



***Insight* — Application Note 2.04**

Dielectric Measurements, Viscosity and Critical Points

Introduction

Dielectric cure monitoring measures the bulk conductance and capacitance of Material Under Test (MUT), which are used to calculate the material properties of conductivity and permittivity.

Conductivity (σ) has both frequency independent (σ_{DC}) and frequency dependent (σ_{AC}) components. In an oscillating electric field, σ_{DC} 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 total measured conductivity:

$$(Eq. 4-1) \quad \sigma = \sigma_{DC} + \sigma_{AC}$$

Resistivity (ρ) is the inverse of conductivity as shown below:

$$(Eq. 4-2) \quad \rho = 1 / \sigma$$

Like conductivity, resistivity has both frequency independent (ρ_{DC}) and frequency dependent (ρ_{AC}) components.

Of particular interest for cure monitoring is the DC resistivity, ρ_{DC} , because of its relationship to a fluid's mechanical viscosity. Crosslink density, which is a measure of cure state, affects both mechanical viscosity and the movement of ions, and therefore influences ρ_{DC} . The term *ion viscosity* was coined to emphasize this relationship between mechanical viscosity and ρ_{DC} . Ion viscosity (IV) is defined as:

$$(Eq. 4-3) \quad IV = \rho_{DC} = 1 / \sigma_{DC}$$

Often differing by only a scaling factor, ρ_{DC} and mechanical viscosity are related to the cure state of thermosets such as epoxies, polyurethanes, polystyrenes, bulk molding compound (BMC) and sheet molding compound (SMC). The measurement of ρ_{DC} requires no mechanical components, and yet provides information about a mechanical property.

For convenience, unless otherwise indicated, this chapter will use the term *resistivity* to refer to ρ_{DC} . Similarly, the term *viscosity* will refer to *mechanical viscosity*.

Viscosity and resistivity

Viscosity is a measure of how easily the molecules of a fluid move past each other in response to shear forces, and in the case of polymeric materials is determined by the motion of polymer chain segments. In contrast, resistivity is a measure of the mobility of free ions through a medium under the influence of an electric field. DC resistivity, ρ_{DC} , is given by equation 4-4.

$$(eq. 4-4) \quad \rho_{DC} = 1 / (q \mu n)$$

Where: q = charge of free ions (coulombs)
 μ = free ion mobility ($\text{cm}^2 / (\text{V}\cdot\text{s})$)
 n = free ion concentration (cm^{-3})

Mobility determines the rate of ionic diffusion through a medium, and is given by the Einstein relationship of equation 4-5:

$$(eq. 4-5) \quad \mu = q D / (k T) \quad (\text{cm}^2 / (\text{V}\cdot\text{s}))$$

Where: D = diffusion coefficient (cm^2 / s)
 k = Boltzmann's constant (eV / K)
 T = temperature in degrees Kelvin (K)

If mobile ions are modeled as spherical particles, then in the limit of low Reynold's numbers, by the Stokes-Einstein Relation of equation 4-6:

$$(eq. 4-6) \quad D = k T / (6\pi \eta r) \quad (\text{cm}^2 / \text{s})$$

Where: η = mechanical viscosity ($\text{g} / (\text{cm}\cdot\text{s})$)
 r = radius of sphere (cm)

Combining equations 4-4, 4-5 and 4-6 yields the following relationship between resistivity and viscosity:

$$\text{(eq. 4-7)} \quad \rho_{DC} = (6\pi \eta r) / (q^2 n)$$

$$\therefore \rho_{DC} \propto \eta$$

Consequently, resistivity is proportional to viscosity. Empirical results show that this relationship is valid in many cases, although some systems for poorly understood reasons obey a power law:

$$\text{(eq. 4-8)} \quad \rho \propto \eta^n \text{ where } n = 1, 2, 3 \dots$$

To emphasize the proportionality between resistivity and viscosity, the term *ion viscosity* was coined as a synonym for resistivity.

Figure 4-1 compares ion viscosity and viscosity from the non-isothermal cure of an epoxy. Ion viscosity was measured with a dielectrometer and viscosity was measured with a Rheological Dynamic Spectrometer. The two curves show strong correlation from the beginning of cure up to gelation at about 135 minutes. After gelation, viscosity increases rapidly and becomes immeasurable. Ion viscosity continues to change as the polymer network grows, and provides useful information about cure state until the end of cure.

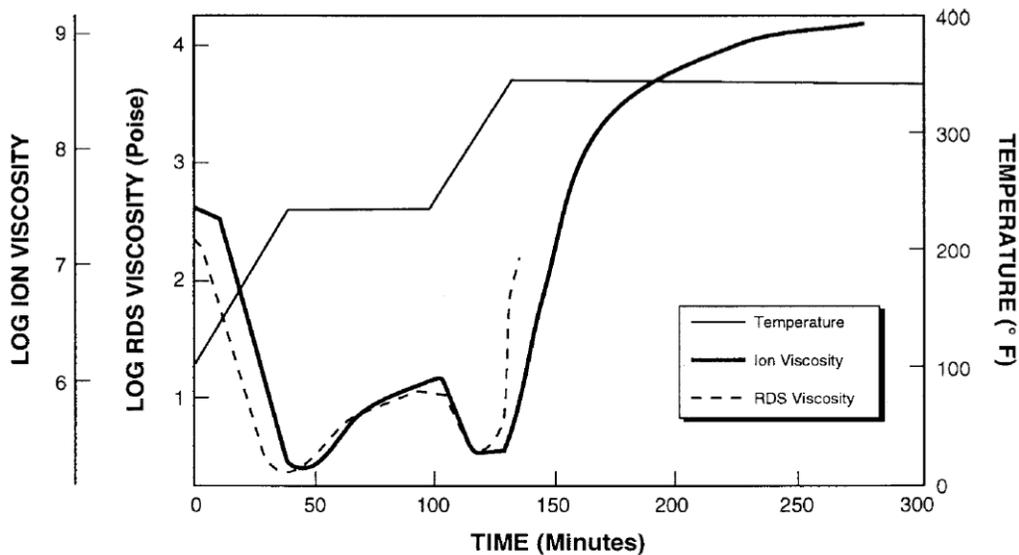


Figure 4-1
Correlation of ion viscosity and viscosity during epoxy cure¹

Critical Points during cure

A thermoset cures because monomers crosslink to form a polymer network. Often this reaction is exothermic—generating heat—or is driven by the heat of a press or oven. Typically the viscosity initially decreases as temperature increases. The material responds by simply melting or becoming less rigid. Resistivity also decreases as mobile ions experience less resistance to movement. At this point the reaction is still slow but eventually accelerates until it dominates the system. Viscosity reaches a minimum—a point of zero slope—and then increases as the material becomes more viscous, gels then becomes more rigid. Resistivity similarly reaches a minimum and then increases due to the growing network, which presents a greater and greater impediment to the flow of ions.

Eventually the reaction slows and viscosity becomes unmeasurable. At this point the resistivity is no longer proportional to viscosity. Resistivity continues to change, but more and more slowly, approaching a limit at the end of cure. Viscosity and resistivity (ion viscosity) typically follow curves like those of Figures 4-2 and 4-3.

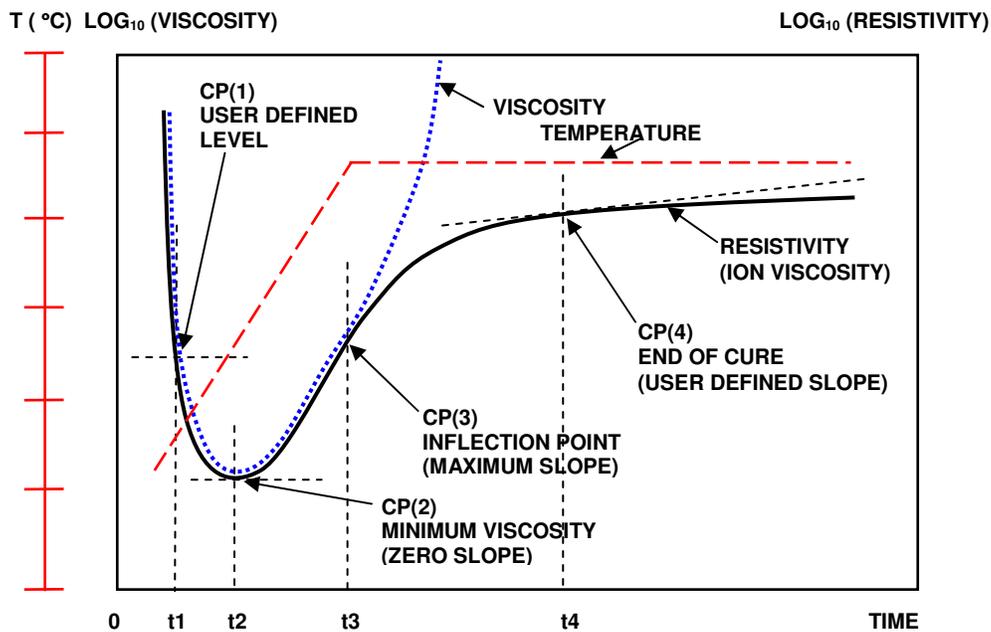


Figure 4-2
Viscosity and ion viscosity (resistivity) in a curing thermoset

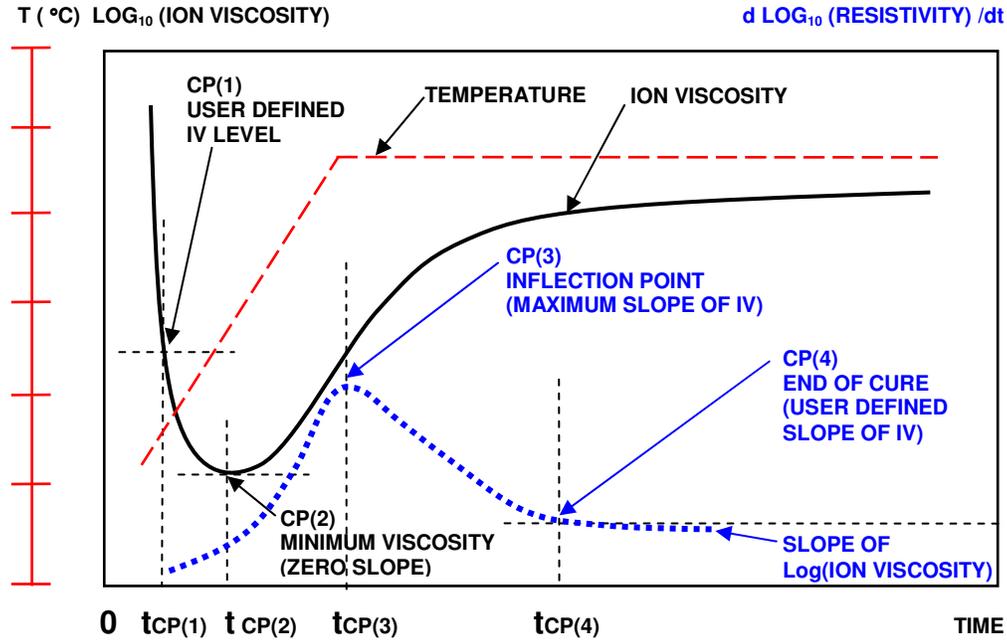


Figure 4-3
Ion viscosity, slope and Critical Points in a curing material

The dielectric cure curve is characterized by four Critical Points:

- CP(1)—A user defined level of ion viscosity, which can identify the onset of material flow at the beginning of cure.
- CP(2)—Ion viscosity minimum, which typically also corresponds to the mechanical viscosity minimum. This Critical Point indicates the time the accelerating crosslinking reaction dominates the behavior of the system.
- CP(3)—Inflection point, which identifies when the crosslinking reaction begins to slow. CP(3) is often used as a signpost that can be associated with gelation.
- CP(4)—A user defined slope that can define the end of cure. The decreasing slope corresponds to the decreasing reaction rate. Note that dielectric cure monitoring continues to reveal changes in the evolving material past the point when mechanical measurement of viscosity is not possible.

The proportionality between ion viscosity and viscosity has proven to be useful in thermoset processing. Knowing when a material has reached the viscosity minimum, for example, allows optimum application of pressure to compress a laminate or to extract air bubbles from a molded part. Even after ion viscosity diverges from viscosity, ion viscosity continues to indicate cure state until polymerization stops.

References

1. *Cure Monitoring of Thermosetting Resins Utilizing Dielectric Sensors*, David Shepard, Holometrix-Micromet



Lambient Technologies LLC
649 Massachusetts Ave., Cambridge, MA 02139
857-242-3963
www.lambient.com
info@lambient.com