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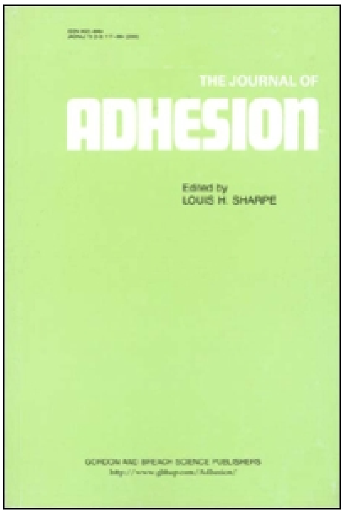

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Environmental Ageing of Adhesively-Bonded Joints. I. Dielectric Studies

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High and low frequency dielectric measurements are reported on adhesively bonded aluminum structures aged by exposure to moisture over an extended period of time. The changes observed are interpreted in terms of initially water diffusing into the adhesive layer and there is little evidence of changes occurring to the surface oxide layer. Differences in the form and rate of change of the dielectric signature reflect the effects of the pretreatment and matrix resin on the water diffusion process. A good correlation is observed between the time domain data and the increased dielectric permittivity resulting from ingress of moisture into the adhesive bond. The paper illustrates the use of high frequency dielectric measurements in non-destructively probing adhesive bonds and indicates the potential for *in-situ* applications.

Keywords: Dielectric studies; epoxy resin; phenolic adhesive; environmental ageing; water ingress; aluminium oxide

INTRODUCTION

An increasing use of adhesively bonded structures in the aerospace industry has highlighted the necessity to develop a more detailed understanding of the mechanisms associated with ageing and also

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non-destructive examination methods for assessment of durability [1–3]. A wide range of techniques exist able to locate defects within a joint structure [4–6]. They include transmission and pulse-echo ultrasonic [7], resonance methods [8–11], X-ray radiography [12], thermography [13, 14] and holography [15–17]. Porosity, cracks or voids in the adhesive layer or at an interface are usually filled with air and these voids [18] are detectable by a number of methods. During the service life of a joint such voids may fill with water making them more difficult to detect since water has a higher acoustic impedance than air. "Zero-volume" voids or debonds may occur when the adhesive or substrate are in contact, but no intrinsic adhesive strength will exist in these areas. Such defects are difficult to detect by void detection methods. In previous publications [18–19] the use of dielectric methods for identification of disbonds and voids have been discussed and this paper focusses on a study in which the methods are applied to characterisation of the changes occurring during ageing.

One of the most hostile environments for the ageing of joints is water. The polar epoxy resins typically used as adhesives are able to adsorb significant amounts of moisture, resulting in loss of mechanical strength [20–22]. Investigations of aluminum or titanium adherends in a range of environmental conditions indicate that water diffusion induces a number of processes: swelling and plasticisation of the resin and permeation of water along interfaces resulting in changes of the metal oxide surface layer. Water can induce micro-crazing – environmental stress cracking within the adhesive which will also lead a deterioration of the joint strength. Build-up of moisture within the joint can promote corrosion and associated deterioration of the joint structure [22].

This paper reports a systematic variation of oxide, pre-treatment and adhesive and investigation of the durability of a set of joint structures over a period of 600 days.

EXPERIMENTAL

Preparation of the Adhesive Joints

The surface preparation of the substrate and chemistry of the adhesive both play important roles in determining the durability of a joint. The

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joints used in this study were prepared using two adhesive systems, phenolic and epoxy, and different surface treatments, Table I. The film adhesive thickness used was controlled to be approximately 250 ± 50 μm, which is optimum for development of maximum bond strength with these materials. Joints were prepared by British Aerospace at their Chester and Filton factories. The joints were prepared from BS L157 Aluminum alloy, plate thickness 4 mm. Each set was prepared using nine pairs of plates, 250 mm. (L) × 250 mm. (W) × ~ 8 mm. (B), which were later machined and cut into eight pieces 240 mm. (L) × 25 mm. (W) × ~ 8 mm. (B), providing 72 test pieces. Six pieces from each set were used for environmental conditioning and two were used as dry controls. In the present study the adherends have been subjected to one or more of the following pretreatments:

i) Vaccum-blasting with Dry Alumina Grit was carried out to remove the natural surface oxide layer. A stream of 10 micron dry alumina was directed on to the substrate through a nozzle using dry air at a controlled pressure of 100 psi (0.69 MPa), allowing a controlled surface oxide layer to be developed in the subsequent processing.

ii) Vapor Degreasing was carried out by suspending the component in hot chlorinated solvent vapor which then condenses on the surface and dissolves and/or rinses away dirt and grease.

iii) Chromic/Sulfuric Etching. During this operation a layer of oxide was developed on the plates. The plates were immersed in an aqueous solution containing sulfuric acid, 150 ml/l, and chromic acid, 50 ml/l, for approximately 2 minutes. The temperature of the water bath was maintained at 60°C–65°C.

TABLE I Structure of joints–adhesive and surface preparation

SET	*Thickness-μm*	*Adhesive Film*	*Surface Preparation*
1	250 ± 50	Phenolic	Etch
2	250 ± 50	Phenolic	Etch + Anodise
3	250 ± 50	Epoxy	Etch
4	250 ± 50	Epoxy	Etch + Anodise
5	250 ± 50	Epoxy	Etch + Primer + Anodise

Phenolic adhesive–Ciba Geigy Redux 775.
Epoxy adhesive–3M AF126.
Primer–3M EC3960.

iv) Chromic Acid Anodising was performed using a solution of 30 g/l in water and a uniformly rising voltage from 0 to 40 Volts over a 10 minute period, then maintaining the voltage constant for 20 minutes prior to finally increasing it to 50 Volts for a period of 5 minutes. On completion of this process the plates were rinsed in cold water. The aluminium at this stage will have a mauve/green bloom typical of a thick surface oxide layer.

It is critical that the freshly-prepared oxide layer is protected by application of a primer coat, which in the case of these joints was a low molecular weight epoxy resin. It is essential that the priming and bonding processes are carried out to a well-defined schedule and both processes are normally completed within twenty-four hours. Two sets of joints were prepared using, respectively, phenolic and epoxy resins:

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i) Phenolic Adhesive Bonded Joints: The primer was brush applied and allowed to dry for 2 hours at room temperature. Adhesive was applied within 24 hours of the primer drying and was then cured at 150°C for a period of 30 minutes. Heating and cooling rates were maintained at the maximum rate of 50°C/minute and the cooling was controlled until a temperature of 50°C was attained. During the entire curing process pressure at the bondline was maintained at 120 psi (0.82 MPa).

ii) Epoxy Adhesive: The primer was spray applied and allowed to dry for 1 hour at room temperature and then hot-air cured at 120°C for 60 minutes. Adhesive was applied within 24 hours of the primer drying and was cured at 125°C for a period of 60 minutes, the cure cycle and pressure conditions being similar to those used for phenolics described above.

DIELECTRIC MEASUREMENTS

Two different techniques were used [18, 19]:

i) Low frequency measurements (10^{-2} Hz–10^{5} Hz). A computer-controlled frequency response analyzer (Schlumberger 1250) was used to make direct measurements of the joints which formed part of a bridge circuit and allowed data to be obtained between 10^{-2} Hz and 65 kHz. Contact can be made directly to the aluminium joint structure. The surface of the joint was lightly abraded so as to remove surface oxide and ensure that a good electrical contact had been established to the aluminium. The technique and method of analysis have been described in detail elsewhere [18].

ii) High frequency measurements (3×10^5 Hz–10^{10} Hz). A computer-controlled network analyzer (Hewlett Packard 8753 A) was used to make transmission line measurements over a frequency range of 300 kHz to 3 GHz. The HP 8753 A network analyzer generates a sine wave voltage of a fixed frequency which is applied to one end of the joint. The reflected signal is measured by the analyzer which then computes the amplitude and phase relationship for the transmitted and reflected waves. The reflection coefficient, ρ, from which the permittivity is calculated is recorded. The high frequency network analyzer can also be used to determine the reflection coefficients in the time domain format. Analysis of the transit time for the pulse to make one round trip along the joint length is related to the dielectric properties of the joint structure. The contact to the aluminium was made through two brass point-contacts and, as with the low frequency measurements, the metal was abraded to remove the surface oxide prior to making the measurements. Poor contacts are immediately evident in terms of erroneous data.

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AGEING MEASUREMENTS

A temperature of 40°C was selected for the ageing study by British Aerospace on the basis of their previous experience [24]; higher temperatures of around 60°C to 80°C are frequently employed by other workers. Each test piece was initially examined dielectrically to establish an "as-received" status, and forms a data reference for this study. Dry control pieces were stored in boxes at room temperature and used as references against which to estimate the observed changes in the dielectric behavior. Test pieces were placed in a glass bath filled with deionized water whose temperature was controlled at 37°C ± 2°C. One set of test pieces was removed after a period of 21 days, and thereafter at 70-day intervals, with the exception of the last withdrawal for each set which was exposed for an extra 40 days in water. A total of nine withdrawals over a period of 600 days were carried out. During the latter part of the investigation a couple of samples from each set were subjected to accelerated ageing at 70°C, as it had become clear that the rate of loss of mechanical properties at the lower temperature was occuring more slowly than had been expected, reflecting the high quality of the joints produced.

RESULTS AND ANALYSIS

Initial Examination of Test Pieces

The test pieces were first milled on their edges to obtain straight faces and inspected using a continuity meter to establish whether any electrical short circuits existed. Short circuits can arise due to small pieces of metal bridging the gap between adhesive/adherend. This was easily dislodged using the tip of a scalpel blade. Six samples were typically measured for each of the conditions examined. Inspection of the adhesive layer showed an uneven spread of the adhesive in a small number of cases and these samples were eliminated from the study, in general, the uniformity of the epoxy was not as good as for the phenolic materials. A typical dielectric response for a good adhesive bonded structure may be split into two regions:

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I) Low Frequency

At low frequencies the structure behaves as a parallel plate condenser and low frequency dielectric measurements were performed on a 15 mm. square piece cut from the end of the strip on completion of the high frequency measurements. Moisture ingress into the polymer has been studied using dielectric methods [25–27], but no literature exists on the use of this technique for investigating moisture ingress into bonded structures. In these samples permeation of water occurs through the four edges of the joint structure. The low frequency region of the dielectric spectrum contains two features; a loss located at approximately 1 KHz associated with rotational relaxation of the pendant hydroxyl dipole and a feature below 1 Hz which is a combination of the high frequency tail of the glass–rubber transition [T_g] process and losses associated with the heterogeneous nature of the matrix–Maxwell Wagner Sillers processes [25]. Water molecules which are associated with the pendant hydroxyl groups relax at a frequency of 10^4 Hz indicated by an increase in amplitude of the process. The fact that the frequency of the relaxation is not shifted due to the association of water implies that the activation energy for the relaxation process is not changed by the binding of the water molecule to the hydroxyl group. Shifts in the shape, amplitude and location of the low frequency process are indicative of changes in the value of T_g as a consequence of plasticization by water.

i) Phenolic Systems; Etched Only, Etched + Anodised. As seen in Figure 1, real and imaginary permittivity values remain almost constant over a narrow range at a frequency around 100 Hz; however, dispersions are observed at the extremes of the frequency range. A large incremental change is observed after a period of 490 days. The imaginary permittivity indicates a weak relaxation process, within the frequency range 10^3 Hz to 10^5 Hz, which grows during the first 350 days and then remains almost constant for the remaining ageing period. This process is assigned to the attachment of water to the polar ether and OH groups within the adhesive [26]. In the case of the anodized and etched samples the increase in real and imaginary permittivity is gradual over the entire frequency range, with substantial increases at lower frequencies. A correlation between the presence of an oxide layer (anodizing) and an increased permittivity is observed in the case of dry samples. On the basis of a three-layer model of oxide, adhesive, oxide for the bond in which d_1 and d_2 are, respectively, the thickness of the oxide and adhesive having real and imaginary permittivities $\varepsilon_1, \varepsilon_2$ and conductivities σ_1, σ_2. The effective real and imaginary permittivity is given by [25]:

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} \tag{1}$$

where

$$\varepsilon_\infty = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 d_1 + \varepsilon_2 \cdot 2d_2}, \quad \varepsilon_S \cong \varepsilon_1\left(\frac{2d_1 + d_2}{2d_1}\right)$$

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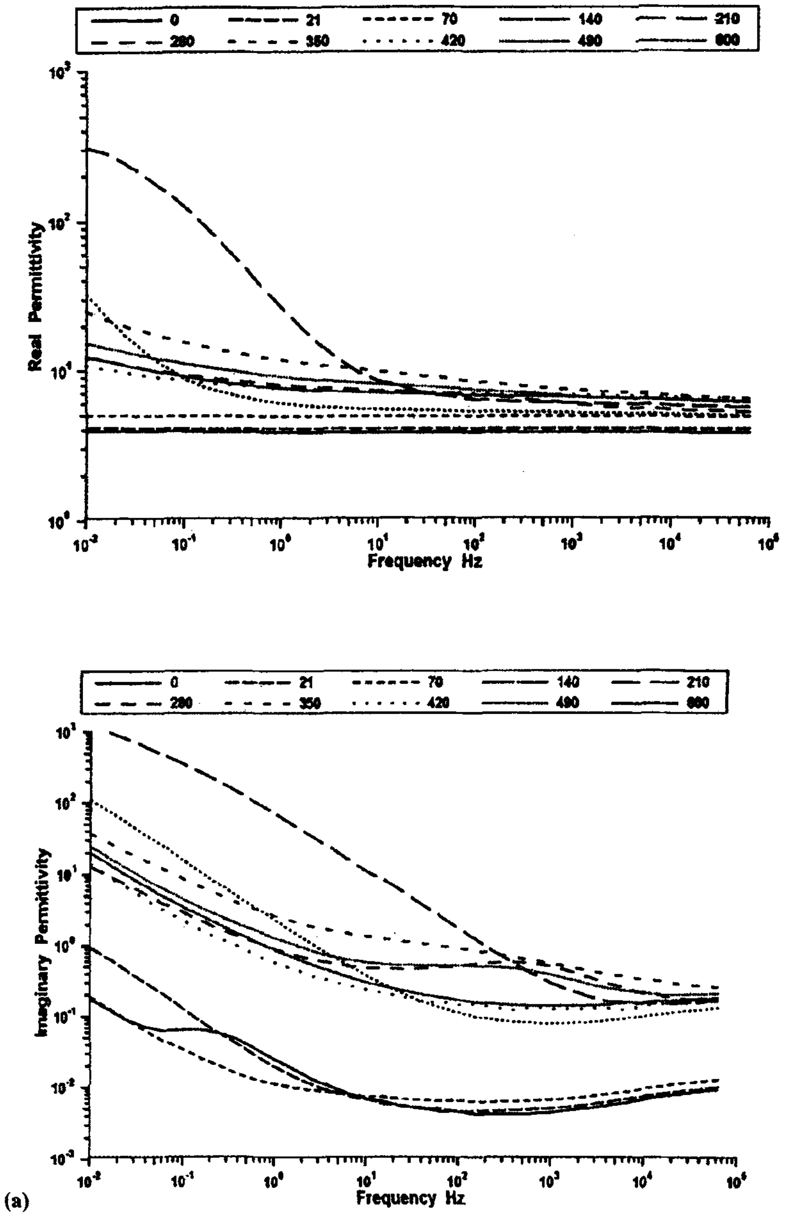

FIGURE 1 Low frequency dielectric response of a phenolic adhesive joint exposed to moisture at 40°C for the exposure time (in days) indicated; etched a) real and imaginary permittivity; etched and anodised; b) real and imaginary permittivity.

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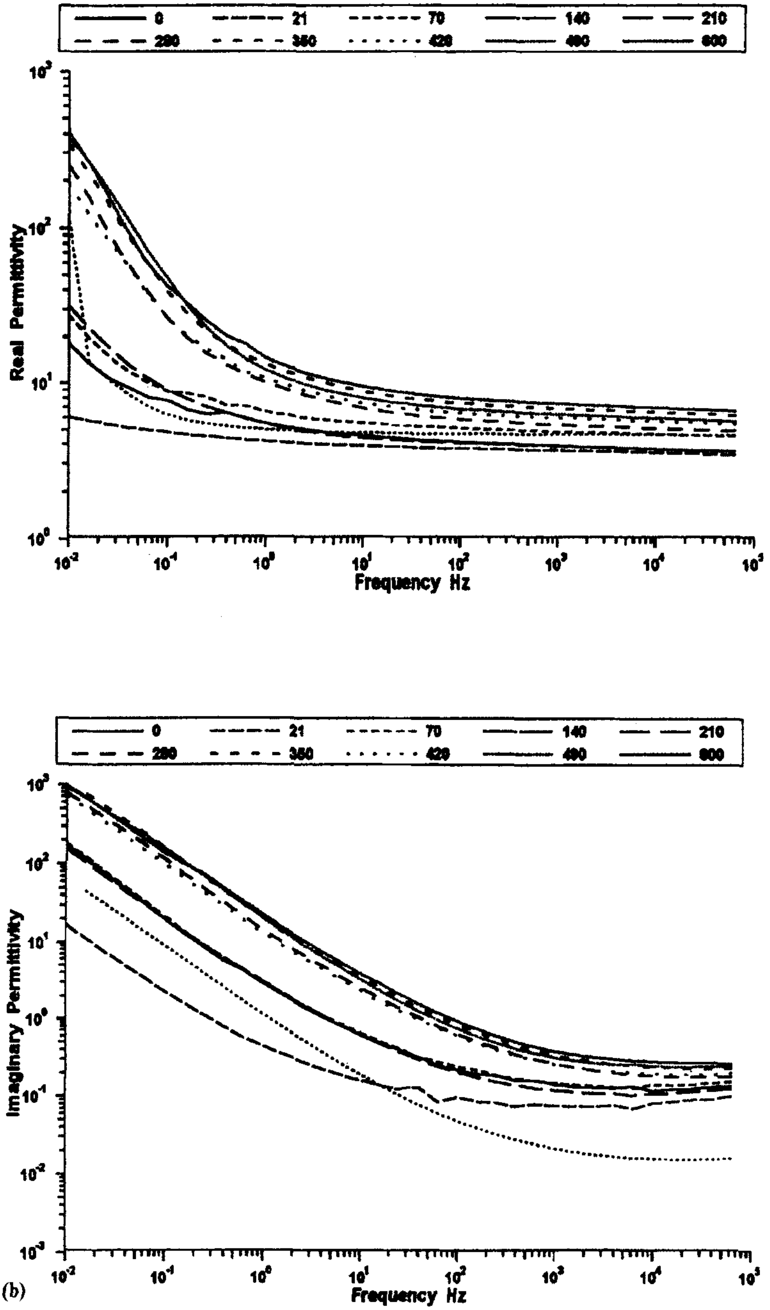

FIGURE 1 (Continued).

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For the case of $d_1 \ll d_2$ and $\sigma_1 \ll \sigma_2$

$$\varepsilon_S \cong \varepsilon_1\left(\frac{d_2}{2d_1}\right) \tag{2}$$

indicating that the surface oxide makes a significant contribution to the observed real and imaginary permittivity values. For an oxide of the order of 100 nm and 250 microns of adhesive, ε_S is of the order of 25×10^3. This situation will exist only if the oxide is more insulating than the adhesive which will not necessarily be the case once the joint becomes exposed to moisture.

The dielectric permittivity data plotted in the time domain indicate that in both cases moisture ingress has reached an equilibrium value around 350 days. The limiting values are presented in Table II.

ii) Epoxy Systems; Etched only, Etched + Anodised, Etched + Anodised + Primer. A definite correlation between surface preparation and permittivity is observed, see Figure 2. An increase in real and imaginary permittivity values is observed with ageing but it is less dramatic than in the case of the phenolic resin and the high frequency contribution is significantly less. No large dispersion in permittivity at the higher end of this spectrum is observed. All epoxy sets tended to share similar values of permittivity in the 10^4–10^5 Hz region, indicating that surface treatment does not significantly affect the dielectric properties in the case of an epoxy joint.

TABLE II Curve fitting parameters for water ingress evaluated at high frequency

Adhesive Film	*Surface Preparation*	*Time* *τ days*	*constant*
Frequency of	*observation–Hz*	*3×10^5*	*3×10^7*
Phenolic	Etch	416	526
Phenolic	Etch + Anodise	208	172
Epoxy	Etch	666	526
Epoxy	Etch + Anodise	545	515
Epoxy	Etch + Anodise + Primer	315	943

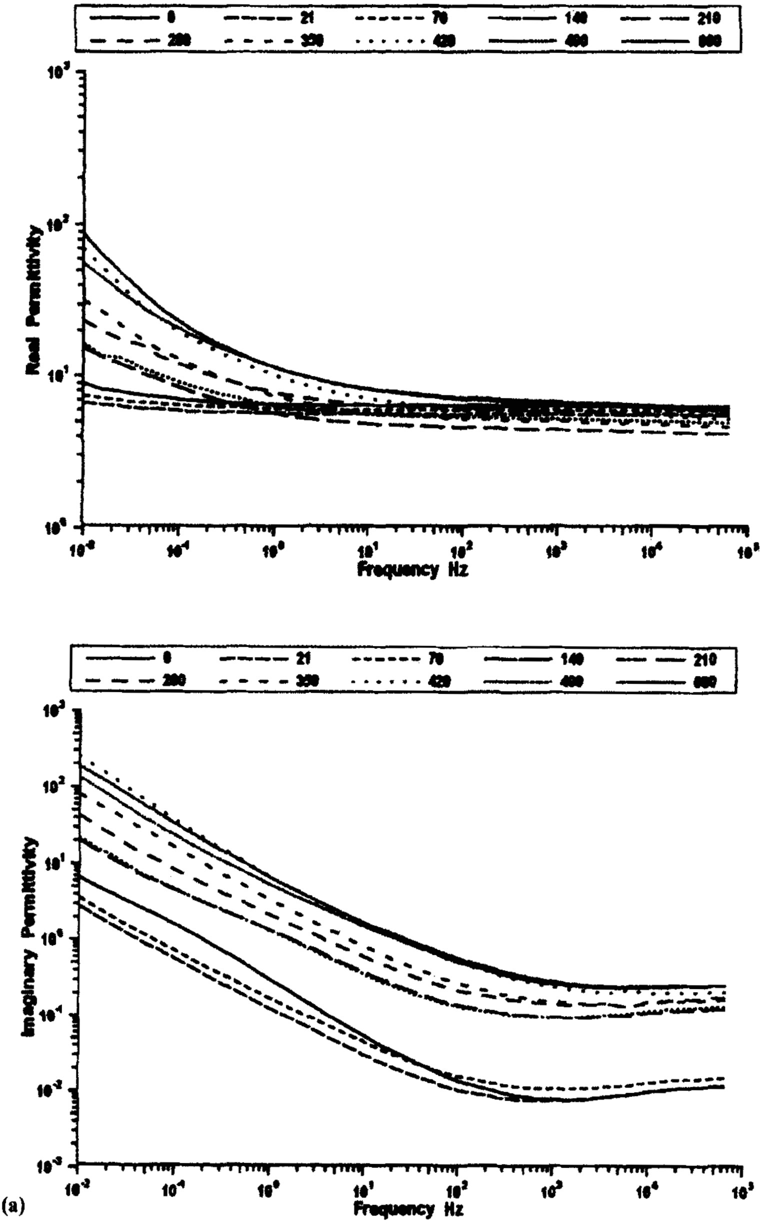

FIGURE 2 Low frequency dielectric response of epoxy adhesive joint exposed to moisture at 40°C for the exposure time (in days) indicated; etched a) real and imaginary permittivity; etched and anodised; b) real and imaginary permittivity; etched, anodised and primed; c) real and imaginary permittivity.

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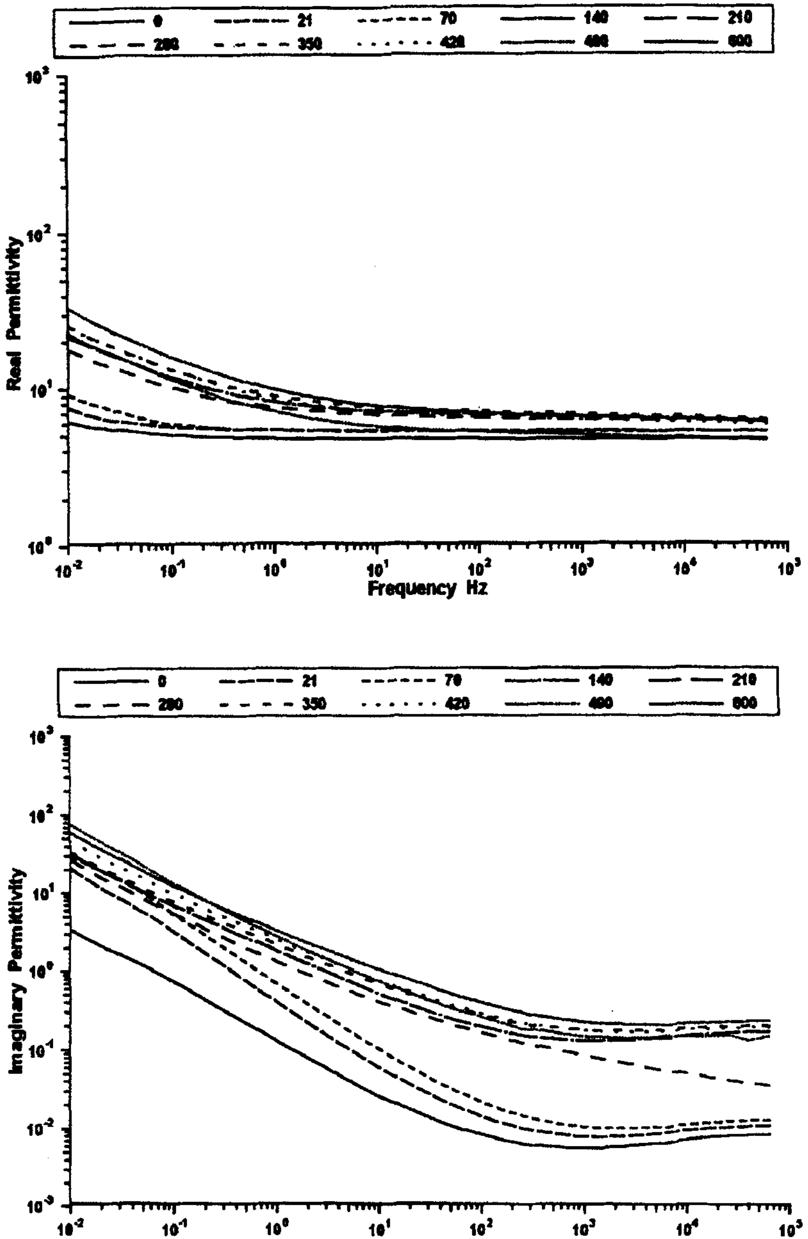

(b)

FIGURE 2 (Continued).

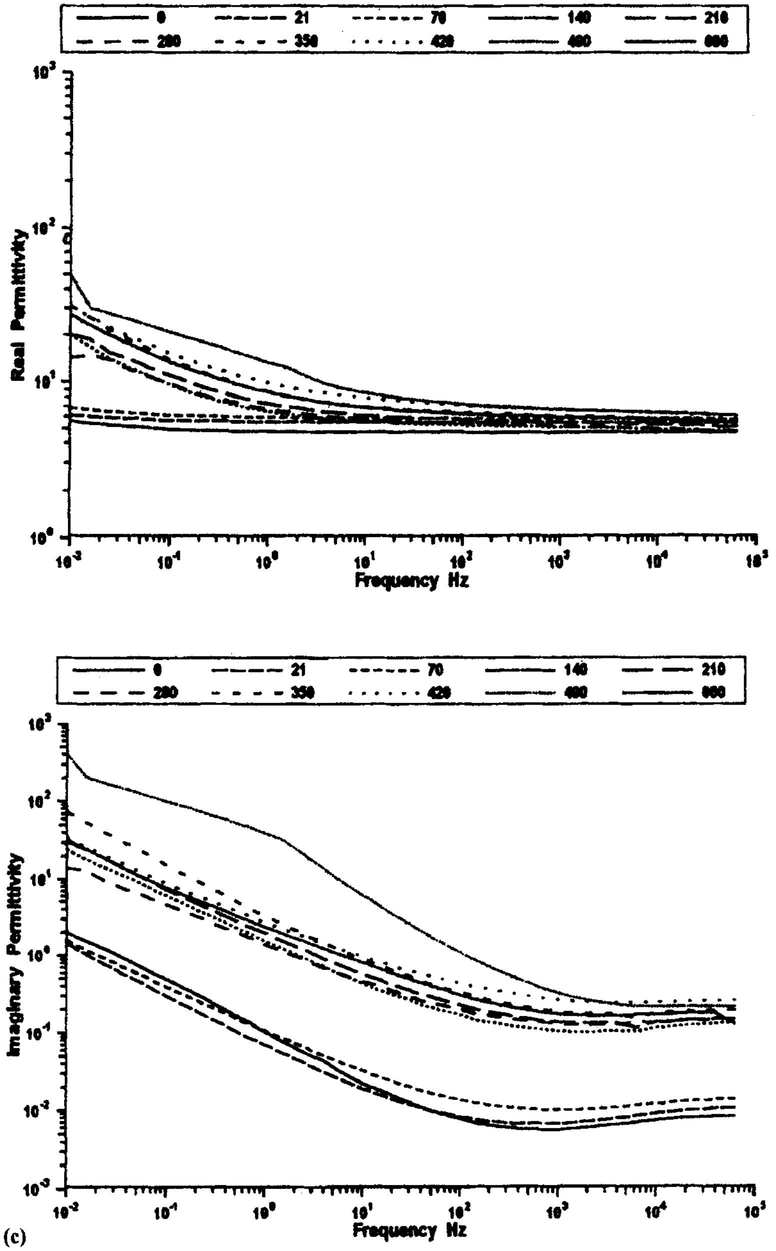

FIGURE 2 (Continued).

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Values obtained for the first two surface preparations, Figure 2, are opposite to those observed in phenolic resins; the presence of an oxide layer has little effect on the permittivity values. The imaginary permittivity data in the region above 10^2 Hz shows a definite relaxation process associated with the —OH group generated during cure of the epoxide [28]. All epoxy systems showed a characteristic change in the imaginary permittivity data after a period of 140 days; the values approach those obtained at 21 days and then increase again.

It can be argued that since the cure is carried out at 120°C the resin will have been quenched to room temperature and will contain stresses which will be frozen within the matrix. The ingress of water will then lead to the perturbation of the matrix which will subsequently lead to stress relaxation, densification and thereby counter the plasticisation process. Further, addition of water will continue to plasticise the matrix, shifting the peak to higher frequencies and result in an increased dielectric loss [28].

Analysis of the change with time of the real and imaginary permittivity measured at 100 Hz indicates that moisture ingress into joints with an etched-only surface is rapid and displays a steady moisture diffusion process which attains a maximum value around 350 days. The slight increase between values measured at 1 and 10^4 Hz reflects the extent to which water is bound to the pendant hydroxyl groups. The variation of the real and imaginary permittivity measured at about 100 Hz will reflect the total water absorption into the resin material which can be visualised as being bound to the hydroxyl groups and also clustered into small droplets in voids and regions of low density.

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II) High Frequency Dielectric Measurements

Frequency Domain

The high frequency data, Figures 3 and 4, are complicated by the effects of reflections arising in the bonded structure and modulating the region above 10^8 Hz. The sharp features observed at high frequency are purely a consequence of standing waves in the joint structure and can be used to provide structural information on the joints. A future paper will describe an analysis of these features using model joint

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structures and indicates how these data can be used for characterisation of the structure of the joints. No attempt has been made to match the real and imaginary permittivity values with those at low frequency, the apparently lower values reflecting the fact that there are significant errors in determining the thickness of the adhesive. The data presented in this paper are based on the measured thickness values. The thickness of the bonds were measured initially and also during the course of the study. Corrosion of the edges as a result of exposure to water lead to large uncertainties in the precise magnitude of the changes which occur in the thickness of the resin layer. The thickness determined during the early stages of the experiments were used in the calculation of the dielectric permittivity when corrosion made precise determination of the thickness impossible. The problem of modelling of the bond line and the associated correction routines will form the basis of a future paper. The values of the real and imaginary permittivity at low frequency do not involve the uncertainties associated with the higher frequency data and, therefore, can be used as an absolute measure of the water absorbed. In this paper we will focus on the data below 10^8 Hz which is influenced by changes in the dipole properties of the bonded structure.

i) Phenolic Systems. Similar variations in the permittivity are observed to those found at lower frequency, Figure 3. There is in certain cases evidence of a process occurring at lower frequency and ascribable to water bound into the matrix. Higher values of the permittivity are observed when anodisation has been carried out during surface preparation. The time evolution of the real and imaginary permittivity as a function of time does not show any significant change in the difference in the values at 10^5 and 10^8 Hz indicating that there is no significant conversion of oxide to hydroxide in these systems.

ii) Epoxy Systems. As in the case of the phenolic systems, an increase of permittivity values as a function of elapsed time is observed, Figure 4. The use of a primer reduces the diffusion of moisture. The variation of the permittivity at 3×10^5 Hz and 3×10^7 Hz frequencies with time were plotted and those plots indicate a steady and increasing diffusion of moisture into the resin over the entire duration of the experiment. In all cases, a steady state value has not been achieved after 600 days. The difference between the low [10^2 Hz] and high

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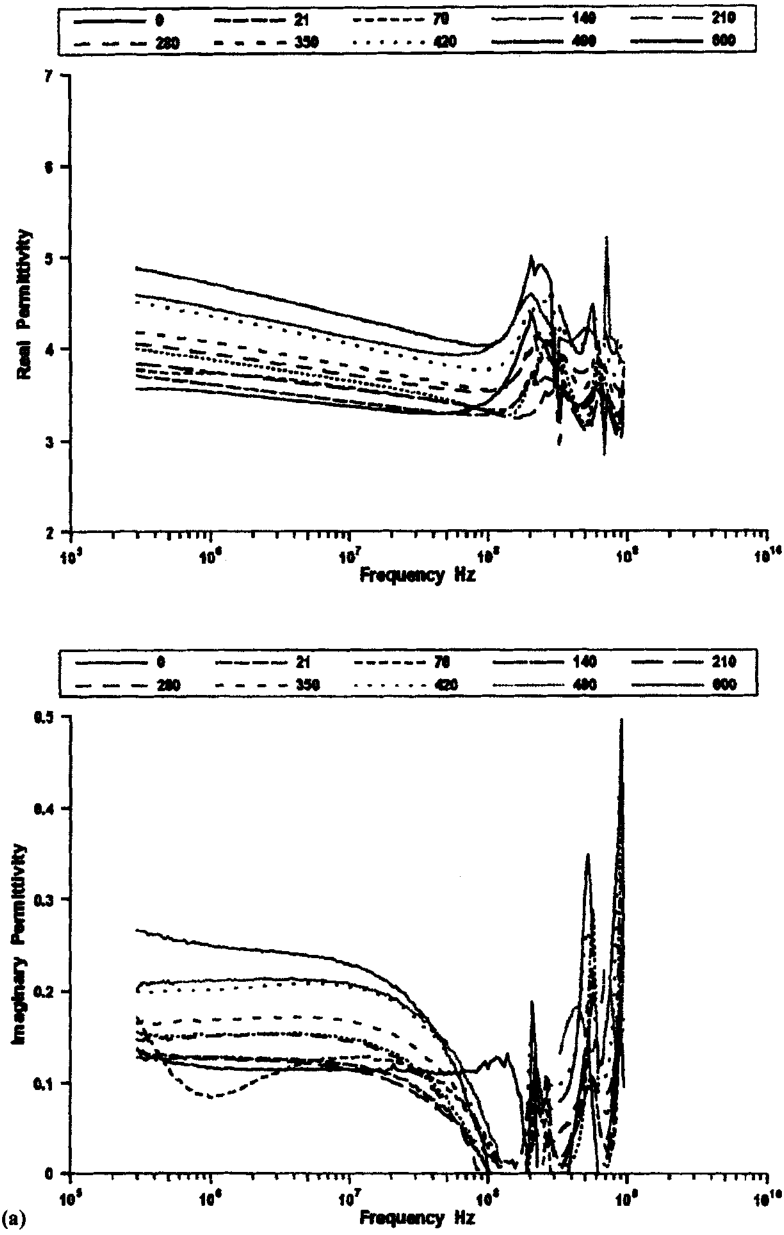

FIGURE 3 High frequency dielectric data for the exposure time (in days) indicated; phenolic–etched a) real and imaginary permittivity, phenolic–etched and anodised, b)real and imaginary permitivity.

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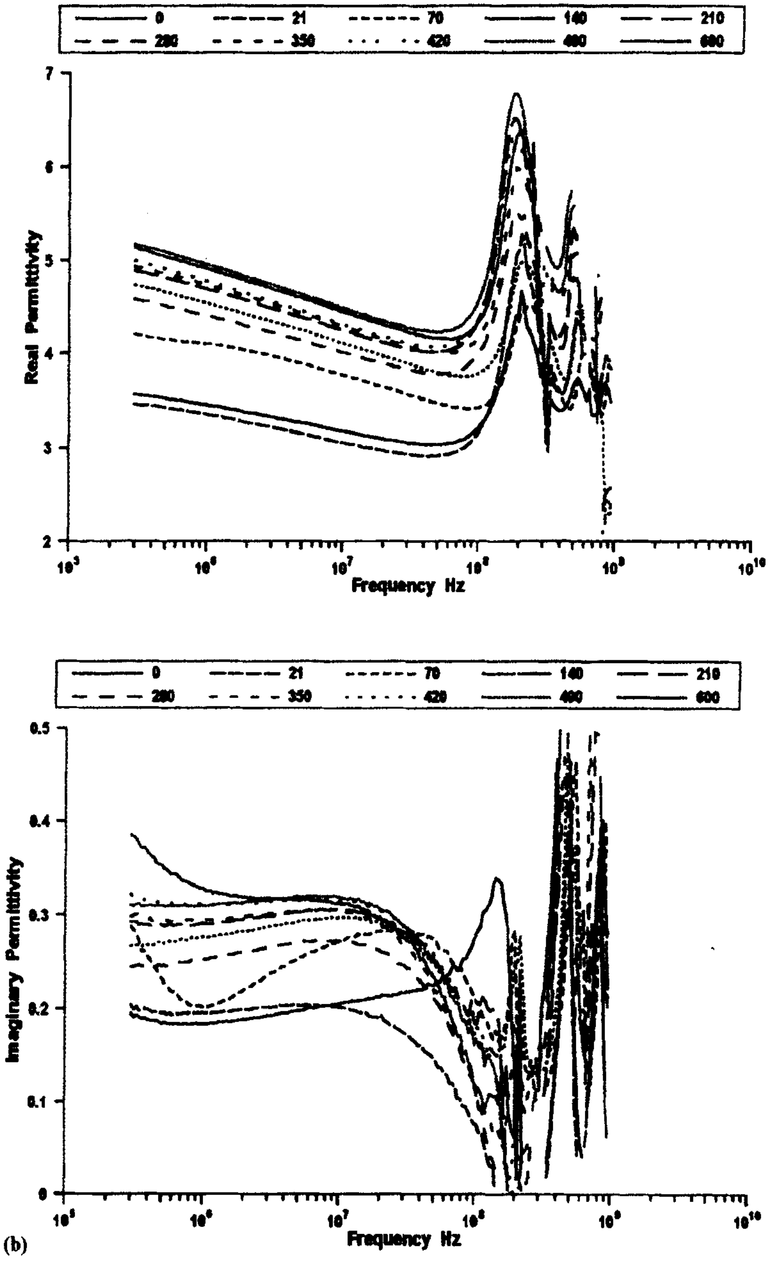

FIGURE 3 (Continued).

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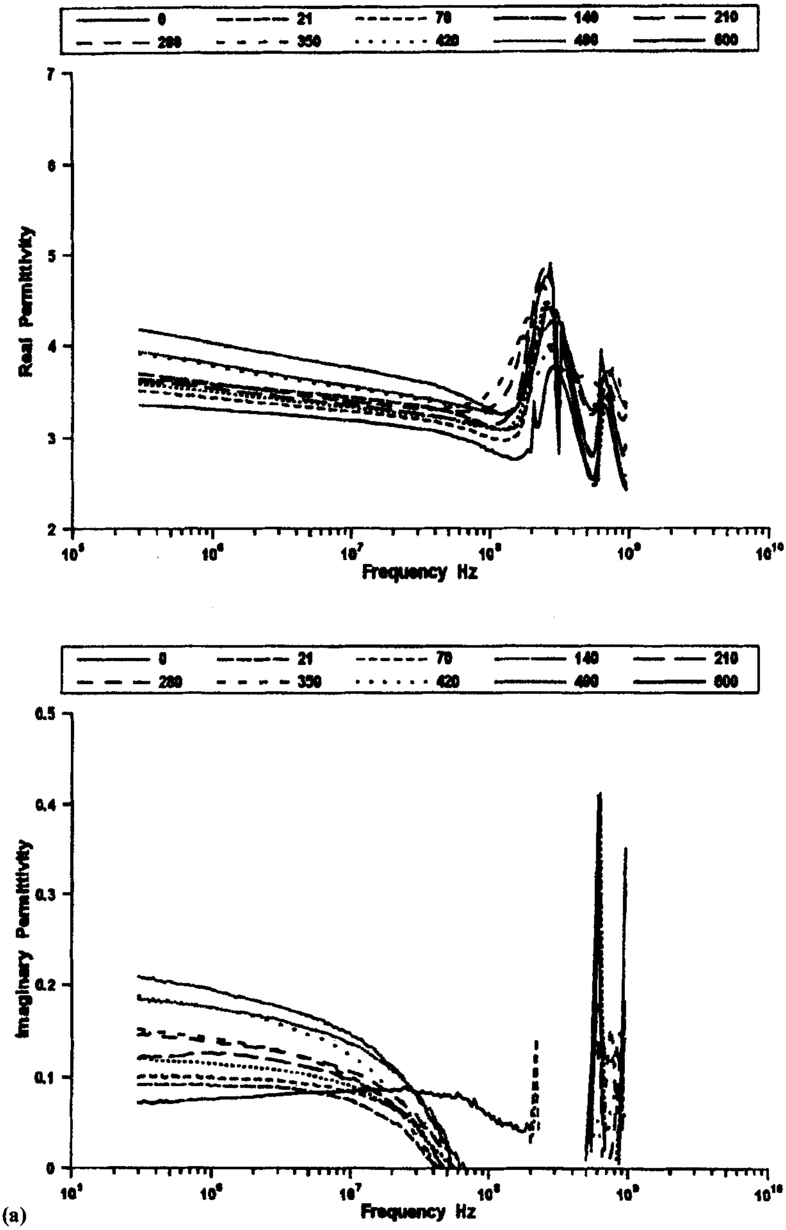

FIGURE 4 High frequency dielctric data for the exposure time (in days) indicated; epoxy–etched a) real and imaginary permittivity, epoxy–etched and anodised, b) real and imaginary permittivity, epoxy–etched, anodised and primed, c) real and imaginary permitivity.

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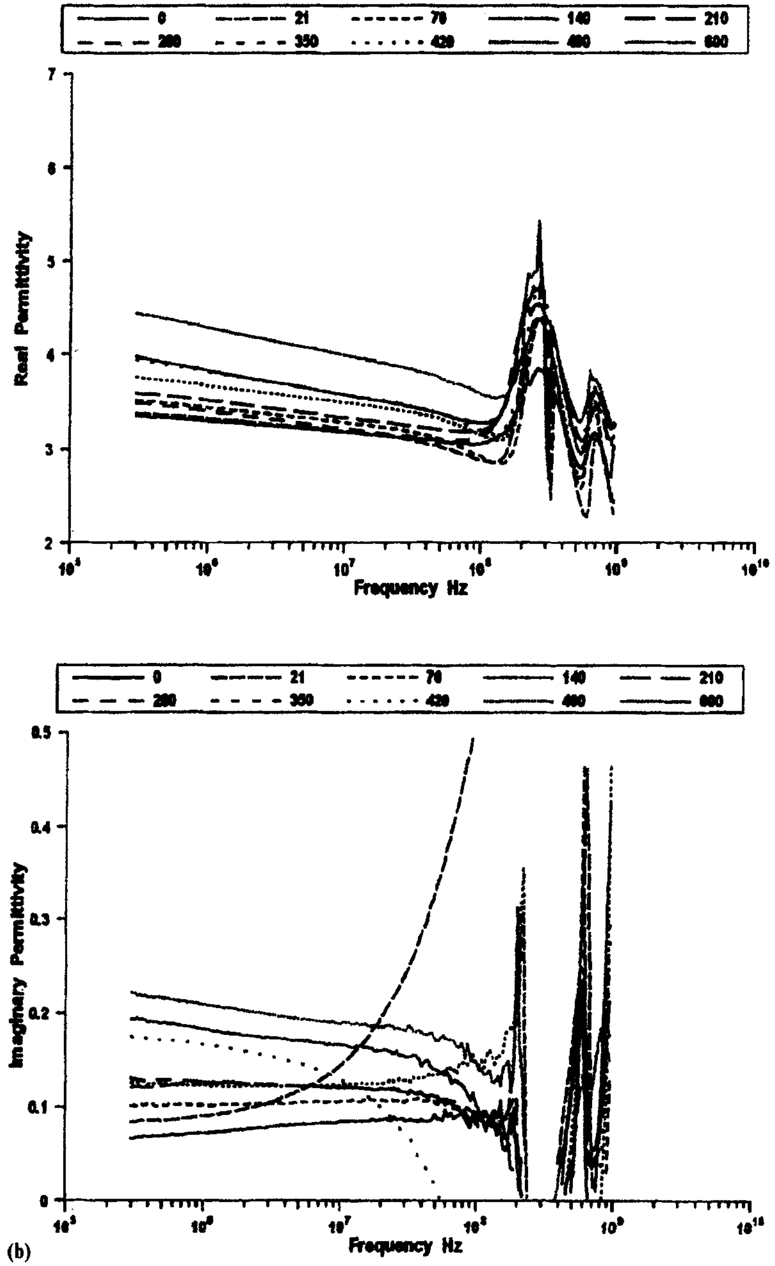

FIGURE 4 (Continued).

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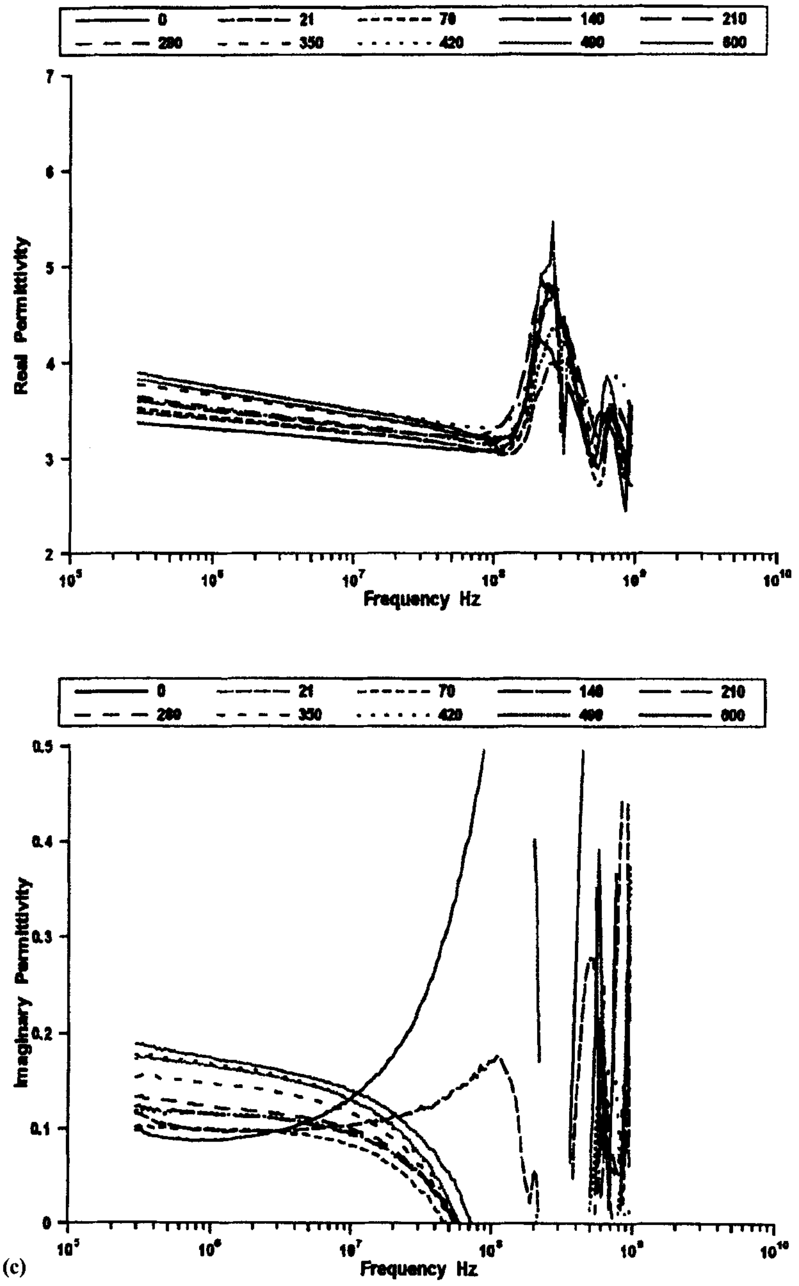

FIGURE 4 (Continued).

frequency [10^5–10^7 Hz] data reflects the way in which the water is dispersed in the resin bond. If there were significant conversion of the surface oxide layer into hydroxide an increasing difference would be observed between the values at 10^5 Hz and those at 10^8 Hz, the latter reflecting the free water content in the resin. Clustered water exhibits a dielectric relaxation which is identical with that of pure water and is termed "free water". It relaxes at a frequency of approximately 18 GHz, which is above the range available for use in the current work but may be assessed by the difference between the high and low frequency values.

TIME DOMAIN MEASUREMENTS

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The network analyzer can perform time domain measurements and can be used to identify the occurrence of voids and defects in the bond line and the resolution of features will be more effective the longer the joint, Figure 5. The transit times were measured by taking the start as the minimum of the largest negative pulse associated with reflection from the front interface and calculating the time to the peak of the first reflected pulse from the end of the bond. Both markers were positioned using the automatic peak location function on the network analyzer. Transit times were also calculated using reflections one, two and three. Data displayed is an average for all these readings. Use of the automatic peak locating function is acceptable provided that the effects of dispersion on the pulse width were minimal, Figure 5, and indicate an increase in peak separation consistent with an increase in permittivity as a function of ageing time. The time domain data have been used to calculate the mean real and imaginary permittivity for the joints using:

$$\sqrt{\varepsilon'} = \frac{C}{(2l/\Delta t)} \tag{3}$$

where C is the velocity of light, l the length of the joint and Δt is the round trip time for the pulse. A linear relationship is observed between the transit time and calculated permittivity for both resin

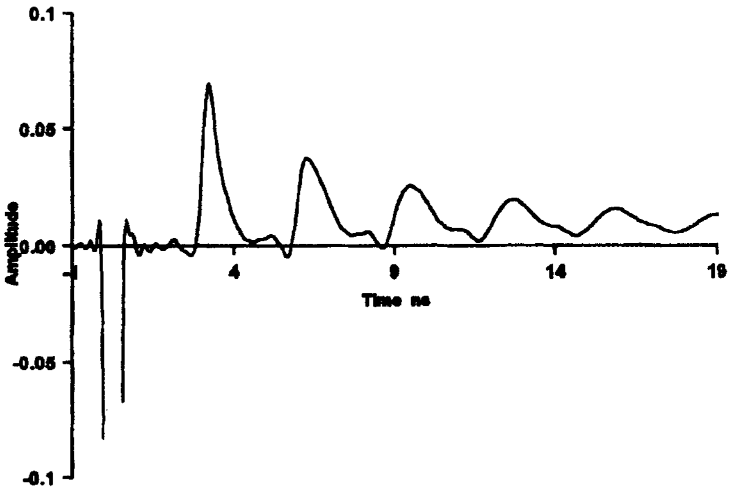

FIGURE 5 Time domain trace for a joint used in this study.

systems. The slope of the line does not vary significantly with surface preparation and reflects the dominance of the adhesive type in controlling diffusion.

HIGHER TEMPERATURE AGEING INVESTIGATIONS

The data presented for the lower temperature ageing indicates that exposure has had little effect on the joint. Previous investigations on aluminum oxide have indicated that hydration leads to the observation of a distinct feature at approximately 10^6 Hz which is absent from the data presented [30]. The joints were all mechanically intact and, hence, it appeared that the ageing process had not led to the catastrophic failures anticipated. Samples of each group of joints were subjected to exposure at 70°C toward the end of the ageing tests. Use of a higher ageing temperature should accelerate the ingress of moisture and, hence, enhance the deterioration of the joint strength. The time domain data indicate that increase of temperature will lead to a corresponding increase in water entering the adhesive. Dielectric data obtained for samples aged at 40°C and subsequently at 70°C are designated

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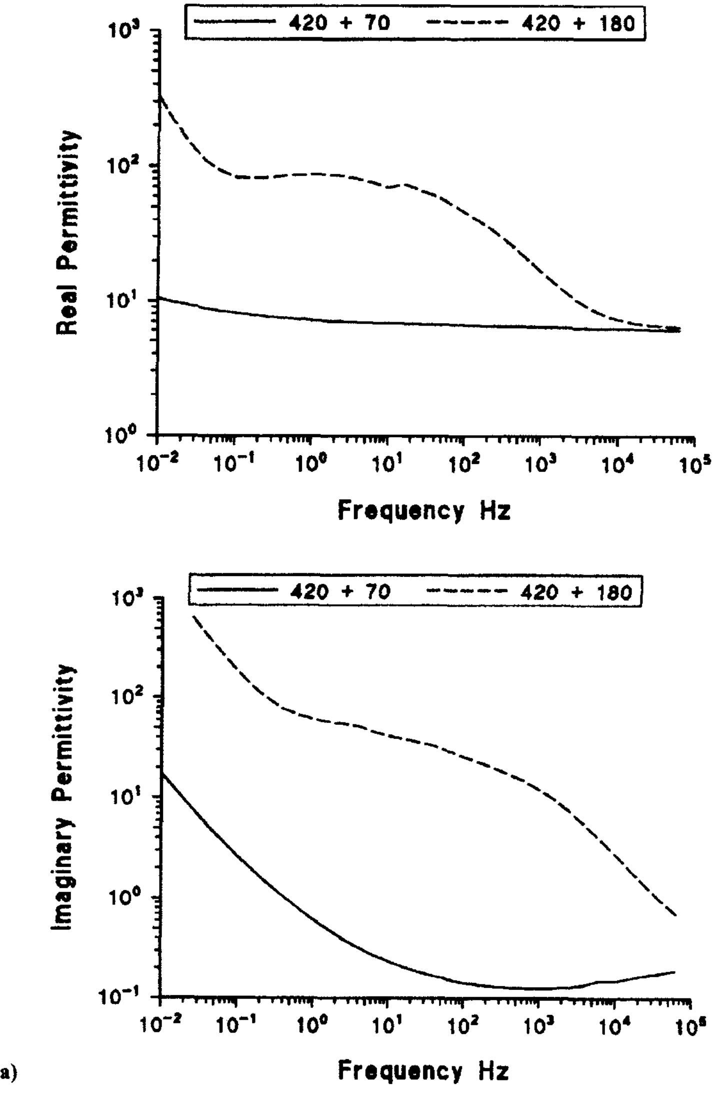

FIGURE 6 Low and high frequency data for samples aged at elevated temperatures; phenolic etched–a) real low frequency permittivity, b) real high frequency permittivity; phenolic etched and anodised–c) real low frequency permittivity, d) real high frequency permittivity.

420 + 70; meaning that they were aged for 420 days at 40°C and 70 days at 70°C, Figure 6. The phenolic samples exhibit larger increases in permittivity in the low frequency domain which is consistent with

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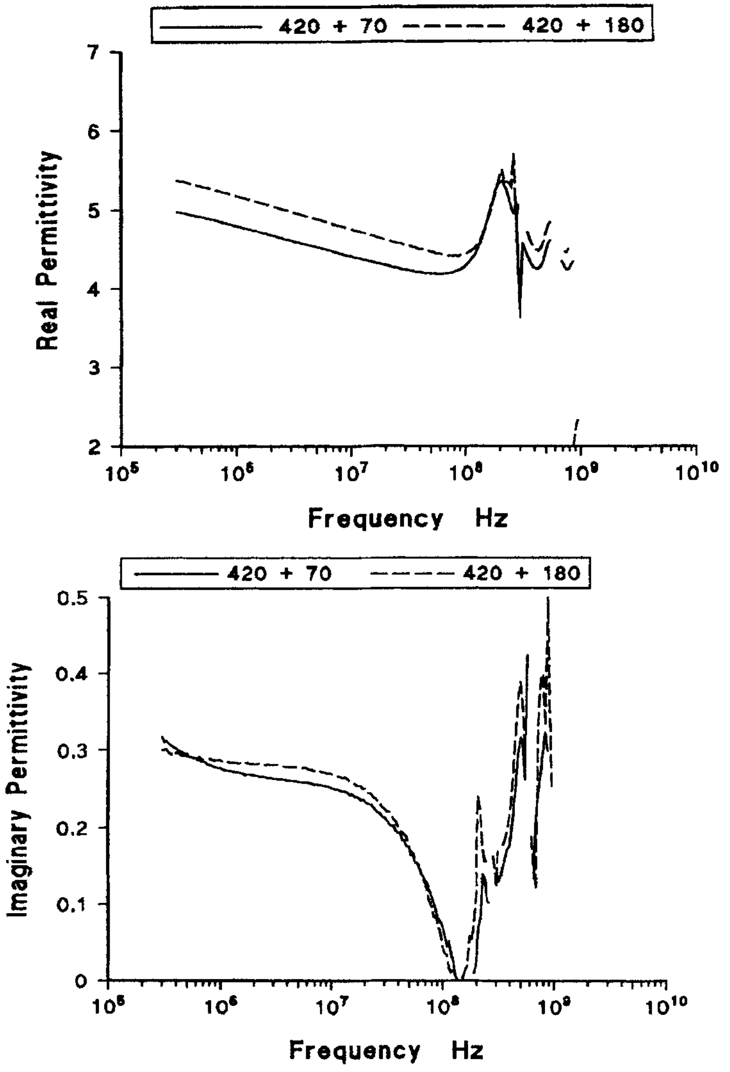

(b)

FIGURE 6 (Continued).

the phenolic's tendency to absorb more moisture, which appears to be present in a bound form in the matrix. The high frequency domain data are not particularly dependent on either the adhesive or surface preparation method, in all cases an overall increase in permittivity is observed.

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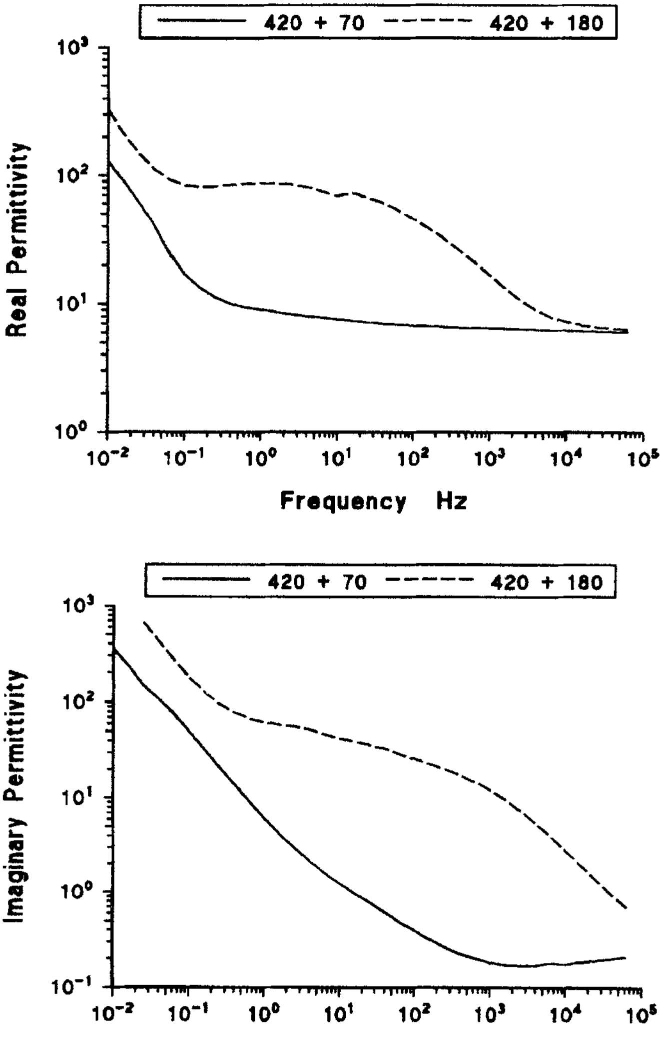
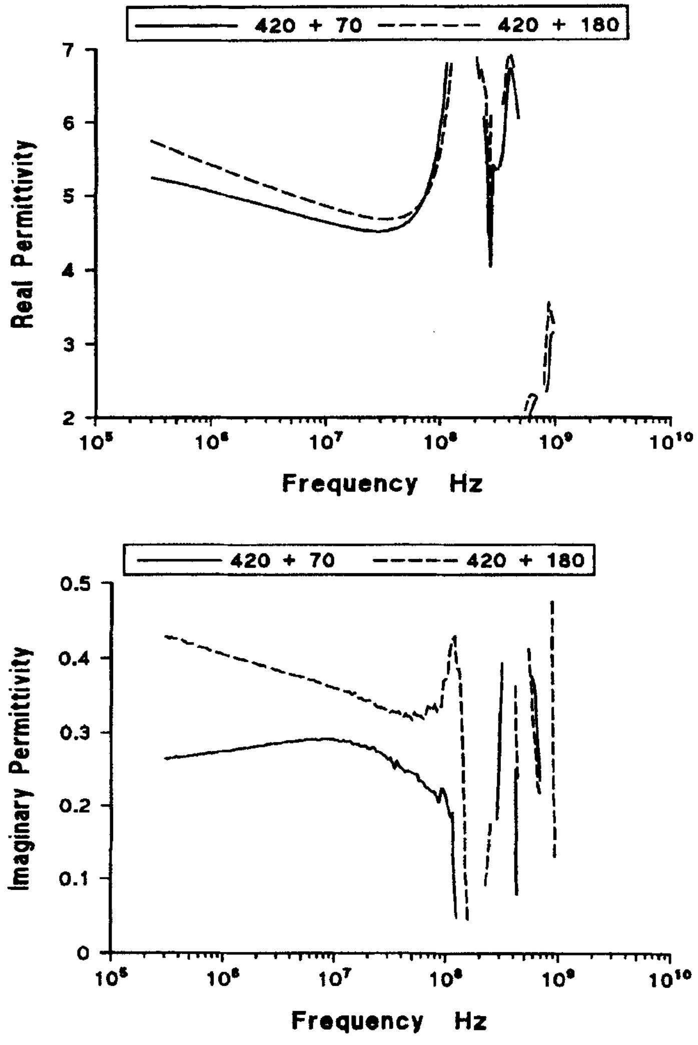


(c)

FIGURE 6 (Continued).

In contrast, the epoxy, Figure 7, does not not appear to show any significant change with increase in the ageing temperature. The etched samples do not show significant change, which is consistent with there being a very thin oxide layer present in these samples, Figures 7a and b. In the anodized and etched sample, the low frequency plots, Figure 7c



(d)

FIGURE 6 (Continued).

do not show significant differences although the high frequency ones do, Figure 7d. This would imply that there conversion of oxide to hydroxide is beginning to occur. The effects in the case of the printed sample are not as dramatic, Figures 7e and f, indicating that the primer is inhibiting the conversion of oxide to hydroxide.

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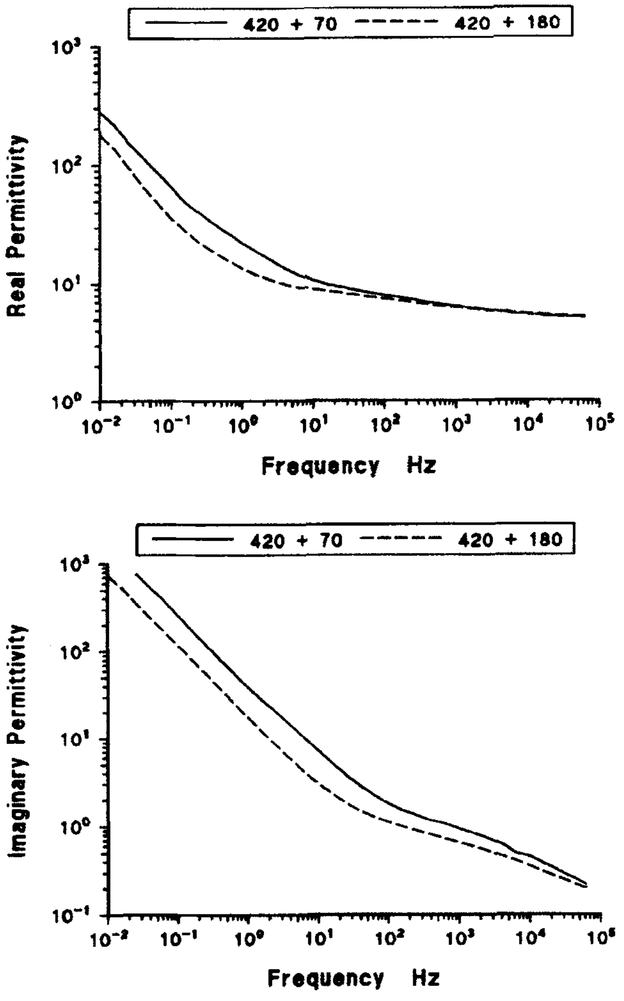

(a)

FIGURE 7 Low and high frequency data for samples aged at elevated temperatures; epoxy etched–a) real low frequency permittivity, b) real high frequency permittivity epoxy etched and anodised–c) real low frequency permittivity, d) real high frequency permittivity epoxy etched, anodised and primed, e) real low frequency permittivity, f) real high frequency permittivity.

ESTIMATION OF WATER CONTENT

The bonds have not reached saturation and Fickian diffusion is not observed, the bond geometry conforming to a very small area in contact with water compared with the joint area. Low frequency data

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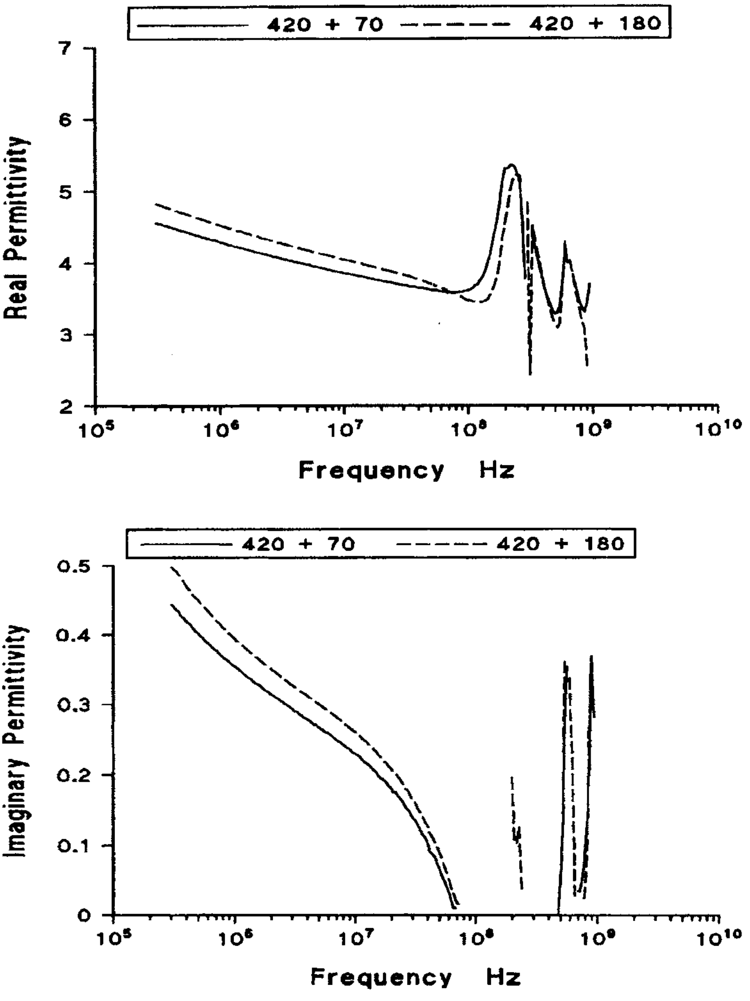

(b)

FIGURE 7 (Continued).

indicate a gradual increase in the permittivity values up to 70 days indicating gradual swelling of the joint. Estimation of bound and free water within the bonds has been attempted from analysis of the real and imaginary permittivity increments measured at two fixed frequencies: 10^4 Hz and 3×10^6 Hz. The high frequency value gives an estimation of free water and the low frequency data of the bound water, Table II. The average for the two frequencies was determined once in

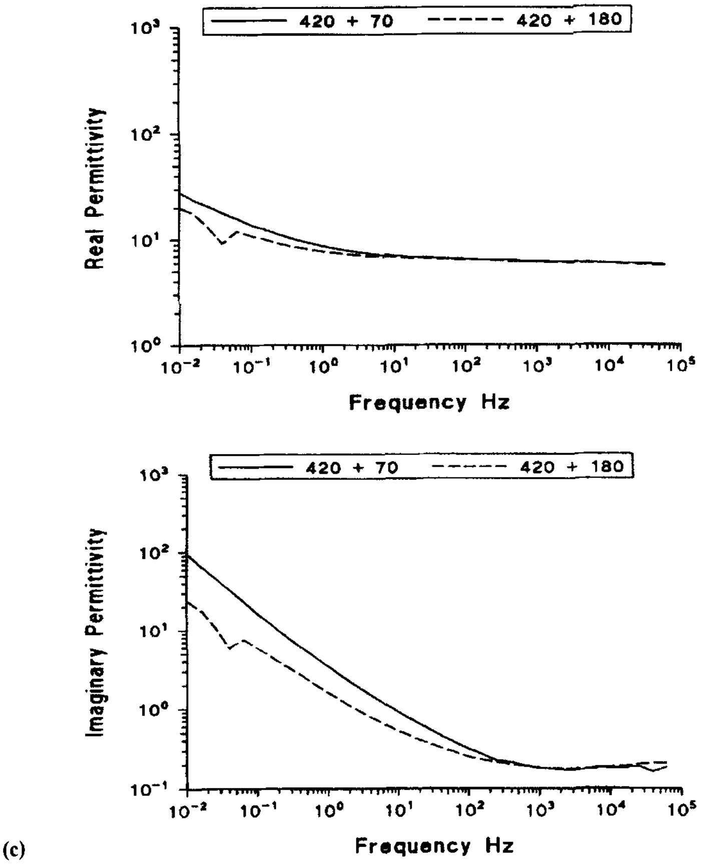

FIGURE 7 (Continued).

the dry state and then for the maximum ageing period. The difference in the two real and imaginary permittivity values will help derive an estimate for water concentration in the joints. Then if $\Delta\varepsilon'$ is divided by 80.36, the permittivity for free water at 25°C, an estimate of free water within the bond [25] can be obtained. The $\Delta\varepsilon'$ for bound water is taken as the difference between the low and high frequency values.

$$\Delta\varepsilon'_{\text{corrected}} = \Delta\varepsilon'_{\text{hf}} - \Delta\varepsilon'_{\text{lf}}$$

This corrected $\Delta\varepsilon'$ will be the contribution from bound water. The permittivity for bound water was obtained from the Kirkwood–Froh-

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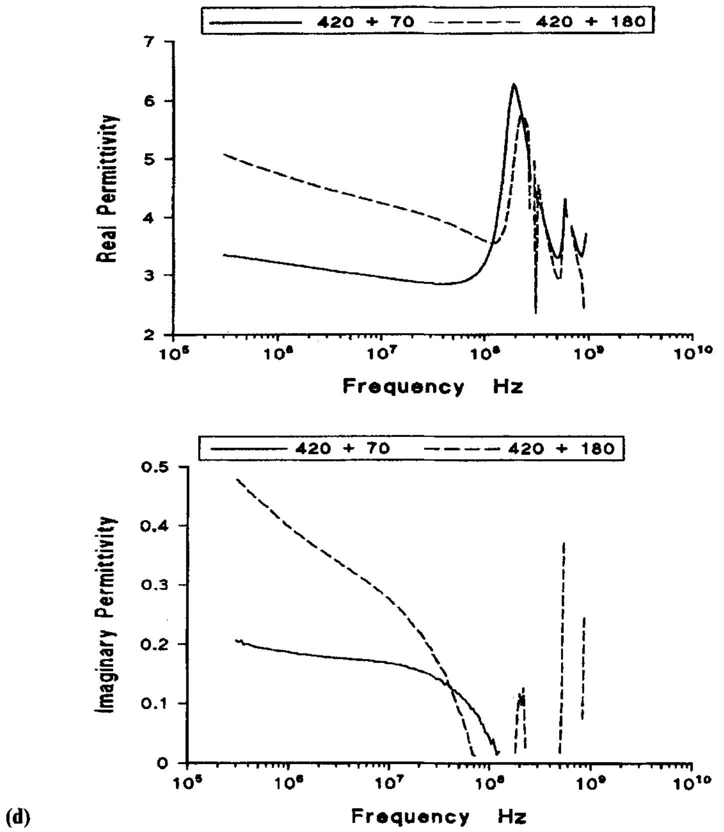

FIGURE 7 (Continued).

lich equation [25]

$$\frac{(\varepsilon_S - \varepsilon_\infty)(2\varepsilon_S + \varepsilon_\infty)}{\varepsilon_S(\varepsilon_\infty + 2)^2} = \frac{4\pi N_0}{9kTv}\cdot(g\mu_0^2) \tag{5.4}$$

where ε_S is the static permittivity, ε_∞ is the permittivity at ∞, g is the Kirkwood factor, μ^2 is the dipole moment, v is the molar volume, k is the Boltzman constant, T is the absolute temperature, and N_0 is Avagadro's number. The Kirkwood factor, g, takes into account short range dipole–dipole interactions, typical of hydrogen bonding between adjacent dipolar molecules. The predicted value of ε_S for bound

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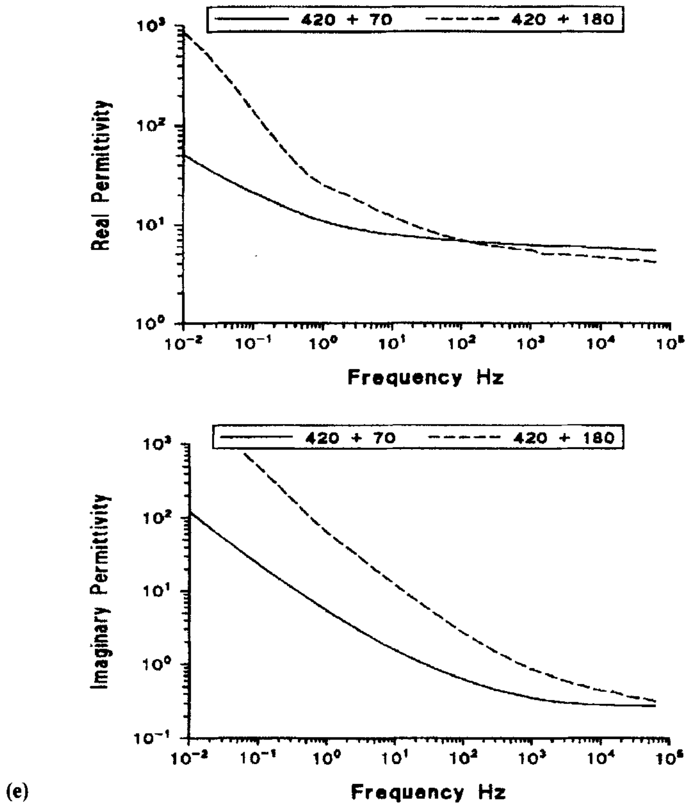

FIGURE 7 (Continued).

water is calculated by taking the Kirkwood-Frohlich equation with g set equal to unity, equivalent to assuming that the bound water molecule is isolated from all other water molecules. This gives us a permittivity value for bound water of 28. This corresponds well with the experimental value of 27.2 obtained from data presented by Pollock [28] and Morel *et al.* [29].

The results for these calculations, Table III, indicate that the phenolic samples have both a greater total quantity of water and a larger concentration of bound water. In contrast, the epoxy samples exhibit a significant percentage of bound water which depends on the surface preparation. The uncertainties arise primarily as a result of the problem of a precise definition of the bond line thickness which controls

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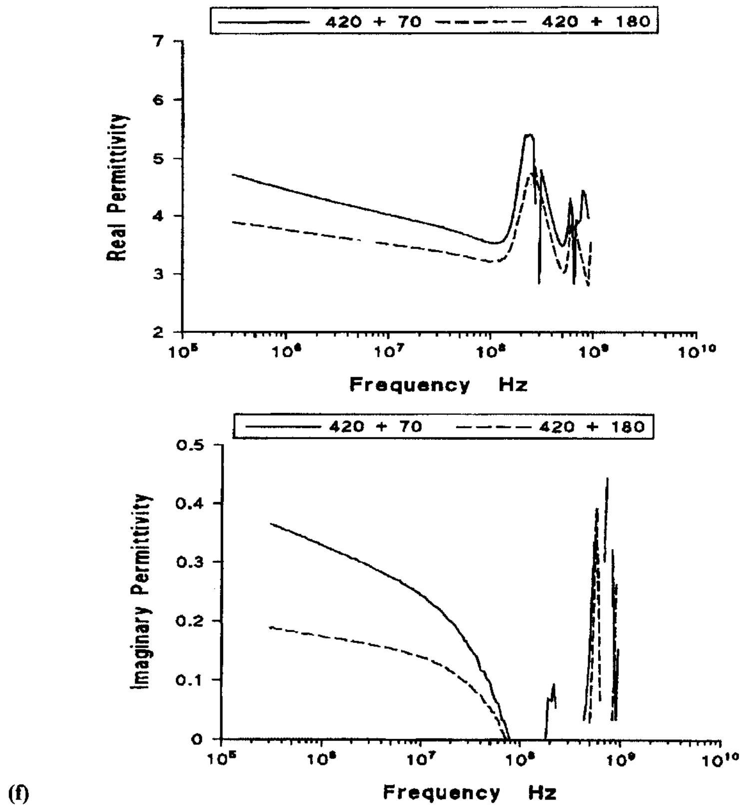

FIGURE 7 (Continued).

TABLE III Estimation of the distribution of water within the sample

Adhesive Film	*Surface Preparation*	*Days*	*ε′(10⁴ Hz)*	*Bound Water %*	*ε′(3 × 10⁶Hz)*	*Free Water %*	*Total Water %*
Phenolic	Etch	0	4.10±0.80	5.92±	3.24±0.02	0.97	6.89±
		600	6.54±0.14	2.92%	4.02±0.22	±0.27%	1.5%
Phenolic	Etch + Anodise	0	4.00±1.30	10.28±	3.26±0.24	1.49	11.77±
		600	8.02±1.61	7.39%	4.40±0.12	±0.53%	3.2%
Epoxy	Etch	0	4.70±0.68	3.28±	3.20±0.41	0.59	3.87±
		600	6.10±0.80	3.74%	3.68±0.24	±0.59%	1.8%
Epoxy	Etch + Anodise	0	5.40±0.91	0±	3.00±0.50	0.99	4.99±
		600	6.20±0.50	3.73%	3.80±1.62	±2.1%	1.6%
Epoxy	Etch + Anodise	0	5.2 ±0.41	0±	3.10±0.02	0.62	6.20±
	+ Primer	600	5.7 ±0.67	2.80%	3.60±0.65	±1.00%	1.5%

the high frequency values of the real and imaginary permittivity. Since the values used are held constant, the differences measured are more precise than the absolute values. Free water in all cases would have entered the oxide layer by capillary action or has segregated into voids in the resin. Water initially on entering the polymer matrix becomes bound to polar groups and is present as a single molecular species.

As far as we are aware there are no dielectric studies of the effects of ageing in water of the prepared surfaces used in this study (i.e. chromic, etching, anodizing, etc.) with which to draw detailed comparisons. The work of Jeffries [30] on aluminium oxide using a series of well-defined preparative routes indicated that the dielectric characteristics were very similar for all the oxides studied. The effects of surface treatment on the dielectric properties of the oxide layer do not appear from this study to introduce any significant changes in the dielectric characteristics initially observed and the dominant process is conversion of oxide into hydroxide.

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CONCLUSION

The permittivity values of adhesively-bonded joints increased as a function of ageing in noist environments, the anodized phenolic samples showing a marginally higher increase in permittivity when compared with epoxy samples with an identical surface preparation. High frequency data, at lower temperature, show no evidence of water attacking the oxide layer as characterized by the change in the dielectric relaxation in the megahertz region [30]. This consistent with the fact that the joints were intact at the end of the study and had not lost all of their mechanical strength. However, at elevated temperatures, increases in the permittivity in the region of 10^6 Hz were beginning to be detected. Transit time measurements support the observations from dielectric analysis and a good correlation is observed between these parameters. A following paper will discuss the mechanical test data obtained on these samples [31].

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