Insight — Application Note 2.09

Cure Monitoring of Sheet/Bulk Molding Compound (SMC/BMC)

Introduction

The curing behavior of Sheet Molding Compound (SMC) was observed using the LT-451 Dielectric Cure Monitor. Bulk Molding Compound (BMC) is the generally the same material as SMC but in bulk form, so the analysis of results apply 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. 9.1) $$\sigma = \sigma_{DC} + \sigma_{AC} \qquad (\text{ohm}^{-1} - \text{cm}^{-1})$$

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

(eq. 9.2) $$\rho = 1/\sigma \qquad (\text{ohm-cm})$$

From its relationship to conductivity, resistivity also has both frequency independent (ρ_{DC}) and frequency dependent (ρ_{AC}) components. Crosslink density, which is a measure of cure state, affects both mechanical viscosity and the movement of ions, and therefore influences 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. 9.3) $$IV = \rho_{DC} \qquad \text{(ohm-cm)}$$

Characteristics of a thermoset Cure

Ion viscosity is defined as the frequency independent resistivity, ρ_{DC}. In many cases ion viscosity is proportional to mechanical viscosity during the early portion of cure, and indicates cure state in the latter portion of cure.

Ion viscosity derived from data at a single frequency produces a curve that characterizes the progress of cure. In simplified form, Figures 10-13 and 10-14 show the behavior of a typical thermoset with one temperature ramp step and one temperature hold step.

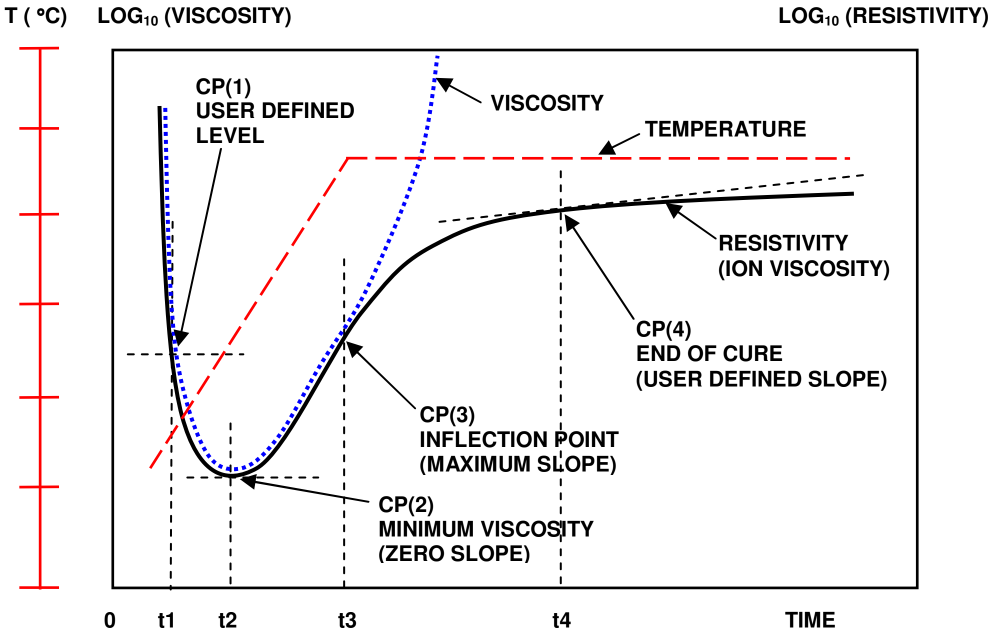

Figure 10-13
Typical ion viscosity behavior of a curing thermoset

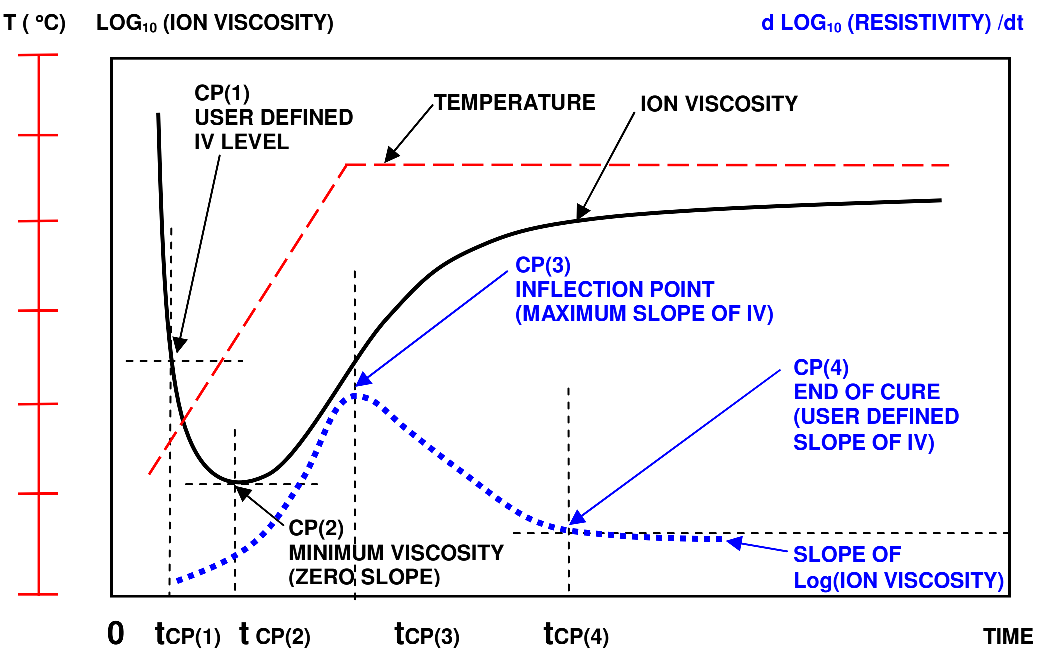

Figure 10-14
Ion viscosity curve and slope of ion viscosity of a curing thermoset

At first, as temperature increases, ion viscosity decreases because the thermoset is melting, becoming more fluid and therefore less resistive. The reaction rate increases as the material becomes hotter. At some time the increase in ion viscosity due to crosslinking overcomes the decrease in ion viscosity due to increasing temperature. This point is the ion viscosity minimum, which also occurs at the time of minimum mechanical viscosity.

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 ion viscosity will have zero slope when cure has stopped completely.

Four Critical Points characterize the dielectric cure curve:

- CP(1)—A user defined level of ion viscosity that is typically used to identify the onset of material flow at the beginning of cure.
- CP(2)—Ion viscosity minimum, which typically also corresponds to the physical viscosity minimum. This Critical Point indicates the time when the crosslinking reaction and resulting increasing viscosity begins to dominate the decreasing viscosity due to melting.

- CP(3)—Inflection point, which identifies the time 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.

Procedure

Samples of SMC were applied to Mini-Varicon sensors and 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. An LT-451 Dielectric Cure Monitor measured the dielectric properties of each sample at 10 Hz for the duration of each test. Lambient Technology's CureView software acquired and stored the data, and performed post-analysis and presentation of the results.

Results

Figures 9-1, 9-2 and 9-3 show data from the cures of SMC at 135 °C, 145 °C and 155 °C, respectively. The data are averaged and filtered to reduce noise.[1]

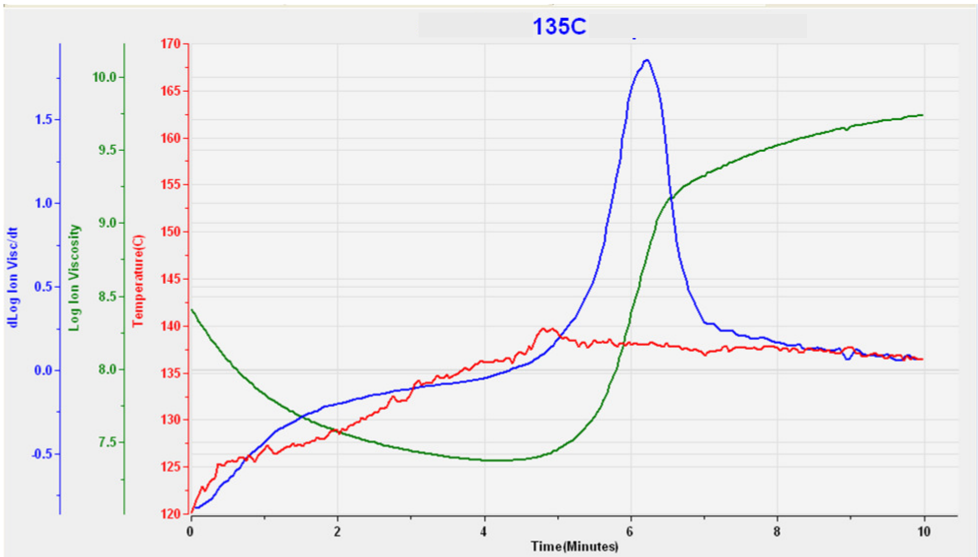

Figure 9-1
135 °C SMC cure data at 10 Hz

[1] CureView data processing parameters: Data Averaging = 1, Slope Span = 3, Data Filtering = 0, Slope Filtering = 1, Slope Filtering Start Time = 0 minutes.

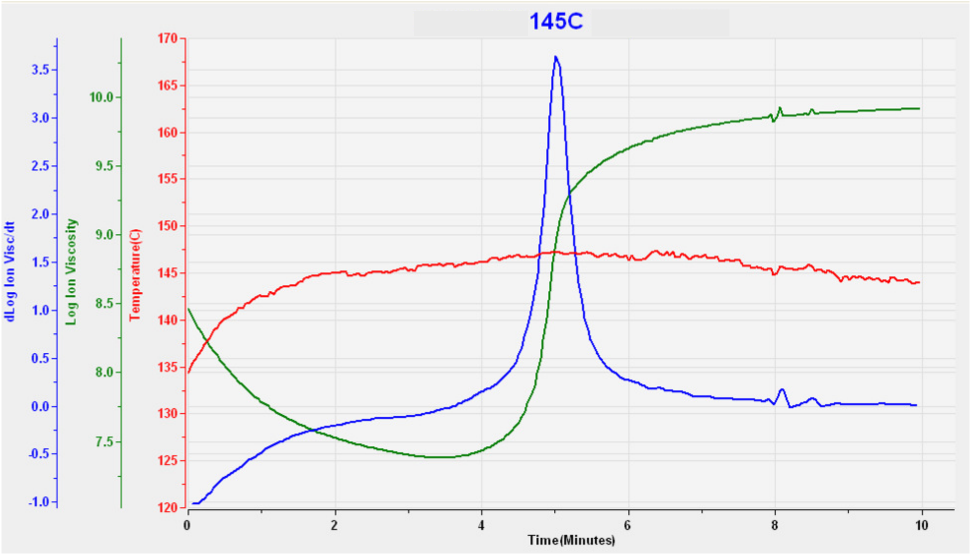

Figure 9-2
145 °C SMC cure data at 10 Hz

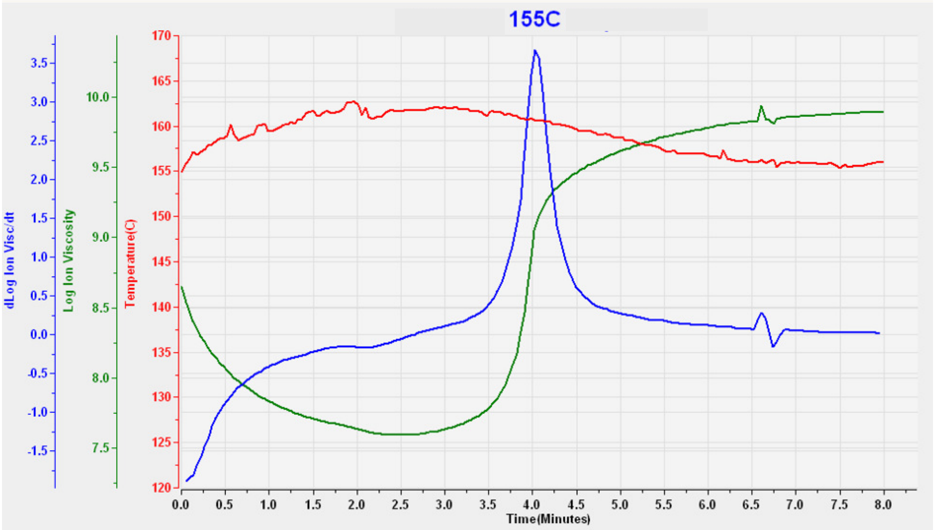

Figure 9-3
155 °C SMC cure data at 10 Hz

The Critical Points that characterize each cure are shown in Table 9-1. **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 appropriate slope to indicate end of cure for the application.

Table 9-1
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 9-4, the times to reach each Critical Point are shorter for cures at higher temperatures, which is expected for thermally driven reactions. Furthermore, the relationship between the time to a Critical Point and the temperature of cure follow a well defined line.

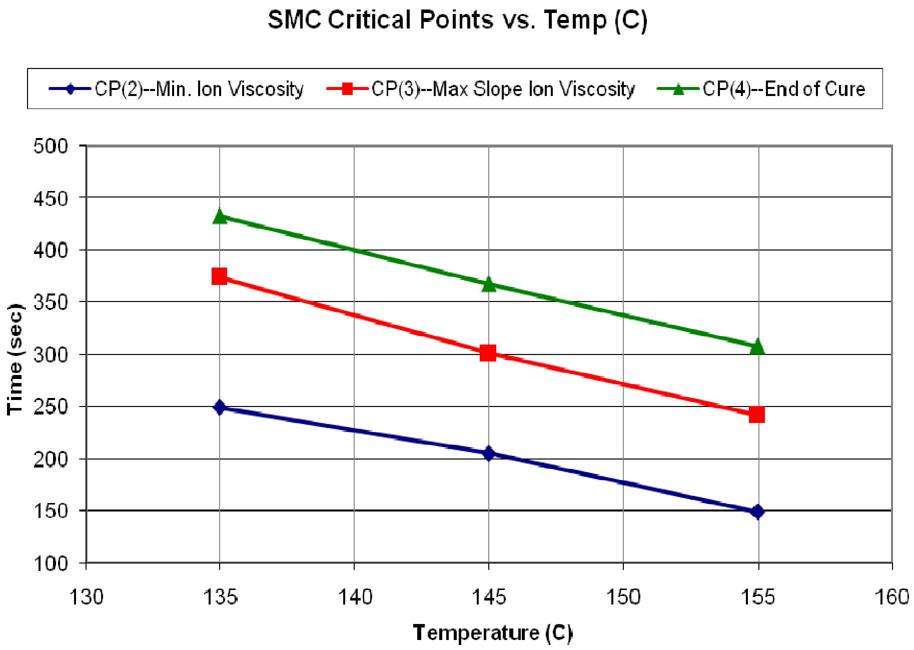

Figure 9-4
Critical Point time vs. cure temperature for SMC

Note that the time to Critical Point 1—CP(1)—is not plotted in Figure 9-4. CP(1) determines when the ion viscosity of the SMC has decreased 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 9-4, 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. Over a wider temperature range this relationship typically follows an Arrhenius function.

Conclusion

Dielectric measurements allow observation of the cure of sheet molding compound and bulk molding compound in real time, and the extraction of Critical Points quantify the characteristics of the reaction. The dielectric data show the direct correlation between temperature and rate of cure.

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