Insight — Application Note 3.17

Cure Monitoring of Carbon Fiber Reinforced Prepreg

Behavior of carbon fiber reinforced prepreg during cure

Samples from of carbon fiber reinforced prepreg (CFRP) were tested for repeatability and the effect of temperature on cure rate. 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 thermally driven reaction.

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. 17-1) $$\sigma = \sigma_{DC} + \sigma_{AC}$$ $(ohm^{-1} – cm^{-1})$

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

(eq. 17-2) $$\rho = 1/\sigma$$ (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. 17-3) $$IV = \rho_{DC}$$ (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***.

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- 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 thermally driven reaction.

Procedure

Samples of CFRP were tested with a Ceramicomb-1″[1] sensor, which was embedded in a press platen as shown in Figure 17-1. Laboratory grade filter paper was placed on the sensor to prevent passage of carbon fibers while allowing resin to flow to the electrodes. Two layers of CFRP approximately 1″ x 1″ were placed on the filter paper.

Figure 17-1
Ceramicomb-1" reusable sensor embedded in press platen

Aluminum foil was placed on the CFRP to prevent the sample from adhering to the upper press platen. During each test a press applied heat and pressure to the lay-up of Figure 17-2.

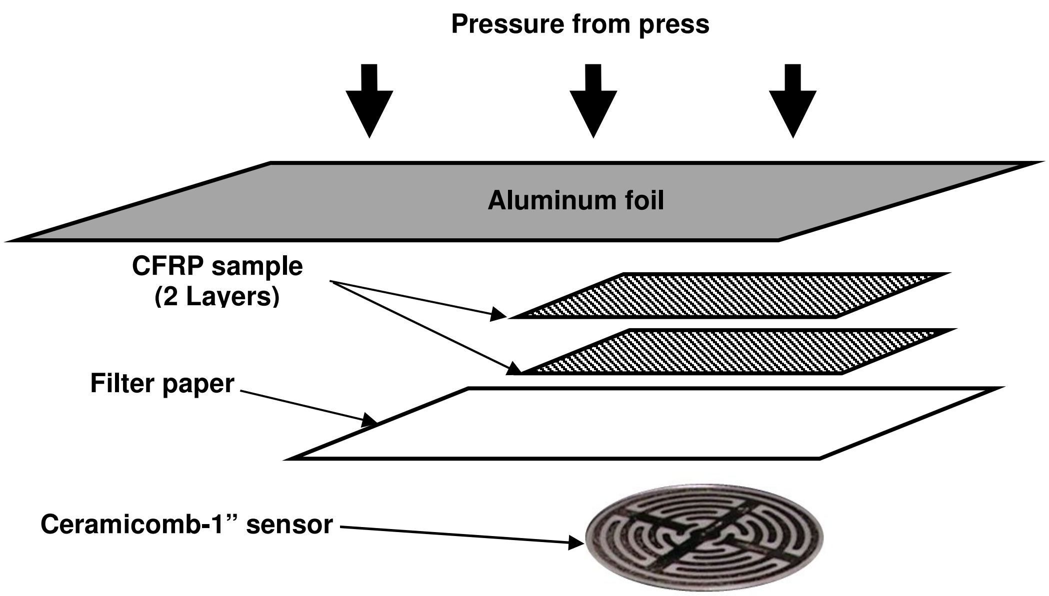

Figure 17-2
Lay-up of carbon-fiber prepreg for tests

An LT-451 Dielectric Cure Monitor[2] measured dielectric properties at 100 Hz and 1.0 kHz excitation frequencies. Previous tests indicated that 100 Hz was an optimum frequency, but 1 kHz was also used to investigate differences when measuring with another frequency. CureView[3] software acquired and stored the data, and performed post-analysis and presentation. Critical Points were determined only for data at the optimal, 100 Hz frequency.

Repeatability of measurements

Figure 17-3 shows the results from an isothermal test of fresh CFRP cured at 120 °C. Minimum log(*IV*)—Critical Point 2 (CP(2))—occurs at the beginning of the test, which is typical for isothermal processing. Minimum mechanical viscosity would occur at about the same time as CP(2), when the increase in viscosity due to curing dominates the decrease in viscosity due to rising temperature.

Maximum slope—Critical Point 3 (CP(3))—occurs at approximately 15 minutes, indicating the time of maximum reaction rate. After this point the reaction slows and the cure is ending. Although some users identify CP(3) with gelation, gelation is actually a mechanical event that has no dielectric equivalent. However, even though CP(3) is not gelation, it may be used as a signpost *associated* with gelation.

By the end of the test the sample is still slowly curing, as indicated by the non-zero slope of log(*IV*). Over time slope would continue to decrease, approaching zero asymptotically until end of cure when the reaction finally stops, the dielectric properties no longer change and the slope reaches zero. In reality, a user would choose a very small, non-zero slope to define end of cure—Critical Point 4 (CP(4))—based on the needs of the application.

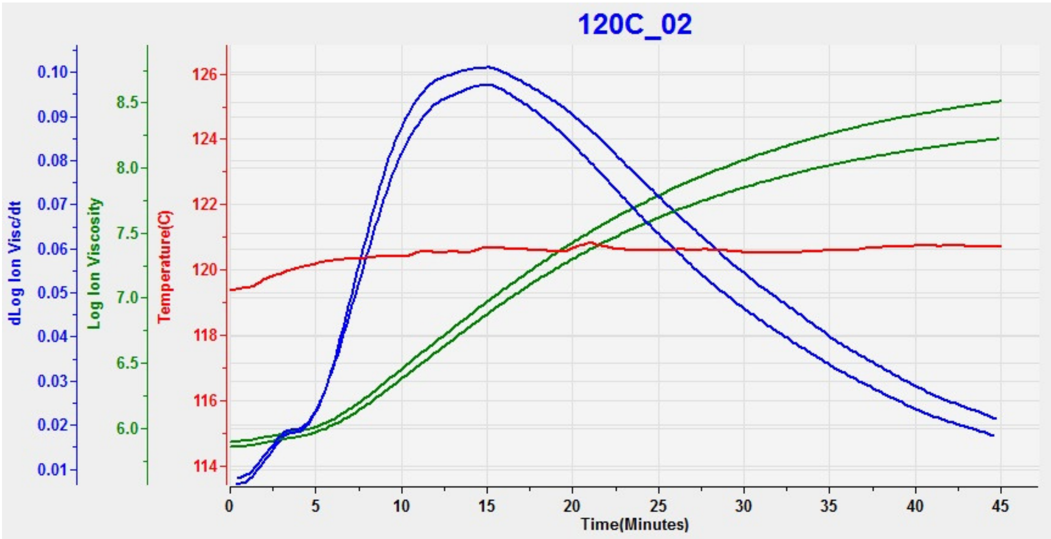

Figure 17-3
CFRP cure at 120 °C, 100 Hz and 1 kHz data

Figures 17-4 and 17-5 are plots of log(*IV*) and slope from six tests with 100 Hz excitation. The curves are superimposed to show typical reproducibility and range of variation. Toward the end of cure, differences in the level of log(*IV*) and resulting slope are likely caused by variability in the amount of resin that passes through the filter.

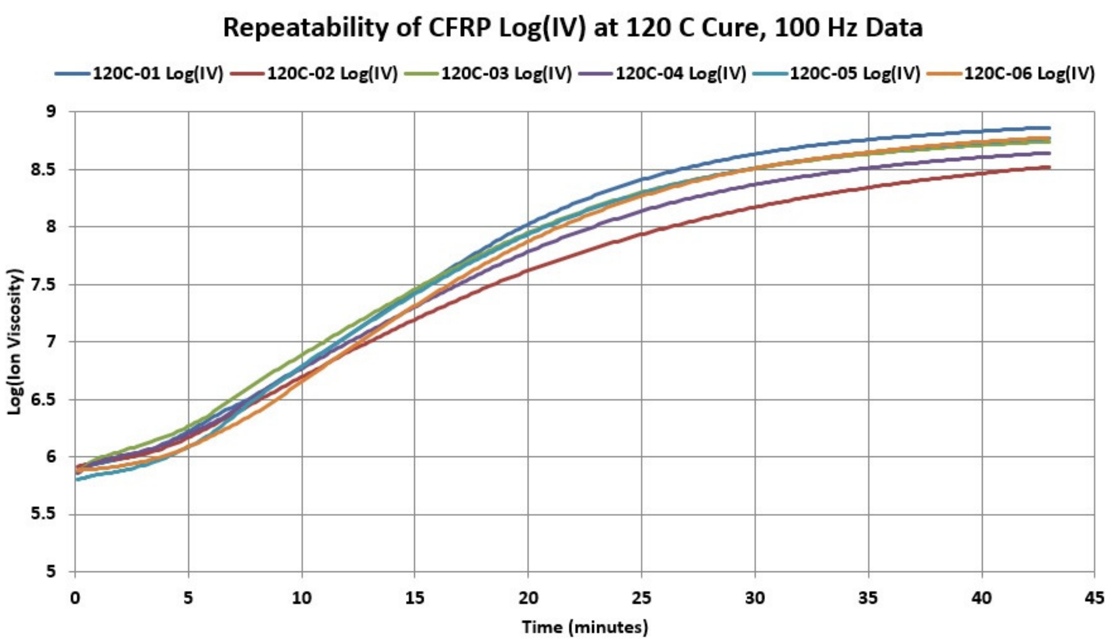

Figure 17-4
Log(*IV*) from cures at 120 °C of six samples of CFRP, 100 Hz data

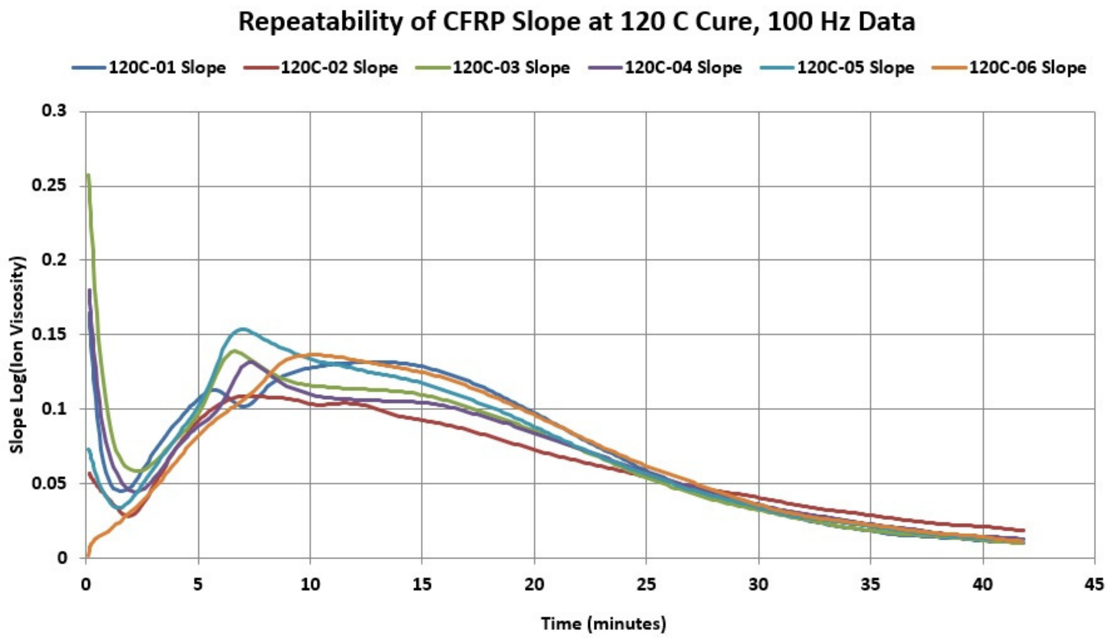

Figure 17-5
Slope from cures at 120 °C of six samples of CFRP, 100 Hz data

Effect of process temperature on cure rate

Figures 17-6 through 17-9 show results from samples of the same fresh CFRP tested at 120 °C, 135 °C, 150 °C and 165 °C.

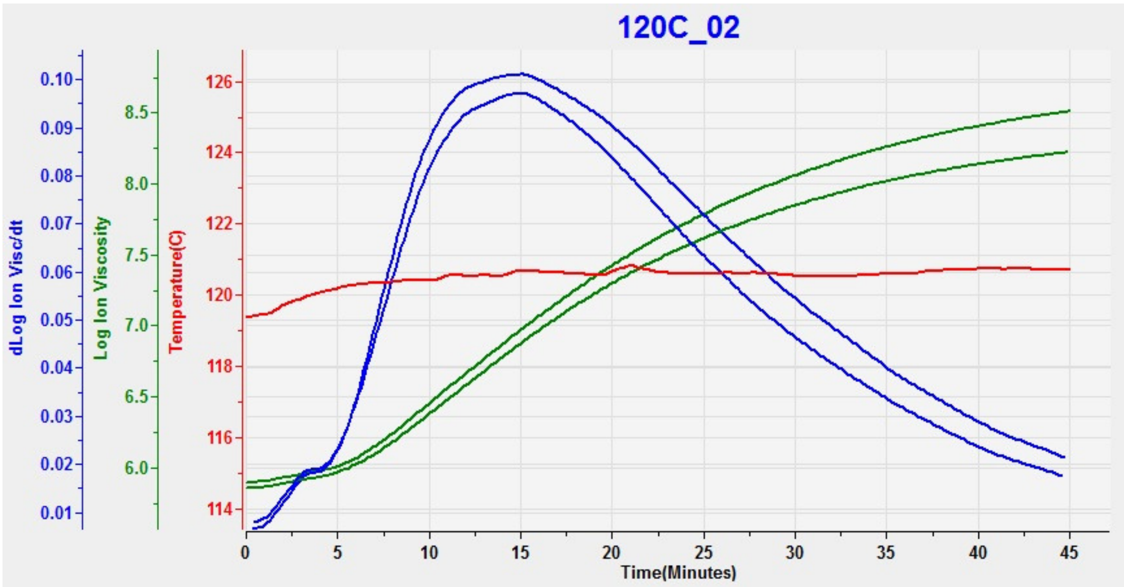

Figure 17-6
CFRP cure at 120 °C, 100 Hz and 1 kHz data

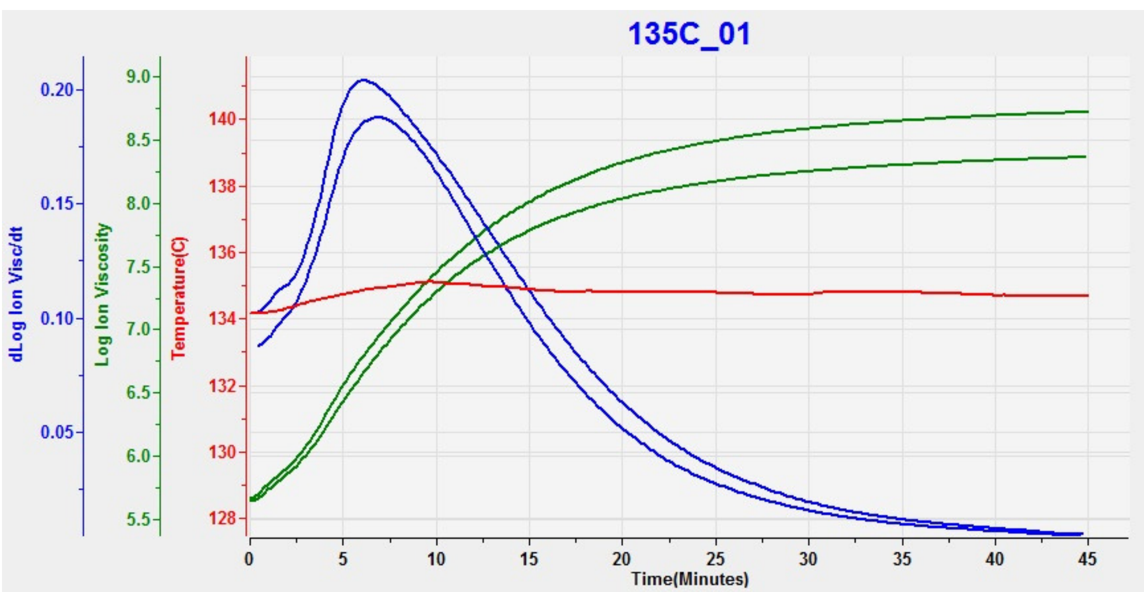

Figure 17-7
CFRP cure at 135 °C, 100 Hz and 1 kHz data

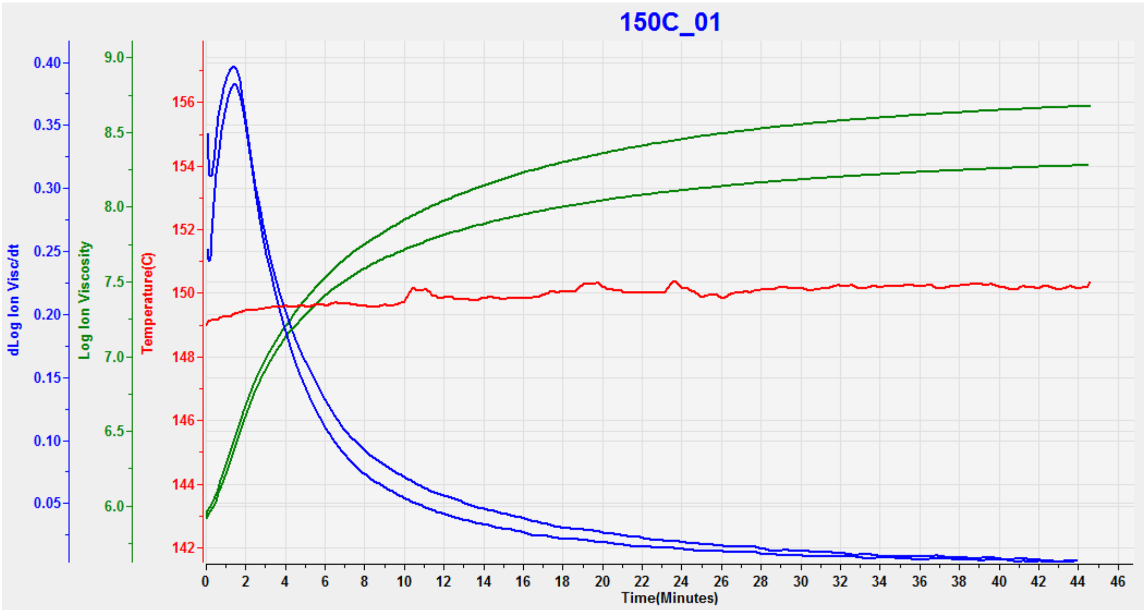

Figure 17-8
CFRP cure at 150 °C, 100 Hz and 1 kHz data

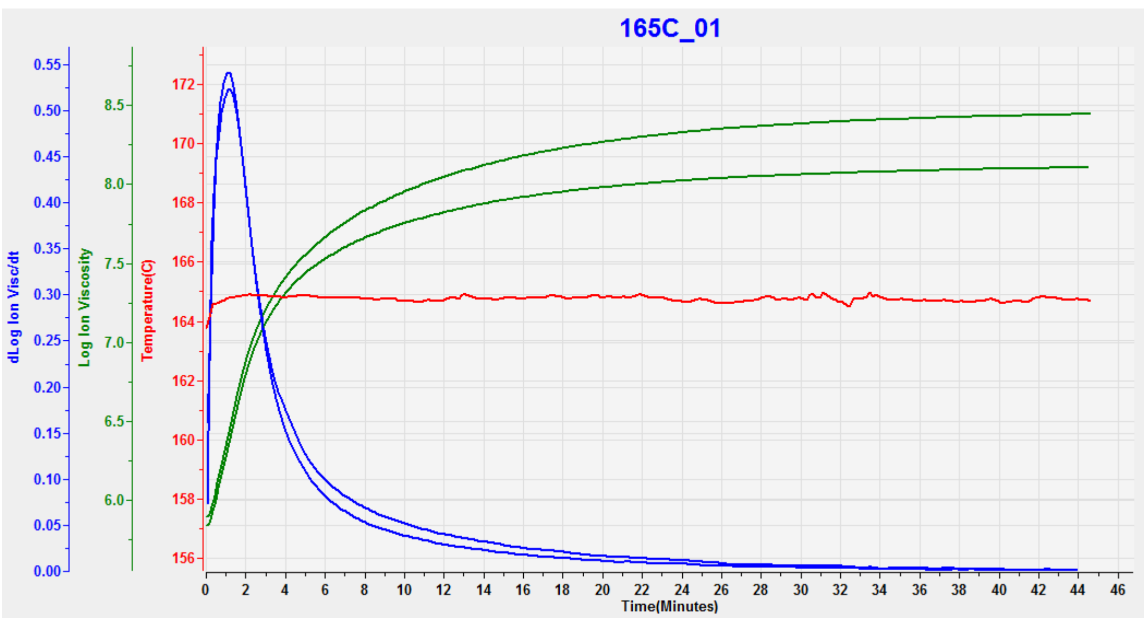

Figure 17-9
CFRP cure at 165 °C, 100 Hz and 1 kHz data

Figure 17-10 overlays 100 Hz log(*IV*) data for the cures at 120 °C, 135 °C, 150 °C and 165 °C. Figure 17-11 overlays slope data for these cures. As expected, higher processing temperatures result in faster cures but the determination of Critical Points is necessary to quantify this relationship.

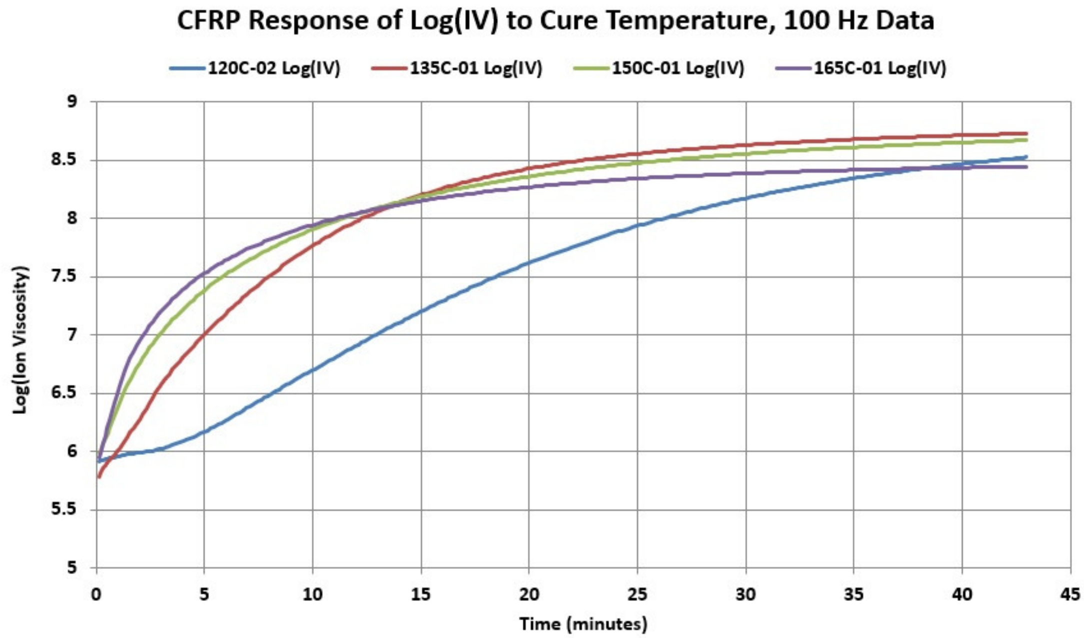

Figure 17-10
Dependence of log(*IV*) with isothermal cure temperature

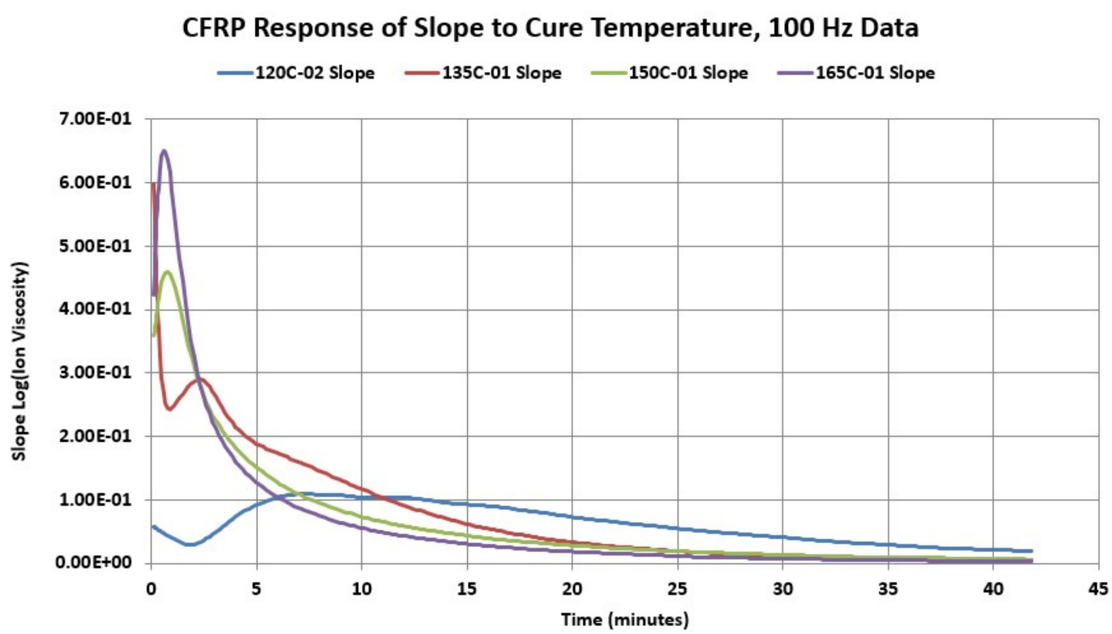

Figure 17-11
Dependence of slope with isothermal cure temperature

Critical Points that characterize each cure are shown in Table 17-1, with the following notes:

- The time to CP(1) indicates onset of flow and is not a measure of cure, so it is not shown
- The time to CP(2), minimum ion viscosity, occurs at or very near time t = 0 for an isothermal cure, does not reflect cure in this case and is not shown
- The slope of 0.05 to define CP(4) was chosen arbitrarily for analytical purposes

Table 17-1
Effect of temperature on Critical Points

Cure Temp. (°C)	CP(1) Crit. Visc.		CP(2) Min. Visc.		CP(3) Max Slope		CP(4) Crit. Slope	
	Value	Time (min)	Value	Time (min)	Value	Time (min)	Value	Time (min)
120	---	---	---	---	8.96E-02	7.282	5.00E-02	26.453
135	---	---	---	---	2.90E-01	2.314	5.00E-02	16.603
150	---	---	---	---	4.58E-01	0.782	5.00E-02	13.612
165	---	---		---	6.50E-01	0.576	5.00E-02	11.970

Figure 17-12 plots the time to CP(3) and CP(4), and shows how they decease with increasing cure temperature. The time to CP(3), which is the time to the point of maximum reaction rate, decreases exponential as temperature increases. The time to CP(3) at 165 °C deviates from the straight trend line at lower temperatures, possibly because of limited accuracy in identifying CP(3) for times less than one minute.

Figure 17-13 shows the level of CP(3)—the level of maximum slope—which indicates maximum reaction rate. Like the time to CP(3), the level of CP(3) shows an exponential relationship with temperature except at the lowest cure temperature of 120 °C.

Figure 17-14 plots the level of CP(3) vs. the time to reach CP(3), showing a rough log-log relationship between the two.

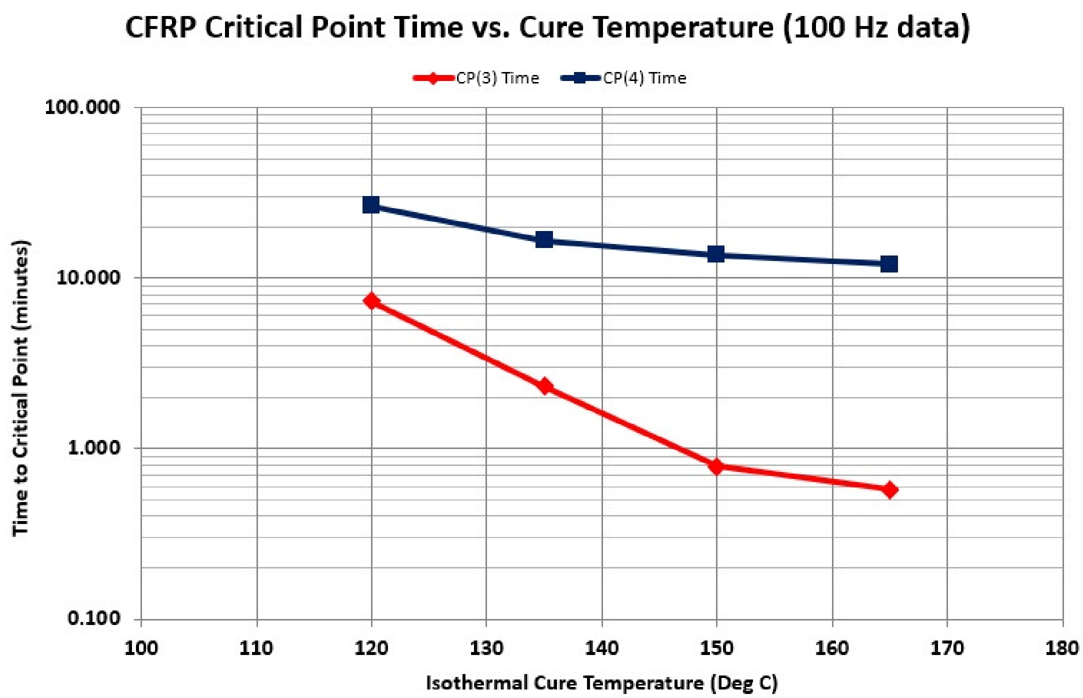

Figure 17-12
Time to Critical Points 3 and 4 vs. cure temperature

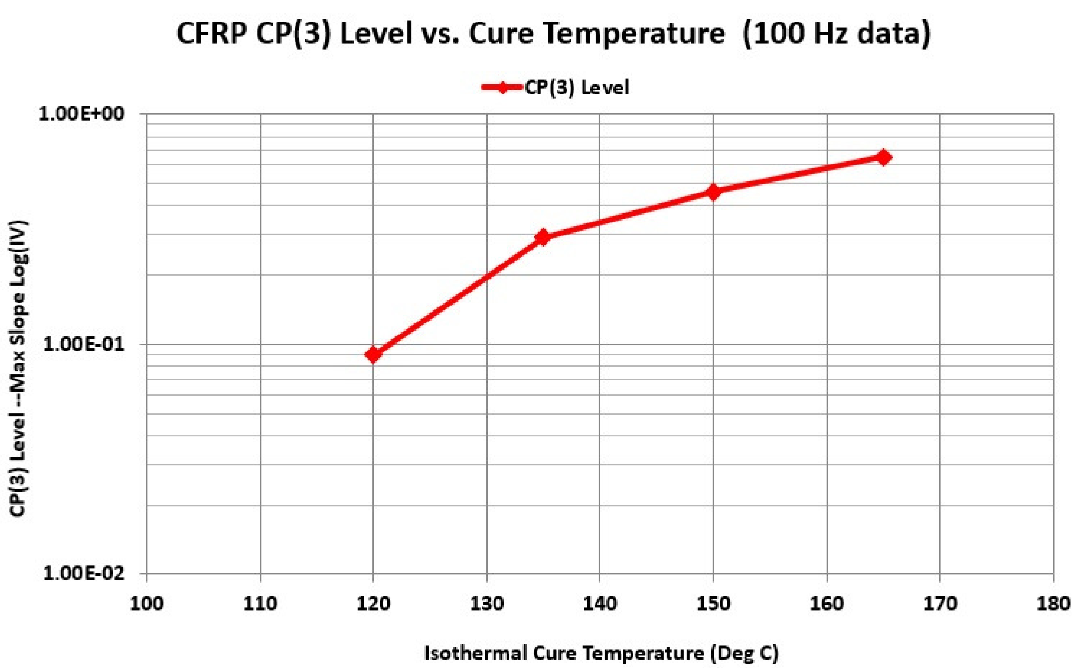

Figure 17-13
CP(3) level vs. cure temperature

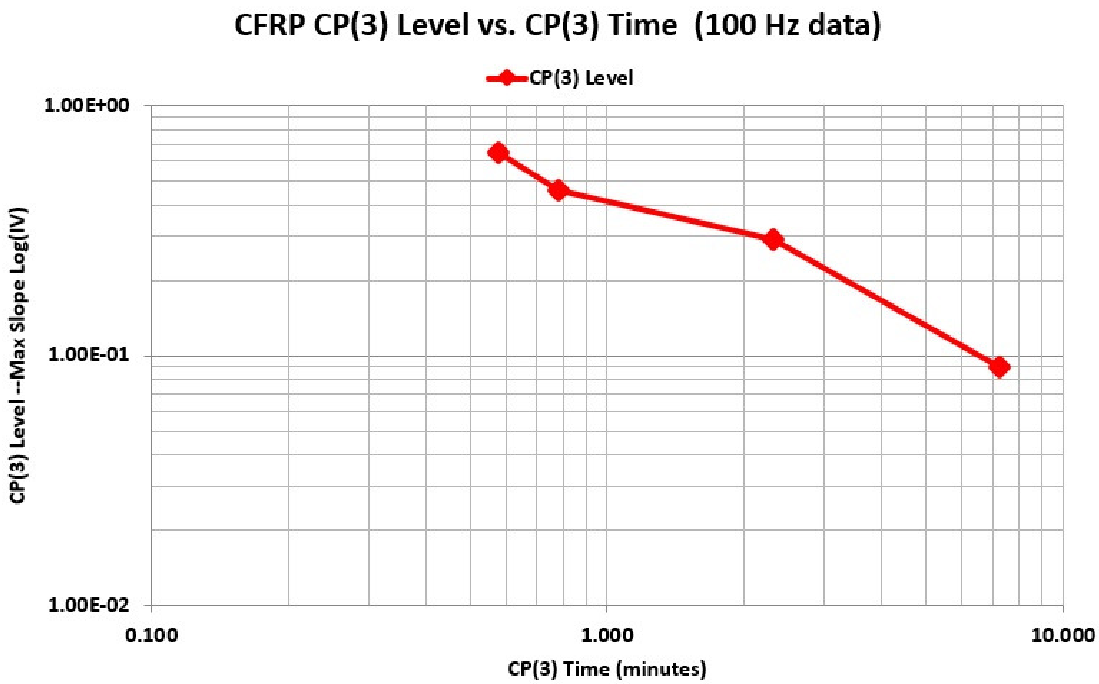

Figure 17-14
CP(3) level vs. CP(3) time

Dielectric measurements allow observation of the cure of thermosets in real time, and the extraction of Critical Points quantify the characteristics of the reaction. The data for CFRP cure show results are repeatable and consistent, with some variation probably caused by differences in the amount of resin that passes through the filter to reach the sensor. Dielectric cure monitoring over temperatures from 120 °C to 165 °C clearly reveal the direct correlation between temperature and cure rate.

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 17-15 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.

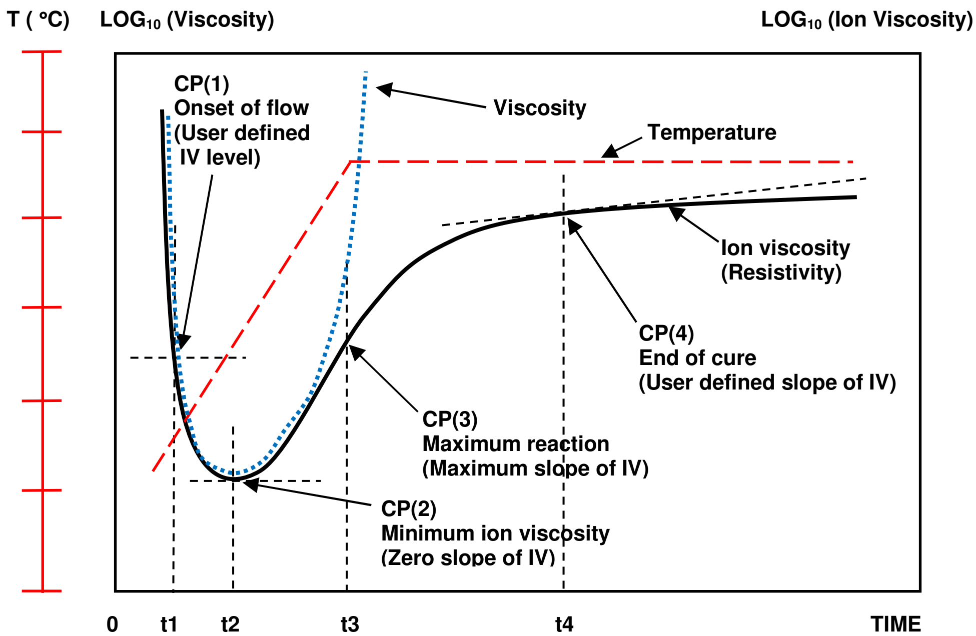

Figure 17-15
Typical ion viscosity behavior of thermoset cure during thermal ramp and hold

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.

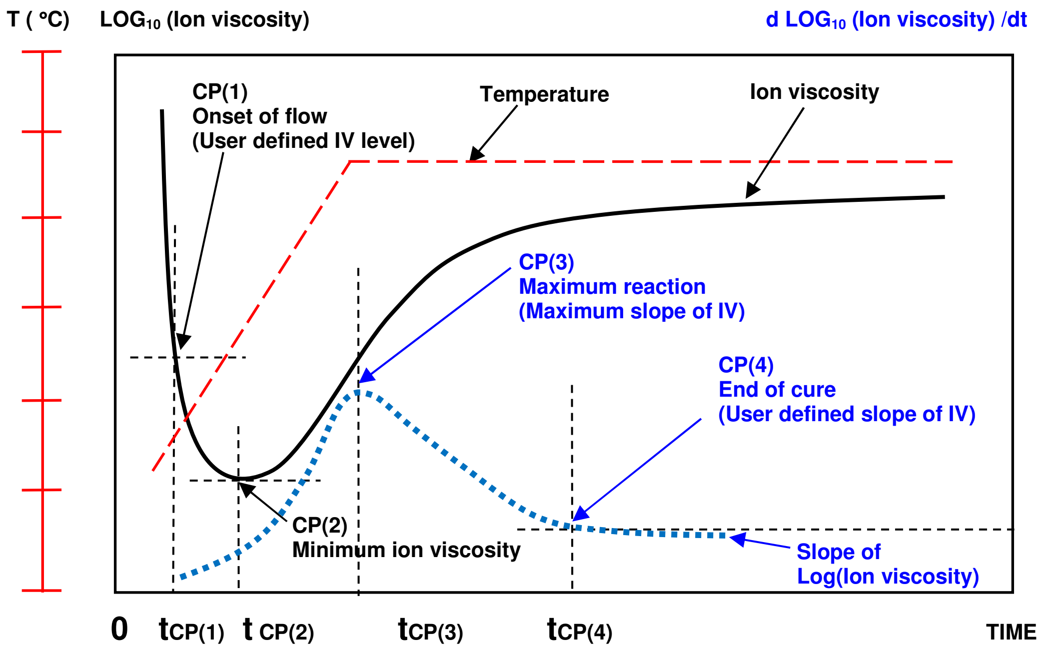

Figure 17-16
Ion viscosity curve and slope of ion viscosity of thermoset cure during thermal ramp and hold

As shown in Figure 17-16, 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 17-15 and 17-16 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 17-17.

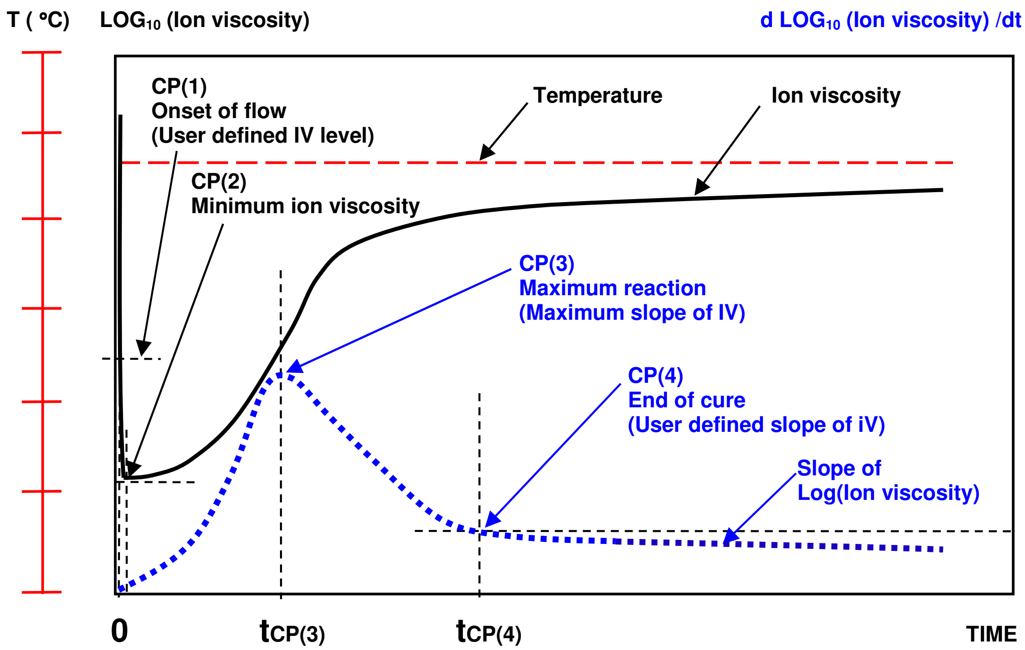

Figure 17-17
Ion viscosity curve and slope of ion viscosity of thermoset cure during isothermal processing

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. Ceramicomb-1" sensor, manufactured by Lambient Technologies, Cambridge, MA USA. https://lambient.com

2. LT-451 Dielectric Cure Monitor, manufactured by Lambient Technologies, Cambridge, MA USA

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

Lambient Technologies, LLC
649 Massachusetts Ave., Cambridge MA 02139, USA
(857) 242-3963
https://lambient.com
info@lambient.com

