Nondestructive examination of epoxy adhesive-bonded structures exposed to a humid environment: A comparison of low- and high-frequency dielectric measurements

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NONDESTRUCTIVE EXAMINATION OF EPOXY ADHESIVE-BONDED STRUCTURES EXPOSED TO A HUMID ENVIRONMENT: A COMPARISON OF LOW- AND HIGH-FREQUENCY DIELECTRIC MEASUREMENTS

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Broadband dielectric measurements (10^{-2} to $3\,GHz$) are reported on the effects of exposure of thick film adhesive-bonded structures to moisture. Measurement of the dielectric properties over a broad frequency range allows identification of water both in voids and as a molecular dispersion in the matrix. Changes in the low frequency region of the dielectric spectrum can be attributed to a combination of processes associated with plasticisation of the adhesive, interfacial polarisation effects, and hydration of the surface oxide layer. The data obtained are complemented by mechanical testing and failure analysis of the bond structure measured as a function of the time of exposure. This study indicates that for thick film adhesives the ageing characteristics are apparently independent of the surface treatment. In one of the joints studied an additional feature is identified which appears to correlate with the premature aging of the joint structure.

INTRODUCTION

The potential use of the high-frequency dielectric technique (300 kHz to 3 GHz) in monitoring the changes which accompany ageing of thin film adhesive-bonded structures in a moist environment at relatively low temperature has been described previously [1–6]. Subsequent measurements of the effects of exposure of the joints to an elevated temperature indicated the possibility of correlating changes in the dielectric profile of the joint and variation in the mechanical properties of the joint with time [7]. It is well established that ageing of an adhesive-bonded structure in a humid warm atmosphere will lead to a loss of mechanical strength, and this phenomenon has been extensively discussed in the literature [8–11]. Comparison of the mechanical strength of joints aged in dry and wet environments [10] indicates the important role that moisture plays in accelerating the loss of strength. Moisture has the capability, in addition to plasticising the adhesive, of inducing changes in the nature of the interfacial oxide layer. Moisture will cause the oxide to be converted to the hydroxide with a corresponding change in the volume of the layer. Moisture entering the adhesive can cause the adhesive layer to swell and allow polymer chain motion that will allow stress relaxation in the adhesive [11]. Combination of the change in the state of the oxide interface and softening of the adhesive layer leads to a loss of the strength of the adhesive bond. Moisture ingress into the joint structure is clearly a key factor in the loss of the adhesive bond strength, and the ability to monitor in situ the ingress is a desirable aim of any nondestructive analysis technique.

A parallel study of the effects of moisture on the resin system has been published recently [12–14]. It was observed that moisture absorption followed a pseudo-Fickian type of behaviour, and saturation was achieved at approximately 4.3%, the matrix being plasticized and the glass transition temperature, Tg, having been lowered to about 65°C. The desorption profiles indicated that not all the moisture from the matrix was observed. In addition, electron microscopic examination of the adhesive indicated that in the case of pure water microcavities were formed. In the case of ageing in NaCl the behaviour was different and the hystresis effects were smaller.

In previous studies, thin bondline adhesives were used and the observations were limited to high-frequency measurements. This study explores the problems of investigating thick bondline adhesives of the type used in automobile applications.

EXPERIMENTAL

Materials—Construction of Joints

Lap-shear joints were produced from 2.0 mm gauge AA5754 aluminium alloy sheets (typical composition, 96.15% Al, 0.10% Si, 0.20% Fe, 0.10% Cu, 0.25% Mn, 3.2% Mg). The joints consisted of 100 mm × 20 mm adherends with an overlap area of 10 mm × 20 mm. The bondline thickness of the joint was 200 μm, controlled by the addition of Ballotini glass spheres to the adhesive (1% by weight). The joints were prepared by firstly guillotining the pretreated aluminium sheets into strips approximately 25 mm in width. The strips were then cut into 100 mm × 20 mm adherends using a die cutter. The substrates were either etched with a hydrofluoric/sulphuric acid cleaning agent or etched and chromate anodised before application of the adhesive. The joints were then bonded together using jigs to achieve the 20 mm × 10 mm overlap, the adhesive being spread on the bonding areas by the use of a spatula. Spring clips were applied to the joint prior to cure to achieve the necessary pressure required to maintain a constant bondline thickness. The adhesive used was a single-part, dicyandiamide-cured, carboxy-terminated, butadiene acrylonitrile-toughened epoxy adhesive. The joints were cured in an oven for 15 min at 145°C followed by 15 min at 190°C. The temperature of the oven was monitored by a thermocouple clipped to one of the joints. After the curing cycle was completed, the joints were removed and allowed to cool slowly overnight. The cure cycle for this adhesive system was optimised by measurement of the cure exotherm for the joint after cure and postcure for several hours at 80°C. In the final cured material, there was no detectable exotherm and the adhesive bond strength exhibited a maximum value at room temperature when it was investigated as a function of the cure temperature. Water absorption studies on this resin system have been reported elsewhere. The glass transition temperature of the resin was observed by dynamic mechanical thermal analysis performed at 10 Hz to be 395 K [12].

Ageing Schedule

The joints were exposed to a warm humid environment (100% RH) and cycled between 42 and 48°C on an hourly basis for a period of two years. A further set of joints was aged in a 70°C water bath to increase their rate of degradation.

Dielectric Measurement—Low Frequency (10^{-2} Hz–6.3×10^5 Hz)

Low frequency measurements were performed using a Solatron 1250 A Frequency Response Analyser (FRA) [15]. Dielectric measurements were performed initially weekly, but as ageing progressed the interval between testing was increased to once a month. The measurements were repeated three times to obtain an averaged value of the frequency response.

Dielectric Measurement—High Frequency (300 kHz–3 GHz)

Measurements were performed between 300 kHz and 3 GHz using a computer-controlled Hewlett Packard HP8753A network analyser. The method used has been discussed previously [1]. To ensure the reproducibility of the results, the instrument was calibrated using a short circuit, open circuit, and a $50\,\Omega$ load after batches of 10 samples had been measured. The day-to-day variation in the calibration parameters was significantly smaller than the effects being observed.

Mechanical Testing of Samples

Mechanical measurements were performed using an Instron Series IX Automated Materials Testing System with a crosshead displacement speed of 2.0 mm/min and a specimen grip length of 75 mm The test method used has been described in detail previously [16] and the mechanical data reported are based on an average of the analysis of 5 test samples for each observation.

Examination of Failure Modes of Mechanical Samples

Fracture surfaces were scanned using a Hewlett Packard 4 C high-resolution flatbed scanner. Comparison of the exposed surfaces for samples aged for different times allowed failure of the joints to be classified as adhesive or cohesive failure.

RESULTS AND DISCUSSION

A key factor in understanding the ageing of joints that are subjected to hydrothermal ageing is the ability to follow the water ingress into the joint. When aluminium substrates are used, surface oxidation can make accurate assessment of the gravimetric changes due to water absorption very difficult, the change in mass due to corrosion often

being greater than the change due to water absorption. In previous studies, thin bondline adhesives were used and the observations were limited to high frequency measurements. This study explores the problems of investigating thick bondline adhesives of the type used in automobile applications. The optimisation of the cure so as to minimise thermally induced stresses which arise when cooling is too quick has been extensively discussed recently [17–19]. Although slow cooling will minimise the vitrification of the outside of the part before the inside, thermal stresses also arise due to a thermal mismatch between the resin and anything that is constraining it (fibres in composites) and can be a cause for additional concern. Similar problems can arise with aluminium–epoxy–aluminium joints and the specimens used in this study were postcured at 80°C to reduce residual stress effects.

A substantial contribution to the development of a molecular understanding of the cure process has been made by Mijovic and his coworkers [20–23]. They have studied a wide range of resin systems including cyanate ester and cyanurate as well as bismaleimide resins. Their studies have also included examination of the cure process using a combination of infrared and dielectric observations.

Low Frequency Dielectric Results (0.01 Hz–6.3 × 10^5 Hz)

The joints selected for this study were prepared from either etched or etched and anodised substrates. The study attempted to show whether any major differences in the ageing characteristics of these thick-film adhesives might occur as a consequence of the difference in surface treatment. The low frequency dielectric measurements for the joints are presented in Figures 1–3. In all cases, there was a marked increase in the dielectric permittivity with ageing time. The low frequency dielectric spectra contain two distinct regions. Above a frequency of 100 Hz there is a steady increase in the dielectric permittivity and an associated increase in the loss that has a maximum observed value in the 10–100 KHz region. From previous studies we have shown that 'bound' water relaxes at approximately 10 KHz and above at room temperature. The observed increase in the permittivity can therefore be ascribed to the diffusion of moisture into the adhesive layer. The peak is attributed to relaxation of the pendant hydroxyl groups of the epoxy resin. As the ageing process proceeds the amplitude of the 10 kHz peak increases due to the relaxation of water molecules which have become bound to the hydroxyl groups [2]. Below 10 Hz marked changes in the dielectric properties are observed. These are associated with a combination of processes related to a lowering of the glass transition temperature, T_g, change in the ionic conductivity, and the
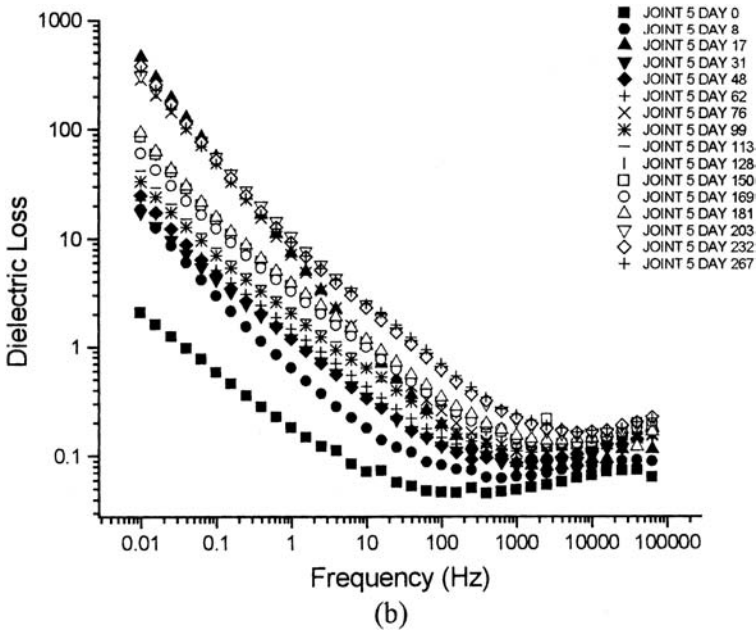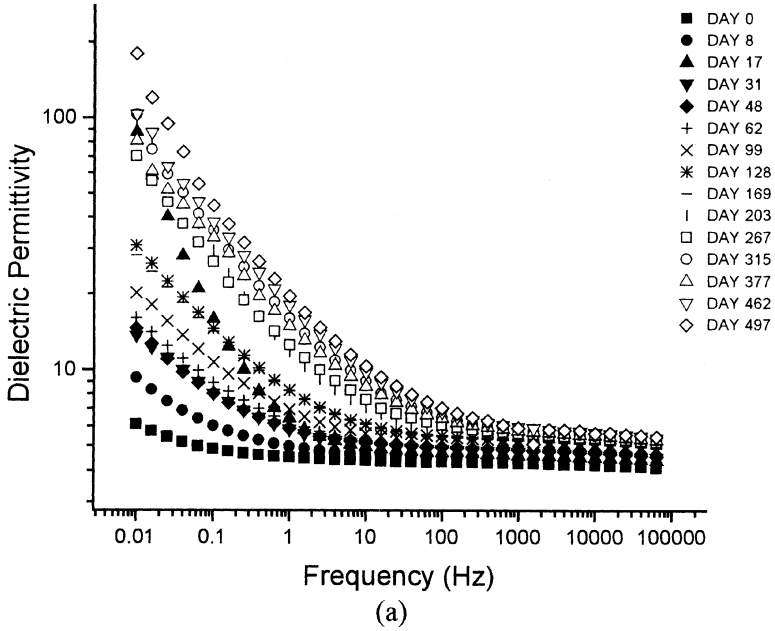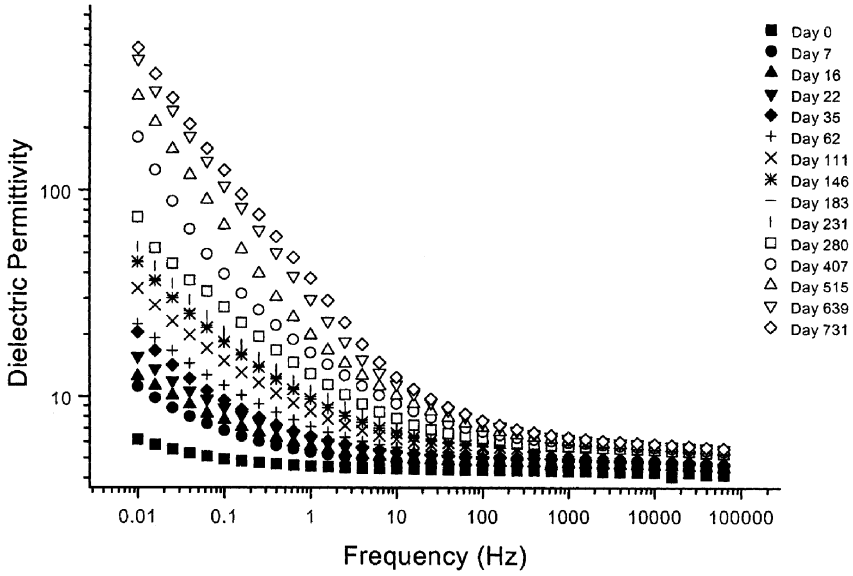
FIGURE 1 Low frequency dielectric data for the etched and anodised system:
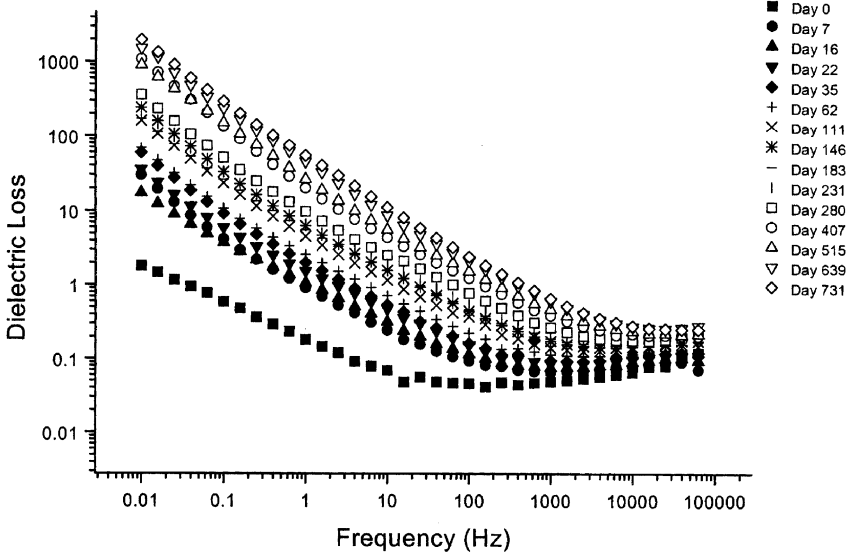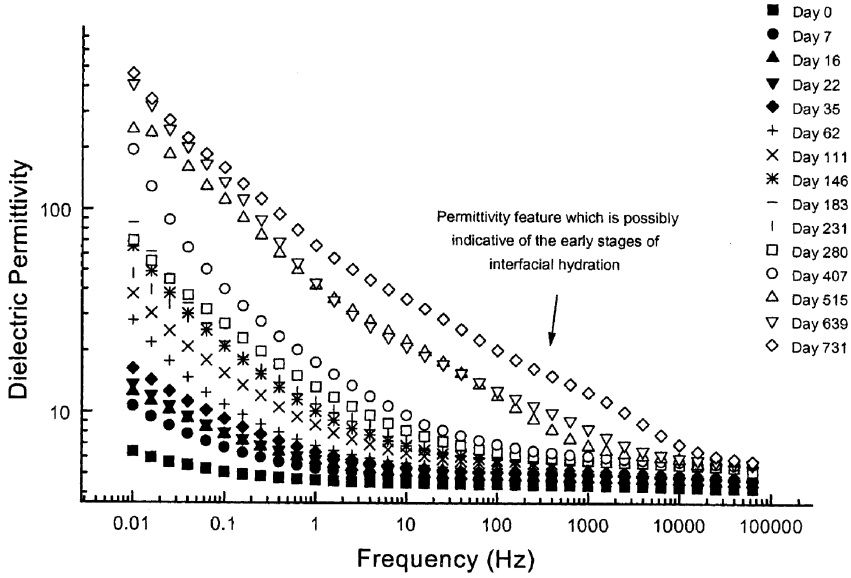(a) dielectric permittivity and (b) dielectric loss.
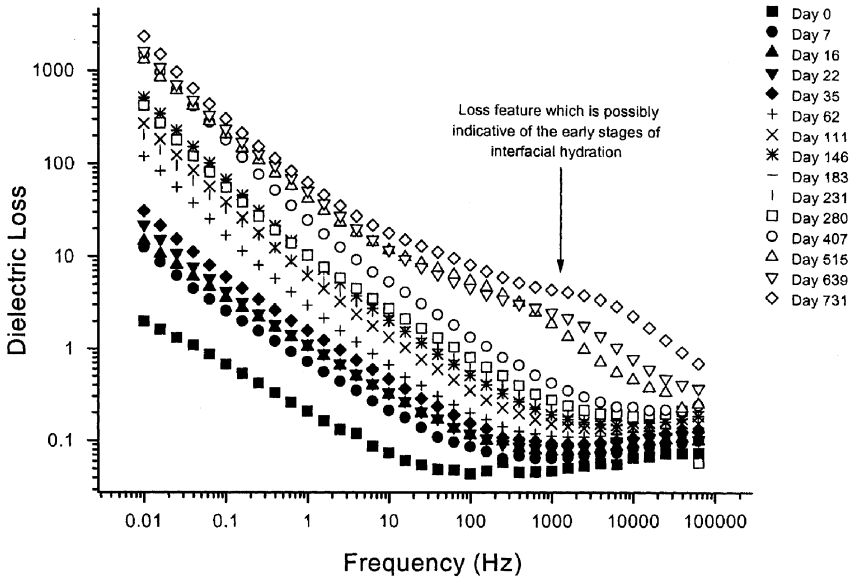
(a)

(b)

FIGURE 2 Low frequency dielectric data for the etched-only system: (a) dielectric permittivity and (b) dielectric loss.

(a)

(b)

FIGURE 3 Low frequency dielectric data for the "prematurely" ageing, etched-only system: (a) dielectric permittivity and (b) dielectric loss.

creation of blocking electrodes at the oxide surface. The dipolar activity of the T_g process would only be expected to contribute an increment to the dielectric permittivity of the order of tens of units. The observed increase, which is much larger than expected from plasticisation, must therefore be attributed primarily to blocking electrodes and the effects of trapped charge conduction. As the T_g is lower due to plasticisation by moisture, there will be increased dipolar activity as the relaxation moves progressively to higher frequency. The observed changes in the dielectric permittivity and loss are of the order of magnitude of that associated with interfacial phenomenon (Maxwell–Wagner Siller [1] processes) associated with trapping at internal interfaces or blocking of long-range mobility of impurities at electrode surfaces. The contributions to the interfacial polarisation can arise from the trapping of charge at various interfaces. Within the adhesive bond structure, charge trapping can occur at the resin-substrate interface and depends on the work function of the metal electrode. This process is assigned the description of a blocking electrode effect. Within the adhesive resin there may exist voids which, when filled with moisture, can exhibit a large differential conductivity relative to the surrounding matrix and will give rise to polarisation effects often referred to as MWS processes. The resin itself, due to differences in crosslink density, will be non-homogeneous and has the potential of creating regions of high and low ionic mobility which, in principle, can also produce MWS-like effects. All these processes can contribute to the low frequency dielectric relaxation behaviour. The resin used in this study is rubber modified and will contain regions of different conductivity and, hence, has been previously observed to exhibit the MWS phenomenon. Charges that cannot be discharged at the oxide layer can also produce similar effects and are observed in uncured resins. It is not possible at this point to differentiate between the dipolar and various interfacial processes. As ageing proceeds, the frequency at which the transition occurs gradually increases, consistent with both a decreasing T_g and a greater ionic mobility in the resin.

The low frequency dielectric data were initially all very similar; however, differences were observed as ageing proceeded. Differences were observed between the etched joints (Figures 2 and 3) during the later stages of the ageing. A loss feature that developed at 1000 Hz after 515 days of ageing is attributed to the early stages of hydration of the interfacial region of the joints.

To aid visualisation of the changes occurring in the dielectric, plots of the variation of permittivity with time were constructed for the data at 10 kHz (Figure 4). This frequency was selected because it is sufficiently high not to be influenced by the effects that cause the
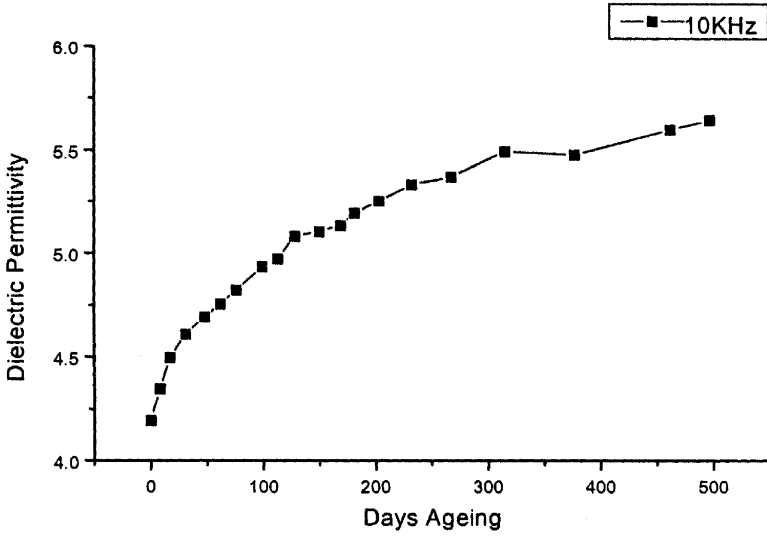
(a)
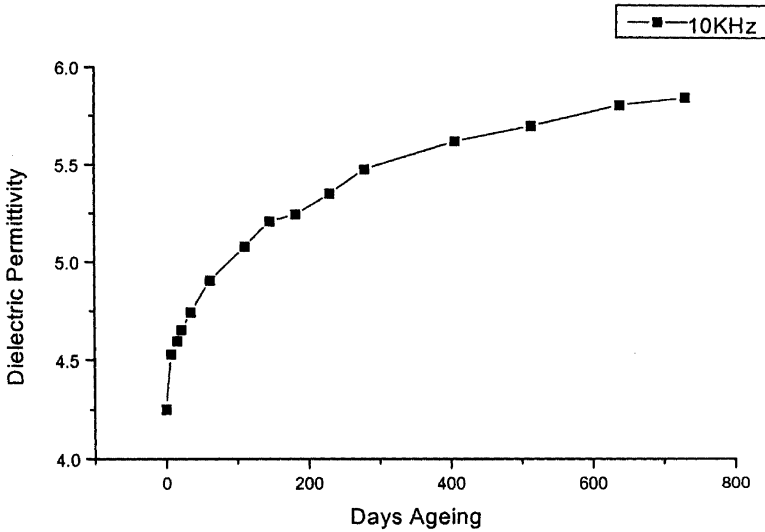
(b)

FIGURE 4 Graph of dielectric permittivity at 10 KHz versus ageing time for the (a) anodised, (b) etched system, and (c) the "prematurely" ageing, etched-only system. (Continued)
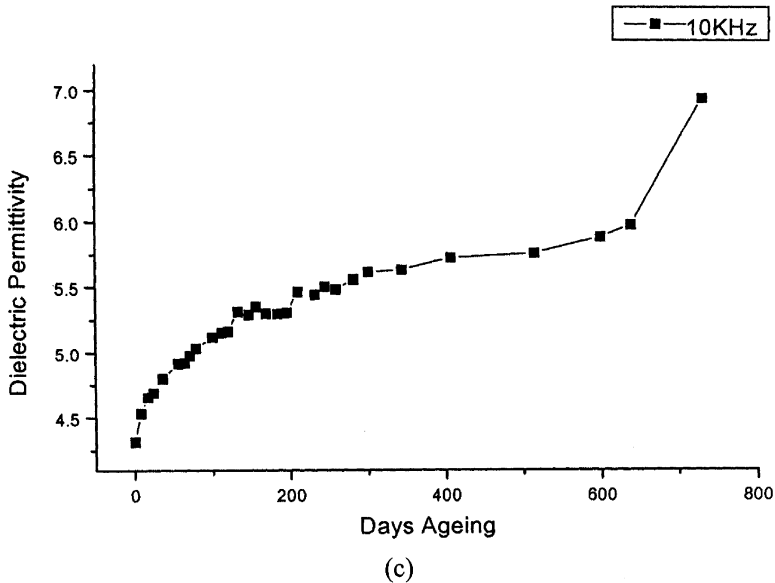
(c)

FIGURE 4 Continued

changes in the lower frequency spectrum. The frequency is sufficiently low that the permitttivity change can be considered to be indicative of the total moisture ingress into the joint structure. The data suggest that the major contribution to the permittivity change will be from the water diffusing into the bonded systems. At 10 kHz both the "bound" and "free" water will contribute to the total permittivity of the sample. There is an initial steep increase in permittivity for the first 70 days of ageing and then a slower increase over the following 670 days. The continuous rise in permittivity over the whole period implies that the saturation level of the epoxy has not been reached. The results from the dielectric analysis of the "prematurely" ageing etched joint, (Figure 4c) show a sharp rise in permittivity at 10 kHz after 600 days ageing, which is interpreted as associated with the initial stages of interfacial hydration. The relaxation of the hydoxyl group of hydrated alumina is known to relax at this frequency [1].

High Frequency Dielectric Results (300 KHz–3 GHz)

The changes in the high-frequency dielectric permittivity are shown in Figures 5–7 for the samples aged in the humidity cabinet. The permittivity values at 1 MHz for the dry adhesive systems ranged from
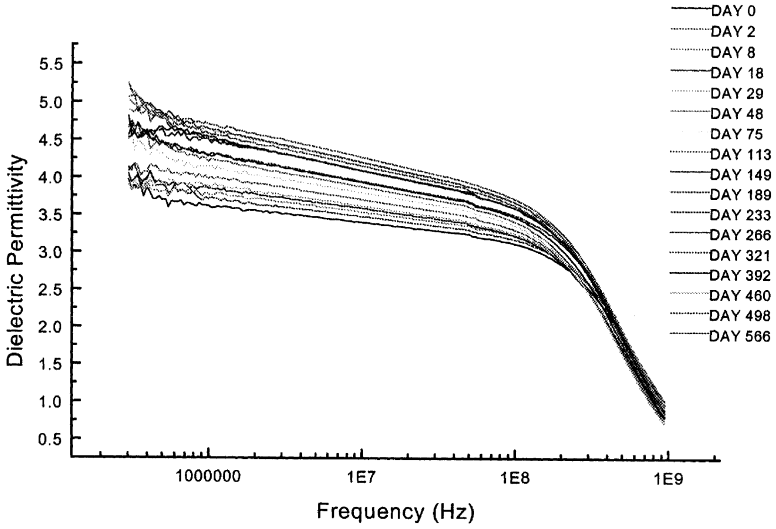
FIGURE 5 High frequency dielectric permittivity data for the etched and anodised system.
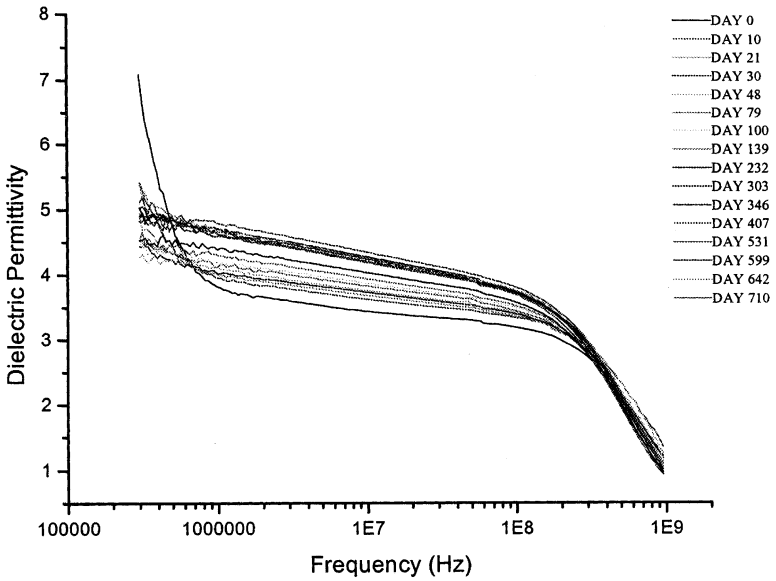
FIGURE 6 High frequency dielectric permittivity data for the etched-only system.
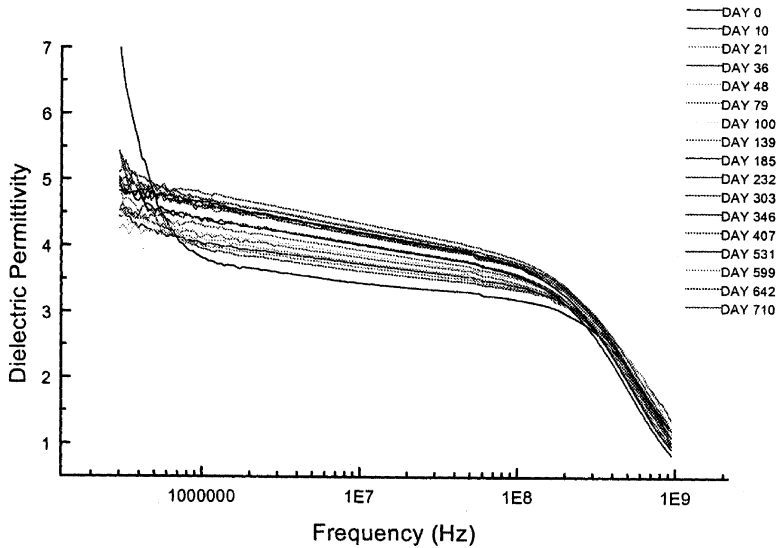
FIGURE 7 High frequency dielectric permittivity data for the "prematurely" ageing, etched-only system.

3.5–3.8 with an average value of 3.7, which is in agreement with the typical values expected for epoxy-bonded adhesive systems [1, 4, 6]. The apparent decrease in permittivity observed above 10^8 Hz is an artefact of the model used in the analysis [2, 3] and is not an indication of a relaxation process but is associated with the finite dimensions of the joint structures used. Current research is aiming to establish the unambiguous assignment of the origins of the dipole processes which occur in this region. The dielectric permittivity increases observed with ageing time are due to increases in the total water content within the adhesive, including that distributed in capillaries and micro-cavities within the epoxy matrix. The relaxation of "free" water occurs at about 18 GHz [3], which is beyond the range of the measuring techniques used for this study; however, an assessment of the rate of ingress of free water into the system can be obtained by monitoring the change in dielectric permittivity at 3 MHz with ageing time [1, 4]. Whilst the precise origins of the dipole relaxation process at this frequency are yet to be unambiguously determined, the magnitude of the dielectric permittivity change can be quantitatively related to the amount of moisture absorbed.

Previous research has indicated that significant hydration of the interfacial aluminium oxide layer may lead to marked increases in the

permittivity contribution observed in the 1 MHz region of the dielectric spectrum [5]. The high frequency dielectric data show no development of a distinct relaxation feature in the high frequency region, indicating that significant oxide-to-hydroxide transformation is not occurring in the joints investigated. The high frequency permittivity results for all of the adhesive systems exhibit no evidence of any change occurring in the composition of the aluminium oxide layer, which would be expected if water changed the dipole activity of the surface oxide layer. It is rather surprising that no change is detected in the dielectric plot for the "prematurely" ageing etched-only joint (Figure 7), since the lower frequency analysis, (Figure 3b), exhibits clear evidence of an increase in dipole activity in a region usually associated with aluminium hydroxide formation.

To aid visualisation of the data, the dielectric permittivity at 3 MHz which indicates the amount of mobile water within the bonded systems, was plotted as a function of ageing time (Figure 8). The results show an initial rise in permittivity throughout the first 70 days of ageing which then slowly approaches an apparent asymptotic value. After 730 days of ageing a steady state had not been achieved, implying that the saturation level of the adhesive had not been reached.

Throughout the ageing period the initial values for the bondline thickness were used in the Mathcad program to calculate the high frequency dielectric results for the joints. This may result in an underestimation of the true permittivity and dielectric loss of the joints during the later stages of the ageing process. Epoxy adhesives can swell as a result of the ingress of moisture and the subsequent plasticisation process, which will ultimately affect the bondline thickness. Any increase in bondline thickness through the ageing period could not be estimated, as corrosion of the aluminium substrate made accurate measurement impossible, resulting in possible errors in the calculation of the permittivity and dielectric loss of the samples. While an underestimation of the total water uptake of the joints may occur, the permittivity results still clearly indicate water uptake of the samples.

MECHANICAL TEST RESULTS

Mechanical tests were performed on the adhesive systems at intervals selected from observation of the dielectric data. The strength of the adhesive joints can be calculated in MPa by dividing the fracture loads in N/mm by 10. Variation of the strength of the joint measured as a function of ageing time is shown in Figure 9. Surprisingly the etched
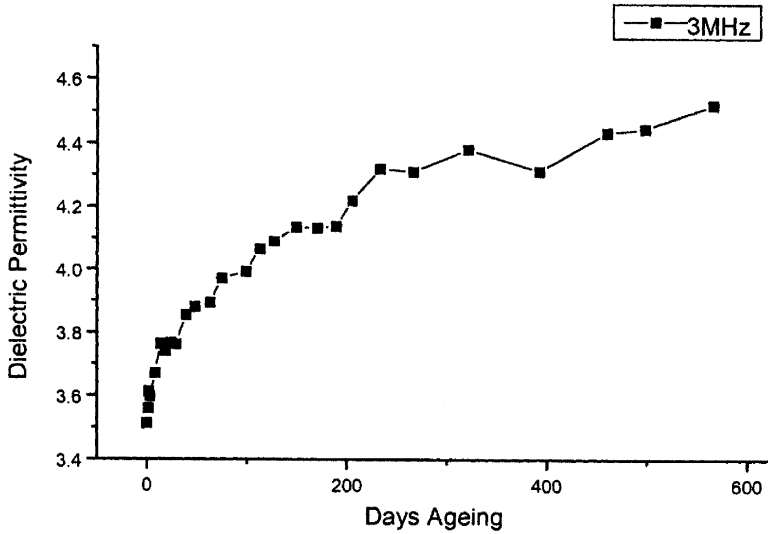
(a)
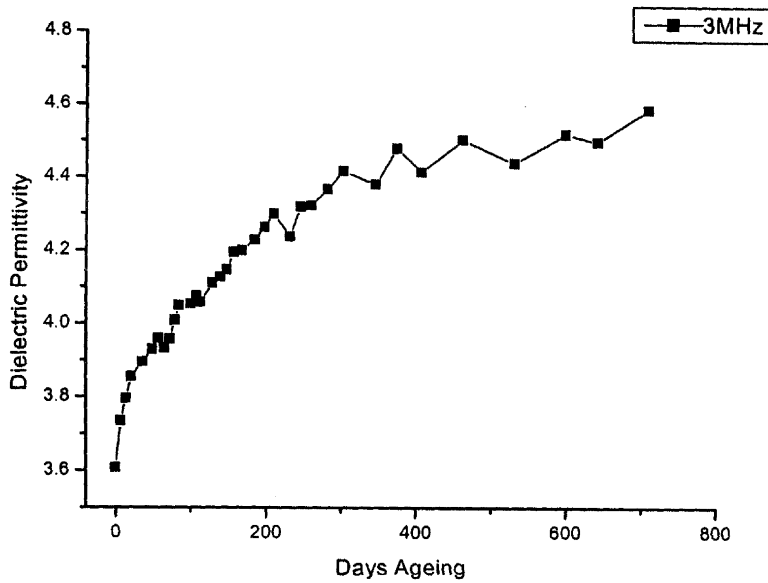
(b)

FIGURE 8 Graph of dielectric permittivity at 3 MHz versus ageing time for the (a) anodized, (b) etched, and (c) prematurely ageing etched-only system. (Continued)
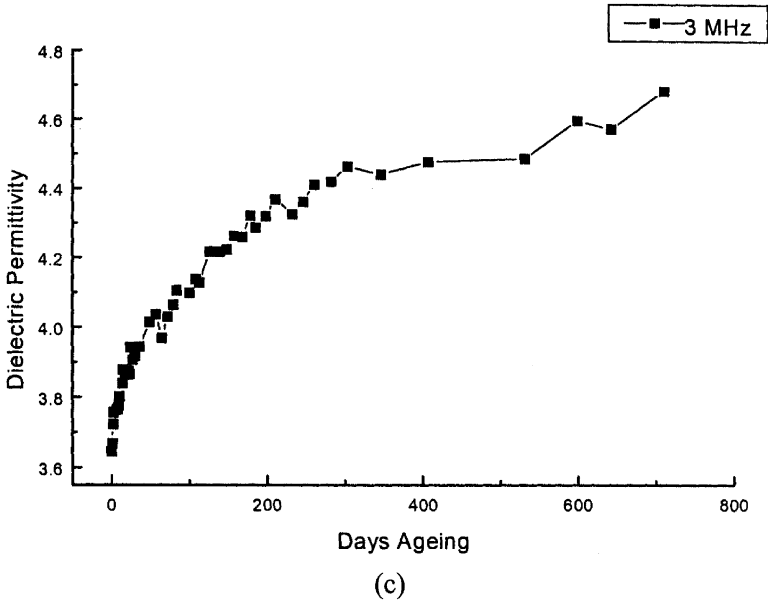
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(c)

FIGURE 8 Continued

system, which intuitively was expected to be the least durable system, demonstrated good long-term durability. The mechanical testing for all the samples exhibited an initial sharp drop in residual strength during the first 5 weeks in the humidity cabinet and then achieved a constant value throughout the rest of the ageing period. The visual inspection of the failure surfaces indicated that the failure mode was predominantly cohesive in all the cases investigated. Plotting the dielectric permittivity values measured at various times from Figure 4 against the corresponding variations in mechanical strength measured at various times from Figure 9 creates Figure 10. Figure 10 contains data for the etched-only and etched and anodised joints, and indicates that their time dependence follows similar characteristics. There is an initial drop in the strength with a corresponding marked rise in the dielectric permittivity. Interestingly, the plots for the two systems coincide without scaling, which implies that water ingress controls the ageing process. The high residual strength of these joints suggests that at the stage at which the study stopped, the destabilisation of the interface is only making a minor contribution to loss of bond strength. The observed decrease can be ascribed to the effects of plasticization of the adhesive and is consistent with the changes observed in the dielectric response of the joints. Recently Mijovic et al. [24] successfully
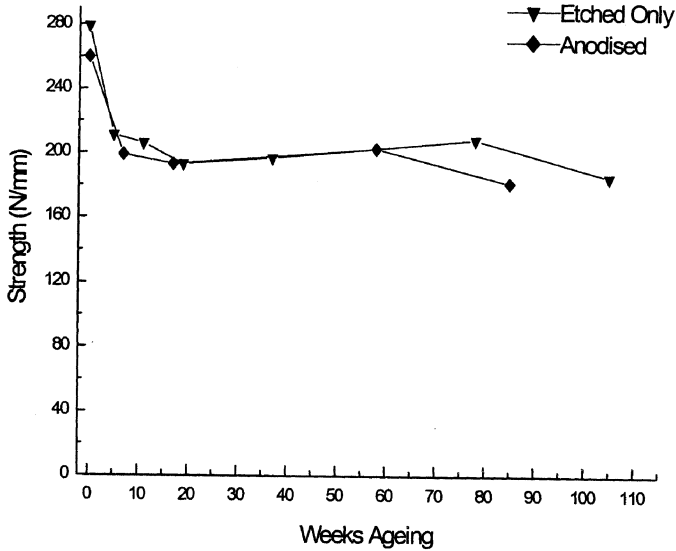
FIGURE 9 Ageing data for the etched-only and etched and anodised joints.

combined FTIR and dielectric measurements and showed that water can exist in more than one form in an epoxy resin matrix. NMR studies [25] have challenged the concept of bound and unbound water in epoxies, and the nature of the state of aggregation and interaction of
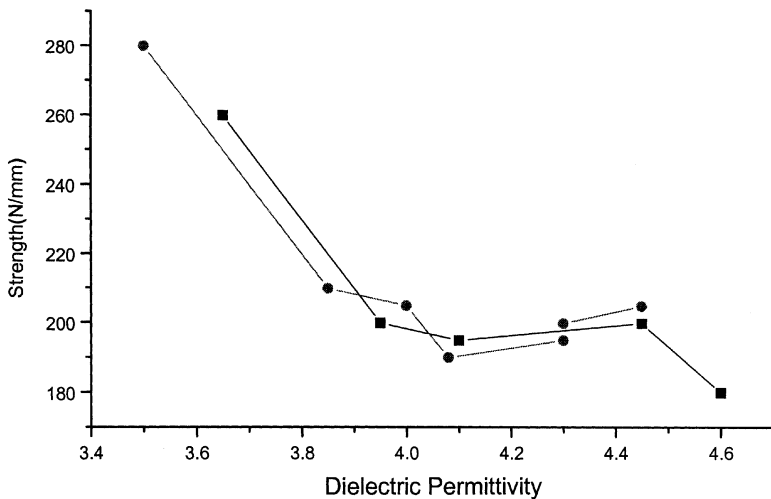

FIGURE 10 Plot of joint strength against dielectric permittivity for: ●, etched-only joints, and ■, etched and anodised joints.

water with the polymer matrix is currently an area of some controversy. However, a comparison of the dielectric increment measured at 10 KHz (1.7) and that at 10 MHz (0.9) indicates that approximately 50% of the water absorbed behaves as though it were in a semi clustered state and able to relax at high frequencies. More aggressive tests of the joints are currently being conducted in which the observations are being extended using both a range of different adhesive systems and also allowing the tests to be extended to a point at which destabilisation of the interfacial oxide layer occurs. These tests will be the subject of a future publication.

CONCLUSIONS

The dielectric data parallels the changes in the mechanical data for these systems that appear to fail cohesively. As was the case for thin bondlines, the thick adhesive layers examined show an interesting correlation of the variation of the dielectric permittivity with the change in the mechanical strength of the joints. This study once more demonstrates the usefulness of the dielectric approach for the assessment of ageing in adhesive-bonded structures and emphasised the importance of extending the dielectric measurements to lower frequencies. The higher frequency measurements have been previously favoured because they can provide time domain data; however, with the small samples used in this study such measurements are no longer practical.

REFERENCES

[1] Hayward, D., Affrossman, S., and Pethrick, R. A., *Non-destructive Testing Evaluation*, **6**, 45–63 (1991).
[2] Joshi, S. B., Hayward, D., Wilford, P., Affrossman, S., and Pethrick, R. A., *European Journal of NDT*, **1**, 190–199 (1992).
[3] Banks, W. M., Hayward, D., Joshi, S. B., Zhi-Cheng, L., Jeffrey, K., and Pethrick, R. A., *Insight*, **37**, 964–968 (1995).
[4] Zhi-Cheng, L., Hayward, D., Gilmore, R., and Pethrick, R. A., *Journal of Materials Science*, **32**, 879–886 (1997).
[5] Joshi, S. B., Pethrick, R. A., Gilmore, R., Yates, L. W., and Hayward, D., *Journal of Adhesion*, **62**, 281–315 (1997).
[6] Zhi-Cheng, L., Joshi, S. B., Hayward, D., Gilmore, R., and Pethrick, R. A., *NDT & E International*, **30**, 151–161 (1997).
[7] Halliday, S., Thesis, University of Strathclyde, Glasgow, UK, (1998).
[8] Culey, A. J., Jewtha, J. K., Kinloch, A. J., and Taylor, A. C., *Proceedings of the 21st Annual Meeting of the Adhesion Society*, Savannah, Georgia, Feb. 22–25, 1998, R. A. Dickie, Ed. (The Adhesion Society, Virginia Tech, Blacksburg, VA, USA 1998), 102–103.

[9] Comyn, J., Brewis, D. M., Shalesh, R. J., and Tegg, J. L., In *Adhesion* 3, K. W. Allen, Ed. (Applied Science Publishers, Barking, London, 1979), p. 13.

[10] Cotter, J. L., In *Developments in Adhesives – 1*, W. C. Wake, Ed. (Applied Science Publishers, Barking, London, 1977), p. 1.

[11] Mahoon, A., In *Adhesion–4*, K. W. Allen, Ed. (Applied Science Publishers, Barking, London, 1980), pp. 71–86.

[12] Ivanova, K. I., Pethrick, R. A., and Affrossman, S., *J. Applied Polymer Science*, **82**, 3468–3476 (2001).

[13] Ivanova, K. I., Pethrick, R. A., and Affrossman, S., *J. Applied Polymer Science*, **82**, 3477–3485 (2001).

[14] Ivanova, K. I., Pethrick, R. A., and Affrossman, S., *Polymer*, **41**, 6787–6796 (2000).

[15] Pethrick, R. A., Hayward, D., and Mahoubian Jones, M. G. B., *J. Phys. E. Sci. Instrum.* **17**, 683–690 (1984).

[16] Joshi, S. B., Gray, T. F., Banks, W. M., Hayward, D., Gilmore, R., Yates, L. W., and Pethrick, R. A., *J. Adhesion*, **62**, 281–315 (1997).

[17] Russell, J. D., Madhukar, M. S., Genidy, M. S., and Lee, A. Y., *Journal of Composite Materials*, **34**, 1926–1947 (2000).

[18] Gopal, A. K., Adali, S., and Verijenko, V. E., *Composite Structures*, **48**, 99–106 (2000).

[19] Prasatya, P., McKenna, G. B., and Simon, L., *J. Composite Materials*, **35**, 826–848 (2001).

[20] Fitz, B. D., and Mijovic, J., *J. Phys. Chem. B*, **104**, 12215–12223 (2000).

[21] Fitz, B. D., and Mijovic, J., *Macromolecules* **33**, 887–899 (2000).

[22] Mijovic, J., Andjelic, S., and Fitz, B., *J. Polymer Science: Polymer Physics*, **34**, 379–388 (1996).

[23] Mijovic, J., Kenny, J., Maffezzoli, A., Trivisano, A., Bellucci, F., and Nicolais, L., *Composites Science and Technology*, **49**, 277–290 (1993).

[24] Mijovic, J., Miura, N., and Soni, S., *J. Adhesion* **76**, 123–150 (2001).

[25] Schadt, R. J., and Vanderhart, D. L., *Macromolecules*, **28**, 3416–3424 (1995).