



Insight — Application Note 3.35

Electrochemical Modeling of AC and DC Cure Monitoring

Introduction

Both AC and DC measurements can probe the cure state of thermosets and composites, so it is important to understand their characteristics when deciding which to use. Dielectric cure monitoring, also called *Dielectric Analysis* (DEA) is an AC technique that excites a sensor with a sinusoidal signal of chosen frequency and amplitude, and a DC bias of zero volts. In contrast, DC resistance cure monitoring uses a constant bias voltage for the excitation. Figure 35-1 illustrates these two types of signals.

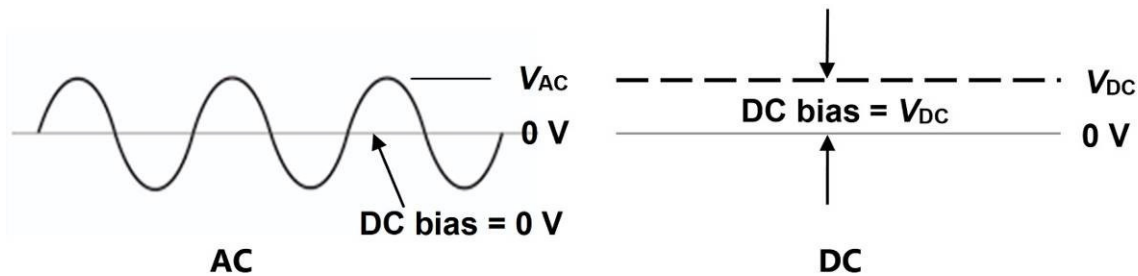


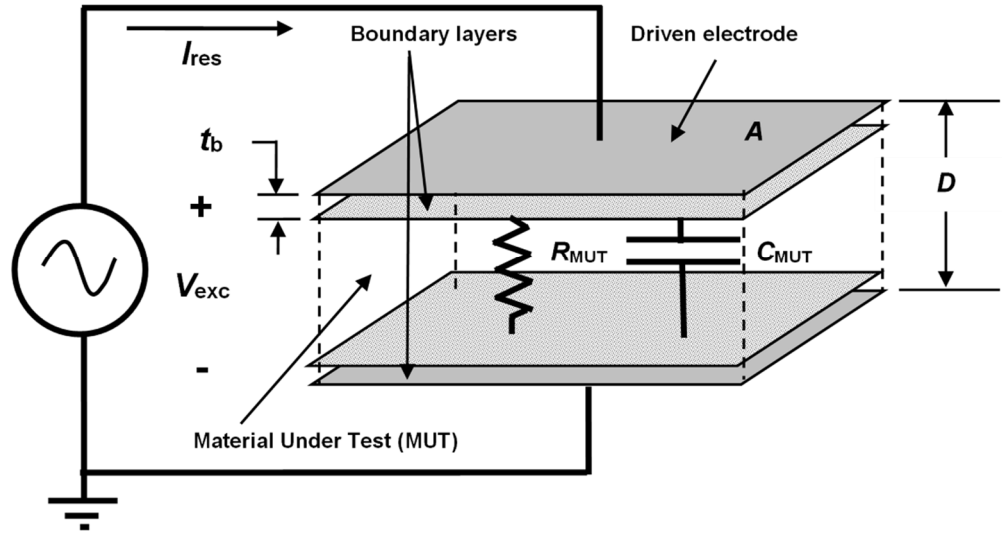
Figure 35-1
AC and DC excitations used for cure monitoring

Ideally, AC frequency independent resistance should be the same as DC resistance. Thermoset resins, however, do not act as ideal electronic components. During early through mid-cure, electrochemical reactions can affect DC results, while these effects are not evident in AC measurements. Consequently, DC measurements have limitations in accuracy for some portion of the cure, but at properly chosen frequencies AC results are accurate through the entire cure.

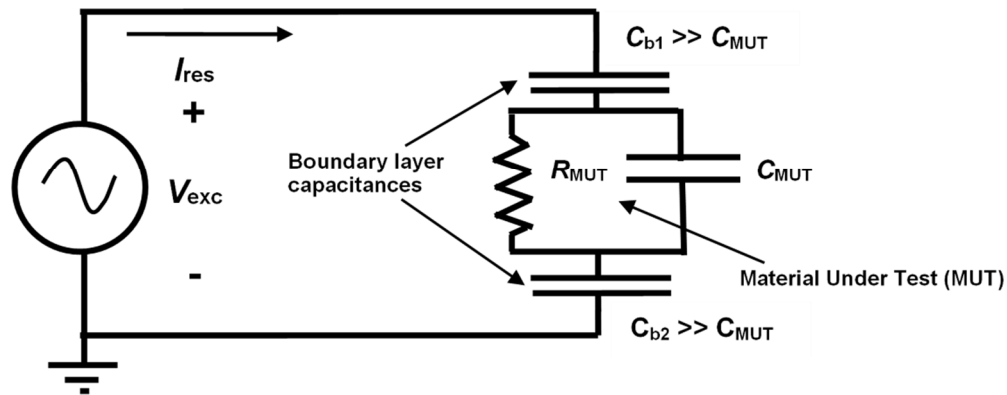
AC and DC measurements converge to the same value at the end of cure and both may be used with equal accuracy during this time. Although the nature of the resin electrochemistry is unknown, a DC electrochemical resistance added to the model of a curing thermoset can reproduce the behavior of DC resistance measurements.

Basic circuit model of a dielectric material

Figure 35-2.a. and Figure 35-2.b show the basic AC electrical model of a dielectric Material Under Test (MUT), consisting of a bulk resistance and capacitance, both in series with boundary layer capacitances caused by electrode polarization.



a.



b.

Figure 35-2

Physical (a.) and circuit (b.) models of thermoset resin for AC measurements Conductivity, resistivity and ion viscosity in materials

Because conductance (G_{MUT}) is the inverse of resistance (R_{MUT}), as described by the equation below:

(Eq. 35-1) $G_{MUT} = 1/R_{MUT}$ (ohm⁻¹)

this model may alternatively be considered a bulk conductance in parallel with the bulk capacitance, both in series with boundary layer capacitances.

Dielectric cure monitoring measures the conductance and capacitance of a Material Under Test, which are used to calculate the material properties of conductivity, resistivity and relative permittivity. Conductivity (σ_{MUT}) is simply the conductance scaled by a sensor's cell constant, or A/D ratio:

$$\text{(Eq. 35-2)} \quad \sigma_{MUT} = G_{MUT} / (A/D) \quad (\text{ohm}^{-1}\text{-cm}^{-1})$$

Conductivity has both frequency independent (σ_{FI}) and frequency dependent (σ_{AC}) components. In an oscillating electric field, σ_{FI} arises from the flow of mobile ions while σ_{AC} arises from the rotation of stationary dipoles. These two responses act like electrical elements in parallel and add together to produce the bulk conductivity:

$$\text{(Eq. 35-3)} \quad \sigma_{MUT} = \sigma_{FI} + \sigma_{AC} \quad (\text{ohm}^{-1} - \text{cm}^{-1})$$

The resistivity of the Material Under Test (ρ_{MUT}) is the inverse of conductivity as shown below:

$$\text{(Eq. 35-4)} \quad \rho_{MUT} = 1 / \sigma_{MUT} \quad (\text{ohm-cm})$$

Like conductivity, resistivity is the bulk resistance scaled by the A/D ratio as follows:

$$\text{(Eq. 35-5)} \quad \rho_{MUT} = R_{MUT} (A/D) \quad (\text{ohm-cm})$$

Also like conductivity, resistivity has both *frequency independent* (ρ_{FI}) and *frequency dependent* (ρ_{AC}) components. Frequency independent resistivity has particular importance for cure monitoring. Before gelation, the amount of polymerization affects both mechanical viscosity and the movement of ions, and therefore influences ρ_{FI} . For many materials, published research has shown the change in ρ_{FI} is proportional to the change in mechanical viscosity. To emphasize this relationship, the term *ion viscosity* (IV) was coined as a synonym for frequency independent resistivity and is defined as:

$$\text{(Eq. 35-6)} \quad IV = \rho_{FI} = 1 / \sigma_{FI} \quad (\text{ohm-cm})$$

Ion viscosity, sometimes called *AC ion viscosity* (IV_{AC})—frequency independent resistivity—is a material property that relates applied voltage to current. Within broad limits, at a fixed state of cure, a valid measurement of ion viscosity is independent of the AC voltage amplitude.

The resistivity (or resistance) of thermosets measured with a DC excitation is called *DC resistivity* (or resistance) and is commonly thought to be the same as frequency independent resistivity (or resistance). In fact, they are different because resins can act as electrolytes and experience reactions driven by a DC bias. To avoid confusion, these properties should be redefined for thermosets and other materials subject to electrochemistry:

- **DC resistivity (ρ_{DC})** – thermoset resistivity measured at $f = 0$ Hz with a DC bias, sometimes called *DC ion viscosity* (IV_{DC}) for convenience
- **Frequency independent resistivity (ρ_{AC})** – thermoset resistivity that is constant or nearly constant across a range of AC frequencies and measured without a DC bias, by convention also called *ion viscosity* (IV), or *AC ion viscosity* (IV_{AC})

AC and DC cure monitoring of PR520 epoxy resin

PR 520N¹ is a pre-mixed epoxy system engineered for resin transfer molding (RTM). At room temperature PR 520N is a thick off-white paste and the manufacturer specifies full cure after two hours at 179 °C. For AC and DC tests, PR 520N was applied to a Mini-Varicon² sensor, like that shown in Figure 35-3, and the sample was heated to 180 °C. Constructed with a Kapton substrate, the Mini-Varicon sensor has electrodes with equal width and separation of 0.004", and $A/D = 80$.

AC measurements were made with the LT-451 Dielectric Cure Monitor³ and a "floating electrode" circuit⁴ widely used for dielectric cure monitoring. DC measurements were made with the LT-440 Dielectric Channel⁵ using the circuit of Figure 35-4, with an adjustable load resistance R_L which determined the current through the sample.

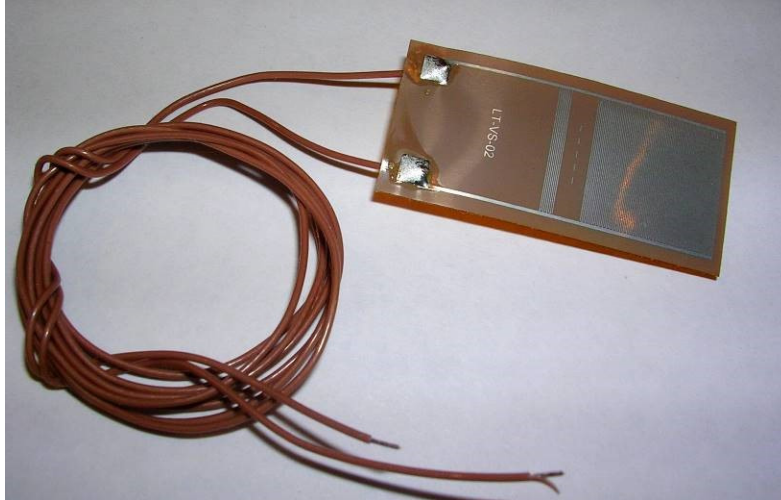


Figure 35-3
Mini-Varicon dielectric/conductivity sensor (A/D = 80)

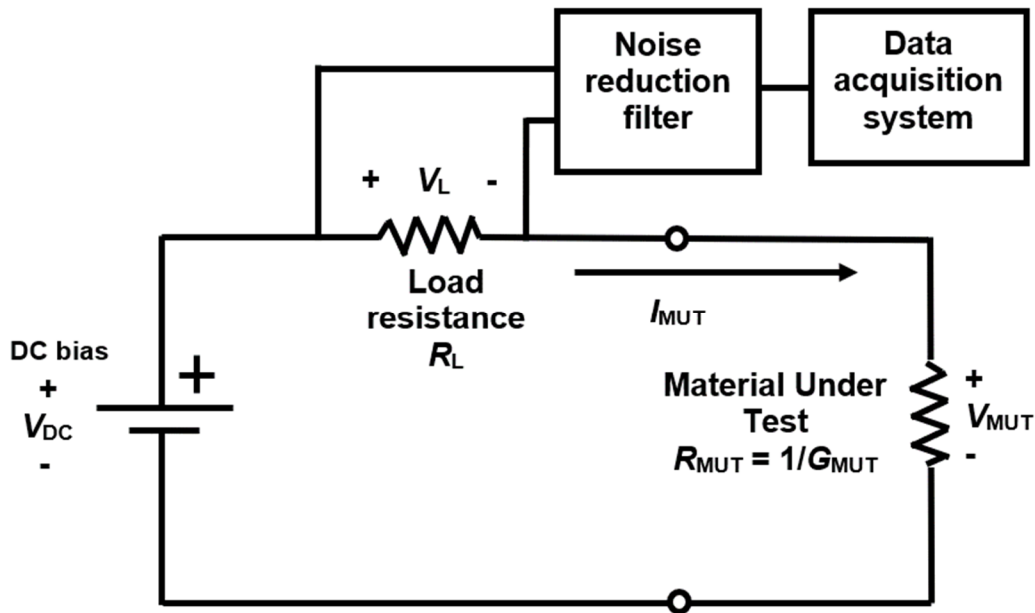


Figure 35-4
Circuit for DC resistance cure monitoring

The DC resistance, R_{MUT} , of the Material Under Test can be calculated with the following expression:

(Eq. 35-7)
$$R_{MUT} = R_L \left(\left[\frac{V_{DC}}{V_L} \right] - 1 \right)$$

With the sensor's cell constant, or A/D ratio, the DC ion viscosity is given by:

$$(Eq. 35-8) \quad IV_{DC} = R_{MUT} (A/D)$$

Figure 35-5 compares AC and DC data from PR 520N cured isothermally at 180 °C on Mini-Varicon sensors. Preliminary tests identified 10 Hz as an optimum excitation frequency that accurately follows the entire cure. At about 120 minutes, the 10 Hz AC ion viscosity curve of Figure 35-5 approaches a constant value, indicating the reaction is slowing and cure is ending. This behavior agrees with the manufacturer's specifications of full cure after two hours at 179 °C. In subsequent tests, the AC ion viscosity curve did not change over a range of excitation voltages (1, 2 or 4 VAC), indicating AC ion viscosity is independent of the details of the measurement circuit.

DC ion viscosity, however, deviated significantly from AC results during early to mid-cure. Furthermore, DC ion viscosity varied with the load resistance (10 MΩ, 50 MΩ or 2 GΩ) and the resulting level of current.

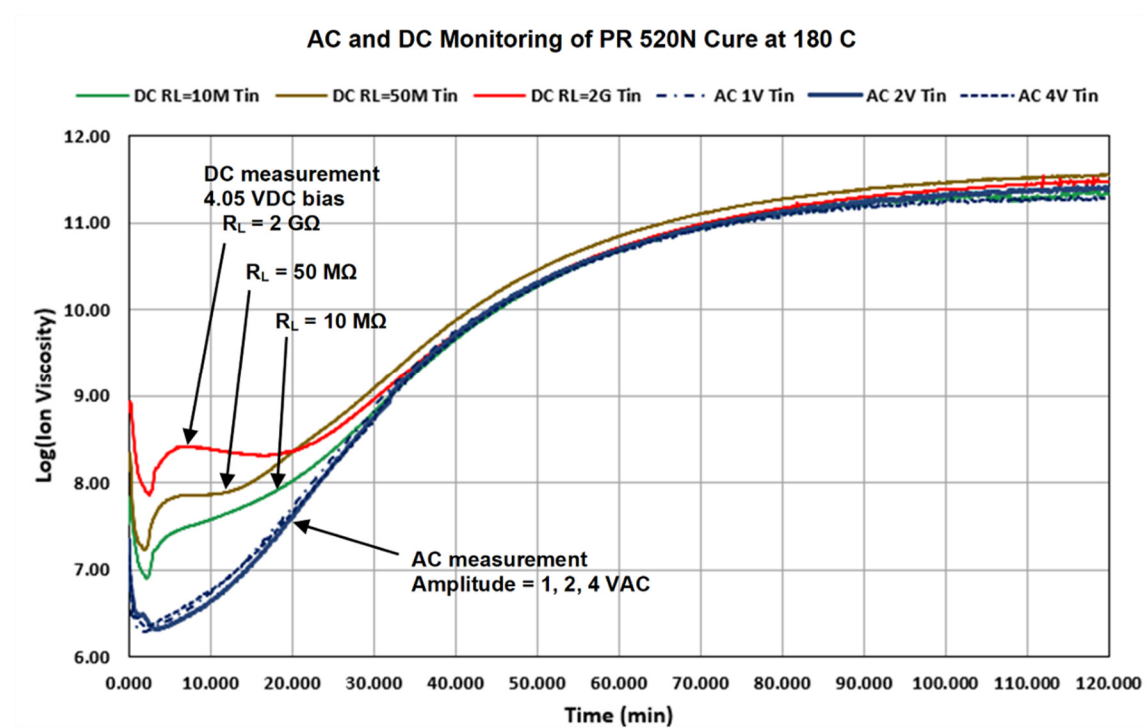


Figure 35-5
AC (10 Hz) and DC ion viscosity of PR 520N cure

Revised model of DC cure behavior

Presumably caused by an electrochemical reaction, the difference between AC and DC ion viscosity is greatest at the beginning of cure and gradually diminishes toward the end of cure. Ignoring the transient behavior during very early cure, the relationship between AC and DC ion viscosity follows an exponential decay of the form:

$$\text{(Eq. 35-9)} \quad IV_{DC}(t) = IV_{AC}(t) \cdot (C_0 e^{-t/T_0} + 1)$$

Where:

$IV_{DC}(t)$ = DC ion viscosity

$IV_{AC}(t)$ = AC ion viscosity

C_0 = Coefficient

t = Time

T_0 = Time constant

Equation 35-9 resembles the kinetics of a first-order chemical reaction, which has a rate that depends linearly on the concentration of only one reactant. A first-order reaction has a rate law with the form:

$$\text{(Eq. 35-10)} \quad [A] = [A]_0 e^{-kt}$$

Where:

$[A]$ = Concentration of reactant

$[A]_0$ = Initial concentration of reactant

k = First-order rate constant

t = Time

Rearranging equation 35-9 results in the following expression for the *difference* between the DC and AC ion viscosity, and highlights the similarity to the rate law for a first-order chemical reaction:

$$\text{(Eq. 35-11)} \quad [IV_{DC}(t) - IV_{AC}(t)] = [IV_{AC}(t)] \cdot C_0 e^{-t/T_0}$$

Although the nature of the electrochemical reaction is unknown, the difference between the AC and DC ion viscosity may be modeled as an additional resistance (R_{EC}) in parallel with the boundary layer capacitance, as shown in Figure 35-6.a. For simplicity, the two boundary layer capacitances (C_b) of

Figure 35-2.b have been combined into the single capacitance C_b' . Because the boundary layer capacitance shunts AC current around this *DC electrochemical resistance*, the additional resistance does not affect AC measurements.

The DC electrochemical resistance is proportional to monomer concentration, decreasing exponentially with time as monomers are consumed in accordance with first-order kinetics. Consequently, DC measurements converge toward AC results at the end of cure when the resin is highly resistive and without significant electrochemistry.

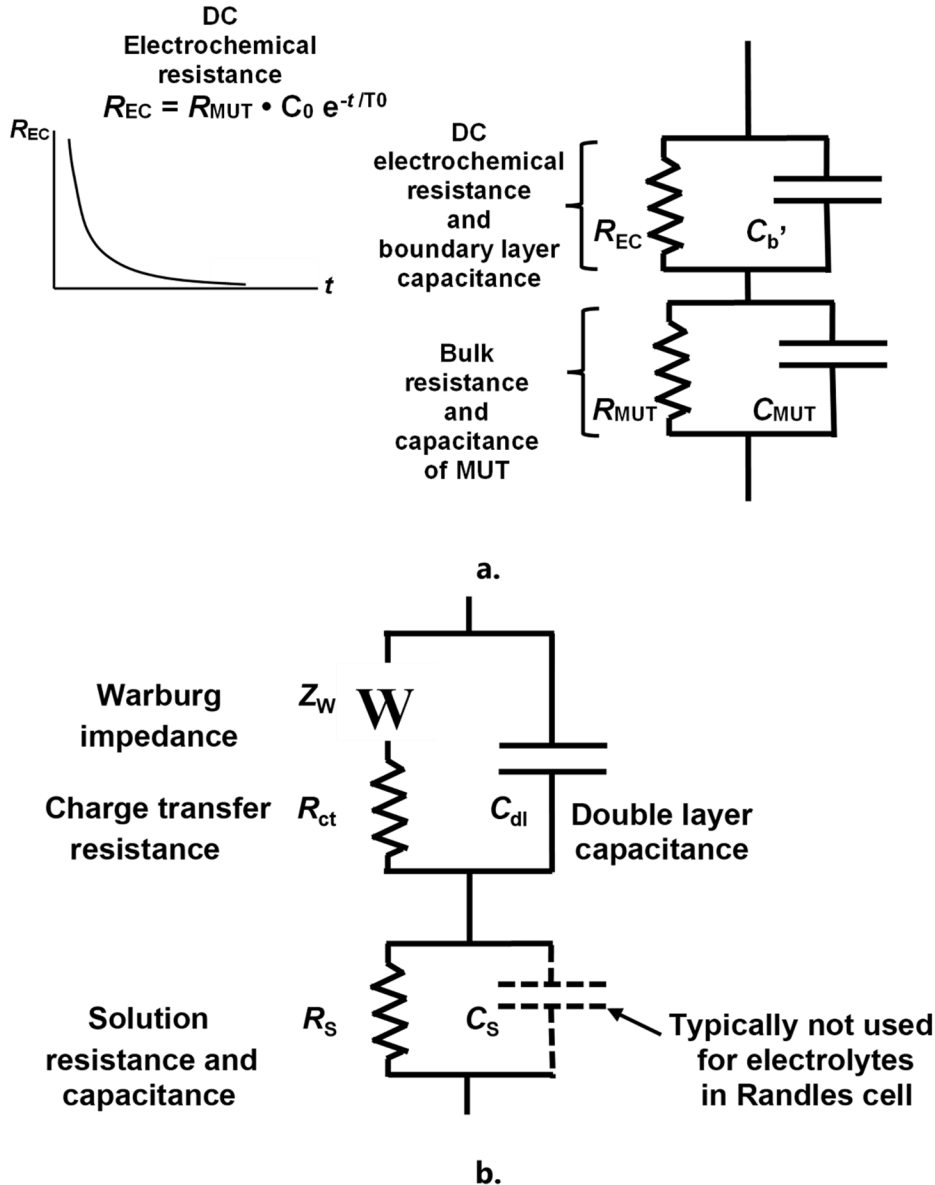


Figure 35-6
Revised model of a thermoset resin (a.) and Randles cell (b.)

The revised thermoset model is analogous to the Randles cell of Figure 6.b., used in electrochemical impedance spectroscopy (EIS) for the study of electrolytes. During early cure, a resin may be treated as a highly resistive electrolyte and its boundary layer capacitance was long ago understood to be an electrolytic double layer capacitance.⁶ Similarly, the resin’s DC electrochemical resistance originates in reactions or ionic diffusion at the electrolyte-electrode interface. Table 35-1 shows the correspondences between elements of the revised thermoset model and the Randles cell.

Table 35-1
Correspondence between thermoset and Randles cell models

Thermoset Model		Randles Cell Model		Description
R_{MUT}	Resistance of thermoset resin	R_s	Resistance of electrolytic solution	Resistance of bulk material
C_{MUT}	Capacitance of thermoset resin	C_s	Capacitance of electrolytic solution	Capacitance of bulk material (Typically not used for electrolytes in Randles cell)
R_{EC}	DC electrochemical resistance	R_{ct} + Z_w	Charge transfer resistance	Resistance due to electrochemical diffusion/reactions at material-electrode interface
			Warburg impedance	
$C_{b'}$	Boundary layer capacitance	C_{dl}	Double layer capacitance	Capacitance due to charge accumulation creating insulating layer at electrode surface

Charge transfer resistance arises from the diffusion of electrons, in both directions, between the electrolyte and electrode. Faradic reactions at the electrolyte-electrode interface are controlled by the diffusion of reactants to the electrode surface and this diffusional resistance is known as the Warburg impedance. These Randles cell resistances vary with applied voltage or current—just as observed with the DC ion viscosity of PR 520N.

For the DC ion viscosity of Figure 35-5, the humps between 5 and 15 minutes are transients caused by current through the DC electrochemical resistance as it charges the bulk capacitance. By basic circuit theory, this transient response can be described with a simple resistor-capacitor (RC) circuit, a time constant and an exponential decay.

The revised thermoset model implies DC ion viscosity may be derived from AC ion viscosity by accounting for only two additional phenomena:

- A transient at the beginning of cure, and
- Consumption of monomers during cure

For the isothermal case, the following expression relates AC and DC ion viscosity by incorporating these two behaviors:

$$\text{(Eq. 35-12)} \quad IV_{DC}(t) = IV_{AC}(t) \cdot ([(1 - C_1 e^{-t/T1}) \cdot C_0 e^{-t/T0}] + 1)$$

Where:

$IV_{DC}(t)$ = DC ion viscosity

$IV_{AC}(t)$ = AC ion viscosity

C_0 = Coefficient during steady state cure

C_1 = Coefficient during transient response

t = Time

T_0 = Time constant during steady state cure

T_1 = Time constant during transient response

Figure 35-7 plots the model of Eq. 35-12 against actual PR 520N DC ion viscosity. For the first two minutes, DC ion viscosity decreased due to initial heating of the material, so data during this time was not included as cure. With proper selection of parameters, the revised thermoset model can reproduce DC ion viscosity from AC ion viscosity over the entire cure.

Knowing the differences between AC and DC measurements, it is now possible to provide guidance for their use:

- AC measurements at an optimum frequency can accurately follow the entire cure of most resins
- DC measurements have uncertain accuracy during early to mid-cure, and are most accurate during mid- to end of cure
- DC measurements can be useful for highly resistive materials like silicones, when AC measurements would require unfeasibly low frequencies and long measurement times

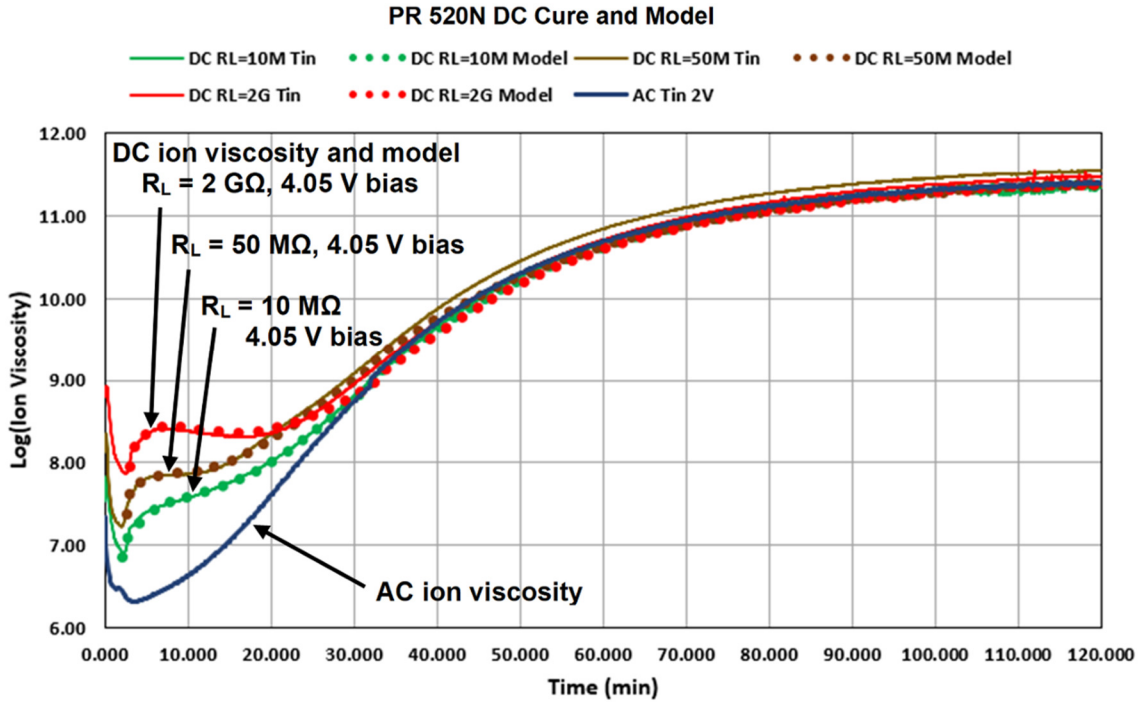


Figure 35-7
Model fit to DC cure data of PR 520N, 180 °C isothermal cure

Conclusion

While frequency independent AC resistance, also known as *ion viscosity*, accurately probes the entire cure of thermosets and composites, DC resistance shows discrepancies in comparison during early to mid-cure. During end of cure, however, AC and DC results agree, indicating DC techniques can also measure cure state but must be used carefully and with an understanding of their limitations.

The ion viscosity of thermoset resins is not affected by the amplitude of the sinusoidal drive voltage and behaves as an ideal, linear electronic component. Furthermore, the change in ion viscosity is proportional to the change in mechanical viscosity before gelation and proportional to the change in modulus after gelation.

Unlike AC ion viscosity, for significant portions of cure the DC resistance of resins does not behave ideally, varying with the magnitude of the applied DC bias and the details of the measurement circuit.

The discrepancies between AC and DC measurements are likely caused by an electrochemical reaction. Although the nature of the electrochemistry is

unknown, the DC response during cure can be reproduced by a *DC electrochemical resistance* added to the standard model of a resin.

This DC electrochemical resistance is proportional to the concentration of unreacted monomers and decreases over time with an exponential rate law. The decay rate is consistent with the kinetics of a first-order reaction, which depends on the concentration of only one component.

Transient effects in DC measurements have erroneously been attributed to an increase in viscosity at the beginning of cure. The revised electrical model of a resin also explains this transient behavior as the charging of the bulk capacitance through the DC electrochemical resistance.

Agreement between the DC model and data indicates this electrochemical resistance can explain both the transient and overall behavior of DC measurements during cure.

References

1. Cycom PR 520N RTM manufactured by Solvay, Brussels, Belgium
2. Mini-Varicon sensor, manufactured by Lambient Technologies, Cambridge, MA USA. <https://lambient.com>
3. LT-451 Dielectric Cure Monitor, manufactured by Lambient Technologies, Cambridge, MA USA
4. Application Note AN 3.25, "Dielectric Measurement Techniques," Lambient Technologies, Cambridge, MA USA
5. LT-440 Dielectric Channel, manufactured by Lambient Technologies, Lambient Technologies, Cambridge, MA USA
6. D.R. Day, J. Lewis, H.L Lee, S.D. Senturia, "The Role of Boundary Layer Capacitance at Blocking Electrodes in the Interpretation of Dielectric Cure Data in Adhesives," *Journal of Adhesion*, **1985**, vol.18, p.73.



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