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Investigation of moisture ingress into adhesive bonded structures using high frequency dielectric analysis

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The effects on the dielectric characteristics of aluminium-adhesive bonded joint structures with different surface treatments on exposure to moisture at elevated temperatures are reported. Analysis of the frequency domain data as a function of the exposure time allows three major ageing processes to be identified; plasticization of the adhesive, changes in the state of interfacial oxide and generation of disbonded areas. Time domain data allows identification of regions where changes in the characteristics of the bond have occurred and complements the data obtained from frequency domain data. Mechanical tests on joints aged for 733 days indicate a large decrease in the shear strength has occurred consistent with the detection of marked changes in the dielectric traces. Anodization of the substrate increases the durability of joints in comparison with etched samples. This study illustrates the potential of this method for *in-situ* characterization of changes occurring both within the adhesive and the adhesive substrate interface.

1. Introduction

The durability of adhesively bonded structures is of considerable concern to designers wishing to produce structural components. A number of studies have been carried out of the change in the strength of bonds generated using adhesive technology and in general loss of strength is correlated with exposure to high temperatures and humidities [1–3]. Surface treatment of substrates before bonding also plays a very important role in achieving both high adhesion strength and durability [1–7]. In aerospace applications, durable high strength bonds are achieved by the use of a thick oxide layer of high surface area [8–10] which are produced by a process of solvent degreasing, grit blasting, etching and anodizing in chromic or phosphoric acid solution. Vapour degreasing in chlorinated or environmentally friendly equivalent solvent systems are employed to remove surface contamination before etching. Grit blasting is used to remove native oxide and the etching process generates a new layer with improved uniformity and strength. The etching process generally are the Forest Products Laboratory (FPL), sulphuric acid/sodium dichromate and sulphuric acid/ferric sulphate processes [9]. Phosphoric acid anodizing is favoured in the United States (ASTM D3933), while chromic acid anodizing is used in the UK (BAEP 0002). The oxide layers produced by phosphoric and chromic acid are similar but have differences in their thickness, topography and porosity. Elevated ageing temperatures increase the rate of water ingress, accelerates physical and chemical degradation and markedly reduces durability [11–22].

Moisture enters a joint by diffusion through the adhesive or transport along the oxide/adhesive interface. Once inside an adhesive joint, water may cause effects on both the bulk adhesive and oxide/adhesive interface. Within the bulk adhesive, water ingress leads to plasticization which will improve the durability of the joint [8–10]. At the substrate/adhesive interface attack by water on the metal oxide layer will produce dimensional changes in the oxide layer leading to generation of shear stresses and displacement of adhesive. Acid anodization inhibits hydration and is very effective in increasing the oxide stability and joint durability [11, 12]. Dielectric studies on the hydration of aluminium oxide by Seitmagzimov *et al.* [13] and Jeffrey [14] indicate that hydration produces a specific dielectric signature associated with the conversion of oxide to hydroxide which is located at ~ 1 MHz. Extensive studies have been carried out on the effect of water uptake in epoxy adhesives and related changes in their dielectric properties [15–20].

This study aims to explore the effects on the dielectric signature of adhesive joints when exposed to water at elevated temperature and attempts to provide an insight into the processes occurring at a molecular level.

2. Experimental procedures

2.1. Joint fabrication

2.1.1. Surface treatment

Strips of aluminium alloy (BS 1470/HE30TF) $150 \times 25 \times 3$ mm were solvent degreased. Four sets of

TABLE I Joints for ageing tests at 70 °C

Codes	Length (mm)	Width (mm)	Thickness (mm)	Surface treatments
Al–A5	121	7	0.2	phosphoric anodized
B1–B5	121	7	0.2	non anodized
Cl–C5	121	7	0.93	phosphoric anodized
D1–D5	121	7	0.93	non anodized
E1–E5	140	14	0.26	non anodized
F1–F5	140	14	0.26	chromic anodized
G1–G5	140	14	0.26	phosphoric anodized

joints were fabricated for this study, Table I. The substrate was degreased with trichloroethylene followed by acid etching in sulphuric acid/sodium dichromate solution at 70 °C for 12–15 min, rinsed in tap water for 10 min and dried in an oven at 50 °C. Phosphoric anodization was carried out using 85% phosphoric acid for 20–25 min at 19–25 °C at 10 V. The substrate was rinsed in tap water for 15 min and dried in an oven at 80 °C for 30 min. Chromic anodization used the same etch process which was followed by anodization in chromic acid solution containing 50 g dm^{-3} chromium trioxide for 20–25 min at 19–25 °C at 10 V. The voltage was raised to 10 V over 5 min and maintained for 20 min at a current density of 0.1–0.6 A dm^{-2}, then the voltage was increased to 50 V over the next 5 min in steps of 2 V and maintained for another 5 min. The substrate was then rinsed in tap water for 5 min and dried in an oven at 50 °C for 30 min. In both cases the surface exhibited a distinct mauve-green colour indicative of the formation of a thick oxide layer.

2.1.2. Adhesive bonding

Layers of adhesive film (Scotch–Weld structural adhesive film AF-30, 5 mil) were applied to the pretreated aluminium alloy. Metal spacers were placed around the edges of the adhesive films to ensure uniform thickness of the cured adhesive layer. Cure was carried out at 125 °C for 60 min at a pressure of 140 kN m^{-2}. The size of the joints were reduced by matching to produce a final structure with dimensions approximately 140 × 14 × 6 or 120 × 7 × 6 mm, Table I; this process removes the sprue and spacers.

Two sets of joints were generated, each containing 20 joints, Table I. One set was aged at 70 °C and the other at 80 °C. Variation of the thickness of the joints aged at the higher temperature were performed using a digital micrometer. The ageing was carried out in deionised water over a period of approximately 730 days.

2.2. Dielectric measurements

Measurements were carried out in reflection mode over the frequency range 300 kHz to 3 GHz using a Hewlett Packard 8753 A network analyser. By inverse Fourier transformation from the frequency domain, time domain data was obtained. The system was calibrated using three independent standards whose reflection coefficients are known over the frequency range of interest; short, open circuit and matched load. Details of the measurement technique and associated theory have been presented elsewhere [21, 22].

2.3. Mechanical measurements

The shear strength was determined using a method which has been described previously [23]. The overlap area was 40 mm in length and 7 mm in width; the test speed used was 5 mm per min.

3. Results and discussion

Dielectric measurements were performed at 0, 21, 51, 82, 112, 141, 172, 202, 232, 262, 305, 335, 370, 400, 431, 460, 491, 537, 568, 603, 631, 659, 687, 705 and 733 days on the joints prepared with the surface treatments indicated in Table I. A comparison of anodized and non-anodized joints and the effects of change in the adhesive bond thickness was undertaken.

3.1. Dielectric measurements on the joints

3.1.1. Thin adhesive-phosphoric anodized joint

A three-dimensional plot of the variation of the dielectric permittivity over the frequency range from 1–100 MHz with ageing time extending from 0–733 days for a phosphoric anodized joint, Fig. 1, indicated an initial rapid increase in amplitude consistent with diffusion of water into the adhesive. A plateau in the dielectric permittivity is reached after about 300 days of ageing and a fall is observed after 700 days. During the first 300 days water is permeating into the adhesive and saturation is achieved towards the end of this period. An increase in water content leads to a lowering of the glass transition temperature T_g until it has a value identical with that used for the ageing experiment. At this point stresses produced in the adhesive layer during cure can relax and this leads to an increase in the thickness of the joint and a subsequent "apparent" lowering of the dielectric permittivity marked by a small ripple in the curve of Fig. 1. The adhesive at this stage will be able to relax the stresses which were introduced during the initial cure process and changes in the mechanical strength may be anticipated to occur at this point in the ageing process. Further absorption of water into the plasticized matrix leads to an increase in permittivity followed by fall after 700 days. The dielectric permittivity does not change significantly with frequency, indicative that the

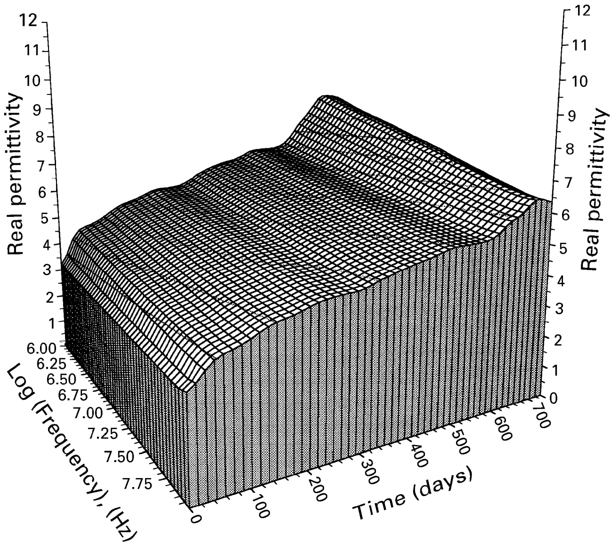

Figure 1 Log frequency and ageing time dependence of the dielectric permittivity for thin adhesive bonded phosphoric anodized aluminium joints exposed at 70 °C.

water absorbed is relaxing above the frequencies used in this investigation and is highly mobile.

The time domain traces presented as a cascade diagram, Fig. 2, indicate that whilst the peak separation increases with time consistent with the increasing value of the dielectric constant of the adhesive layer as water is absorbed, the basic pattern remains unchanged. The fall in the dielectric constant which occurs after 700 days of ageing can readily be seen as a reduction of separation between neighbouring pulses. The time difference is related to the "average" permittivity of the adhesive of joint by;

$$\bar{\varepsilon} = \frac{c^2}{(2l/\Delta t)^2} \qquad (1)$$

where l is the length of the joint, Δt, is the time difference between the first and second pulse, c is the velocity of light and $\bar{\varepsilon}$ is the average dielectric constant. The drop in the apparent permittivity can be attributed to a change in thickness. The dominant process in this joint is plasticization and stress relaxation induced by water ingress.

3.1.2. Thin adhesive-etched only joint

The three-dimensional diagram of the variation of the dielectric permittivity with frequency and ageing time, Fig. 3, is significantly more complex than in the previous case. The initial rapid increase and drop in permittivity on stress relaxation in the joint is similar to that observed in the anodized joint. The development of a marked frequency dependence and oscillatory behaviour of the permittivity is in marked contrast to that observed in Fig. 1. The increased permittivity and frequency dependence observed after 300 days is consistent with hydration of surface oxide and reflects the greater susceptibility of the oxide generated by etching compared with that formed during the anodization process to conversion to the hydroxide. The subsequent falls in the permittivity can only be

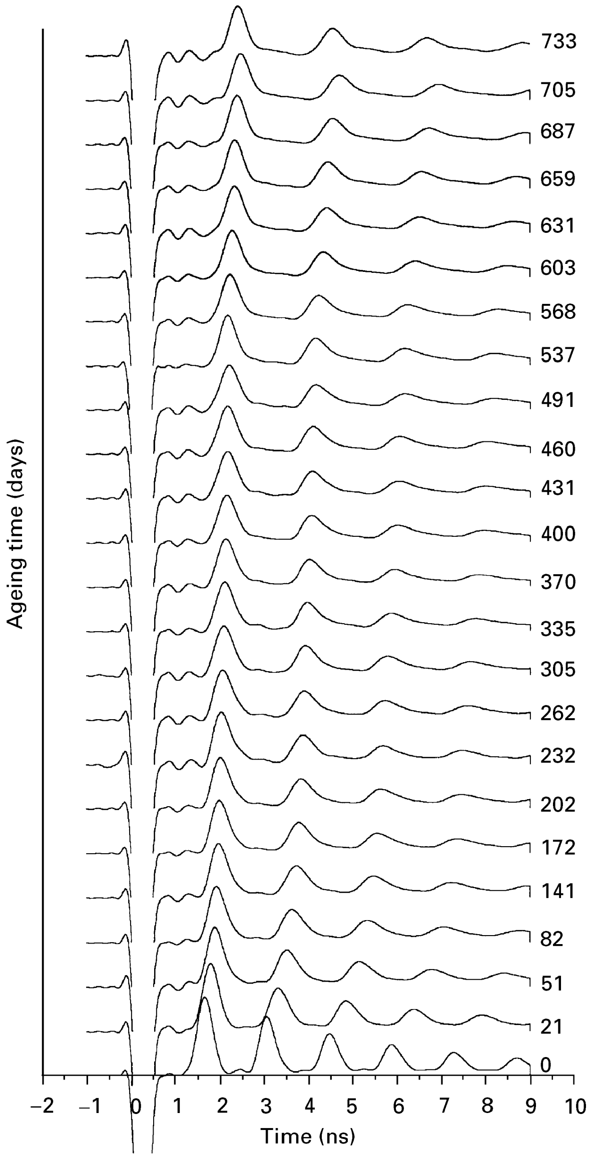

Figure 2 Variation of the time domain traces with ageing time for thin adhesive bonded phosphoric anodized aluminium joints exposed at 70 °C.

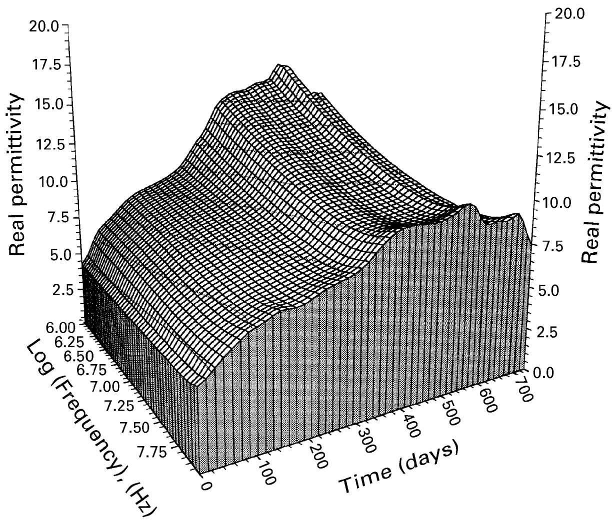

Figure 3 Log frequency and ageing time dependence of the dielectric permittivity for thin adhesive bonded etched aluminium joints exposed at 70 °C.

explained if voids are generated within the bond line. The composite dielectric media contains therefore resin, oxide and air, the latter leading to a lowering in the observed permittivity value. Air gaps introduced between the resin and the metal substrate have characteristic features in the time domain and can be differentiated from the lowering of the permittivity as a result of changes in bond line thickness.

Time domain studies of the joint, Fig. 4, in the initial stages of ageing are very similar to those observed for the phosphoric acid anodized thin joint. The dramatic change of the time domain pulses implies either the introduction of some disbonds or non-uniform expansion of the adhesive layer along the length of the joint as its T_g drops to the ageing temperature of 70 °C.

The ageing of this joint is characterized by conversion of oxide to hydroxide after the initial plasticization of the adhesive structure. The generation of disbonded areas are identified by the observation of impedance changes in the time domain trace corresponding to the formation of air gap rather than simple non-uniform adhesive expansion. The joint fell apart after 705 days of exposure to water at elevated temperature.

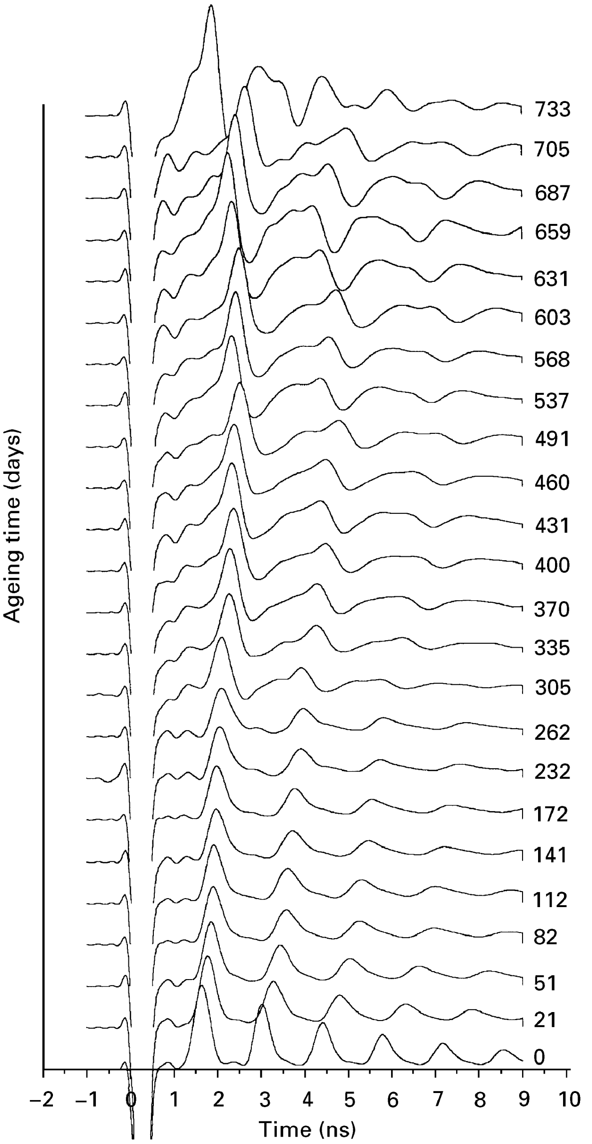

Figure 4 Variation of the time domain traces with ageing time for thin adhesive bonded etched aluminium joints exposed at 70 °C.

3.1.3. Thick adhesive-phosphoric anodized joint

The frequency domain response on ageing, Fig. 5, exhibits an increase in dielectric constant reaching an initial plateau at 300 days, then rising again to another plateau after 550 days, and finally dropping after 700 days. The initial behaviour up to 300 days can be associated with water absorption into the glass adhesive, subsequent changes correlate with the idea that the adhesive changes into a rubbery state and conversion of oxide to hydroxide at the substrate interface begins to occur. The drops after 550 and 700 days correspond to the development of disbonds or changes in the bond line thickness.

The corresponding time domain responses, Fig. 6, do not provide evidence for disbonds implying that the changes are associated with thickness variations. There are, however, small peaks after the main reflection which can be assigned to the beginning of the generation of defects in the adhesive bond. It is clear that using the thick adhesive structure there is a loss of sensitivity of the changes which are occurring at the interface.

3.1.4. Thick adhesive-etched joint

The dielectric permittivity changes with ageing time show the initial marked increase and development of a plateau after 100 days and then subsequent dips associated with the occurrence of disbonds, Fig. 7. A drop of the dielectric permittivity after 500 days indicates that early disbonds were formed due to the weak non-anodized substrate surfaces under the attack of water. The time domain traces clearly indicate the occurrence of these disbonded areas and the general deterioration of the joint, Fig. 8.

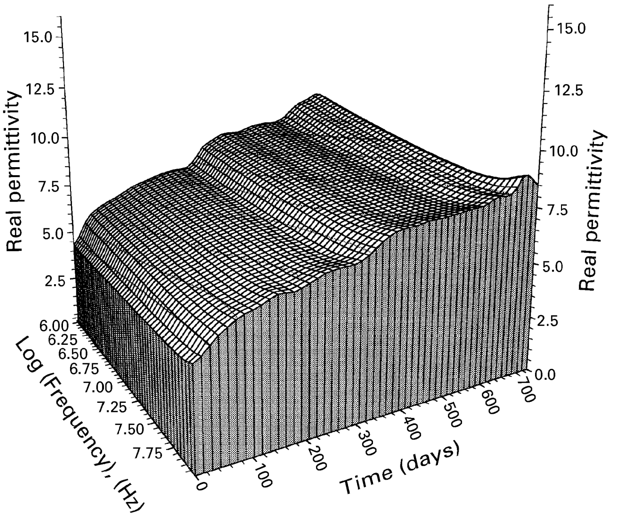

Figure 5 Log frequency and ageing time dependence of the dielectric permittivity for thick adhesive bonded phosphoric anodized aluminium joints exposed at 70 °C.

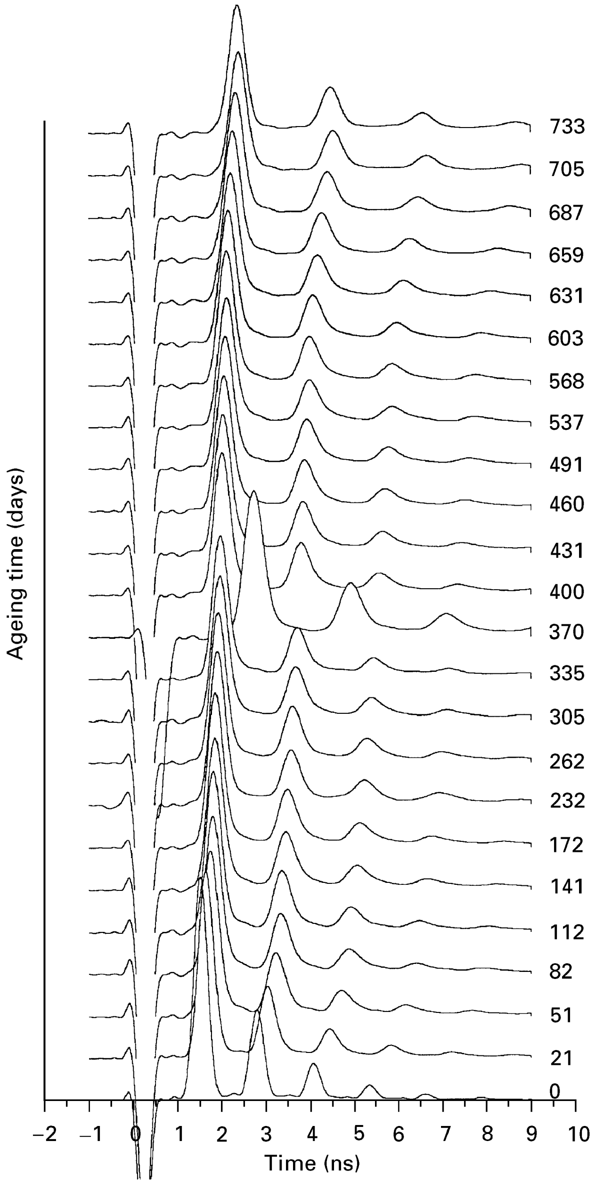

Figure 6 Variation of the time domain traces with ageing time for thick adhesive bonded phosphoric anodized aluminium joints exposed at 70 °C.

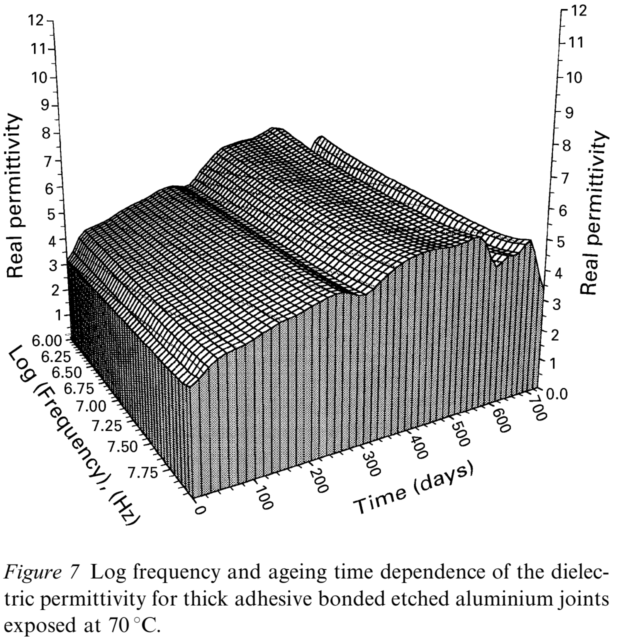

Figure 7 Log frequency and ageing time dependence of the dielectric permittivity for thick adhesive bonded etched aluminium joints exposed at 70 °C.

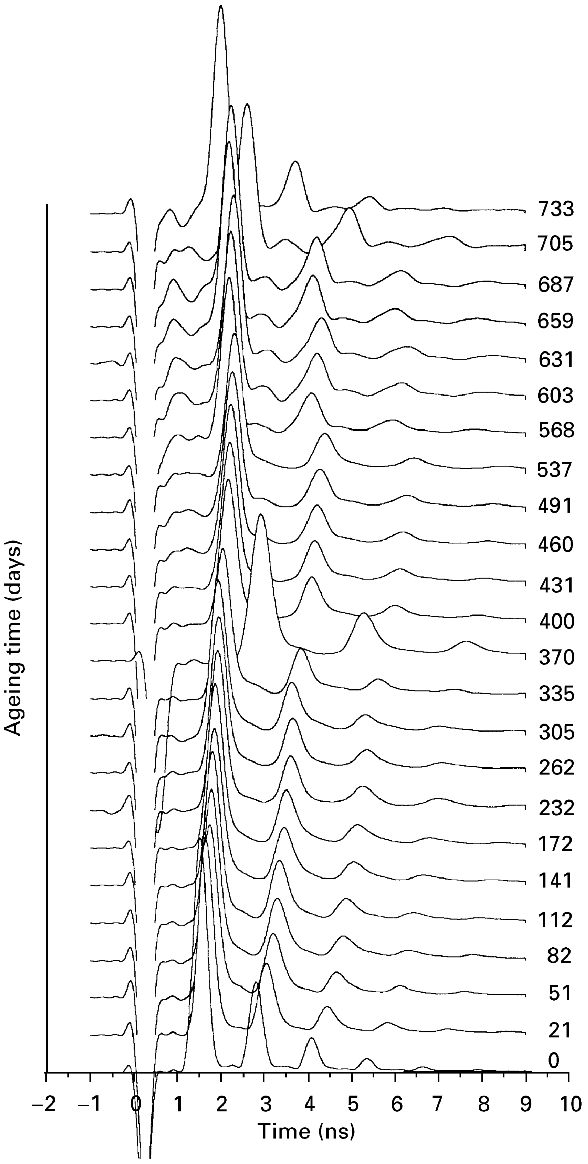

Figure 8 Variation of the time domain traces with ageing time for thin adhesive bonded etched aluminium joints exposed at 70 °C.

In summary, all the frequency and time domain traces displayed in the period up to about 300 days a rapid increase in the dielectric permittivity associated with the ingress of water. The adhesive used has an initial value of T_g above 100 °C, which on the uptake of water can easily be depressed to 70 °C, the ageing temperature. Stresses in the joint structure are then able to relax and in all cases a small decrease in the dielectric permittivity is observed associated with a thickening of the adhesive. The subsequent changes which occur depend on the nature of the surface treatment and the thickness of the adhesive layer.

3.2. Comparison of chromic and phosphoric anodized treatments

A study was undertaken over a limited period of 175 days and as expected only reflects the uptake of moisture by the joint. A typical three-dimensional plot of the dielectric permittivity as a function of ageing time for the chromic acid treatment is shown in Fig. 9, the bump at high frequency is an artefact. A comparison of the change in dielectric constant at 3 MHz for chromic, phosphoric and etched joints. Fig. 10, indicate that the ageing process of these joints is still in the stage of plasticization of adhesive layer and no noticeable change of oxide layer at the interfaces has been reflected from the dielectric responses. The thickness variation of these joints with ageing were measured at a specific point on the joint using a micrometer, Fig. 11. The difference between these three joints is the initial thickness of the adhesive. The accuracy of the thickness measurement becomes less reliable with extension of the ageing time due to corrosion on the surface of the joint. These data imply that in the early stages of ageing there is no significant difference between the surface treatments for good joints.

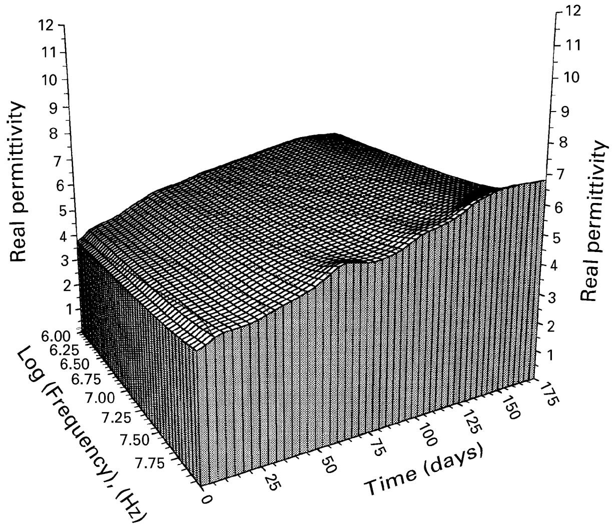

Figure 9 Log frequency and ageing time dependence of the dielectric permittivity for thin adhesive bonded chromium anodized aluminium joints exposed at 70 °C.

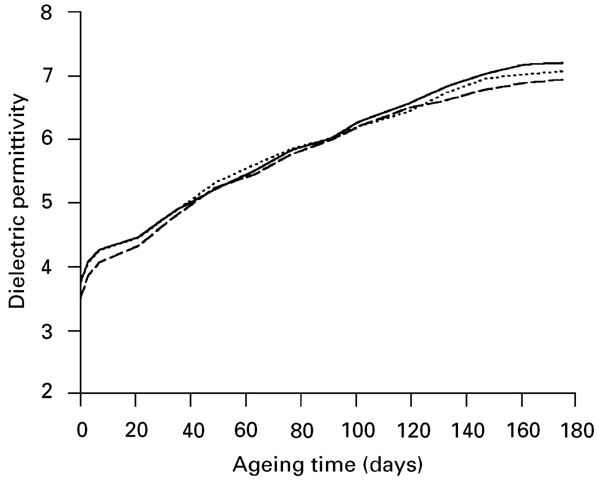

Figure 10 Dielectric permittivity variation measured at 3 MHz for (- -) chromic anodized, (· · · ·) phosphoric anodized and (——) etched aged at 80 °C.

3.3. Estimation of water content and diffusion coefficient

Dielectric measurements have been successfully employed to study water ingress into thermoset resins [13, 15], but no literature exists on the use of this technique for the investigation of moisture ingress into bonded structures. It is well known that water can exist within a moist polymer in two distinct states; bound water and free water [14, 18], the bound water being associated with hydroxyl groups within the polymer and was found to relax at 100 kHz, and free water clustered in larger voids relaxes approximately at a frequency of 18 GHz. No satisfactory theory exists which enables the dielectric properties of a moist material to be accurately related to its total water content. However, the amount of water ingress in a joint can be estimated from the increment of dielectric constant at a frequency below the relaxation of water. Estimations have been attempted by Joshi [22] from analysis of the increment of dielectric constant measured at two fixed frequencies, 10 kHz and 30 MHz, respectively. In this paper only the amount of free water is calculated from the increment of dielectric constant at 3 MHz.

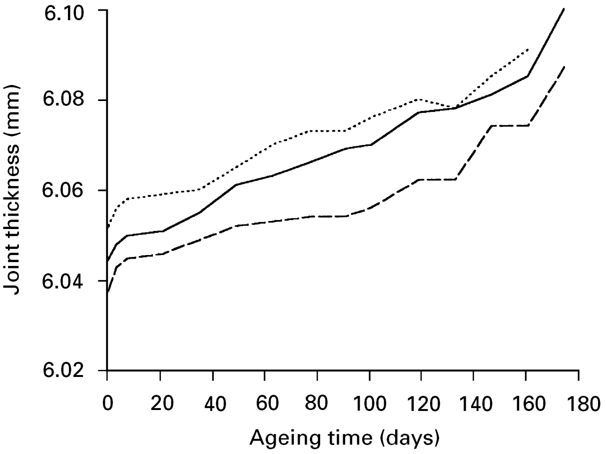

Figure 11 Thickness variation with time for (– – –) chromic anodized, (· · · ·) phosphoric anodized and (——) etched aged at 80 °C.

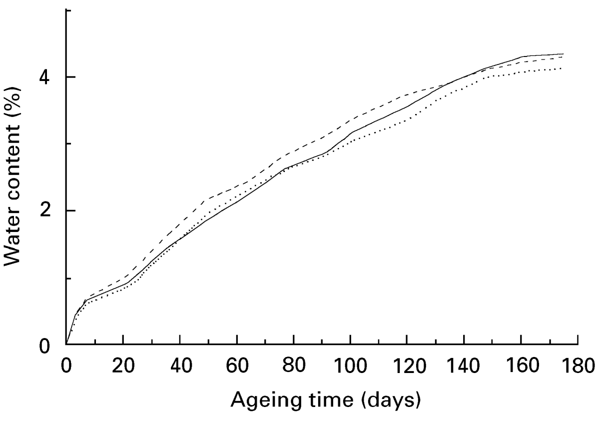

Figure 12 Variation of the water uptake as a function of ageing time for (– – –) chromic anodized, (· · · ·) phosphoric anodized and (——) etched aged at 80 °C.

TABLE II Shear strength of aged and unaged joints

Thin layer-phosphoric anodized	Strength (MPa)	Thin layer-etched	Strength (MPa)	Thick layer-phosphoric anodized	Strength (MPa)	Thick layer-etched	Strength (MPa)
1	4.68	1	0.57	1	2.07	1	0.21
2	6.07	2	3.75	2	2.29	2	0.00
3	5.00	3	0.71	3	1.64	3	1.29
4	4.29	4	0.00	4	0.71	4	0.86
5	5.36	5	2.86	5	1.96	5	0.75
average	5.08		1.58	5	1.73	5	0.62
unaged*	> 12		> 8.6		> 8		> 11.5

* Substrate failure.

The variation of the dielectric permittivity with ageing time at a fixed frequency 3 MHz, Fig. 10, shows a gradual increase with ageing due to the contribution from the uptake of free water. Differences in the dielectric constant between the aged and dry joint was calculated, then divided by 80, the permittivity of free water at 25 °C [23] allowing an estimation of the volume fraction of free water within the joint to be obtained. The increment of the amount of free water entering joints with the ageing time is shown in Fig. 12. In principle, it is possible to calculate "apparent" diffusion coefficients from this data, however the geometry used does not allow a simple analysis to be applied with any confidence.

3.4. Mechanical measurements

The phosphoric acid anodized joints were subjected to mechanical testing at the end of the study, Table II. The data indicates that the strength of all the joints deteriorate after ageing in water. Joints with thin adhesive layers and phosphoric anodization are clearly more durable than the thicker adhesive or those which were only etched. The joints with the greatest strength displayed a combination of interfacial and cohesive failures. Increase of the adhesive thickness leads to interfacial failures being observed even with phosphoric anodized substrates. Voids at the adhesive/substrate interface due to corrosion of substrates during ageing were also observed in the etched samples consistent with the observation in the time domain traces. The presence of corrosion at the failed surfaces does not necessarily imply that it was a key aspect in the mechanism of environmental attack. It is very likely that corrosion only occurs after the stable oxide layer at the adhesive/substrate interface has deteriorated due to the attack of water. The substrate surface is now exposed and a liquid electrolyte is present so that post-failure corrosion of the substrate occurs. The dielectric analysis reveals that the loss of strength is the result of a combination of adhesive disbonding from the substrate and changes in the oxide surface layer.

4. Conclusions

This study indicates clearly the value of the high frequency dielectric technique for the *in-situ* investigation of adhesive bond failure. The results of the mechanical testing are consistent with those previously reported in the literature, however this study reveals that the failure mechanisms are complex and involve a combination of plasticization, stress relaxation of the adhesive and destabilization of the interface by conversion of the oxide into hydroxide. The generation of voids as seen from the time domain traces are a clear indication of the loss of interfacial shear strength.

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