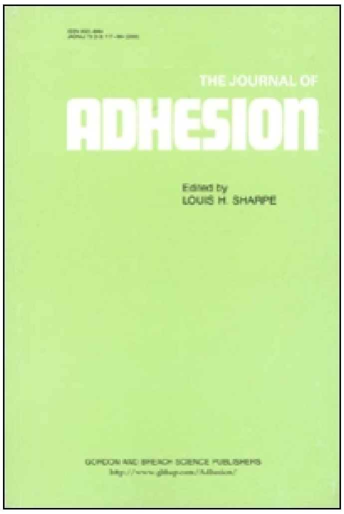
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

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

Ageing of Adhesive Bonds with Various Surface Treatments, Part 1: Aluminium-Dicyandiamide Cured Epoxy Joints

Robert Comrie[a]; Stanley Affrossman[a]; David Hayward[a]; Richard A. Pethrick[a]; Xiaorong Zhou[b]; George E. Thompson[b]

[a] Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK [b] Corrosion and Protection Centre, University of Manchester Institute of Science and Technology (UMIST), Manchester, UK

To cite this Article Comrie, Robert , Affrossman, Stanley , Hayward, David , Pethrick, Richard A. , Zhou, Xiaorong and Thompson, George E.(2005) 'Ageing of Adhesive Bonds with Various Surface Treatments, Part 1: Aluminium-Dicyandiamide Cured Epoxy Joints', The Journal of Adhesion, 81: 12, 1157 — 1181

To link to this Article: DOI: 10.1080/00218460500371673

URL: http://dx.doi.org/10.1080/00218460500371673

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Journal of Adhesion, 81:1157–1181, 2005

ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460500371673

Ageing of Adhesive Bonds with Various Surface Treatments, Part 1: Aluminium–Dicyandiamide Cured Epoxy Joints

Robert Comrie
Stanley Affrossman
David Hayward
Richard A. Pethrick
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK

Xiaorong Zhou
George E. Thompson
Corrosion and Protection Centre, University of Manchester Institute of Science and Technology (UMIST), Manchester, UK

Ageing studies on adhesive-bonded aluminium–dicyandiamide cured epoxy joints prepared using a variety of different surface treatments were carried out using 100% humidity and cycling the joints between 42–48–42°C every hour. The pretreatments include a chromic acid, silica/siloxane pretreatment, nonrinse chrome pretreatment, titanium/zirconium (Ti/Zr) pretreatment, and anodised substrate with no pretreatment. Dielectric spectroscopy measurements were used to characterise the rate of the water uptake and monitor the conversion of the surface oxide to hydroxide. These data were correlated with the changes that occurred in the mechanical strength of the bonds. The changes in the surface structure were observed using electron microscopy and elemental analysis conducted using X-ray photoelectron spectroscopy. The dielectric permittivity changes observed were similar for all the different pretreatments, indicating that the predominant process was water absorption. However, small differences were observed that reflect the different surface treatments used. Ageing at an elevated temperature of 70°C provided definite evidence of hydration of the surface oxide layer. Electron microscopy of the fracture surface indicated oxide-to-hydroxide conversion and was reinforced by X-ray photoelectron spectroscopy. Predominantly, the changes in the mechanical strength observed at low temperature are consistent with the plasticization of the adhesive. However, at the elevated temperature of 70°C, evidence for weakening of the interfacial layer by hydration becomes evident as a

Received 27 July 2004; in final form 11 August 2005.

Address correspondence to Richard A. Pethrick, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow Gl 1XL, UK. E-mail: r.a.pethrick@strath.ac.uk

reduction in the mechanical strength. The dielectric measurements allowed the changes in the bond to be followed nondestructively. The mechanical strength of the etched-only pretreatment aged surprisingly well and at the lower temperature of ageing was comparable with the no-rinse chrome and titanium/zirconium pretreatments. The least durable was the PT2Cr-free treatment; however, all treatments showed a significant level of durability at low temperature.

Keywords: Anodised; Chromic acid; Dielectric analysis; Durability; Nonrinse chrome pretreatment; Silica/siloxane pretreatment; Titanium/zirconium (Ti/Zr) pretreatment

INTRODUCTION

Adhesive bonding of aluminium structures plays an important role in the creation of aerospace and automobile structures [1]. Loss of the strength of aluminium adhesive bonds, because of exposure to moisture and/or elevated temperatures, has long been recognised as being a determining factor defining their useful life [2], Numerous studies have been performed attempting to understand the mechanisms associated with the loss in strength of the joints. Key to understanding this problem is the question of whether hydration of the oxide, which is grown on the substrate to improve adhesion, occurs under the adhesive layer. Currently there are conflicting views as to whether hydration is the cause of bond failure or whether hydration occurs on the bare surface after bond failure has occurred [3–8]. Evidence appears to exist that hydration is occurring before the bond failure is observed; however, other studies point to significant growth in thickness of the oxide layer only after bond failure has occurred. Hydration of an aluminum oxide surface under an adhesive film has been reported when the specimen was immersed for extended periods in hot water [9], Migration of moisture through the adhesive was inferred from the absence of cracks and a lack of access of the water to the specimen edges. The increase in volume as the hydration occurred created a sufficient force to allow the oxide to erupt through the adhesive layer.

In practice, stabilisation of the oxide layer is achieved by careful pretreatment of the oxide interface, resulting in adhesive-bonded structures that are durable for long periods of time. The pretreatments aim to either enhance bonding between adhesive and oxide interface and/or suppress conversion of aluminium oxide to the weaker hydroxide [10]. Growth of a thick cellular oxide layer, $\sim$350 nm, has been shown to provide a lock-and-key mechanism that promotes a good stable bond between the substrate and adhesive [11, 12]. This cellular oxide layer is usually grown by either chromic [13] or phosphoric acid [14] treatment, and its structure has been established by electron-microscopic examination [12, 15]. The nature of the oxide interface and the properties of the adhesive are critical in determining the bond durability. In applications where high volumes of metal are used, it is not possible to grow the thick oxide layers typically used in the aerospace industry, which typically require a number of minutes to grow, and alternative approaches are required. The typical treatment involves a rapid hot etch of the aluminium followed by a phosphoric acid anodising pretreatment system. This process differs from the conventional anodisation process in that the surface is anodised for a much shorter time but the growth conditions are more rapid. Typical conditions would be 50–70 °C with 50 V and a current density of 1–4 kAm^{-2} for a time of 0.25–6 s depending on the line speed through the bath. The oxide grown is 5–200 nm thick.

In this article, the durability of a series of dicyandiamide-cured epoxy aluminium-bonded systems with different oxide pretreatments are reported. The surface treatments either involve different methods of growth of the original oxide layer or, alternatively, subsequent treatment once the oxide layer was created The systems reported are as follows:

Chromic Acid Treatment

The chromic acid treatment involves etching the metal at 65 °C in a solution of sodium dichromate and sulphuric acid [13]. The surface morphology created consists of a cell structure with oxide whiskers that are approximately 5 nm in diameter and extend 40 nm from the surface. Concerns about the environmental problems with the use of chromium have favoured the use of alternative treatments.

Phosphoric Acid Anodised Treatment (PAA)

The PAA treatment is widely used for the bonding of aluminium and its alloys and is widely accepted by the aircraft industry as a method of achieving good adhesion and bond durability. The porous anodic film produced has been studied by electron microscopy [12, 14]. Anodic films can be grown using phosphoric acid and the detailed morphology and chemistry of the surfaces produced are influenced by the conditions used in their growth [14]. Anodising aluminium at 10 V d.c. for 20 min in a 10% solution of phosphoric acid at room temperature produces a whiskered, porous, oxide structure that is about 0.5 μm thick. PAA suppresses the hydration of the aluminium oxide layer

[14] through the formation of an insoluble thin film of AlPO4, which will approach monolayer dimension in places.

Silica/Siloxane Pretreatment

A stable surface layer can be created using a silica/siloxane [16]. The silica/siloxane pretreatment system consists of silica particles dispersed within a silicate/siloxane matrix that is applied to the hot, previously anodised, substrate. The silicate particles produce a rough surface, enhancing the mechanical interlocking between the substrate and adhesive.

Nonrinse Chrome Pretreatment

The surface is treated with a silica suspension deposited onto a partly reduced chromic acid mixture. This produces films with a silica-rich surface and chromium-rich interfacial zone between the silica and the metal substrate [17]. The chromium-rich layer consists of a mixture of trivalent and hexavalent compounds. These compounds are formed as a consequence of the acid dissolution of the metallic-substrate oxide film, followed by the dissolution of the metal and precipitation of chromium hydroxides resulting from reduction of chromium ions [17]. Bond durability is enhanced by the production of a convoluted surface topography resulting from the presence of colloidal silica particulates that are bonded through silanol groups to the epoxide groups in the adhesive. Exposure of films containing Cr(VI) compounds to moisture releases ions, which react with the aluminium and stabilise the oxide layer.

Titanium/Zirconium (Ti/Zr) Pretreatment

The titanium/zirconium (Ti/Zr) pretreatment [18] uses a mixture of polyacrylic acid and a mixture of fluorozirconic (H_2ZrF_6), fluorotitanic (H_2TiF_6), and fluorosilicic acids (H_2SiF_6) in an aqueous solution. Hydrofluoric acid is added to provide a source of free fluoride, which dissolves the aluminium surface. The resultant rise in pH leads to precipitation of the coating mixture that is then heated to form a stable coating [18, 19].

Anodisation and No Pretreatment

As a reference, a simple anodisation process [19] that involves passage of a current through a strong acid electrolyte for short period of time and formation of a thin oxide layer was carried out. Aluminium is often hot- and cold-rolled prior to use, may be deformed, and may have its surface damaged up to a thickness of 300–1000 nm. Etching involves removal of the surface with a system of H_2SO_4/HF and nonionic surfactants. The hydrofluoric acid consumes the aluminium, forming an aluminium fluoride, which remains in solution [20].

In this study, a comparison is made between changes occurring in the dielectric spectrum during ageing characteristics of aluminium–epoxy bonded adhesives, changes that are observed using electron microscopy, surface analysis, and mechanical test data. The nature of the oxide surfaces and the effects of the pretreatments generated are demonstrated in the electron-microscopy studies.

EXPERIMENTAL

Sample Preparation

Lap-shear joints were produced from 2.0-mm-gauge AA5754 aluminium alloy (typical composition: 96.15% Al, 0.10% Si, 0.20% Fe, 0.10% Cu, 0.25% Mn, 3.2% Mg) sheets, which were subjected to the pretreatments indicated previously. The joints consisted of 100 mm × 20 mm adherends with an overlap area of 10 mm × 20 mm and were bonded using a jig. The bond line thickness of the joint was 200 μm, controlled by the addition of 1% by weight of Ballotini glass spheres to the adhesive, and spring clips were used to achieve a constant pressure during cure. The adhesive was a rubber-toughened diglycidyl ether of bisphenol A cured with dicyandiamide and containing fused silica. The cure conditions used were 15 min at 145 °C followed by 15 min at 190 °C. Fifteen joints were prepared for each of the pretreatments studied.

Ageing of Samples

A humidity cabinet that creates (100%) humidity with the temperature cycling between 42–48–42 °C every hour was used for ageing the joints. This particular ageing regime has been shown previously by Alcan to encourage the disbonding in thick film adhesives [20]. Dielectric measurements were conducted on the joints initially on a weekly basis, which was decreased to once every two months as the ageing progressed. The dielectric measurements involved removing the joints from the ageing bath, removing surface moisture, and cooling to ambient temperature. This procedure is not believed to induce any effects on the joints. The joints used for mechanical testing were removed from the bath until they were tested. The ends of the aluminium joints for dielectric testing were abraded to remove the surface oxide, enabling good electrical connection for the dielectric measurements. Prior to ageing, the bond-line thickness for each of the joints was measured by taking the average of several measurements across the bonded area and was typically 0.17 mm ± 0.05 mm. Three joints were studied for each of the surface treatments investigated, and the data presented are the average of the measurements. The dielectric measurements were performed using a Solatron 1250A Frequency Response Analyser (FRA) Franborough, Hants, UK that generates frequencies between 10^{-3} Hz and 63 kHz. The high-frequency dielectric measurements, between 3×10^5 and 13×10^9 Hz, were carried out using a Hewlett Packard HP8753A network analyser, Hewlett Packard, Queensferreg, Scotland, UK. The method used for the measurement and the analysis of data has been described previously [21].

Mechanical Testing

Tensile tests were carried out on batches of three joints using a crosshead displacement speed of 2.0 mm/min and a specimen grip length of 75 mm, with the maximum loads being recorded using an Instron Series IX Automated Materials Testing System (Instrou Ltd, HighWycombe, Buckinghamshire, UK) as described previously [15] The joints used for mechanical testing had not previously been used for dielectric examination and were, therefore, continuously exposed to moisture. Checks were carried out to ensure that the dielectric test joints that were studied had mechanical properties identical to those of the joints used in the mechanical tests.

Modes of Failure

The failure surfaces of the mechanical test pieces were scanned images using a Hewlett Packard 4C high-resolution flatbed scanner. These images allowed visual assessment and differentiation between adhesive (interfacial) and cohesive failure.

Electron Microscopy of Sections of the Joints

Transmission electron microscopy was conducted using a JEOL 2000FX TEM (JEOL, Tokyo, Japan) in the Corrosion Science Centre at UMIST. The adhesive/substrate interfacial region of ultrathin cross-sectioned samples, obtained by microtoming the joints perpendicular to the bond line, were examined. The ultrathin slices were less than 100 nm in thickness.

X-ray Photoelectron Spectroscopy Analysis (XPS)

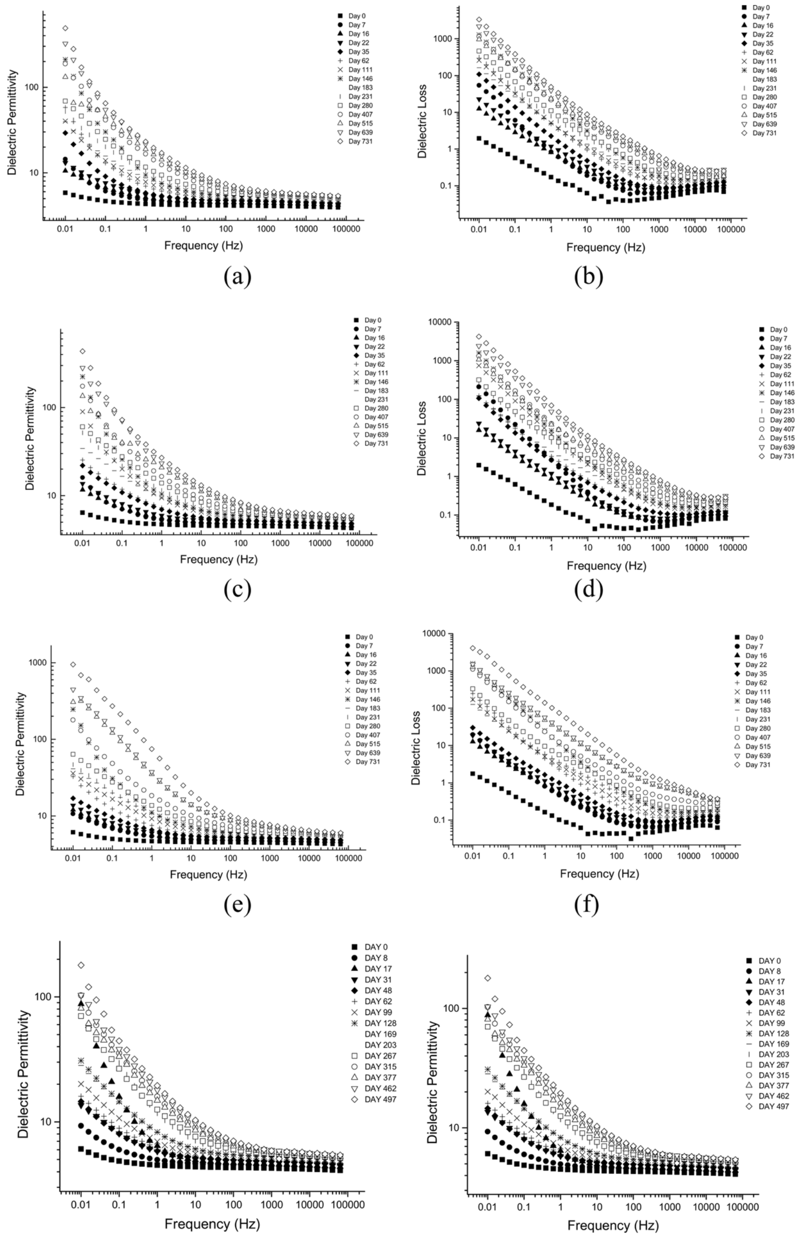
XPS analysis of the fracture surfaces of the joints was undertaken using a Kratos Axis HS XPS spectrometer equipped with a 127-mm-radius hemispherical analyser and a triple channeltron detection system for improved sensitivity (Kratos, Manchester, UK). A magnesium anode X-ray source was used and the survey spectra were recorded between 0 and 1000 eV. The spot size used was 0.8 mm × 0.3 mm.

RESULTS

The initial tests were carried out at 42–48–42 °C; however, to achieve a significant level of ageing within an acceptable time, selected samples were subsequently aged at 70 °C. The results from the ageing at 42–48–42 °C are considered first.

Low-Frequency Dielectric Results (0.01 Hz–63 kHz)

The permittivity of the joints, Figure 1, was observed to increase throughout the period of the study as a consequence of moisture ingress into the adhesive bond. Because the adhesive is common to all the joints the apparent initial similarity between the plots is not surprising and reflects the dominance of the moisture-diffusion process into the bond line. Close inspection of the data, however, reveals that significant differences in the dielectric permittivity and loss curves are observed later in the exposure. These differences may be attributed to the effect of the pretreatment on the moisture-uptake process as a consequence of the surface treatment. The low-frequency dielectric spectrum can be divided into two distinct regions. The region between 0.01 Hz and 10 Hz is associated with a combination of a dipole relaxation process, associated with the glass-to-rubber transition, T_g, and effects arising from interfacial polarisation (Maxwell Wagner Sillers, MWS) processes associated with the heterogeneous nature of the matrix and d.c. conductivity [22–24]. As ageing occurs, the upper frequency limit of this large loss moves gradually to higher frequency with time and indicates a lowering of the T_g as a result of plasticization by moisture. The increased mobility of ions also shifts the MWS and ion-conduction processes to higher frequency. The MWS process is associated with the polarisation of mobile charges constrained within occlusions in

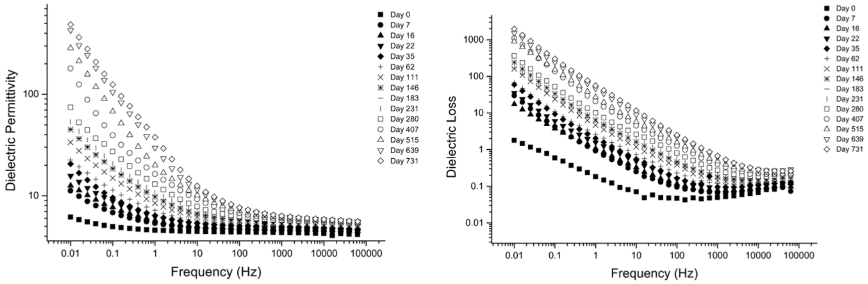

Dielectric Permittivity
Dielectric Loss
Frequency (Hz)
0.01
0.1
1
10
100
1000
10000
100000
Day 0
Day 7
Day 16
Day 22
Day 35
Day 62
Day 111
Day 146
Day 183
Day 231
Day 280
Day 407
Day 515
Day 639
Day 731
DAY 0
DAY 8
DAY 17
DAY 31
DAY 48
DAY 62
DAY 99
DAY 128
DAY 169
DAY 203
DAY 267
DAY 315
DAY 377
DAY 462
DAY 497

(a) (b)

(c) (d)

(e) (f)

(g) (h)



(i) (j)

FIGURE 1 Continued.

the matrix and can give rise to very large dielectric relaxation processes. The second region lies above 10 Hz and is identified by a loss feature at about 10 KHz observable in the dry pristine material. This peak is associated with the relaxation of the pendant hydroxyl groups of the epoxy resin and increases in its amplitude can be attributed to relaxation of water molecules that are bound to the hydroxyl groups [25–27]. The low-frequency dielectric results for all of the joints indicate similar ageing behavior however, there are subtle differences that reflect the way in which moisture is interacting with the surface pretreatments. Plotting the variation of the permittivity as a function of time at 10 KHz, Figure 2, shows that the increase in the permittivity is initially very similar. This is consistent with the assumption that the moisture is predominantly absorbed by the polymer matrix and the permittivity at 10 KHz is indicative of bound and free water. However, differences in the profile and the magnitude of the increment are observed that reflect the way in which moisture can create new dipolar entities when interacting with the pretreatments [27]. The silica/siloxane system and the titanium/zirconium systems show a slightly greater permittivity increase, reflecting additional dipole entities in these systems

FIGURE 1 Low-frequency dielectric data for the high-strength adhesive, no-rinse chrome system (a) dielectric permittivity and (b) dielectric loss; silica/siloxane system (c) dielectric permitticvity and (d) dielectric loss; titanium zirconium (Ti/Zr) system (e) dielectric permittivity and (f) dielectric loss; anodised system (g) dielectric permittivity and (h) dielectric loss; and Etched-Only System (i) dielectric permittivity and (j) dielectric loss. The traces are in ascending order: 0, 7, 16, 22, 35, 62, 111, 146, 183, 231, 280, 407, 515, 639, and 731 days.

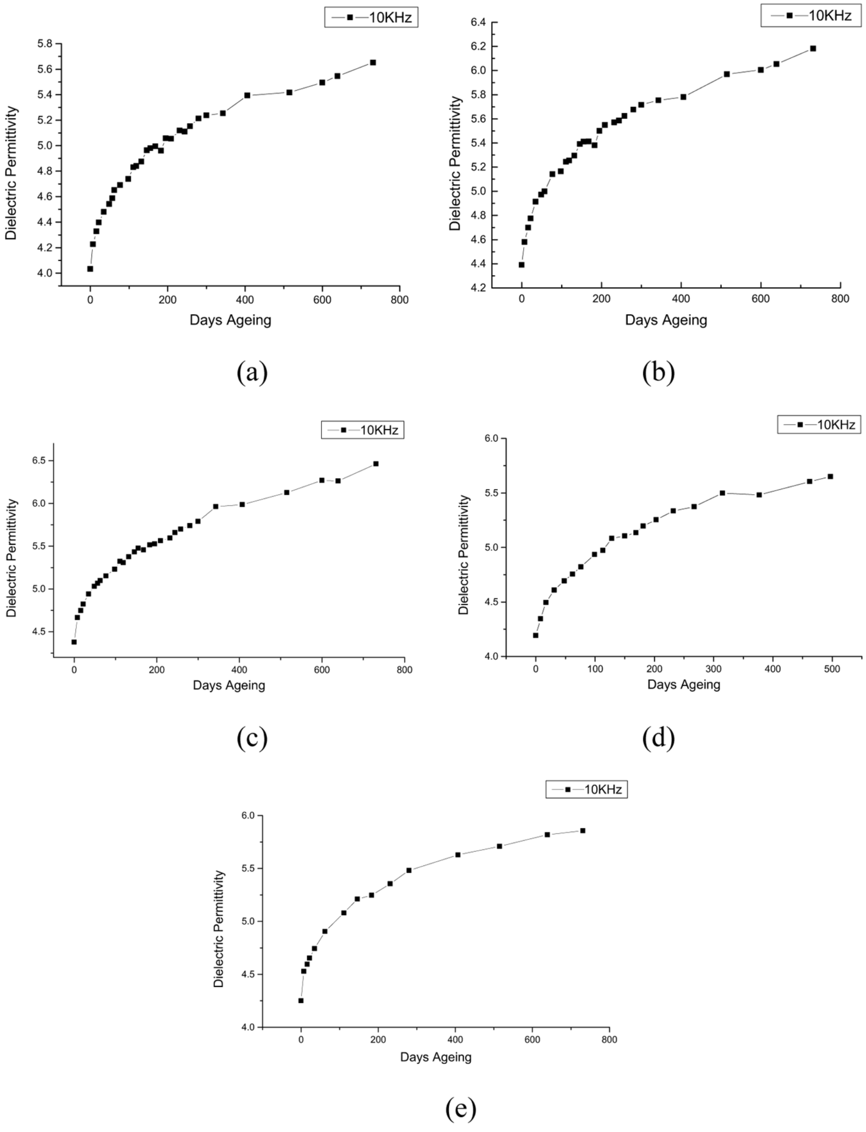


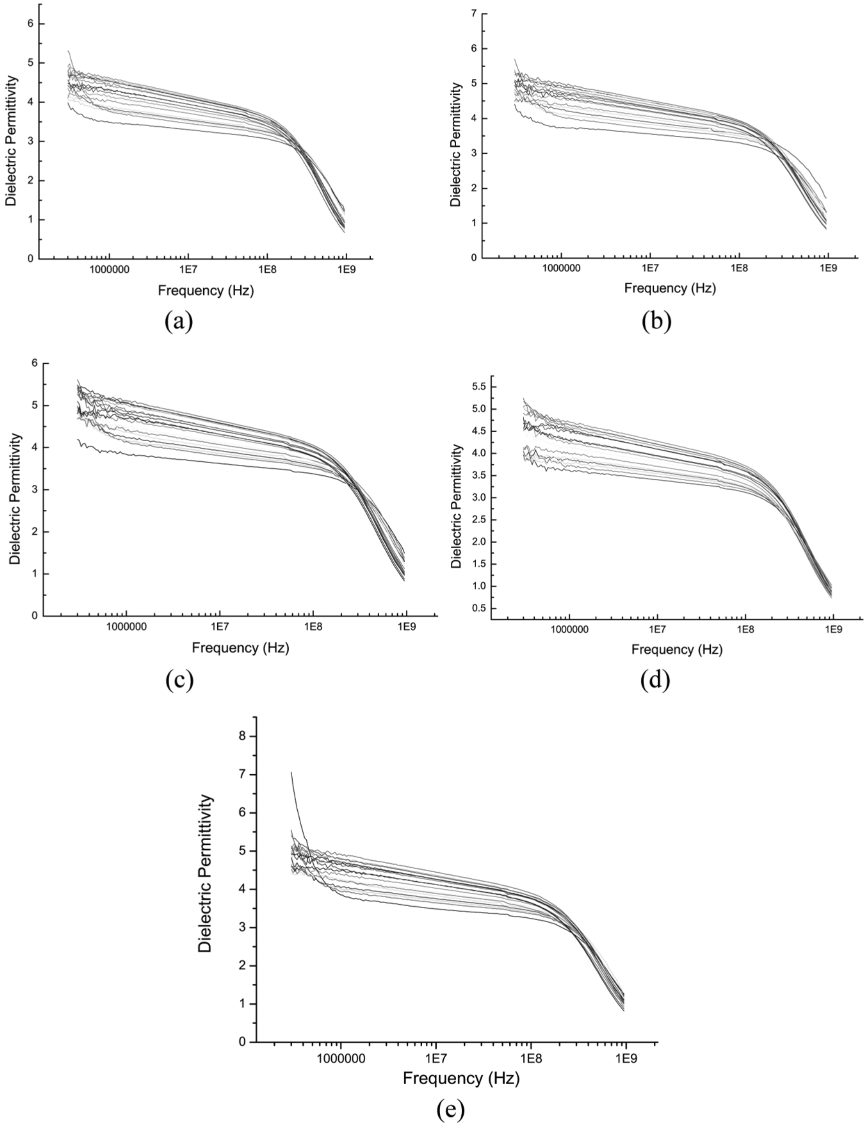
FIGURE 2 Graph of dielectric permittivity at 10 KHz *versus* ageing time for the high-strength adhesive: (a) no-rinse chrome system, (b) silica/siloxane loxane system; (c) titanium/zirconium (Ti/Zr) system, (d) anodised system, and (e) etched-only system.

consistent with additional hydration sites being available on the pretreatment. The heterogeneous nature of the matrix as a result of the surface treatment gives rise to specific features that reflect the structure of the surface and are revealed when partial hydration is occurring.

High-Frequency Dielectric Results (300 KHz–3 GHz)

The permittivity increase observed using high-frequency dielectrics with ageing is attributed to the presence of "free" water within the adhesive. Free water can be associated with molecules that are clustered and reside in capillaries and microcavities within the epoxy matrix. The relaxation of the free water occurs at about 18 GHz [24] that is beyond the range of the measuring techniques used for this study. However, an assessment of the rate of creation of free water can be obtained by monitoring the permittivity at 3 MHz with ageing time, Figure 3. As water molecules bind more strongly to the matrix, their relaxation frequency is lowered and they contribute to the permittivity changes at lower frequencies. If changes were to occur in the surface oxide layer, then distinct frequency dependence would be expected in the range 1–10 MHz associated with the creation of hydroxyl dipoles [25]. No such changes were observed in this region over the period of the study, indicating a lack of significant changes in the interfacial region, Figure 4. The variation in the permittivity at 3 MHz indicates the amount of free water present in the system, which progressively increases with exposure to moisture. This is consistent with the idea that the moisture clusters into microvoids formed during the cure of the matrix or that are associated with the pretreatment. These microvoids have submicron dimensions and are found in all cured epoxy matrices or within the structure of the pretreatment. Once more, the silica/siloxane system and the titanium/zirconium systems exhibit higher values of the permittivity consistent with the idea that there are additional microvoids created in this system that allow clustering of the water. There is no evidence from these traces of corrosion occurring in the joints.

The general conclusions that can be drawn at this point are that the dielectric data indicate that plasticization of the adhesive has occurred and that there are small changes in the nature of the interface, but there is no evidence of any oxide-to-hydroxide conversion at this stage. The process of oxide growth as a consequence of exposure to moisture is a process that appears to be most prevalent under forcing conditions; however, conversion of oxide to hydroxide appears to occur at lower temperatures.



(a) (b) (c) (d) (e)

FIGURE 3 High-frequency dielectric permittivity results for the high-strength adhesive: (a) no-rinse chrome system, (b) silica/siloxane system, (c) titanium/zirconium (Ti/Zr) system, (d) anodised system, and (e) etched-only systems. Data are in ascending order: Day 0, 10, 21, 30, 49, 79, 100, 139, 178, 232, 303, 346, 407, 531, 599, 642, and 710.

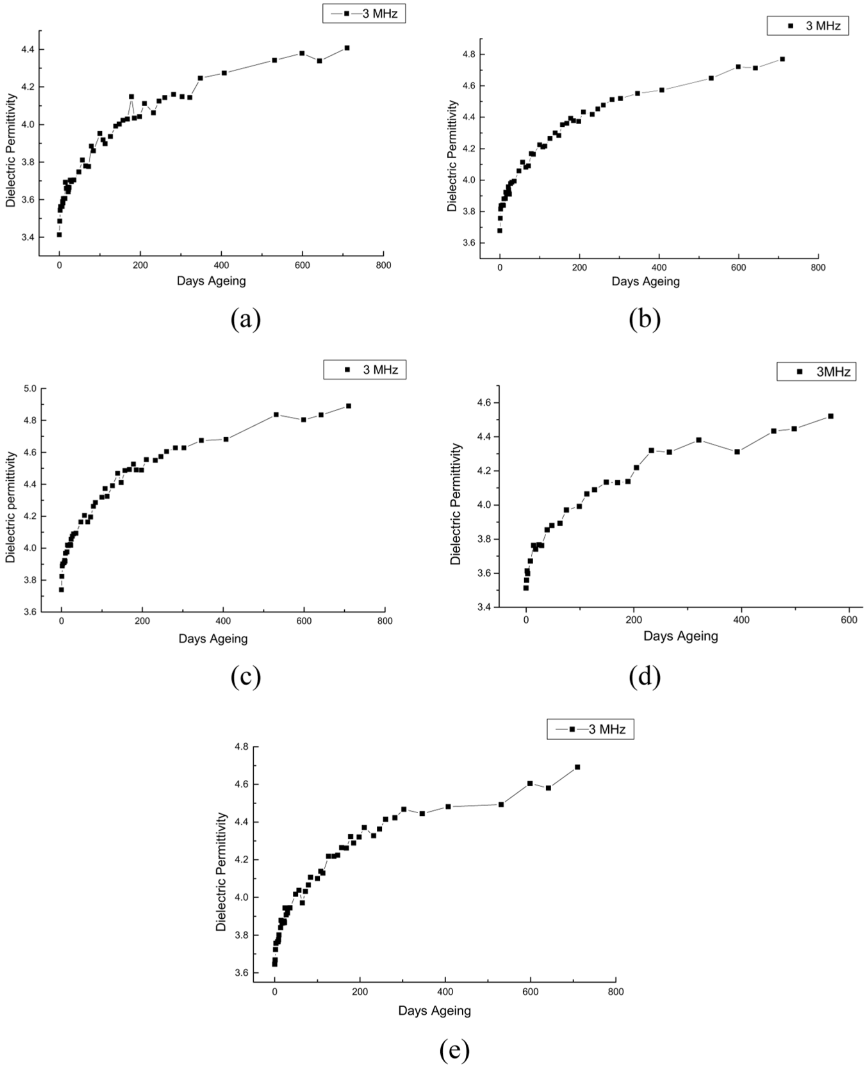


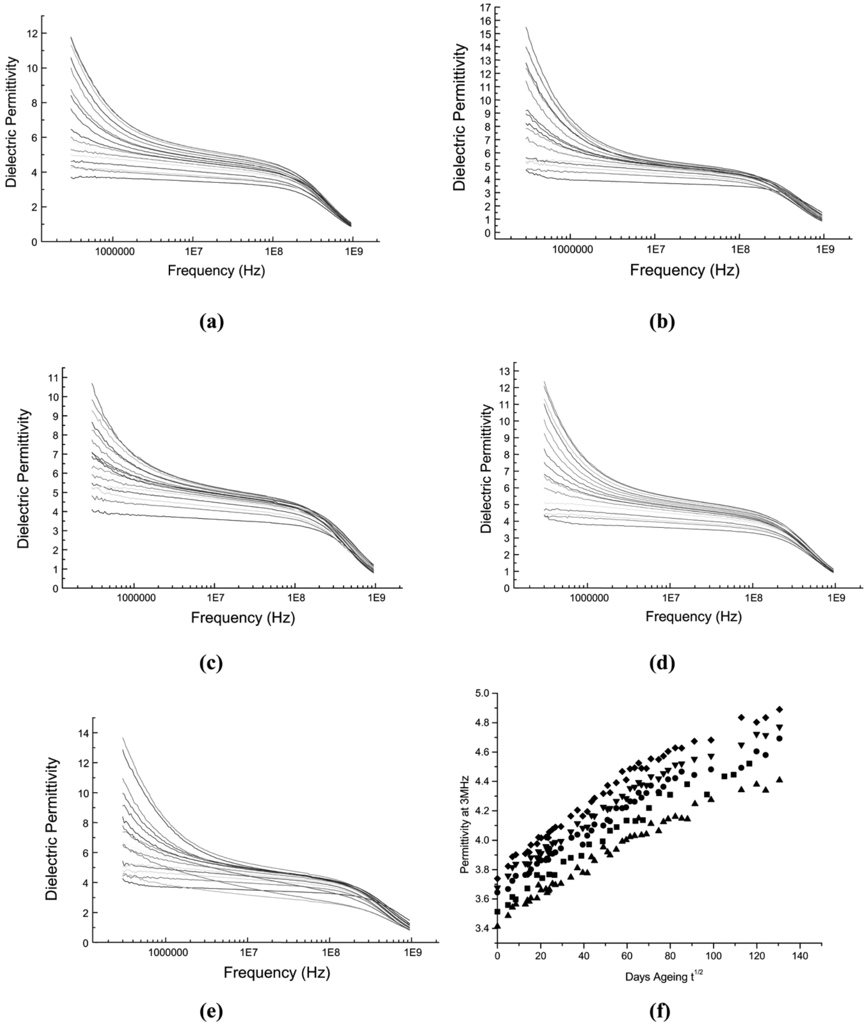
FIGURE 4 Graph of dielectric permittivity at 3 MHz *versus* ageing time for the high-strength adhesive: (a) no-rinse chrome system, (b) silica/siloxane system, (c) titanium/zirconium (Ti/Zr) system, (d) anodised system, and (e) etched-only system.

Results—70 °C Water Bath Samples

A small number of joints were exposed to accelerated ageing at 70 °C to accelerate the joint ageing to a point where failure is observed. The samples were initially aged for 73 days in a humidity cabinet (48–42–48 °C cycling, 100% relative humidity) before being transferred to a 70 °C water bath. The high-frequency dielectric results, Figure 5, show a dramatic increase in permittivity in the megahertz region as the ageing process proceeds, which indicates that hydration of the interfacial region of the aluminium substrate is occurring [1]. The distinct permittivity feature that can be observed developing at 10^6 Hz indicates that hydration of the aluminium substrate is occurring. After 175 days ageing, a dramatic decrease in permittivity can be seen, which indicates that the adhesive has disbonded from the aluminium substrate. The drop in permittivity arises from the presence of air gaps within the bonded structure, which create regions of low dielectric permittivity. As ageing proceeds, the disbonded areas then begin to fill with water and an apparent increase in permittivity can be observed from the dielectric results obtained during the following 26 days. Li [29] and Halliday [30] have reported a similar effect during previous ageing studies conducted on aluminium/epoxy-bonded systems. The dielectric properties mechanical test samples that had not been subjected to the stresses created in the withdrawl process were changes similar to those of the dielectric test samples, which implies that the withdrawl process is not the primary cause for the creation of the air gaps. Furthermore, there appears to be no particular pattern for the appearance of the air gaps in the bond line. Ageing at the elevated temperature has, as expected, encouraged the hydration of the oxide, and this has commensurate effects on the bond strength.

Mechanical Testing of the Joints

Lap shear measurements of the joints, Figure 6, indicated an approximately 40% decrease independent of the surface treatment. The etched-only pretreatment was expected to give the least durable systems but during the period of study it is as good as any of the other pretreatments. The general loss in strength can be ascribed to plasticization of the epoxy resin. However, the significant differences in the apparent plateau values of the strengths reflect the influence of changes in the pretreatments on ageing. In all cases, the interfaces exhibit a high level of stability; however, it is apparent that changes are occurring as reflected in differences in the time–permittivity profiles, Figure 2. The mechanical test results mirror the water-uptake



(a) (b) (c) (d) (e) (f)

FIGURE 5 High-frequency dielectric permittivity results for the (a) silica/siloxane system, (b) titanium/zirconium (Ti/Zr) system, (c) anodised system, (d) etched-only system, and (e) no-rinse chrome system. Data are in ascending order: 0, 11, 18, 27, 40, 54, 62, 76, 82, 89, 96, 104, 111, and 118 days. (f) Plot of the dielectric permittivity at 3 MHz against $t^{1/2}$ in days. Key: silica/siloxane system, ◆; titanium/zirconium (Ti/Zr) system, ■; anodised system, ●; etched-only system, ▲; no-rinse chrome system, ▼.

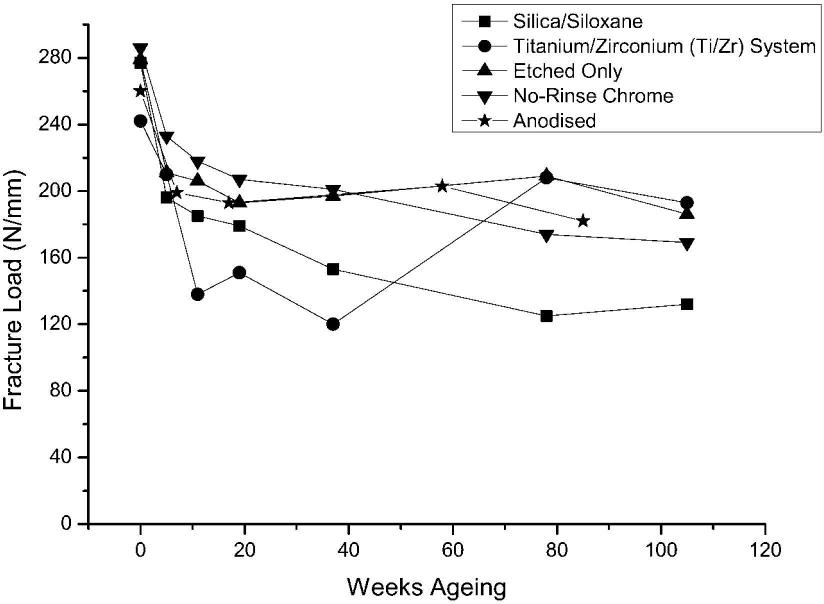


FIGURE 6 Lap-shear testing results. The spread of the data was typically ±10N/mm, being the average of five measurements.

profiles, as reflected in the dielectric data. The titanium/zirconium (Ti/Zr) system shows a substantial drop in mechanical strength during the first 40 weeks of ageing, and then the strength appears to rise again during the following period of the ageing programme. A possible explanation for this rise in mechanical properties is that the pretreatment has undergone hydrolysis to give gel particles, which are effective in energy dissipation and, hence, increase the toughness of the matrix. There is microscopic evidence for this process occurring, and it is consistent with the observed changes. The mechanical data are consistent with the dielectric observation that the low-temperature ageing is consistent with moisture ingress plasticizing the adhesive.

Failure Mechanisms

Optical examination of the failure surfaces indicated that with the exception of the titanium/zirconium (Ti/Zr) system, where some joints exhibited signs of interfacial failure, all the joints failed predominantly cohesively, indicating that the interface was stable for the period of the ageing study. These observations are consistent with the dielectric data, which indicate that the oxide has not been significantly converted to hydroxide, although there is evidence that some hydration of the pretreatments has occurred.

TEM Analysis of Humidity Bath Samples

Joints were carefully microtomed and subjected to transmisson electron microscopy (TEM) examination. Certain pretreatments were selected for TEM study as representative of the ageing occurring in the adhesive. Scanning electron microscopy (SEM) of a typical anodised surface (5754 aluminium alloy) is shown in Figure 7. The porous structure required for lock-and-key bonding is clearly shown.

No-Rinse Chrome Pretreated System

This system, Figure 8 was examined after 0, 140, and 381 days of ageing for the samples aged in the humidity cabinet (42–48 °C cycling, 100% relative humidity). It is clear that the interface is stable up to 140 days; however, there are signs of deterioration of the interface after 381 days. It was found that failure was introduced during microtoming along the adhesive/pretreatment interface, although in some regions failure has occurred along the pretreatment/metal interface, indicative of the weak nature of the interface. In other regions, it

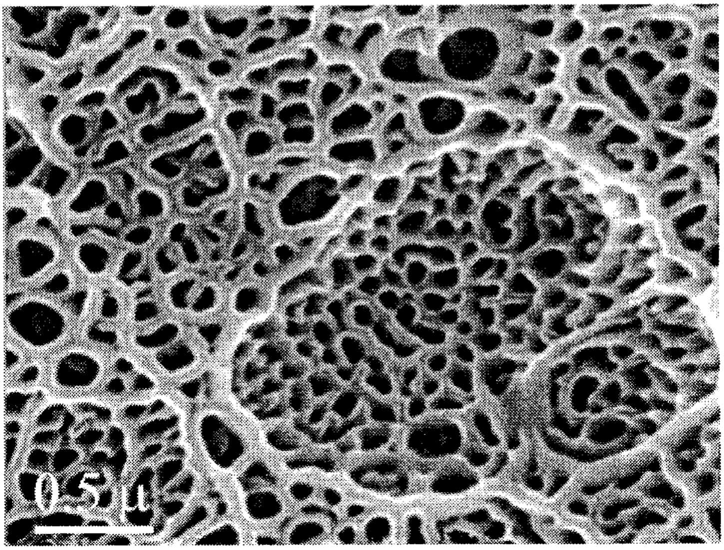


FIGURE 7 SEM image of a typical anodised surface (5754 aluminium alloy).

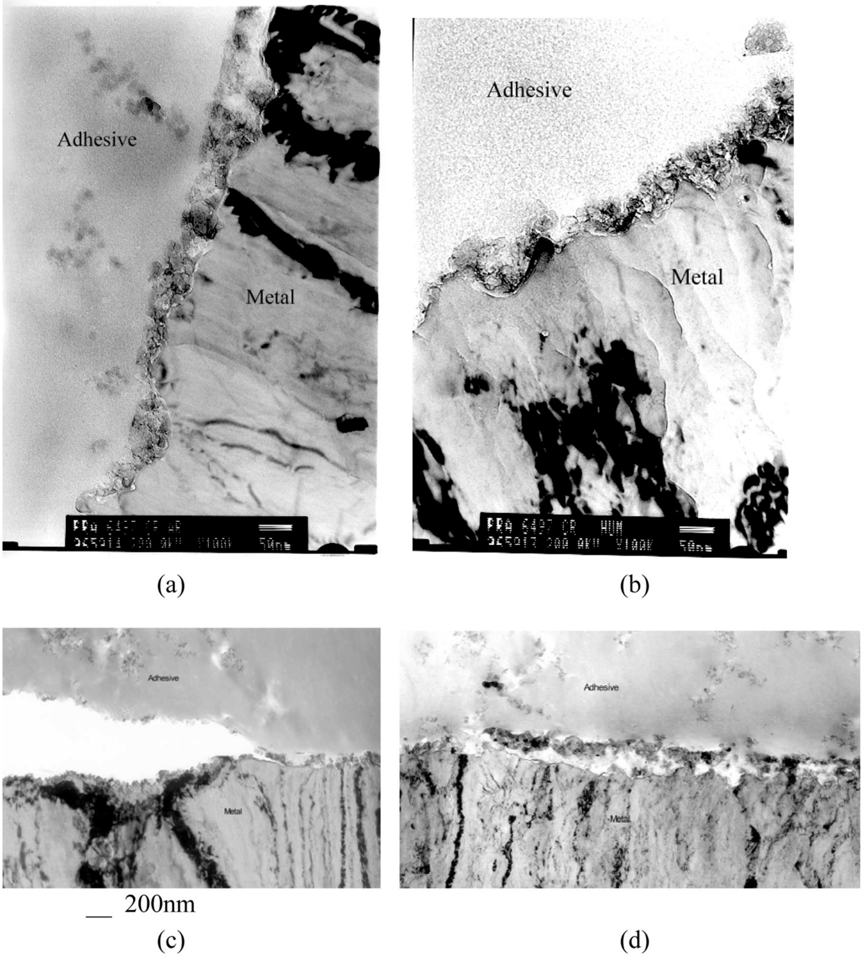


FIGURE 8 Cross section of adhesive/metal interface for the no-rinse chrome pretreated: (a) 0 days, (b) 140 days, and (c) and (d) 381 days ageing.

was observed that the pretreatment layer appears to be pulling away from the metallic substrate. These results indicate that the adhesive/pretreatment and pretreatment/metal interfacial regions are weakened as a consequence of the ageing process and that, ultimately, bond failure may be occurring along these interfacial boundaries. However, these joints have still retained approximately 60% of their initial strength, indicating that even though failure is occurring within the vicinity of the interfacial region, bond durability is still being maintained. There is no evidence from the TEM analysis of hydration of the aluminium substrate that is consistent with the dielectric analysis.

Silica/Siloxane System

The silica/siloxane pretreatment layer can be seen between the adhesive and aluminium substrate in Figure 9 with the silica particles particularly visible. After 350 days ageing in the humidity cabinet

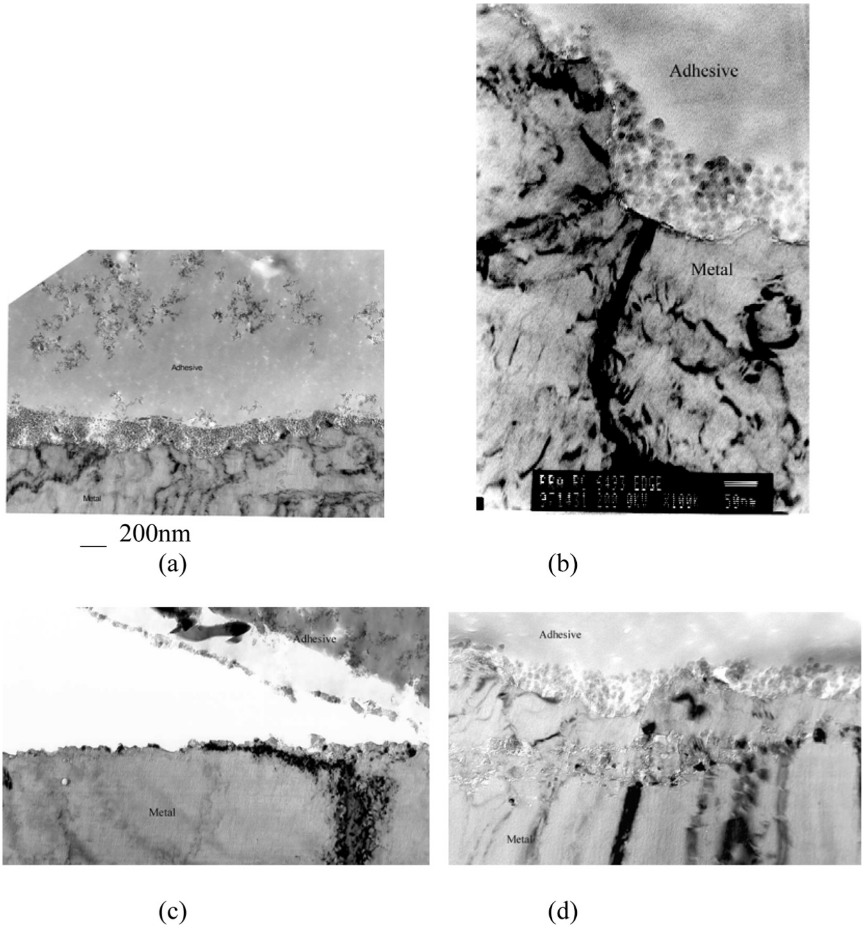
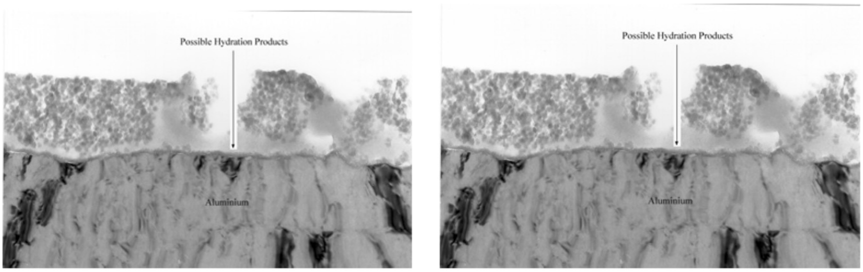


FIGURE 9 Cross section of silica/siloxane adhesive/metal interface: (a) 0 days, (b) 350 days, and (c) and (d) 381 days ageing.

there is no evidence of any changes in the interface. The TEM analysis on a sample aged for 381 days indicates that the interfacial region of the sample had been weakened as a consequence of the ageing process. From Figure 8 it can be seen that the microtoming of the sample had resulted in the disintegration of the joint, with the locus of failure being located mainly along the pretreatment/metal interface. Figure 9 shows an interfacial region of the joint that has remained intact throughout the microtoming process. The silica particles within the pretreatment layer retain their spherical shape but appear less well defined after 381 days ageing in comparison with the images of the same layer obtained from a joint that had not been exposed to the ageing environment, indicative of the early stages of hydration of the pretreatment layer. There is no obvious evidence for hydration of the aluminium substrate. After 78 weeks, the silica/siloxane system still retained approximately 45% of its residual strength. The mechanical testing results indicated that although these joints were less durable than the no-rinse chrome pretreated samples, there was not a dramatic drop in residual strength even though failure was apparently occurring within the vicinity of the interfacial region of the samples after 381 days of ageing.

Similar studies on the other pretreatments indicated that even after 380 days the joints were failing in the adhesive, and little change was observed either in the oxide or in the pretreatment layer.

TEM analysis, Figure 10, of joints aged at 70 °C showed apparent evidence of changes in the aluminium substrate/pretreatment interface as a consequence of ageing. Because no TEM analysis was conducted prior to the observation of the increase in the dielectric permittivity measured at 3 MHz, it is not possible to state categorically that hydration of the substrate had not occurred before. Although



(a) __ 50nm (b) __ 100nm

FIGURE 10 Cross section of adhesive/metal interface: 73 days ageing in the humidity cabinet plus 240 days ageing at 70 °C.

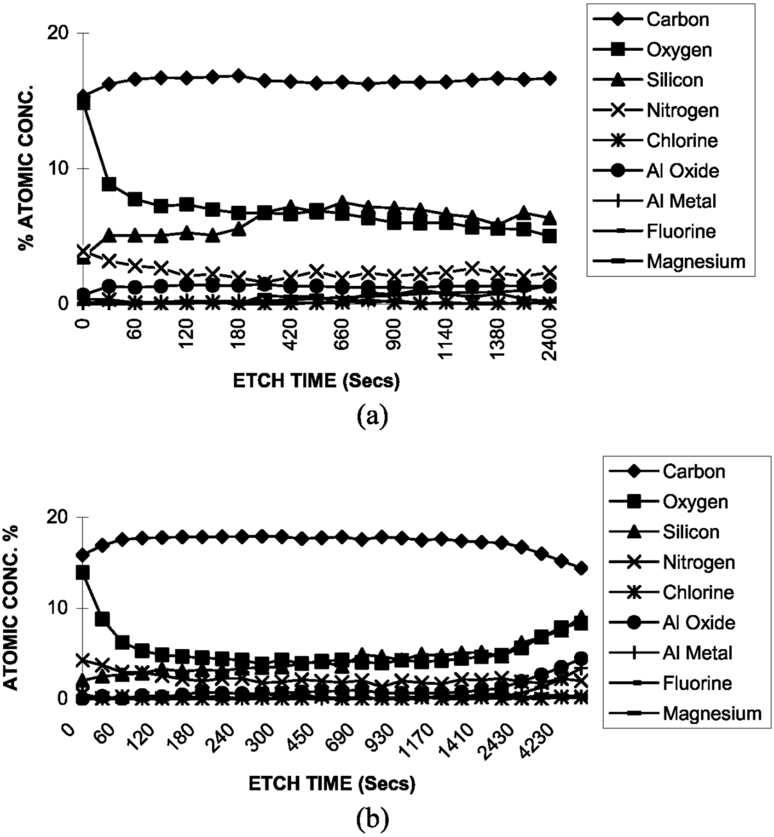


FIGURE 11 Variation of elemental percent atomic concentrations with etch time for the silica/siloxane system: (a) unaged {C%/5}; (c) aged; {C%/5}.

there may be evidence of the aluminium substrate being modified as a consequence of exposure to the ageing regime, no TEM analysis was conducted on the samples prior to the significant changes being observed in the megahertz region of the dielectric spectrum.

X-Ray Photoelectron Spectroscopy (XPS)

Two samples were analysed by XPS depth profiling at intervals during the course of the project. The samples were an unaged and aged silica/siloxane joint. The aged joint was initially aged for 73 days in the humidity cabinet followed by 118 days at 70 °C. The dielectric results, Figure 5, indicated that a change in the aluminium oxide layer had occurred during the ageing period. Once the joints had been fractured, the XPS analysis was carried out on the half of the joint that had an extremely thin layer of epoxy still remaining on the surface. The XPS was used without depth profiling to determine the locus of failure in adhesively bonded joints. The results of the percentage atomic concentrations of the elements present at the surface of both the unaged and aged samples prior to etching are shown in Table 1.

From the high carbon, oxygen, and nitrogen concentrations at the surface of both joints it appears that fracture has occurred within the adhesive itself adjacent to the adhesive/pretreatment interface. The high carbon, oxygen, and nitrogen concentrations are consistent with the presence of the dicyanamide-cured epoxy. The detection of chlorine on the sample surface can be attributed to residual sodium chloride being present within the epoxy as a result of the synthesis of the DGEBA (digylicidyl ether of bisphenol A) resin from epichlorohydrin. The silicon concentrations for both samples rise appreciably within the first few minutes of etching, indicating that there is only a thin adhesive layer covering the silica/siloxane pretreatment after the joints were fractured. It appears from these initial XPS analysis results that there was no obvious change in the locus of failure between the aged and unaged joints as a result of the ageing. The variation in the percentage atomic concentration of the elements present at the surface of the silica/siloxane unaged sample are shown in Figure 10 as a function of the ion-etch time. To obtain the depth profile of the atomic species, an ion-etching experiment was performed, which slowly removes the surface and reveals the atomic composition through the interface and into the substrate. The carbon concentration is observed to dominate throughout the depth profile and indeed after an etch time of 2400 s more than 80% of the surface of the sample is still composed of carbon. However, it should also be noted that

TABLE 1 Percentage Atomic Concentrations at the Surface of the Silica/Siloxane Systems

Element	Unaged % concentration	Aged % concentration
Carbon	76.7	79.3
Oxygen	14.9	13.9
Silicon	3.5	2.0
Nitrogen	3.9	4.2
Chlorine	0.4	0.5
Aluminium oxide	0.7	0
Aluminium metal	0	0

aluminium metal (Al°) is detected after the sample had been etched for 120 s. This result implies that in some regions the initial fracture of the sample must have been within 60 Å of the underlying metal substrate because the maximum inelastic escape depth of the photoelectrons is 5 mm and the etch rate of the argon ion beam is approximately 5 Å per minute. After an etch time of 2400 s the concentration of the aluminium metal exceeds that of the aluminium oxide. This implies that after the duration of the argon ion etch, small areas of the sample have been etched through to the aluminium substrate itself. The high remaining carbon concentration indicates that across the majority of the sample the ion etching has not even broken through the adhesive fragments remaining on the surface of the aluminium substrate after the joint had been fractured. It can also be observed that the silicon concentration also remains much higher than the aluminium concentration throughout the whole of the etching period. The silicon signal may arise from both the silica used within the pretreatment layer and from the silicate filler used within the adhesive itself. A further complication with the interpretation of the variation in the silicon concentration throughout the depth profile is that the thickness of the silica/siloxane pretreatment layer on the surface of the aluminium substrate has been shown to dramatically vary across the sample. The TEM results show that the pretreatment layer may vary in thickness by as much as 0.3 μm. It is possible that after the profiling has been conducted some areas of the sample will have been etched down to the aluminium substrate. In other areas, however, penetration through the pretreatment layer in these thicker regions may not have occurred.

CONCLUSIONS

The dielectric data indicated that at low temperatures, the predominant process was moisture absorption by the adhesive, although there were indications that some changes were occurring to the pretreatment after extended periods of ageing. The TEM examination showed that the silica/siloxane-bonded systems were considerably less durable than joints produced using aluminium that had undergone the no-rinse chrome pretreatment. Differences in the failure modes of these systems were observed from the mechanical testing of the joints; the no-rinse chrome pretreated joints failed cohesively throughout the ageing period whereas the silica/siloxane systems failed more adhesively. The TEM analysis showed that the interfacial region of the silica/siloxane systems was weakened as a result of the ageing process and that bond failure was apparently occurring along the adhesive/pretreatment and metal/pretreatment interfaces. The mechanical test results indicated that the loss in strength mirrors the water uptake, as determined by dielectric measurements, and the joints still retained about 50% of their initial strength after 105 weeks of ageing, consistent with the dominant change being plasticization of the adhesive.

The high-frequency dielectric results obtained for the samples ageing at 70 °C showed that possible hydration of the interfacial region of the aluminium substrate may be occurring. TEM analysis provided evidence of changes occurring at the aluminium/pretreatment interface as a consequence of the ageing regimen and showed that the sample failed along the adhesive/pretreatment interface during microtoming. These results indicated that during the later stages of the ageing process, the loss in joint strength may be attributed to interfacial changes occurring at the adhesive/pretreatment interface. These changes vary slightly with pretreatment but are dominated by changes in the nature of the oxide when the joints are exposed to high temperatures and high humidity.

ACKNOWLEDGEMENTS

One of us (R. O.) thanks Alcan International PLC for support during the period of this project. We also acknowledge the support of the Air Force Office of Scientific Research for the NDT research during the period of this investigation.

REFERENCES

[1] Kinloch, A. J., *Proc. Unstn. Mech. Engrs.* **221**, 308–335 (1997).
[2] Cotter, J. L., in *Developments in Adhesives—I*, W. C. Wake (Eds.) (Applied Science Publishers, London, 1977).
[3] Korenberg, C. F., Kinloch, A. J., and Watts, J. F., *J. Adhes.* **80**, 169–201 (2004).
[4] Davis, G. D., Krebs, L. A., and Dacres, C. M., *J. Coatings Technol.* **74**, 69–74 (2002).
[5] Davis, G. D. and Harkless, B. J., *International J. Adhes. Adhesives* **22**, 323–329 (2002).
[6] Vine, K., Cawley, P., and Kinloch, A. J., *J. Adhes.* **77**, 125–161 (2001).
[7] Vine, K., Cawley, P., Kinloch, A. J., *NDT & E International* **35**, 241–253 (2002).
[8] Curley, A. J., Hadavinia, H., Kinloch, A. J., and Taylor, A. C., *International J. Fracture* 41–69 (2000).
[9] Davis, G. D., Whisnant, P. L., and Venables, J. D., *J. Adhes. Sci. Technol.* **9**(4), 433–442 (1995).
[10] Jethwa, J. K. and Kinloch, A. J., *J. Adhes.* **61**, 71–95 (1997).
[11] Kinloch, A. J., *Adhesion and Adhesives—Science and Technology* (Chapman and Hall, London 1987), p. 302.
[12] Podoba, E. A., Kodali, S. P., Curley, R. C., McNamara, D., and Venables, J. D., *Appl. Surface Sci.* **9**, 359–376 (1981).

[13] Packham, D. E. (Ed.), *Handbook of Adhesion* (Longman Scientific and Technical, Harlow, 1992).

[14] Thompson, G. E., *Thin Solid Films* **297**, 192–201 (1997).

[15] Ahearn, J. S. and Davis, G. D., *J. Adhes.* **28**, 75–102 (1989); Ahearn, J. S., Venables, J. D., and Davis, G. D., *Adhesion Aspects of Polymeric Coatings*, K. L. Mittal (Ed.) (Plenum Press, New York, 1983).

[16] Hartman, N., European Patent 92905413.8–2103 (1997).

[17] Vussey, C. A., Albon, C., and Holker, K., U.S. Patent 3,706,603 (1972).

[18] Dollman, D. Y. and O'Grady, T. J., U.S. Patent 4,191,596 (1990).

[19] Ball, J., Limbach, J. D. B., and Sharman, J. D. B., *Proceedings of the International Symposium on Aluminium Surface Science and Technology* **31**, p. 101 (1997).

[20] Personal communication, Alcan Research, UK.

[21] Halliday, S. T., Banks, W. M., Pethrick, R. A., *J. Materials: Design and Applications* **213**, 27–35 (1999).

[22] Boinard, P., Pethrick, R. A., Banks, W. M., and Crane, R. L., *J. Materials Sci.* **35**, 1331–1337 (2000).

[23] Affrossman, S., Banks, W. M., Hayward, D., and Pethrick, R. A., *Proc. I. MechE J. Mechanical Engineering Science* **214** Part C, 87–102 (2000).

[24] Hastead, J. B., *Aqueous Dielectrics* (Chapman and Hall, London, l973).

[25] Pethrick, R. A., Hayward, D., Jeffrey, K., Affrossman, S., and Wilford, P., *J. Mater. Sci.* **31** (10), 233 (1996).

[26] Li, Z., Ph.D. Thesis, High Frequency Dielectric Measurements of Adhesive Bonded Structures, University of Strathclyde (1995).

[27] Halliday, S., Ph.D. Thesis, High Frequency Dielectric and Mechanical Investigations of Adhesive Bonded Structures, University of Strathclyde (1998).

[28] Pethrick, R. A., North, A. M., and Wilson, A. D., *Polymer* **19**, 913–922 (1978).

[29] Pethrick, R. A., North, A. M., and Wilson, A. D., *Polymer* **19**, 923–930 (1978).

[30] Hayward, D., Pethrick, R. A., and Siriwittayakorn, T., *Macromolecules* **25**, 1480–1486 (1992).