Insight — Application Note 2.16

Electrode Polarization and Boundary Layer Effects

Introduction

When the incorrect model is used to determine dielectric properties, low frequency measurements of highly conductive materials may appear to have unusually low conductivity. This phenomenon is caused by electrode polarization, the accumulation of charge against the electrodes, which occurs when the material under test:

- Has high loss factor (high ionic conduction at low frequency)

  AND

- Has a non-conductive film, an oxide layer or an electrochemical potential barrier, resulting in an insulating boundary layer

If the effects of electrode polarization and boundary layers are properly considered, then it is possible to account for their influence and correctly calculate bulk permittivity and conductivity.

Effects of electrode polarization

Electrode polarization distorts dielectric data by artificially increasing *apparent* relative permittivity (ε') and decreasing *apparent* loss factor (ε''). When plotted against time, loss factor curves may display anomalous behavior as shown in Figure 16-1.

This distortion increases as loss factor increases. In addition, lower frequencies correspond to higher loss factors for a given conductivity, and therefore display even greater distortion. As a result, the 10 Hz loss factor data of Figure 16-1 shows a double hump—a depression with two satellite peaks instead of a single peak. The first satellite peak has been attributed to softening, and the second satellite peak to gelation—but they both are artifacts from use of an incorrect model and do not describe actual dielectric events. In fact, the expected—but unseen—single loss factor peak corresponds to the point of minimum viscosity, an event that would be completely lost if the data were misinterpreted.

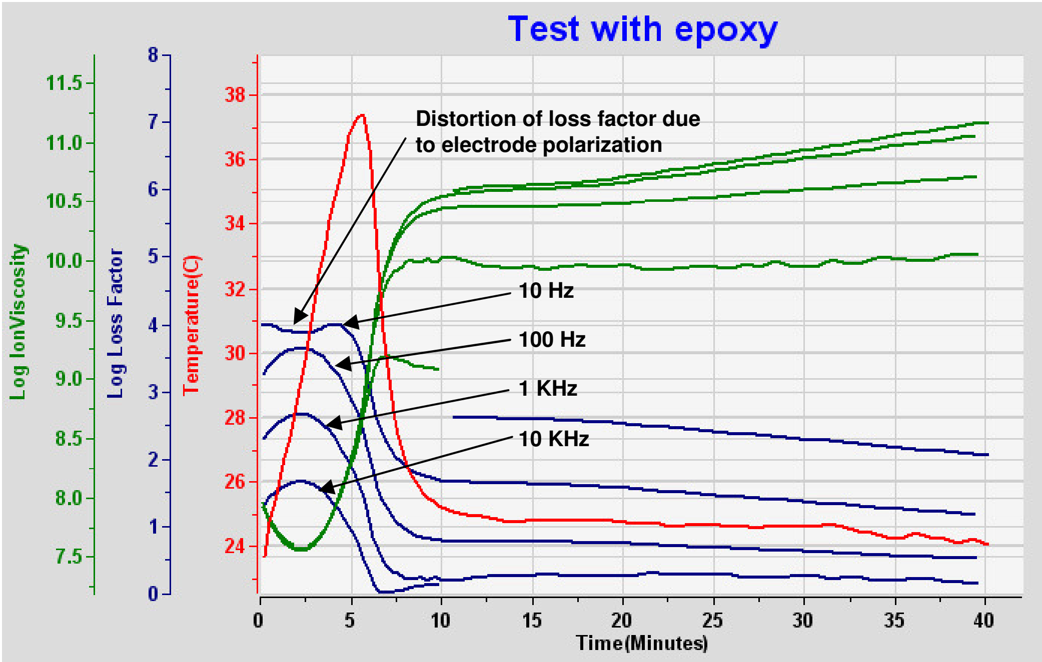


Figure 16-1
Plot showing distortion of loss factor due to electrode polarization

The loss factor data of Figure 16-1 can be plotted against permittivity to highlight the nature of these relationships, as shown in Figure 16-2.

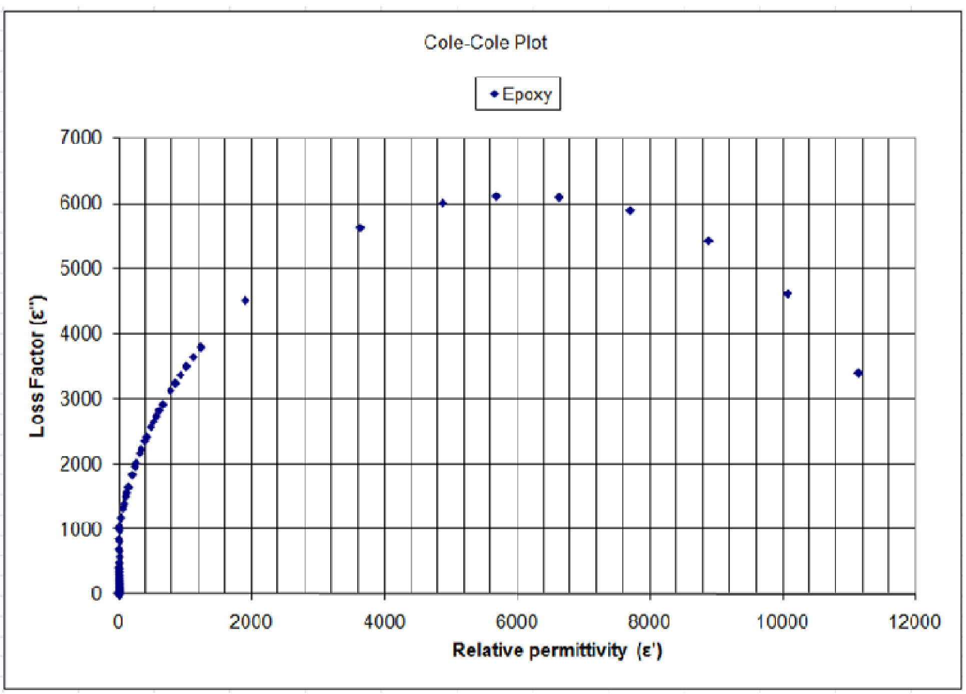


Figure 16-2
Cole-Cole plot of epoxy cure data distorted by electrode polarization

In older literature this Cole-Cole plot behavior has been erroneously explained by a large dipole relaxation response.

Basic Circuit Model of a Dielectric Material

The basic model of a dielectric Material Under Test consists of a conductance G_{MUT} in parallel with a capacitance C_{MUT} as shown below in Figure 16-3.

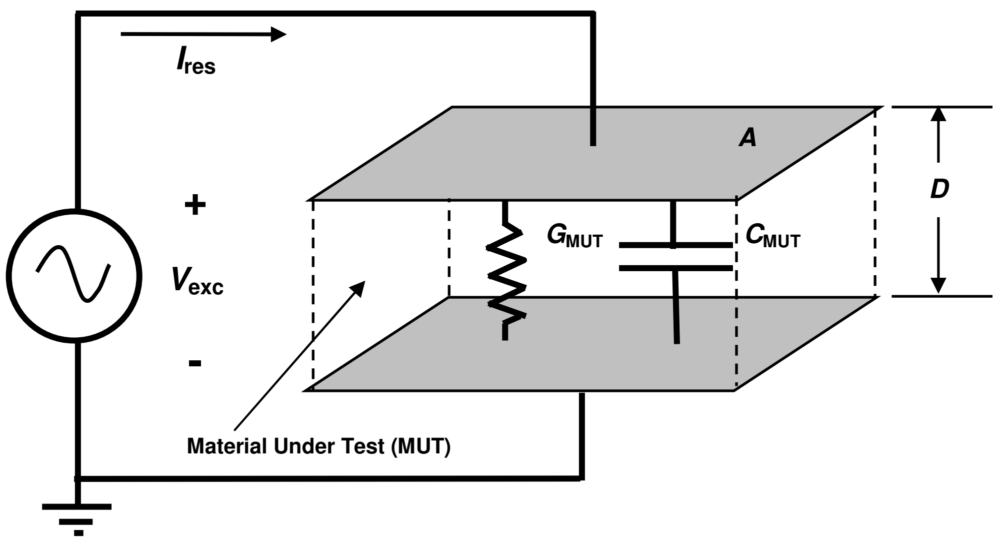


Figure 16-3
Basic model of a dielectric material

This configuration has a simple relationship between the excitation voltage V_{exc} across the material and the response current I_{res} through the material, given by equation 16-1:

(eq. 16-1) $$I_{res} / V_{exc} = G_{MUT} + i\omega C_{MUT} = Y_{MUT}$$

Boundary Layers

Electrode polarization creates a boundary layer at the interface with the material and changes the model to that shown in Figure 16-4:

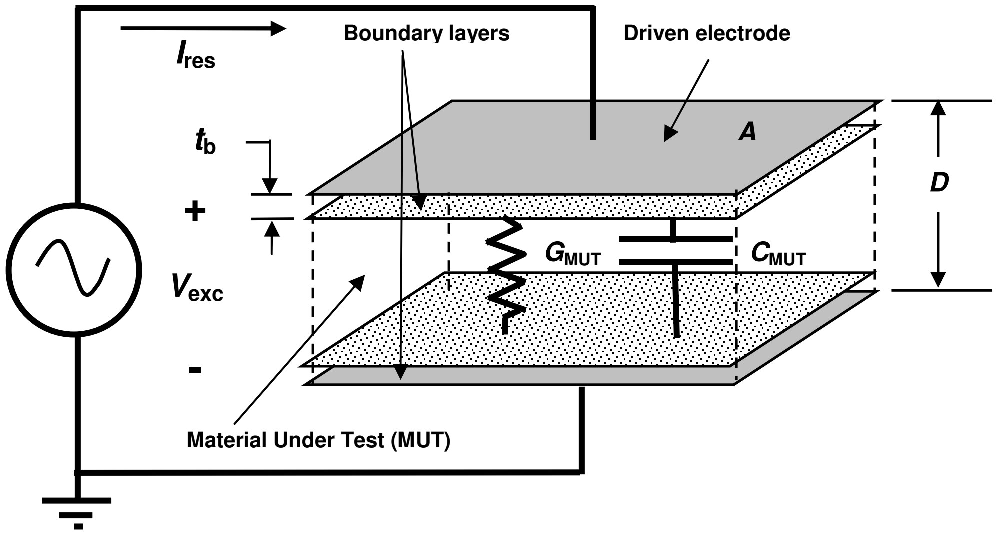


Figure 16-4
Model of dielectric material with boundary layer

The boundary layers are very thin (thickness = t_b) and have the surface area of the electrodes. Consequently they have a very large *A/D* ratio, resulting in a very large capacitance C_B in series with the bulk material. This arrangement is shown in the circuit model of Figure 16-5.

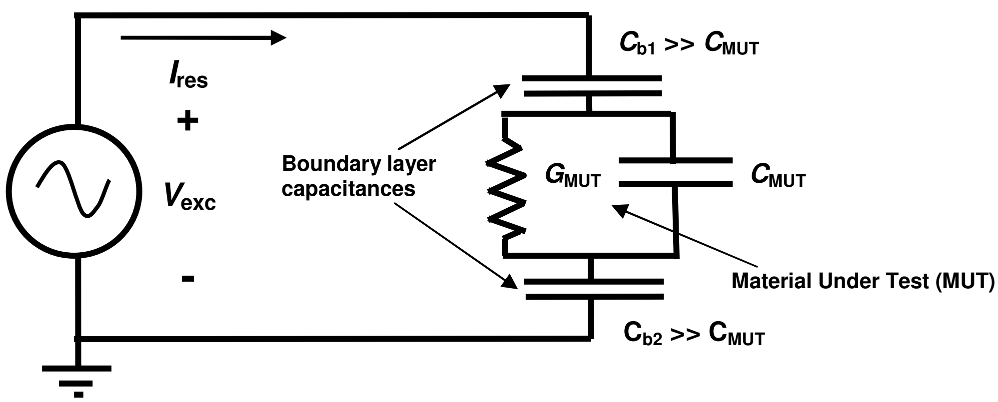


Figure 16-5
Circuit model of dielectric with boundary layer capacitances

Analysis of the boundary layer model is much more complicated than for the basic model, but it is possible to quickly understand the circuit behavior in certain limiting cases.

Low Frequency Response of Boundary Layers

For situations with low excitation frequency or high bulk conductivity, the boundary layer capacitances dominate the circuit response and the model reduces to that of Figure 16-6. Capacitances act as open circuits at low frequencies, so the electrode boundary layer blocks DC current. Measurements of DC conductance are impossible in this case and the material appears primarily capacitive.

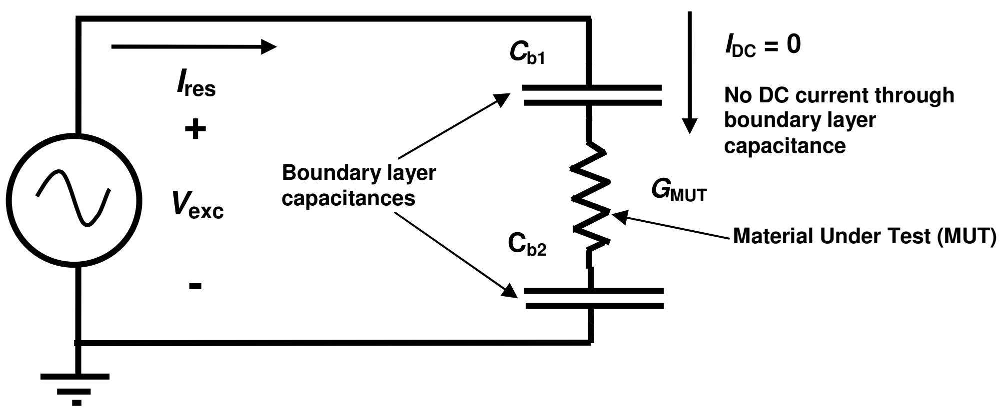


Figure 16-6
Circuit model of dielectric with boundary layer capacitances

In reality these boundary layer capacitances may be "leaky" and some DC current passes through them. The boundary layer conductances G_{b1} and G_{b2}, shown in Figure 16-7, would be uncertain and can range from being very high (and negligible), to being very low (and significant). Furthermore, G_{b1} and G_{b2} may vary with temperature and the state of the material, which itself will vary during cure.

If the basic model of Figure 16-3 is used to interpret measurements, the apparent bulk conductance would be the conductance of the series configuration of G_{b1}, G_{MUT} and G_{b2}, i.e. the inverse of the sum of their resistances, given by equation 16-2:

(eq. 16-2) $$R_{MUT\ (apparent)} = R_{b1} + R_{MUT} + R_{b2} \quad \text{(where } R = 1/G\text{)}$$

At best the boundary layer resistances are negligible, but in the worst case for high R_{b1} and R_{b2} the apparent bulk resistance would appear much higher than it should be, because the bulk conductance (and therefore conductivity) would appear much lower than it should be.

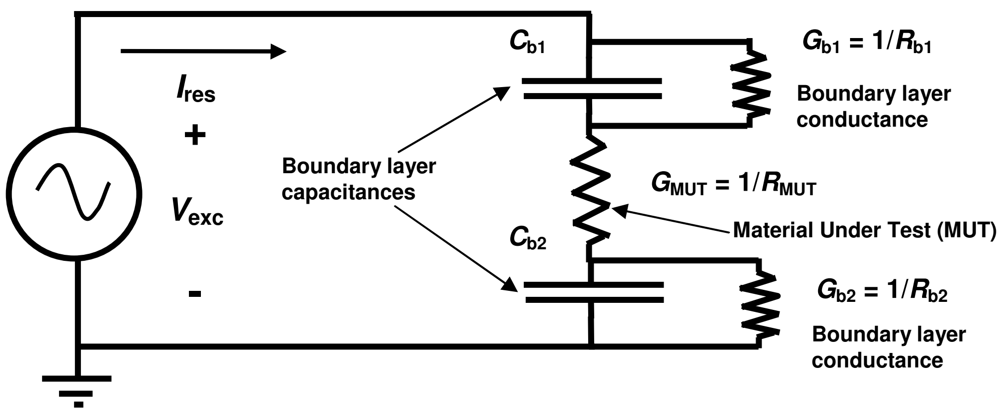


Figure 16-7
Circuit model of dielectric with “leaky” boundary layer capacitances

For qualitative measurements where accuracy is not critical, DC measurements can yield useful information; however, there will always be uncertainty about the magnitude of the boundary layer effect.

High Frequency Response of Boundary Layers

For the limit of high frequency or low bulk conductivity, boundary layer admittance is high compared to the Material Under Test, and boundary layer capacitances act like short circuits. In this case the circuit of Figure 16-7 reduces to the simpler one of Figure 16-8, which is identical to the basic model of a dielectric material. Therefore the high frequency behavior of a dielectric material is the same with or without boundary layers.

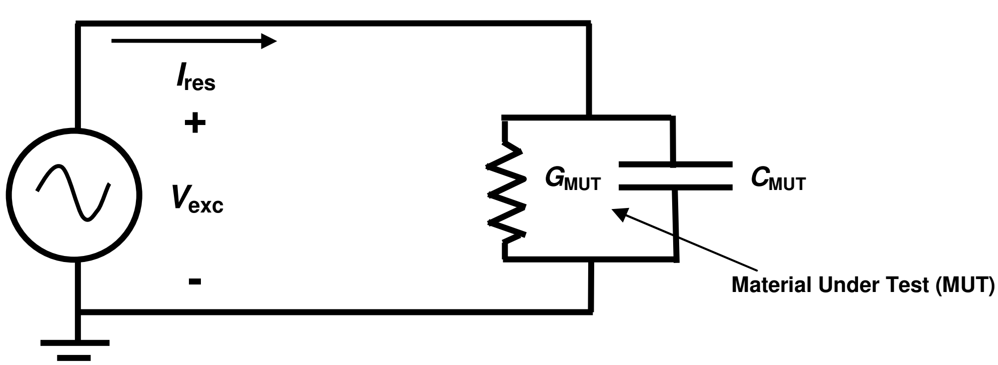


Figure 16-8
Circuit model of dielectric with boundary layer capacitances
(Limiting case of high frequency or low bulk conductivity)

Boundary Layer Effect on Dielectric Cure Monitoring

With the known quantities of:

$\omega = 2\pi f_{exc}$
$\varepsilon_0 = 8.85 \times 10^{-14}$ F/cm
A/D = ratio of area to distance for electrodes

it is possible to calculate the following dielectric material properties from measurement data:

(eq. 16-3) $\sigma = G_{MUT} / (A/D)$ (conductivity)
(eq. 16-4) $\varepsilon' = C_{MUT} / (\varepsilon_o A/D)$ (relative permittivity)
(eq. 16-5) $\varepsilon'' = \sigma / (\varepsilon_o \omega)$ (loss factor)
(eq. 16-6) $\rho = (A/D) / G_{MUT}$ (resistivity)

A common convention describes the cure of a polymeric material in terms of relative permttivity ε' and loss factor ε''. The boundary layer model of Figure 16-6 can be solved using these terms as follows[1]:

(eq. 16-7)
$$\varepsilon'_x = \varepsilon' \,(D / 2t_b)\, \frac{(\varepsilon''/\varepsilon')^2 + (D / 2t_b)}{(\varepsilon''/\varepsilon')^2 + (D / 2t_b)^2)}$$

(eq. 16-8)
$$\varepsilon''_x = \varepsilon'' \,(D / 2t_b)\, \frac{(D / 2t_b) - 1}{(\varepsilon''/\varepsilon')^2 + (D / 2t_b)^2)}$$

(eq. 16-9) $\tan \delta_x = \varepsilon''_x / \varepsilon'_x = \tan \delta \,[((D / 2t_b) - 1) / ((\tan \delta)^2 + (D / 2t_b))\,]$

Where:
- t_b = boundary layer thickness
- D = distance between electrodes or plate separation
- ε'_x = uncorrected (apparent) permittivity
- ε''_x = uncorrected (apparent) loss factor
- ε' = actual permittivity
- ε'' = actual loss factor
- $\tan \delta = \varepsilon''/\varepsilon'$

Figure 16-9 shows how boundary layer thickness, temperature, frequency and state of cure influence the Cole-Cole plot of a curing material. With no boundary layer, loss factor decreases with advancing cure, while permittivity remains constant at the value ε_r, called the relaxed permittivity. Thicker boundary layers cause the Cole-Cole plot to develop a curvature which in extreme cases can become a complete semi-circle.

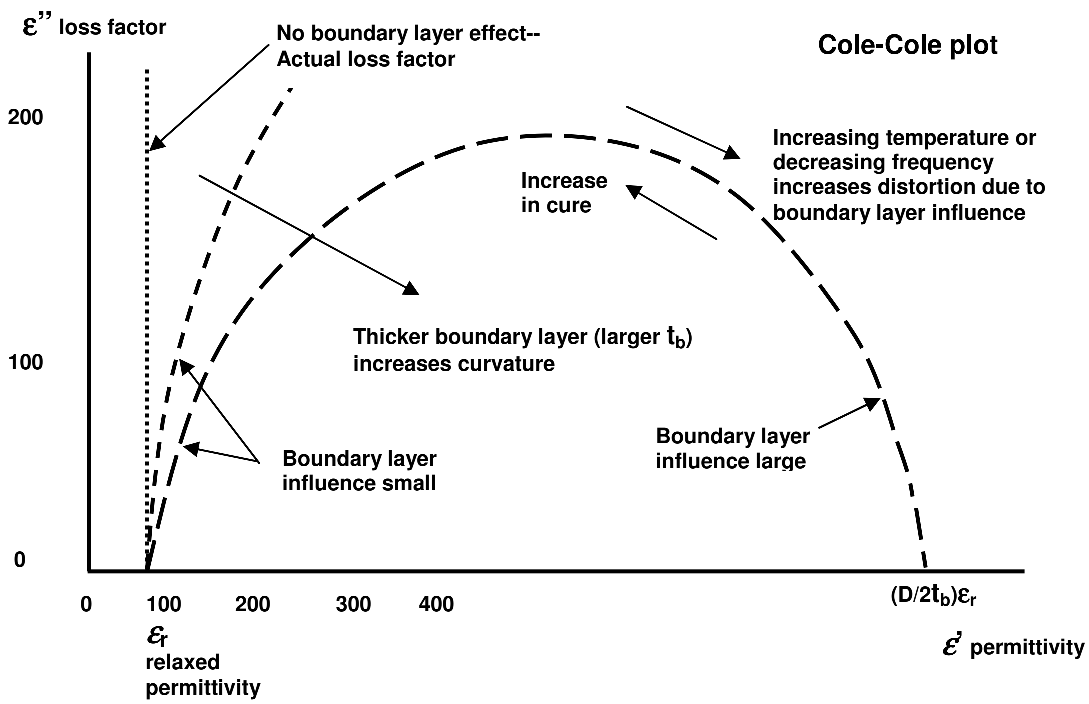


Figure 16-9
Cole-Cole plot of curing material with boundary layer effect

The left intercept of the semi-circle is the relaxed permittivity ε_r, and the right intercept is determined by both ε_r and the ratio $D/2t_b$. This information can be used to calculate the boundary layer thickness t_b. In the absence of an artificial blocking layer such as an applied insulator or an oxide coating, the boundary layer thickness can be used to calculate an approximate mobile ion concentration [C] and ion mobility μ[2]:

(eq. 16-10) $$[C] = (t_b^2 q^2) / (2kT\varepsilon' \varepsilon_0)$$

(eq. 16-11) $$\mu = \sigma / ([C]\, q)$$

Where : k = Boltzmann's constant (eV/K)
T = temperature in degrees Kelvin (K)
q = magnitude of electronic charge (coulombs)
μ = free ion mobility (cm^2 / (V-s))

Electrode Polarization Correction

It is possible to manipulate equations 16-7, 16-8 and 16-9 to correct the effect of electrode polarization in certain cases. Figure 16-10 shows data that has been adjusted in this manner.

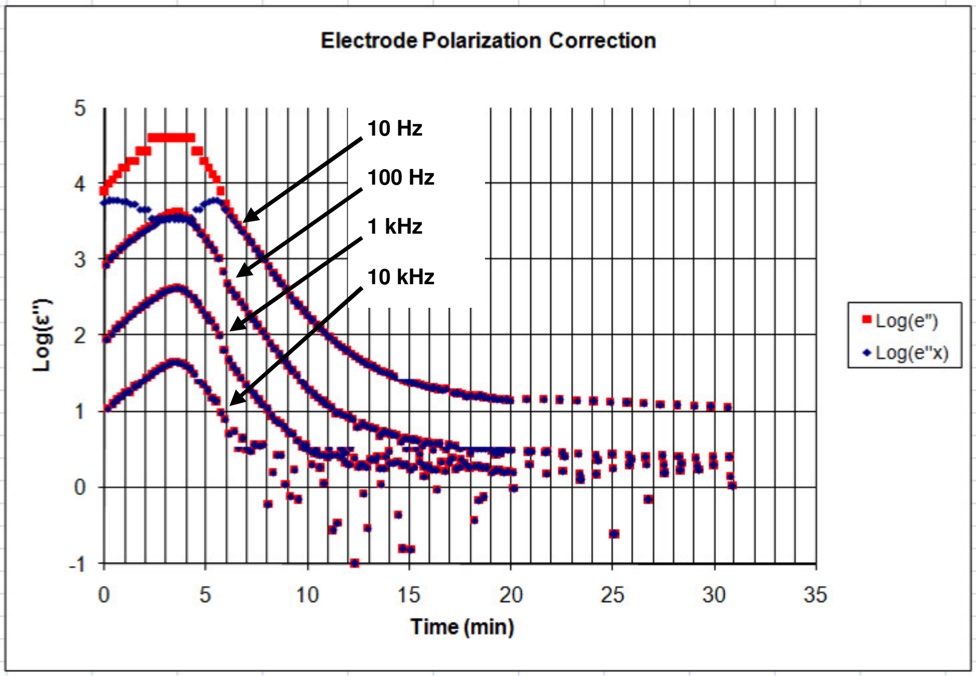
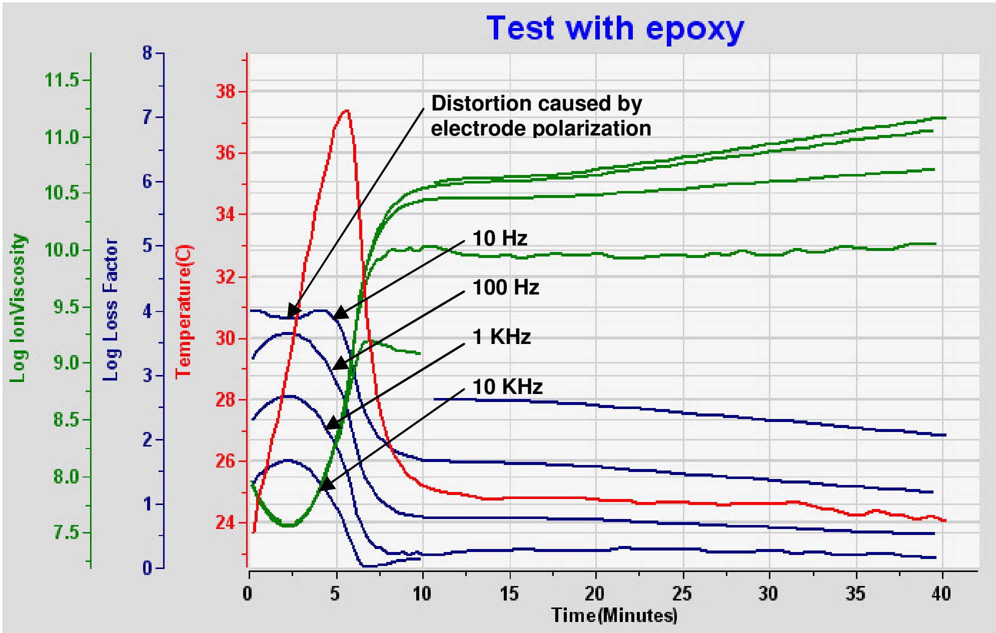


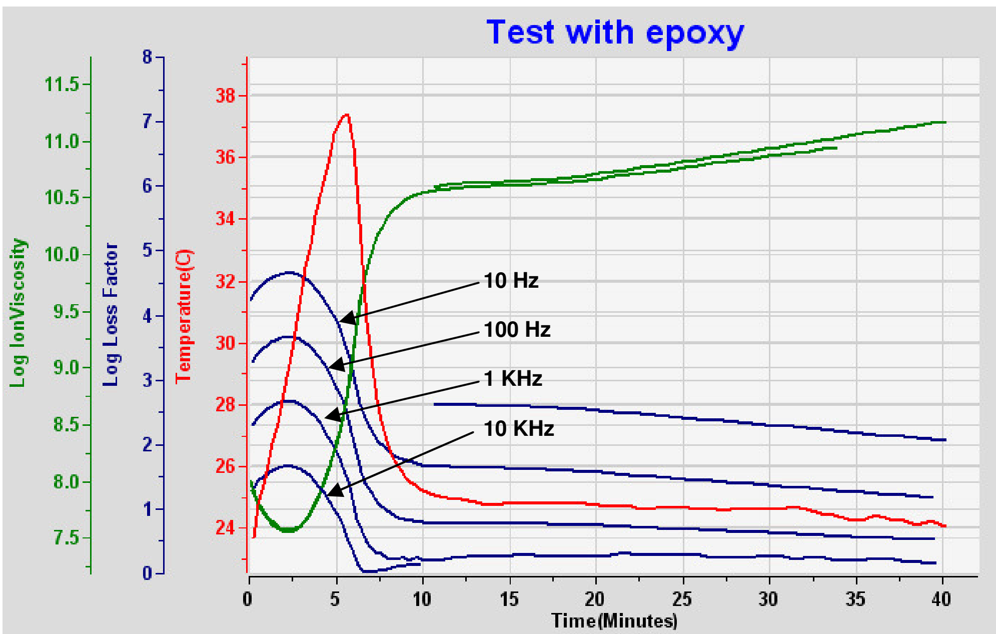
Figure 16-10
Correction of the boundary layer effect

Log(*e*″*x*) is the logarithm of the original loss factor *e*″*x*, which was acquired during cure of an epoxy resin. Log(*e*″*x*) data at 10 Hz shows distortions and the characteristic double hump from the boundary layer effect. This anomaly occurs at the time of maximum loss factor—maximum conductivity—as indicated by peaks from data at the higher frequencies of 100 Hz, 1.0 kHz and 10 kHz. Log(*e*″) is the logarithm of the corrected loss factor *e*″, and the corrected 10 Hz curve shows a loss factor peak consistent with peaks for higher frequencies.

Figure 16-11 compares data from the cure of this epoxy both before and after boundary layer correction.



Epoxy cure data showing distortion due to boundary layers



Epoxy cure data after electrode polarization correction

Figure 16-11
Comparison of data before and after electrode polarization correction

Note that loss factor is inversely proportional to frequency, as given by equation 16-5, repeated below:

(eq. 16-5) $$\varepsilon'' = \sigma' / (\varepsilon_o\ \omega)$$

During the early portion of cure, frequency independent DC conductivity σ_{DC} typically dominates loss factor and the corrected curves for 10 Hz, 100 Hz, 1 kHz and 10 kHz are all parallel and separated by factors of 10, as expected.

References

1. Day, D.R.; Lewis, J.; Lee, H.L. and Senturia, S.D., *Journal of Adhesion*, V18, p.73 (1985)

2. MacDonald, J.R., *Phys. Rev.*, v92, p.4 (1953)

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