

A precision capacitance cell for measurement of thin film out-of-plane expansion. II. Hygrothermal expansion

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(Received 17 August 1998; accepted for publication 25 January 1999)

The data reduction techniques necessary for utilizing the capacitance cell described previously by us for thickness measurements [C. R. Snyder and F. I. Mopsik, *Rev. Sci. Instrum.* **69**, 3889 (1998)] in a humid environment are presented. It is demonstrated that our data reduction techniques provide thicknesses that are equivalent to those measured under dry conditions within the expected experimental uncertainty. The utility of this technique is demonstrated by the measurement of the hygrothermal expansion (swelling) of a bisphenol-A based epoxy with novolac hardener and fused silica filler. Our technique is shown to have a higher sensitivity than most current thermomechanical analysis techniques and is readily amenable to humid conditions. [S0034-6748(99)01705-0]

I. INTRODUCTION

One of the main concerns for plastic integrated circuit surface mount devices (SMDs) is the effect of moisture inside the plastic package during the solder reflow process, e.g., infrared, convection, or vapor phase reflow.¹ Most of the damage is due to the pressure caused by the rapid expansion of the moisture as the high solder reflow temperatures (in excess of 200 °C) rapidly volatilize it. The most severe case is known colloquially as the “popcorn” phenomenon, due to the fact that the internal stresses cause the package to bulge and then crack with a “popping” sound.^{2,3} Some examples of less severe damage caused by the pressure from the moisture are internal cracks which do not propagate to the surface, delamination of the polymer from the chip, bond damage, bond lifting, cratering beneath the bonds, and/or wire necking.¹ An additional issue regarding moisture uptake in electronic packaging is the hygrothermal expansion coefficient (the degree of swelling due to moisture uptake as a function of temperature). This is important since mechanical stresses build up when the polymeric resin expands more than the conductor (e.g., copper) or substrate to which it is bound.⁴

There have been a large number of studies on the effect of moisture on epoxy resins (neat, filled, and in composites). These studies have examined the rate of moisture uptake,^{5–10} the effect of moisture on the glass transition temperature,^{11–13} the irreversible effects of hygrothermal aging,¹⁴ and the nature of moisture in the epoxy.^{15–19}

In the electronic packaging industry, there is an ever present drive towards denser packages and hence, thinner polymeric films. With the increased use of thinner films there is a need for better metrology techniques. Current techniques such as thermomechanical analysis (TMA) do not have the sensitivity required to measure either the coefficient of thermal expansion (CTEs) or the hygrothermal expansion coefficients of these thin polymeric films perpendicular to the

plane of the film.²⁰ Furthermore, these techniques are ordinarily not readily amenable to varying environmental conditions.

We shall demonstrate in this work that our capacitance cell technique is easily utilized with varying humidity conditions and that its sensitivity is such that phenomena which cannot be readily observed by techniques such as TMA are easily seen with our cell. In the first article in this series, henceforth referred to as I, we introduced the design of our capacitance cell and introduced the necessary equations for data reduction for a dry air atmosphere.²¹ In this article, we will provide the necessary techniques for data reduction in a humid environment, examine the errors associated with measurements performed in a humid environment, and report the behavior of a commercial epoxy-molding compound when it is exposed to varying degrees of moisture.

II. EXPERIMENT

A. Material

The molding compound was B8 epoxy obtained from Plastkon.²² The compound is a bisphenol-A based epoxy with novolac hardener and fused silica filler. The manufacturer cured the molding compound at 160 °C for 4 h.

B. Thickness measurements

All thickness measurements were performed in the capacitance cell described in our previous publication.²¹ The cell was assembled in a laminar flow hood equipped with a high efficiency particle arresting (HEPA) filter to minimize dust uptake. The cell and sample surface were cleaned with ethanol and distilled water and dried with lens tissue. For the measurements performed in this article, the total surface area supporting the top electrode was determined to be 16.02 cm². With the top electrode having a mass of 223.3 g, the load was determined to be 1.366 kPa.

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C. Zerodur

To verify the validity of our calculations, with respect to calculation of the plate separation under humid conditions, measurements were performed on the Zerodur^{22,23} wedges which were used for calibration of the electrode area in article I. Measurements were performed at 60 °C at relative humidities of 0%, 19%, 38%, 57%, and 75%.

D. Thermal analysis

Thermogravimetric Analysis (TGA) was performed on a Perkin–Elmer TGA7. Differential scanning calorimetry (DSC) was performed on a Perkin–Elmer DSC7 at a heating rate of 10 °C/min. Temperature and enthalpy calibration of the DSC was performed with tin and indium standards (both of purity 99.999%, obtained from Aldrich Chemical Company). A sample size of 23.33 mg was used for the DSC measurements.

E. Mass uptake

All mass uptake measurements were performed on an analytical mass balance sensitive to 0.1 mg. These measurements were performed on a coupon (sample with dimensions of approximately 10.00 cm × 4.45 cm × 0.0393 cm) of the B8 epoxy that was free standing in the environmental chamber. Measurements were taken after the capacitance cell indicated equilibration, i.e., no apparent increase/decrease in film thickness.

F. Temperature/humidity calibration

The sample and the capacitance cell were placed in a environmental chamber that used a platinum resistance thermometer and solid state humidity sensor. Both sensors were calibrated prior to use.

1. Temperature calibration

The temperature of the cell was calibrated in terms of the environmental chamber temperature with a resistance temperature device (RTD) mounted to the cell with thermally conducting paste. The RTD was calibrated against an NIST certified ITS-90 standard reference thermometer.

2. Humidity calibration

It is important to note that the humidity/temperature chamber was equipped with a dry air purge with a manufacturer's quoted dew point of −90 °C (this corresponds to a vapor pressure of 9.3×10^{-3} Pa). The relative humidity of the chamber was calibrated by the following method. The humidity of the chamber was equilibrated until the fluctuations in humidity were as low as possible. The outlet of the chamber was then passed through a tube into a cold finger immersed in a temperature bath with a temperature range of −40–100 °C, with a temperature control of ± 0.1 °C. The bath was allowed to equilibrate at each temperature, and the bath temperature at which condensation appeared on the inside of the cold finger was recorded. From this dew point and the known temperature of the chamber, the relative humidity was determined. This was performed over a range of tem-

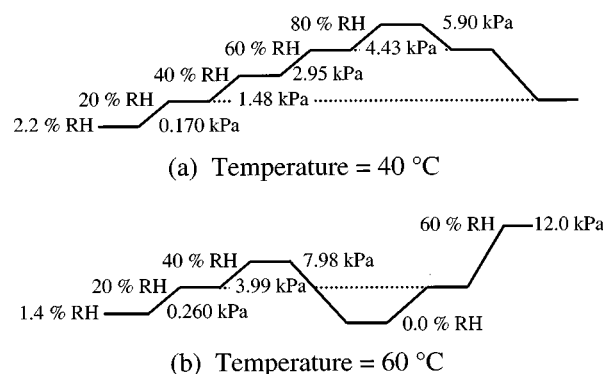


FIG. 1. Environmental profile used in the experiments on the epoxy. Relative humidity and partial pressure are shown for both temperatures examined: (a) 40 °C and (b) 60 °C.

peratures and humidities. The relative humidity of the chamber was controlled to within $\pm 0.5\%$. Vapor pressure was determined from reference data (see Sec. III A) and an external pressure sensor.

G. Dielectric spectroscopy

Dielectric spectroscopy was performed using the time domain dielectric spectrometer, described by one of us previously, over times ranging from 10^{-5} to 3000 s.²⁴ These time domain data were converted to the equivalent frequency domain data (10^{-4} Hz–10 kHz) by a Laplace transform. Temperature was controlled to ± 0.01 °C. The sample designated as “neat” was tested as received from the manufacturer after drying overnight under vacuum at room temperature. The sample was metallized with aluminum to eliminate air layer effects.

H. Environmental history

Two temperatures were studied: 40 and 60 °C. Figure 1 shows the environmental history at both temperatures in terms of the relative humidities (or partial pressure) experienced by the epoxy.

III. RESULTS AND DISCUSSION

A. Data reduction

In article I we presented the necessary equations for analyzing the capacitance data for samples measured under dry conditions. For the case of varying humidity conditions, the data reduction is more involved.

1. Digital filtering

The first problem that was encountered was due to the fact that the humidity sensor was not at the same location as the capacitance measurement, therefore spikes in the humidity did not correspond directly to spikes in the capacitance. To account for this fact, we utilized the technique of digital filtering. This is superior to a moving average because trends are not obscured by the filter and spikes do not unnaturally bias the results. We chose a double-pole Bessel filter due to the fact that Bessel filters are well behaved in the time domain. The filtering equation is given by²⁵

$$g_i = A \times (f_i + 2f_{i-1} + f_{i-2}) + B \times g_{i-1} + C \times g_{i-2}, \quad (1)$$

where A , B , and C are the filter coefficients, f_x is the x th raw experimental datum, and g_x is the x th filtered datum. The initial values of g_{i-1} and g_{i-2} were obtained with a 50 point moving average to accelerate the response of the filter. The Bessel filter coefficients are given by^{26,27}

$$A = \frac{\omega_c^2}{\theta}, \quad (2)$$

$$B = \frac{1}{\theta} \left(2\omega_c^2 - \frac{2\omega_c}{\tan(\tau\omega_c/2)} \right), \quad (3)$$

$$C = \frac{1}{\theta} \left\{ \left[\frac{\omega_c}{\tan(\tau\omega_c/2)} \right]^2 + \omega_c^2 - \alpha \frac{\omega_c^2}{\tan(\tau\omega_c/2)} \right\}, \quad (4)$$

where θ is given by

$$\theta = \left(\frac{\omega_c}{\tan(\tau\omega_c/2)} \right)^2 + \omega_c^2 + \alpha \frac{\omega_c^2}{\tan(\tau\omega_c/2)}. \quad (5)$$

In the above equations τ is the time interval between samples, α is a constant for the Bessel filter ($\alpha = 1.732051$), and ω_c is given by

$$\omega_c = 2\pi\nu_c\beta, \quad (6)$$

where β is the 3 dB cutoff multiplier ($\beta = 1.272$) and ν_c is the cutoff frequency in Hertz (for $\tau = 10$ s, we chose $\nu_c = 0.001$ Hz).

2. Calculation of the dielectric constant of air containing water vapor

For calculation of the sample thickness, we utilized the following equation for a parallel plate capacitor:

$$d = \frac{\epsilon\epsilon_0 A}{C}, \quad (7)$$

where C is the measured capacitance, A is the electrode area (the calibration of which is described in article I), ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.854$ pF/m), and ϵ is the dielectric constant of the medium separating the plates. To determine ϵ in the above equation, the molar polarization per unit volume is needed. In article I, we used the molar polarization of dry air from the literature ($P_{\text{air}} = 4.31601 \times 10^{-3}$ L/mol).²⁸ To convert this value to the proper units, the molar polarization was divided by the molar volume v given by the ideal gas law to be

$$v = \frac{RT}{p}, \quad (8)$$

where T is the temperature, p is the pressure, and R is the gas constant ($R = 8.314507$ L kPa/mol K).²⁹ As stated in the previous article, the error in using the ideal gas law for air is well below the resolution of our technique. This is not the case for water vapor.

The sensor in the environmental chamber recorded temperature and relative humidity. An external sensor measured atmospheric pressure p_{atm} . For calculations, the relative humidity must be converted into a partial pressure of air. For this, the saturation pressure p_{sat} of the water vapor must be

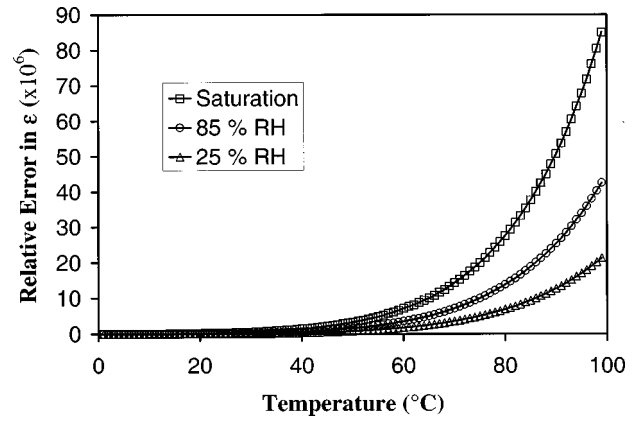


FIG. 2. Error in ϵ due to the use of the ideal gas law. Comparison has been made with calculations performed using data obtained from steam tables at 25%, 85%, and 100% (i.e., saturation) relative humidities.

known at the temperature corresponding to the temperature at the humidity sensor. The vapor pressure equation that was utilized³⁰

$$p_{\text{sat}} = \exp \left(\frac{F_0}{T_{\text{chamber}}} + F_1 + F_2 T_{\text{chamber}} + F_3 T_{\text{chamber}}^2 + F_4 (\ln T_{\text{chamber}}) \right) \quad (9)$$

yields the pressure in units of Pascal, where ($F_0 = -6043.6117$, $F_1 = 18.9318833$, $F_2 = -2.8238594 \times 10^{-2}$, $F_3 = 1.7241129 \times 10^{-5}$, and $F_4 = 2.858487$, and where T_{chamber} is the temperature of the chamber in Kelvin. (Note that where no subscript is present on T it refers to the temperature of the capacitance cell.) The partial pressure p_w is then calculated by

$$p_w = p_{\text{sat}} \times \frac{\text{RH}}{100}, \quad (10)$$

where the relative humidity (RH) is assumed to be in %. The molar polarization of water is temperature dependent and is given in the literature to be²⁸

$$P_w = \frac{20.847 \text{ K L mol}^{-1}}{T} + 0.0039 \text{ L mol}^{-1}, \quad (11)$$

where T is the temperature of the cell. The partial pressure of air is given by

$$p_{\text{air}} = p_{\text{atm}} - p_w. \quad (12)$$

As was mentioned previously, the ideal gas law cannot be used for water vapor due the errors it introduces in ϵ . Figure 2 shows the error in ϵ as a function of temperature and relative humidity due to the use of the ideal gas law. This calculation was performed by comparison of ideal gas law predictions with steam table data.³¹ It is apparent that the error in epsilon due to the use of the ideal gas law is completely unacceptable at temperatures above 70 °C. Therefore, it was deemed necessary to account for the difference between the ideal gas law predictions and the true water vapor behavior.

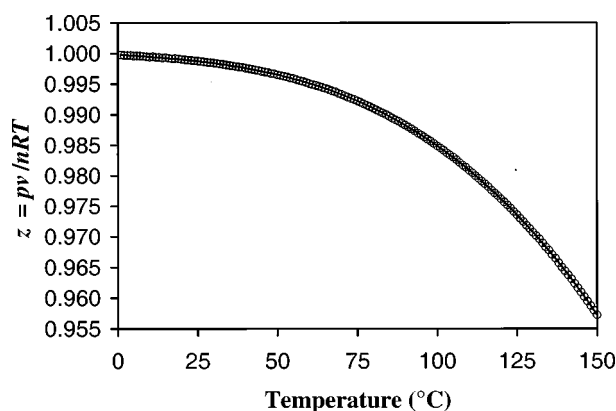


FIG. 3. Compressibility factor of saturated water vapor ($z = pv/RT$) as a function of temperature. The solid line corresponds to a cubic polynomial fit to the compressibility factor calculated from steam table data (solid circles).

To properly determine ϵ , the compressibility factor ($z = pv/RT$) for saturated water vapor was calculated as a function of temperature (see Fig. 3) from steam table data.³¹ This was fit well to a cubic equation between 0 and 150 °C of the form

$$z = \frac{pv}{RT} = AT^3 + BT^2 + CT + D, \quad (13)$$

where $A = -1.026 \times 10^{-8} \text{ } ^\circ\text{C}^{-3}$, $B = -1.289 \times 10^{-7} \text{ } ^\circ\text{C}^{-2}$, $C = -3.382 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$, $D = 0.9998$, and T is the temperature of the cell. However, the compressibility factor will increase towards unity at lower relative humidities, therefore the relative humidity corrected value of the compressibility factor (z') is³²

$$z' = 1 - \left((1 - z) \times \frac{\text{RH}}{100} \right). \quad (14)$$

The molar polarizability per unit volume is

$$\frac{P_w}{v_w} = P_w \times \left(\frac{P_w}{z' RT} \right). \quad (15)$$

We then assumed additivity for the molar polarizabilities, i.e.,

$$P_{\text{total}} = (P_w v/v_w) + (P_{\text{air}} v/v_{\text{air}}) = P_w \chi_w + P_{\text{air}} \chi_{\text{air}}, \quad (16)$$

where χ_i is the mole fraction of the i th component and from this, the dielectric constant of the medium was calculated through the definition

$$\frac{\epsilon - 1}{\epsilon + 2} v = P_{\text{total}}. \quad (17)$$

It should be apparent that Eqs. (8)–(17) serve to define the dielectric constant as a function of relative humidity. From the combined equation, which is too lengthy to include here, the error in ϵ due to a standard deviation of $\pm 1\%$ in the RH can be calculated, i.e., $d\epsilon/d(\text{RH})$. While it is a strong function of temperature, it is weakly relative humidity dependent, which can be seen in Fig. 4 which is a plot of $d\epsilon/d(\text{RH})$ versus temperature at relative humidities of 10% and 90%. For constant error in RH, the error in ϵ increases with increasing temperature. This error sets the ultimate sensitivity

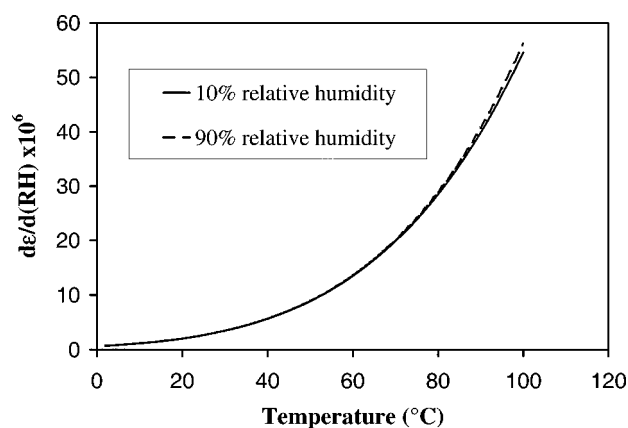


FIG. 4. Error in epsilon due to a standard deviation in the relative humidity (RH) of $\pm 1\%$, i.e., $d\epsilon/d(\text{RH})$, as a function of temperature T at 10% and 90% relative humidity.

of our technique, as this relative error in epsilon carries over directly to the calculation of thickness [Eq. (7)].

B. Zerodur results

The data obtained from the experiments performed on the Zerodur were reduced using the above equations. The results of the calculations are shown in Fig. 5. The error bars on the thickness at a relative humidity of 0% are the best estimate of two standard deviations in the experimental uncertainty obtained from previous measurements on Zerodur. The error bars on the thickness at higher humidities correspond to the standard uncertainty in the thicknesses with a coverage factor of 2 assuming a 1% error in the RH as calculated from the data in Fig. 4. It is apparent that there are no differences between the calculated thicknesses within the experimental error. This demonstrates the validity of our data reduction technique.

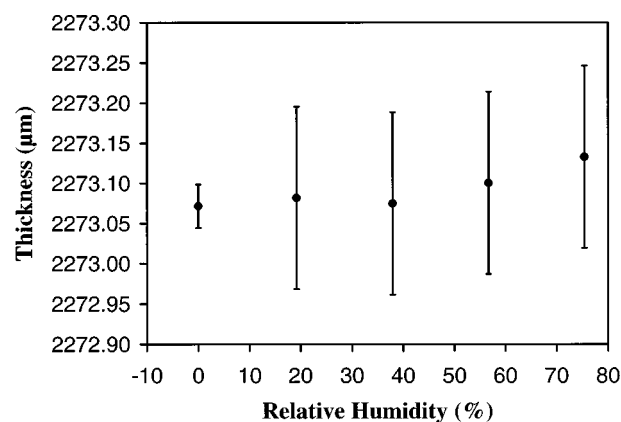


FIG. 5. Calculated thickness of Zerodur spacers as a function of relative humidity. (The error bars correspond to the best estimate of the experimental standard deviation with a coverage factor of 2. The error bars on the thickness at a relative humidity of 0% were estimated from previous results on Zerodur. The error bars on the thicknesses corresponding to higher relative humidities were estimated by assuming a standard deviation in the relative humidity of $\pm 1\%$; see Fig. 4.)

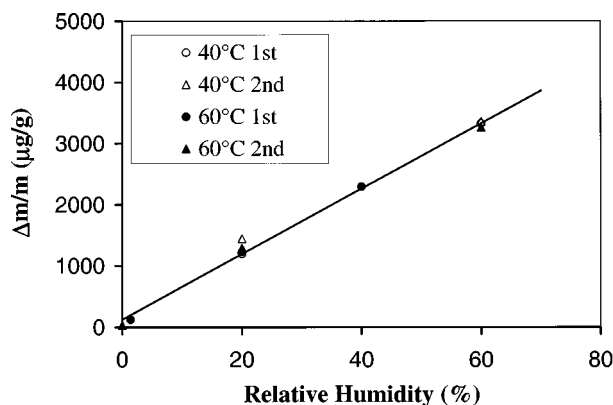


FIG. 6. Relative mass increase (relative to dried epoxy) of the B8 epoxy as a function of relative humidity. Note: At 40 °C, the second run refers to a decrease in humidity from the previous data point. At 60 °C, the second run refers to a reduction to 0% relative humidity followed by a subsequent increase in humidity. (The best estimate of two standard uncertainties in $\Delta m/m$ corresponds to $\pm 31 \times 10^{-6}$ which is less than the size of the plot symbols.)

C. Bisphenol-A epoxy results

Initially, the sample was examined at 40 °C at a relative humidity of 0%. The change in sample thickness with time was too great, so the temperature was raised to 100 °C. After several days at 100 °C, the sample was still dimensionally changing, so the temperature was raised to 120 °C. (It was reasoned that the film might contain some moisture that could not be driven out at 100 °C or that there might be some residual curing taking place.) The sample was stabilized by heating to 120 °C for 3 days to remove any residual moisture and to minimize the possibility of further curing at 40 and 60 °C. The mass of the coupon in the oven was determined after cooling to room temperature under an argon purge. The chamber was then lowered to 40 °C and the humidity profile shown in Fig. 1 was followed.

In Figs. 6 and 7, we have plotted the results of the moisture uptake measurements; as there are disagreements whether partial pressure or relative humidity (related to an

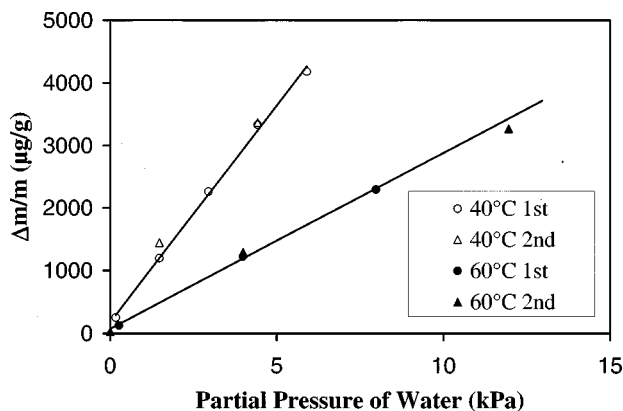


FIG. 7. Relative mass increase (relative to dried epoxy) of the B8 epoxy as a function of partial pressure of water. Note: At 40 °C, the second run refers to a decrease in humidity from the previous data point. At 60 °C, the second run refers to a reduction to 0% relative humidity followed by a subsequent increase in humidity. (The best estimate of two standard uncertainties in $\Delta m/m$ corresponds to $\pm 31 \times 10^{-6}$ which is less than the size of the plot symbols.)

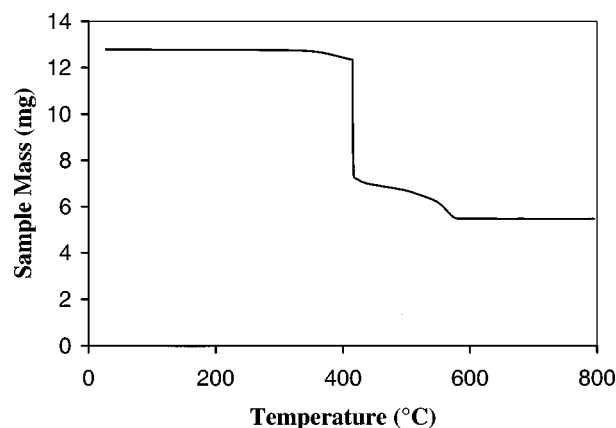


FIG. 8. Thermogravimetric analysis (TGA) scan of B8 epoxy. A heating rate of 10 °C/min was utilized.

activity term) is the correct parameter to plot moisture uptake against, we have plotted against both. The fact that the mass uptake retraced (with one exception) at 40 and 60 °C described in the Sec. II A, indicates that our criterion for equilibration (i.e., no change in film thickness as a function of time as measured by the capacitance cell) was sufficient. The exception was that the second mass uptake measurement performed at 40 °C and a partial pressure of water of 1.48 kPa (RH=40%) was not equal to the first measurement within experimental error. This will be discussed at a later point in this article.

The observed initial dimensional instability of the material at 40 °C and a relative humidity of 0% was considered to be an important issue. It is important because we were uncertain whether this was caused by residual moisture in the epoxy causing plasticization or whether the resin was not fully cured. If it were the latter, there would be important implications regarding the possible molecular interactions of the resin with the moisture. Therefore, TGA and DSC were performed on a piece of the as-received epoxy material to determine if there were large amounts of moisture present in the resin. TGA does not display a large loss of mass until approximately 350 °C (see Fig. 8). The DSC trace (Fig. 9) does not show the endothermic peak that would be expected for moisture boiling off. However, the data indicate that a residual exotherm spanning the range of 100–250 °C may be

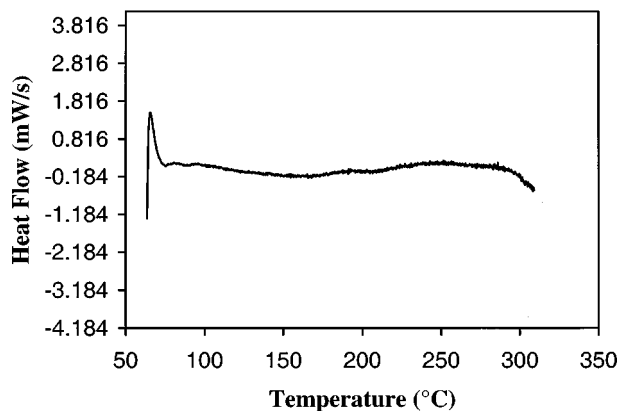


FIG. 9. DSC scan of B8 epoxy. A heating rate of 10 °C/min was utilized.

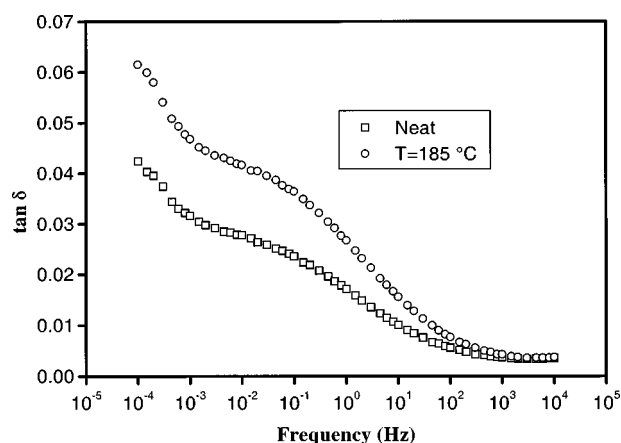


FIG. 10. Dielectric spectrum of B8 epoxy at 50 °C. The squares correspond to the sample as received after drying under vacuum at room temperature. The open circles correspond to the sample after annealing at 185 °C for 1.5 days.

present. Due to the inconclusive nature of the DSC data, dielectric spectra were obtained for the material at 50 °C. Figure 10 shows the dielectric spectrum of the material dried under vacuum at ambient temperatures overnight and after 1.5 days at 185 °C. It is apparent from the spectra that the magnitude of the relaxation has decreased; this indicates a decrease in mobility. Thus, it is apparent that the material was not fully cured as received and therefore, there are undoubtedly free hydroxyl groups present in the material.

Figure 11 shows the sample thickness as a function of partial pressure of water at 40 °C. As can be seen from the plot, the sample expands (swells) with increasing moisture uptake up to a partial pressure of water of 4.43 kPa. However, upon increasing the relative humidity from 60% (vapor pressure of water = 4.43 kPa) to 80% (vapor pressure of water = 5.90 kPa) two events were observed simultaneously. (1) The sample rapidly contracted, even though the mass uptake curve displayed an increase, and (2) the sample began to “creep,” i.e., the thickness decreased as a function of time (see Fig. 12). To verify that the first event was not creep, the

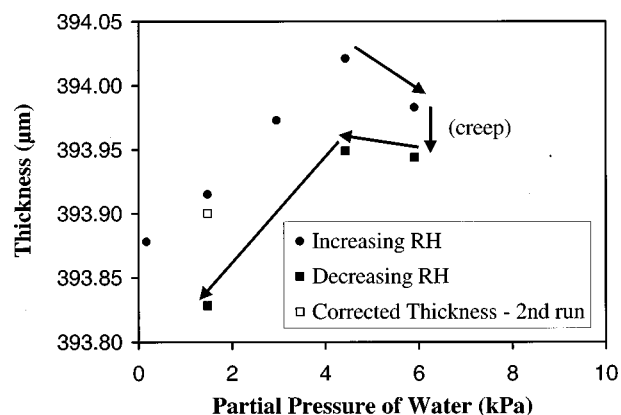


FIG. 11. Thickness of the B8 epoxy at 40 °C as a function of the partial pressure of water. Note that the open square is the 1.48 kPa (20% RH) thickness corrected by the thickness change in the 4.43 kPa (60% RH) measurements. Also note that the error bars corresponding to the best estimate of two standard uncertainties in the thickness are smaller than the plot symbols.

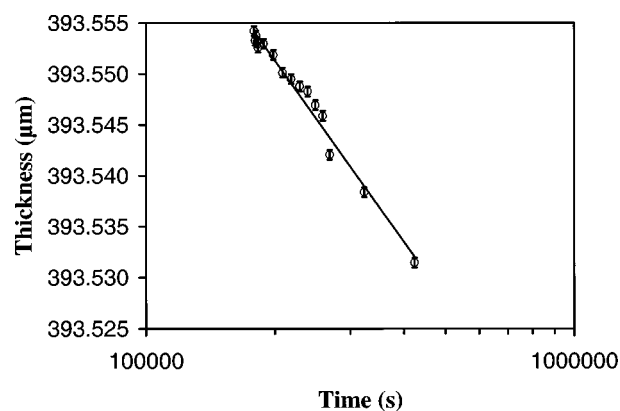


FIG. 12. Example of the change in thickness as a function of time at 40 °C and 5.90 kPa. Note that the time scale is logarithmic. The error bars correspond to the best estimate of two standard deviations in the experimental uncertainty.

humidity was decreased to a partial pressure of water at 4.43 kPa. The final thickness increased from the last reading at 5.90 kPa of water (RH=80%) and was displaced from the initial value by an amount close to the measured creep at 5.90 kPa of water, plus what can be estimated by considering the creep that occurred in going to or from 5.90 kPa. Therefore, events (1) and (2) were separate.

Analysis of the increase in thickness from 0.170 to 2.95 kPa corresponds to a hygroscopic expansion coefficient of $37.7 \times 10^{-3} (\text{g water})^{-1}$, which was calculated through the following relationship:

$$\alpha_{\text{water}} = \left(\frac{d - d_0}{d_0} \right) \left(\frac{1}{m - m_0} \right), \quad (18)$$

where d is the thickness at a mass uptake of water m , and d_0 is the thickness at the reference condition of a mass uptake of water m_0 . The total volume occupied by the B8 epoxy coupon at 40 °C was determined to be approximately 1.75 cm³ (corresponding to a moisture uptake of 8.2 mg of water). If it is assumed that the volumetric expansion is equal to three times the linear expansion, then the total volumetric increase (on a basis of per unit mass water uptake) is 0.18 cm³/g. Given that water has a specific volume of 1.008 cm³/g at 40 °C,³³ it is obvious that the expansion is almost an order of magnitude less than would be expected from simple volumetric additivity.

One possible explanation is that the resin is porous, or that it contains regions of low density. Therefore the water could be condensing in the voids (or low density regions). Further supporting evidence for this is that the expected equilibration time for a pure epoxy resin of this type is ordinarily at least an order of magnitude longer than what we determined. This implies that the diffusion of the water is occurring at a faster rate than expected. This observation could be attributed to porosity (or regions of low density), which would be in agreement with the observations of Wong and Broutman on Shell Chemical Company's Epon 828.⁶ They observed, by sorption measurements, that the diffusion rate was far higher than would ordinarily be expected for an epoxy resin for moisture uptakes of less than 1.2%. Additionally, the expansion of their material was far less than

would be expected from strict volumetric additivity. At higher moisture uptakes (i.e., above 1.2%) they observed a large decrease in diffusion rate and also an increase in the rate of resin expansion with moisture uptake. They explained these results by postulating that the moisture enters the low density regions first (up to 1.2% moisture uptake) which allows for a higher diffusion coefficient and less swelling, followed by a slower diffusion into the denser epoxy regions with an associated increase in swelling.

Adamson provided an alternative explanation in his study on Hercules 3501-5 resin.³⁴ In this work, three "regimes" were observed. The first two regimes corresponded to Wong and Broutman's two regimes. The change from the first regime to the second regime occurred at around 3% moisture uptake (by mass). A third regime was observed around 6% moisture uptake. In this third regime, the swelling again dropped below the volume of moisture absorbed. Adamson explained this behavior with free volume arguments. In the first regime, some of the moisture occupies the free volume without swelling the resin while the remainder disrupts the interchain hydrogen bonds which results in swelling. The second region corresponds to a domination of the hydrogen bond disruption mechanism, hence the large degree of swelling. Finally, in the third regime, the moisture diffuses primarily into the high density micelles which contain primarily covalent (rather than hydrogen) bonds and therefore do not swell. Both Wong and Broutman's⁶ and Adamson's³⁴ observations mirror our own observations. As our highest relative mass uptake is approximately 0.4%, it is apparent that the epoxy resin is in the first "regime" of both works. Therefore, their explanations can be applied to our measurements. However, neither article reports a reduction in thickness with time (i.e., creep), therefore it is appropriate to discuss the behavior of the epoxy at 40 °C and 80% relative humidity (5.90 kPa of water).

It has been well documented that moisture uptake can plasticize epoxy resins,¹³ therefore, creeping at temperatures which are low relative to the glass transition temperature is not an unreasonable explanation. A second explanation for the decreasing thickness with time derives from the fact that the resin was only partially cured. Therefore, the addition of water to the system at temperatures above room temperature could have catalyzed further curing, resulting in a densification of the resin. Johncock stated that the two major roles of water in an epoxy resin are as a plasticizer and as a catalyst for further reaction of the epoxy groups, therefore both are possibilities.⁹ Although it is uncertain which is the correct result, we would like to point out that this shrinkage would not ordinarily be observed by most of the current TMA techniques.

The volumetric contraction observed at 40 °C under increased mass uptake is far more difficult to explain than the expansion behavior or the creep (structural recovery). Because of the proprietary nature of the material examined, it is impossible to determine exactly what might be causing this contraction. Several possibilities are the interaction of the moisture: (1) with the free hydroxyl groups which must be present in a partially cured resin; (2) with the filler particles, e.g., hydrate formation, as certain hydrates are known to

have higher densities than their corresponding anhydrous analogs;³³ (3) with the filler particles' adhesion promoter; or (4) with a mold release agent. It is well documented that under many conditions a minimum (maximum) in the volume versus composition can occur when there is not an ideal noninteracting solution or mixture. A simple example is the ethanol-water system that has a minimum in the partial molar volume of ethanol at a volume fraction of 0.009.³¹ Further studies of this phenomenon should include production of the neat resin (i.e., no fillers) and production of a filled resin with varying amounts of filler.

It was reasoned that this volumetric contraction effect might be even more pronounced at 60 °C, however "creep" occurred at a faster rate and it was difficult to obtain good equilibrium thickness values. Before further discussion of the 60 °C data, we will address the question of dimensional reversibility of the samples at both 40 and 60 °C. As can be seen from Fig. 7, the mass uptake measurements were reproduced within experimental error upon raising and lowering the humidity (with the exception of 40 °C and 1.43 kPa of water); this was not true for the thickness measurements. At 40 °C this discrepancy can be attributed almost entirely to the creep. In Fig. 11, we have plotted both the second data point taken at 1.48 kPa of water as measured, and after shifting upwards by the difference in thickness between the two measurements taken at 4.43 kPa. Note that the first measured data point and the second data point (after shifting) are close (a difference of 15 nm), but do not overlap. There are two possible reasons for this. (1) The material has been changed by the presence of moisture and therefore it behaves differently. (2) The second measurement made at 1.48 kPa was not in equilibrium as evidenced by the mass uptake, i.e., the second data point does not fall on the line with the rest of the data. While the mass uptake measurement would support a lack of equilibrium, the fact that the mass of moisture is greater than the equilibrium value would predict that the thickness measurement would be too high. This is the opposite of what was observed. Therefore, the first option is far more likely. Furthermore, only the first option can be used to explain the data at 60 °C.

From the mass uptake measurements plot, Fig. 7, it is clear that all the measurements of mass uptake fall onto the same line at 60 °C. But it is apparent from Fig. 13 that the thickness measurements do not. The discrepancy between the two runs at high humidities is not the basis for this conclusion, since neither the initial nor the final thicknesses (before and after creep) are exact. (The initial measurement is obtained from a back extrapolation whereas the second is taken after some arbitrary time and it is therefore uncertain how much the material creeps after a reduction in the chamber's humidity until equilibrium is re-established.) However, the low humidity data (where there was no creep observed) are not reproduced. Even with the corrections made for the change in thickness due to creep, the data measured at vapor pressures of less than 5 kPa of water at 60 °C would not overlap. This indicates that the material has changed in some fashion. This phenomenon is not new. Irreversible effects have been seen repeatedly in epoxy systems exposed to moisture (see for example the work of Xiao *et al.*)¹⁴ Without

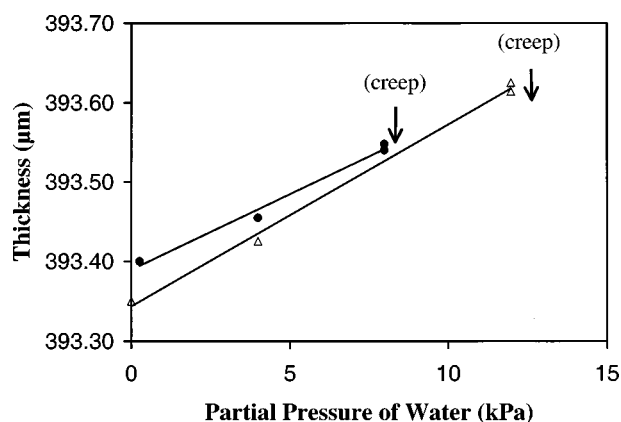


FIG. 13. Thickness of the B8 epoxy at 60 °C as a function of the partial pressure of water. The diamonds indicate the first run while the triangles indicate the second run. Note that the initial and final positions of the data points labeled with "creep" are approximations only, since the creep never actually stopped therefore the final thickness is an overestimate and the initial thickness is a rough back extrapolation.

further studies, it is impossible to state what changes have occurred in the epoxy; this will be the topic of a future study.

D. Adsorbed moisture

In discussions regarding our capacitance cell, the question of a layer of moisture on the electrode has arisen. There are two principal cases which must therefore be considered. The first case is where the adsorbed layer of moisture is providing a source for increased humidity. This case has been proven to be unlikely by the experiments on the Zero-dur. Had a large effect on the humidity been present, the thicknesses that were calculated would not have agreed as well as they did. The second case is the decrease in electrode separation due to the presence of moisture. Because of the high surface energy of nichrome, the presence of a layer of liquid water can be ruled out. We therefore will consider only the case of an adsorbed layer. If there is a layer of moisture ($n/2$) Å thick on each electrode, then an n μm/m error in the thickness will be present for a sample thickness of $n \times 10^2$ μm. For the adsorbed layer, it is reasonable to assume that n is 2, or less, since only a few monolayers could be present with nichrome's high surface energy. If n is less than 2, then for a 20 μm thick sample, the error would be 20 μm/m. However, it is apparent from our measurements that this magnitude of error can arise solely from the variation in ϵ due to the error in the relative humidity. Therefore, since we stated in our previous article that the sample limit of the dry air measurement is on the order of 2 μm and since the humid conditions have errors that are an order of magnitude larger, we would have recommended a lower limit of sample thickness of between 15 and 20 μm for full accuracy. Under these conditions, the calculated thicknesses will not be measurably affected by an adsorbed monolayer.

ACKNOWLEDGMENT

C.R.S. would like to acknowledge the support of the NIST-NRC Postdoctoral Research Associate Program.

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