Insight — Application Note 2.38

Dielectric Cure Monitoring of Bulk Molding Compound

Introduction

The curing behavior of Bulk Molding Compound (BMC) was observed using the LTF-631 High Speed Dielectric Cure Monitor. Bulk Molding Compound is generally the same material as Sheet Molding Compound (SMC) but in bulk form, so the analysis of results can 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(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(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. 38-1) $$\sigma = \sigma_{DC} + \sigma_{AC} \qquad (\text{ohm}^{-1} - \text{cm}^{-1})$$

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

(eq. 38-2) $$\rho = 1/\sigma \qquad (\text{ohm-cm})$$

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

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result, the term *Ion Viscosity* was coined to emphasize the relationship between mechanical viscosity and ρ_{DC}. Ion viscosity (*IV*) is defined as:

(eq. 38-3) $$IV = \rho_{DC}$$ (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***.

Characteristics of thermoset Cure

In many cases the change of *log(IV)* is proportional to the change of mechanical viscosity before gelation and continues to indicate cure state even after gelation.

A plot of Ion viscosity is a simple way to characterize the progress of cure. In simplified form, Figures 38-1 and 38-2 show the behavior of a typical thermoset with one temperature ramp step and one temperature hold step.

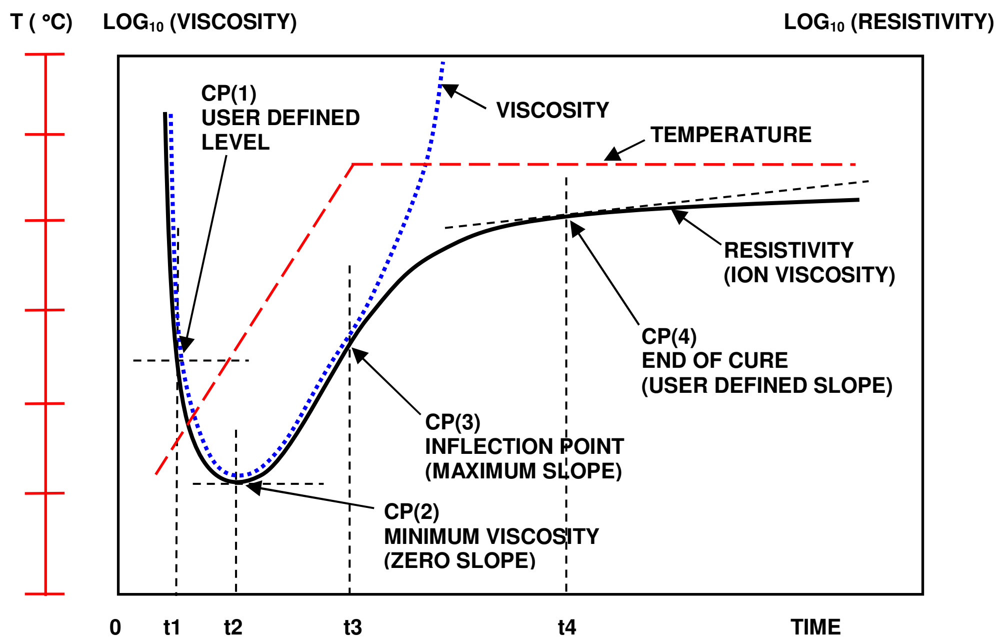

Figure 38-1
Typical ion viscosity behavior of thermoset cure during thermal ramp and hold

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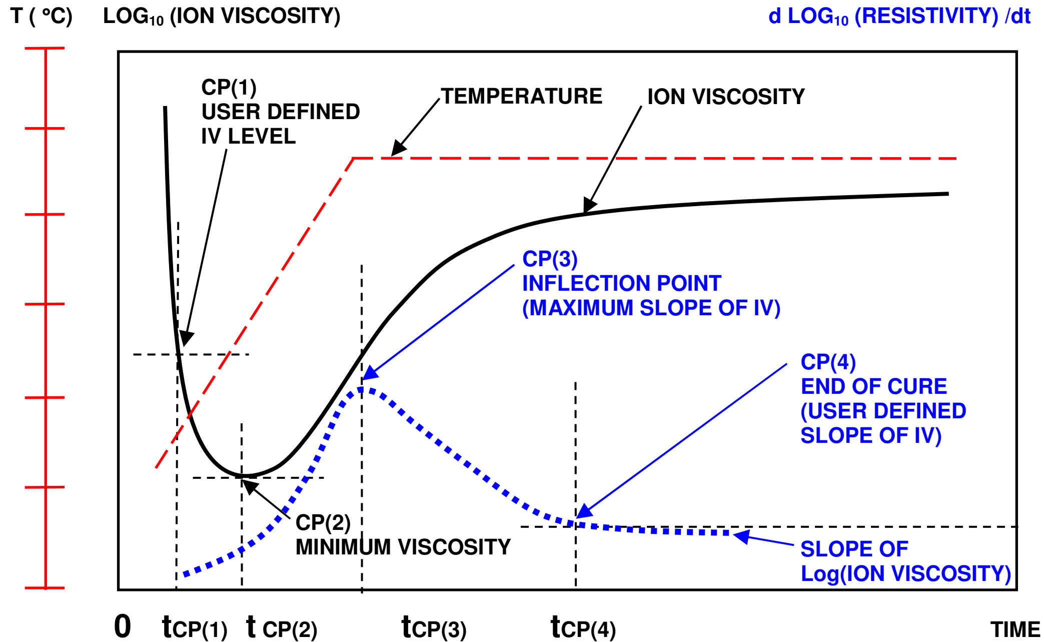

Figure 38-2
Ion viscosity curve and slope of ion viscosity of thermoset cure during thermal ramp and hold

At first, as temperature increases, ion viscosity decreases because the thermoset becomes 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 polymerization 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 *log(IV)* that is typically used to identify the onset of material flow at the beginning of cure.
- CP(2)—Ion viscosity minimum, which also corresponds to the physical viscosity minimum. This Critical Point indicates the time when polymerization and the resulting increasing viscosity begin to dominate the decreasing viscosity due to heating.

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- CP(3)—Inflection point, which identifies the time when the curing reaction begins to slow. CP(3) is often used as a signpost that can be associated with gelation. The height of CP(3) is a relative measure of the reaction rate.
- 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 measurement of mechanical viscosity is not possible.

Figures 38-1 and 38-2 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 38-3. In this case CP(1) either is meaningless or occurs at t = 0, immediately after the application of heat, when material flows to make contact with 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.

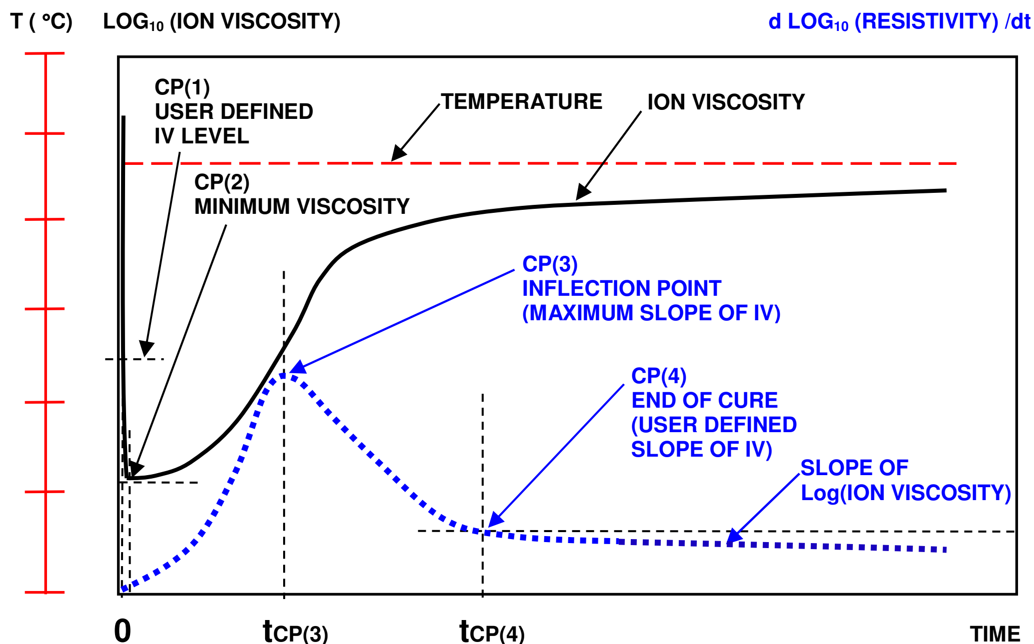

Figure 38-3
Ion viscosity curve and slope of ion viscosity of thermoset cure during isothermal processing

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Procedure

Samples of BMC were placed on disposable Mini-Varicon sensors, shown in Figure 38-4, then compressed and cured in the Lambient Technologies LTP-250 MicroPress, 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.

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. Lambient Technology's CureView software acquired and stored the data, and later performed Critical Point analysis and presentation of the results.

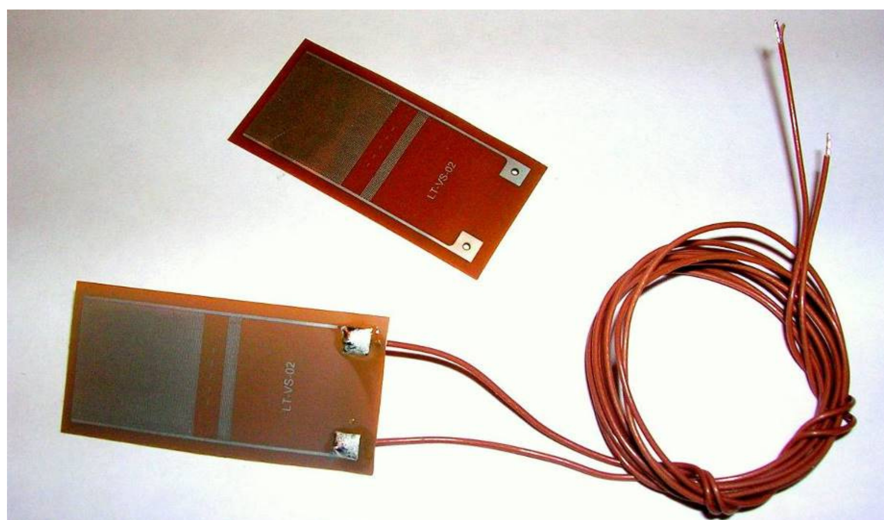

Figure 38-4
Mini-Varicon sensor

Results

Figures 38-5, 6, 7, 8 and 9 show data from the cures of BMC at 130 °C, 140 °C, 150 °C, 160 °C and 170 °C, respectively. For each cure *log(IV)* and *slope* follow the typical behavior of Figure 2. 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

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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.

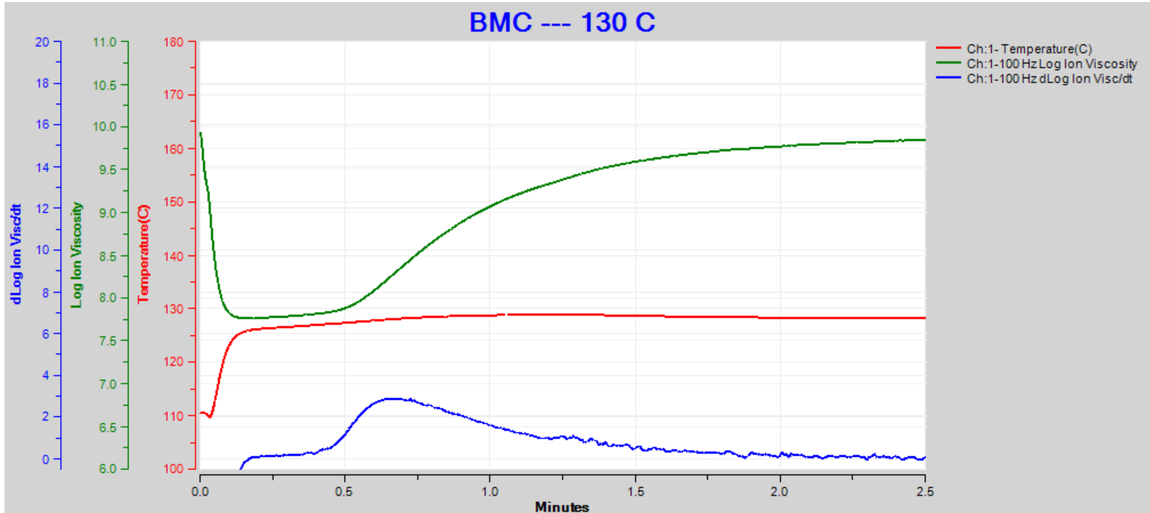

Figure 38-5
130 °C BMC cure data at 100 Hz

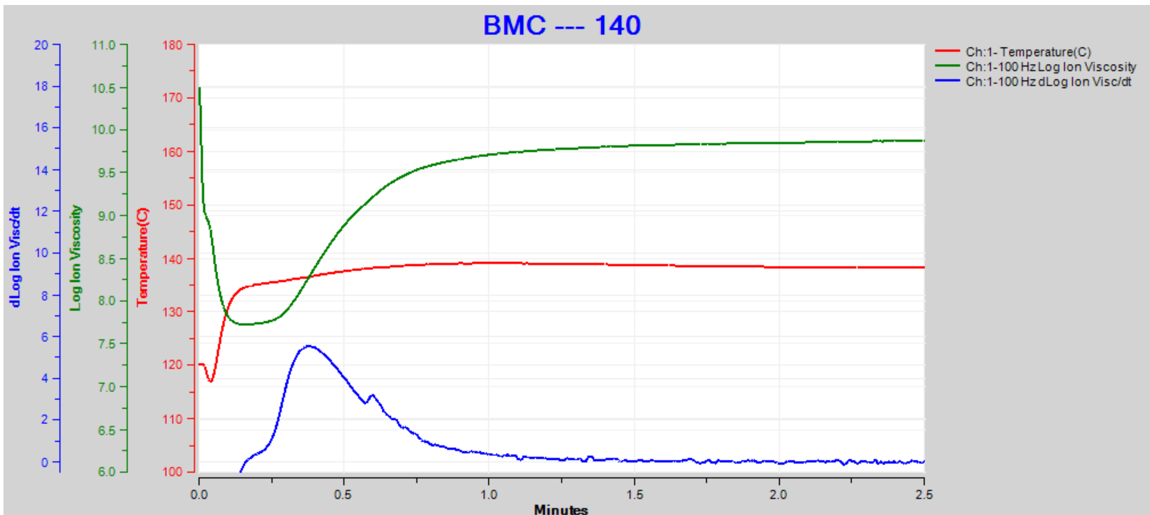

Figure 38-6
140 °C BMC cure data at 100 Hz

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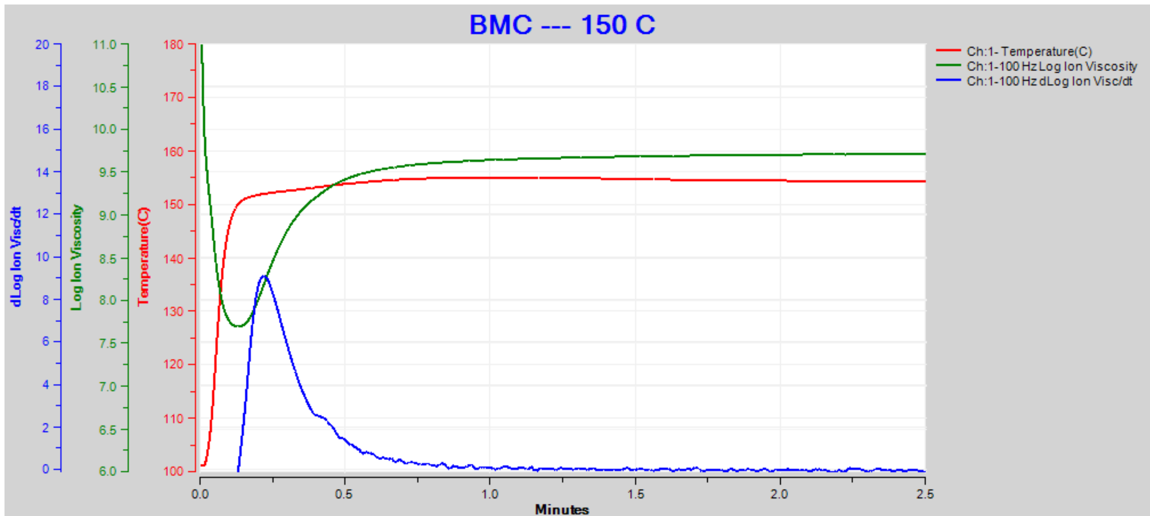

Figure 38-7
150 °C BMC cure data at 100 Hz

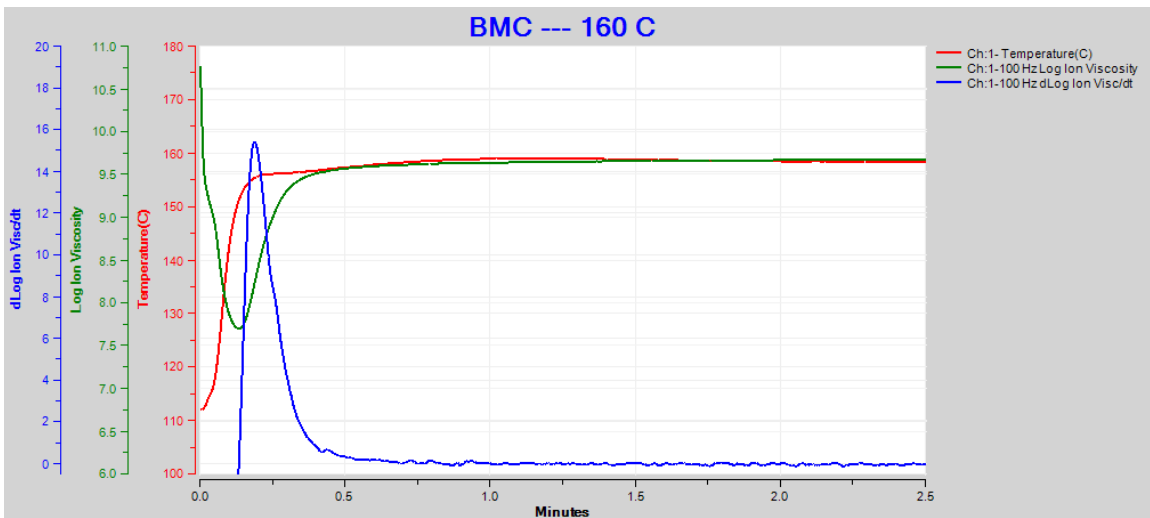

Figure 38-8
160 °C BMC cure data at 100 Hz

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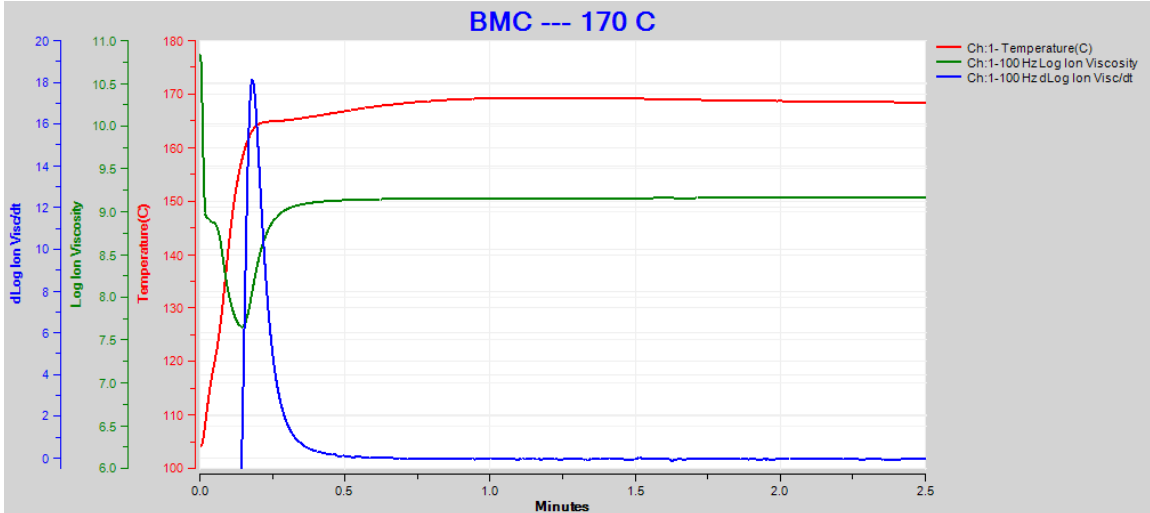

Figure 38-9
170 °C BMC cure data at 100 Hz

Figure 38-10 overlays the *log(IV)* and *slope* curves for 140 °C, 150 °C and 160 °C on top of one another. 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 temperature differences.

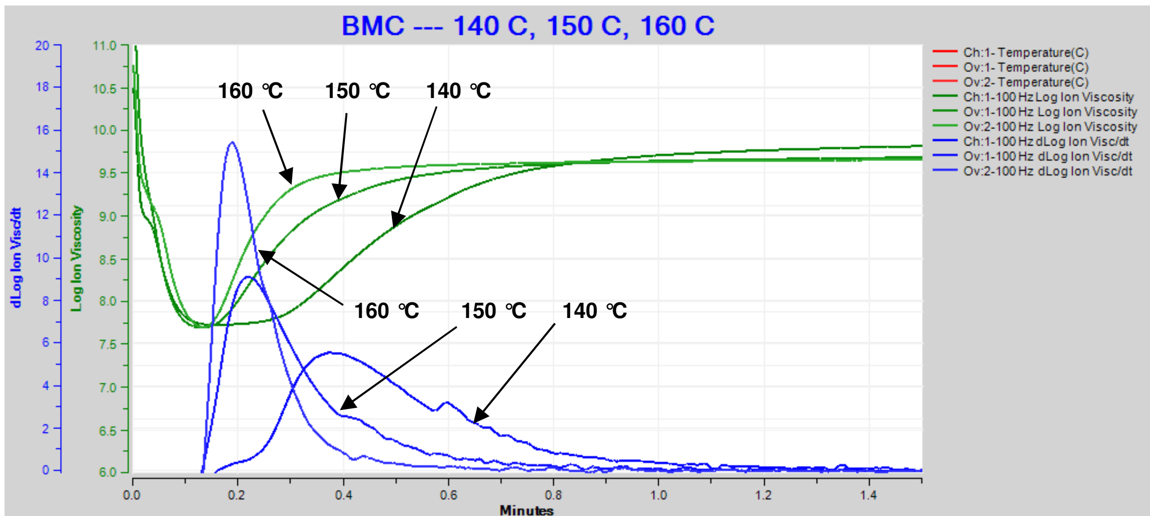

Figure 38-10
Overlay of 140 °C, 150 °C and 160 °C BMC cure data at 100 Hz

As expected, the maximum value of *slope* increases with process temperature, showing the relationship between reaction rate and temperature.

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Critical Points that characterize each cure are shown in Table 38-1, 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 38-1
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 38-11, the times to reach each Critical Point are less 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.**

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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.

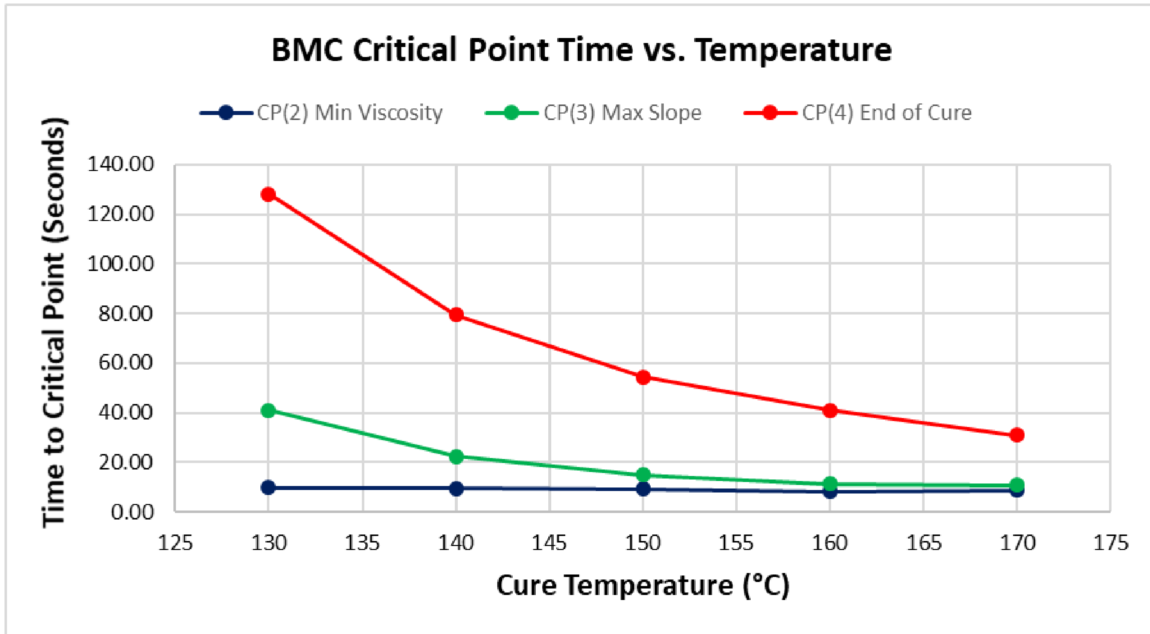

Figure 38-11
Critical Point time vs. cure temperature for BMC

Figure 38-12 shows how the maximum value of *slope* increases with temperature. Again, this relationship is expected because the height of CP(3) is a relative measure of the maximum reaction rate.

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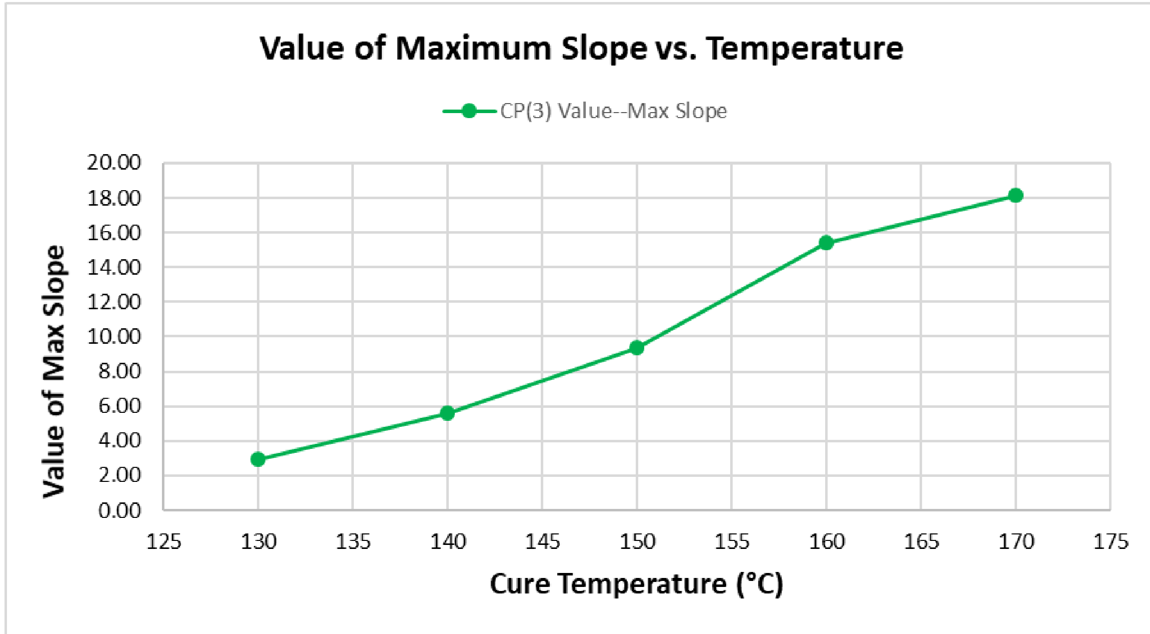

Figure 38-12
Value of maximum slope vs. cure temperature for BMC

DEA in quality control and manufacturing

Temperature measurements, which vary with the thermal environment, configuration of the mold, volume of material and other factors, have sometimes been used to indirectly observe cure. In fact, several brands of thermoset curing ovens market their use of thermocouples for exactly this purpose.

In contrast, dielectric cure monitoring (DEA) directly measures material properties—ion viscosity, in particular—that indicate cure, giving immediate, real time insight. Because of the ease and repeatability of DEA, manufacturers of BMC and SMC use dielectric cure monitoring in their quality control departments. Samples of each batch of BMC or SMC are tested at a controlled temperature. Critical Points like those listed in Table 38-1 characterize the ion viscosity curve and these Critical Points are recorded to monitor consistency in the material.

Good batches of BMC or SMC will have Critical Points that stay within a narrow range. Results outside this range suggest a process that may be out of control, warranting investigation or remediation. In this way a manufacturer can maintain the quality of outgoing material.

Similarly, molders of end products using BMC or SMC can test incoming material to confirm that it will cure as expected. Some have installed reusable dielectric sensors in their molds to monitor and record the processing of every part, accumulating a manufacturing history for statistical quality control.

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DEA in closed loop process control of BMC and SMC

The real time information available with dielectric cure monitoring opens the possibility of closed loop process control. Manufacturers of molded thermosets use timers to determine when products are cured and may be removed from a press. This standard practice must allow for normal variation in process temperature and other factors that affect cure. To be conservative, demold time is chosen to guarantee that all parts are good, with the result that some parts may be cured longer than necessary. Over many thousands of parts, the use of timers wastes considerable time, effort and productivity.

One study of closed loop process control used the hardware of Figure 38-13 at a company that manufactures commercial SMC products. A reusable dielectric sensor was embedded in the lower mold. The sensor was coated with mold release before each charge of SMC was loaded. Then the 2000-ton press was closed. Upon detecting end of cure, the dielectric cure monitor automatically issued a signal to open the press.

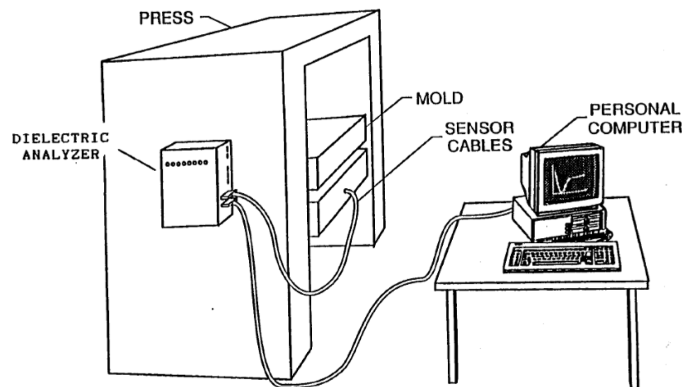

Figure 38-13
Closed-loop process control with dielectric cure monitoring[1]

Figure 38-14 shows the distribution of cure time during the production of about 1000 parts. A fixed timer setting would have been 60 seconds to ensure 100% good parts. In comparison, closed loop control with dielectric cure monitoring reduced average press cycle time to 50 seconds.[1] This 10 second reduction would have saved $70,000/year/press in labor costs alone.

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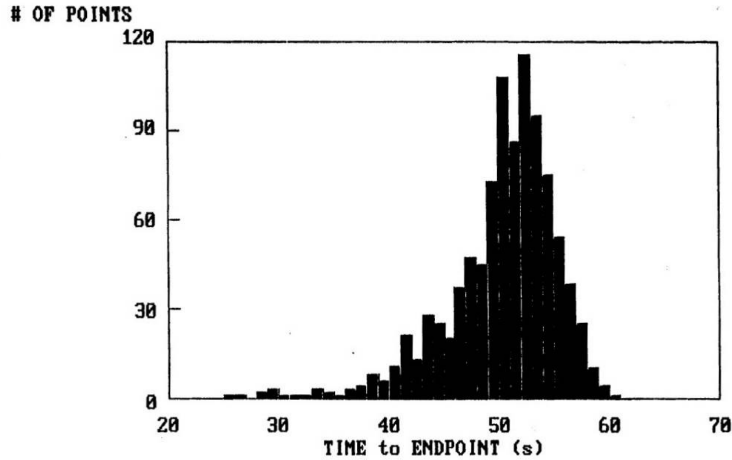

Figure 38-14
Distribution of SMC cure time for 1000 parts[1]

Conclusion

Dielectric cure monitoring (DEA) enables observation of bulk molding compound (BMC) cure in real time, and the extraction of Critical Points quantify the characteristics of the reaction. Critical Points allow direct comparison of the cure of materials under different conditions. The ion viscosity data show the direct correlation between temperature and rate of cure.

As the only method that can measure cure state in real time under actual process conditions, dielectric cure monitoring offers the ability to generate results in the laboratory that are directly applicable in manufacturing processes.

References

1. Day, D.R. and Lee, H.L., "Analysis and Control of SMC Part to Part Variations," Session 13-C of *Proceedings of the 17th Annual Conference, Composites Institute*, *the Society of the Plastics Industry, Inc., Feb 3-6, 1992.*

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