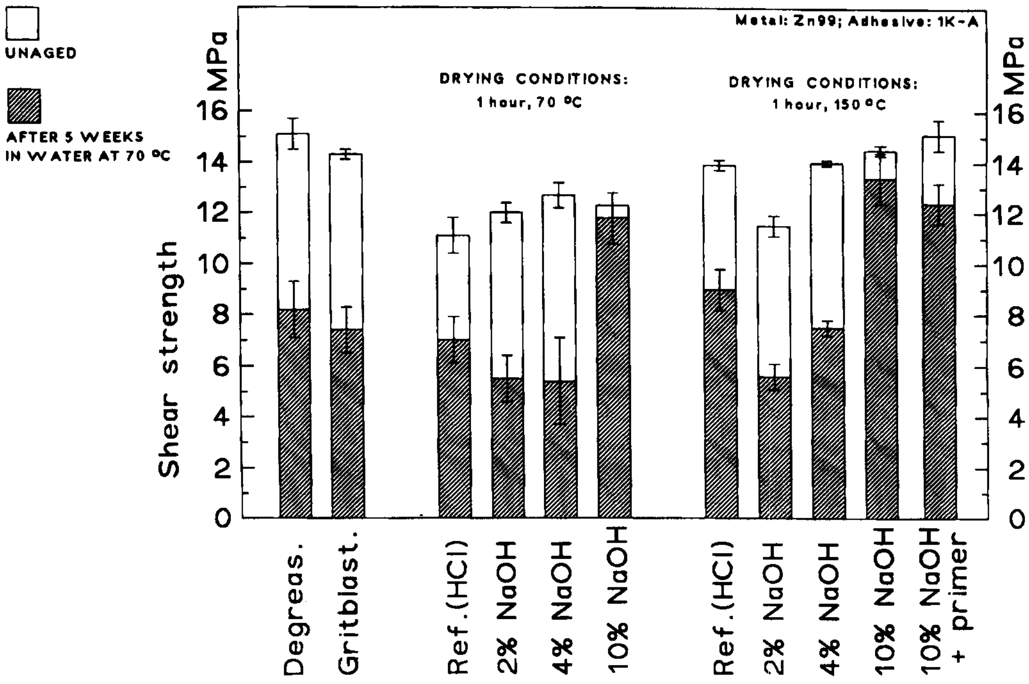

FIGURE 3 Hydrolytic stability of anodized zinc specimens bonded with the hot-curing epoxy adhesive 1K-A (Durability test: 5 weeks immersion in water at 70 °C).

along with the performances of the specimens anodized in 2, 4, or 10% NaOH (anodizing time: 10 min.).

The unaged bonded joints anodized in the 2% NaOH solution failed inside the oxide layer, whereas the failure was cohesive well inside a layer of adhesive for the specimens anodized in the 4 and 10% NaOH solution. The degreased and grit-blasted specimens had residual shear strengths of, respectively, 8.2 and 7.4 MPa after 5 weeks of immersion test at 70 °C, as against *ca.* 15 MPa before the ageing test. This was significantly higher than the strengths measured for the specimens anodized in the 2% NaOH (5.5 MPa; drying conditions of the specimens after anodization: 1 hour, 70 °C) and 4% NaOH (5.4 MPa; drying conditions: 1 hour, 70°C) solutions, but *ca.* 30% lower than what was obtained with the 10% solution (11.8 MPa; drying conditions: 1 hour, 70°C). The fracture surfaces of the degreased or gritblasted specimens were also largely delaminated and only 20 to 30% of the surfaces were covered with a fine pellicle of adhesive after the ageing test. In contrast, the failure of the specimens anodized in 10% NaOH (drying conditions: 1 hour, 70°C) was mainly in a layer of adhesive (*ca.* 80/90%), suggesting that the anodizing treatment greatly contributed to enhancing the hydrolytic stability of the interface (Figure 4).

Figure 3 also presents results obtained by drying the metal samples at 150°C before bonding with 1K-A. At the beginning of the investigations, some unaged bonded joints anodized in the 10% NaOH solution displayed fracture surfaces with a few zones of

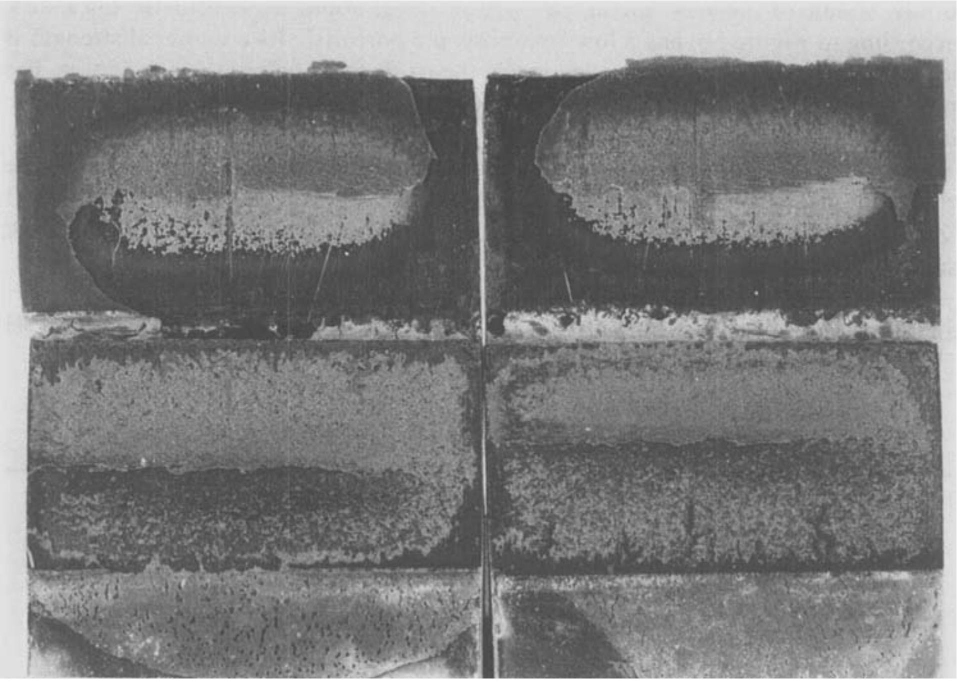

FIGURE 4 Fracture surfaces of degreased (top) and anodized (bottom, anodizing conditions: 10% NaOH, 10 min., $i = 30\,\mathrm{mA/cm^2}$) specimens bonded with 1K-A after ageing in water for 5 weeks at 70 °C. (See Color Plate III.)

adhesional failure covering up to 20% of the fracture surfaces. The initial drying temperature of 70°C was arbitrarily chosen to dry the metal probes under smooth conditions. It was found later to be too low to guarantee a satisfactory drying of the highly porous anodized layer obtained from the 10% NaOH solution and hence was raised to 150°C. More reproducible results and also slightly improved durability properties were obtained after the immersion test: *ca.* 13.4 MPa as against 11.8 MPa for the specimens dried at 70°C.

A study of the morphology of the outer surface of the anodic coating before bonding as well as a close examination of Figure 2 is necessary to understand these results. Zinc coupons anodized with a current of 30 mA/cm^2 were able to passivate in the 2% NaOH solution (part C-onwards of the anodizing curves) but stayed in an active state for the 4 and 10% NaOH solutions (O-B). In other words, the 2% solutions allowed the growth of an oxide layer, whereas it was only possible in the 4 and 10% solutions to develop an etched structure (*i.e.* the substrate was anodically dissolved in the solution). A short summary of the main characteristics of zinc specimens anodized in 2 or 10% NaOH solutions is given in Table I.

Figure 5 presents SEM pictures (magnification: 2000 × in all cases) of zinc specimens simply degreased or anodized for 10 minutes in 2, 4, or 10% NaOH under the experimental conditions mentioned above. On the degreased specimen (Figure 5a), the characteristic lines coming from the milling stage of the manufacturing process of the metal sheet are clearly visible. The compact oxide layer produced in the 2% solution is firmly bound to the base metal, partly insulating, about 2 micrometer thick and, according to Figure 5b, has a low "macroscopic porosity". Its cohesional strength is low so that the bonded joints failed inside the oxide layer before the ageing test. The results presented later will show that it is possible to obtain a cohesional failure in the unaged state and to improve the durability properties for shorter anodizing periods. The black colour of the surface is probably attributable to the big excess of zinc in the zinc oxide lattice.[12] The XPS analysis of the surface revealed *ca.* 56% Zn and 35% O (Zn/O ratio 1.6), as against 18.5% Zn and 47.7% O (Zn/O ca. 0.39) for the degreased substrate (Table II).

In Figure 5c, the metal coupons display a structure modified significantly after anodization in 4% NaOH, compared with the samples anodized in the 2% NaOH

TABLE I

Characteristics of zinc specimens (Zn 99) anodized in 2 or 10% NaOH solutions

NaOH conc.	Current density	Oxide layer	Anodizing time (t)/Oxide layer thickness (l)	Mode of failure of bonded joints made from the specimens and the epoxy adhesive 1K-A	
				unaged	aged in water
2%	30 mA/cm^2 $\Rightarrow$ passivation of the surface	compact oxide layer/very low porosity	● $t \leq 5$ min $\Rightarrow l \leq 1$ µm ● 5 min $\leq t \leq 30$ $\Rightarrow 1 \leq l \leq 5$ µm	● cohesive fail. in the adhesive ● failure in the oxide layer	● cohesive fail. in the adhesive ● failure in the oxide layer
10%	30 mA/cm^2 $\Rightarrow$ etching of the surface	surface etched/ high porosity	● $t \leq 30$ min $\Rightarrow l \leq 2$ µm	● cohesive fail. in the adhesive	● cohesive fail. in the adhesive

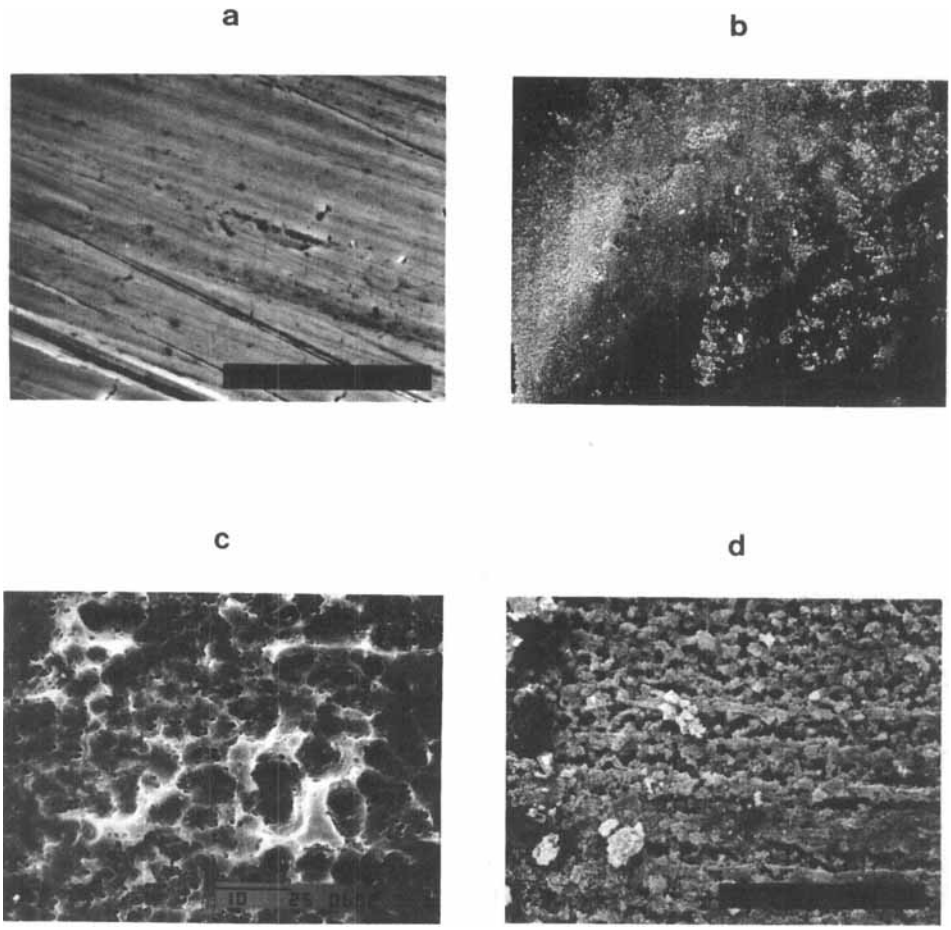

FIGURE 5 Scanning electron micrographs (2000 x) of zinc specimens degreased (a), or anodized for 10 minutes in 2% (b), 4% (c) or 10% (d) NaOH solutions ($i = 30$ mA/cm^2).

solution. However, the macroscopic porosity of the oxide layer remains low. The failure of the bonded joints in the unaged state occured inside an adhesive layer and the residual shear strengths after the ageing test was low, *ca.* 7.5 MPa (drying conditions: 1 hour, 150°C) compared with 5.6 MPa (drying conditions: 1 hour, 150°C) for the specimens anodized in 2% NaOH. In addition, the metal side of the fracture surfaces was fully delaminated after the ageing test.

The most significant change occurred on the surface of the specimens anodized in the 10% NaOH solution. The oxide layer developed on these specimens had a thickness of about 1 micrometer and displayed, in Figure 5d, a much higher porosity than that observed so far for the previous samples. Such an oxide structure is likely to enable a dissipation of the stress during mechanical testing in a much larger volume of polymer than it is normally observed for simply degreased specimens. Surprisingly enough, the oxide layer in this case is not firmly bound to the base material and can be destroyed

TABLE II

Atomic composition of interfacial fracture surfaces of bonded joints made from grit-blasted or anodized zinc specimens and polypropylene (PP)

Element (*At.*%)	%C	%O	%Zn	%Cl	%Ti	%Cu	%F
Zinc (Zn99, degreased or degreased and grit-blasted) and Polypropylene (PP)							
Zn99 degreased	33.9	47.7	18.5				
Zn99 gritblasted	30.0	39.0	31.0				
Polypropylene, as received	80.0	4.5					15.5
Zn99 gritblasted/PP joint: unaged							
Interf. PP side	98.2	1.8					
Interf. zinc side	60.0	27.4	12.7				
Zn99 gritblasted/PP joint: aged for 8 weeks in water at 70°C							
Interf. PP side	91.1	6.4	2.5				
Interf. zinc side	59.3	25.4	15.3				
Zinc (Zn99) substrates anodized in 2 or 10% NaOH for 10 min. ($i = 30\,\mathrm{mA/cm^2}$)							
Zn anodized 2% NaOH	9.0	35.0	56.0	1.0			
Zn anodized 10% NaOH	18.2	46.2	26.2	3.2	4.0	3.0	
Zn99 (anodized in 10% NaOH)/PP joint: unaged							
Interf. PP side	96.5	2.7	0.8				
Interf. zinc side	82.5	11.6	5.9				
Zn99 (anodized in 10% NaOH)/PP joint: aged for 8 weeks in water at 70°C							
Interf. PP side	91.1	6.3	2.6				
Interf. zinc side	81.4	12.7	5.8				

just by touching it with the fingers. An interesting analogy is provided by the oxide layers created on aluminium following anodization in phosphoric acid. The latter are very fragile and the freshly-anodized substrates have to be stored with great caution before bonding.[15] A TEM picture (Figure 6) of the metal/adhesive cross-section illustrates the looseness of the oxide layer: it partly separated from the metal and the adhesive flowed underneath the oxide during curing of the bonded joints. The loose part of the oxide layer is about 1 μm thick and 3 to 4 μm away from the adhesive/metal interface.

To verify the possibility of protecting the anodized substrate with a layer of primer without losing its good bonding properties, a series of zinc coupons freshly anodized in a 10% NaOH solution was primed with a 10% solution of a model epoxy adhesive (having the same dicyandiamide/epoxy resin ratio as the adhesive 1K-A) in isopropanol. The specimens were primed by dipping the metal coupons for 5 seconds in the solution and subsequently cured at 200 °C for one hour (same conditions as for the epoxy adhesive). A weight gain of about 4.8 mg was measured for the primed specimens (surface area primed *ca.* $30\,\mathrm{cm}^2$) so that it could reasonably be assumed that the deposited layer of primer was *ca.* 1 to 2 μm thick. The primed specimens which were bonded 48 hours later with the epoxy adhesive performed well after the immersion test (see right hand side of Figure 3), with a residual lap shear strength of 12.4 MPa after 5 weeks of testing in water at 70°C. Moreover, as was observed for unprimed specimens

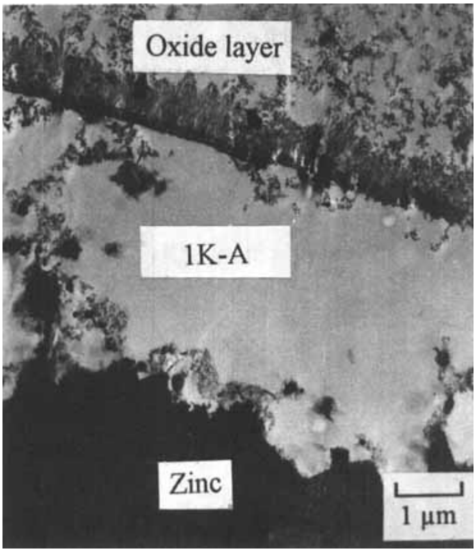

FIGURE 6 TEM image of the zinc/1K-A interface (10500 *x*) obtained from a zinc specimen anodized in 10% NaOH for 10 minutes ($i = 30$ mA/cm^2). Note the diffusion of the oxide layer into the adhesive.

directly bonded after anodization treatment, the failure occurred for both the unaged and aged specimens well inside a layer of adhesive.

As already mentioned above, the specimens anodized in the 2% NaOH solution for 10 min. had very poor durability properties. This was attributed to both the low porosity of the oxide layer and the length of time the specimens were anodized; time which was shown to be responsible for a failure of the bonded joints inside the oxide layer in the unaged state.

Figure 7 compares the durability performances of zinc specimens anodized in 2 or 10% NaOH solutions for anodizing periods ranging from 20 seconds to 30 minutes. The residual shear strengths of the specimens anodized in the 10% NaOH solution were on average 30% better than those of degreased specimens after 5 weeks of immersion in water at 70°C, and 50% better after 2 weeks in water at 90°C. For most specimens anodized in the 10% solution, the failure occured on average 70 to 80% cohesively inside a layer of epoxy adhesive, whereas it was maximum 30% cohesive for the best specimens anodized in the 2% NaOH solution.

The results presented in Figure 7 demonstrate, however, that it is possible to improve significantly the durability of the bonded joints using a 2% NaOH solution for anodizing periods ranging from 1 to 5 minutes. The improvement is, however, much less significant than that observed for the specimens anodized in the 10% NaOH solution. The difference is particularly remarkable after storing the specimens in water at 90°C.

In both cases, probably because of the electronic-conductor character of zinc oxide, the oxide layer is not insulating (according to corrosion measurements carried out with salt bridges) and its protection against electrochemical corrosion should be limited.[16]

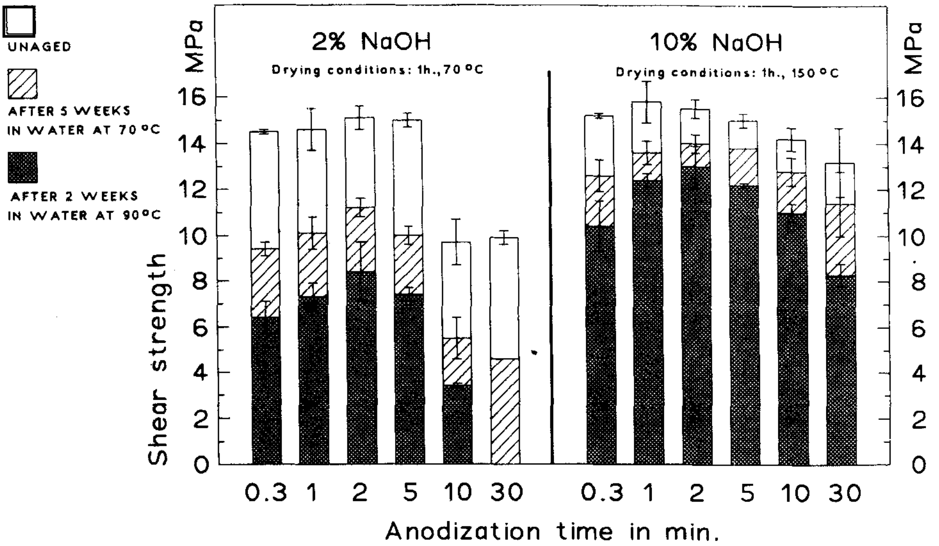

FIGURE 7 Influence of the anodizing periods on the hydrolytic stability of Zn99/1K-A bonded joints.

According to Kaesche, the current densities measured on "passive" zinc substrates are so high that it is not possible to consider this state of passivity as being technically useful.[17]

The increase in size of the true surface area of the oxide layer and the possibility for the polymeric molecules to diffuse into its pores could well account for the improved durability properties. This possibility will now be studied.

4 INVESTIGATION OF "MECHANICAL INTERLOCKING EFFECTS" USING POLYPROPYLENE AS A MODEL ADHESIVE

A study was carried out with polypropylene (PP) as a model adhesive (used as a hot-melt) to study the influence of mechanical interlocking effects on the performance of the bonded joints. The characteristics of PP, in particular its high chemical and thermal stability, make it an appropriate choice to minimize the chemical interactions at the metal/polymer interface. The Differential Scanning Calorimetry (DSC) spectrum of PP used in this study displayed an endothermal peak with a minimum at 168.4°C (melting of PP) and an exothermal peak starting at *ca.* 225°C (decomposition of PP). In addition, polypropylene is stable in hot water at 70 °C for more than 10 years so that the degradation of metal/PP joints should be dominated by the degradation of the metal substrate.[18]

The metal coupons were grit-blasted or anodized prior to bonding with a 0.5 mm thick polypropylene film supplied by Goodfellow (UK). The joints were heated at 200 °C for 1 hour. Attempts to produce bonded joints from degreased substrates were unsuccessful. The morphology of the surface produced by grit-blasting allows the polymer to anchor itself mechanically to the surface, as has been shown for aluminium substrates.[19] Electrostatic interactions at the metal/polymer interface can also play a significant role.[20]

Figure 8 compares the shear strengths of specimens bonded with the epoxy adhesive and polypropylene. In this case, the zinc specimens were only degreased prior to the anodizing treatment (no preliminary etching in HCl) in order to assess better the influence of the gradual modification of the surface structure.

The shear strength of bonded joints made from zinc anodized in 10% NaOH and polypropylene gradually increases as a function of the time of anodization to reach a maximum of 12.4 MPa for a 10 min. anodization period. This value is surprisingly high and directly comparable with the shear strength of specimens bonded with the epoxy adhesive. It is likely that anodization periods greater than 5 min. allow full development of the morphology of the oxide layer. The latter would enable an optimal wetting of the surface as polypropylene flows upon melting into the pores of the oxides. This is illustrated in Figure 9 which reproduces the interfacial anodized zinc side (9a) and polypropylene side (9b) of an unaged bonded joint. For the purpose of comparison, the polypropylene interfacial side of a grit-blasted/PP unaged bonded joints is also reproduced (9c). In the latter case, PP does not have the lamellar structure observed for the anodized specimen and the penetration depth of PP into the surface is, accordingly, likely to be smaller. This is confirmed by the low initial shear strength of bonded joints made from grit-blasted zinc and polypropylene: *ca.* 3.8 MPa.

An anodization period of five minutes is also appropriate to achieve excellent durability properties. For anodizing periods greater than 5 minutes, the strength retentions of the Zn99/polypropylene bonded joints exceed those of the Zn99/1K-A

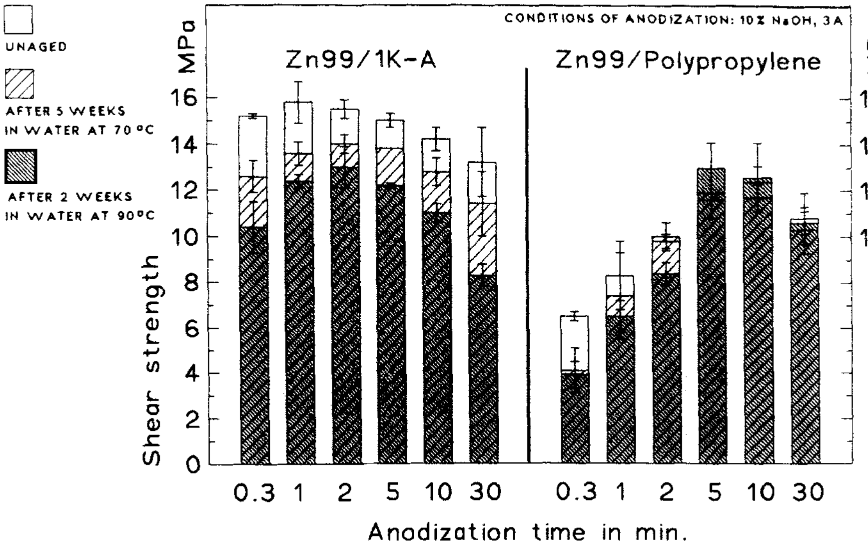

FIGURE 8 Comparison of the durability properties of bonded joints made from anodized zinc specimens (10% NaOH, $i = 30\,\mathrm{mA/cm^2}$) and the epoxy adhesive 1K-A or polypropylene used as a model adhesive.

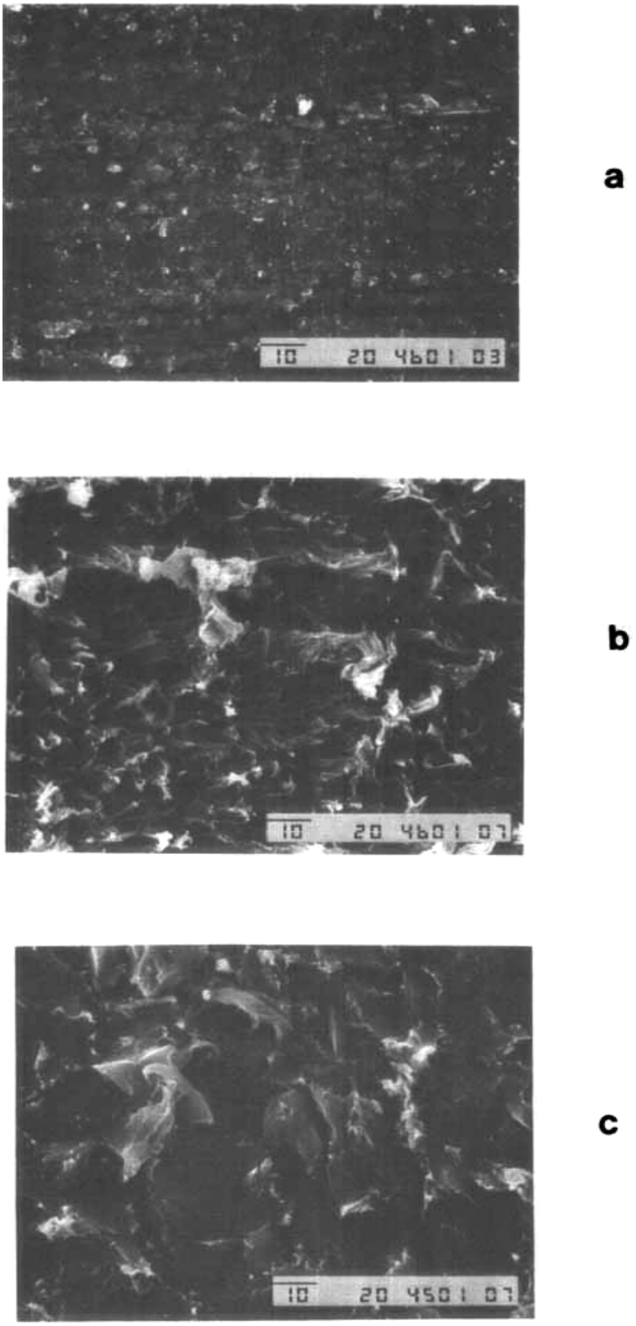

FIGURE 9 Scanning electron micrographs (500 *x*) of the interfacial zinc (**a**) and polypropylene (**b**) sides of unaged anodized zinc (10% NaOH, 10 min., $i = 30$ mA/cm^2)/PP joints, (**c**) PP interfacial side of unaged grit-blasted zinc/PP joints.

bonded joints. No decrease in shear strength after 5 weeks of immersion in water at 70 °C was detectable. The slight increase (103% with respect to the initial strength) is most likely to be due to the plasticization of the polymer by water.

Figure 10 presents the interface of a zinc specimen anodized in 10% NaOH, bonded with polypropylene, and aged in water for 2 weeks at 90°C. As was observed above in Figure 6 for the epoxy adhesive, the layer of zinc oxide generated after the anodizing

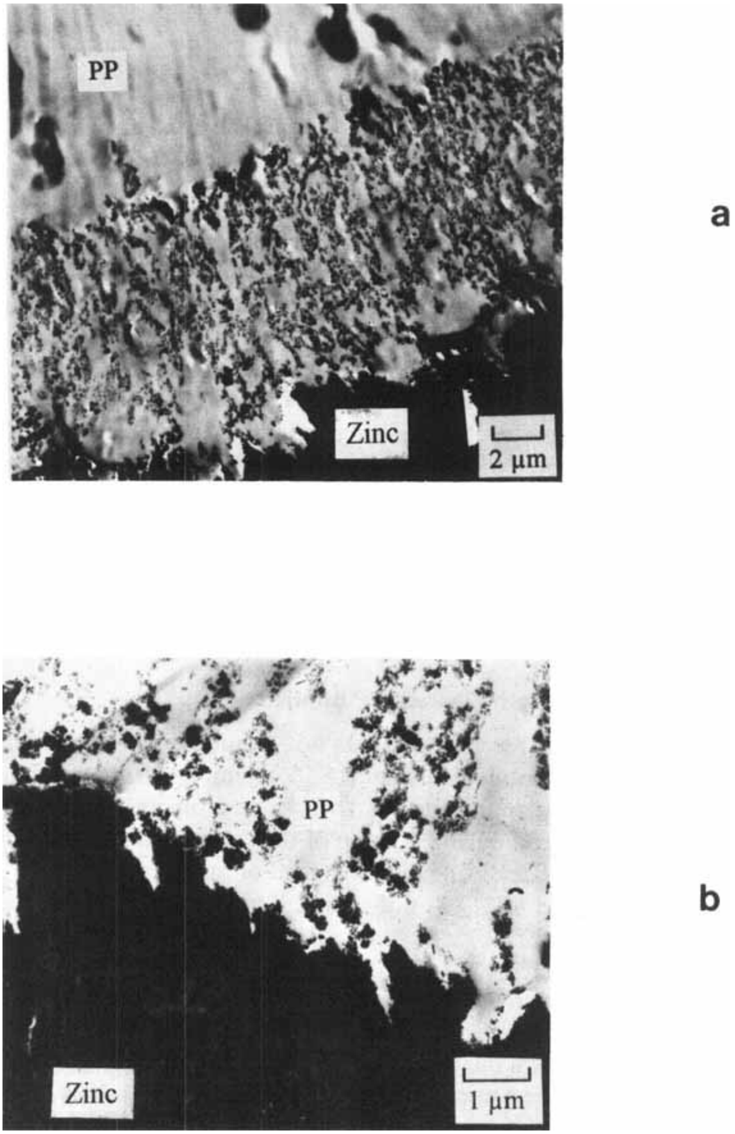

FIGURE 10 TEM image of a zinc (anodized in 10% NaOH, 10 min., $i = 30$ mA/cm^2)/PP interface (a) unaged state (3900 x), (b) after 2 weeks in water at 90 °C (10200 x).

treatment diffused in polypropylene during curing of the joints (Figure 10a). The diffusion of PP occurred deep into the surface and no signs of destruction caused by the ingress of water are detectable at the metal/polymer interface after the ageing test (Figure 10b). The thickness of the oxide layer has, therefore, little influence on the durability of the bonded joints. Although it is not possible to assess, at this stage of this investigation, the stability of the oxide layers located at the metal/adhesive interface (see Section 6 below), the morphology of the metal surface (see Fig. 10b) clearly shows that "mechanical interlocking effects" are likely to explain the good performances of the bonded joints.

5 XPS-ANALYSIS OF THE FRACTURE SURFACES

5.1 Introduction

It is particularly important to be aware of the chemical transformations occuring at the metal/polypropylene interface during heating of the joints and after the ageing test. It is well known that Teflon, which is probably the polymer with the worst adhesional properties, can be bonded adequately if its surface is oxidised through plasma treatment, for example. An oxidized surface can be easily wet and the formation of hydrogen bonds in the interphase region would contribute to the strength of the joint.[21] Recent works cast some doubts about the need for a surface to be oxidized in order to give better adhesional properties. Schonhorn *et al.* studied the tensile shear strengths of aluminium-epoxy-gold-polyethylene-gold-epoxy-aluminium composites; the strengths were very high although no sign of oxidation of the gold/polymer interface could be detected by XPS.[22]

In the present case, XPS analyses of the interfacial polypropylene or metal sides of Zn99/PP bonded joints (grit blasted or anodized) in the unaged state or after ageing in water for 8 weeks at 70°C are presented in Table II.

5.2 XPS Analysis of Zn99 (grit blasted)/PP Bonded Joints

Polypropylene was used as received and was not cleaned prior to bonding. Carbon, oxygen, and a significant amount of fluorine (15.5%) stemming from the manufacturing process (lubricating oil, wrapping paper...) was found on its surface. This surface contamination was displaced during heating of the system and no fluorine could be detected on the metal interfacial side in the unaged or aged state.

There were 98.2% C and 1.8% O on the unaged polypropylene failure surface and 60% C, 27.4% O, and 12.7% Zn on the corresponding substrate failure surface. Therefore, the failure mainly occurred at the zinc/polypropylene interface. Nevertheless, the O/C ratio from the metal failure surface, 0.46, is significantly lower than the value of 1.3 obtained from the clean grit-blasted surface, indicating partial adsorption of polypropylene on the metal interfacial side. After 8 weeks of ageing in water at 70°C, there was little change in the composition of the fracture surfaces. The failure was still mainly at the zinc/PP interface and the polypropylene interfacial side was only slightly more oxidized than it was just after curing of the joints: the O/C ratio increased from 1.8 to 7%. However, around half of the oxygen on PP could be attributed to the presence of

2.5% Zn (*ca.* 1% ZnO and 1.5% Zn $(OH)_2$). It shows that partial dissolution of the zinc substrate occurred under the polypropylene and that the failure partly took place in a layer of zinc corrosion products.

5.3 XPS Analysis of Zn99 (anodized)/PP Bonded Joints

The Zn(2p) binding energies of ZnO and Zn $(OH)_2$ are relatively close to each other (1021.3 and 1021.8 eV, respectively). It is, however, possible to resolve ZnO and $Zn(OH)_2$ without ambiguity by checking the positions and ratios of the O(1s) bands which are well separated for both species (530.4 and 531.9 eV, respectively).

The percentage of zinc increased on the surface of the specimen anodized in 10% NaOH: 26.2% compared with 18.5% for the degreased substrate. While ZnO accounts for 65.5% of Zn on the surface of the degreased substrate as against 34.5% for $Zn(OH)_2$, it only accounts for 49.6% of the total amount of Zn, as against 50.4% for $Zn(OH)_2$ on the surface of the anodized specimen. 4% of Ti and 3% Cu account for a segregation of alloying elements initially present in Zn99 to the surface during anodization.

The study of the failure mechanisms of anodized zinc/PP joints offers other interesting features. 82.5% C, 11.6% O, 5.9% Zn were detected on the metal failure surface (O/C ratio *ca.* 0.14), as against 18.2% C, 46.2% O, and 26.2% Zn for the freshly-anodized substrate (O/C ratio *ca.* 2.6). Moreover, the carbon peak on the metal interfacial side revealed only one component at 284.8 eV (C-C). The failure was, therefore, mainly cohesive within a layer of polypropylene very close to the metal side. A very small amount of zinc (0.8%) was detectable on the polypropylene side. The degree of oxidation of PP was approximately that determined on the PP side of the grit-blasted zinc/PP system in the unaged state (O/C, respectively, *ca.* 2.8 and 1.8%).

After total immersion in water, the failure was still mainly within the polypropylene and the slight zinc concentration increase (+ 1.8%) on the polymer side accounted for the small amount of corrosion products formed during ageing test.

5.4 Conclusion

The failure, which was mainly adhesive when zinc was grit-blasted prior to bonding, occurred mainly within the polypropylene for the anodized substrate. The degree of oxidation of the polypropylene in the boundary layer was very small and stayed practically constant throughout the ageing test. There was no sign of degradation of the polypropylene.

6 ANODIZATION OF HOT-DIPPED GALVANIZED STEEL

It was demonstrated in a previous study that the hydrolytic stability of bonded joints made from an ultrasmooth hot-dipped galvanized substrate (G2F) and 1K-A is jeopardized by the ability of zinc to corrode in media deprived of oxygen, as well as by intergranular corrosion phenomena occuring on the whole surface of the metal substrate (the top layers of G2F consist of *ca.* 2 thirds of aluminium oxide and 1 third of zinc oxide).[1]

The zinc layer on G2F is about 10 μm thick so that the anodizing treatment for this substrate should be "as smooth as possible" in order to exclude a chemical attack of the zinc coating. The degreased G2F coupons were anodized in 2% NaOH using a current of 3 A/dm^2 for periods ranging from 5 seconds to 10 minutes. The edges of the metal coupons were not protected prior to anodization.

As was mentioned above, zinc specimens anodized under these conditions develop a compact oxide layer with a very low porosity (see Table I). Figure 11 presents the results obtained after the immersion test in water or salt-spray test for G2F specimens. The improvement is significant for anodization periods as short as 5 seconds. An average increase of about 20% on the initial shear strength and *ca.* 70% on the residual strength after the immersion test is obtained for anodization periods of up to 2 minutes. The residual shear strength of the galvanized specimens anodized for 2 minutes is directly comparable with what was obtained for Zn99 anodized under the same conditions: in both cases, 74% of the initial shear strengths after 5 weeks of immersion in water at 70°C. Five minutes and certainly 10 minutes are too long anodization periods and the failure of the bonded joints took place inside the oxide layer (the adhesive interfacial side was partly covered with a black layer of zinc oxide). After the salt spray test, the bonded joints performed well in all cases (degreased or anodized specimens) with an average strength retention of *ca.* 12 MPa after 6 weeks of testing (see Figure 11).

It is noteworthy that the corrosion resistance of bonded joints made from zinc or galvanized steel (degreased or anodized) specimens and the epoxy adhesive 1K-A was very good in all cases. Bonded joints which cohesively failed inside a layer of adhesive in the unaged state had residual lap shear strengths greater than 80% after 6 weeks of salt spray testing (these results are not presented in detail in this paper).

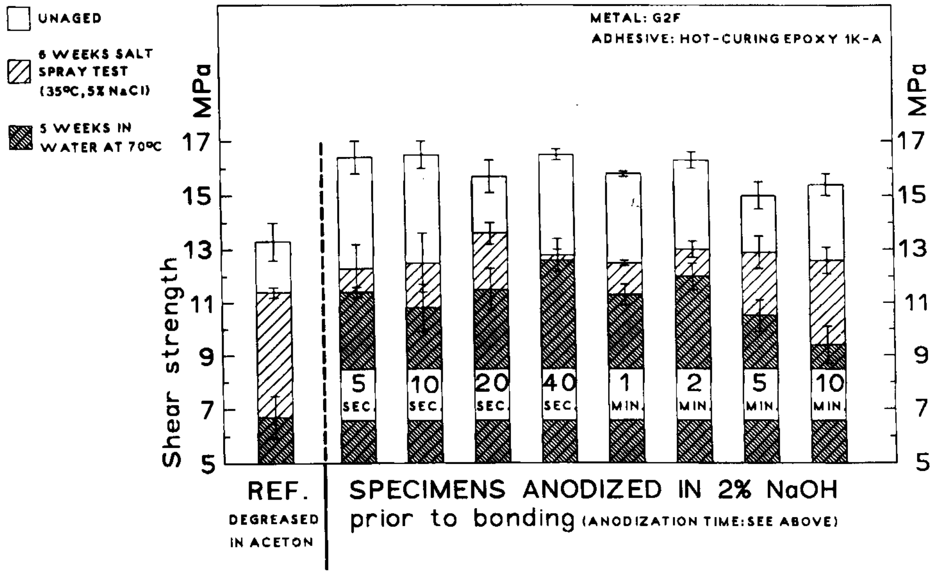

FIGURE 11 Durability of anodized hot-dipped galvanized steel (G2F)/1K-A bonded joints. (anodization conditions: 2% NaOH, $i = 30\,\text{mA/cm}^2$).

During the course of this study, it was necessary to investigate a possible contamination of the surface from the unprotected edges of the galvanized substrate during the anodizing treatment. A series of zinc-coated specimens was treated with a special coating used for protection purposes during electrochemical treatments.[23] The edges of the metal coupons were coated carefully in order to avoid a contamination of the surface before anodization, dried overnight at room temperature (following the instructions of the coating manufacturer), anodized and bonded the next day. Identical initial shear strengths and results after durability tests were obtained as for unprotected specimens.

In order to check the chemical modifications occurring on the surface of the metal coupons during anodization, an XPS analysis of the galvanized substrates was also carried out. Both the center and a zone very close to the edges of the anodized coupons were analyzed to check the eveness of the surface treatment. The results of the analysis presented in Table III show that the composition of the galvanized substrate was drastically modified after anodization. A comparison of the analyses of both zones show that the anodizing treatment produces a surface with a reproducible atomic composition. The concentration of aluminium was reduced to 0.6% after anodization, compared with 12.5% for the clean metal substrate. The concentration of zinc was multiplied by *ca.* 6. The intergranular corrosion effects between zinc and aluminium are likely to be limited in comparison with the observed results for degreased G2F specimens.

Another interesting feature of this set of data is the great difference in the ZnO/$Zn(OH)_2$ ratio: respectively, 1.4 and 3.6 in the degreased and anodized state. Therefore, the oxide layer of the hot-dipped galvanized substrates anodized under these conditions mainly consists of ZnO (as is the case for Zn99 anodized under the same conditions, see Table II). In contrast, the zinc coating produced on the surface of zinc coupons treated in a 10% NaOH solution consisted of approximately an equal amount of ZnO and $Zn(OH)_2$. A cross-cut of the metal/adhesive interface in the unaged state is presented in Figure 12: we can evaluate the thickness of the oxide layer for a galvanized specimen anodized in 2% NaOH for 1 minute at *ca.* 150 to 200 nm.

As observed before, the same residual strength was obtained from G2F or Zn99 specimens anodized for 2 minutes in 2% NaOH and aged for 5 weeks in water at 70°C, *ca.* 74%, as against 50% (G2F) and 54% (Zn99) for degreased specimens. Attempts to produce joints bonded with PP from specimens anodized in 2% NaOH (G2F or Zn99) were unsuccessful. The morphologies of the oxide layers of the anodized (Figure 12) and degreased (Figure 1a) specimens are comparable and the improved durability properties in this case can mainly be attributed to the higher hydrolytic stability of the oxides.

TABLE III
Atomic composition of the hot-dipped galvanized substrate (G2F)

Element (At.%)	%C	%O	%N	%Zn	%Al	%Pb	%Cl
G2F degreased	36.0	41.7	3.2	6.1	12.5	0.7	
G2F anodized/2% NaOH ($i = 30$ mA/cm^2)/1 min:							
center	15.3	41.4		40.6	0.6		2.2
near the edges	16.6	42.2		38.1	0.9		2.2

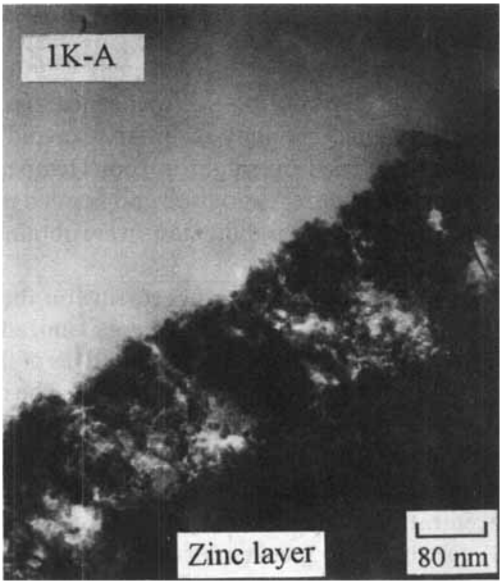

FIGURE 12 Cross-section (TEM image, 120000 x) of the G2F/1K-A interface, anodization conditions: 2% NaOH, 1 min., $i = 30$ mA/cm^2.

Conclusion

This anodizing treatment carried out under mild conditions (2% NaOH solution; anodizing current: 30 mA/cm^2; anodizing time: 5 seconds to 2 minutes) gives satisfactory results. Fracture surfaces of joints after an ageing test in water demonstrate that the corrosion of the bonded joints is restricted to an area close to the edges of the bonded parts. Corrosion phenomena at grain boundaries which were responsible for the accelerated degradation of the degreased hot-dipped substrate are not detectable and the hydrolytic stability of the bonded joints is significantly improved.

SUMMARY

Zinc-coated substrates were anodized in sodium hydroxide solutions and bonded with a commercial one-component epoxy adhesive. Lap shear joints were aged following immersion and salt spray tests. The morphology of the oxide layers was investigated with SEM and TEM imaging analyses and their composition by XPS.

Two possibilities leading to an improved hydrolytic stability of the bonded were found. The anodization of zinc metal coupons in 10% NaOH (30 mA/cm^2) allowed the development of an etched structure covered with a porous oxide layer. A study carried out with polypropylene as a model adhesive demonstrated that the diffusion of the polymer into the oxide structure ("mechanical interlocking effects") was essential to achieve good durability properties.

The anodization of zinc-coated substrates in dilute sodium hydroxide solutions (2% NaOH, 30 mA/cm^2) allowed the growth of a compact oxide layer with a low porosity. For short anodizing times (< 2 min.), the speed of dissolution of zinc during the storage of the adhesively-bonded joints in hot water was significantly reduced compared with simply degreased specimens. Bonded joints made from hot-dipped galvanized coupons anodized under such smooth conditions displayed residual shear strengths up to 70% higher than simply degreased specimens after an immersion test. Thus, car manufacturers could make the most of these results by using a short anodizing process to pretreat some parts of the car body prior to bonding with hot-curing epoxy adhesives.

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