Dielectric Spectroscopy as a Non-Destructive Technique to Assess Water Sorption In Composite Materials

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ABSTRACT

Over the last ten years, the application of high frequency dielectric spectroscopy techniques for the assessment of composite structures has been investigated. Novel approaches to assess non-destructively the evolution during ageing of adhesively bonded carbon fibre reinforced plastic (CFRP) structures and bulk glass fibre reinforced plastic (GRP) structures are presented in this paper and the results are critically assessed.

The applicability and limitations of dielectric measurements, in both frequency and time domain, to the monitoring of water ingress at 30°C and 60°C are examined. The correlation between gravimetric and high frequency dielectric spectroscopy data demonstrates the suitability of the techniques regarding the assessment of water uptake in composites structures and illustrates its potential as a non-destructive evaluation (NDE) technique. The dielectric time domain response (TDR) study of adhesively bonded structures indicates a new way to assess such structures. The approach for frequency domain analysis of bulk GRP using a coaxial probe technique indicates the potential portability of the technique for in-situ measurements.

INTRODUCTION

The application of dielectric spectroscopy for the assessment of water permeation into polymeric materials has been the subject of a number of investigations /1-3/. The effect of the water on the dielectric characteristics of polymeric materials has been discussed in terms of both the conductivity of water occlusions and the dipolar nature of the water. The applicability of either perspective depends on whether the water exists as droplets (free water) or as individual molecules (bound water) /4/.

Over the past decade, the application of high frequency dielectric spectroscopy to the assessment of aluminium adhesively bonded structures has been investigated. Its potential as a non-destructive technique to assess the quality and integrity of such structures and to monitor their ageing has been demonstrated /5/. The high conductivity of the aluminium adherent allowed the successful use of high frequency dielectric spectroscopy techniques by providing an efficient wave-guide structure. However, the aerospace industry is increasingly using adhesively bonded composite materials with a much lower conductivity than aluminium and there is a requirement for non-destructive techniques to assess the integrity of these structures.

This paper explores the potential of high frequency dielectric spectroscopy as a non-destructive evaluation (NDE) method for composite structures. Two approaches are presented in this paper. The first one consider the application of the method successfully used on adhesively bonded aluminium structures to adhesively bonded CFRP structures, the second one present a novel approach to the application of dielectric spectroscopy to bulk GRP structures.

EXPERIMENTAL METHODS

Materials

Carbon fibre reinforced plastic (CFRP) adherents were manufactured from Hexcel Composites Ltd unidirectional carbon fibre pre-impregnated film (914C-TS(6K)-5-34%). The pre-impregnated film contained 66% by weight of high-tensile surface treated carbon fibres. The adhesive system used was a 3M structural epoxy system (Scotch-Weld Brand AF-163-2U).

Two glass fibre reinforced plastic (GRP) composites prepared from woven-rowing E glass fibre reinforced thermoset resins were used: a 50% weight glass fibre hand lay-up reinforced unsaturated isophthalic polyester resin (Crystic 489/Y0530, Scott-Bader Ltd) and a 70% weight E glass fibre reinforced vinyl ester resin (Derakane 411, Dow Chemicals) manufactured using the Seamann Composites Resin Infusion Moulding Process (SCRIMP).

Gravimetric measurement

Gravimetric measurements were performed by removing the samples from the ageing environment, water at 60°C for CFRP structures and water at 30°C for GRP structures, rapidly blotting and weighing them. The times for the weighing experiments were assumed to be sufficiently short not to influence the values of the mass measured.

Dielectric Spectroscopy

High frequency dielectric measurements of adhesively bonded CFRP structures were carried out in reflection mode over the frequency range 300kHz to 3GHz using a Hewlett Packard 8753A Network analyser (Fig.1). Time domain response (TDR) data were obtained by using the network analyser's inverse Fourier transformation over the frequency range.

Low frequency dielectric spectroscopy measurements of GRP structures were carried out using a computer controlled frequency response analyser (Schlumberger 1250A) allowing measurements at frequencies between 10^{-4} and 10^{5} Hz. A capacitor was formed by evaporating a layer of metal on the surfaces of the sample (Fig. 2a). High frequency measurements of GRP structures were performed using an open ended cylindrical coaxial line sensor and a vector network analyser, Hewlett Packard 8720C, which allowed measurements to be made over a frequency range of 0.05 GHz to 5 GHz. The probe used was a 15-mm diameter GR900-L15 connector (Fig. 2b). The system was operated in reflection mode.

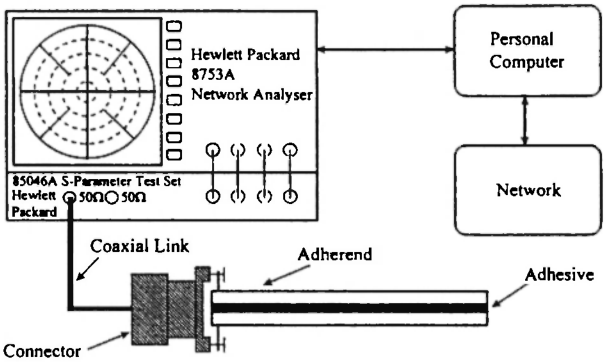


Fig. 1: Set up for dielectric spectroscopy measurement of adhesively bonded composite joint.

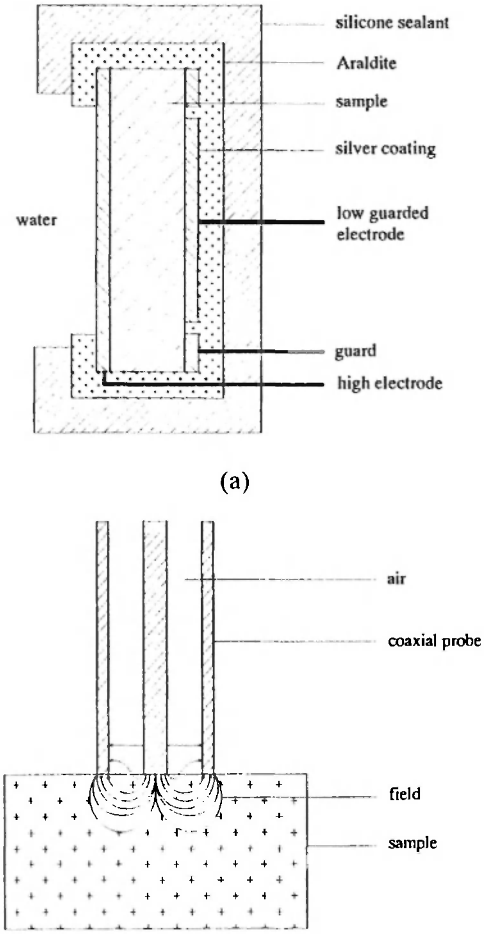
RESULTS AND DISCUSSION

Adhesively Bonded Carbon Fibre Reinforced Composites

Figure 3 presents the gravimetric results for the joint structure, the CFRP adherents alone and the adhesive. From these results, it is possible to dissociate the amount of water in the adherent from the amount of water absorbed by the adhesive.

The time difference between two neighbouring peaks is related to the effective permittivity $\bar{\varepsilon}$ of the material between the wave-guides by /6/:

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



(a)

(b)

Fig. 2: Set up for (a) low frequency and (b) high frequency dielectric spectroscopy measurement of GRP structures.

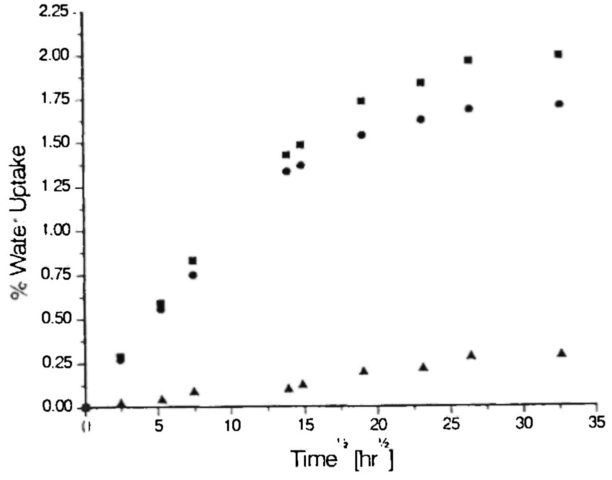


Fig. 3: : Water uptake of (■) the joint structure, (●) the CFRP adherents and (▲) the adhesive.

where c is the velocity of light in vacuum, l is the physical length of the joint and Δt is the time difference between the impulse peak and the first response peak. Figure 4 shows the displacement of the response peaks towards longer response time values during ageing. This is caused by the evolution of the dielectric permittivity of the adhesive due to the absorption of water which decreases the electrical wave velocity, consequently increasing the response time.

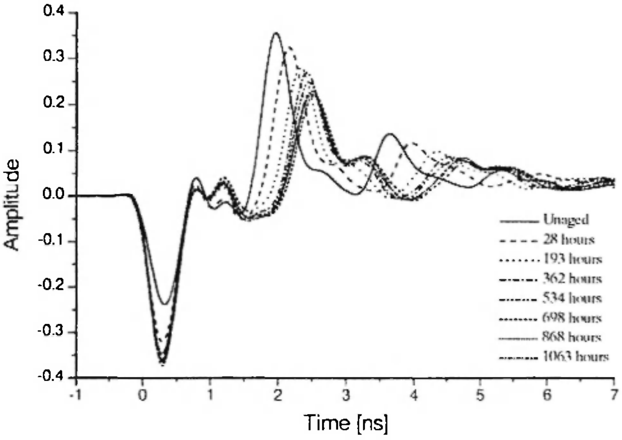


Fig. 4: Evolution of the TDR during ageing.

A high correlation coefficient (0.96) between the evolution of the average dielectric permittivity and the gravimetric results shown in Figure 5 confirms that water penetration in adhesively bonded structure could be assessed by high frequency TDR measurement.

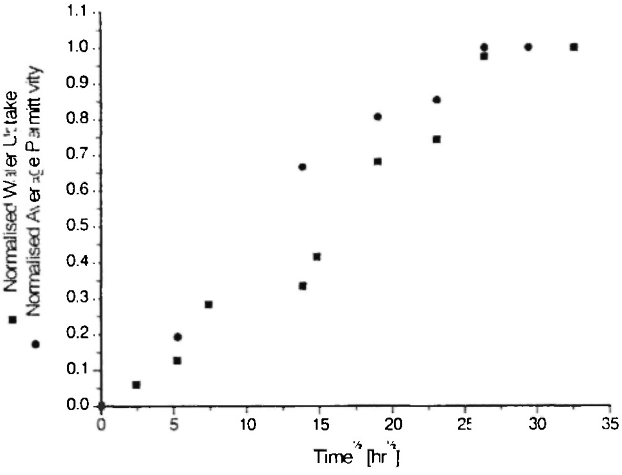
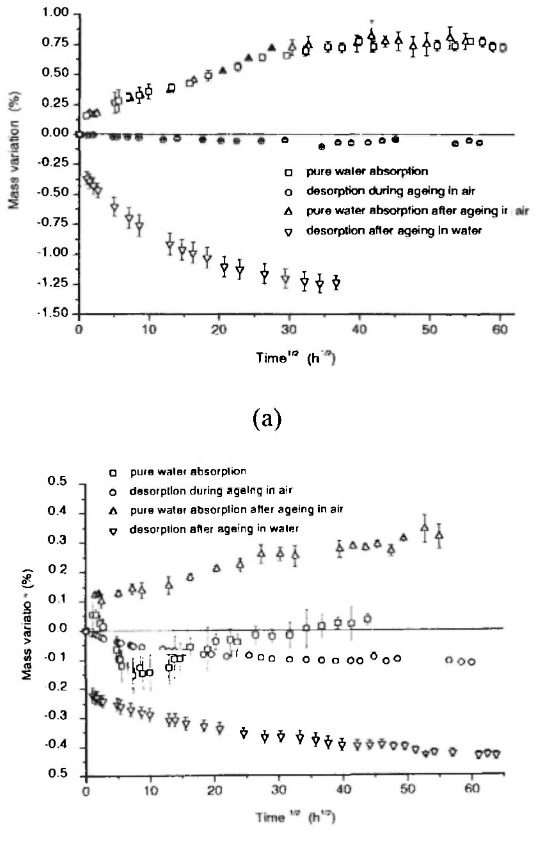


Fig. 5: Correlation between water uptake and average dielectric permittivity.

Glass Fibre Reinforced Composites

As shown in Figure 6, samples aged in air lost some low molar mass material. The apparent larger amount of water lost by the polyester laminate during desorption implies a loss of unreacted monomer and degradation (Fig.6a). Hydrolysis of the resin is one possibility and is supported by the observation of blistering and a change in colour of the laminate. The absorption curve of the vinyl ester laminate (Fig.6b) shows that the amount of water desorbed after ageing in water equals the amount absorbed after ageing in water added to the loss in weight during ageing in air. This implies that no leaching is occurring during exposure to water.



(a)

(b)

Fig. 6: Sorption of (a) polyester and (b) vinyl ester GRP structures.

The Kirkwood-Fröhlich equation, which describes the dielectric response of dipoles in condensed material, has the form /7,8/:

$$\frac{(\varepsilon_S-\varepsilon_\infty)(2\varepsilon_S+\varepsilon_\infty)}{\varepsilon_S(\varepsilon_\infty+2)^2}=\frac{4\pi N}{9kT}g\mu_0^2$$

where ε_∞ is the dielectric permittivity at a frequency so high that dipole orientation contributions have vanished, k is the Boltzman constant, T is the temperature, N is the number of molecules per unit volume, μ_0 is the dipole moment of the molecule and g is the orientation correlation function. Water uptake can be assessed by assuming that the variation in the dielectric permittivity during exposure is caused by the increasing number of water dipoles. Comparison of low and high frequency dielectric data allows differentiation between water molecules free to rotate and those undergoing interactions with the resin since the former rotates at a frequency of about 10 GHz whereas the latter relaxes at frequencies in the 10 kHz region /4/.

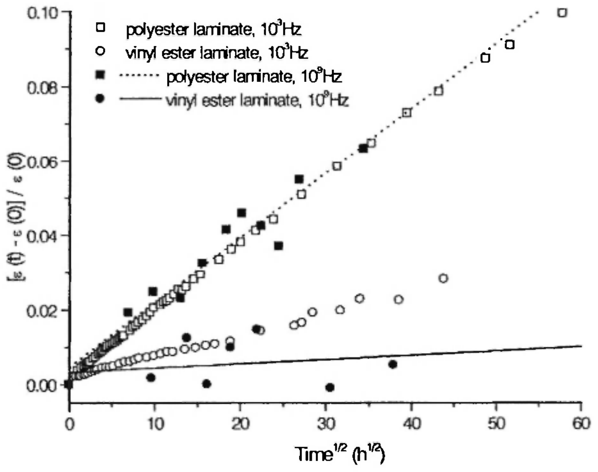


Fig. 7: Dielectric permittivity of polyester and vinyl ester laminates at 10^3 Hz and 10^9 Hz.

As shown in Figure 7, the dielectric permittivity increment of the polyester laminate increases for a longer time than that required for the gravimetric measurement to reach equilibrium. The similarity between the 10^3 Hz and 10^9 Hz increments implies that a pseudo-equilibrium is actually observed in the gravimetric measurement between water uptake and leaching of compound. Most of the water present in the polyester laminate is in a free state whereas free water in the vinyl ester laminate is limited. This is in agreement with the previous results that showed debonding and blistering in the polyester laminate, creating space for the water to cluster, whereas none of these degradation processes seemed to occur in the vinyl ester, agreeing with the absence of free water. Comparison of the high and low frequency data provides an assessment of the distribution between free and bound states.

CONCLUSIONS

The study on adhesively bonded CFRP structure has established that non-isotropic adherents can provide good wave-guides for electrical wave propagation. Correlation between TDR and gravimetric data validated the use of TDR to relate the change in the dielectric permittivity of the bond line to the water uptake of the adhesive. This study demonstrated the potential of high frequency dielectric TDR as a NDE method to assess the water uptake of the bond line present in bonded structures. Further work is currently being done to relate TDR measurements to the evolution of the mechanical characteristics of the joint.

The study on GRP structures showed the possibility of developing an in-situ monitor for water diffusion in resistive polymeric materials. The main limit in using low frequency measurement is the formation of the capacitor that cannot be applied in real conditions. The limit of high frequency measurement is that it only measures the free water present in the material. These limitations are currently being investigated in an attempt to develop an instrument able to make in-situ measurement using low frequency measurement (10^5 Hz) combined with a high frequency probing technique.

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