



Insight — Application Note 3.14

Cure Monitoring of Bulk Molding Compound (BMC)

Cure of bulk molding compound

The curing behavior of Bulk Molding Compound (BMC) was observed using the LTF-631 High Speed Dielectric Cure Monitor.¹ Bulk Molding Compound is generally the same material as Sheet Molding Compound (SMC) but in bulk form, so the overall results apply to SMC as well. The data from dielectric cure monitoring (DEA) clearly show:

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

Definitions

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

$$\text{(eq. 14-1)} \quad \sigma = \sigma_{DC} + \sigma_{AC} \quad (\text{ohm}^{-1} - \text{cm}^{-1})$$

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

$$\text{(eq. 14-2)} \quad \rho = 1/\sigma \quad (\text{ohm-cm})$$

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:

$$(eq. 14-3) \quad IV = \rho_{DC} \quad (\text{ohm-cm})$$

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 BMC were placed on disposable Mini-Varicon² sensors, shown in Figure 14-1, then compressed and cured in an LTP-250 MicroPress,³ which applied pressure and heat for separate runs at 130 °C, 140 °C, 150 °C, 160 °C and 170 °C. Previous tests had identified 100 Hz as an optimum excitation frequency for cure monitoring.

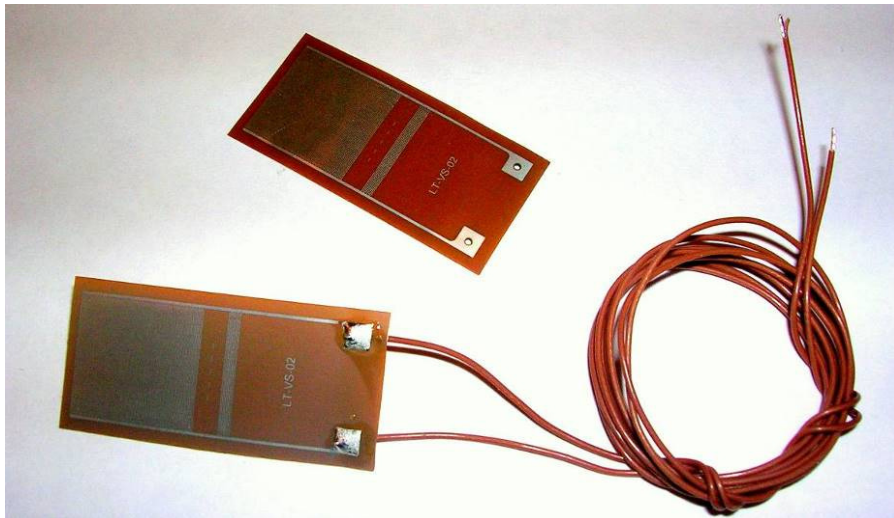


Figure 14-1
Mini-Varicon disposable sensor

The cure time for these samples is less than two minutes so an LTF-631 High Speed Dielectric Cure Monitor measured the dielectric properties of each sample. The measurement interval was 100 ms/data point and a trigger on the LTP-250 initiated data acquisition at a consistent point in the compression cycle. CureView⁴ software acquired and stored the data, and later performed Critical Point analysis and presentation of the results.

Results

Figures 14-2, 3, 4, 5 and 6 show data from the cures of BMC at 130 °C, 140 °C, 150 °C, 160 °C and 170 °C, respectively. The ability of dielectric cure monitoring to observe the effect of temperature on cure is apparent in this sequence of plots.

As expected for a thermally activated reaction, the $\log(IV)$ curves rise and flatten more quickly with increasing temperature. The ion viscosity minimum—CP(2)—and the peak slope—CP(3)—also occur sooner at higher temperatures. Furthermore, the peak value of CP(3), which is related to the maximum reaction rate, increases with temperature. After acquiring these data, CureView was able to extract the Critical Points that characterize each cure and allow direct comparison of their behavior across the temperature range.

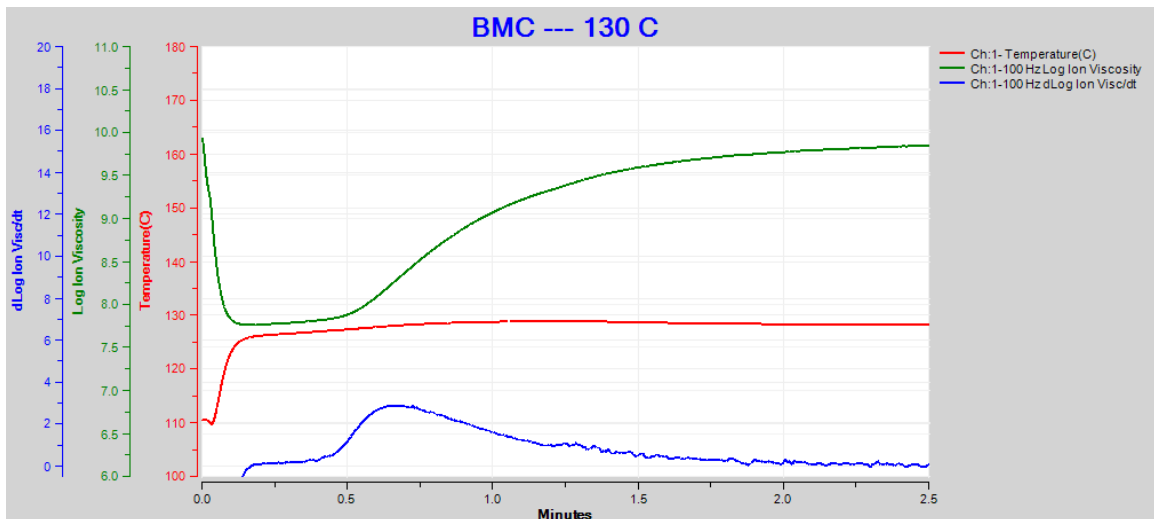


Figure 14-2
130 °C BMC cure data at 100 Hz

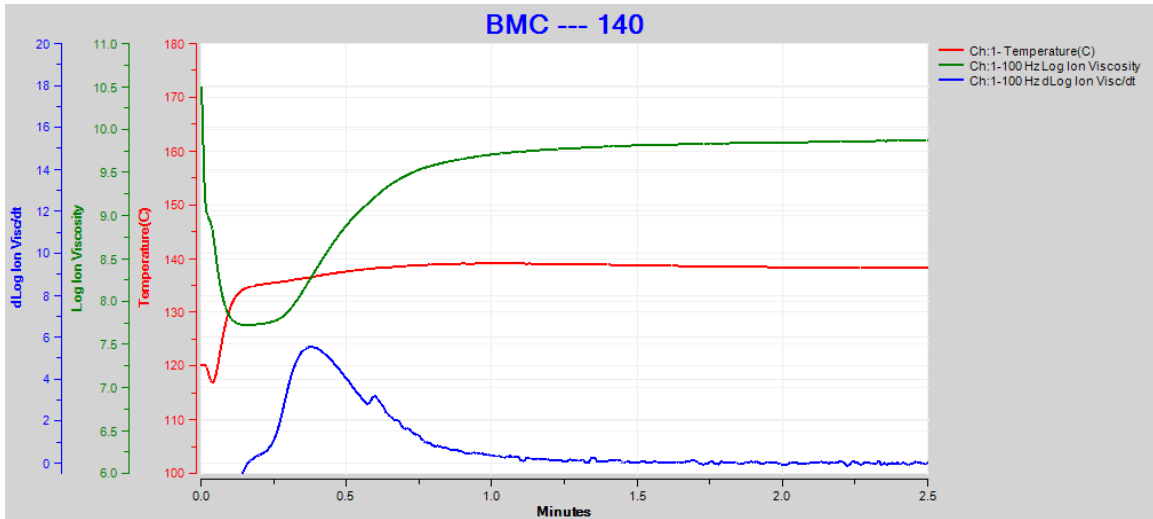


Figure 14-3
140 °C BMC cure data at 100 Hz

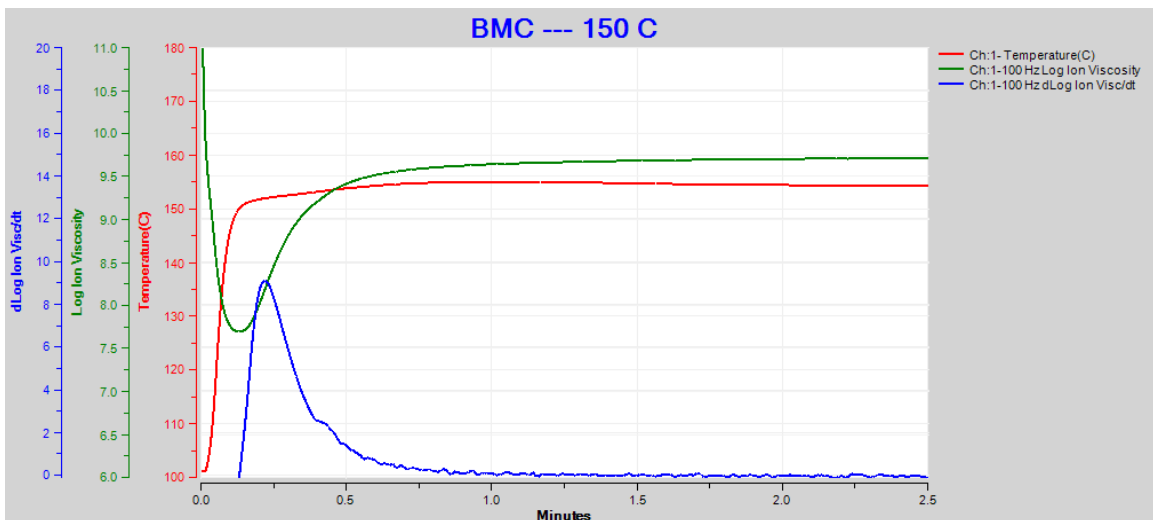


Figure 14-4
150 °C BMC cure data at 100 Hz

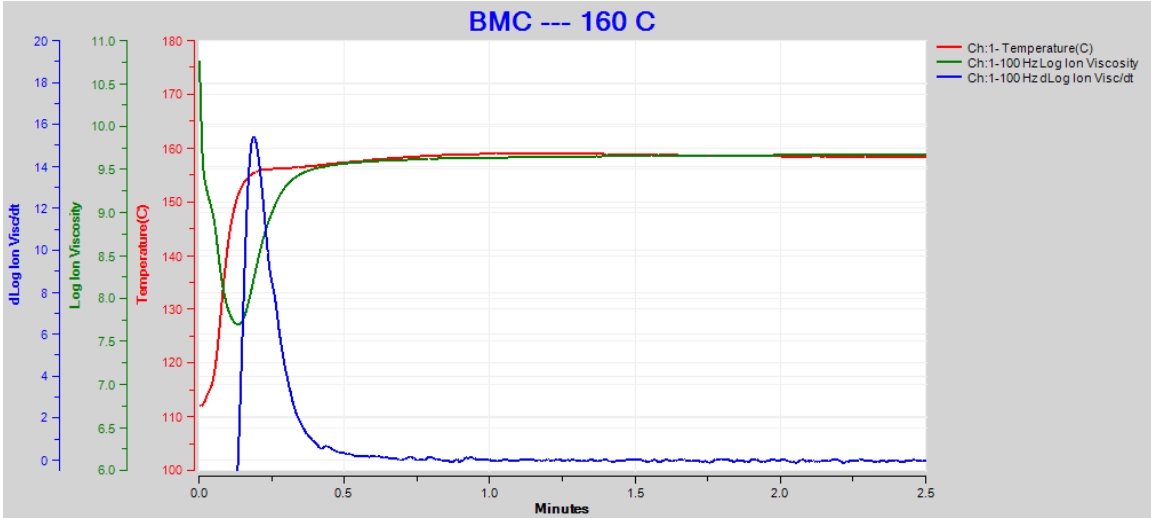


Figure 14-5
160 °C BMC cure data at 100 Hz

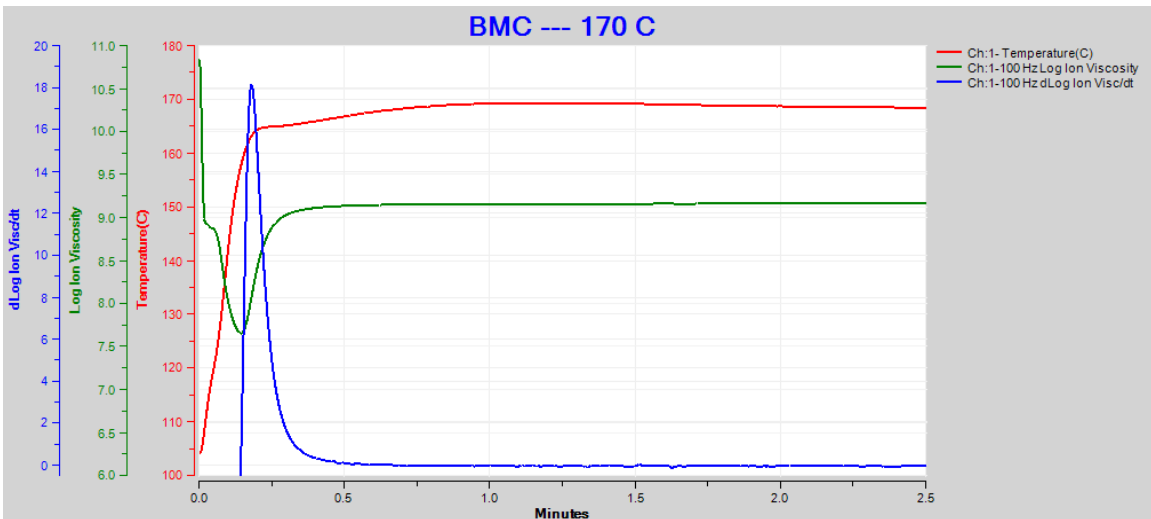


Figure 14-6
170 °C BMC cure data at 100 Hz

Figure 14-7 overlays the $\log(IV)$ and $slope$ curves for 140 °C, 150 °C and 160 °C. For clarity, the data for 130 °C and 170 °C are omitted. This comparison shows the sensitivity of dielectric cure monitoring to changes in cure due to differences in process temperature.

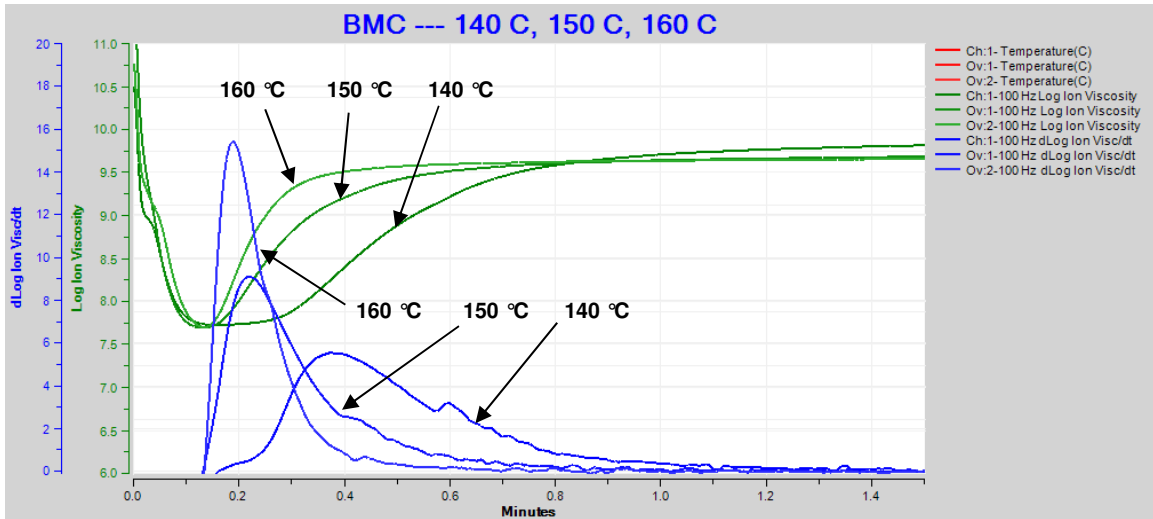


Figure 14-7
Overlay of 140 °C, 150 °C and 160 °C BMC cure data at 100 Hz

As expected, the maximum value of *slope* increases with process temperature, showing the relationship between reaction rate and temperature. Critical Points that characterize each cure are shown in Table 14-1, with the following notes:

- The time to CP(1) indicates onset of flow and is not a measure of cure, so CP(1) data are not shown
- The slope of 0.1 to define CP(4) was chosen arbitrarily; in fact, a user must determine a suitable slope based on the needs of the application to indicate end of cure.

Table 14-1
Critical Points from BMC cure monitoring

Cure Temp. (°C)	CP(1) Crit. Visc.		CP(2) Min. Visc.		CP(3) Max Slope		CP(4) End of Cure	
	Value	Time	Value	Time	Value	Time	Value	Time
130	---	---	7.77	0.164 m (9.8 s)	2.93	0.681 m (40.9 s)	0.10	2.138 m (128.3 s)
140	---	---	7.74	0.157 m (9.4 s)	5.58	0.373 m (22.4 s)	0.10	1.321 m (79.3 s)
150	---	---	7.72	0.153 m (9.2 s)	9.36	0.249 m (14.9 s)	0.10	0.908 m (54.5 s)
160	---	---	7.71	0.135 m (8.1 s)	15.42	0.189 m (11.3 s)	0.10	0.681 m (40.9 s)
170	---	---	7.66	0.144 m (8.6 s)	18.14	0.180 m (10.8 s)	0.10	0.517 m (31.0 s)

As plotted in Figure 14-8, the times to reach each Critical Point decrease for cures at higher temperatures, which is expected for thermally driven reactions.

The time to Critical Point 2—CP(2)—is the point when the BMC has the lowest mechanical viscosity. This information is often useful for identifying the optimum time to apply compression to squeeze out voids, consolidate the layers of a laminate or fill a mold.

The time to Critical Point 3—CP(3)—indicates the moment of fastest reaction. Before CP(3) the reaction is accelerating as temperature increases from the exotherm and external heating. After CP(3) the reaction slows as the network grows and monomers are depleted. *Although CP(3) is not the gel point, CP(3) is often used as a signpost associated with the gel point.*

The time to Critical Point 4—CP(4)—is the time to a user defined slope indicating end of cure. True end of cure occurs when the reaction stops and the material is no longer changing; at this time the slope is zero. The reaction may continue at a very low level for considerable time, so for practical purposes a small, non-zero slope is usually selected, with a value depending on the needs of the application.

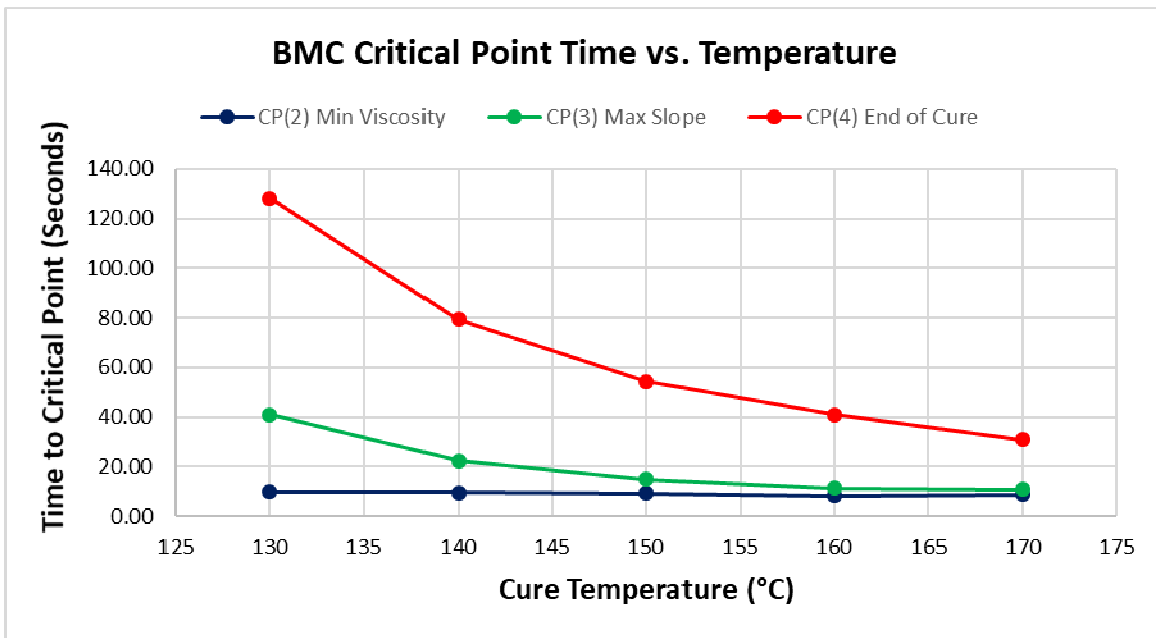


Figure 14-8
Critical Point time vs. cure temperature for BMC

Figure 14-9 shows how the maximum value of *slope*, which is a relative measure of reaction rate, increases with temperature. Again, this relationship is expected for a thermally driven reaction.

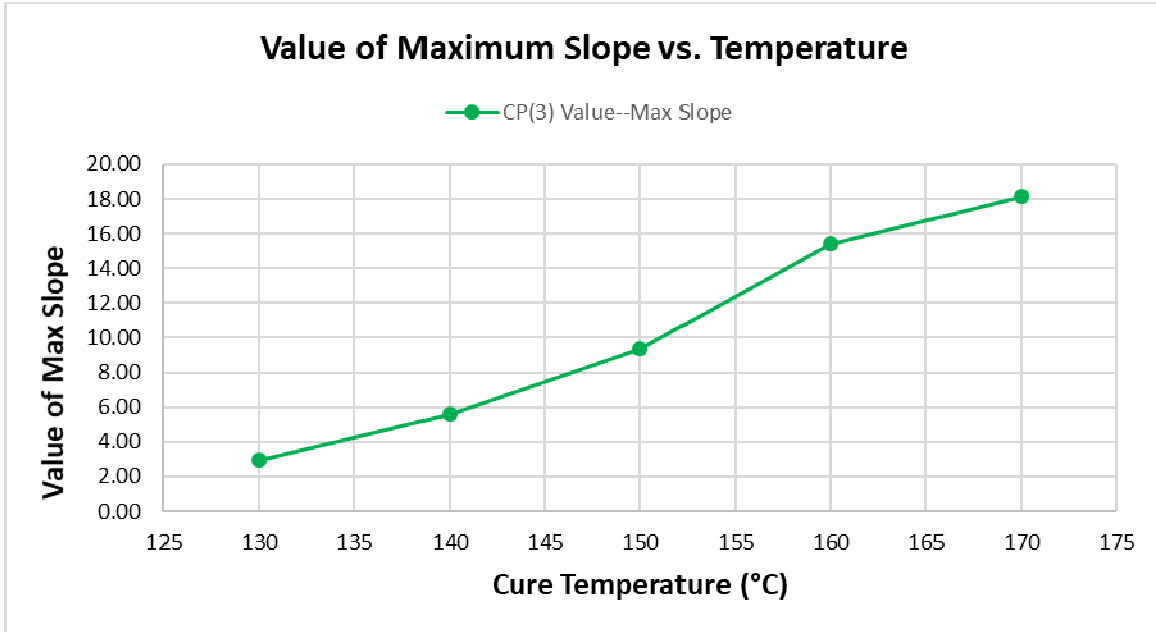


Figure 14-9
Value of maximum slope vs. cure temperature for BMC

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 $\log(\text{ion viscosity})$ is a simple way to characterize the progress of cure and Figure 14-10 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.

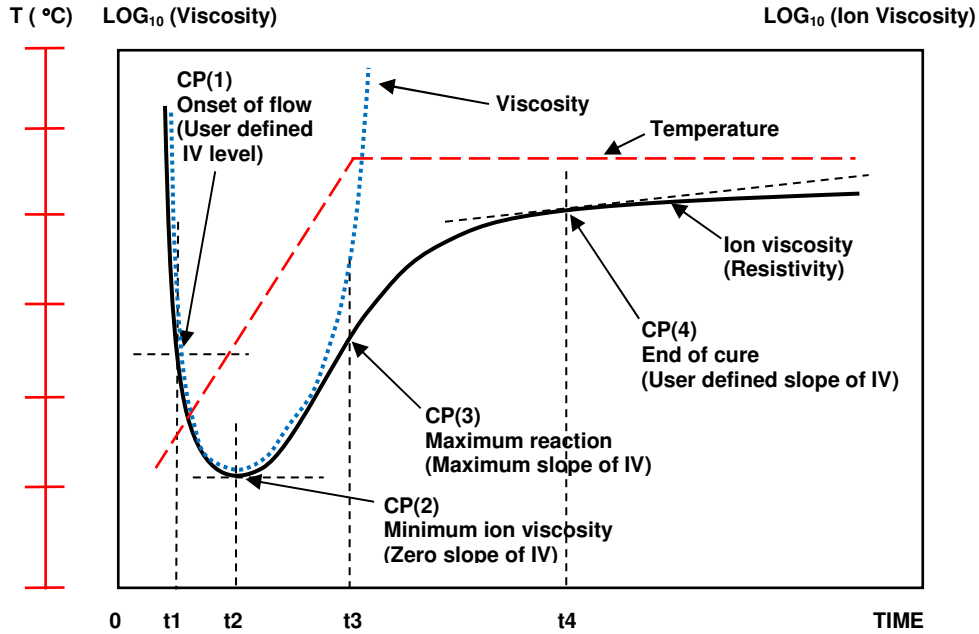


Figure 14-10
Typical ion viscosity behavior of thermoset cure
during thermal ramp and hold

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.

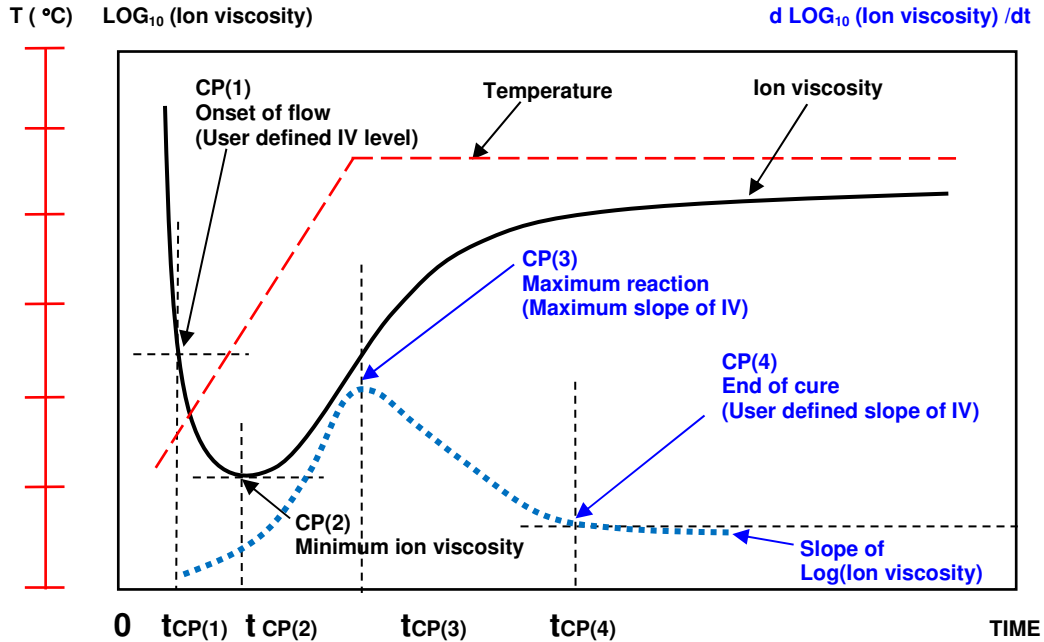


Figure 14-11
Ion viscosity curve and slope of ion viscosity of thermoset cure
during thermal ramp and hold

As shown in Figure 14-11, 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 14-10 and 14-11 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 14-12.

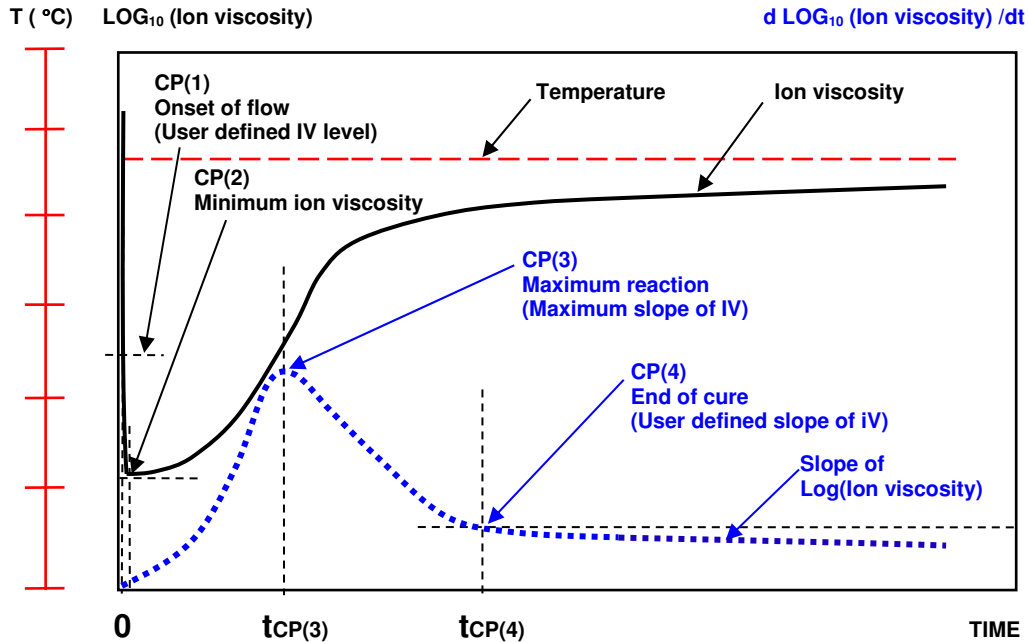


Figure 14-12
Ion viscosity curve and slope of ion viscosity of thermoset cure
during isothermal processing

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. LTF-631 High Speed 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. LTP-250 MicroPress, manufactured by Lambient Technologies, Cambridge, MA USA
4. CureView software, manufactured by Lambient Technologies, Cambridge, MA USA



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