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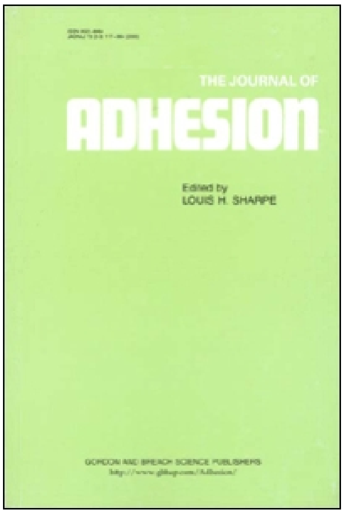

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B. J. Nairn[a]; P. A. Dickstein[a]; D. J. Plausinis[a]; J. K. Spelt[a]
[a] Department of Mechanical Engineering, University of Toronto, Ontario, Canada

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Dielectric Response of Adhesive Joints to Water Absorption

B. J. NAIRN, P. A. DICKSTEIN, D. J. PLAUSINIS and J. K. SPELT*

Department of Mechanical Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario, M5S 1A4, Canada

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Dielectric measurements have been used to infer the average moisture content of aluminum adhesive joints bonded with three commercial epoxy adhesives. Measurements were made on both aluminum-adhesive-aluminum joints and aluminum-adhesive specimens in order to assess the influence of moisture diffusion gradients. Similar experiments were also performed with foil electrodes embedded in the bondline. For average water concentrations less than approximately 2%, there existed a linear relationship between the permittivity and the average moisture level which was independent of the spatial nonuniformity produced by water diffusion. At higher moisture levels, the dielectric response varied considerably from one adhesive to another, but, in general, could be approximated as a linear dependence on the average moisture concentration. The dielectric response was recoverable upon drying.

KEY WORDS adhesive joints; permittivity; dielectric; water concentration; epoxy adhesives; aluminum adherends.

INTRODUCTION

The durability of an adhesive joint is strongly affected by the absorption of water from the service environment.[1] Numerous studies have been made of the relationships between joint properties, such as strength, and the time of exposure to hot-wet environments under various mechanical loading conditions.[1] This type of experiment would be facilitated by the development of methods for the *in situ* measurement of the amount of absorbed water which do not require the weighing of the test specimen. Furthermore, if such methods could be applied to bonded structures in service, it may be possible to use the time history of the water absorption levels to predict better the integrity of the joint.

The objective of the present work was to examine the feasibility of measuring the moisture content of adhesive joints by means of dielectric measurements utilizing conducting adherends and embedded foils as the electrodes. Particular emphasis was placed on the investigation of techniques which may allow *in situ* measurements, applicable to both complete structures and laboratory test specimens.

Dielectric measurements have been used to monitor the curing process in adhesive joints[2] and epoxy resins,[3,4] to study water absorption in epoxy resins and composites,[5–8] and to detect flaws in joints.[9] The application of the approach to the measurement of water absorption in adhesive joints is complicated by the influence of concentration gradients and the possible presence of two forms of water, bound (chemisorbed) and free (bulk water in cavities),[10] both of which give different dielectric responses. Furthermore, commercial structural adhesives often contain inorganic filler particles which can affect water absorption and the dielectric properties.

DIELECTRIC SPECTROSCOPY

The response of a nonconducting material to an applied electric field is governed by the dielectric properties. For parallel-plate electrodes connected to an alternating current, the capacitance, C^*, is related to the complex permittivity, ε^*, by

$$C^* = \varepsilon^* \varepsilon_0 A/d \tag{1}$$

where A is the area of each electrode, d is the distance between the electrodes, and ε_o is the permittivity of free space, 8.854×10^{-12} F/m. The complex permittivity may be expressed as

$$\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \tag{2}$$

where $\varepsilon'(\omega)$ is the permittivity, $\varepsilon''(\omega)$ is the dielectric loss, and ω is the frequency. The permittivity of a pure material is a function of the structure and state of its molecules, particularly the ability of permanent dipoles to respond to an applied electric field.[11] It is also dependent on both the frequency of the electric field and the temperature, and there exists a frequency (and temperature) at which the dipoles will be unable to reorientate in response to the alternating field. This is the relaxation frequency above which the dipoles no longer contribute to the dielectric response, thereby causing a decrease in the permittivity, ε', and a maximum dielectric loss, ε''.

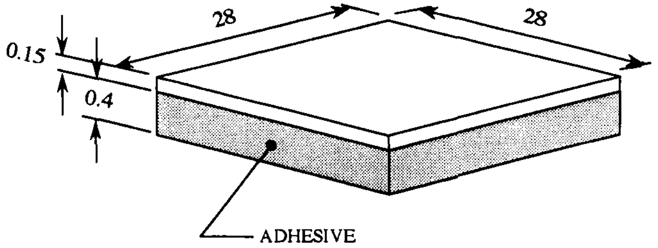
The dielectric properties of a heterogeneous material are described approximately by a mixture relationship, which is dependent upon the amount, shape (*e.g.* fibres, flakes, clusters), and dielectric properties of the constituent materials.[12] This assumes that the constituent materials do not interact with each other. Although water absorbed in an adhesive will interact, the following linear mixture rule has been found to describe adequately how the permittivity of the mixture varies with water uptake in several resins at low moisture levels[5]

$$\varepsilon'_m = aV_w \varepsilon'_w + (1 - V_w)\varepsilon'_p \tag{3}$$

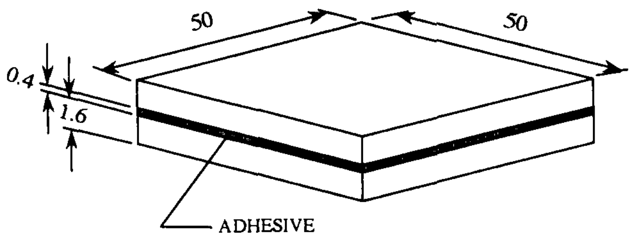
where a is a proportionality constant such that $a\varepsilon'_\omega$ is the apparent permittivity of the absorbed water, V_w is the volume fraction of the water, and ε'_p is the permittivity of the epoxy.

EXPERIMENTS

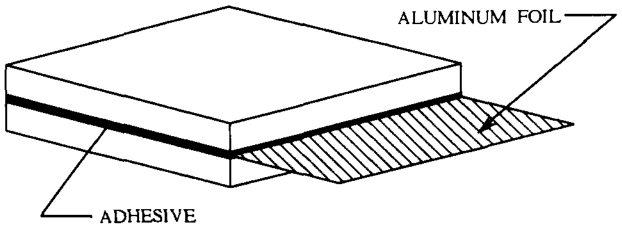
Experiments were performed to investigate the effect of moisture content on the dielectric response of structural adhesive joints. Three different types of specimens



(a) 1-D Sample



(b) 2-D Sample



(c) Embedded Foil Sample

FIGURE 1 Specimen geometries (all dimensions in mm): a. 1-D diffusion specimen, b. 2-D diffusion specimen, c. embedded foil specimen.

(Figure 1) were bonded using three different epoxy adhesives and FPL-etched (ASTM Standard Test Method D-2651, Method G) aluminum adherends. It is recognized that, although aluminum is not a standard electrode material it is a commonly used joint adherend, and in the present experiments is actually bonded to the dielectric material (adhesive) so that interfacial contact resistance is minimized. The effects of water diffusion gradients were isolated by comparing the average dielectric response for one-dimensional (1-D, Figure 1a) and two-dimensional (2-D, Figure 1b) specimens. The 1-D specimens were used to provide an unambiguous correlation between moisture content and permittivity for a particular adhesive system. The embedded foil specimens (Figure 1c) were used to demonstrate the feasibility of bondline dielectric sensors for moisture determination. Table I shows the test matrix of adhesives and specimen geometries which was used.

The 1-D specimens were made by casting 0.4 mm of adhesive onto an AA7072-H22 aluminum sheet and then cutting individual coupons (28 mm square) from the larger piece using a sharp steel knife. The adhesive and sheet were sandwiched between 12.5 mm aluminum plates, one of which was coated with a mold release agent which was subsequently washed from the cured adhesive surface. The 2-D specimens consisted of two sheets of 1.6 mm thick 6061-T6 aluminum bonded with 0.5 mm of adhesive and cut to the final dimensions (50 mm square) using a carbide-tipped circular saw. The embedded foil specimen was essentially a 2-D specimen with a rectangular piece (11 × 25 mm or 14 × 25 mm) of AA7072-H22 aluminum foil in the middle of the bondline. The sizes of these specimens were chosen to give a capacitance of approximately 55pF assuming an error in the capacitance measurement of less than 2 pF.

Permabond E-04 (Permabond Int'l, Englewood, NJ, USA) is a two-part epoxy which was cured at room temperature for 24 hours. Permabond ESP-308 is an aluminum-filled, single-part epoxy which was cured at 140 °C for 2 hours, while Cybond 4523 GB (American Cyanamid, Havre de Grace, Maryland, USA) is a single-part epoxy, with a relatively large amount of mineral filler (approximately 45% by weight) and glass spacer beads, which was also cured at 140°C for 2 hours.

All specimens were immersed in a 70°C distilled water bath for periods up to 250 days, and moisture absorption was calculated from the weight gain of each sample. The weight gain due to aluminum oxide growth was accounted for using samples of FPL-etched aluminum that were immersed along with the three adhesive joints. The joints were assumed to be dry in the as-cured state, at which time the initial dielectric measurements were made.

Before weight gain and dielectric measurements were made, all samples were removed from the bath and placed under a forced flow of room temperature air for 30 minutes. This removed unabsorbed surface moisture and ensured that the specimens were at room temperature.

Dielectric measurements were performed over a frequency range of 240 Hz to 20 kHz using a GenRad GR1688 Precision LC Digibridge (GenRad Inc., Concord, Mas-

TABLE I
Experimental test matrix of adhesives and specimen geometries

Adhesive	Specimen Geometry 1-D	 2-D	 Embedded Foil
Permabond E-04	X	X	X
Permabond ESP-308	X		X
American Cyanamid 4523GB	X	X	

sachusetts). The aluminum adherends were used as electrodes in all cases. The additional electrode required for the 1-D samples was provided by applying a conducting silver paint[13] to the adhesive. This meant that the specimens could not be used again in the water bath. Electrical contact was made with each electrode by means of a spring clip having a sharp point to penetrate the aluminum oxide film. In addition, the dielectric properties of several 2-D specimens were measured over an extended frequency range of 20 Hz to 2 MHz by using specially-built instrumentation.

To investigate the reversibility of the dielectric response to moisture content, a 1-D E-04 specimen was dried in a desiccator and a vacuum oven after the water absorption experiments had run for 22 days.

After each time interval, three 2-D or 1-D specimens were weighed and the permittivities were measured. The 2-D specimens were then returned to the bath while the 1-D specimens were removed from the experiment because they had been coated on one side with the silver electrode paint. Two batches of specimens were used for each set of 1-D and 2-D experiments. The 1-D experiments were typically conducted over immersion periods of up to 30 days , while the 2-D experiments ran for periods of up to 8 months.

RESULTS

Dielectric measurements displayed an initial transient response following the connection of the leads. The amplitude of the transient was a function of the moisture content, but it always less than 5% of the steady state value reached after a standardized waiting period of 5 minutes.

Figure 2 shows the moisture content as a function of time for the 1-D and 2-D specimens of E-04 and 4523GB. As expected, the 1-D specimens (Figure 2a) saturate relatively quickly at 3% for E-04 and 3.5% for 4523GB. Note that there is considerable variability in the the rate of water uptake between the two batches of 4523GB, and that the E-04 specimen absorbed water faster than the 4523GB specimens. The 2-D 4523GB specimens (Figure 2b) showed no evidence of saturation after almost 250 days in the water bath and an average moisture content of 5 to 7%. In contrast, the 2-D E-04 samples (Figure 2c) reach an initial saturation level of approximately 2.2% before continuing to gain water. A similar type of two-stage water uptake, in which Fickian diffusion is followed by water ingress through microcracks, has been documented in several epoxies[14–16] and in polycarbonate.[17] If the first and second stages overlap, the saturation plateau may not be apparent. It is believed that this may be the reason for the absence of any saturation with the 2-D 4523GB specimens (Figure 2b).

The frequency dependence of the permittivity, ε', and the dielectric loss, ε'', are shown in Figure 3 for moist 2-D specimens of Cybond 4523GB. All other specimens showed a similar frequency response, such that ε' and ε'' increased with moisture content, with the difference in ε' between wet and dry specimens being greater at lower frequencies. At 10 kHz, the standard measurement frequency used in this study, the permittivity was essentially independent of frequency.

The relationship between the moisture content (percentage by weight of water in adhesive) and the permittivity at a fixed frequency is illustrated in Figure 4 for 1-D samples of Permabond E-04 measured at 10kHz. The lines through the data are linear

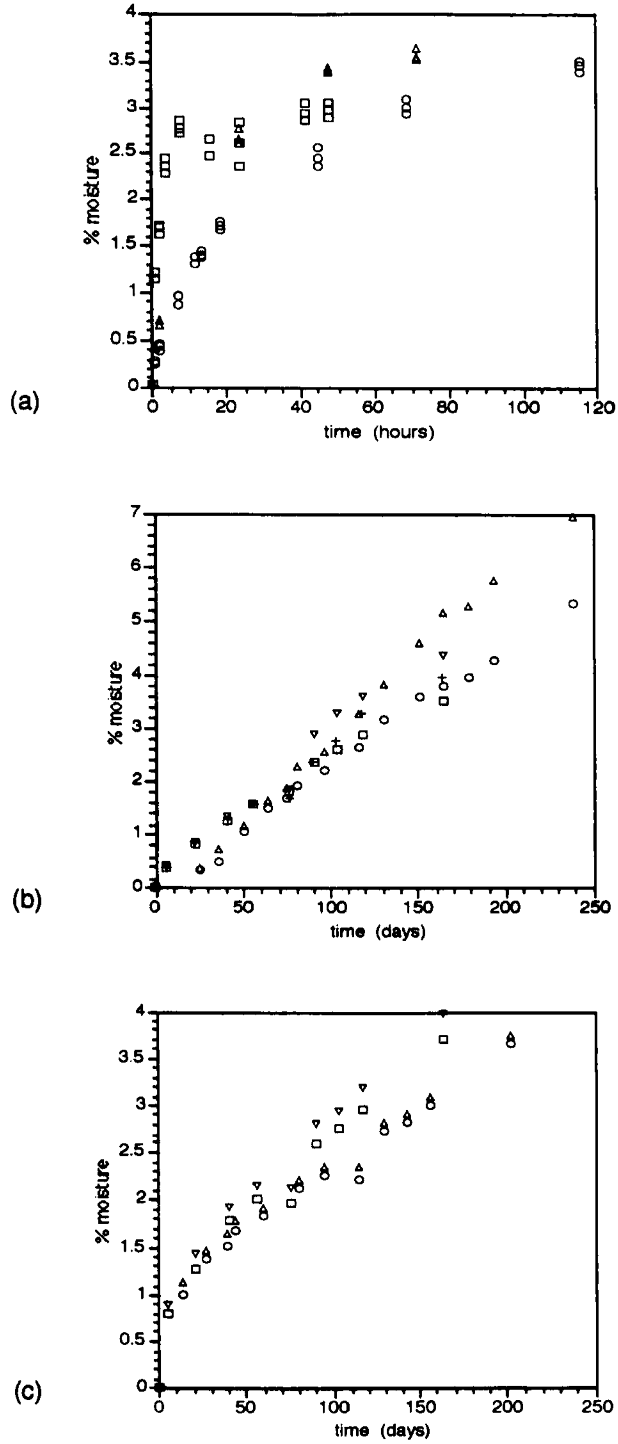


FIGURE 2 Water content of adhesive as a function of immersion time in bath: a. (Δ)(○) 2 batches of 1-D 4523GB and (□) 1 batch of E-04, b. (○ Δ) (▽ + □) 2 batches of 2-D 4523GB, c. (○ Δ) (□ ▽) 2 batches of 2-D E-04.

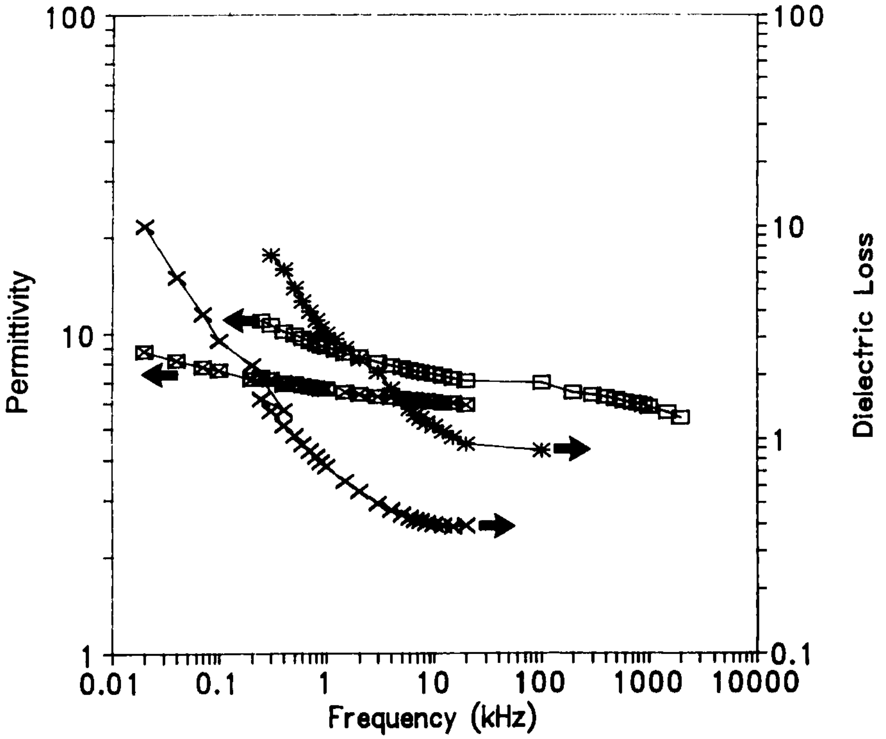


FIGURE 3 Average permittivity (ε') and dielectric loss (ε'') *versus* frequency for 2-D Cybond 4523GB samples over an extended frequency range: ☒ ε'2% moisture, ☐ ε'3% moisture, × ε''2%, ✳ ε''3%.

least-squares fits over two moisture ranges: less than and greater than 1.8%. The scatter in the data are due mostly to errors in the determination of the adhesive moisture content and in specimen variability.

Results for the Permabond ESP-308 adhesive (not shown) illustrated the same general trend; however, there was a larger amount of scatter which was attributed to the presence of an electrically-conducting filler (aluminum powder). The permittivity was also abnormally large (16–20 *versus* 2–5 for typical dry epoxies) which is consistent with the filler creating conducting pathways which extended over a significant fraction of the bondline. This hypothesis was qualitatively supported by microscopic examination of the distribution of the aluminum powder within the adhesive layer.

Figure 5 shows the results of two separate experiments with 1-D 4523GB specimens at 10 kHz. As with the 1-D E-04 data (Figure 4), ε' increases approximately linearly with moisture up to about 1.5%. Above this, ε' increases rapidly to relatively high values, again in an approximately linear fashion.

Figure 6 gives the average permittivity of two batches of 2-D Permabond E-04 specimens as a function of the measured average moisture content at 10 kHz. The dashed lines are the 1-D 10 kHz correlations of Figure 4 at moisture levels below and

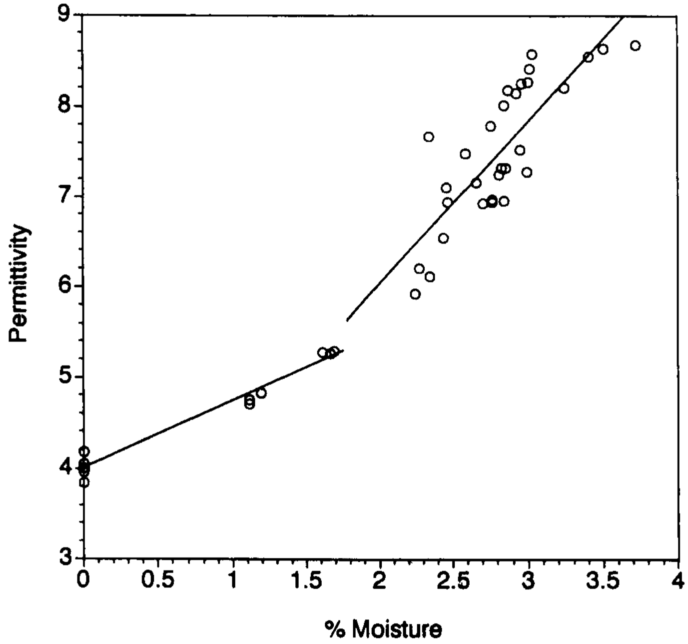


FIGURE 4 Permittivity (ε') *versus* moisture content for two batches of 1-D Permabond E-04 samples at 10 kHz. Least-squares lines— % < 1.8: $y = 0.744x + 3.98$ ($r^2 = 0.97$); % > 1.8: $y = 1.68x + 2.75$ ($r^2 = 0.72$).

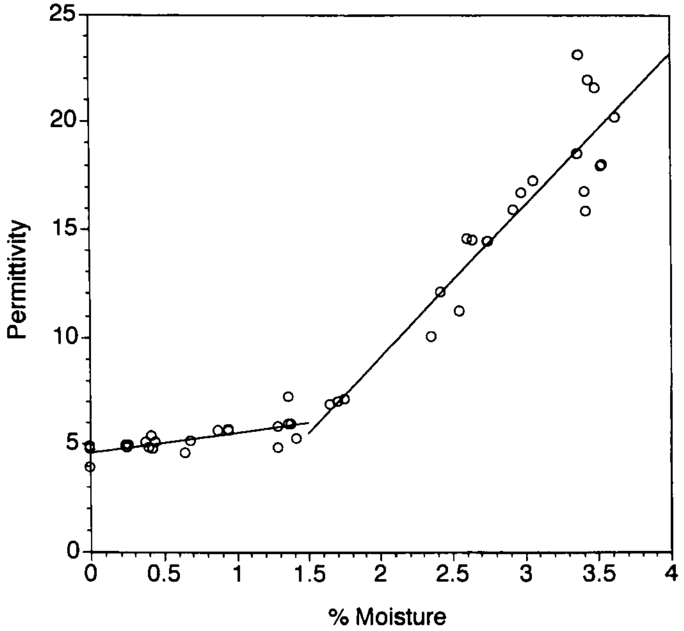


FIGURE 5 Permittivity (ε') *versus* moisture content for two batches of 1-D 4523GB samples at 10 kHz. Least-squares lines—% < 1.5: $y = 0.934x + 4.62$ ($r^2 = 0.52$); % > 1.5: $y = 7.10x - 5.08$ ($r^2 = 0.87$).

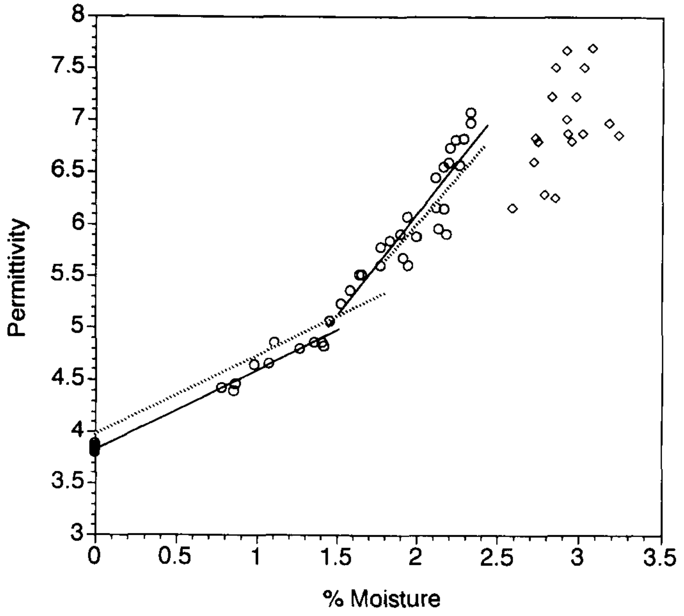


FIGURE 6 Average permittivity (ε') *versus* average moisture content for two batches of 2-D Permabond E-04 samples at 10 kHz. Dashed lines are the 10 kHz 1-D correlations from Figure 4. Least-squares lines —% < 1.5: $y = 0.755x + 3.84$ ($r^2 = 0.98$); % > 1.5: $y = 1.97x + 2.15$ ($r^2 = 0.85$). Data above 2.5% (◇) not fitted.

above 1.8%. The solid lines are linear least-squares fits through the 2-D E-04 data over two ranges: less than 1.5% and between 1.5% and 2.5%. Over these two ranges of moisture content, the 1-D and 2-D specimens behave approximately the same. Beyond 2.5% (the expected saturation level, Figure 2c) both batches of 2-D E-04 specimens showed a marked change in response which was attributed to the onset of the second stage of water uptake. This was supported by the observation that the adhesive layer in fractured specimens showed evidence of delamination along the periphery of the joint. For this reason, the data above 2.5% were not included in the linear curve fit.

Figure 7 shows the data for the 2-D specimens of Cybond 4523GB at 10 kHz. The data are again fitted to two straight lines, below and above 1.5%. The dashed lines are the least-squares fits of the 1-D 4523GB data at moisture levels below and above 1.5% (Figure 5). As with the 2-D E-04 data (Figure 6), at low moisture levels the 1-D and 2-D specimens behave similarly. Above 1.5% however, the 1-D 4523GB specimens show a markedly different response from the 2-D specimens, with ε' increasing much more quickly with the moisture content.

Table II gives the linear least-squares slopes and intercepts for the lower moisture curves of Figures 4–7, along with the 95% confidence limits for each. It is seen that the slopes of the fitted 1-D and 2-D lines for each adhesive lie within these limits, but that the intercepts are slightly beyond them. For the E-04 system, the slopes of the 1-D and 2-D specimen responses at higher moisture levels (> 1.8% and > 1.5%, Figures 4 and 6, respectively) are also very similar; respectively, 1.81 ± 0.39 and 1.97 ± 0.64 (± 95%

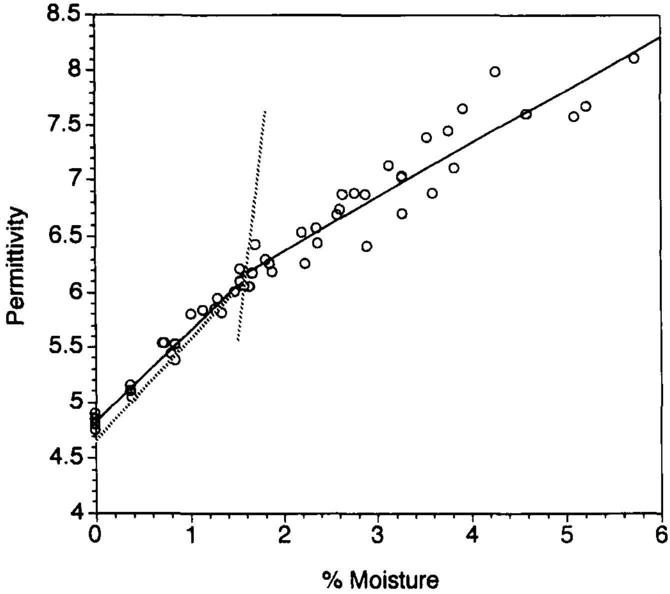


FIGURE 7 Average permittivity (ε') *versus* average moisture content for two batches of 2-D Cybond 4523GB samples at 10 kHz. Dashed lines are the 10 kHz 1-D correlations from Figure 5. Least-sequares line —% < 1.5: $y = 0.827x + 4.83$ ($r^2 = 0.96$); % > 1.5: $y = 0.483x + 5.41$ ($r^2 = 0.88$).

TABLE II
Confidence limits (95%) for slopes and intercepts of linear least-squares lines for E-04 and 4523GB permittivity *vs.* % moisture data at moisture levels below 1.8% (Figures 4, 5, 6 and 7)

System	Slope	±95%	Intercept	±95%
1-D E-04 (Fig. 4)	0.744	0.097	3.98	0.034
2-D E-04 (Fig. 6)	0.755	0.062	3.84	0.015
1-D 4523GB (Fig. 5)	0.934	0.410	4.62	0.073
2-D 4523GB (Fig. 7)	0.827	0.144	4.83	0.040

confidence interval). The slopes at higher moisture levels for the 4523GB 1-D and 2-D specimens are very different (Figures 5 and 7); 7.07 ± 1.32 and 0.483 ± 0.064, respectively.

The average dielectric response of the 2-D embedded foil specimens (Permabond E-04) *versus* immersion time is shown in Figure 8a. Using the calibration curve obtained from the 1-D E-04 experiment (Figure 4), average moisture levels can be calculated, as shown in Figure 8b. The dielectric response is reported as a normalized change in capacitance with respect to the initial value. This is convenient because it makes it unnecessary to measure the area and spacing of the embedded foil sensor since,

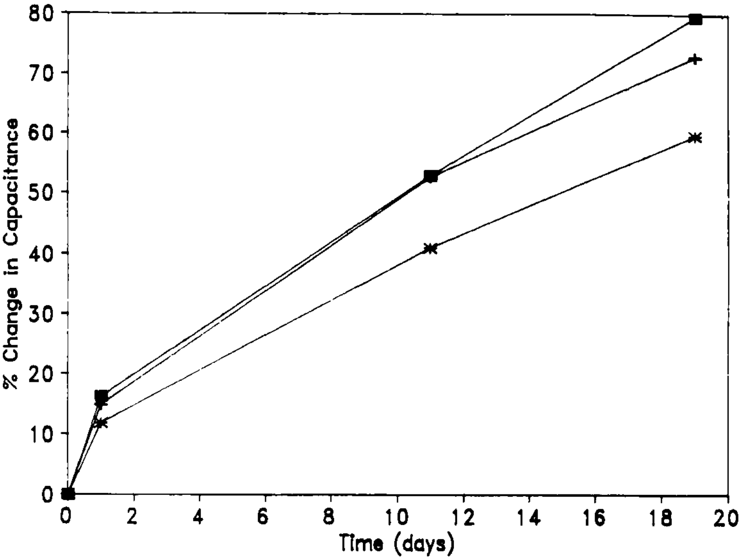


FIGURE 8a Percentage change in capacitance *versus* water immersion time for Permabond E-04 samples with embedded foil electrodes of two sizes at 10 kHz: (+ ■) 11 × 25 mm, (✳) 14 × 25 mm.

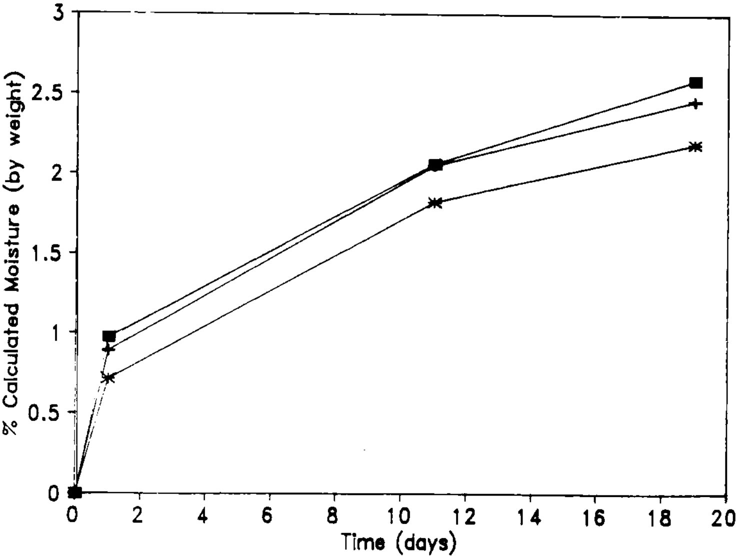


FIGURE 8b Calculated average moisture content (from 1-D specimen data) *versus* water immersion time for Permabond E-04 specimens with embedded foil electrodes of two sizes at 10 kHz: (+ ■) 11 × 25 mm, (✳) 14 × 25 mm.

as seen from equation (1), all parameters except ε^* remain constant. The general shape of this graph is as expected from Figure 2c, showing an approximately Fickian diffusion uptake of moisture into the adhesive joint, approaching an initial saturation plateau at approximately 2.5%. Samples 1 and 2 are approximately the same size, while sample

3 is approximately 27% larger. The latter lies below the other two because, in a given time, the relative amount of water absorbed by a specimen is proportional to the ratio of the bondline length to the bond area.

Measurements on the Permabond ESP-308 embedded foil samples proved impossible due to shorting of the electrodes by the aluminum filler particles.

Figure 9 shows the permittivity of a single 1-D specimen of E-04 as a function of moisture content during an initial immersion period of 22 days followed by a period of drying in a vacuum oven. The data for the wetting and drying phases are very similar, indicating that changes in the permittivity are a function primarily of the amount of absorbed water. It was found that the initial weight of the specimen (0% moisture) was greater than the final weight after the immersion and subsequent drying in the vacuum oven (−1% moisture). This was probably due to the leaching of certain adhesive constitutents during the experiment, and to the absorption of a small amount of water from the atmosphere prior to experiment.

DISCUSSION

The use of a mixture relation, such as equation (3), to model the dielectric response of adhesive joints as a function of the water content, assumes that the constituent materials (adhesive, filler, water) contribute linearly to the dielectric response. The present experimental results indicate, however, that there is a nonlinear relationship between the permittivity and the moisture content (Figures 4–7). Figures 4 and

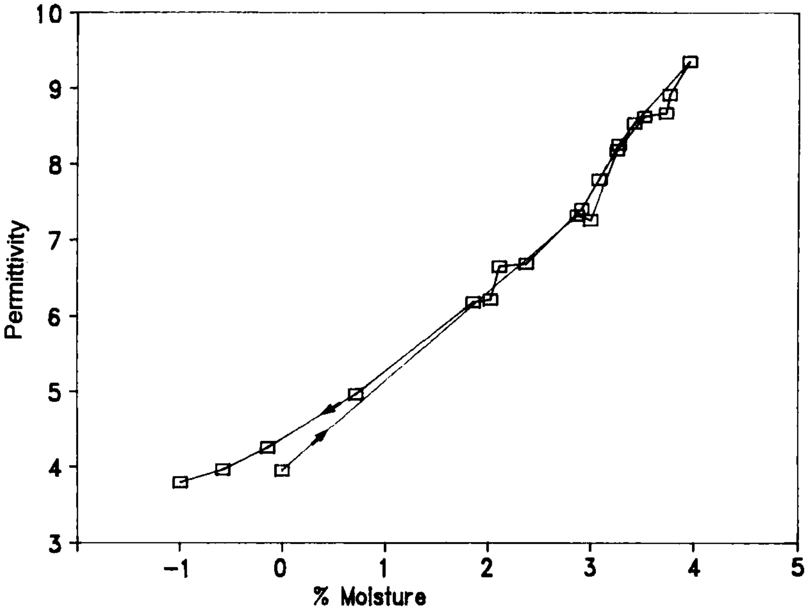


FIGURE 9 Permittivity (ε') *versus* moisture content for 1-D sample of Permabond E-04 at 10 kHz during immersion at 70 °C and subsequent drying.

5 suggest that the absorbed moisture is present in both bound and free (bulk) forms. The lower initial slopes of the bilinear correlations are consistent with the reduced mobility expected from water molecules which are bound to the adhesive, and corresponds to the first (Fickian) stage of water uptake shown in Figure 2a. Subsequent moisture absorption (beyound the saturation plateau at approximately 2%, Figure 2c) into cavities and voids as free water would result in a greater slope or, equivalently, an increased change in the permittivity per unit increase in the amount of water. Reid *et al.*[6] reported similar moisture sorption patterns in a cast epoxy resin, with the transition from bond to free water occurring at a moisture concentration of 1.4%. As well, Bair *et al.*[17]observed evidence of clustered water in polycarbonate saturated at an elevated temperature and subsequently cooled to varying degrees of supersaturation. Below the glass transition temperature, water was believed to condense in microscopic cavities if the polymer had been hydrolytically degraded.[17] This is consistent with the present situation, since the approximate glass transition temperatures of the E-04 and 4523GB adhesives are 35°C and 114°C, respectively. As with polycarbonate, however, it was found that there was only a very weak dependence of the saturation water content on temperature (over the range 20–70°C).[17] Aldrich *et al.*[7] also reported a linear correlation between water content and permittivity in cast epoxies at moisture levels below 1.8% (higher levels were not investigated).

The empirical mixture formula (equation (3)) can be extended to the case of clustered water, if bound and free water are treated as different materials so that

$$\varepsilon'_m = aV_{fw}\varepsilon'_{fw} + bV_{bw}\varepsilon'_{bw} + (1 - V_{fw} - V_{bw})\varepsilon'_p \tag{4}$$

where, respectively, V_{fw} and V_{bw} are the volume fraction of free and bound water, and a and b are constants of proportionality such that $a\varepsilon'_{bw}$ and $b\varepsilon'_{fw}$ are the apparent permittivities of free and bound water, respectively. While this formula contains enough variables to be able to represent the entire moisture range of the experimental data of Figures 4 and 5, it is not possible to use it to predict the total moisture content since both V_{fw} and V_{bw} are unknown. For this reason, a calibration curve, similar to Figures 4 or 5, must be obtained for the adhesive system in question.

In their study of the dielectric response as a means of nondestructively evaluating bonded joint integrity, Hayward *et al.*[9] reported a dielectric relaxation process occurring in the 100 kHz range which was attributed to hydrated aluminum oxide in an aluminum/epoxy joint. However, the samples and test methods used were very different from those of the present study, making comparisons difficult. Nevertheless, assuming an oxide layer thickness of at least 60 nm[18] and combining the dielectric properties of the adhesive and oxide as capacitors in series, leads to a prediction that both the permittivity and loss should be insensitive to changes in the oxide film.

The effect of a moisture concentration gradient on the average permittivity is important, since it can be expected in most measurement applications. The measured permittivity is an average of all the dielectric properties between the electrodes (area A)

$$\varepsilon'_{avg} = 1/A \int \varepsilon'(x, y)\, dA \tag{5}$$

and the moisture content, w, can be related to the permittivity at a given point (x, y) by

$$w(x, y) = f(\varepsilon'(x, y)) \tag{6}$$

The average moisture content is then

$$w_{avg} = 1/A \int f(\varepsilon'(x, y))\, dA \tag{7}$$

requiring a knowledge of both the permittivity—moisture content correlation, f (obtained from 1-D specimens), and the moisture distribution, $w(x, y)$. However, if the dielectric response of the adhesive is a linear function of absorbed moisture content ($w = f(\varepsilon') = C_1 \varepsilon' + C_2$), equation (7) simplifies to the linear relation

$$w_{avg} = C_1 \varepsilon'_{avg} + C_2 \tag{8}$$

While this linear response is predicted from the mixture relations, the presence of two forms of water (bond and free) results in a nonlinear correlation for both the E-04 and 4523GB adhesives (Figures 4 and 5). As a result, equation (8) does not apply exactly. Nevertheless, as shown in Figures 4–7, a linear approximation can be made over certain ranges of moisture levels. The data of Figure 4 have been modelled with two linear regions, below and above 1.8% moisture content. Equation (8) predicts that the 2-D response should be given by the same linear functions, f, as the 1-D response. Figure 6 shows that this is approximately true; *i.e.*, the 1-D and 2-D responses are essentially colinear below and above about 1.5%. The reason for the delayed onset of the second 1-D line at 1.8% is possibly due to the fact that a 2-D specimen may contain free water near the edges at a lower average water concentration than a 1-D specimen. The behavior of 4523GB is markedly different, as seen in Figure 7. Below about 1.5%, the 1-D and 2-D specimens do indeed follow almost the same linear functions. Above this moisture level, however, the permittivity of the 1-D specimens increases much more rapidly with absorbed water. The reason for this is unknown, although the difference between this behaviour and that observed with E-04 may be related to the relatively large amount of mineral filler in 4523GB (approximately 45% by weight) which may promote the adsorption and clustering of water molecules.

The use of equation (8), to infer the average water content from the average permittivty, requires that there be an approximately linear correlation between them at a given point. Figures 4 and 5 indicate that this is the case at low and high moisture contents; below or above 1.8% and 1.5%, respectively, for E-04 and 4523GB. If joints have large diffusion gradients such that there are significant regions of both high and low water content at the same time, then equation (8) is no longer applicable. In practice then, the average permittivity can be used to find the average water content as long as the local water concentration at every point is within the range of a single linear correlation with the permittivity.

Maffezzoli *et al.*[20] found that electrode polarization can produce high values of the permittivity in cured films of epoxy adhesives, with the effect being greatest at low frequencies (below 1 kHz) and at high moisture levels. At 10 kHz and higher, polarization was negligible at all moisture levels up to saturation. In the present experiments, all dielectric measurements were performed at both 10 kHz and 1 kHz. The 1 kHz data were similar to those at 10 kHz, supporting the hypothesis that electrode polarization effects were negligible, and that the primary reason for the differing behaviour at low and high moisture levels was due to the presence of two forms of water; bound and free (or "clustered"). Figure 3 illustrates that at frequencies of 10 kHz and more, the dielectric response was essentially independent of frequency.

The use of embedded electrodes (Figure 1c) permits localized measurements of moisture content and is essential in situations where the adherends are either nonconducting or are electrically connected by rivets, for example. In the latter case, the optimum configuration is a Schering bridge[13,19] in which one lead is grounded and connected to both adherends. With the other lead connected to the embedded sensor, not only is a localized measurement obtained, but also stray capacitance to the ground is eliminated. Also, since an embedded foil electrode coupled to both adherends has effectively twice its area and 1/2 the bondline spacing, equation (1) shows that such an electrode can be 1/4 the area of the present 2-D specimens to give the same capacitance. This can serve to make the measurement of the permittivity more localized and thereby reduce the influence of moisture diffusion gradients.

The use of the normalized change in the capacitance (Figure 8a) is convenient because it makes the results independent of both the geometry of the embedded sensor and the spacing between the electrodes. Strictly, however, this is only true if the dielectric material is homogeneous and isotropic. In the case of the present embedded foils, water diffusion gradients create inhomogeneities which will lead to a dependence on the electrode shape and size. This source of error can be minimized by using the smallest possible electrode area (limited by the sensitivity of the capacitance measurement), or rectangular electrodes with the smaller dimension parallel to the diffusion gradient.

The results obtained with Permabond ESP-308 adhesive make it apparent that dielectric measurements are difficult with adhesives containing a large fraction of a conducting filler such as aluminum powder. Conduction through the filler particles reduces the effective separation between electrodes, resulting in an abnormally high permittivity and more scatter in the data. Random variations in the amount and orientation of the filler particles, changing the effective electrode spacing, is believed to be the cause of this scatter. In addition, the thinner bondlines used in the embedded foil samples (0.2 mm) resulted in conducting paths between the electrodes, making it impossible to obtain measurements.

The drying of a 1-D E-04 specimen showed a reversible dielectric response which was only a function of the water concentration in the adhesive. The data of Figure 9 were obtained for a single specimen which had been immersed at 70°C for 22 days. Upon drying in a vacuum oven, essentially the same dielectric response was observed. This is similar to the findings of Apicella *et al.*[15] and Aldrich *et al.*[7] who examined cast samples of several filled and unfilled epoxy resins. It would be of interest to perform even longer term studies to investigate at what point adhesive degradation influences the dielectric response. Some idea of this for 2-D specimens is provided by the E-04 data of Figure 6, which shows the effect of edge delamination beyond 2.5% average moisture content after approximately 100 days immersion (Figure 2c).

CONCLUSIONS

Dielectric measurements were found to possess high sensitivity to absorbed moisture within structural adhesive joints. Calibration curves have been obtained from adhesive layers cast onto a single aluminum adherend, and immersed in water to produce spatially uniform moisture concentrations. The application of these curves to actual adhesive joints with moisture concentration gradients was discussed. At average moisture concentrations below approximately 2%, two commercial epoxy adhesives displayed a linear relationship between the average moisture content and the average permittivity which was independent of the distribution of the absorbed water within the joints. At higher moisture levels, one of the epoxies exhibited similar behavior but with a linear slope different from that at lower moisture concentrations, while the other epoxy showed a strong dependence on the distribution of the absorbed water. The measurements appear to be reversible upon drying and are insensitive to the presence of an aluminum oxide layer. Although more testing is required, the use of embedded foil sensors should allow these measurements to be applied, *in situ*, to both field structures and laboratory test specimens.

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