



***Insight* — Technical Overview 2.01**

Ion Viscosity and Its Use in Dielectric Cure Monitoring

What Does Dielectric Cure Monitoring Measure?

Dielectric cure monitoring, also known as 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.

The term *ion viscosity (IV)* was coined in the early 1980's as a synonym for frequency independent resistivity. Ion viscosity has units of ohm-cm and is defined below:

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

Why? Because ρ_{DC} is determined by ionic mobility, and the state of a material's polymer chains or networks affects *both* ionic mobility and mechanical resistance to flow. Consequently, ion viscosity 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.

Figure 1 presents data from the non-isothermal cure of an epoxy. A dielectrometer measured ion viscosity and a Rheological Dynamic Spectrometer (RDS) measured mechanical viscosity. The two curves show strong correlation from the beginning of cure up to gelation at about 135 minutes. After gelation, mechanical viscosity increases rapidly and becomes immeasurable; however, ion viscosity continues to provide information about material state until the end of cure.

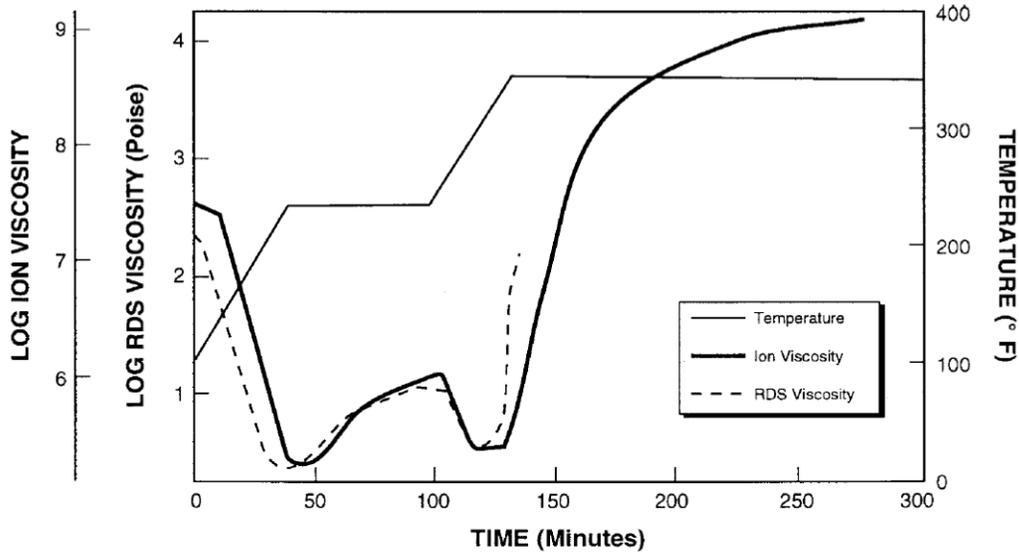


Figure 1
Correlation of ion viscosity and viscosity during epoxy cure

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

Note that the minimum RDS viscosity, at about 40 minutes, actually happens a little before the time of minimum ion viscosity. This behavior is common in comparisons between rheological and dielectric data. Mechanical viscosity starts to increase as monomers react and begin chain extension, which 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.

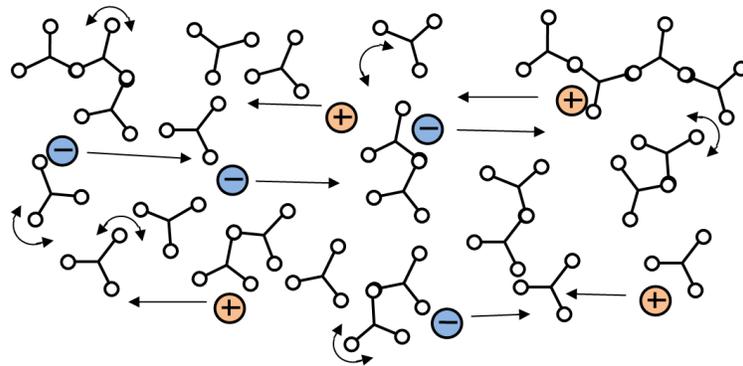


Figure 2
Mobile ions during early polymerization

When chain extension begins, free ions do not yet experience “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 behind mechanical viscosity.

Resistivity and Viscosity

The relationship between ion viscosity and mechanical viscosity can be examined rigorously. For convenience, unless otherwise indicated, *resistivity* will refer to ρ_{DC} . Similarly, *viscosity* will refer to *mechanical viscosity*.

Resistivity is a measure of the mobility of free ions through a medium under the influence of an electric field. Resistivity is given by equation 2.

$$(eq. 2) \quad \rho_{DC} = 1 / (q \mu n)$$

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 3:

$$(eq. 3) \quad \mu = q D / (k T)$$

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, the diffusion coefficient is given by the Stokes-Einstein relation of equation 4:

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

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

Combining equations 2, 3 and 4 yields the following relationship between resistivity and viscosity:

$$\text{(eq. 5)} \quad \rho_{DC} = (6\pi \eta r) / (q^2 n)$$

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

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:

$$\text{(eq. 6)} \quad \rho \propto \eta^n \text{ where } n = 1, 2, 3 \dots$$

Ion Viscosity and Gelation

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

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

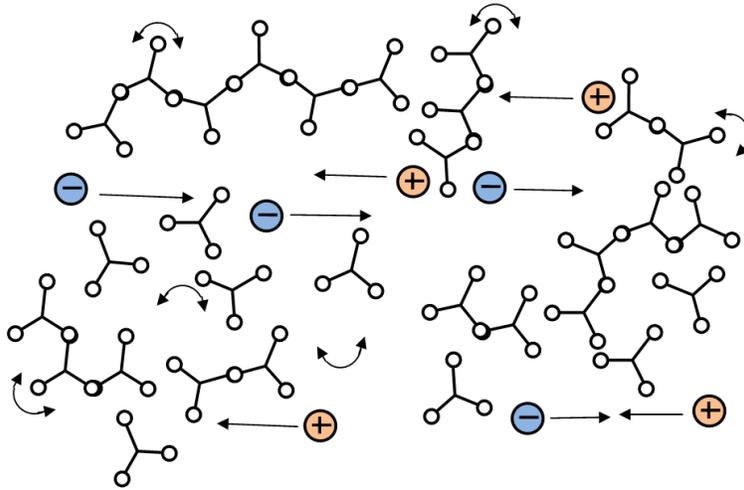


Figure 3.a. Polymer just before gel point

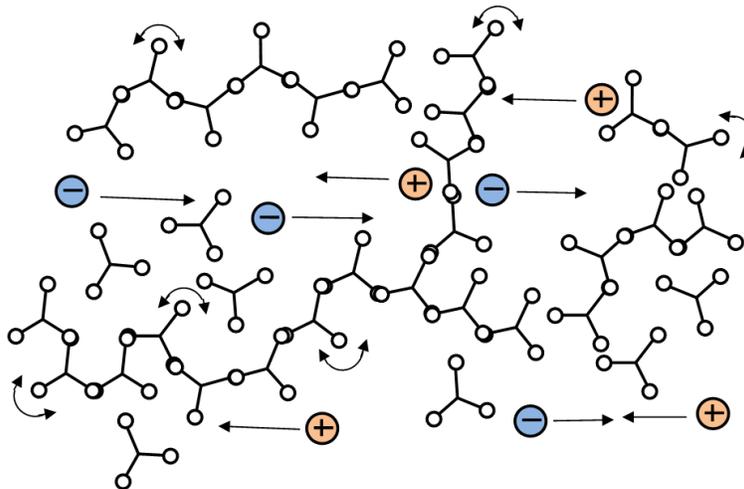


Figure 3.b. Polymer at gel point (beginning of network formation)

Determining Ion Viscosity

Ion viscosity (I/V) is the frequency independent resistivity (ρ_{DC}) of a polymer, which correlates with viscosity before gelation and modulus after gelation. For dielectric cure monitoring it is important to understand how to identify ion viscosity and isolate it from other factors.

Many in this field are more familiar with loss factor (ϵ''), so it is easiest to begin by looking at the loss factor during cure of a familiar thermoset, in this case "Five-minute" epoxy, shown in Figure 4.

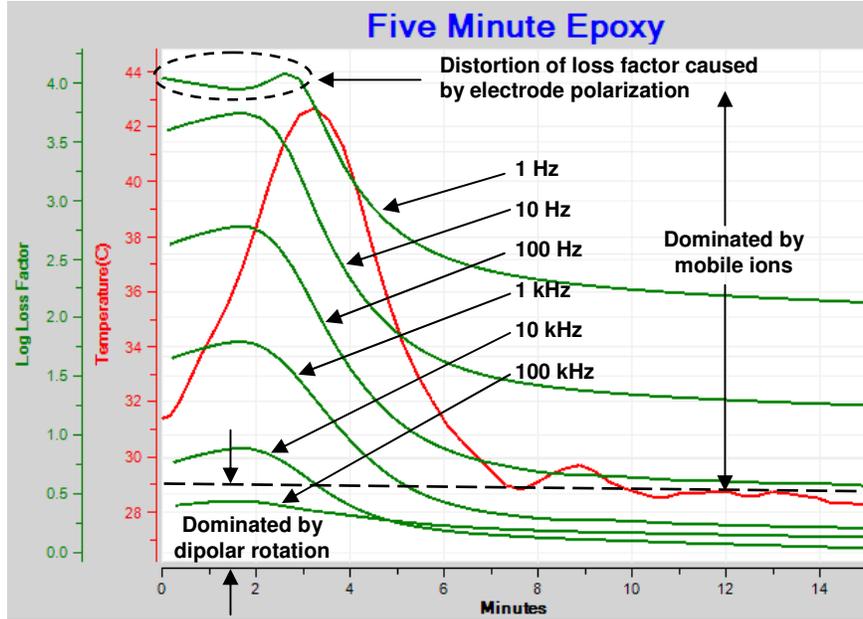


Figure 4
Loss factor of curing epoxy

During early cure, loss factor is inversely proportional to frequency for 10 kHz or less—the effect of mobile ions dominates here. Loss factor for 1 Hz shows distortions characteristic of a boundary layer caused by a phenomenon called 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.

Figure 5 shows resistivity (ρ), defined by equation 7, derived from the loss factor data of Figure 1.

(eq. 7)
$$\rho = 1/(\omega \epsilon_0 \epsilon'_{MUT})$$

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

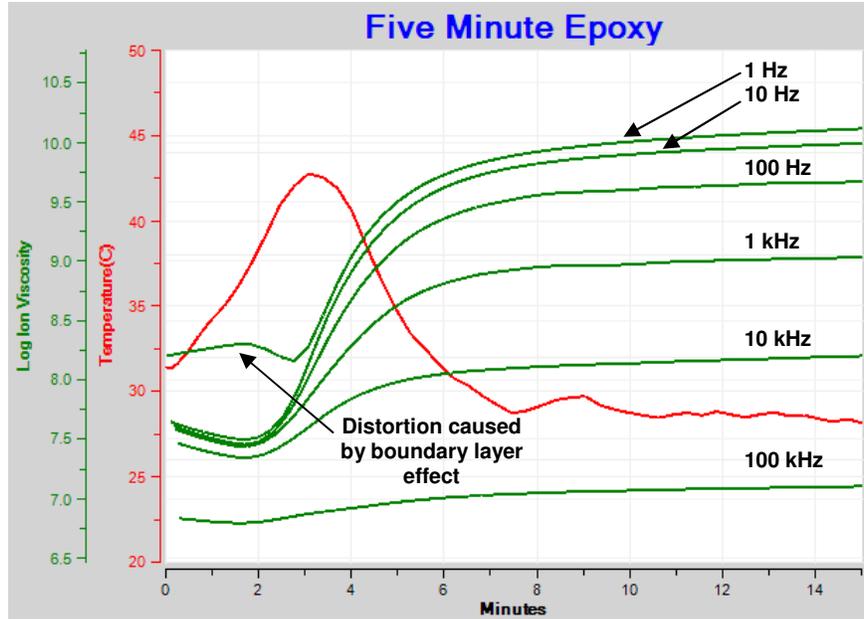


Figure 5
Resistivity of curing epoxy (plotted against log(ion viscosity) axis)

Resistivity has both frequency independent (ρ_{DC}) and frequency dependent (ρ_{AC}) terms. 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.

Note that the resistivity of Figure 5 is the sum of both frequency independent and frequency dependent components ($\rho_{DC} + \rho_{AC}$). When this total resistivity is unknowingly represented as ion viscosity, misleading interpretations of cure state may result. Which curve is ion viscosity? Which curve follows viscosity? Or Modulus? Therefore it is necessary to correctly identify ion viscosity.

Figure 6 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*, that indicates cure state of the material.

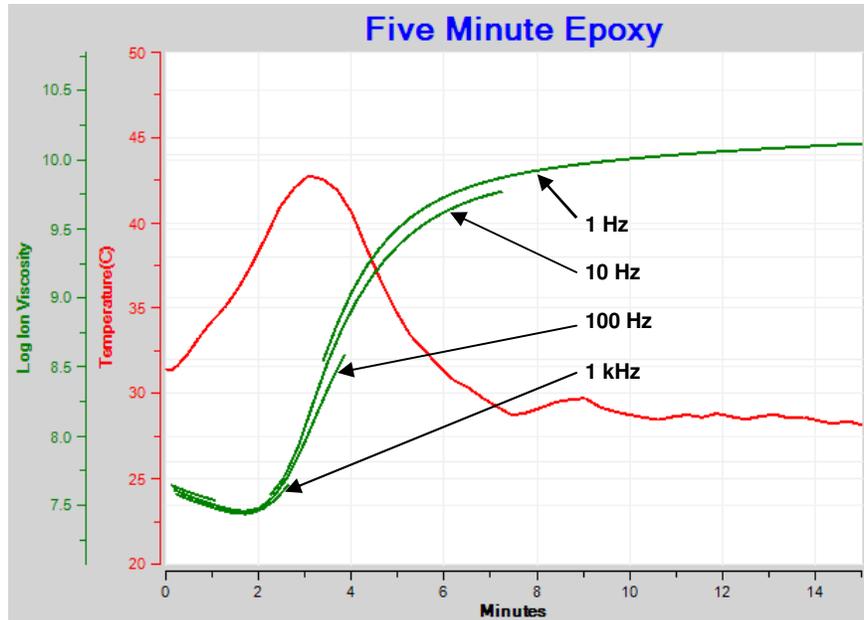


Figure 6
Ion viscosity—frequency independent resistivity component only

To determine the time of maximum reaction rate or the time to end of cure, we must calculate the slope of $\log(\text{ion viscosity})$, here simply called *slope* for brevity. Unfortunately, the ion viscosity segments of Figure 6 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 7. This simplification is possible because ion viscosity from a properly chosen frequency usually is very similar to the composite from multiple frequencies.

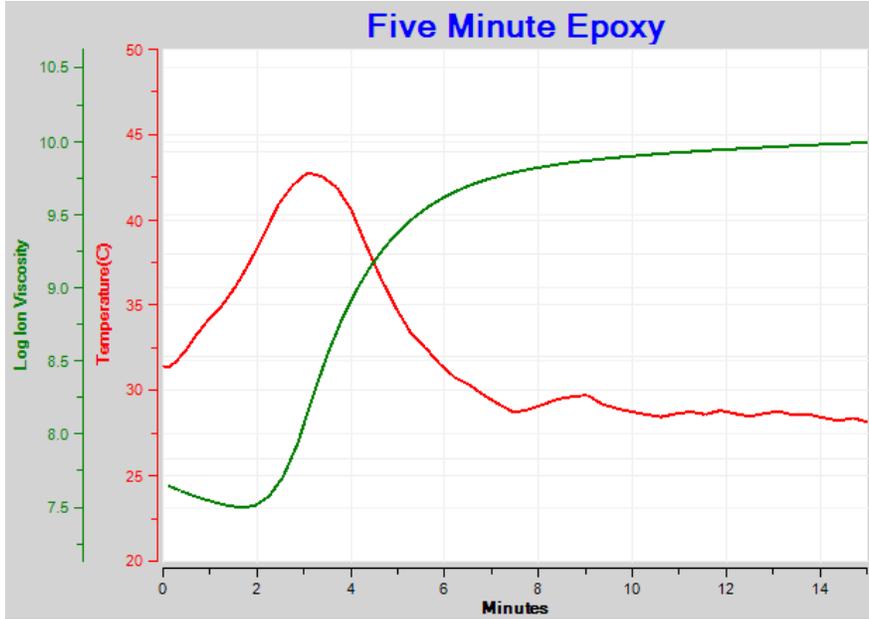


Figure 7
Ion viscosity for 10 Hz frequency only

Figure 8 shows ion viscosity from 10 Hz data as well as the resulting curve for slope.

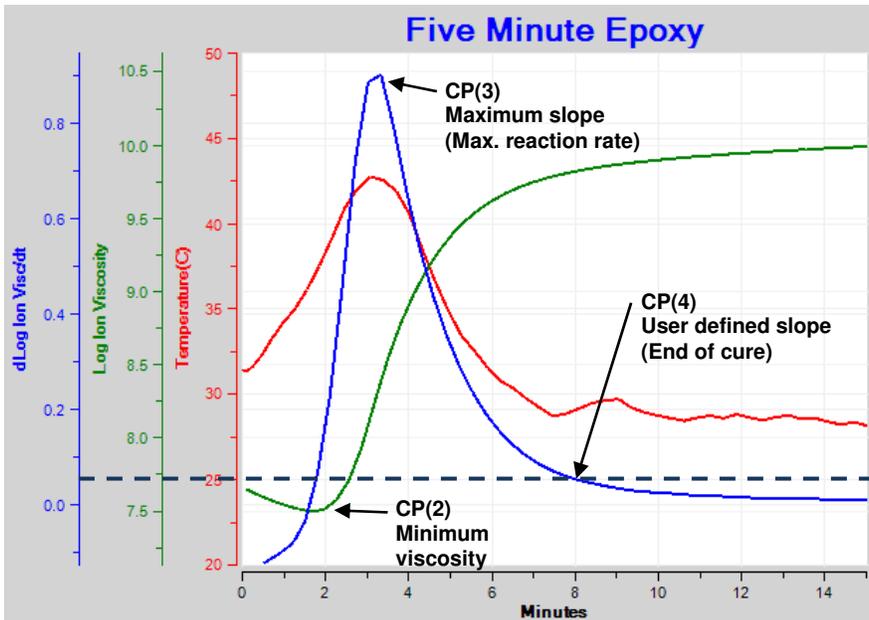


Figure 8
Ion viscosity and slope for 10 Hz frequency only, showing Critical Points

Four Critical Points, which identify particular events, characterize the cure of a thermoset:

- **Critical Point 1—CP(1)—Onset of flow**
 - Ion viscosity passes a user defined level
 - Indicates material has reached the sensor
- **Critical Point 2—CP(2)—Minimum viscosity**
 - Ion viscosity reaches minimum
 - Hardening from cure overcomes softening from temperature increase
 - Approximately same time as minimum mechanical viscosity
- **Critical Point 3—CP(3)—Maximum slope**
 - Slope of ion viscosity reaches maximum
 - Ion viscosity inflection point
 - Point of maximum reaction rate
 - Associated with gelation but not indicating gelation
- **Critical Point 4—CP(4)—Critical slope**
 - Slope of ion viscosity reaches user defined value
 - Chosen slope represents degree of cure that depends on application
 - Can identify end of cure

In Figure 8 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 Cure

A thermoset cures because monomers react to form polymer chains then a network. The reaction is usually exothermic—generating heat—or is driven by the heat of a press or oven. Mechanical viscosity and ion viscosity typically follow curves with Critical Points like those of Figures 9 and 10.

Initially, mechanical viscosity decreases as temperature increases and the material softens or melts. Ion viscosity also decreases as mobile ions experience less resistance to movement. At this point the reaction is still slow.

Mechanical viscosity reaches a minimum—a point of zero slope—when the accelerating reaction dominates and the material becomes more viscous. Ion viscosity reaches a minimum at about the same time then increases due to chain extension, which presents a greater and greater impediment to the flow of ions.

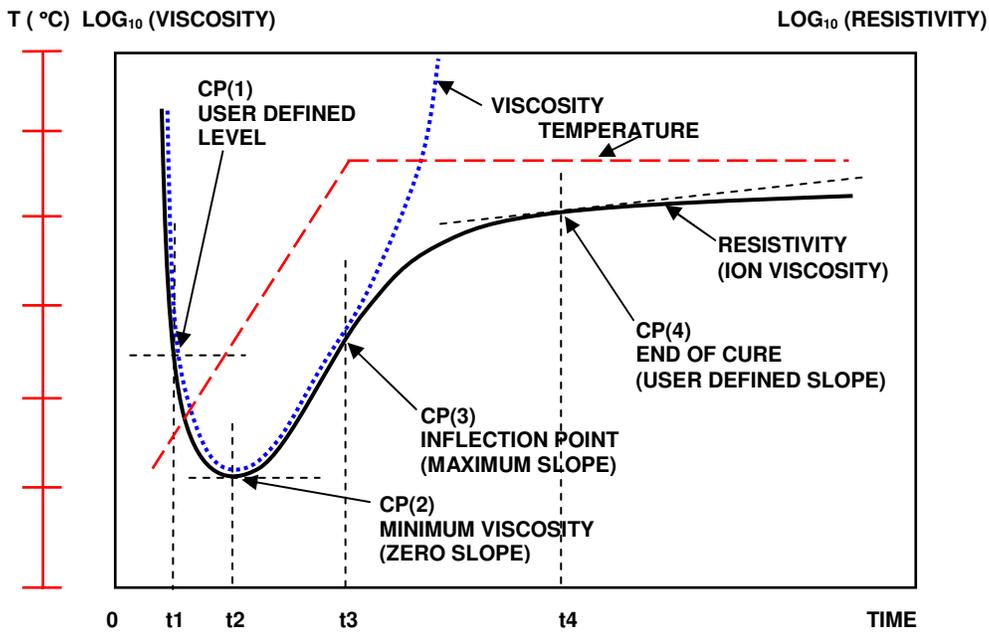


Figure 9
Mechanical viscosity and ion viscosity in a curing thermoset

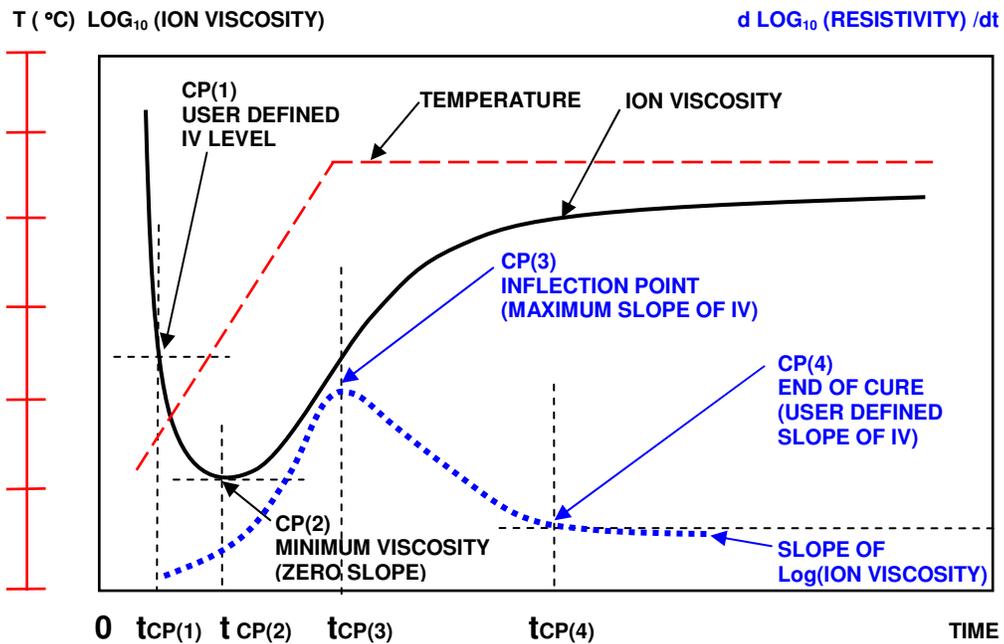


Figure 10
Ion viscosity, slope and Critical Points in a curing material

Eventually the reaction slows and mechanical viscosity becomes immeasurable at the gel point. At this point ion viscosity is no longer proportional to mechanical viscosity. Ion viscosity continues to change, but more and more slowly, approaching a limit at the end of cure.

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 when mobile ions dominate the dielectric response and therefore identify ion viscosity.

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

The relationship between ion viscosity and mechanical 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 a molded part. Even after ion viscosity diverges from mechanical viscosity, ion viscosity continues to indicate material state and can indicate a user defined end of cure.



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