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### Use of dielectric spectroscopy to assess adhesively bonded composite structures, Part II: Dielectric study

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## USE OF DIELECTRIC SPECTROSCOPY TO ASSESS ADHESIVELY BONDED COMPOSITE STRUCTURES, PART II: DIELECTRIC STUDY

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*A study of the sorption and desorption of moisture in a structural adhesively bonded composite structure using low- and high-frequency dielectric spectroscopy is reported when the adhesive is subjected to a hot and wet environment. As water penetrates the structure, variations in the dielectric permittivity and dielectric loss can be used to understand the nature of the absorption process. A new dielectric tool is introduced to aid interpretation of the dielectric data based on the Kirkwood-Fröhlich equation of the dipolar activity. The data are correlated with gravimetric and dynamic mechanical thermal analysis of the adhesive during exposure to moisture reported in Part I of this series of three articles.*

**Keywords:** Bonded structures; Composite structures; Joints; Adhesive; Moisture; Dielectric spectroscopy.

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## INTRODUCTION

Dielectric spectroscopy (DS) is an extremely effective method of characterising, over a very large frequency range, the molecular dynamics of liquids and solids containing mobile polar groupings. The technique is sensitive to the orientational motions of permanent dipoles contained in the material and the translational contribution of ions due to the applied electric field. Over the past 2 decades, the DS method has been extensively used for the characterisation of polymeric materials and, in particular, for the study of the cure process in thermosets [1–5]. The development of interdigital electrodes as embedded probes has provided new insight and in situ information into the processes associated with cure [6]. In principle, the DS technique can provide detailed information on the dipolar activity of the material investigated. In certain systems ionic conduction may, however, give rise to larger contributions and, in the fluid state, mask the dipole processes. However, in semi rigid solids these ionic conduction processes are suppressed, and dipole relaxation is the dominant cause of the frequency dependence of the electric properties. The technique is ideally suited to the investigation of the motion of a polar substance such as water. Over the last 20 years, Mashimo and coworkers [7–10] have investigated the dynamics and structure of water in biological materials and polymers in solution. They have successfully identified relaxation processes associated with 2 different states of water which they designate “free” and “bonded”. Eadline and Leidheiser [11] and Kolek [12] used the DS method to determine the water penetration in polymer coatings on metal substrates. However, the evolution of computer-controlled network analysers has allowed the determination of the dielectric characteristics of adhesively bonded metallic structures as well as the effect of water ingress on such structures [13, 14].

In this article results are presented on adhesively bonded composite joint structures. The aim of this investigation is to demonstrate that the success achieved over the past 10 years in the study of metallic structures can be transferred to the increasingly used composite structures.

## EXPERIMENTAL PROCEDURE

### Materials

The adherends were manufactured from unidirectional carbon fibre preimpregnated epoxy film (trade name 914C-TS-5-34) supplied by Hexcel Composites. The preimpregnated film contains 66 wt % of high

tensile Torayca surface-treated carbon fibres. The adhesive film used is supported by a polymeric woven film and is a blend of approximately 70% of bis[2-chloro-N,N-bis(2,3epoxypropyl)-4-aminophenyl]methane and 30% of diglycidylether of bisphenolA which was cured with about 3–7.0% of dicyandiamide and between 0.5 and 1.5% of (N,N'-(methyl-1,3-phenylen)bis (N,N'dimethylurea)).

## Manufacturing

Carbon fibre prepreg layers were used to produce a series of different lay-up designs using a vacuum bag procedure in an autoclave. Curing was achieved at a temperature of 170°C under a pressure of 7 bar. A post cure at 190°C for 4 h was performed. Joints were manufactured by joining two carbon fibre reinforced plastic (CFRP) plates with a lay-up of adhesive films. The assemblage, placed in an autoclave chamber, was cured using a vacuum bag system at a temperature of 125°C and a pressure of 2 bar for 1 h. The final system was a single lap joint made of 150 mm length, 50 mm width, and 1.8 mm thick CFRP plates bonded over a 10 mm wide overlap by a 1 mm thick adhesive.

## Gravimetric Measurements

As soon as the samples were manufactured, they were placed in a desiccator at room temperature in order to avoid absorption of moisture. Gravimetric measurements during ageing were performed by removing the samples from a water bath held at a constant temperature of 60°C and rapidly blotted and weighed using an electronic balance (Mettler AJ100) with an accuracy of  $\pm 0.1$  mg. The times for the weighing experiments were assumed to be sufficiently short so as not to influence the values of the mass measured.

## Dielectric Measurements

The dielectric technique was based on one of two different methods, depending on the frequency range used. At low frequency (0.1 Hz to 65 kHz) the impedance measurement was used. At high frequency (300 kHz to 0.3 GHz) the method was based on the transmission line principle, in which an electromagnetic wave is propagated along the bonded structure. In each technique, no external nor embedded electrodes were used. The bonded structure acts as a capacitor where the adhesive is the dielectric and the carbon fibre (CF) composite laminates are the electrodes. The percentage in weight of CF and conductivity of each was high enough to produce percolation and an

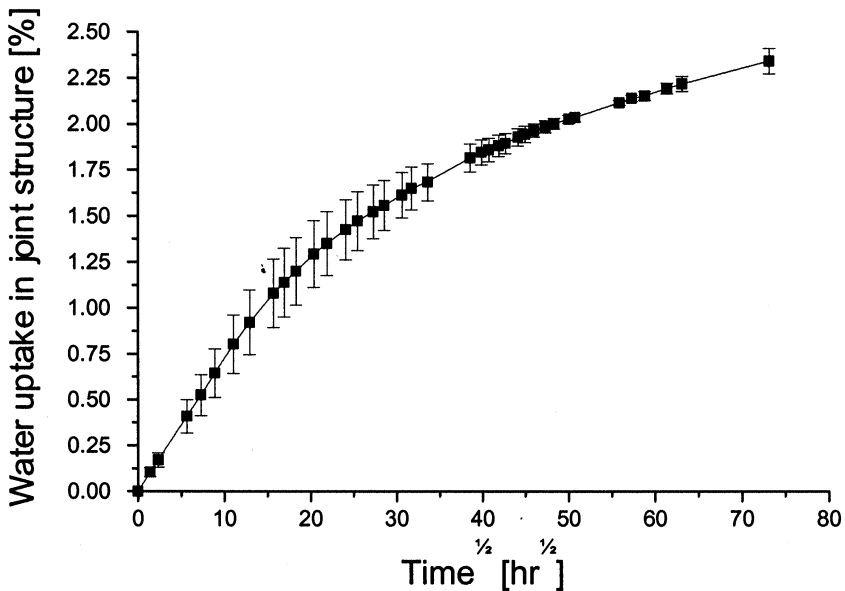
electrical path through the thickness and along the electrode. The geometry of the joint was designed to match the impedance at any frequency, especially in the transmission line procedure [19]. Each technique is capable of providing dielectric permittivity and dielectric loss data on the materials under investigation. Details of the measurements can be found elsewhere [15–19].

## RESULTS AND DISCUSSION

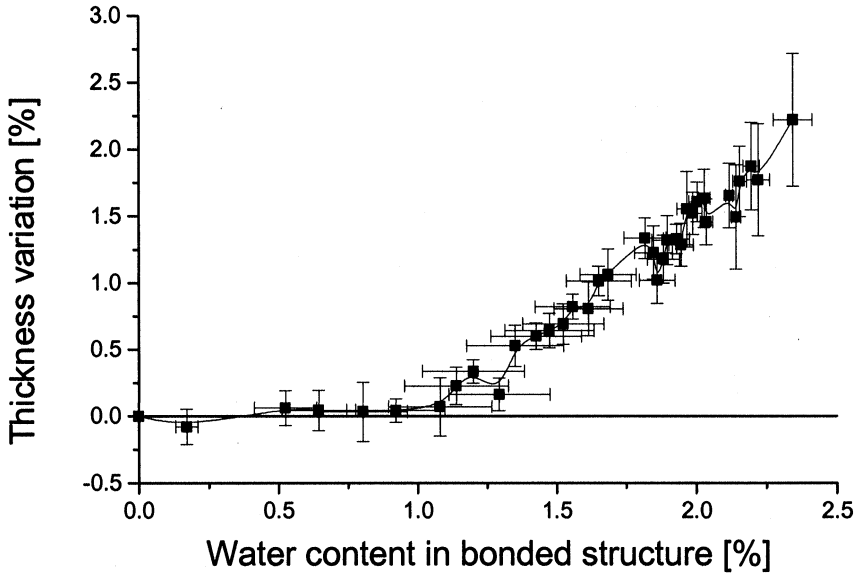
### Water Uptake Behaviour

Figure 1 presents the water content evolution in the adhesively bonded joint as a function of the exposure time. The specimens have spent 5350 h immersed in water at 60°C.

The trace indicates that the water absorption process follows non-Fickian behaviour. This type of behaviour is expected as there will be only a small surface of the adhesive exposed to the moist environment. The water uptake in such a bonded structure is mainly driven by the absorption in the CFRP adherends. Once the adherends are at pseudo-equilibrium, the adhesive starts to absorb moisture from the interface.



**FIGURE 1** Water content in the adhesively bonded structure as a function of the exposure time.



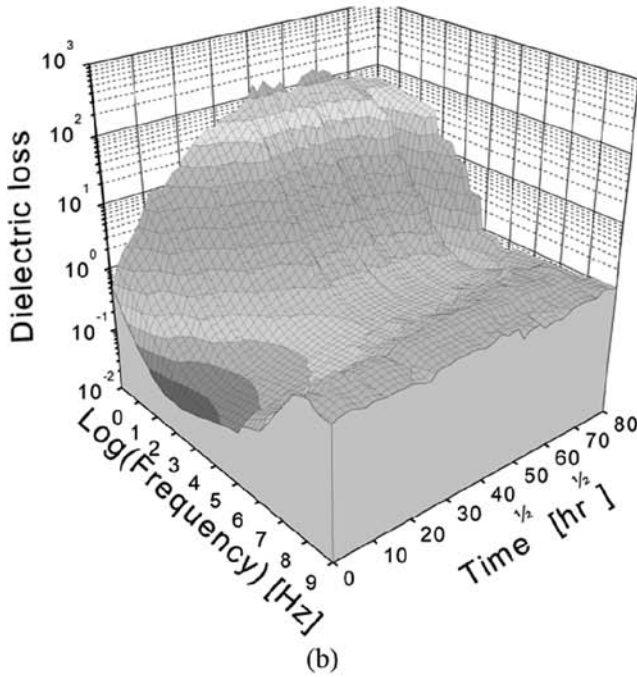
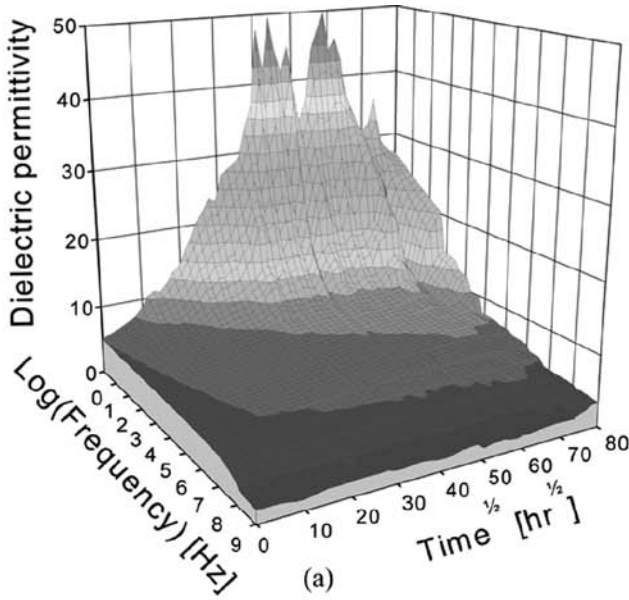
**FIGURE 2** Evolution of the thickness of the bonded structure as a function of water content in the joints.

In conjunction with gravimetric experiments, measurements of the thickness of the adhesively bonded structure were carried out. Figure 2 shows the variation of the thickness of the joints as a function of the water content in the bonded structure.

The thickness does not change initially, but once a moisture content of approximately 1.25% has been exceeded swelling of the joint is observed and it continues linearly with time. In the first stage of moisture absorption, water enters the polymer and fills micro and macro voids without changing the volume. Subsequently, as the water content increases and all the voids are filled, the water molecules start to penetrate the dense crosslinked network and swell the matrix, producing a water front which progresses through the bulk of the material [20–22].

### Effect of Water on the Dielectric Spectroscopy

Dielectric spectroscopy data were collected at regular intervals over 9 decades of frequency. Figures 3a and 3b show the evolution of the dielectric permittivity and dielectric loss, respectively, as a function of the exposure time and frequency. The dielectric permittivity and loss

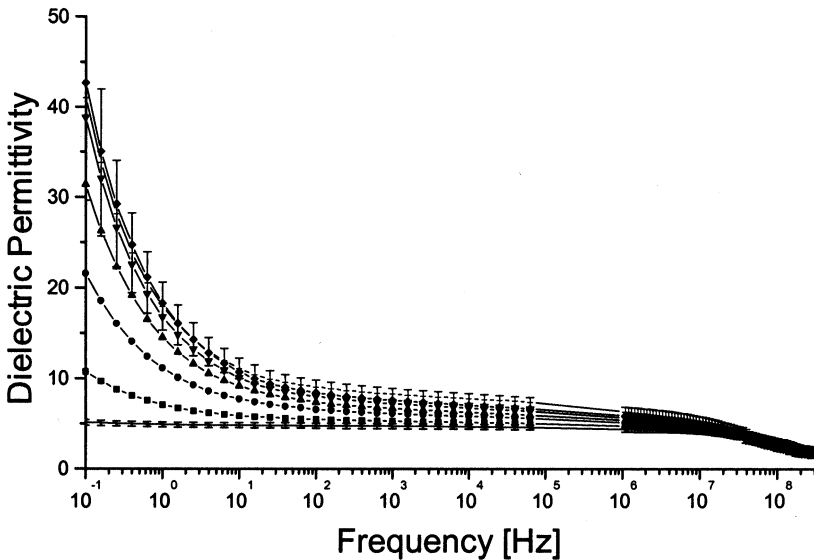


**FIGURE 3** 3D representation of (a) the dielectric permittivity and (b) the dielectric loss as a function of the frequency and exposure time (see Color Plate III).

give information concerning the polarisability of the medium and allow investigation of the relaxation processes associated with water permeation and conductivity phenomena. Figure 3b shows that two separate relaxation processes can be identified, one at high frequency and one at low frequency. The ingress of water molecules which have a high static permittivity ( $\epsilon_S \approx 80$ ) increases the dielectric permittivity with exposure time.

Figures 4a and 4b represent the evolution of the dielectric permittivity and loss, respectively, as a function of frequency.

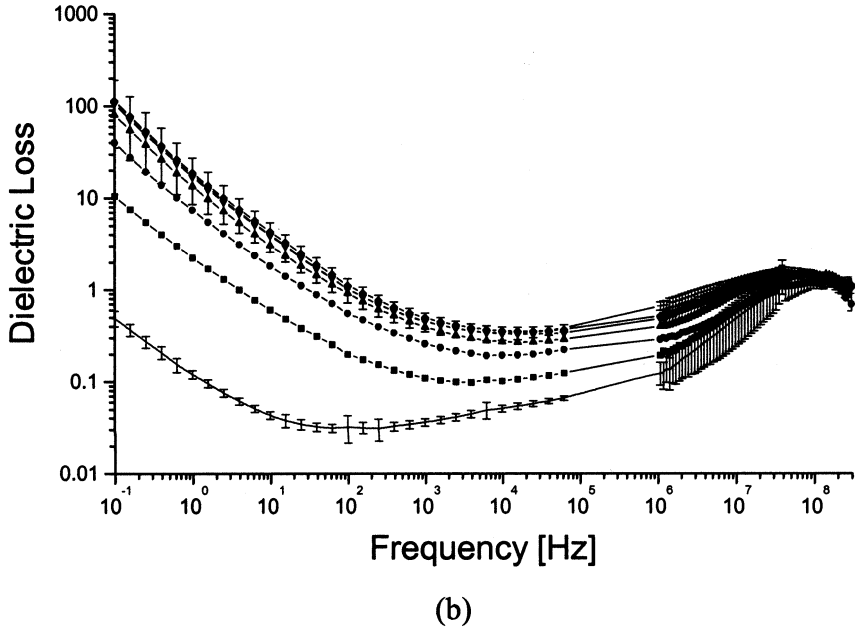
As the time of exposure increases, there is a large increase in the permittivity at low frequency. No significant variation occurs in the higher range of frequency. Indeed, up to 580 h the permittivity is, within experimental error, identical with that of the unexposed material. As exposure to the humid environment continues, departure from the initial value occurs. Water molecules will exhibit different relaxation processes dependent on their interaction with the surrounding environment [23]. Relaxation processes for water molecules free to rotate occur in the GHz region, whereas water molecules



(a)

**FIGURE 4** Dielectric (a) permittivity and (b) loss as a function of the frequency during exposure: (—) as manufactured, (—■—) 122 h, (—●—) 580 h, (—▲—) 1,007 h, (—▼—) 1,590 h, (—◆—) 2,019 h, and (—⊠—) 5,350 h.





**FIGURE 4** (Continued).

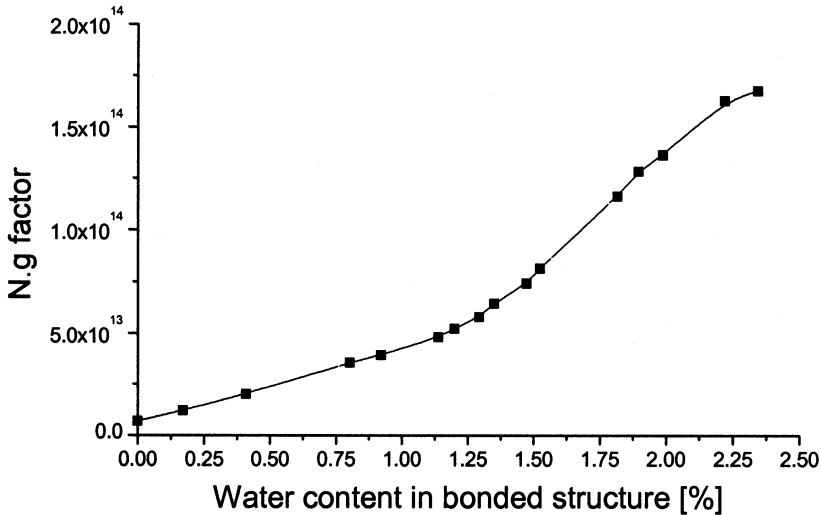
undergoing hydrogen-bonding interactions exhibit relaxation processes which stretch down to the kHz region. The two states of water are commonly named *free water* and *bonded water*, respectively. At the end of the ageing process, the water molecules may be expected to exist in both free and bound states. Figure 2 indicates that there is no increase of the thickness up to 1.25% water absorption. It is thus believed that the micro voids filled by the water up to this stage are small enough to enable only a few molecules to enter the cavities. These molecules are either bonded to the polymer at the surface of the voids, are constrained in their ability to move by the volume they occupy, or are interacting with other water molecules [23]. The initial large increase in permittivity at low frequency should not be associated with dipolar activity but should be associated with the movement of mobile ionic charges in the adhesive towards the electrodes. These ionic charges are related to species such as sodium chloride generated by the epichlorohydrin during the manufacture of the epoxy resin. It has to be said that other charged entities such as protons and hydroxyl ions could be responsible for the large increase in the low frequency range. However, commercial epoxy adhesives do

have high chloride ion content, which would not be the case in the electrochemical grades used in the electronic industry. It is well known that the reduction of chloride ion content reduces intrinsic conductivity and sensitivity to water [24]. Another possible source of charged species would be the unreacted low molar mass materials which arise from the decomposition of dicyandiamide as it reacts with the epoxy. Dicyandiamide and these degradation products can dissolve in hot water [25]. These small ionic species can migrate in the presence of an applied field and create a space charge near the electrodes or migrate within voids and microcavities. These processes lead to large dielectric loss contributions and are identified with blocking electrodes or the Maxwell-William-Sillars (MWS) effects [26, 27]. It is rather difficult to identify the exact process involved in the low frequency range; besides, it is not the focus of this study to determine an absolute value for the low frequency behaviour but rather to observe differences between dielectric properties at different values of moisture content.

The Kirkwood-Frölich equation [28, 29] relates the dielectric permittivity,  $\epsilon_s$ , of a material to the number of dipoles per unit volume,  $N$ , present in that material:

$$\frac{(\epsilon_S - \epsilon_\infty)(2\epsilon_S + \epsilon_\infty)}{\epsilon_S(\epsilon_\infty + 2)^2} = \frac{4\pi\mu_0^2}{9kT}Ng, \quad (1)$$

where  $\epsilon_\infty$  is the dielectric permittivity at very high frequency and a constant,  $g$ , is the orientation correlation function and a measure of the constraints applied to the rotation of the dipole in the material,  $k$  is Boltzmann's constant,  $T$  is the temperature, and  $\mu_0$  is the dipole moment of the molecule. The  $g$  factor indicates the nature of the interactions between the water molecule and the surrounding matrix. The permittivity changes that occur at high frequency can be attributed purely to the effects on the dielectric characteristics due to the presence of water molecules and can be separated from the lower frequency processes associated with charge migration. Therefore, water uptake could be assessed by assuming that the variation in the dielectric permittivity of a material during exposure to water is caused by a variation in the number of dipoles present and their interaction with the matrix [30]. The dielectric characteristics of the adhesively bonded structure can be expressed in terms of dipolar interactions by the product  $Ng$ , termed the *Ng factor*, which represents the number of dipoles present in the material and their interaction with the surroundings.



**FIGURE 5** Evolution of the  $Ng$  factor as a function of the water content in the joint structure.

In terms of exposure time, the  $Ng$  factor provides information on the number of dipoles in the material. Figure 5 depicts the  $Ng$  factor as a function of the water content and, therefore it is a representation of the dielectric characteristics versus the number of water molecules contained in the joint.

Two types of behaviour can be identified by separating the graph into regions above and below 1.25% water content. Below 1.25% water content, the water enters the polymeric materials and exhibits pseudo-Fickian diffusion behaviour. Above 1.25% water content, the mechanism of diffusion changes and a different slope reflects a change in the dipole interaction and a change in the local ordering factor,  $g$ .

Below 1.25% water content, the water molecules penetrate the medium in such a way that they fill the voids and free volume without changing the physical dimension of the structure and behave as single dipoles with a  $g$  factor that approaches 1. Above 1.25%, the water molecules exhibit a greater degree of interaction with either themselves or the polymeric network. These molecules swell the resin structure and form strong bonds with the polymer at hydrophilic sites. Water molecules will also form clusters in macro voids. As the number of interactions between the water dipole and its surroundings increase, so the  $g$  factor will also increase and produce a change in the slope of the graph.

## CONCLUSION

Dielectric spectroscopy of adhesively bonded composite structures proves to be an efficient method of gaining information concerning the state of water in the adhesive layer. Dielectric relaxation processes have been identified which may be correlated with changes in the morphology induced by ingress of water into the adhesive. Moreover, some new insight has been gained concerning the interaction of water within the adhesive, and a new tool is proposed to aid understanding of the changes in the dipolar activity, termed the “ $N_g$  factor,” as absorption of moisture occurs. The  $N_g$  factor allows interpretation and separation of plasticisation from clustering processes.

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