Insight — Technical Overview 3.02

Ion Viscosity in Dielectric Cure Monitoring

What does dielectric cure monitoring measure?

Dielectric cure monitoring, also known as *Dielectric Analysis* (DEA), measures a polymer's resistivity (ρ) and permittivity (ε'), which are a material's dielectric properties. 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.

Although often called DC resistivity, frequency independent resistivity actually extends across a range of frequencies that includes DC (0 Hz). Because frequency independent resistivity correlates with cure state, it is a useful material probe of epoxies, polyurethanes, polystyrenes, bulk molding compounds (BMC), sheet molding compounds (SMC) and other thermosets

To emphasize the relationship with mechanical viscosity, the term *ion viscosity* (*IV*), which depends on ionic mobility, was coined in the early 1980's as a synonym for frequency independent resistivity. Ion viscosity is defined below:

(Eq. 2-1) $$IV = \rho_{DC}$$

Ion viscosity and thermoset cure

The state of a material's polymer chains or networks affects *both* ionic mobility and physical resistance to flow. Ionic mobility therefore is a measurable link to mechanical viscosity, which from this point will simply be called *viscosity*. Figure 2-1 presents data from the cure of an epoxy. A dielectrometer measured ion viscosity and a Rheological Dynamic Spectrometer (RDS) measured viscosity. 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 unmeasurable; however, ion viscosity continues to provide information about material state, specifically modulus, until the end of cure.

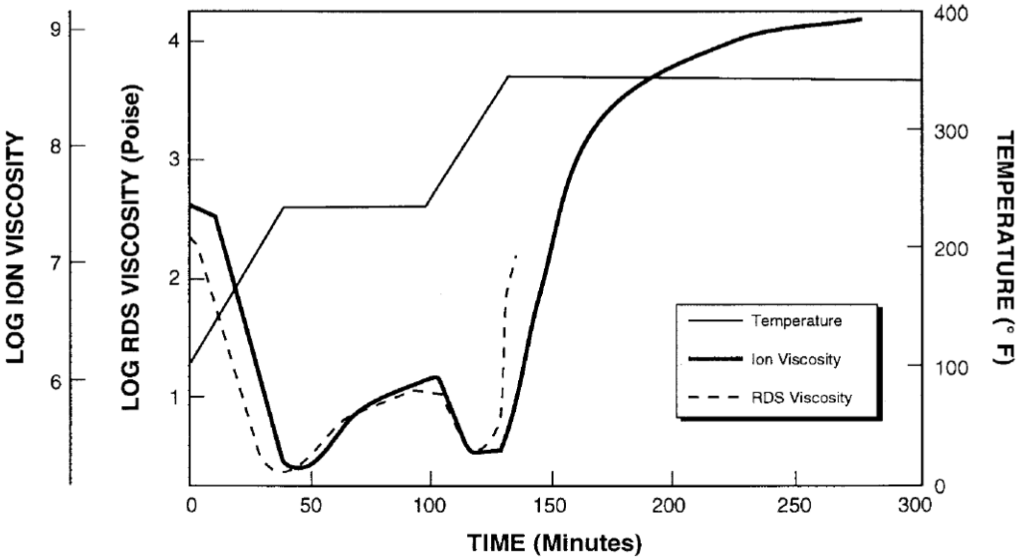

Figure 2-1
Correlation of ion viscosity and viscosity during epoxy cure

(From: *Cure Monitoring of Thermosetting Resins Utilizing Dielectric Sensors*, David Shepard, Holometrix-Micromet)

Note the minimum RDS viscosity, at about 40 minutes, actually occurs a short time before the minimum ion viscosity. This behavior is common in comparisons between rheological and dielectric data. Viscosity starts to increase when the first monomers react and polymerize, a process that occurs on a relatively large physical scale. Mobile ions only respond to local conditions, and on average are distant from the first scattered chains at this time, as shown in Figure 2-2.

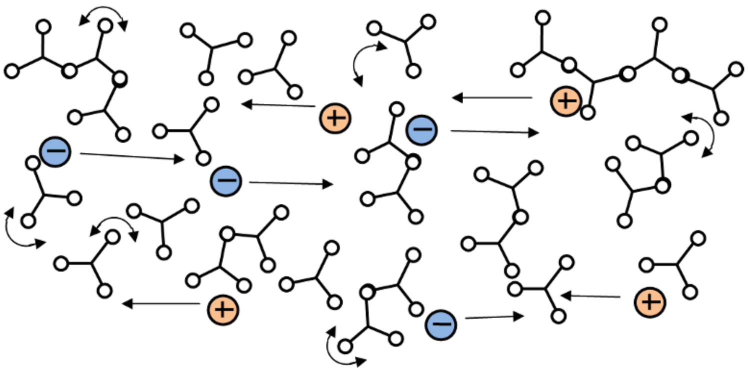

Figure 2-2
Mobile ions during early polymerization

When chain extension begins, free ions do not yet experience the "crowding" that reduces their mobility. It is like a jogger running on a city street—his motion is affected by the cars driving around him but not by the traffic jam three blocks away.

The growing polymer chains eventually do affect ionic mobility and then ion viscosity increases, although lagging slightly behind viscosity. Nevertheless, it is a reasonable to say the ion viscosity minimum and viscosity minimum occur at approximately the same time.

Ion viscosity and gelation

In Figure 2-1, around 135 minutes, viscosity becomes unmeasurable at the gel point, when network formation begins. Although ion viscosity increases rapidly around this time, no distinct dielectric event indicates the start of crosslinking.

Ion viscosity is a probe of the microscopic environment, which changes only gradually around a mobile ion. An ion traveling between polymer chains just before gelation, as in Figure 2-3.a., doesn't experience much difference as the first chains connect to form a network, as in Figure 2-3.b. Increasing crosslink density does present greater and greater impediment to the overall flow of ions. As a result, ion viscosity responds continuously, becoming a measure of rigidity or modulus after gelation.

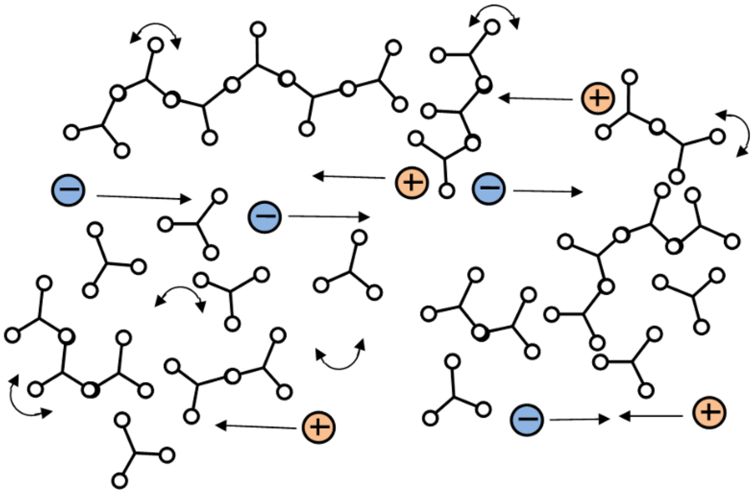

Figure 2-3.a. Polymer just before gel point

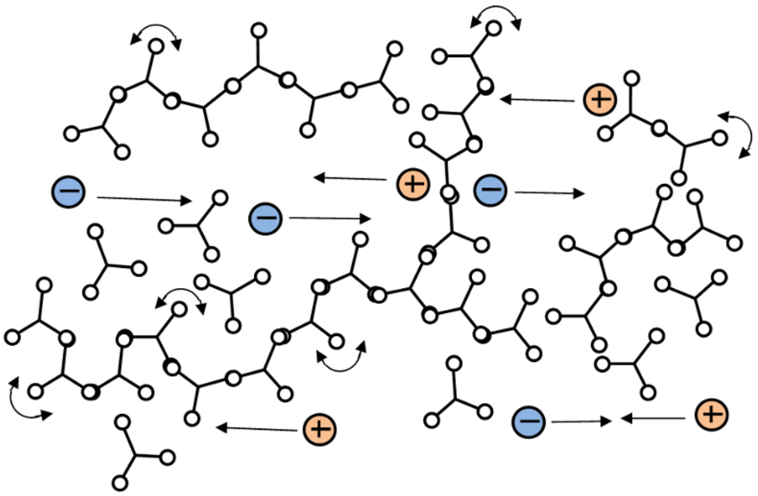

Figure 2-3.b. Polymer at gel point (beginning of network formation)

Determining ion viscosity

Figure 2-4 shows resistivity (ρ) across a range of frequencies for the cure of five-minute epoxy. For convenience all resistivity data are labeled ion viscosity, although *only frequency independent resistivity (*ρ_{DC}*) is true ion viscosity*.

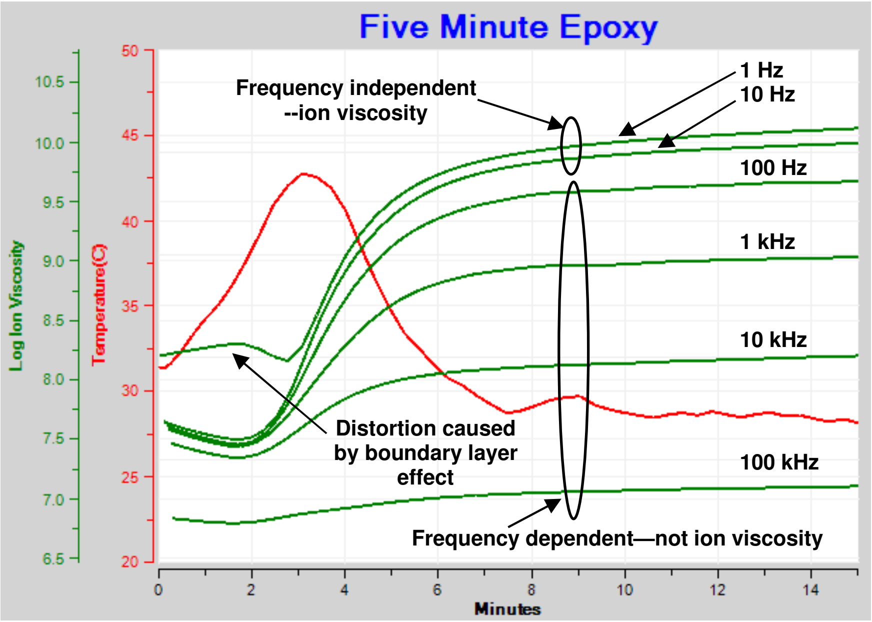

Figure 2-4
Resistivity of curing epoxy (plotted against log(ion viscosity) axis)

When total resistivity, which combines both frequency independent and frequency dependent responses, is unknowingly represented as ion viscosity, misleading interpretations of cure state may result. Which curve follows viscosity? Or modulus? Therefore, it is important to identify ion viscosity and isolate it from other factors.

Frequency independent resistivity, which correlates with cure state, dominates where curves overlap, although sometimes the overlap may not be perfect because of a non-ideal response. Figure 2-5 shows the resistivity after using an algorithm to present only data dominated by overlapping curves. This plot now shows the progression of frequency independent resistivity, properly called *ion viscosity*, that indicates cure state of the material.

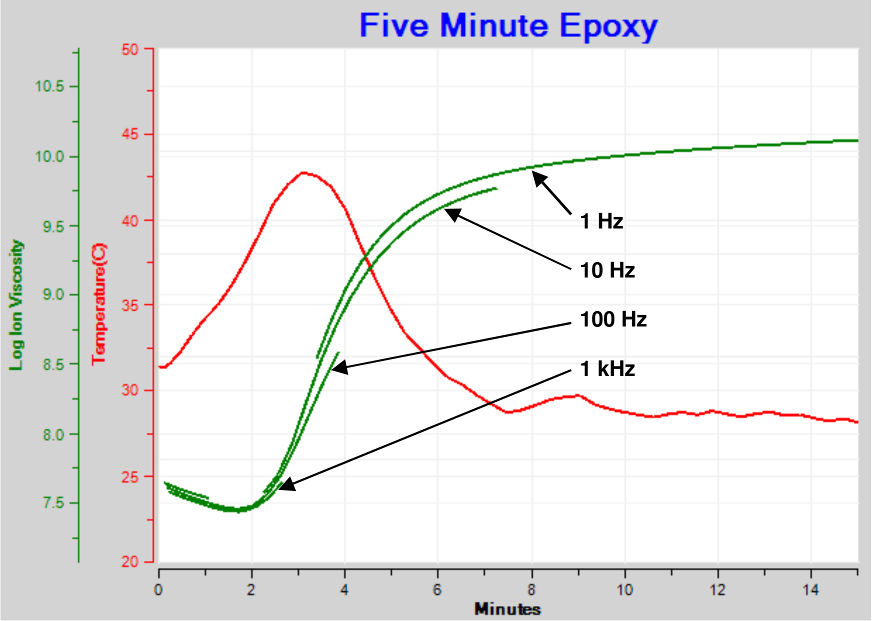

Figure 2-5
Ion viscosity—frequency independent resistivity component only

To determine the time of maximum reaction rate or the time to end of cure, we must calculate the slope of log(*ion viscosity*), here simply called *slope* for brevity. Unfortunately, the ion viscosity segments of Figure 2-5 do not overlap perfectly and would yield a series of discontinuous curves for slope. To avoid this problem, we should calculate slope of ion viscosity from a single frequency, such as from the 10 Hz data of Figure 2-6. This simplification is possible because ion viscosity from a properly chosen frequency is often very similar to the composite from multiple frequencies.

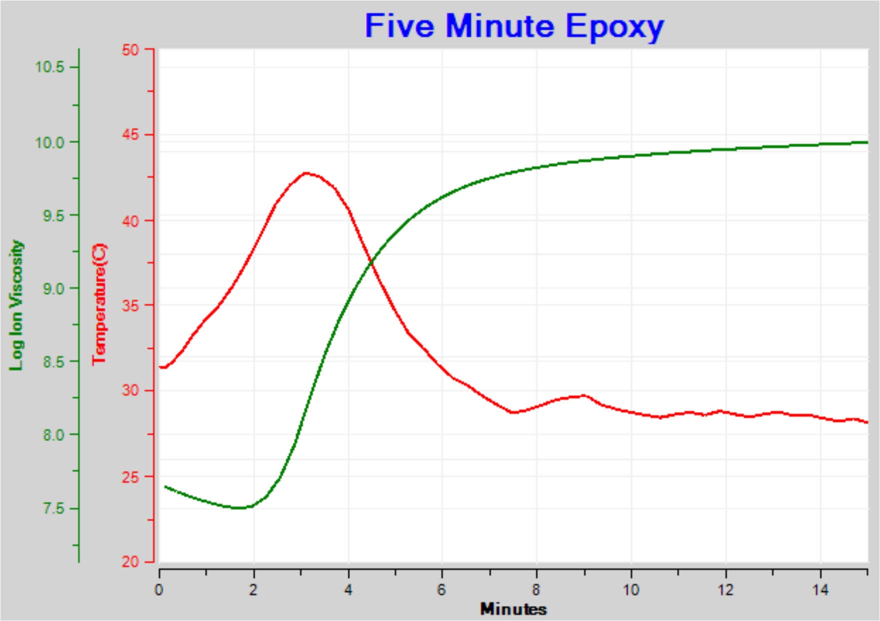

Figure 2-6
Ion viscosity for 10 Hz frequency only

Figure 2-7 shows ion viscosity from 10 Hz data as well as the resulting curve for slope.

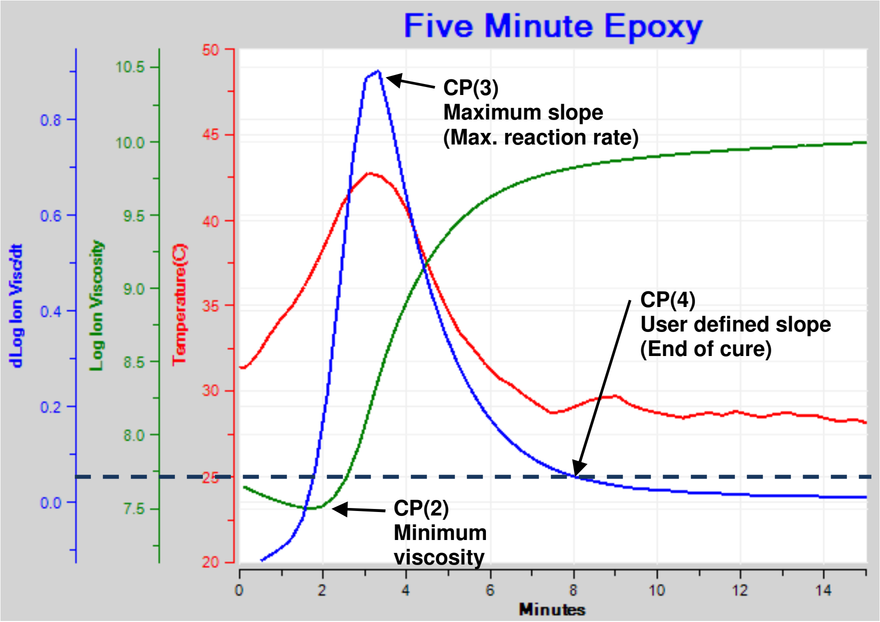

Figure 2-7
Ion viscosity and slope for 10 Hz frequency only, showing Critical Points

Four Critical Points characterize the dielectric cure curve:

- CP(1)—A user defined level of *log(IV)* to identify the onset of material flow.
- CP(2)—Minimum ion viscosity, which closely corresponds to minimum mechanical viscosity, indicating when polymerization and increasing viscosity begin to dominate the material's behavior.
- CP(3)—Maximum *slope*, which identifies the time of maximum reaction rate. The height of CP(3) is a relative measure of the reaction rate and CP(3) is often used as a signpost 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.

In Figure 2-7 Critical Points CP(2), CP(3) and CP(4) are clearly visible. The epoxy was applied to the sensor before the start of this test, so the material had already flowed by time *t* = 0 and CP(1) is not shown.

Ion viscosity behavior during thermoset cure

A plot of log(*ion viscosity*) is a simple way to characterize the progress of cure. Figures 2-8 and 2-9 show the behavior of a typical thermoset with one ramp and hold step in temperature.

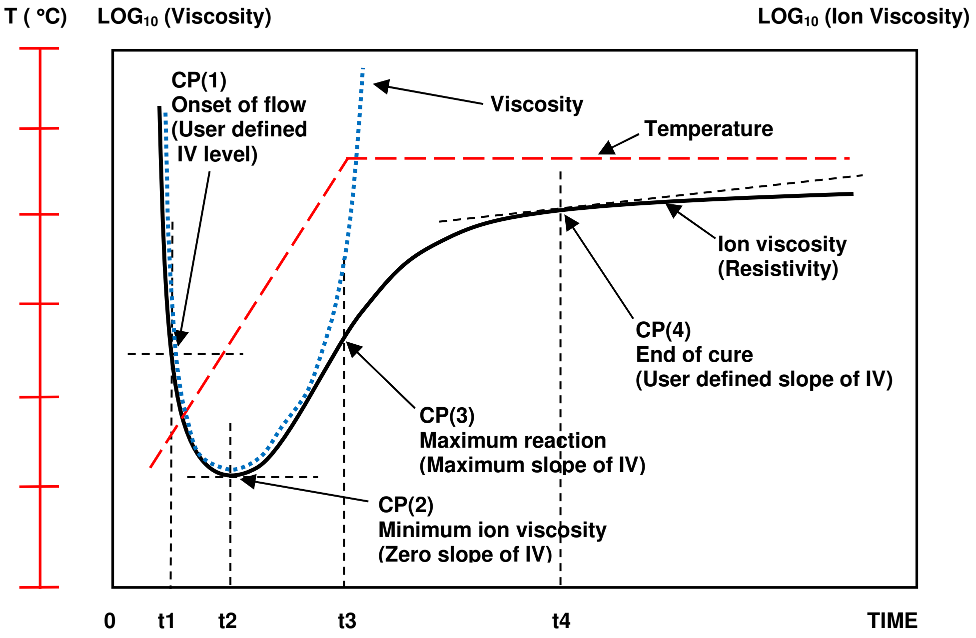

Figure 2-8

Typical ion viscosity behavior for thermoset cure during thermal ramp and hold

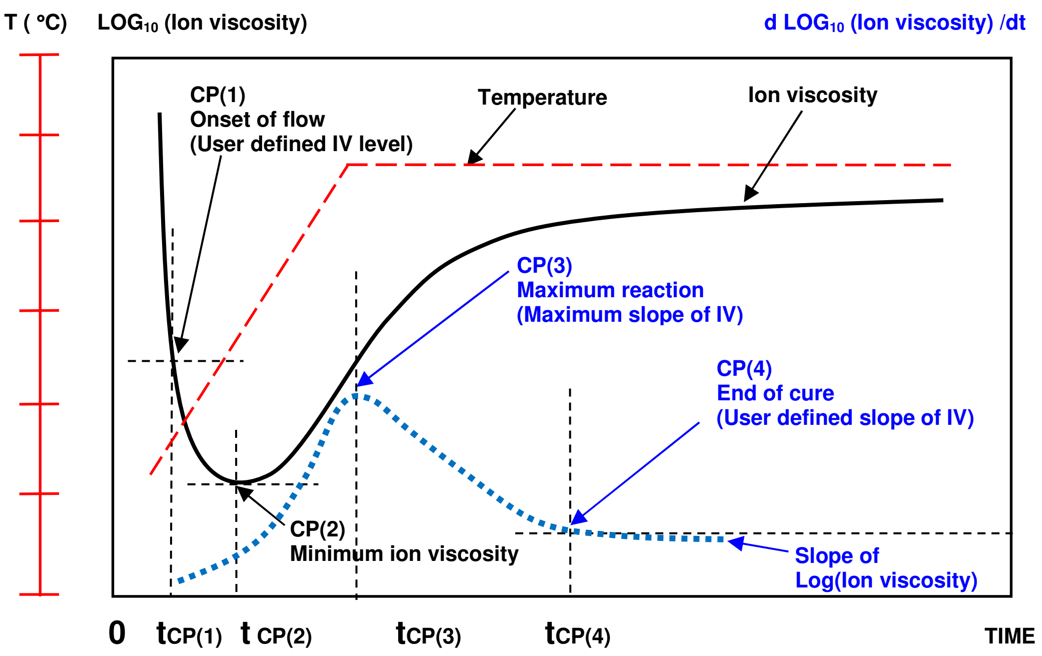

Figure 2-9
Ion viscosity curve and slope of ion viscosity for thermoset cure during thermal ramp and hold

At first, as temperature increases, the material softens or melts and viscosity decreases. Mobile ions also experience less resistance to movement and ion viscosity also decreases. At this point the reaction is still slow.

As the material becomes hotter, the cure rate increases. At some time the accelerating reaction begins to dominate; viscosity reaches a minimum then the material becomes more viscous. Electrically, the increase in ion viscosity due to polymerization overcomes the decrease in ion viscosity due to higher temperature. Ion viscosity also reaches a minimum then increases due to chain extension, which presents a greater and greater impediment to the flow of ions.

After the minimum point, ion viscosity increases continuously until the concentration of unreacted monomers diminishes and the reaction rate decreases. Consequently, the slope of ion viscosity also decreases and eventually reaches a value of zero when cure has stopped completely.

Conclusion

Ion viscosity is the frequency independent resistivity (ρ_{DC}) of a material due to mobile ions. Curves of resistivity measured at different frequencies overlap or closely overlap when mobile ions dominate the dielectric response and therefore identify ion viscosity.

During thermoset cure, the change of ion viscosity is often proportional to the change of viscosity before the gel point and proportional to the change of modulus afterward. Consequently, ion viscosity is a useful probe of material state through the entire cure. Critical Points on the ion viscosity curve can characterize the progress of cure.

The relationship between ion viscosity and viscosity has proven to be useful in thermoset processing. Knowing when material has reached the viscosity minimum, for example, allows optimum application of pressure to compress a laminate or a molded part. Even after ion viscosity diverges from mechanical viscosity, ion viscosity continues to indicate material state and can identify a user defined end of cure.

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