The Role of Boundary Layer Capacitance at Blocking Electrodes in the Interpretation of Dielectric Cure Data in Adhesives

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The Role of Boundary Layer Capacitance at Blocking Electrodes in the Interpretation of Dielectric Cure Data in Adhesives§

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The use of dielectric measurement techniques for monitoring the cure of adhesives and matrix resins used in composite materials is well known. Either parallel-plate electrodes or recently introduced dielectric microsensors can be used. During a typical cure, the quantitative results obtained from dielectric measurements early in cure, where the resin is a viscous liquid, have been shown to depend on the presence or absence of blocking layers at one or both electrodes. This paper reports a quantitative evaluation of the effects of blocking layers on the interpretation of such dielectric data. The approach follows that used for dilute electrolytes, which is a reasonable model for the liquid resins, in which ion conduction will always be present to some degree. It is shown, first, that blocking layers can be modeled as capacitances in series with the bulk adhesive; second, that when the dielectric loss factor of the material is high (which is typically true early in cure), the

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apparent dielectric response is dominated by the charging and discharging of boundary layer capacitances through the bulk resistance of the sample; and, third, that this phenomenon leads to behavior that is similar to a Debye model for dipole orientation, but with an apparent permittivity (dielectric constant) that is inversely proportional to the boundary layer thickness and, thus, can be much larger than the actual bulk permittivity of the material under measurement. Data are presented with demonstrate this effect with a DGEBA resin in the presence of blocking layers that vary in thickness from .0023 to 1.5 μm. The implications for the interpretation of data obtained while monitoring adhesive cure are discussed.

I. INTRODUCTION

Dielectric and conductivity measurements have been used to study chemical reactions in resins for more than 50 years[1]. Typically, an AC capacitance bridge or impedance meter is used in conjunction with a pair of electrodes, such as parallel plates or foils, or comb electrodes. Applications of such measurements to the cure of epoxy resins and other thermosets began in earnest in about 1958[2,3]. A vast literature has developed since then, including studies of epoxies, phenolics, polyesters, and polyimides, to name a few, both as neat resins, and in structures such as fiber-resin composite laminates and adhesive joints. In 1981 a new integrated-circuit measurement technique was introduced, called microdielectrometery, which combines comb electrodes with built-in amplification and temperature sensing in a single probe[4,5]. In all these measurements, the goal is to follow changes during cure in the dielectric *permittivity* ε' (*dielectric constant*), which for most resins ranges from 2 to 15, and in the dielectric *loss factor* ε'', which can vary by many orders of magnitude, depending on the conductivity of the sample.

Parallel-plate and comb-electrode methods typically operate in the 10 Hz–100 kHz range. The calibration of parallel-plate electrodes depends on plate spacing and area, as illustrated in an ideal case in Figure 1. Two plates of area A spaced apart by distance L and filled with a homogeneous medium having permittivity ε' and loss factor ε'' can be represented by an equivalent circuit having capacitance C and parallel resistance R given by:

$$C = \frac{\varepsilon' \varepsilon_0 A}{L} \qquad R = \frac{L}{\omega A \varepsilon'' \varepsilon_0} \qquad (1)$$

where ε_0 is the absolute permittivity of free space (8.85 × 10^{-12} F/m). Measurement of C and R at some angular frequency ω is then used to
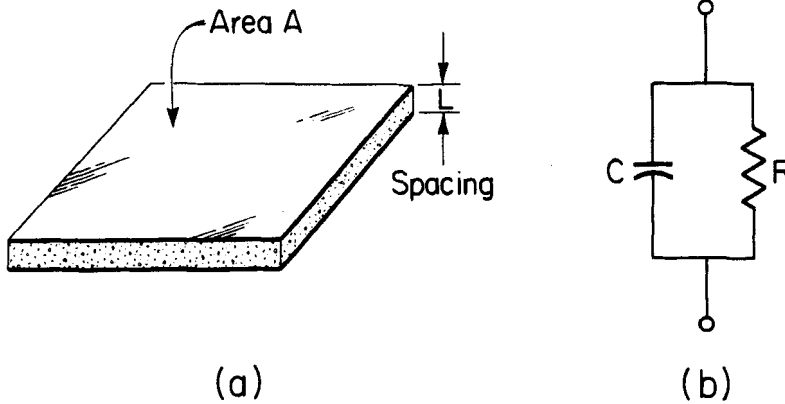
FIGURE 1 (a) Schematic of ideal parallel-plate capacitor filled with homogeneous medium; (b) equivalent circuit.

extract values for ε' and ε''. Typical plate spacings for parallel-plate geometries are in the range of a few tenths of a mm to a few mm. If the spacing can change during cure, as might occur when pressure is applied to a laminate or adhesive joint, then the separate quantitative determination of both ε' and ε'' is not possible. As a result, it has been common practice to measure the ratio of ε'' to ε', called the loss tangent (tanδ, which is also equivalent to the dissipation factor D of the parallel plate capacitor), because in the absence of blocking-electrode effects, the calibration of parallel plates for tanδ is independent of plate spacing. In terms of the experimentally measured quantities, R and C, tanδ is expressed as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{1}{\omega RC} \tag{2}$$

Since the geometrical quantities L and A cancel out of tanδ when the medium is homogeneous, it has been widely assumed that all parallel-plate measurements of tanδ are geometry-independent. However, one result of the present paper is to show that the conventional practice of placing a thin release film, which functions as a blocking layer, between parallel plates during cure studies can make the calibration depend directly on plate spacing, even when measuring only tanδ.

The comb electrodes, in contrast to parallel plates, do provide a fixed

calibration both for ε' and ε'', because electrode size and spacing does not change during cure. However, comb electrodes typically have limitations of sensitivity and frequency range due to practical instrumentation issues, and comb electrodes are also affected by blocking layer effects.

The microdielectrometry approach, with interelectrode spacings measured in tens of μm, provides both the stable calibration of the comb electrode, and the ability to measure to arbitrarily low frequencies because of the built-in amplification. Microdielectrometry equipment is now available which covers the frequency range 0.005 Hz–10 kHz.

The combination of low measurement frequency plus small interelectrode spacing of microdielectrometry has brought out an effect, which while noticed in even the earliest conventional measurements[1], has only occasionally been analyzed in cure experiments[6]. The effect is the exact homologue of the polarization of blocking electrodes in electrolytes[7], and arises in the case of adhesives and resins from the ionic conductivity due either to intrinsic ions or to residual impurity ions. These ions are relatively mobile during the early portions of a typical
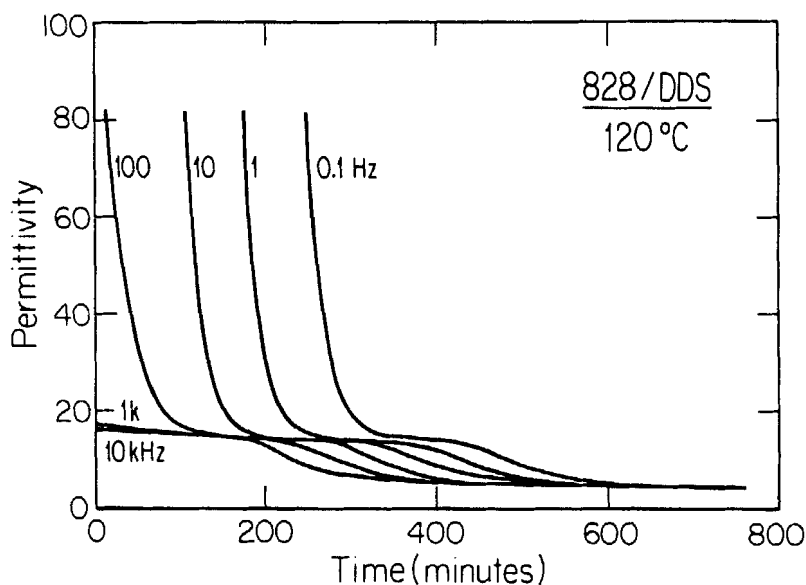

FIGURE 2 Typical experimental cure data in which blocking layer effects produce a large measured permittivity (ε'_x) early in cure, particularly at low frequencies.

cure sequence, when the sample viscosity is relatively low, and it is in this portion of the cure cycle that polarization effects are observed.

Figure 2 illustrates the effect. The permittivity measured using micro-dielectrometry at a range of frequencies from 0.1 Hz to 10 kHz is shown as a function of cure time for an isothermal 120°C cure of Shell EPON 828®, which is a resin based on diglycidyl ether of bis-phenol A (DGEBA), with diamino diphenyl sulfone (DDS). Starting at about 200 minutes, the data show a clear sequence of dielectric relaxations at each frequency which is due to the increasingly hindered dipole orientation as vitrification is approached[8]. However, early in cure, and particularly at low frequencies, the measured permittivity is very large. The purpose of this paper is to demonstrate that this large apparent permittivity early in cure can be attributed to the polarization of blocking electrodes, and can be quantitatively modeled by assuming a blocking layer capacitance in series with the dielectric sample.

II. EXPERIMENTAL METHODS

The experiments consist of making dielectric measurements as a function of frequency on a non-curing sample material whose dielectric properties are varied by making temperature changes, and using a variety of electrode configurations and blocking layers. The sample material was Epirez 510®, a commercial DGEBA resin. The dielectric permittivity of Epirez 510 is independent of frequency in the range 0.1 Hz to 10,000 Hz, and varies from $\varepsilon' = 9.5$ at room temperature to $\varepsilon' = 7.5$ at 90°C. Over this same temperature range, the dielectric loss factor is dominated by residual ionic conduction, and varies between $\varepsilon'' = 0.013$ (room temperature, 10,000 Hz) and ε'' values in excess of 3000 (90°C, 10 Hz). For the purposes of the experiments reported here, the small variation in ε' with temperature is negligible compared to the enormous variation in apparent ε' due to blocking layer effects. Therefore, for the parallel plate experiments reported below, data from temperatures throughout the range 20–90°C were merged in order to approximate the experimental ideal of a nominally constant ε' and a widely varying ε''.

Two different electrode metals were used. Aluminum was used both for parallel-plate electrodes and as the electrodes on the microdielectrometry probe. Gold was also used for parallel-plate measurements. For aluminum parallel-plate measurements, the interelectrode spacing

was varied between 32 μm and 5 mm. For gold, a single 60 μm spacing was used. It should be noted that the smallest of these spacings (achieved by using Kapton® film spacers) is much less than that typically used with parallel plates. No intentional blocking layers were used with the parallel plates; however, both metals yielded polarization characteristics indicating blocking behavior. Measurements on parallel-plate electrodes were made over the frequency range 10 Hz–10,000 Hz with a GenRad 1689 Digibridge®. In the case of the microdielectrometry probe, the interelectrode spacing is fixed at 12 μm. However, blocking layer thickness was varied by spin-coating and curing films of DuPont 2555 polyimide onto some of the sensors prior to the measurements. Two polyimide thicknesses were used, 150 nm, and 1.2 μm. Microdielectrometry measurements were made over the frequency range 0.1–10,000 Hz using equipment equivalent to the Micromet Instruments System II Microdielectrometer.

The typical experimental sequence involved placing a sample of the resin either between the parallel plates or on the microdielectrometry probe, and measuring ε' and ε'' as a function of frequency at a series of temperatures between 20 and 90°C. The primary effect of varying temperature is to vary the ionic conductivity of the resin. Thus, we were able to make a controlled change in the conductivity part of the dielectric properties of the sample without the complications of dipolar changes that would accompany a typical cure. This permits a clear isolation of the effects of polarization of blocking electrodes.

It should be emphasized that our experiments are designed to highlight the effects of ionic conductivity of the neat resin. In actual cures, such as that of Figure 2, there can also be additional ionic contributions from the curing agent. Furthermore, in actual cures, while the ionic effects dominate earlier in cure, dipole effects can appear later in cure.

III. POLARIZATION MODEL

As a prelude to the presentation of experimental data, it is useful to examine a simple model of the polarization of blocking electrodes. Figure 3 illustrates the polarization schematically using the parallel-plate geometry. The sample is initially uncharged and unpolarized. When a voltage is applied to the plates, polarization of the material proceeds by dipole orientation (the normal permittivity) and polarization of the blocking electrodes proceeds by ionic conduction. The ions

RANDOM
DIPOLES

RANDOM
IONS

(a)

ORIENTATION
STARTS

CONDUCTION
STARTS

(b)
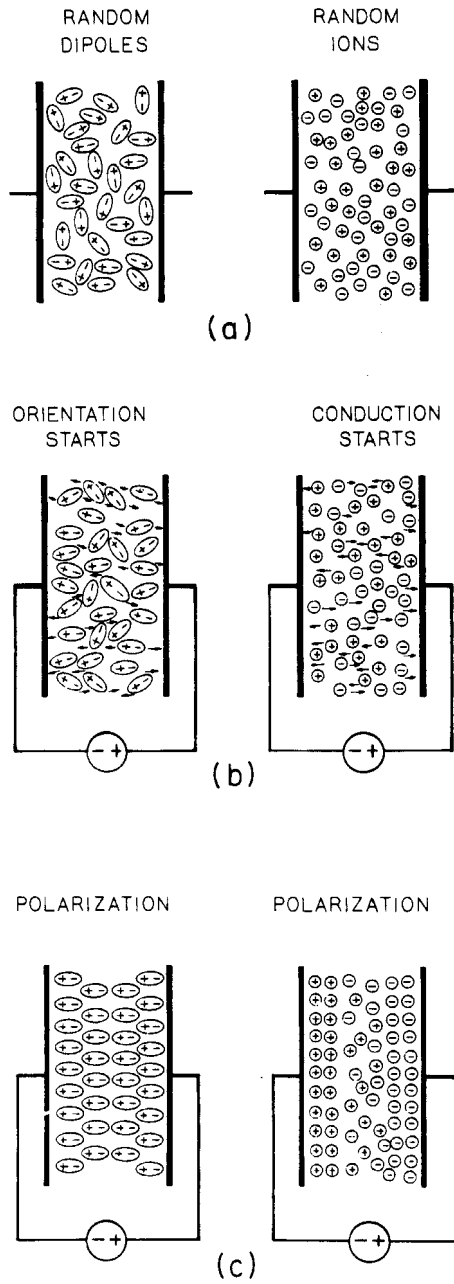
POLARIZATION

POLARIZATION

(c)

FIGURE 3   Idealized view of the polarization due to dipoles and ions: (a) unpolarized;
(b) orientation and conduction begins; (c) fully polarized. In actual materials, both
processes can occur simultaneously.

accumulate at the electrodes, forming a charge layer which is qualitat-ively similar to the layer of bound charge established by dipole orient-ation, but which can have a much greater charge per unit area. Thus, viewed from the electrodes, the measured capacitance C, which depends on the total polarization charge, can be much larger than would result from dipoles. Since the parallel equivalent circuit of Figure 1 is conven-tionally used to interpret dielectric measurements, the use of Equation 1 to extract ε' from C would result in an *apparent* permittivity which can be quite large.

A simple equivalent circuit that includes blocking layers is shown in Figure 4. The two charge layers that form at the electrodes, each of thickness t_b, are combined into a single blocking capacitor C_b with a plate spacing of $2t_b$. In order to distinguish between an *apparent* measu-red permittivity and the *actual* bulk permittivity of the medium, we shall denote the experimentally measured permittivity, loss factor, and loss tangent as ε'_x, ε''_x, and $\tan\delta_x$, respectively, where the x subscript represents an *experimental* result. These experimental values are what would be inferred from the measurement using the parallel R–C equivalent circuit of Figure 1 together with Eq. 1. Quantities without the x subscript represent the actual values for the bulk resin, and are what would be measured when blocking layers are absent.
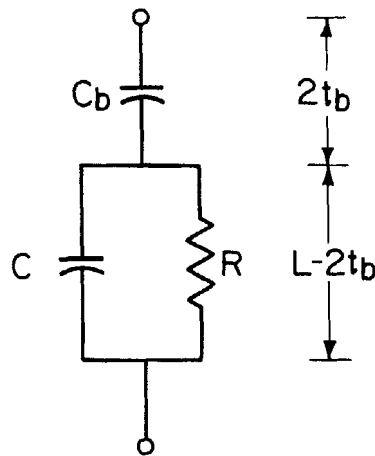

FIGURE 4   Equivalent circuit that includes a blocking layer.

We assume for simplicity that the permittivity within the blocking layer has the same value as that in the bulk. C_b is then given by

$$C_b = \frac{\varepsilon' \varepsilon_0 A}{2t_b} \qquad (3)$$

The bulk permittivity is represented by a capacitor C as in Figure 1, and the ionic conductivity mechanism by a resistor R in parallel with C. If we allow for the blocking layer thickness, then the remaining thickness for the bulk portion of the sample is $L - 2t_b$. Hence, the value of C is

$$C = \frac{\varepsilon' \varepsilon_0 A}{L - 2t_b} \qquad (4)$$

Assuming that the ionic conductivity σ is the only contribution to ε'' (*i.e.* $\varepsilon'' = \sigma/\omega\varepsilon_0$, with no dipolar contribution), then R is given by

$$R = \frac{L - 2t_b}{A\sigma} \qquad (5)$$

The intrinsic loss tangent, $\tan\delta$, then becomes

$$\tan\delta = \frac{\sigma}{\omega\varepsilon_0\varepsilon'} \qquad (6)$$

The critical issue is that when ionic conductivity is present, $\tan\delta$ can become arbitrarily large as the frequency is lowered. Therefore, when measuring at low frequencies early in cure (where relatively large ionic conductivity is present) the intrinsic $\tan\delta$ is large, and it is in this domain that polarization effects are observed. We now examine how this comes about.

Qualitatively, it is apparent that if the conductivity is low, hence making R large, the sample will behave as a simple dielectric with permittivity ε'. However, when the conductivity is large enough so that the impedance of R becomes less than that of C (the impedance of C is $1/\omega C$), then $\tan\delta \rangle 1$ and the charging of C_b through R becomes the dominant behavior of the circuit. Under these circumstances, the relative impedances of R and C_b determine whether or not significant charging of C_b can take place at the frequency of measurement. As long as R

represents the larger of the two impedances, then charging of C_b (*i.e.*, electrode polarization) is not significant. However, when $R < 1/\omega C_b$, the charging of C_b becomes important. These arguments lead to two inequalities that must be satisfied if blocking layer effects are to be observed:

$$\tan\delta \gg 1 \tag{7}$$

and, by combining $R < 1/\omega C_b$ with Eqns. 3, 5, and 6

$$\tan\delta \gg \frac{L - 2t_b}{2t_b} \tag{8}$$

A useful method for demonstrating the effect of the blocking layer is with a plot of the experimental ε_x'' *vs* ε_x', with frequency as the parameter (a Cole-Cole plot). We have analyzed the circuit of Figure 4, and extracted the experimental ε_x' and ε_x'' values using Equation 1. The results are

$$\varepsilon_x' = \varepsilon' \frac{L}{2t_b} \left[\frac{(\tan\delta)^2 + \left(\dfrac{L}{2t_b}\right)}{(\tan\delta)^2 + \left(\dfrac{L}{2t_b}\right)^2} \right] \tag{9}$$

$$\varepsilon_x'' = \varepsilon'' \frac{L}{2t_b} \left[\frac{\left(\dfrac{L - 2t_b}{2t_b}\right)}{(\tan\delta)^2 + \left(\dfrac{L}{2t_b}\right)^2} \right] \tag{10}$$

$$\tan\delta_x = \frac{\varepsilon_x''}{\varepsilon_x'} = \tan\delta \left[\frac{\dfrac{L}{2t_b} - 1}{(\tan\delta)^2 + \dfrac{L}{2t_b}} \right] \tag{11}$$

It is interesting to note that in the ideal case of no blocking layer, *i.e.*, $L \gg t_b$, the equations become $\varepsilon_x' = \varepsilon'$, $\varepsilon_x'' = \varepsilon''$, $\tan\delta_x = \tan\delta$, as expected.

In these equations, the frequency appears implicitly in $\tan\delta$, with high

frequencies corresponding to small tanδ and low frequencies to large tanδ. Figure 5 shows a set of Cole-Cole plots illustrating the effect of the blocking layer thickness on the resulting dielectric parameters. For an infinitesimally thin blocking layer compared to the interelectrode spacing $(L/2t_b \gg 1)$, the Cole-Cole diagram approaches a vertical line which intersects the ε'_x axis at the bulk (dipolar) permittivity ε'. As the ratio $L/2t_b$ decreases, either due to a smaller interelectrode spacing or a
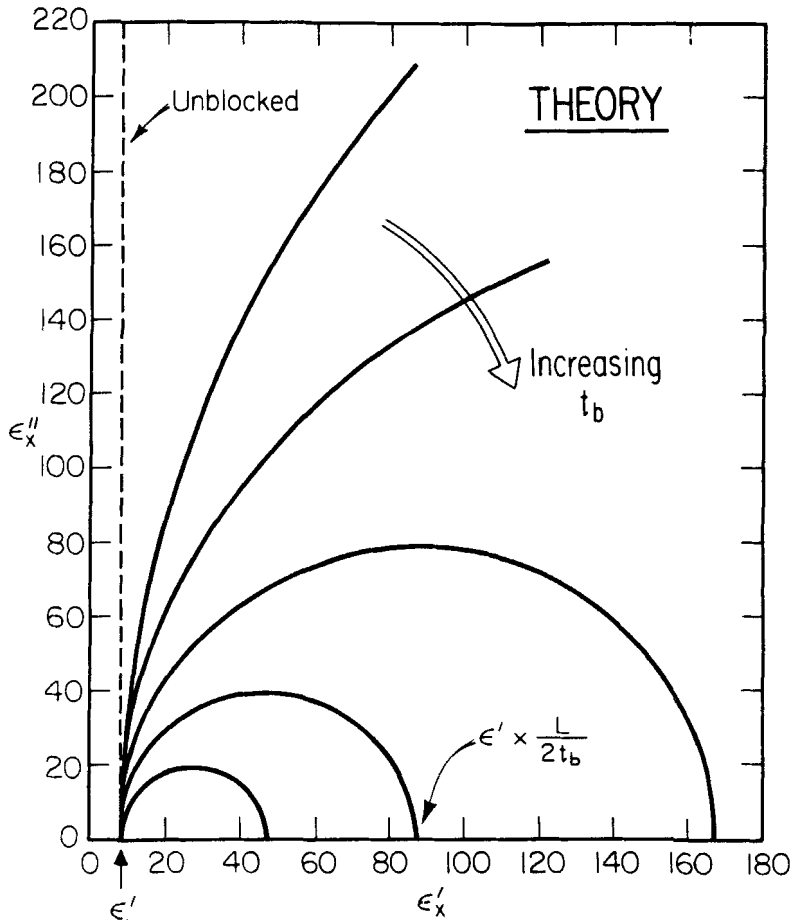

FIGURE 5   Cole-Cole plots from Eqs. 9 and 10 for various $L/2t_b$.

thicker blocking layer, the Cole-Cole diagram becomes semicircular, with one ε'_x-axis intercept at the bulk permittivity, and the second intercept at the bulk permittivity multiplied by $L/2t_b$. In the experimental discussion to follow, data of this type will be exhibited, and will be used to extract information about the blocking layer thickness t_b.
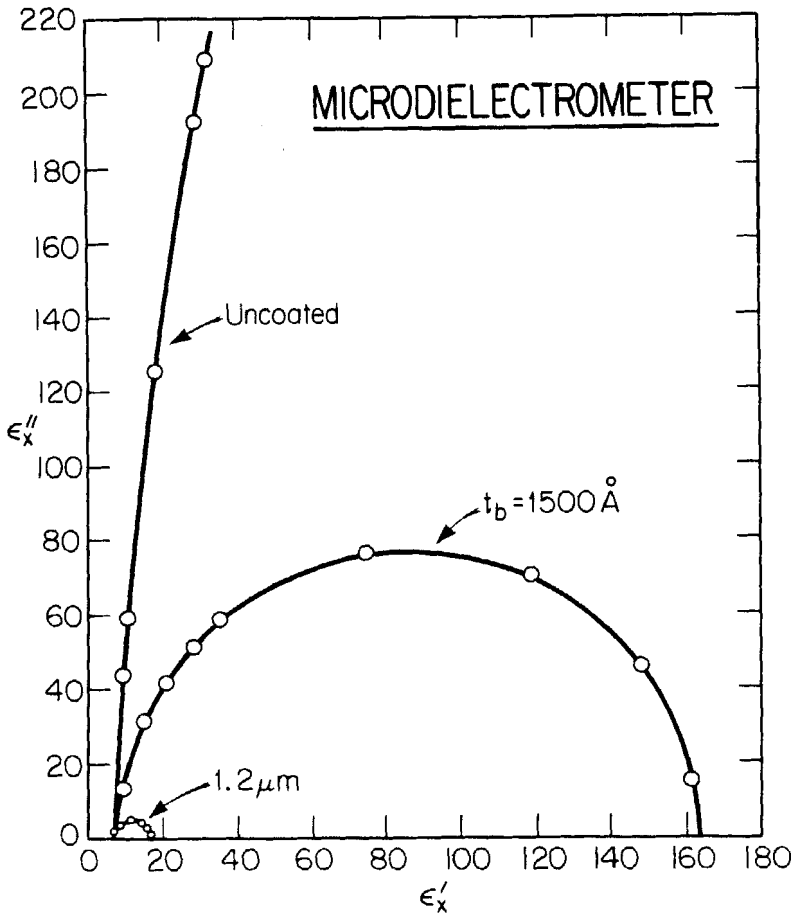

FIGURE 6 Experimental Cole-Cole plots from the microdielectrometer at room temperature.

IV. EXPERIMENTAL RESULTS

Figure 6 shows Cole-Cole diagrams measured at room temperature for the microdielectrometer sensor with various thicknesses of blocking layers. It is seen that the Cole-Cole diagrams all show the semicircular characteristic of a blocking layer, with a common ε'_x intercept at the bulk permittivity, and a second intercept that moves to arbitrarily large ε'_x

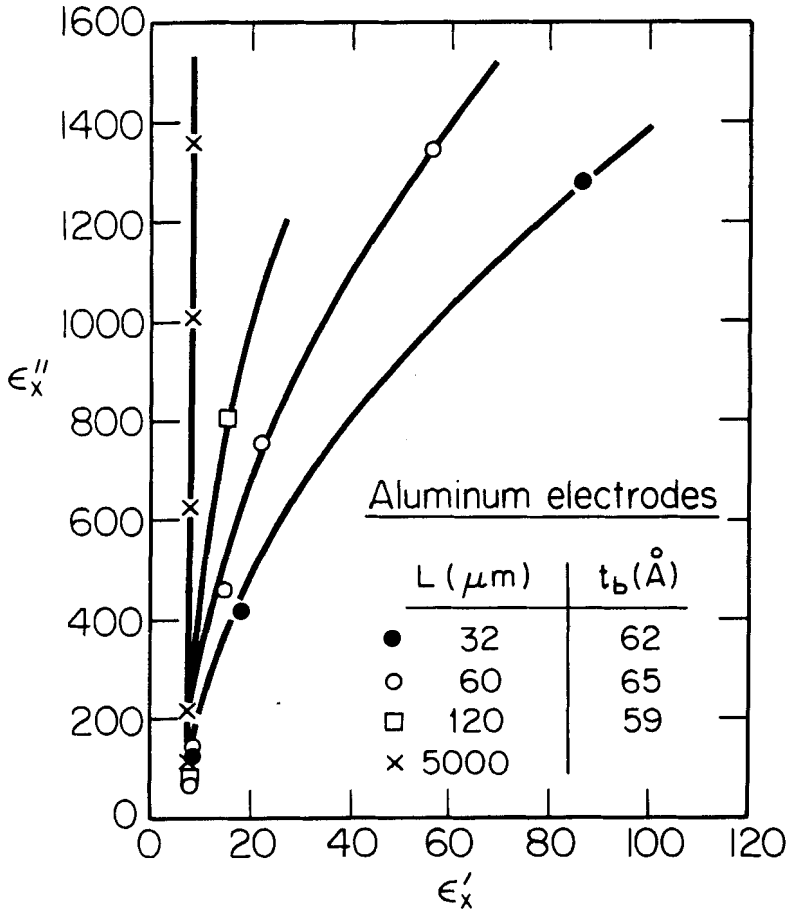| L (μm)	t_b(Å)
● 32	62
○ 60	65
□ 120	59
× 5000	

Aluminum electrodes

FIGURE 7 Experimental Cole-Cole plots from aluminum parallel plates with varied spacing. Data from the temperature range 20–90°C were merged for these plots.

values as the blocking layer becomes thinner. Even in the case of the
uncoated microdielectrometer sensing electrodes, where the blocking
layer thickness is measured in Angstroms (see below), the presence of the
semicircular trend in the data is evident.

Figures 7 and 8 show parallel-plate results for various interelectrode
spacings on aluminum and gold electrodes, respectively. In order to
keep the plots of reasonable scale, some additional data points at higher
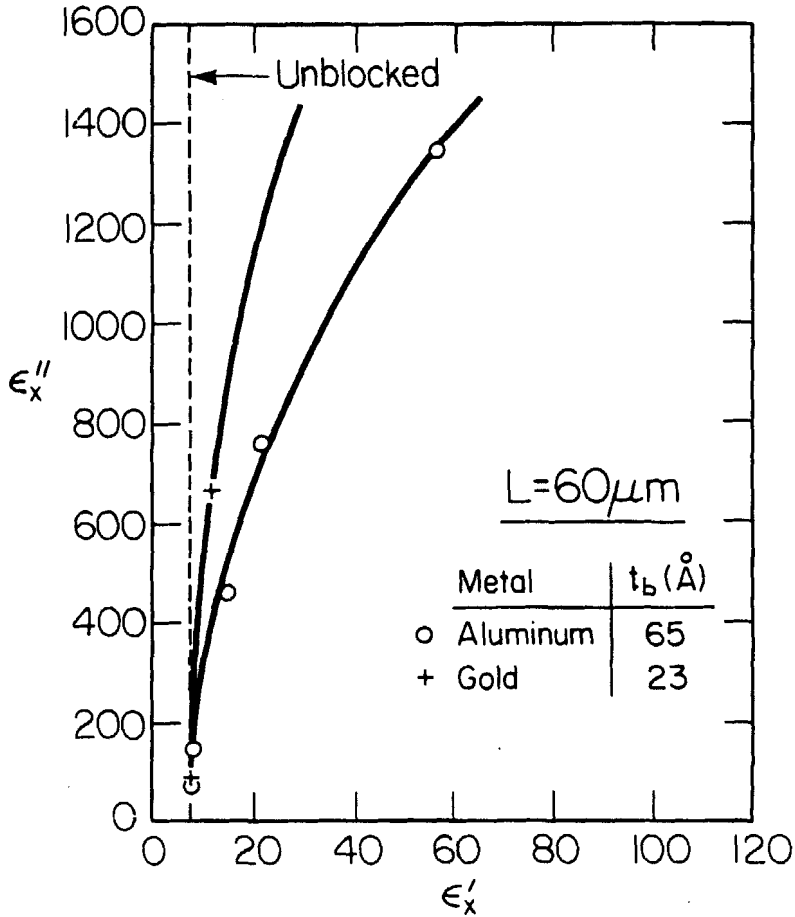

FIGURE 8   Experimental Cole-Cole plots for gold and aluminum parallel plates. Data
from the temperature range 20–90°C were merged for these plots.

values of ε'_x and ε''_x have been omitted from the diagrams; however, the solid lines are based on semicircular fits to all the data. The intercept of the semicircle is used to infer a blocking layer thickness for each inter-electrode thickness.

We note first that in the case of the aluminum electrodes with the smaller interelectrode spacings, the various Cole-Cole plots yield good agreement on the value of t_b, which is 62 Å. This shows that it is reasonable to attribute a well defined blocking layer thickness to the resin-electrode interface. The corresponding value of t_b on gold electrodes (Figure 8) is 23 Å. Since aluminum forms a native oxide and gold does not, one can attribute the result for the gold electrode to an intrinsic blocking layer in the resin, and the thicker blocking layer on aluminum to the combination of the native aluminum oxide and the intrinsic resin blocking layer. Furthermore, using MacDonald's analysis of blocking layer capacitances in electrolytes[7], one can use the 23 Å thickness on gold to estimate an equivalent ion concentration for the resin. That is, the intrinsic blocking layer thickness is estimated as equal to the Debye length L_D for the electrolyte, which is given by

$$L_D = [\frac{2\ kT\varepsilon''\varepsilon_0}{q^2 N}]^{1/2} \tag{12}$$

where kT is thermal energy, q is the electronic charge, and N is the ion concentration. Using a bulk permittivity of 9, the 23 Å blocking layer corresponds to an overall ion concentration of 4×10^{18} cm^{-3}, or roughly 100 ppm. While this is a reasonable value for residual impurities in a commercial resin, we do not have an independent confirmation of the accuracy of this estimate.

V. DISCUSSION OF RESULTS

These results show that blocking layer effects can be observed in parallel-plate experiments when the $L/2t_b$ value becomes small enough. For conventional spacings without an added blocking layer, however, such as the 5 mm spacing in Figure 7, the Cole-Cole plot looks almost ideal. The problem is that it is common practice to add a release film which functions as an extrinsic block layer when doing dielectric cure monitoring. To show how important this effect can be, consider placing a 25 μm (one mil) blocking layer between 5 mm parallel plates. The ratio
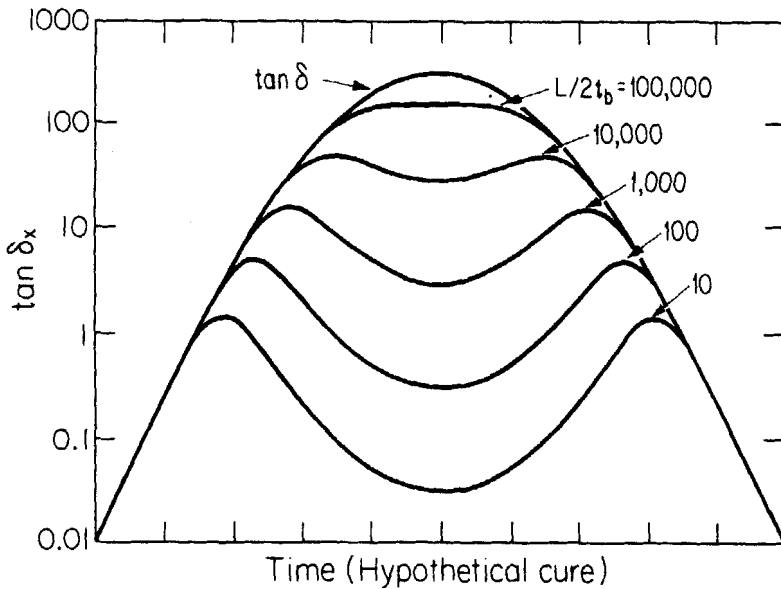
FIGURE 9   Hypothetical cure data for tanδ and for the corresponding tanδ_x that would be observed experimentally for various values of $L/2t_b$.

$L/2t_b$ in this case would be 100, which might appear to be large. However, the data of Figure 7 clearly show significant blocking layer effects even when $L/2t_b$ is as large as 10,000. Therefore, much of the conventionally reported dielectric cure data carried out with parallel plates in which a blocking layer is used have significant blocking layer effects in the data.

We can illustrate this effect for a hypothetical cure experiment by comparing tanδ to the experimental tanδ_x obtained from Equation 11. For illustration purposes, we assume that tanδ begins at a low value, increases to a maximum, then decreases. This would be typical behavior in a ramped resin cure. Figure 9 shows a hypothetical cure behavior for tanδ versus time together with the corresponding behavior of what would be the experimentally observed tanδ_x for various values of $L/2t_b$. Note that as the blocking layer thickness increases, one changes from observing a maximum in tanδ_x to a minimum. Furthermore, when there is a minimum in the experimental tanδ_x, two subsidiary maxima occur. Most important, since these blocking layer artifacts depend on the ratio

of the interelectrode spacing to the blocking layer in thickness, attempts to repeat parallel-plate cure studies without carefully controlling both the interelectrode spacing and blocking layer thickness could be expected to yield non-reproducible cure results.

There are many examples in the literature of data which resemble the $\tan\delta_x$ curves shown in Figure 9. As a result of this work, we are now reexamining much of the published data with a goal of clarifying the interpretation of the various $\tan\delta$ maxima and minima which have been reported. An evaluation of that literature will be the subject of a future publication.

VI. SUMMARY AND DISCUSSION

It has been demonstrated that the presence of capacitances at the boundaries of blocking electrodes affects the interpretation of dielectric measurements in materials which have ionic conductivity as the dominant polarization mechanism. Analysis of experimental data using Cole-Cole plots has shown that the polarization effect is determined by the ratio of the interelectrode spacing to the blocking layer thickness. Results from a range of electrode spacings were used to extract an intrinsic blocking layer thickness for a DGEBA resin, and a Debye-length interpretation of that thickness corresponds to reasonable levels of ionic contamination. It has been further shown that even in conventional parallel-plate measurements, if an extrinsic blocking layer is used, one must take careful account of blocking layer effects when interpreting dielectric data. In particular, for commonly used blocking layer thicknesses, maxima in the intrinsic $\tan\delta$ appear in the data as $\tan\delta_x$ minima, with the appearance of secondary maxima. Furthermore, the widespread practice of assuming that $\tan\delta$ calibration of parallel-plate measurements is independent of plate spacing may lead to non-reproducible results in cure studies where plate spacing and blocking layer thickness are not carefully controlled.

Acknowledgements

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