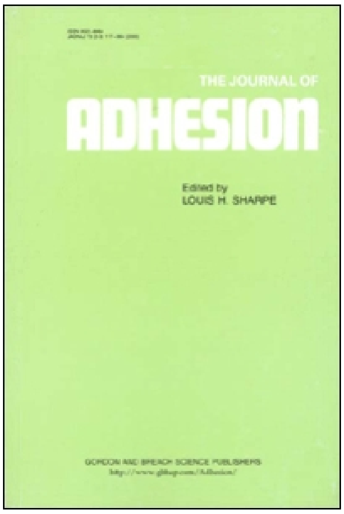

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Ageing of Adhesive Bonds with Various Surface Treatments, Part 3: Aluminium-Dicyandiamide Cured Aluminium Filled Epoxy Joints

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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 3: Aluminium-Dicyandiamide Cured Aluminium Filled Epoxy Joints', The Journal of Adhesion, 81: 12, 1199 — 1215

To link to this Article: DOI: 10.1080/00218460500371756

URL: http://dx.doi.org/10.1080/00218460500371756

The Journal of Adhesion, 81:1199–1215, 2005

ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460500371756

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Ageing of adhesive-bonded aluminium–dicyandiamide cured epoxy alumina-filled joints prepared using a variety of different surface treatments and exposed to elevated temperatures and high humidity are reported. The uptake of moisture was followed using broadband dielectric spectroscopy, and attempts are made to correlate these changes with observations of variations in the mechanical properties and surface structure monitored by electron microscopy. It was found that the absorption of moisture, as indicated by the dielectric measurements, is similar for all the joints. Small differences observed may be ascribed to the influence of the pretreatment on the absorption behaviour. There was no evidence of changes in the oxide layer of the substrate. Detailed electron microscopic examination of the surfaces did indicate, after prolonged exposure, that change in the pretreatment is consistent with small differences in the dielectric data. Predominantly, the changes that were observed in the mechanical strength of the joints are consistent with the plasticization of adhesive in the joint rather than failure at the substrate interface. Ageing at 70°C did, however, indicate that there were changes in the interfacial layer and these can be correlated with the change in the failure mechanism. It was also observed that the titanium/zirconium (Ti/Zr) pretreatment showed signs of being less durable than the others used in this study.

Received 17 July 2004; in final form 17 September 2005.
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Keywords: Adhesive durability; Dicyandiamide cure; Dielectric spectroscopy; Epoxy resin; Moisture ageing; Pretreatments

INTRODUCTION

In previous articles [1, 2], the effects of exposure of a series of joints created using a unfilled dicyandiamide-cured epoxy and an acrylic modified resin were reported. It was observed that the dielectric analysis indicated that the water absorption correlated well with the loss of the mechanical properties and, further, that there were small differences in behaviour that reflect the nature of the pretreatment. In this article, the effects of the inclusion of aluminium powder in the dicyandiamide-cured epoxy and the nature of the pretreatments used in the preparation of the adhesive bonds are investigated. Loss of strength of aluminium adhesive bonds, due to exposure to moisture and elevated temperatures, has long been recognised as a problem [3, 4]. However, with careful pretreatment of the interface, it is possible to generate adhesive bonds that are durable for long periods of time.

Pretreatments aim to enhance bonding between the adhesive and the interface and suppress conversion of aluminium oxide to the weaker hydroxide [5]. Aluminium oxide will naturally occur as a thin layer on the metal substrate and any fillers that are incorporated in the adhesive. Growth of a thick cellular oxide layer provides a lock-and-key mechanism that promotes a good stable bond between the substrate and adhesive [5]. Chromic [6] and phosphoric acid [7] treatments are commonly used to create thick oxide layers. A variety of other surface treatments have been proposed to create a stable surface layer and include silica/siloxane [8], titanium/zirconium (Ti/Zr) [9], and no-rinse chrome pretreatments [10]. The nature of these pretreatments has been discussed previously [1, 2], and each has potential benefits in terms of improving adhesion and durability of the joints.

In this study, a comparison is made between changes occurring in the dielectric spectrum during ageing of aluminium–epoxy adhesive bonds, changes which are observed using electron microscopy and mechanical test data.

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 described previously [1, 2].

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 diglycidyl ether of bisphenol A resin cured by a modified dicyandiamide. The adhesive contains approximately 40% by weight aluminium-based inorganic filler. Curing conditions were 30 min at 180°C. Fifteen joints were prepared for each of the pretreatments studied.

Ageing of Samples

A humidity cabinet that creates (100%) humidity with temperature cycling between 42–48–42°C every hour was used for ageing the joints. This form of cycling has been used to accelerate ageing of joints for use in the automobile industry by Alcan. The joints were initially examined dielectrically on a weekly basis, which was decreased to once every two months as the ageing progressed.

Dielectric Analysis

The joints were removed from the ageing bath, dried, and cooled to ambient temperature. The ends of the joints were abraded to remove the surface oxide to ensure good electrical connection was achieved. Prior to ageing, the bond-line thickness for each of the joints measured was determined by taking the average of several micrometer measurements across the bonded area of each joint and was found to be 0.17 mm ± 0.05 mm. Three joints were studied for each of the surface treatments investigated, and the data represent the average of these data. The measurements were performed using a Solatron 1250 A Frequency Response Analyser (FRA), Franborough, Haxts, UK, which generates frequencies between 10^{-3} Hz and 63 kHz. The high-frequency dielectric measurements were carried out using a Hewlett Packard HP8753A network analyzer (Queensferry, Scotland, UK), and the method used has been described in detail previously [1, 2].

Mechanical Testing

Tensile tests were carried out on batches of three joints using a cross-head 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 (Ingtorn Ltd., High Wycoube, Buckinghampshire, UK).

Modes of Failure

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

Electron Microscopy of Sections of the Joints

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

RESULTS

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

The low-frequency dielectric results for the joints aged in the humidity cabinet are shown in Figure 1. The absorption of water leads to large changes in the dielectric permittivity and loss. The dielectric loss and permittivity are initially very similar to those observed for any epoxy resins; however, because the adhesive is filled with aluminium powder, a large Maxwell Wagner Siller (MWS) contribution is observed once the conductivity of the matrix is increased by water absorption. The water provides the necessary mobile ions to allow the heterogeneity of the matrix to be observed. The water also produces plasticization of the adhesive, and this contributes to the low frequency losses. Moisture also gives rise to increases in the dielectric loss at higher frequencies and adds to the inherent dipole relaxation associated with the pendant hydroxyl groups of the epoxy resin [11]. Interfacial polarisation effects, arising from the presence of water associated with the surface of the metallic filler, dominate the region below 10 Hz during the later stages of the ageing process. At l0 kHz the dielectric spectrum is indicative of water binding to the pendant hydroxyl groups of the epoxy resin. The data in Figure 2, for 10 kHz, show that

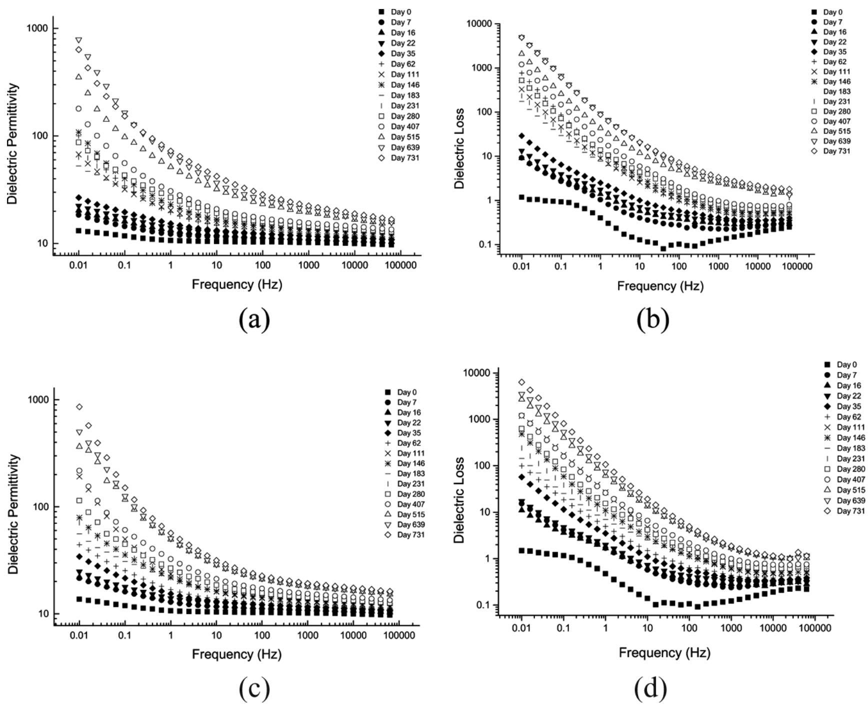

FIGURE 1 Low-frequency dielectric data for the no-rinse chrome system (a) dielectric permittivity and (b) dielectric loss; silica/siloxane system (c) dielectric permittivity and (d) dielectric loss; titanium/zirconium (Ti/Zr) system (e) dielectric permittivity and (f) dielectric loss; anodised system (g) dielectric permittivity and (h) dielectric loss; and etched-only system (i) dielectric permittivity and (j) dielectric loss.

there is initially a sharp rise in the permittivity for all the samples during the initial 100 days of ageing. The ingress of moisture into the samples then appears to plateau off during the following 250 days, and then another dramatic rise in permittivity can be observed after the joints had been ageing for 350 days. This second rise in permittivity may possibly be attributed to the water beginning to swell the matrix as a consequence of hydration of the surface of the aluminium filler and plasticization of the matrix. Zi et al. [12] and Halliday et al. [13] have previously reported similar effects. A study of the effects of water distribution on the mechanical properties of the adhesive is currently being undertaken.

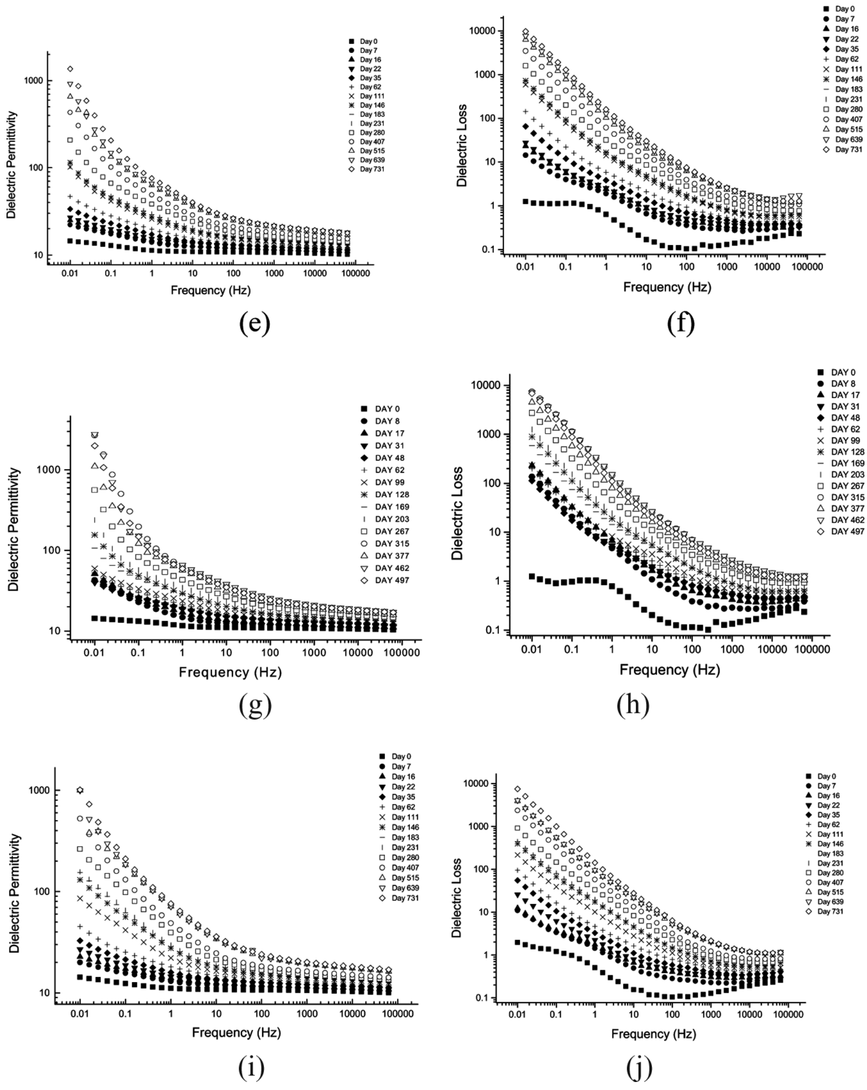

FIGURE 1 Continued.

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

The initial permittivity at 1 MHz ranges from 8.7 to 9.3 with an average value of 9.1. These initial high values arise because of the presence of the metallic filler within the adhesive, Figure 3. The metal will

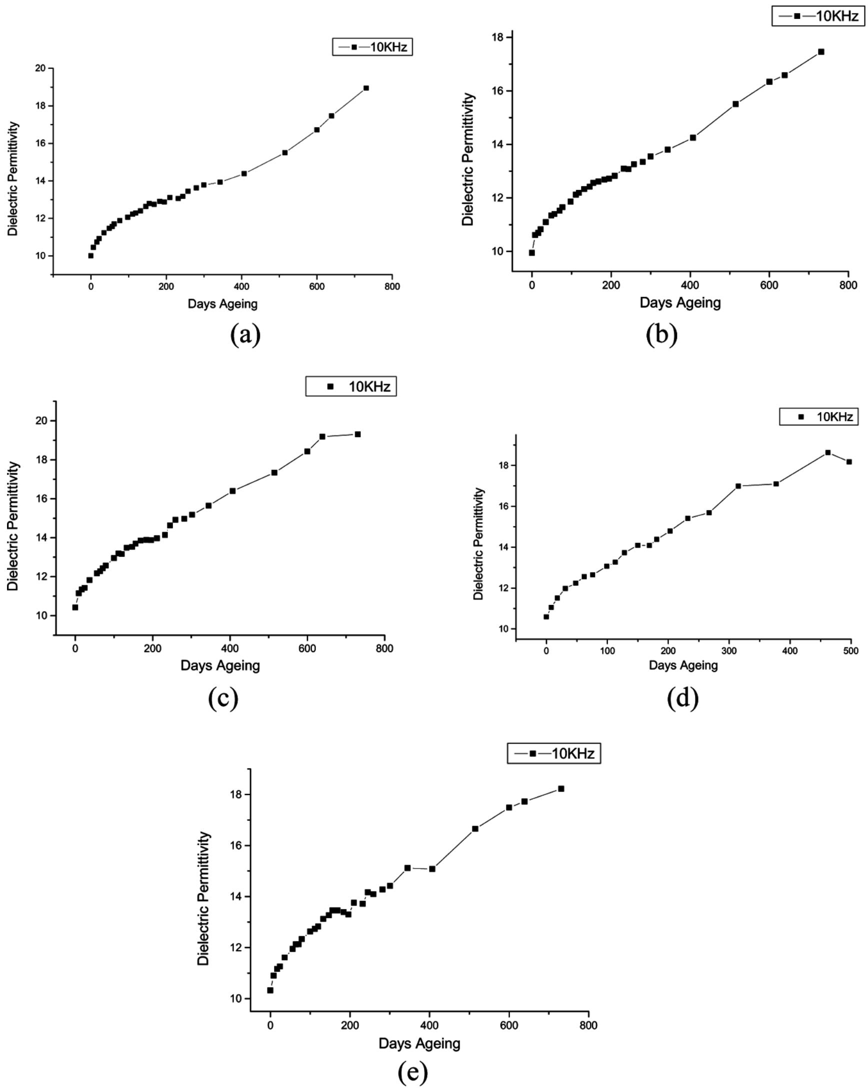

FIGURE 2 Dielectric permittivity at 10 KHz *versus*, ageing time for (a) the no-rinse chrome system, (b) silica/siloxane system, (c) titanium/zirconium (Ti/Zr) system, (d) anodised system, and (e) etched-only system.

increase the high-frequency limiting value of the permittivity because of the polarisation of the conducting electrons. The increase in the high-frequency dielectric relaxation can be attributed to the absorption of "free" water. The absence of a major permittivity contribution in

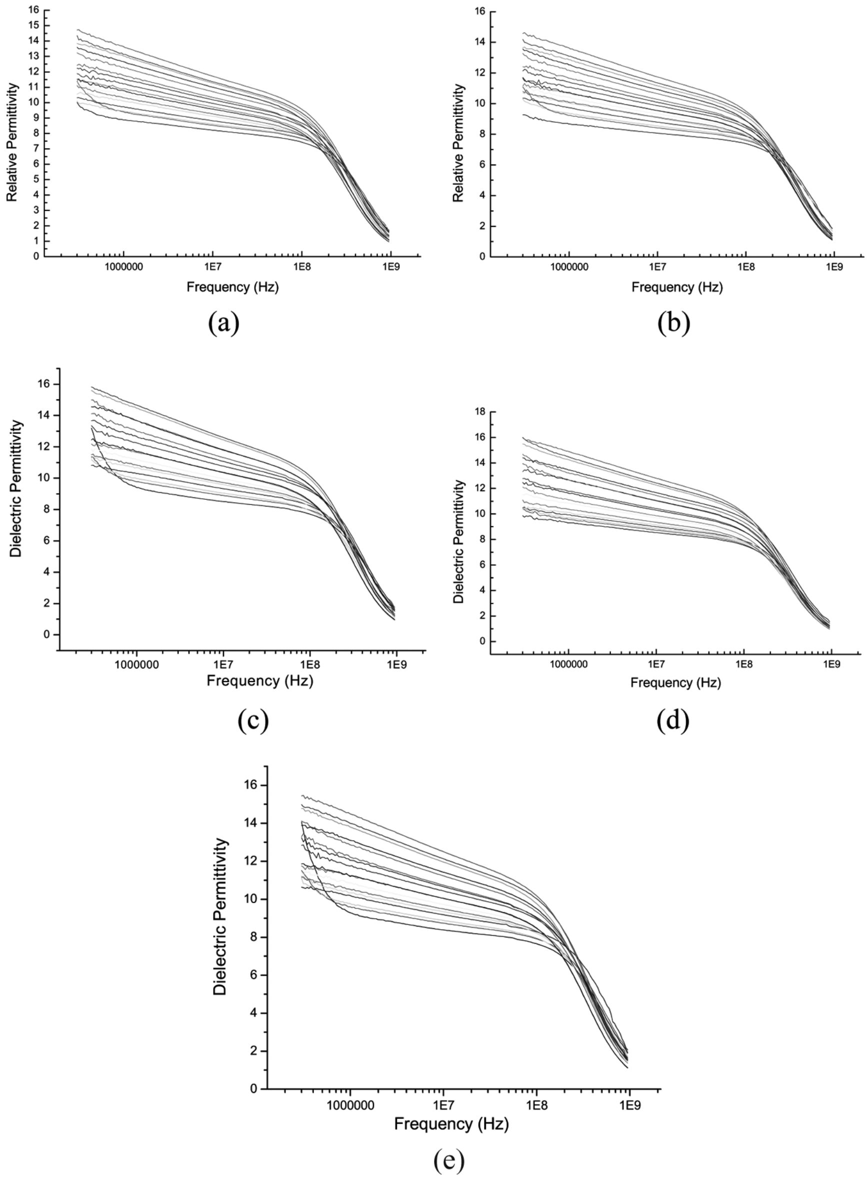

FIGURE 3 High-frequency dielectric permittivity results for (a) the no-rinse chrome system, (b) silica/siloxane system, (c) titanium/zirconium (Ti/Zr) system, (d) anodised system, (e) etched-only system. Data in ascending order Day 0, 10, 21, 30, 49, 79, 100, 139, 178, 232, 303, 346, 407, 531, 599, 642,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

the megahertz region of the dielectric spectrum indicates that no significant oxide-to-hydroxide conversion at the substrate–resin interface occurs during the first 710 days of ageing. The change of dielectric permittivity at 3 MHz with ageing time, Figure 4, shows an initial sharp rise in permittivity, which appears to begin to plateau off after 350 days. However, in certain samples, the permittivity began to rise again at an increased rate. The second rise in permittivity can be attributed to hydration of the aluminium-based filler within the epoxy. The largest increase is observed with the anodised treatment, followed by the Ti/Zr treatment; the no-rinse chrome, the etched-only, and the silica/siloxane treatments are almost indistinguishable.

Ageing at 70°C

The high-frequency dielectric results obtained for joints that had been initially aged for 73 days at 201 days of the ageing programme in the 70°C bath are shown in Figure 5. The permittivity results show that the initial ingress of water gives rise to a general increase in permittivity across the whole frequency range. At a later stage hydration effects are indicated by an increased permittivity at approximately 1 MHz. The hydration effects are particularly noticeable in no-rinse chrome and silica/siloxane systems, Figure 5. The titanium/zirconium (Ti/Zr) system exhibits a larger increase in permittivity throughout the ageing period in comparison with the other systems being examined and indicates a greater quantity of free water after 201 days of ageing in comparison with the other systems. Because the same adhesive was used for all of the joints, the dielectric results indicate that the titanium/zirconium (Ti/Zr) pretreatment is less resistant to water than the others used.

Mechanical Testing of the Joints

The mechanical testing results for joints, Figure 6, show that the etched-only system demonstrates as good long-term durability as all the other pretreatments. The mechanical testing profiles for the no-rinse chrome, etched-only, and Ti/Zr systems show the same trends with an initial sharp reduction in strength during the first 20 weeks and then an apparent plateau. The anodised and the silica/siloxane systems did not perform as well throughout the durability study in comparison with the other pretreatments. The failure was clearly interfacial, whereas in the other systems it was within the adhesive. The mechanical strength profiles of the samples appear to mirror

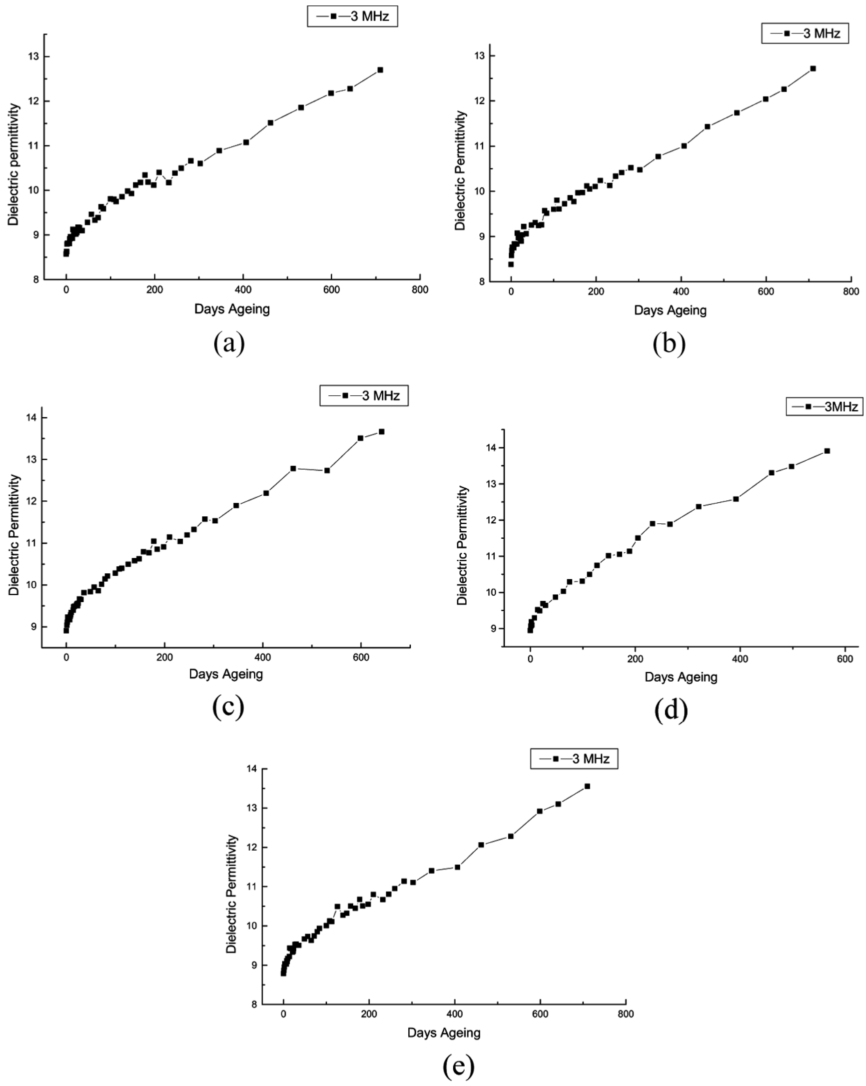

FIGURE 4 Dielectric permittivity at 3 MHz *versus* ageing time for the (a) no-rinse chrome system, (b) silica/siloxane system, (c) titanium/zirconium (Ti/Zr) system, (d) anodised system, (e) etched-only system.

the water-uptake curves obtained from the dielectric testing of the joints and reflect plasticization of the adhesive by the ingress of water. The anodised system is the one that has the largest increase in the high-frequency permittivity (3 MHz) with time, which is consistent

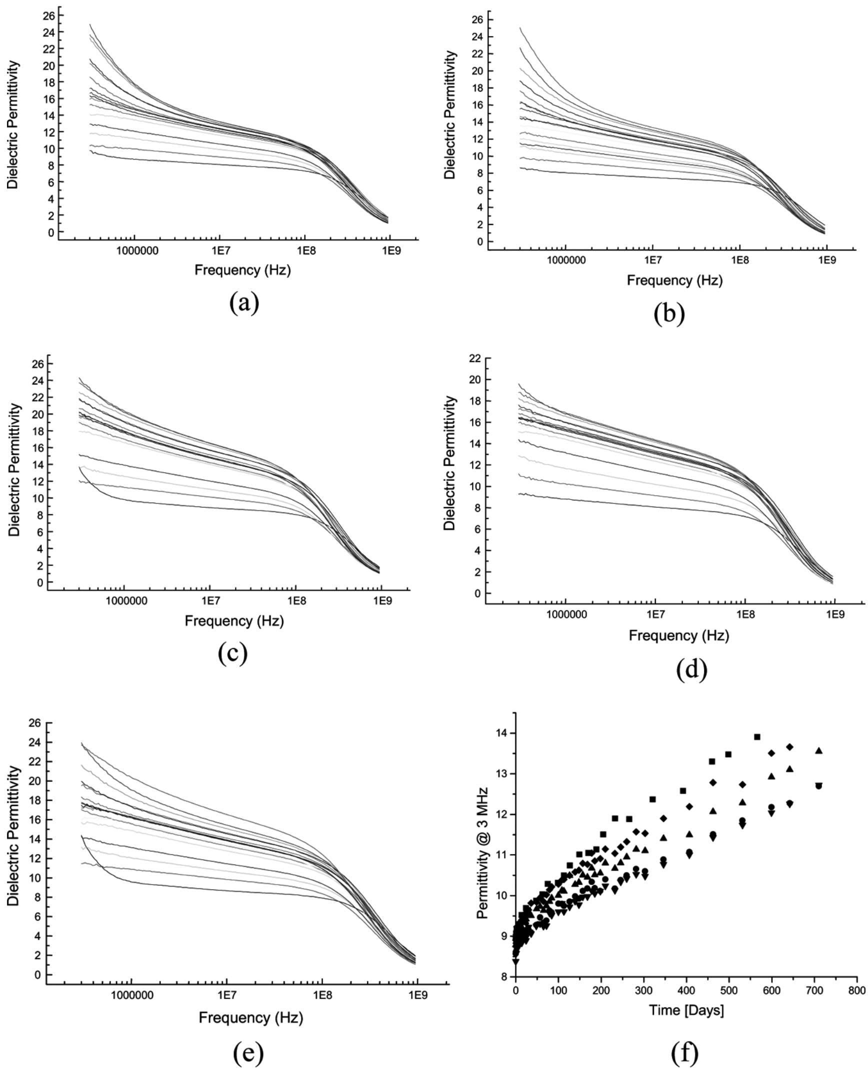

FIGURE 5 High-frequency dielectric permittivity results for joints aged at 70°C for the (a) no-rinse chrome system, (b) silica/siloxane system, (c) titanium/zirconium (Ti/Zr) system, (d) anodised system, and (e) etched-only system, (f) Plot of the permittivity at 3 MHz against time; ■, anodized; ▲, no-rinse chrome; ▼, silica siloxane; ◆, Ti/Zr; and ●, etched-only. Data in ascending order are Day 0, 11, 18, 27, 40, 54, 76, 82, 89, 104, 111, 131, 157, 174, 190, 201, and 240.

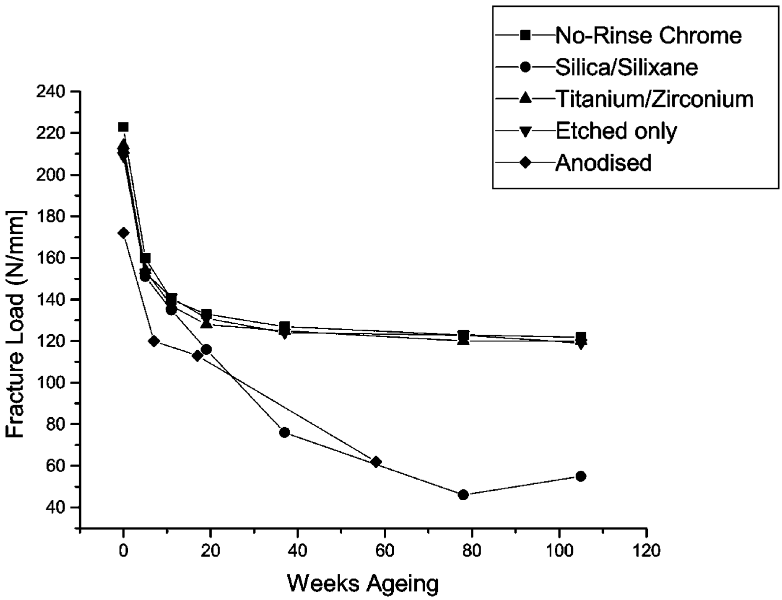

FIGURE 6 Lap-shear testing results for the adhesive system.

with water being trapped in microvoids. For example, after 105 weeks in the ageing cabinet, the etched-only system still retained 57% of its initial strength whereas the silica/siloxane system had retained only 26%. A more detailed analysis of the data is not possible with these small joints; however, an analysis in which it is possible to distinguish between water in the adhesive and the interface has been completed recently on another joint system and will be reported in the near future.

Mechanical Testing Results of the Neutral Salt-Spray Samples

Figure 7 summarises the mechanical testing results of joints that were aged at 43°C in a 5% neutral salt spray. The data are less dramatic than for the water-aged system. They appear to reflect only plasticization effects of the adhesive, and there was little evidence of interfacial failure contributing to the decrease in the mechanical properties.

Failure Mechanisms

During the study the failure mode was observed to be predominantly cohesive but as ageing proceeded the failure modes became more

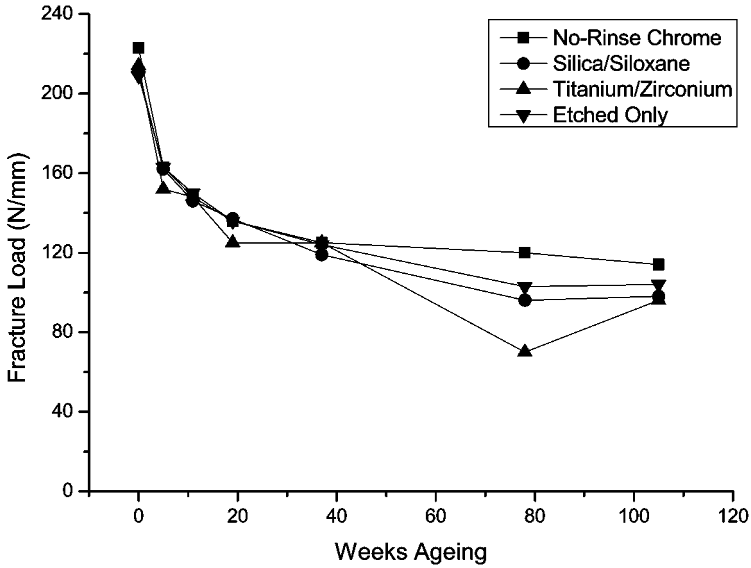

FIGURE 7 Lap-shear testing results for the joints ageing under neutral salt-spray conditions.

adhesive in nature, which was paralleled by a significant loss in joint strength and a greater scatter in the data.

TEM Analysis of Humidity Bath Samples

No-Rinse Chrome System

The results for the no-rinse chrome pretreated systems after 0 and 312 days of ageing in the humidity cabinet are shown in Figure 8. Prior to ageing, the pretreatment layer is clearly visible between the adhesive and the metal substrate. After 312 days of ageing the interfacial region remained intact throughout the microtoming process, indicating that the interfacial region of the samples had not been significantly weakened during the initial 312-day ageing period. The aluminium substrate analysed after 312 days still retains a micro-grain, which exists for a depth of $\sim$600 nm. The deformed surface structure arises from the hot- and cold-rolling of the aluminium, and the TEM results show that the aluminium substrate was not properly cleaned using the HF/H_2SO_4 etching solution prior to application of the no-rinse chrome pretreatment. After 312 days of ageing there is no evidence of hydration of the aluminium substrate occurring,

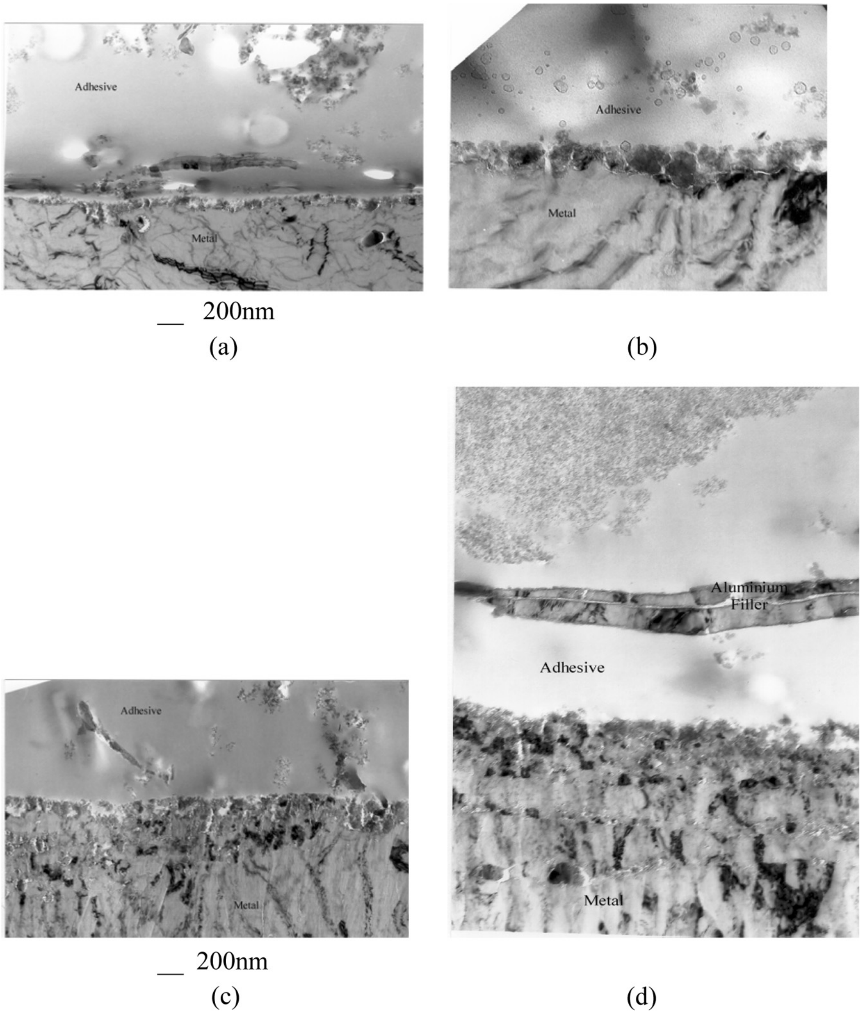

FIGURE 8 Cross section of adhesive/metal interface for the no-rinse chrome system: (a) and (b) 0 days of ageing, and (c) and (d) 312 days of ageing.

which correlates with the dielectric results obtained for these systems during the ageing period.

Silica/Siloxane System

These joints were chosen for TEM examination because throughout the ageing period the silica/siloxane-bonded system showed an

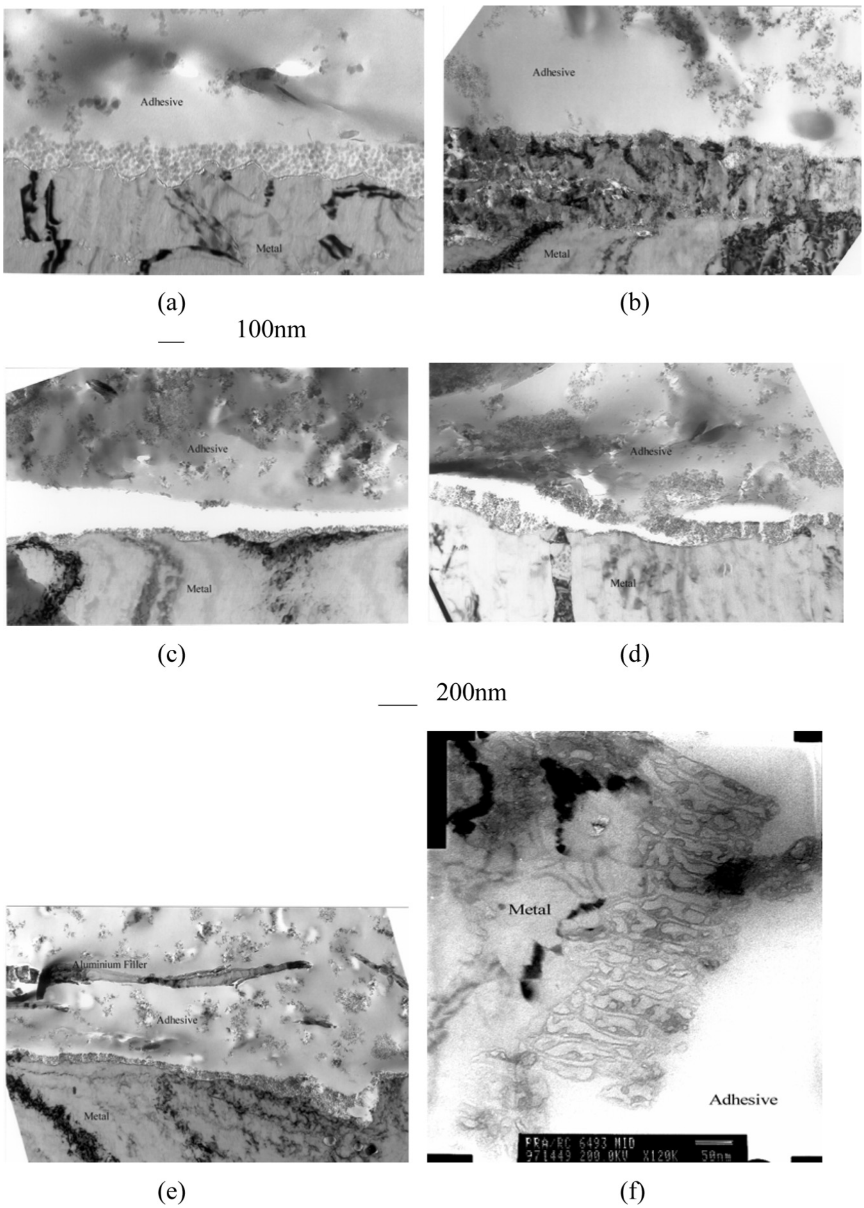

FIGURE 9 Cross section of adhesive/metal interface for the silica/siloxane system: (a) and (b) 0 days of ageing, (c) and (d) 312 days of ageing, (e) and (f) 350 days of ageing.

increasing degree of failure within, or adjacent to, the interfacial region of the joint, Figure 9. There is evidence that regions of the substrate may not have been completely cleaned, with the silica/siloxane pretreatment penetrating into the resultant crevices. The TEM analysis correlates well with the failure modes of the mechanically tested specimens. Only when samples failed adhesively during mechanical testing did joints from the same pretreatment systems and aged for approximately the same time period show apparent interfacial failure resulting from the microtoming of the sample prior to TEM analysis. The presence of aluminium filler particles can be clearly observed along with a second type of filler, which may be silicate based. A sample was analysed after 350 days of ageing. It appeared to give evidence that the silica layer had become heavily hydrated as a result of the ageing process, consistent with dielectric observations.

CONCLUSIONS

The dielectric results obtained for the samples ageing in the humidity cabinet (42–48°C cycling, 100% relative humidity) shows that ingress of water into the adhesive bonds has occurred. Differences in behaviour between the different pretreatments being examined were observed. However, little difference in the dielectric behaviour was observed between the no-rinse chrome and silica/siloxane pretreatments, but the traces for the other pretreatments showed progressively larger changes in the dielectric permittivity when plotted against time. The apparent similarity between the dielectric traces is in contrast to the differences observed in the TEM analysis and mechanical testing, which showed that the silica/siloxane-bonded systems were less durable. The no-rinse chrome pretreated joints failed cohesively throughout the ageing period whereas the silica/siloxane systems failed more adhesively. Subsequent 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 dielectric studies of the Ti/Zr treatment indicate that ageing creates microvoids that are filled with moisture.

The mechanical test data indicated that the etched-only pretreatment systems exhibited as good long-term durability as any of the other pretreatments, implying that, provided the metal has been properly cleaned, good bond durability can be achieved without the need for any further pretreatment. The conclusion that the etched-only treatment gives as good long-term durability as any other treatment may be warranted in this experiment, but as a general conclusion it is contrary to practical experience with many bonded systems

ACKNOWLEDGEMENTS

One of us (R. C.) thanks Alcan for a studentship for the period of this study.

REFERENCES

[1] Comrie, R., Affrossman, S., Hayward, D., Pethrick, R. A., Zhou, X., and Thompson, E. *J. Adhes.* **81**(12), xx–xx (2006).
[2] Comrie, R., Affrossman, S., Hayward, D., Pethrick, R. A., Zhou, X., and Thompson, E. *J. Adhes.* **81**(12), xx–xx (2006).
[3] Kinloch, A. J., *Proo. Instn. Mech. Engrs.* **221**, 308–335 (1997).
[4] Cotter, J. L., in *Developments in Adhesive—1*, W. C. Wake (Ed.) (Applied Science Publishers, London, 1977), p. 1.
[5] Kinloch, A. J., *Adhesion and Adhesives—Science and Technology* (Chapman and Hall, London, l987), p. 302.
[6] Packham, D. E. (Ed.) *Handbook of Adhesion* (Longman Scientific and Technical, Harlow, 1992).
[7] Ahearn, J. S., in *Adhesion Aspects of Polymeric Coatings*, K. L. Mitta (Ed.) (Plenum Press, New York, 1983).
[8] Hartman, N., European Patent 92905413.8-2103 (1997).
[9] Dollman, D. Y. and O'Grady, T. J., U.S. Patent 4,191,596 (1990).
[10] Vussey, C. A., Albon, C., and Holker, K. U.S. Patent 3,706,603 (1972).
[11] Pethrick, R. A. and Maxwell, I. D., *J. Appl. Polym. Sci*. **28**, 2363–2480 (1983).
[12] Li, Z. C., Joshi, S., Hayward, D., Gilmore, R., and Pethrick, R. A. *NDT&E International*. **30**(3), 151–161 (1997).
[13] Halliday, S. T., Banks, W. M., and Pethrick, R. A. *J. Materials: Design Applications*. **213**(L1), 27–35 (1999).