Insight — Technical Overview 2.04
Electrode Polarization and DC Resistance Cure Monitoring

Introduction

Dielectric cure monitors measure the electrical properties of a thermoset with AC signals across a range of frequencies. Measurement of resistance with DC methods can also reveal information about a material, but has disadvantages and limitations that the user must consider. In particular, the phenomenon of electrode polarization can distort DC resistance data and cause misinterpretation of the cure state.

Dielectric Cure Monitoring

Dielectric cure monitoring (also known as Dielectric Analysis, or DEA) measures a polymer's resistivity (ρ) and permittivity (ε'), which are the material's dielectric properties. In general resistivity provides the most useful information about cure state. Resistivity itself has a frequency independent (ρ_{DC}) component due to the flow of mobile ions and a frequency dependent (ρ_{AC}) component due to the rotation of stationary dipoles.

Ionic mobility determines frequency independent resistivity (ρ_{DC}), while the state of a material's polymer chains or networks affects *both* ionic mobility and mechanical resistance to flow. Consequently, ρ_{DC} often differs from mechanical viscosity by only a scaling factor and is a useful probe of the cure state of epoxies, polyurethanes, polystyrenes, bulk molding compounds (BMC), sheet molding compounds (SMC) and other thermosets.

The term *ion viscosity* (*IV*) was coined in the early 1980's as a synonym for frequency independent resistivity, which is proportional to the change in mechanical viscosity before gelation and proportional to the change in modulus after gelation. Ion viscosity has units of ohm-cm and is defined below:

(Eq. 1) $$IV = \rho_{DC}$$

DC resistance measurements

AC measurements of thermosets can obtain the full range of information about cure state. Simpler DC methods provide data that are limited but still useful. Resistance monitors are essentially highly sensitive ohmmeters that use a

DC voltage source to drive current through the material between a pair of electrodes. Resistivity differs from resistance by only a scaling factor that depends on sensor geometry, so issues about resistivity apply equally to resistance.

Instruments using DC measurements achieve simplicity while sacrificing flexibility, and possibly accuracy, because of the following disadvantages:

- DC measurements can only obtain DC resistance
    - AC methods measure capacitance, frequency *independent* resistance and frequency *dependent* resistance
    - Frequency independent resistance is the more accurate term that describes DC resistance
    - Frequency independent resistance can be measured across a range of frequencies that includes DC
- DC measurements may have systematic errors
    - Offset voltage drifts, thermal drifts and leakage currents in circuits cannot be distinguished from the true DC signal
- DC measurements are not possible with release layers
    - Release layers are very thin insulating sheets used to prevent material from adhering to a mold or platen.
    - Release layers block DC current and prevent DC resistance measurement
- DC measurements may produce distorted data caused by *electrode polarization*

Electrode Polarization

It is often *not* useful to measure ρ_{DC} or DC resistance using DC signals. The phenomenon of electrode polarization can create a blocking layer across sensor electrodes during early cure, when material is most conductive. In the presence of electrode polarization, dielectric data from very low excitation frequencies are distorted, as shown in Figure 1 for the cure of a graphite-epoxy prepreg.

Note the flattening of the loss peak at 10 Hz and the *dip in place of the loss peak* at 1 Hz. This distortion becomes worse at lower and lower frequencies, and with DC signals a conductive material can even appear *non-conductive* because the blocking layer prevents the passage of DC current.

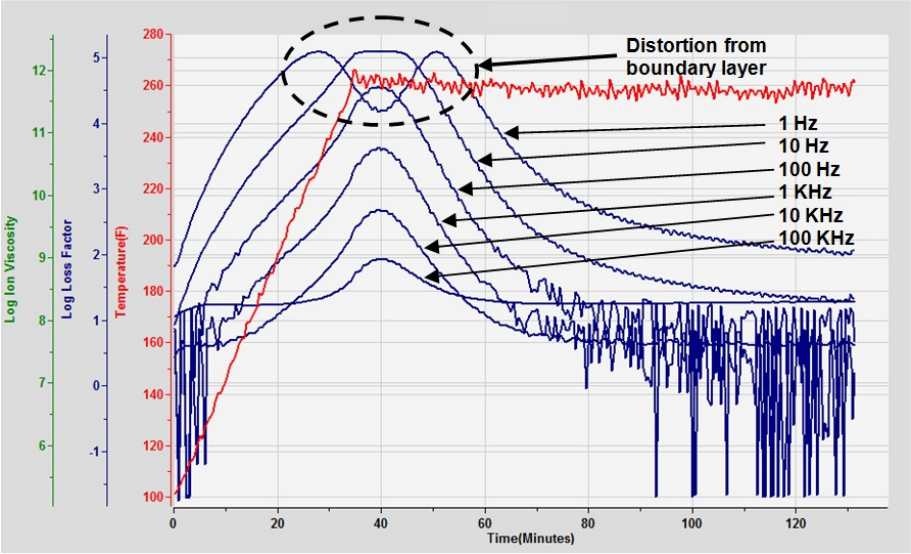


Figure 1
Distortion in loss factor data from a blocking layer

Electrode Polarization Correction

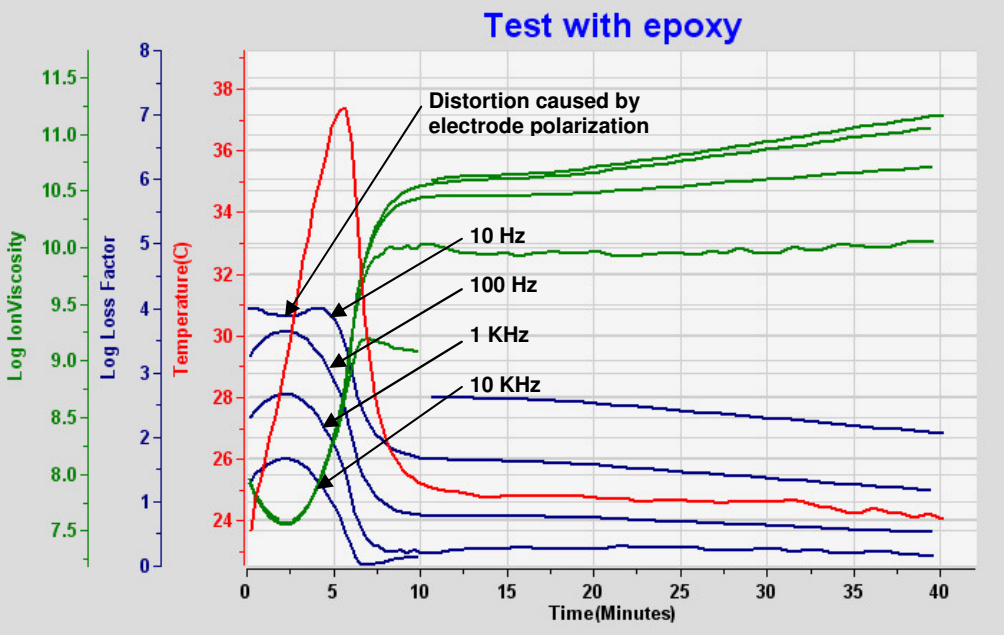
With only DC resistance, it is not possible to correct erroneous data caused by a boundary layer. However, AC dielectric measurements provide additional information, which enables electrode polarization correction.[1] Figure 2.a. shows the raw loss factor, with distortions at 10 Hz and the characteristic dip from a boundary layer. This anomaly occurs at the time of maximum loss factor—maximum conductivity—as indicated by peaks from data at higher frequencies. Figure 2.b. shows the corrected 10 Hz loss factor, which now has a peak consistent with the higher frequencies.

When frequency independent conductivity dominates the dielectric response, loss factor is inversely proportional to frequency, as given by equation 2:

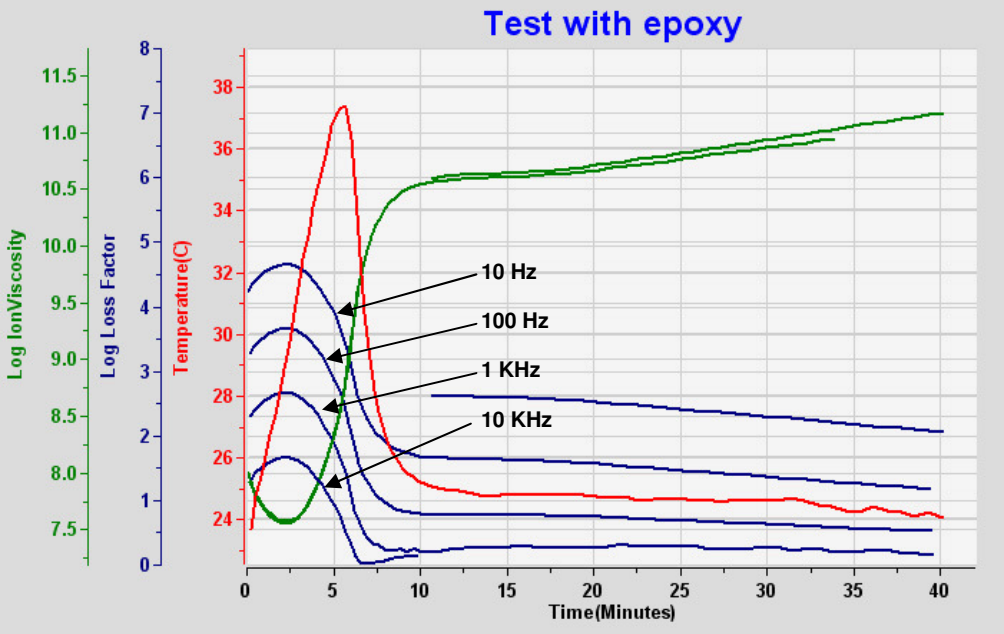
(eq. 2) $$\varepsilon'' = \sigma_{DC} / (\varepsilon_0 \omega)$$

Where: σ_{DC} = Frequency independent conductivity
ε_0 = Permittivity of free space
ω = $2\pi f$ (s^{-1})
f = Frequency (Hz)

Frequency independent conductivity (σ_{DC}) typically dominates during early cure. In Figure 2.b. the corrected curves for 10 Hz, 100 Hz, 1 kHz and 10 kHz are all parallel at this time, with levels inversely proportional to frequency, as expected.



a. Uncorrected cure data showing distortion due to boundary layers



b. Cure data after electrode polarization correction

Figure 2
Loss factor before and after electrode polarization correction

Frequency independent resistivity is the inverse of frequency independent conductivity, as given in equation 3:

(eq. 3) $$\rho_{DC} = 1/\sigma_{DC}$$

The ion viscosity of Figure 2.b. is the family of overlapping resistivity data, and represents cure state throughout the test.

Ion Viscosity

The loss factor (ε'') during cure of a "Five-minute" epoxy is shown in Figure 3.

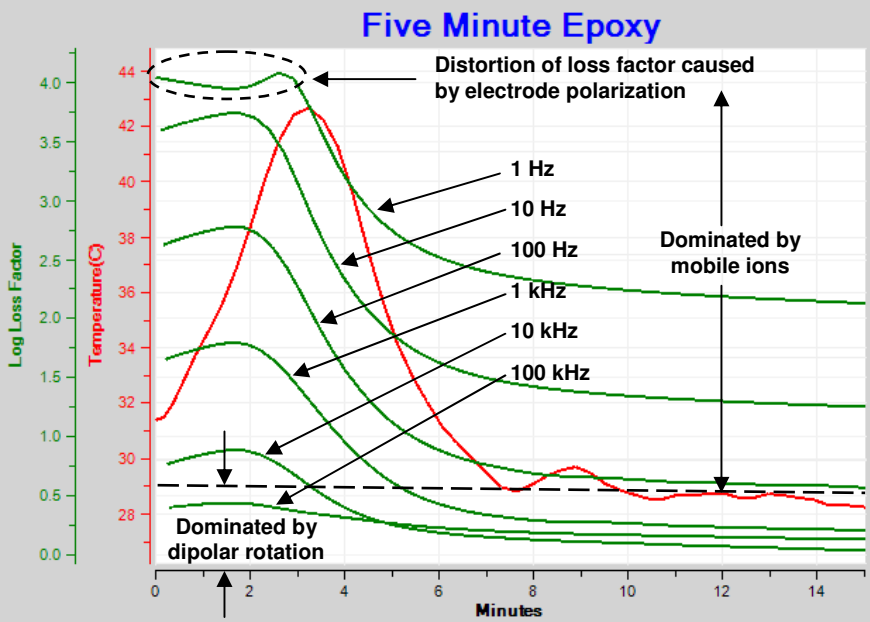


Figure 3
Loss factor of curing epoxy

During early cure of this material, loss factor is inversely proportional to frequency for 10 kHz or less—the effect of mobile ions dominates at this time. Loss factor for 1 Hz shows distortions characteristic of a boundary layer caused by electrode polarization. As cure progresses, the relative influence of dipole rotation grows; after a time loss factor is no longer inversely proportional to frequency for 1 kHz or greater. At the end of cure, loss factors for 1 Hz and 10 Hz are still inversely proportional to frequency.

The relationship between resistivity and loss factor is defined by equation 4. Figure 4 shows resistivity derived from the loss factor data of Figure 3.

(eq. 4) $$\rho = 1/(\omega \varepsilon_0 \varepsilon'')$$

Where: ε_0 = Permittivity of free space
ω = $2\pi f$ (s^{-1})
f = Frequency (Hz)

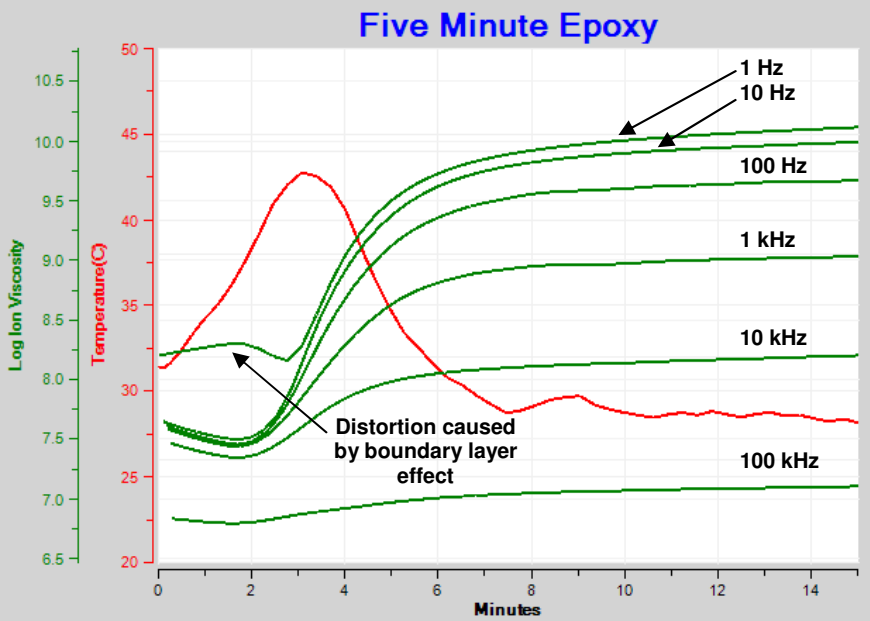


Figure 4
Resistivity of curing epoxy (plotted against log(ion viscosity) axis)

Frequency independent resistivity, from mobile ions, dominates where curves overlap, although sometimes the overlap may not be perfect because of a slightly non-ideal response.

Figure 5 shows the family of resistivity curves after using an algorithm to present only data dominated by mobile ions. This plot now shows the progression of frequency independent resistivity, properly called *ion viscosity*, which indicates cure state of the material.

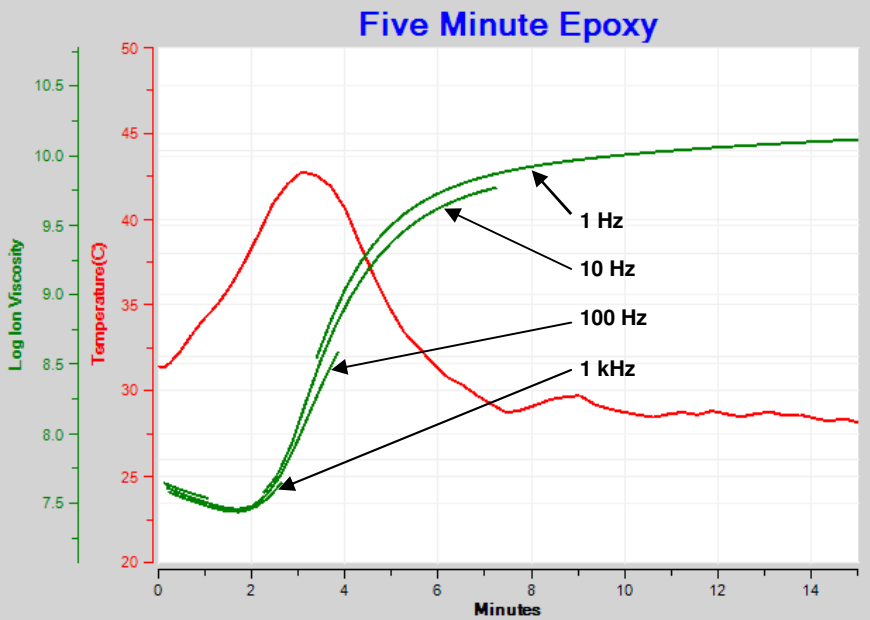


Figure 5
Ion viscosity—frequency independent resistivity component only

Ion viscosity from an appropriate frequency can be very similar to the composite from multiple frequencies, so it is often possible to observe the entire cure with a single frequency, such as the 10 Hz data of Figure 6.

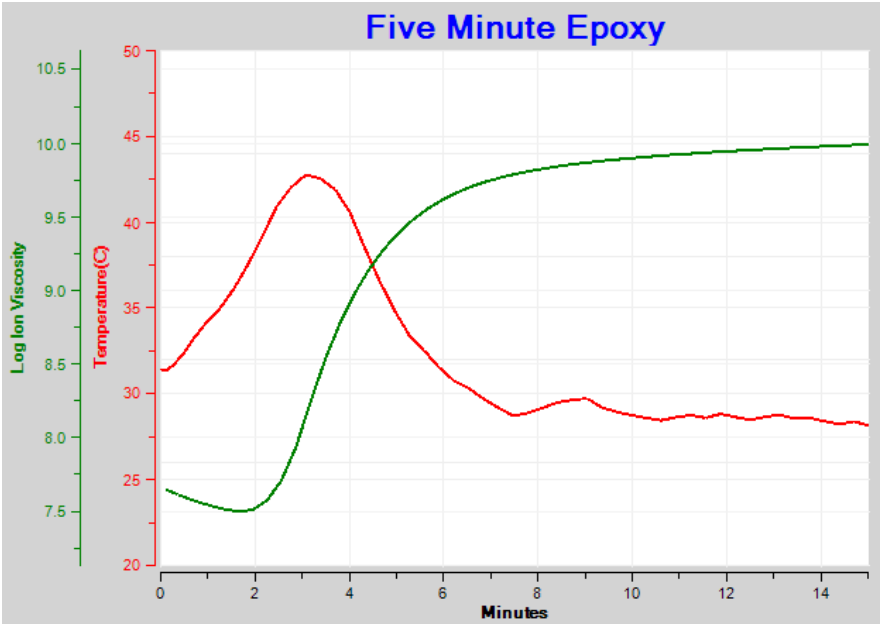


Figure 6
Ion viscosity for 10 Hz frequency only

Conclusion

While DC measurements of resistance are simple to make, they have disadvantages compared to AC measurements of dielectric properties. For thermoset cure monitoring, electrode polarization may distort DC data and cause misinterpretation of cure state.

Although electrode polarization can also affect low frequency AC measurements, the additional information gained from dielectric properties allows correction of the distorted data.

Frequency independent resistance is a more accurate description of DC resistance, and when sensor geometry is taken into account, bulk resistance can be converted to the material property of resistivity (ρ). Often AC measurements at a single appropriate frequency can determine frequency independent resistivity (ρ_{DC}), also known as *ion viscosity*, which is proportional to the change in mechanical viscosity before gelation and proportional to the change in modulus after gelation.

References

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

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