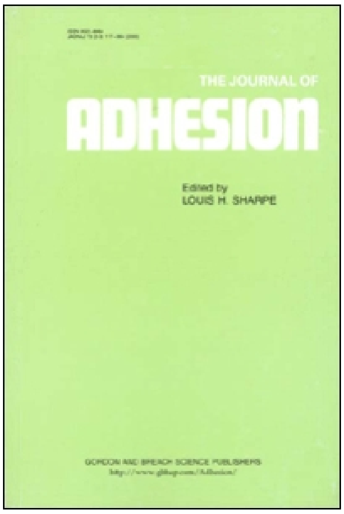

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Influence of Thermal Spikes on the Ageing of Adhesively Bonded Structures - A Dielectric Study

B. K. McConnell[a]; R. A. Pethrick[a]
[a] Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow

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Influence of Thermal Spikes on the Ageing of Adhesively Bonded Structures – A Dielectric Study

B. K. McConnell and R. A. Pethrick
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow

Dielectric measurements are reported on epoxy bonded aluminium joints exposed to moisture at 75°C. The observed changes in the dielectric spectrum that occur with time of exposure are correlated with the variation in the mechanical strength. Certain joints were subjected to periodic cooling to −20°C to simulate the shock of aircraft flight. The effects of dehydration were examined for joints that had been exposed to moisture for a prolonged period of time. The data indicate that the initial hydration process lowers the glass transition temperature and the stress released creates micro-voids. Further ageing leads to hydroxide formation in the interfacial layer. Freezing of water during the thermal spike experiments induces cracking in the adhesive, and leads to greater water uptake. Plasticisation of the resin appears to be to a large extent reversible and dehydration allows some recovery of the bond strength. The shock cooling of the joints has only a relatively small effect on the ageing of the joints but does, however, produce differences in the dielectric data. This study illustrates the power of the dielectric technique for the assessment of ageing in adhesively bonded structures.

Keywords: Adhesive bonding; Aluminium epoxy joints; Dehydration effects; Dielectric relaxation; Hydrolytic ageing; Spiked temperature studies

1. INTRODUCTION

In a previous paper [1], the effect on the physical properties of exposure of the dicyandiamide (DICY) cured epoxy resins to moisture was discussed. It was observed that water entering the resin is able to

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Address correspondence to Richard A. Pethrick, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK. E-mail: r.a.pethrick@strath.ac.uk

plasticise the polymer, leading to a consequent lowering of the modulus and glass transition temperature (T_g). Water was observed to segregate into microvoids formed as a consequence of gas entrapment during the cure process or formed as a result of osmotic effects associated with the swelling of the resin. Heating the resin indicated that whilst plasticisation appears to be a reversible process, densification of the resin and the changes in the void distribution appear to be irreversible. The application of the dielectric technique to the study of bond ageing has been the subject of a number of previous publications [2–10]. The studies have focussed on isothermal ageing or a slowly cycling temperature regime about a temperature close to ambient. In practice, joints are likely to be exposed to a range of environments and in aerospace applications cooling to -50°C will be frequently encountered during aircraft flight.

In this paper, measurements are described of ageing of a common aerospace resin, subjected to isothermal ageing at 75°C and periodically frozen to -20°C for short periods of time. Aircraft are likely to be subject to elevated temperatures and dry conditions allowing dehydration of the joints. To simulate this process a study was undertaken of the dehydration of previously hydrated joints.

2. EXPERIMENTAL

2.1. Materials

The AF 163-2 K adhesive was obtained from 3 M (Bracknell, UK) and is a DICY cured epoxy resin supplied on a nylon mesh. The aluminium adhesive joints were fabricated from aluminium sheet supplied by British Aerospace (Prestwick, UK) and designated Series 2000-MTL Spec L166 T4 material, clad in 99.5% pure aluminium. A 2000 series aluminum alloy contains about 3.60 to 4.25 w% copper, about 1.00 to 1.60 w% magnesium, about 0.30 to 0.80 w% manganese, about 0.05 w% silicon, about 0.07 w% iron, about 0.06 w% titanium, about 0.002 w% beryllium, with the remainder as aluminium. The sheet was surface pre-treated at British Aerospace and consisted of the following procedures: a degrease, alkaline clean, chromic/sulphuric acid pickle, chromic acid anodise, and application of a corrosion resistant primer (low viscosity epoxy resin). An oxide layer of around 400 nm was produced and the substrates were stored in polyethylene sheets and bonded within 2 weeks. For the aluminium joints, the bondline thickness was 0.2 mm; Teflon® inserts were used to keep the bondline thickness constant. Cure involved heating from room temperature to 125°C at 5°C/min, then holding for 60 min, followed by cooling cycle at 5°C/min to room temperature. The T_g of the adhesive is 110°C.

2.2. Exposure to Moisture

Sandwich specimens were cut for dielectric and mechanical testing with dimensions $75 \times 10 \times 3.5$ mm. The strips were aged in jars filled with deionised water and held at 75°C in an oven. This temperature is below the T_g of the adhesive (110°C). Measurements were performed at regular intervals, with half of the joints also exposed to temperatures of −20°C for 24 h, after every testing schedule. This temperature was selected for the study as it was possible with the refrigeration equipment available to maintain it accurately for long periods of time. After approximately 805 days exposure, all of the samples were removed from water and desorbed in the oven at 75°C. The same procedure (without the cryogenic exposure) was used to follow their desorption profiles. Previous studies have indicated that the T_g decreases by ~10°C for every 1% of water absorbed [1].

2.3. Dielectric Analysis

Permittivity and loss values were recorded over the frequency range 0.1 Hz to 63 kHz using a frequency response analyser and over the frequency range 30 kHz to 6 GHz using a network analyser as described previously [8–10].

2.4. Mechanical Tests

Mode II tests were carried out according to ASTM D 3165–9—tension loading of single lap joint laminated assemblies. The aluminium joints were prepared by notching parallel grooves on either side of the joints, creating a reproducible shear area of 13 (length) × 10 mm (width). Five such joints were tested at each stage in the ageing cycle. Analysis was carried out on a Zwick tensile testing machine (Zwich, ULm, Germany). The joints were loaded at a free cross-head speed of 1.27 mm/min, with the load and extension recorded from zero load through to failure load. Details of the method have been discussed previously [8,9].

3. RESULTS AND DISCUSSION

Ageing in adhesively bonded joints can be attributed to a number of factors. At low temperatures, degradation of the resin is not normally considered to be a factor and the changes observed may be attributed to the slow reaction of uncured monomer and physical ageing associated with densification due to matrix relaxation. In moist conditions, lowering of the T_g aids matrix relaxation [11–13].

3.1. Absorption of Moisture in Aluminium/AF 163-2K Joints

A previous study by Brewis *et al.* [13] suggests that ice crystals formed in the epoxy matrix could lead to damage. To simulate aircraft flight, two sets of samples were created: frozen (75°C and −20°C ageing, five samples) and non-frozen (just 75°C ageing, six samples) joints. Although water freezes at 0°C, previous studies have shown that water molecules can retain mobility in a polymer matrix down to −35°C [14].

3.1.1. Joint Thickness Variation

Due to corrosion of the metal substrate, it is not possible to use changes in weight to monitor moisture uptake in the joints. Surface corrosion and hydroxide formation in the interfacial (oxide) layer will effect a change in joint thickness, which will also be influenced by swelling of the resin (Fig. 1). This contributes to the scatter observed at longer exposure times, caused by an increase in the standard deviation of the samples. Figure 1 shows that after 50 $\text{hrs}^{1/2}$ (104 days) of ageing, there is a substantial increase in thickness. This correlates with significant surface corrosion of the substrate. Since the adhesive

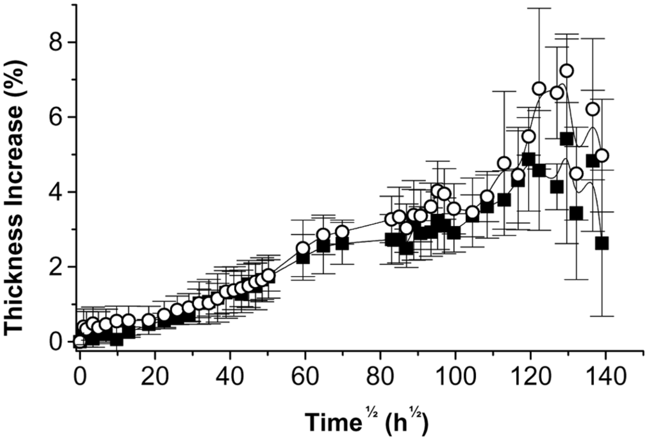


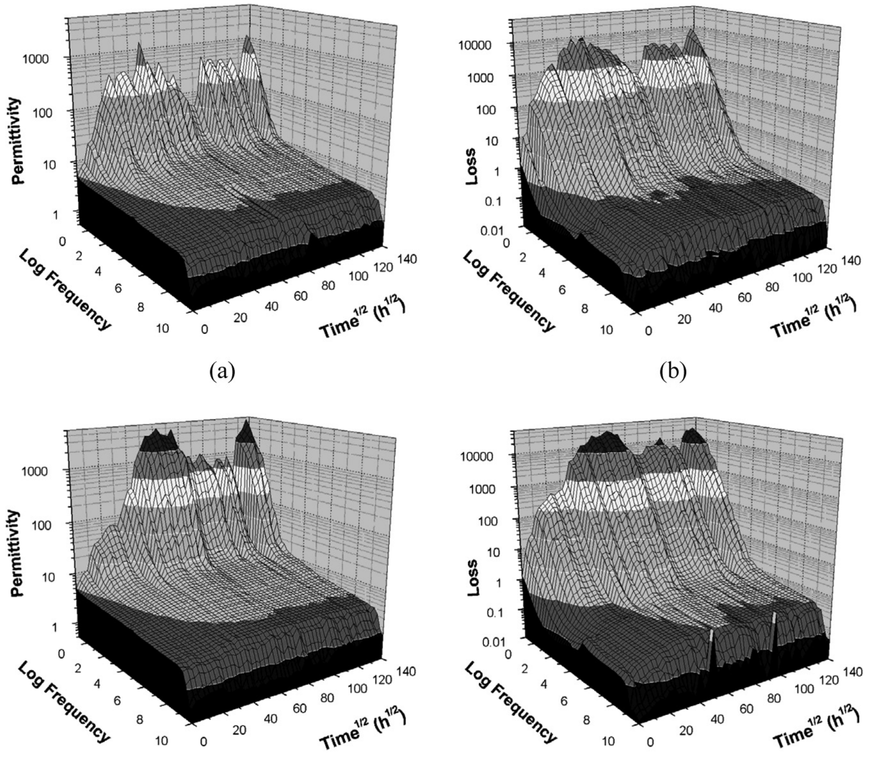
FIGURE 1 The effect of moisture ingress upon the thickness of aluminium/AF 163-2 K joints, aged at 75°C (-■-) and at 75°C/−20°C (-○-).

thickness is small in comparison with the adherend, the observed increase is attributed to growth of aluminium hydroxide. However, the initial increase in thickness may be attributed to swelling, paralleling changes seen in the pure adhesive [1]. The greater thickness increase of frozen samples suggests that the cryogenic spiking has led to both an increased level of corrosion and hydroxide growth on the aluminium adherend. Freezing of water molecules trapped within the growing hydroxide layer will open up the aluminium surface to further corrosion, aid greater hydroxide growth, and increase exposure to atmospheric oxygen.

3.1.2. Dielectric Analysis – Frequency Domain

The permittivity and loss data were measured as a function of ageing time for the frozen and non-frozen joints. 3-D plots showing these data plotted against frequency are presented in Fig. 2. Small differences in the data were observed and the increase in permittivity with time is indicative of water ingress. Increase in the GHz region is associated with the presence of clusters of free water molecules located in microscopic voids and cracks. Increases in the permittivity in the kHz-MHz frequency range are due to the interaction of individual water molecules with polar groups on the resin. The apparent drop off in dielectric permittivity at very high frequencies is an artefact and associated with the finite dimensions of the joint structures under analysis [15,16]. The major feature at low frequency is associated with blocking electrode effects and heterogeneity in the matrix. A slightly greater low frequency contribution in thermally spiked samples is consistent with the freezing process creating cracks and microvoids within the adhesive layer, which results in an increase in free water. Blocking electrode effects are associated with space charge polarization, which is associated with the inability of mobile charges to be discharged at the metal substrate. The moisture ingress liberates the mobile charges allowing these effects to develop.

The 3-D plots are unsuitable for spotting trends at specific frequencies. In order to visualise more clearly the differences between the two sets of joints, increases in dielectric permittivity with time are plotted at the frequencies: (a) 10 kHz and (b) 3 MHz (Fig. 3). The frequencies 10 kHz and 3 MHz were selected being, respectively, below the relaxation frequency for "bound" and "free" water. These 2-D graphs clearly demonstrate how water ingress results in significant changes to the permittivity of joints. Over the initial 40 $\mathrm{hr}^{1/2}$ (approx 67 days) ageing period there is a linear increase in permittivity, with almost no difference observed between non-frozen and frozen samples. At 10 kHz the



(a) (b)

(c) (d)

FIGURE 2 Average permittivity and loss data for non-frozen joints, aged at 75°C (a,b), and frozen joints, aged at 75°C/−20°C (c,d). The grey scaled, bands designate decades of change in, respectively, the dielectric permittivity and dielectric loss.

gradients are 0.076 and 0.082, respectively, whilst at 3 MHz they both have a gradient of 0.045.

After this initial period of rapid increase in permittivity, both sets of joints then enter a plateau region, which endures for the rest of their absorption cycle. For frozen joints this occurs at a higher permittivity than with their non-frozen counterparts, confirming that the freezing of samples to −20°C has resulted in greater water uptake. This correlates with the very low frequency data (Fig. 2), since the formation of cracks and voids within the adhesive layer would also result in an increase in bound water interactions, by opening up the adhesive to further water ingress. The fact that the commencement of the plateau

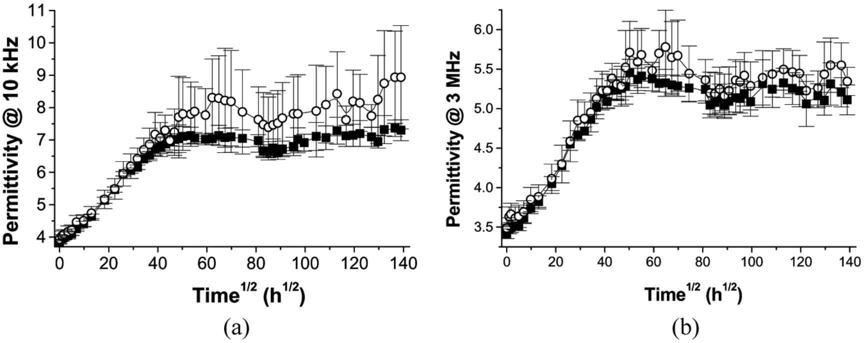


FIGURE 3 Comparison of dielectric ageing profiles of non-frozen (-■-) and frozen joints (-○-) at (a) 10 kHz and (b) 3 MHz.

region also coincides with a large increase in the error bars of the frozen samples also suggests greater degradation. This is a common sight in aged joints, and is indicative of ingressing water affecting essentially identical joints to differing degrees. The apparent dip in the permittivity at 80 hr$^{1/2}$ is consistent with the densification of the resin and the effects of stress relaxation changing the bond line thickness. The degradation of the interface could be compounded by residual stress caused by the difference in coefficient of thermal expansion between the adhesive and substrate, which is compounded by decreasing the temperature.

A plateau region in the dielectric data would appear to indicate saturation of the adhesive layer. However, 70 days of ageing is not enough time for saturation levels to have been reached, as shown by ageing of the free adhesive [1]. The adhesive bondline is a sixth of the sample used for tests on the free adhesive but the surface area exposed to the water is significantly reduced by the substrate, hence very long exposure times are required to reach saturation levels in the resin. Similar behaviour was observed by Armstrong *et al.* [9]. The increased bondline thickness associated with hydroxide formation in the interfacial layer, and swelling of the resin, reduces the capacitance of the joint and hence there is an apparent plateau in the permittivity, although further water ingress must be taking place.

To overcome the problem of interfacial polarisation and conductivity swamping the dipolar relaxations, the electric modulus representation will be considered. This is defined as the reciprocal of the dielectric constant. Permittivity and loss have their electric

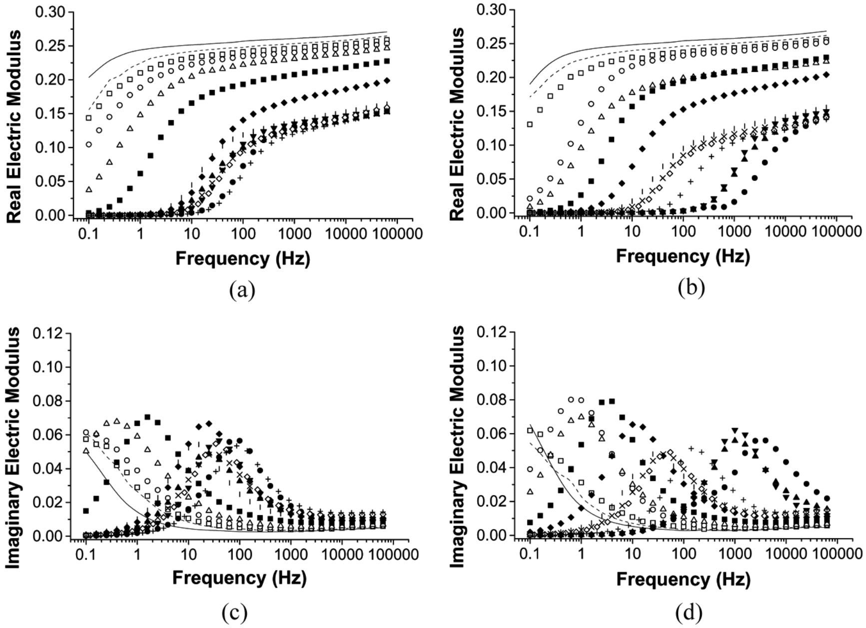


FIGURE 4 The real and imaginary electric modulus of an average non-frozen (a,c), and frozen joint (b,d). Key: — Unaged joints; - - 1 hour exposure; □ 0.5 days; ○ 1 day; △ 2 days; ■7 days; ◆21 days; ▼ 84 days; ● 126 days; ▲ 203 days; |315 days; × 567 days; ◇ 728 days; +805 days.

modulus equivalent, calculated using the following equations:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \qquad \text{and} \qquad M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{1}$$

where ε' is permittivity and ε'' loss, and M' and M'' are the real and imaginary electric moduli, respectively. The modulus data for the non-frozen and frozen joints are presented in Fig. 4.

The real electric modulus data show a decrease in amplitude with exposure time, consistent with a reduction in the capacitive contribution. The relaxation in the imaginary data shifts to higher frequencies with moisture ingress, consistent with the effects of plasticisation within the adhesive. The more plasticised the polymer, the higher the frequency at which the relaxation will occur reflecting the faster motion of the polymer chain.

3.1.3. Dielectric Analysis – Time Domain

Time domain reflectometry has been used previously to identify changes occurring in the structural integrity of joints during exposure to water [9,10]. Figure 5 shows data for a non-frozen aluminium/AF 163-2 K joint. The traces were obtained over 805 days of ageing in water. The vertical line indicates the locus of the original first reflection and shows the shift in this peak as the sample is exposed to moisture, indicative of a rising permittivity increasing the transit time.

The data confirm that, even after 805 days of ageing, there are no significant changes to the bondline profile which would lead to degradation in the signal pattern. Therefore, it is reasonable to assume that despite water ingress and subsequent hydration of the adhesive layer, there is little actual mechanical degradation occurring in the bondline. When the wave reaches a defect, the change in permittivity generates a reflected wave which produces a weak response peak [17]. Figure 6 shows the time domain data for a typical frozen joint. The graph is virtually identical to that of the non-frozen samples, indicating that although freezing of joints has led to a greater degree of water ingress, there has not been any significant extra degradation to the bondline of the joint.

3.1.4. Mechanical Analysis

In order to follow the physical effects of ageing on frozen joints, mechanical testing and visual inspection of the oxide layer of samples

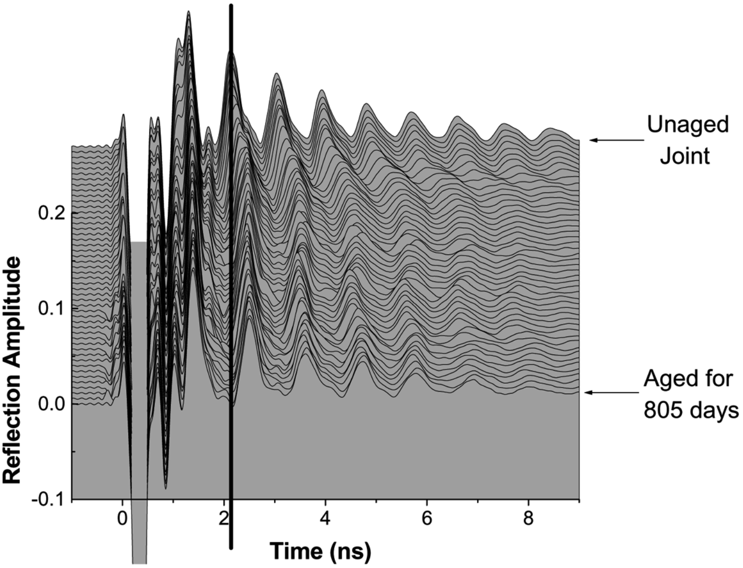


FIGURE 5 Time domain data for a non-frozen joint, aged in water at 75°C.

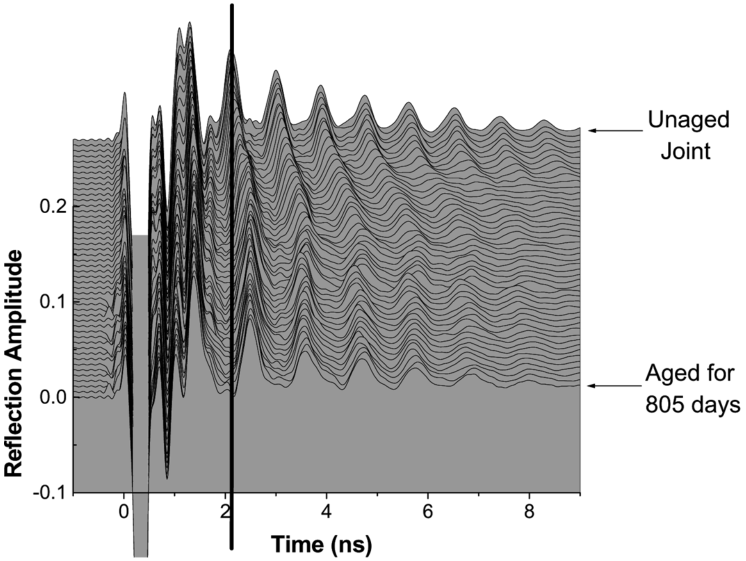


FIGURE 6 Time domain data for a frozen aluminium/AF 163-2 K joint, aged in water at 75°C/−20°C.

was carried out. This also allowed direct correlation with the dielectric data. Mode II mechanical shear testing was carried out at regular intervals on the fozen joints and the results are presented in Fig. 7. The average maximum stress and ultimate strain values are plotted against ageing time. A very large increase in the size of error bars as ageing progresses is observed due to the effects of ingressing water degrading identical joints to differing amounts. Initially, there is a large decrease in strength, before a plateau is reached after approximately 50 $\mathrm{hrs}^{1/2}$ (104 days) of ageing. This behaviour matches that observed in the dielectric data, indicating that the strength of the joints is linked to water ingress and associated with a lowering of the T_g. However, after $50+\mathrm{hrs}^{1/2}$ of ageing the formation of significant amounts of hydroxide in the interfacial layer changes the failure mode from cohesive to adhesive. Further water uptake by the *adhesive* has less of an effect on joint strength, because failure is mainly occurring in the interfacial layer. A further drop in strength is anticipated to occur beyond 120 $\mathrm{hr}^{1/2}$ (600 days) as the oxide layer is further weakened.

Examination of the strain data (Fig. 7) shows that there is the usual expected drop in the ultimate strain. However, after 504 days of ageing there is an apparent recovery before once more decreasing.

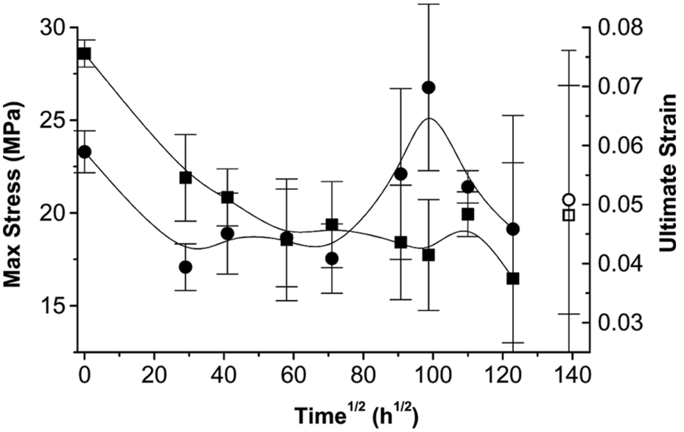


FIGURE 7 Average maximum stress (-■-) and ultimate strain (-●-) values for frozen aluminium/AF 163-2 K joints. Open points on the far right-hand-side of the graph refer to the desorbed joints (Section 3.2.4).

This behaviour is linked to plasticisation of the adhesive layer. The initially cured resin will have a significant internal stress relating to the initial conditions used in the cure process. Once T_g becomes comparable with that of the ageing temperature, stress relaxation and densification of the matrix can occur. The net result of these changes in the resin is an apparent increase in the strain of the joint. The ultimate strength or the failure mechanism of the joint, however, is dependent upon the stability of the adhesive—aluminium oxide interface. Visual examination of the failed joints indicates that whereas the initial failure is cohesive, ageing increases the preponderance for adhesive failure. After approximately 340 days of ageing, there are signs of corrosion in the interfacial layer around the edges of the joints, where water concentration is at its highest. However, in other samples areas of the interfacial region have actually been removed along with the adhesive, suggesting conversion of the oxide layer has taken place *prior* to disbonding but has not led to complete loss of strength. It is probable that there is a critical level of oxide conversion before the strength of the interface drops to a critical value and loss of strength is observed.

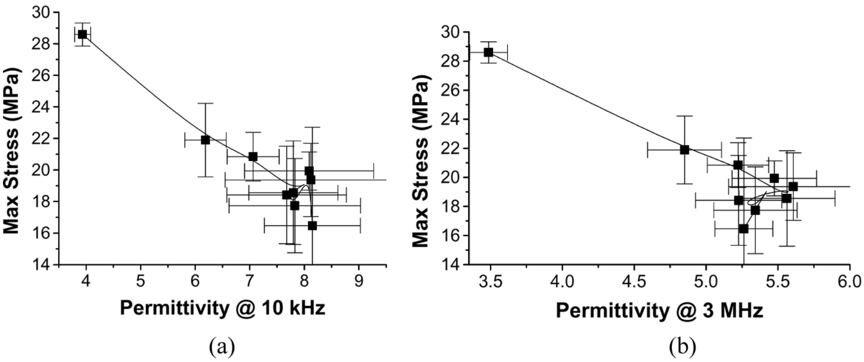
Ageing studies by Sargent [18] on aluminium/AF 163-2 K joints found that samples aged in normal *tap* water failed much earlier than those aged in distilled water (these studies were performed in *deionised* water). It is assumed that the ions present in the tap water promote the growth of the surface hydroxide layer and the consequent loss of strength. Work by da Silva *et al*. [19] has shown that the nylon carriers can improve the strength of a joint, through their fibres strengthening the adhesive, as well as acting as crack-stoppers, and will influence the stress distribution in the joint. As both sets of joints aged, the colour of the oxide layer on certain areas of the surface was observed to change from white to aqua-blue and red, which reflects the progressive galvanic corrosion of the metal adherends [20]. The observation of this change was rather surprising, but it is expected to be connected to the relatively large amount of copper present in the adherend.

3.1.5. Correlations Between Mechanical and Dielectric Data

Plots for the mechanical and permittivity results (Fig. 8) show a general correlation between the increase in permittivity and the decrease in the bond strength (the large error bars are a consequence of the expected variation between individual joint samples). This shows that the factors controlling the strength of the joints, namely plasticisation and hydroxide formation, also influence the dielectric behaviour and highlights the use of dielectric spectroscopy as a NDE technique.

3.2. Desorption of Aluminium/AF 163-2 K Joints

After 805 days of ageing at 75°C, the non-frozen and frozen joints were removed from water and allowed to desorb in the oven at 75°C. Testing of the joints continued at regular intervals. The results are presented below.



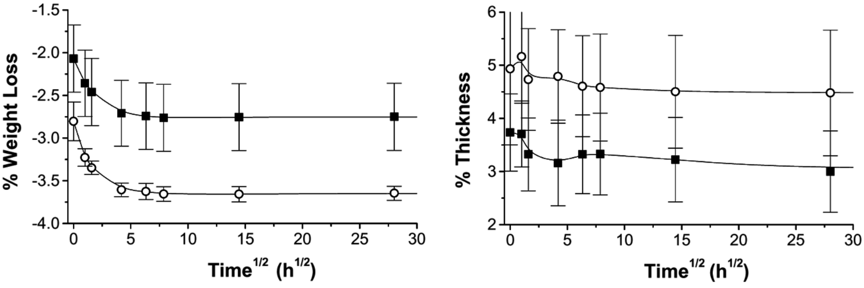
(a) (b)

FIGURE 8 Maximum stress *versus* permittivity at (a) 10 kHz and (b) 3 MHz for frozen aluminium/AF 163-2 K joints.

3.2.1. Gravimetric Analysis

Figure 9 indicates (a) the weight loss and (b) the change in thickness of the joints over the course of their desorption cycle. The joints were desorbed for a total of 296 days (84 hrs$^{1/2}$). However, very little difference was observed between the final testing and the values at 33 days (28 hrs$^{1/2}$). Therefore, these data points are omitted for clarity. The graphs show changes with respect to *unaged* data. Both show an overall drop in magnitude as water leaves the joints and reduces the swelling in the resin. Comparison of the non-frozen and frozen joints indicates that the frozen samples have lost more weight than their non-frozen counterparts, but suffered less of a drop in thickness due to greater hydroxide formation. The frozen joints have lost, on average, 1% more of their mass which signifies greater hydroxide formation in these samples. After complete desorption, frozen joints are nearly 5% thicker than their unaged state, whereas non-frozen samples are just over 3% thicker. This implies greater hydroxide formation through partial freezing of the joints. The relatively small amount of change in the thickness data during desorption also suggests that most of the thickness increases during ageing of the joints was due to hydroxide formation, with only a small contribution from swelling of the adhesive layer.

Using the above data, it is possible to estimate the percentage water present in the adhesive layer, just before commencement of the desorption studies. For non-frozen and frozen joints the water contents are, respectively, 27% and 33%, and highlight the greater water content in the frozen samples. These observations are consistent with our previous study of the water absorption characteristics of the pure resin [1].

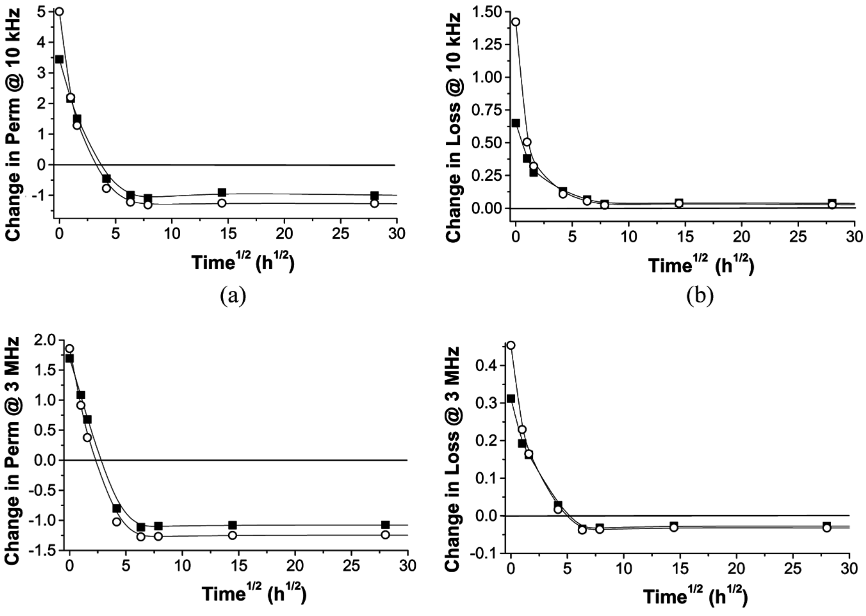


(a) (b)

FIGURE 9 Changes in (a) the weight and (b) the thickness of the non-frozen (-■-), and frozen joints (-○-) during desorption at 75°C (changes relative to unaged joints).

3.2.2. Dielectric Analysis – Frequency Domain

The dielectric behaviour during desorption are presented in Fig. 10 as the variation in permittivity and loss as a function of time. The graphs highlight the very rapid loss of water, also observed in the gravimetric data. Very little difference exists between the non-frozen and frozen samples, except that the initial permittivity and loss values are higher for the frozen joints. The solid horizontal line indicates the base line for the measurements using the unaged samples as a reference. The removal of water from the samples has resulted in an overall *decrease* in permittivity from the unaged state and indicates that ageing has produced an irreversible change to the dielectric behaviour. A negative change in permittivity is consistent with an increase in thickness of the bond line due to the conversion of aluminium oxide to hydroxide. The formation of this thick hydroxide layer would also lead to a smaller reduction in the loss values. The lower value of permittivity for frozen joints suggests greater damage caused by the freezing action of water.



(a) (b)

(c) (d)

FIGURE 10 Changes from the unaged 10 kHz values of (a) permittivity and (b) loss, and changes from the unaged 3 MHz values of (c) permittivity and (d) loss, all during desorption of joints at 75°C. Key: non-frozen (-■-) and frozen joints (-○-).

3.2.3. Dielectric Analysis – Time Domain

Dielectric time domain analysis was also carried out on these joints during the desorption process. Figure 11 shows the waterfall plot for an average non-frozen joint. The vertical line drawn through the centre of the *aged* trace indicates the relative shift in the peaks. The shift in position of the peaks reaches a constant value very early into the desorption process, showing that water egress is a rapid event. There are no significant points of inflection, implying a lack of any major degradation in the adhesive. If cracks and voids do exist within the adhesive layer, they are not large enough to disturb the electrical signal-and are, therefore, not detected. Another important feature of Fig. 11 is highlighted by the dashed vertical line. This is drawn through the middle of the *unaged* trace. It shows that not long into the desorption process the second positive peak has shifted back to response times *shorter* than that of the unaged adhesive. This effect is caused by hydroxide formation in the interfacial layer, increasing the distance between the two conducting adherend plates. Similar behaviour was observed for the frozen joint (Fig. 12). One of the frozen joint samples did, however, show signs of significant delamination at one end of the joint (Fig. 13a). Its time domain trace (Fig. 13b) indicates an increase in peak height, indicative of delamination at the testing end of the joint. Since delamination was occurring at the

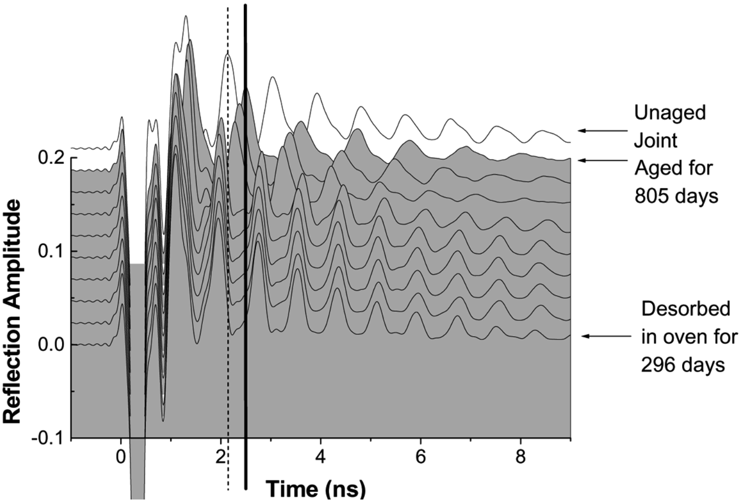


FIGURE 11 Time domain data for a non-frozen joint, during desorption at 75°C.

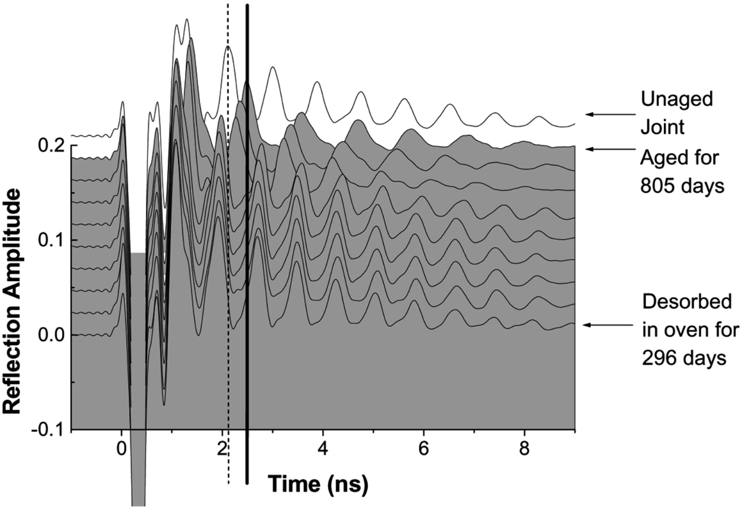


FIGURE 12 Time domain data for a frozen joint, during desorption at 75°C.

end of the joint sample, the mechanical measurements (which only tested the strength of the *middle* of the joint) indicated that it still possessed good shear strength. However, dielectric spectroscopy was able to pick up on this degradation.

It is possible to make an estimate of the fraction of air introduced into the bondline, caused by the effects of delamination and

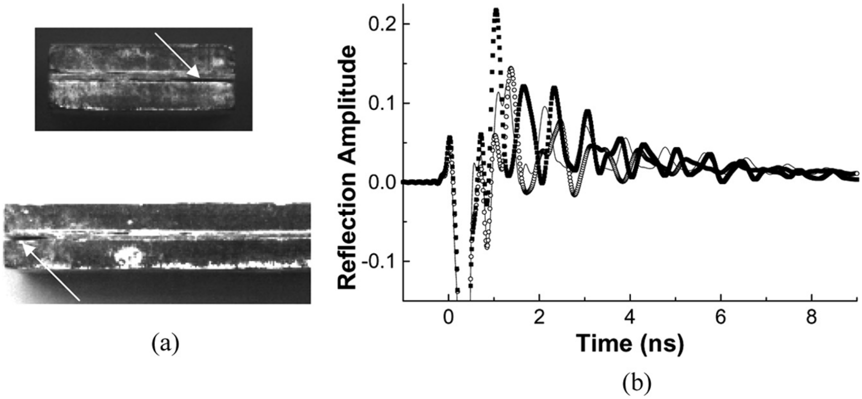


FIGURE 13 Data for a frozen, pre-mechanically tested aluminium/AF 163-2 K joint. (a) Image showing damage to its bondline after desorption and (b) its time domain behaviour. Key: —Unaged joint; ○ 805 days aged joint; ■ fully desorbed joint.

hydroxide growth, using the unaged (ε_{unaged}) and desorbed ($\varepsilon_{desorbed}$) permittivities-and the following equation:

$$Air\ Fraction = \frac{\varepsilon_{unaged} - \varepsilon_{desorbed}}{(\varepsilon_{desorbed} - 1)\varepsilon_{unaged}}. \tag{2}$$

The equation is based on the assumptions that the joints are completely dry after desorption, and that the actual permittivity of the adhesive itself does not change with time. Also, that the desorbed dielectric contributions are solely due to air-and relaxations in the adhesive. It is possible that these assumptions slightly overestimate the amount of air present in a desorbed sample. However, using the 10 kHz data, the estimate for the non-frozen joints is 18.5%, whereas for the frozen joints it is 23.5%, consistent with the theory that exposure to cryogenic temperatures has created more delamination and degradation in the joint.

3.2.4. Mechanical Analysis

After complete desorption, the adhesive joints were mechanically tested and it was found that the maximum stress had recovered to an average value of 19.9 MPa (−30.5% of unaged joints), with the ultimate strain recovered to 0.051 (−13.8%) (Fig. 7). This indicates that after removal of the water the adhesive has regained a significant proportion of its unaged strength. Some joints, however, did not show this level of strength recovery with stress (−84.9%) and strain values (−70.3%). This shows that the interfacial layer is still susceptible to failure. However, the recovery in strength of the majority of joints does seem to support the argument that, in general, the extreme absorption/desorption cycle has failed to affect significantly the strength and integrity of the samples. Desorption will allow the thick aluminium hydroxide layer to re-establish contact with the adhesive and this increases the apparent strength of the joint. van den Brand *et al.* [20] have reported that this process occurs during the ageing of epoxy coated aluminium. The results reported here also suggest that during the latter stages of absorption-the strength of the joints is not simply dependent upon the interfacial layer. Instead, it is likely to be influenced by both the integrity of the interfacial layer *and* the amount of plasticisation in the adhesive.

3.2.5. Correlations Between Data

Since there are no changes to the weight of the adherend during desorption, it is possible to correlate permittivity changes with

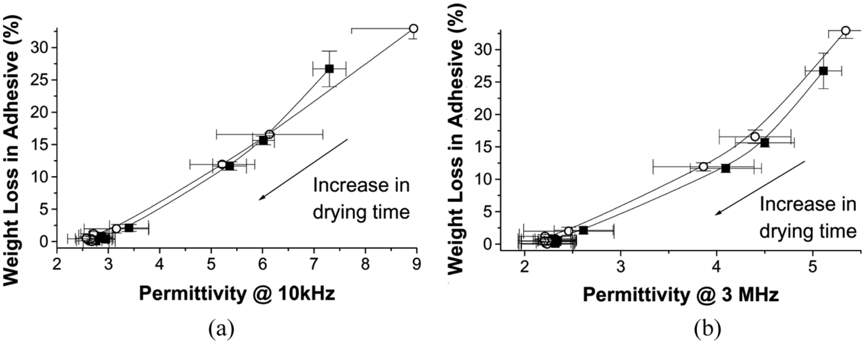


FIGURE 14 Correlations between the weight loss in the adhesive layer and permittivity at (a) 10 kHz and (b) 3 MHz during desorption of non-frozen (-■-) and frozen joints (-○-) at 75°C.

changes to the moisture content during water egress. Figure 14 indicates that a simple relationship exists between the permittivity and the amount of moisture present in the adhesive bondline. There are no significant differences between the correlation curves of non-frozen and frozen joints.

4. SUMMARY

This study indicates that the ageing of aluminium joints at elevated temperatures produces small but consistent differences between samples which have been periodically frozen and those which have not. The differences in the data are believed to be a result of the freezing action of water encouraging greater water uptake in the samples, as well as causing slightly more hydroxide conversion. The cyclic stressing of the bondline due to the thermal cycling may cause additional oxygen ingress, which will encourage the hydroxide formation. However, it is not believed to have degraded the adhesive layer to any significant level. Indeed, after desorption, both the adhesive layer and the joints as a whole were shown to regain their integrity and a significant proportion of their strength. The only significant irreversible damage inflicted upon the joints by this study has been severe corrosion of the outside surfaces of the adherend, as well as the formation of hydroxide in its interfacial layer. It is believed that the major changes to the durability of the joints are mainly due to the effects of water absorption, and not exposure to cryogenic temperatures.

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