Insight — Application Note 3.13

Cure Monitoring of Sheet Molding Compound (SMC)

Cure of sheet molding compound

The curing behavior of Sheet Molding Compound (SMC) was observed using the LT-451 Dielectric Cure Monitor.[1] Bulk Molding Compound (BMC) is the generally the same material as SMC but in bulk form, so the overall behavior applies to BMC as well. The data from dielectric cure monitoring clearly show:

- Critical Points identify characteristic features of the cure such as minimum ion viscosity, maximum slope of log(ion viscosity) and the time to a chosen end of cure.
- Cure time decreases as cure temperature increases, as expected for a reaction that is thermally driven.

Definitions

This application note presents and discusses data for *log(ion viscosity)* and *slope of log(ion viscosity)*, which indicate the state of cure. The plots show characteristic features such as minimum ion viscosity, maximum slope of log(ion viscosity) and the time to a chosen end of cure. For brevity, log(ion viscosity) will be called *log(IV)* and slope of log(ion viscosity) will simply be called *slope*.

Electrical 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 are added together as expressed below:

(eq. 13-1) $$\sigma = \sigma_{DC} + \sigma_{AC} \qquad (\text{ohm}^{-1} - \text{cm}^{-1})$$

Resistivity (ρ) is the inverse of conductivity and is defined as:

(eq. 13-2) $$\rho = 1/\sigma \qquad (\text{ohm-cm})$$

From its relationship to conductivity, resistivity also has both frequency independent (ρ_{DC}) and frequency dependent (ρ_{AC}) components. The amount of polymerization or crosslink density, which are measures of cure state, affect both mechanical viscosity and the movement of ions, and therefore influence ρ_{DC}. As a result, the term *Ion Viscosity* was coined to emphasize the relationship between mechanical viscosity and ρ_{DC}. Ion viscosity (*IV*) is defined as:

(eq. 13-3) $$IV = \rho_{DC} \qquad \text{(ohm-cm)}$$

Although the strict definition of ion viscosity is frequency independent resistivity, ρ_{DC}, for convenience ion viscosity may also be used to describe resistivity in general, which has both frequency independent (ρ_{DC}) as well as frequency dependent (ρ_{AC}) components. ***Note, however, that cure state and mechanical viscosity relate best to frequency independent resistivity, ρ_{DC}, which is true ion viscosity***.

Procedure

Samples of SMC were placed on Mini-Varicon[2] sensors, shown in Figure 13-1, with the lay-up of Figure 13-2. The samples were cured in a laboratory press at 135 °C, 145 °C and 155 °C. Previous tests had identified 10 Hz as an optimum excitation frequency for cure monitoring.

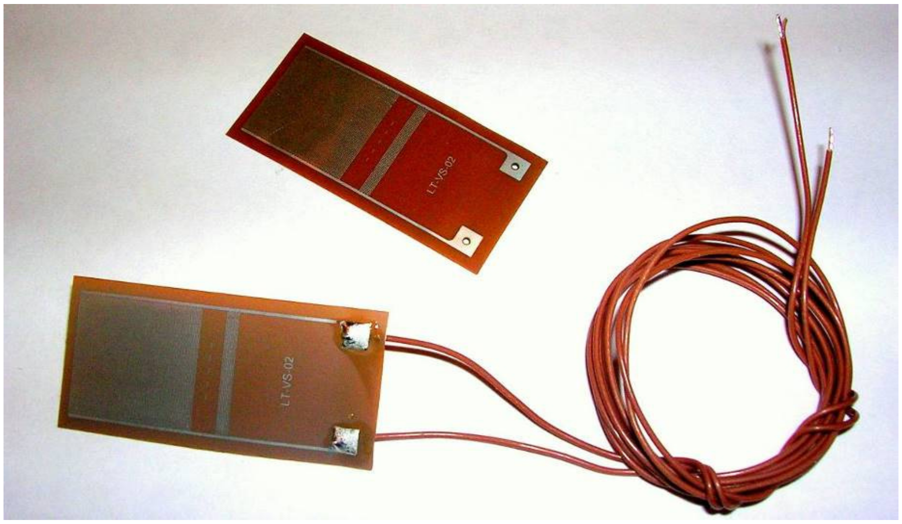

Figure 13-1
Mini-Varicon disposable sensor

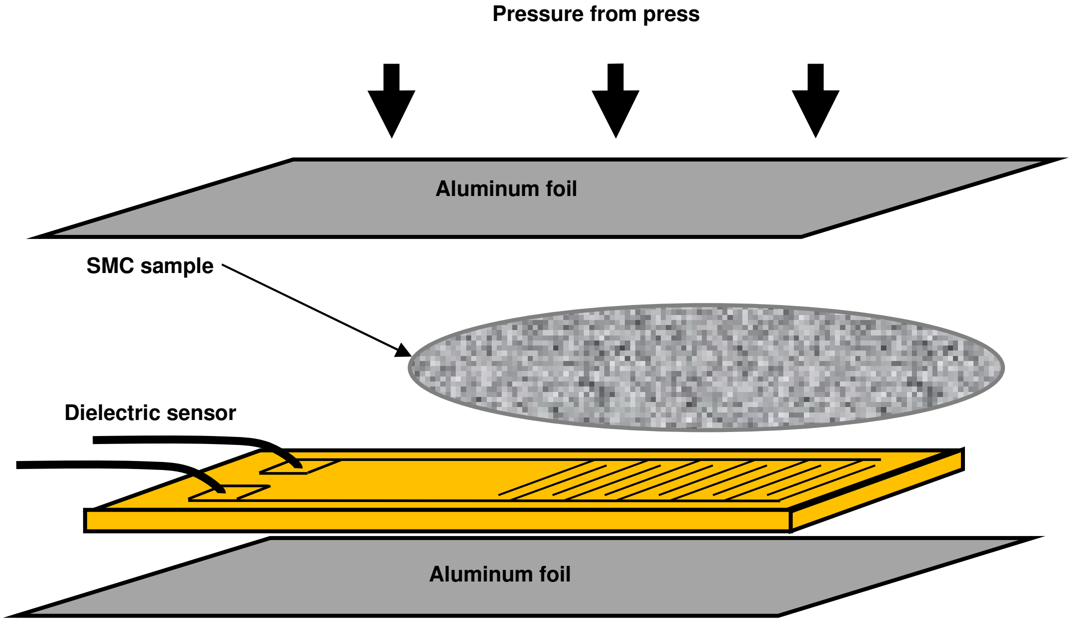

Figure 13-2
Lay-up of SMC for cure monitoring

An LT-451 Dielectric Cure Monitor measured the dielectric properties of each sample at 10 Hz and was triggered to start data acquisition when the press closed. CureView[3] software acquired and stored the data, and performed post-analysis and presentation of the results.

Results

Figures 13-3, 13-4 and 13-5 show data from the tests of SMC at 135 °C, 145 °C and 155 °C, respectively, and demonstrate how SMC cures more quickly at higher process temperatures. The time of minimum ion viscosity, which indicates the start of accelerating cure, occurs sooner at higher temperatures. Furthermore, once cure dominates, ion viscosity rises more steeply at higher temperatures until the curve flattens as it approaches the end of cure.

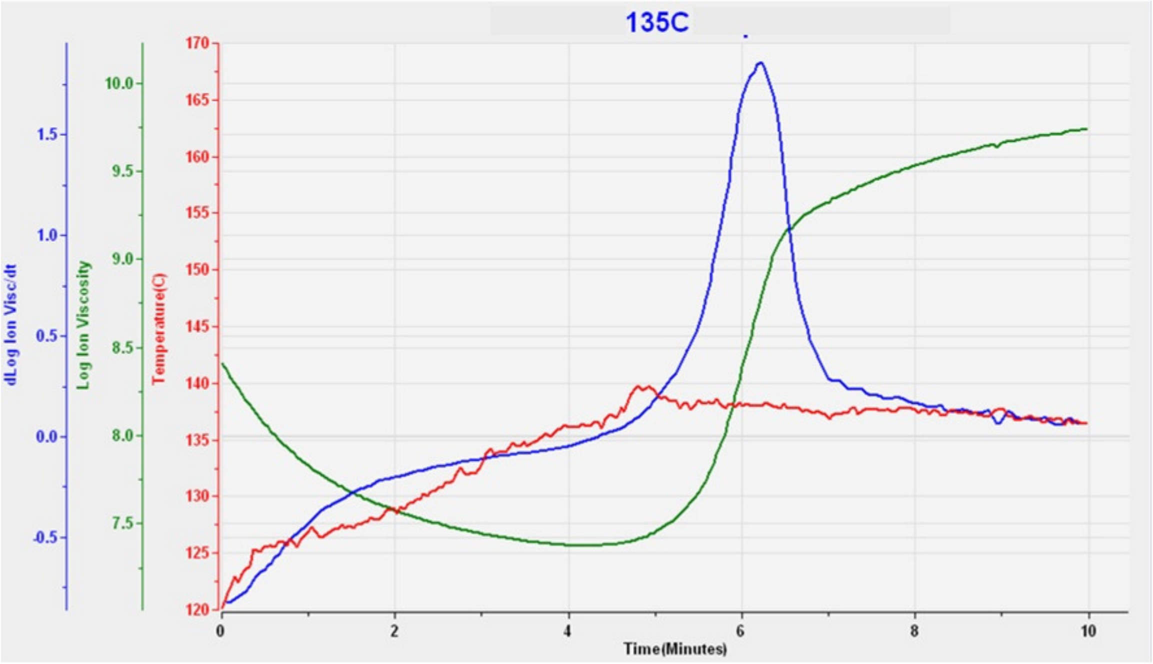

Figure 13-3
135 °C SMC cure data at 10 Hz

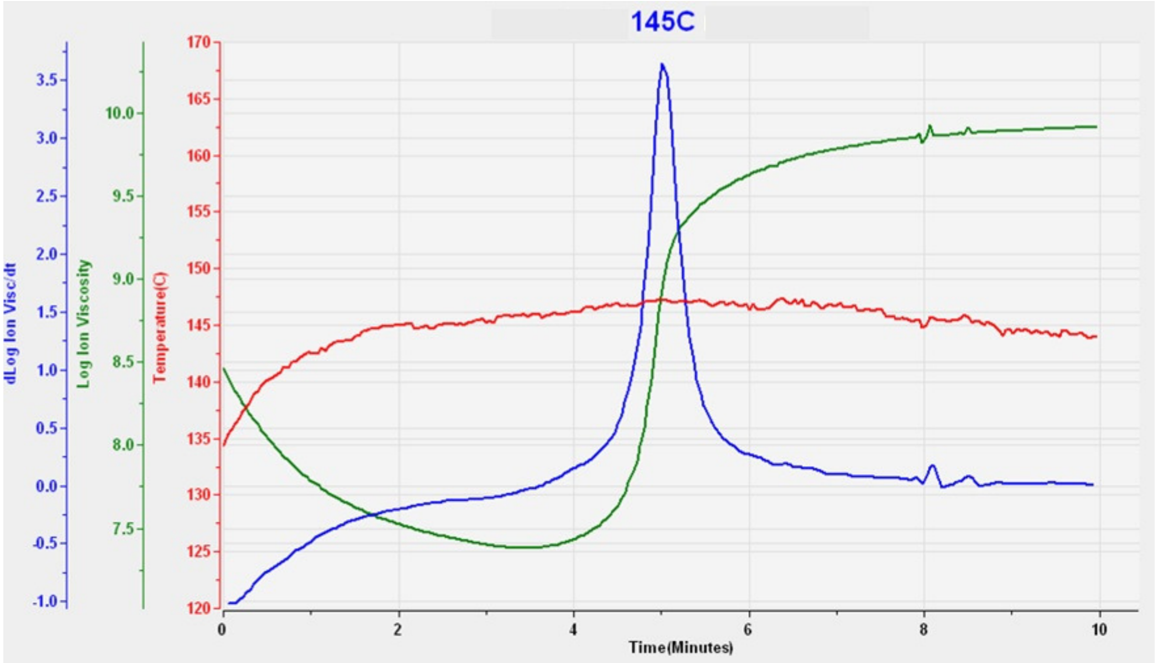

Figure 13-4
145 °C SMC cure data at 10 Hz

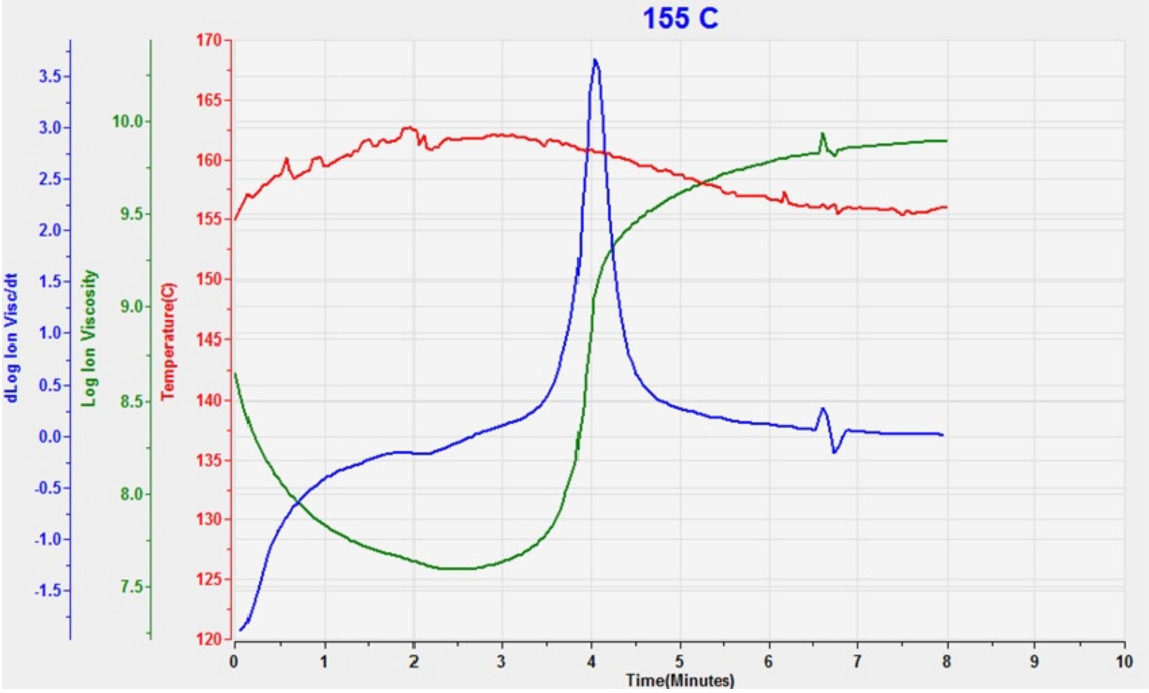

Figure 13-5
155 °C SMC cure data at 10 Hz

The Critical Points that characterize each cure are shown in Table 13-1. *Note that the slope of 0.25 to define CP(4), the end of cure, was chosen arbitrarily.* In actuality a user must determine the slope to indicate end of cure based on the needs of the application.

Table 13-1
Critical Points from SMC cure monitoring

Cure Temp. (°C)	CP(1) Crit. Visc.		CP(2) Min. Visc.		CP(3) Max Slope		CP(4) Crit. Slope	
	Value	Time	Value	Time	Value	Time	Value	Time
135	8.0	0.65 min (39 s)	7.38	4.17 min (250 s)	1.86	6.23 min (374 s)	0.25	7.21 min (433 s)
145	8.0	0.60 min (36 s)	7.39	3.42 min (205 s)	3.65	5.01 min (301 s)	0.25	6.13 min (368 s)
155	8.0	0.65 min (39 s)	7.60	2.48 min (149 s)	3.67	4.03 min (242 s)	0.25	5.14 min (308 s)

As plotted in Figure 13-6, the times to reach each Critical Point are shorter for cures at higher temperatures, which is expected for thermally driven reactions.

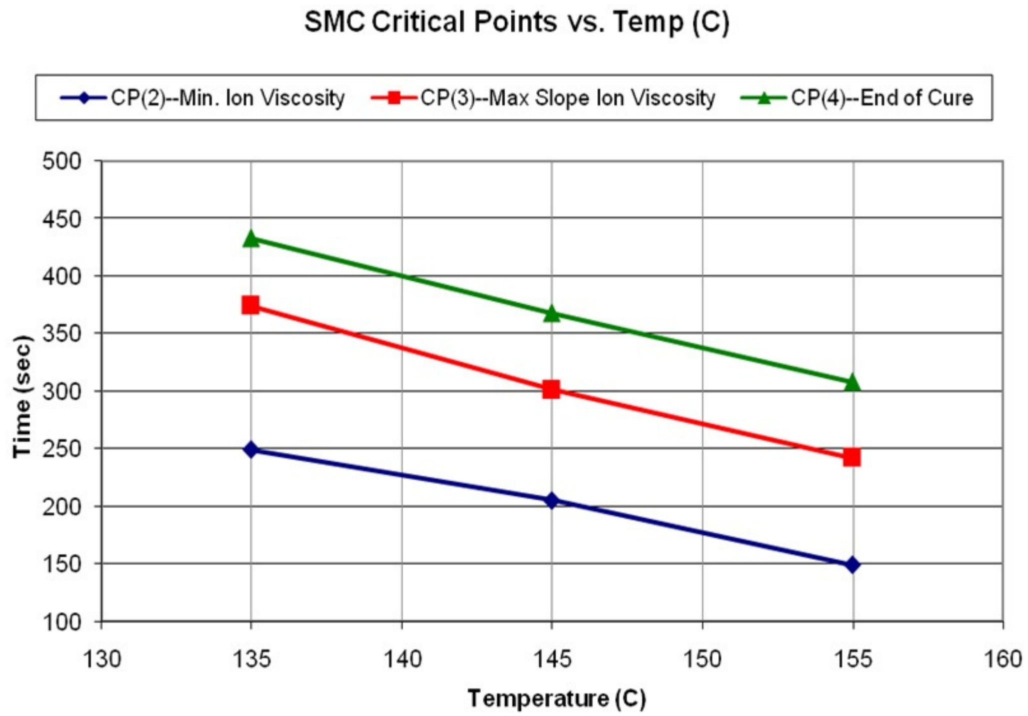

Figure 13-6
Critical Point time vs. cure temperature for SMC

The time to Critical Point 1—CP(1)—is not plotted in Figure 13-5. CP(1) determines when the ion viscosity of the SMC has decreased to the user selected value of 8.0, which was chosen to indicate the onset of flow. The time to flow is a measure of heating time and not of curing, consequently CP(1) has been omitted for clarity.

Within the 20 °C range of the plot of Figure 13-6, the time to reach CP(2)—the ion viscosity minimum—decreases by approximately 50 seconds for each 10 °C increase in processing temperature. The times to reach CP(3) and CP(4) vary by a similar amount with temperature.

Critical Points during thermoset cure

A thermoset cures when monomers react to form polymer chains then a network. The reaction is usually exothermic—generating heat—and may additionally be driven by the heat of a press or oven. A plot of log(*ion viscosity*) is a simple way to characterize the progress of cure and Figure 13-7 shows the behavior of a typical thermoset with one ramp and hold step in temperature.

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

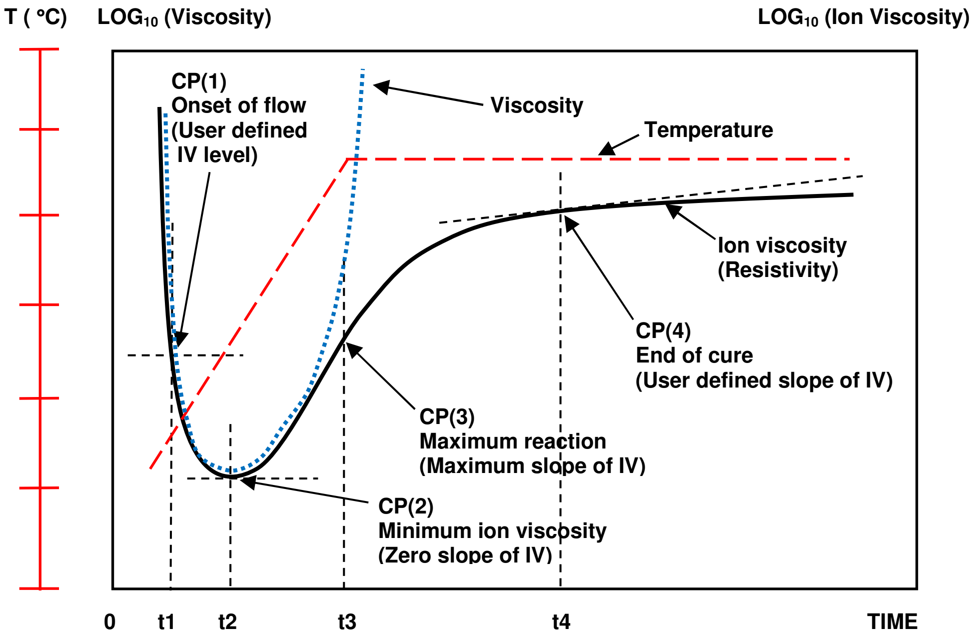

Figure 13-7
Typical ion viscosity behavior of thermoset cure during thermal ramp and hold

As the material becomes hotter, the cure rate increases. At some time the accelerating reaction begins to dominate; mechanical 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.

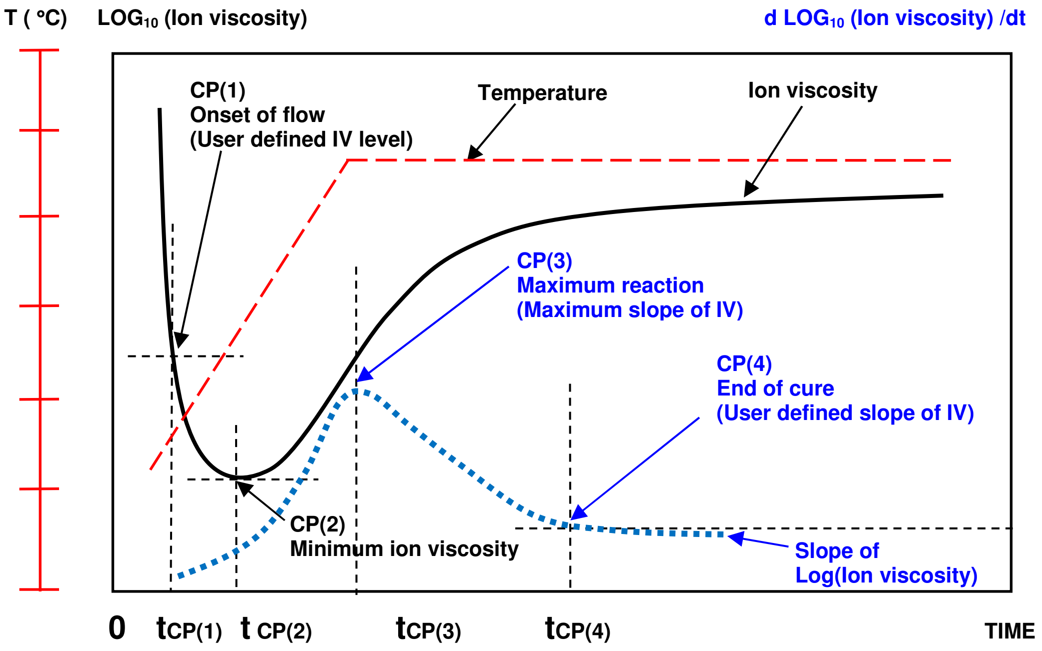

Figure 13-8
Ion viscosity curve and slope of ion viscosity of thermoset cure during thermal ramp and hold

As shown in Figure 13-8, 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.

Figures 13-7 and 13-8 illustrate the typical behavior of curing thermosets when temperature gradually ramps to a hold value. The response is slightly different when the material under test is essentially isothermal, as shown in Figure 13-9.

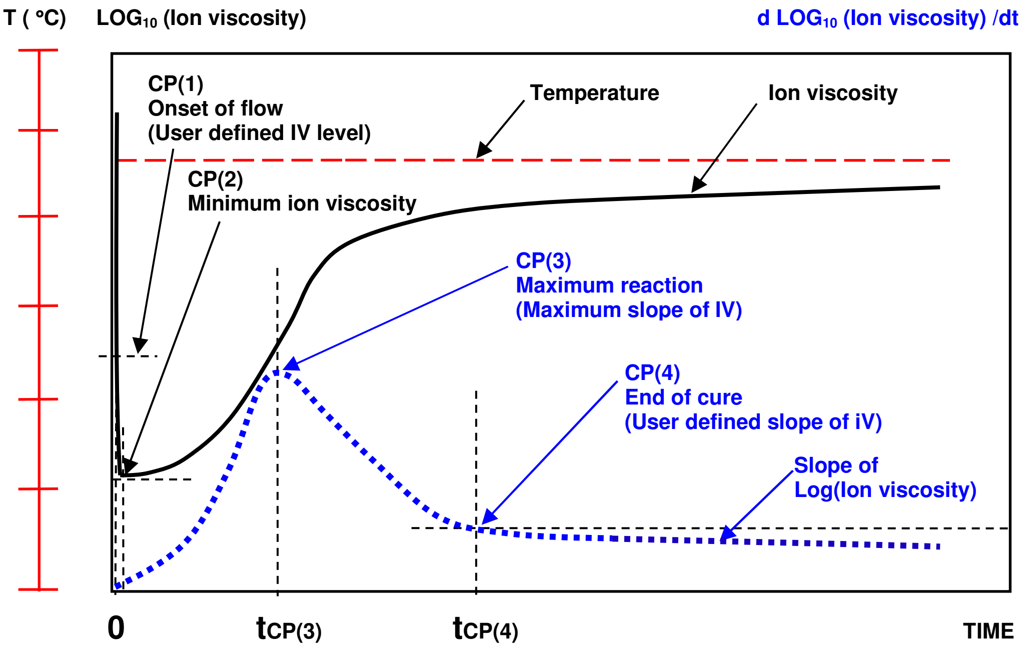

Figure 13-9
Ion viscosity curve and slope of ion viscosity of thermoset cure during isothermal processing

In this case CP(1) either is meaningless or occurs immediately after the application of heat, when material flows and contacts the sensor. Minimum ion viscosity also occurs at t = 0 or shortly afterwards because cure begins immediately. For isothermal cures, CP(3) and CP(4) are conceptually the same as for ramp and hold conditions.

References

1. LT-451 Dielectric Cure Monitor, manufactured by Lambient Technologies, Cambridge, MA, USA. https://lambient.com

2. Mini-Varicon sensor, manufactured by Lambient Technologies, Cambridge, MA USA

3. CureView software, manufactured by Lambient Technologies, Cambridge, MA USA

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