Insight — Application Note 2.31

Cure Monitoring of
Epi-Kote MGS LR135 Epoxy

Introduction

Lambient Technologies tested Epi-Kote MGS LR 135 resin cured with Epi-Kure MGS LN 134 catalyst at 55 °C, 70 °C and 85 °C to observe the effect of process temperature on cure rate. Epoxies in the Epi-Kote product family are widely used in the fabrication of wind turbine blades, often using the process of resin transfer molding with fiberglass reinforcement. The data from dielectric cure monitoring clearly show 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. 31.1) $$\sigma = \sigma_{DC} + \sigma_{AC} \qquad (\text{ohm}^{-1} - \text{cm}^{-1})$$

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

(eq. 31.2) $$\rho = 1/\sigma \qquad (\text{ohm-cm})$$

From its relationship to conductivity, resistivity also has both frequency independent (ρ_{DC}) and frequency dependent (ρ_{AC}) components. Degree of cure 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. 31.3) $IV = \rho_{DC}$ (ohm-cm)

Procedure

Epi-Kote MGS LR 135 resin was mixed with Epi-Kure MGS LN 134 catalyst in the ratio of 2.9:1 by weight. A small amount of the mixture was placed on a Mini-Varicon sensor, shown in Figure 31-1, which was placed on the lower heater platen of a press. One sample each of the resin with catalyst was cured at 55 °C, 70 °C and 85 °C.

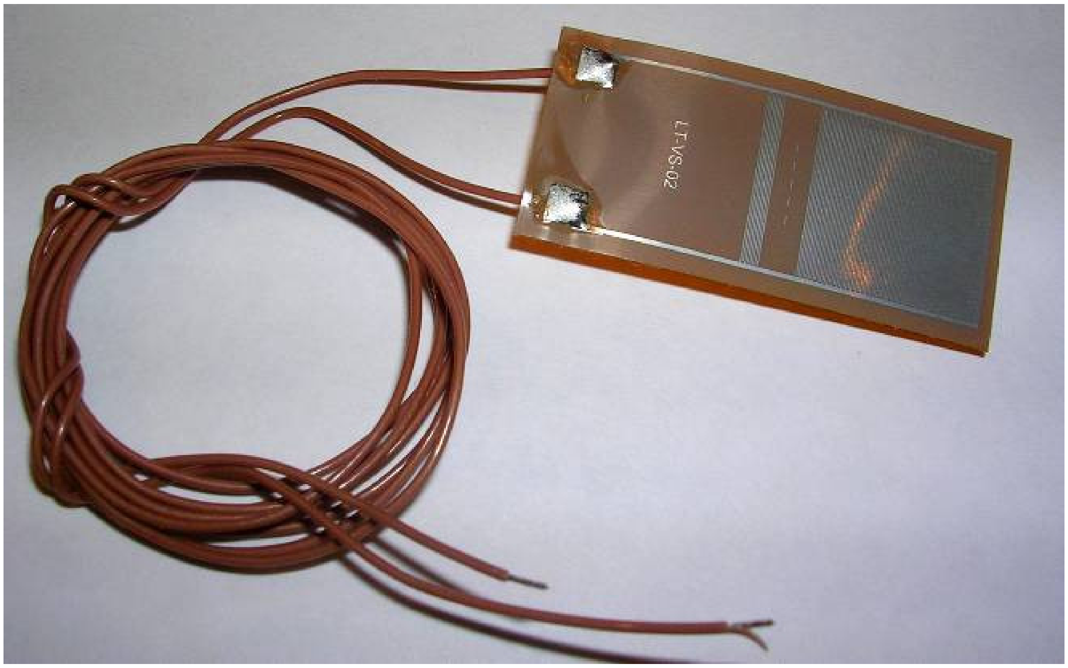


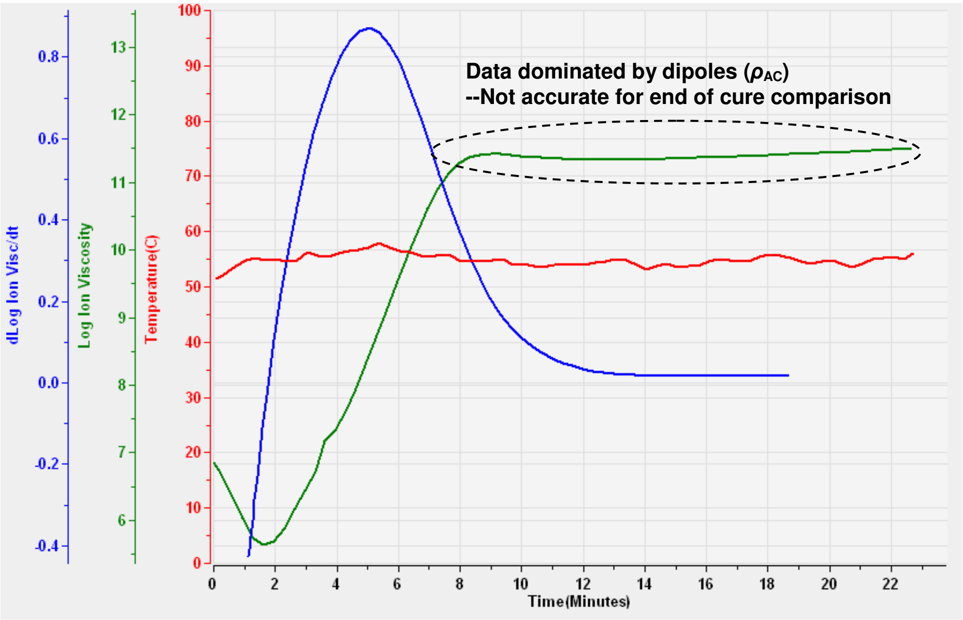
Figure 31-1
Mini-Varicon sensor

To determine the optimum excitation frequency, an LT-451 Dielectric Cure Monitor measured dielectric properties using 10 Hz, 100 Hz and 1.0 KHz for 25 minutes. Lambient Technology's CureView software acquired and stored the data, and performed post-analysis and presentation of the data.

Results

The 10 Hz data was optimal because the signal level was high and the noise level was low. In addition, the ion viscosity measured at 10 Hz was dominated by frequency independent resistivity (ρ_{DC}), therefore the following discussion will consider the results at 10 Hz only. All data was smoothed by averaging and filtering algorithms, with the same averaging and filtering parameters used for each test.[1]

For the 55 °C cure, in Figure 31-2, the log(*IV*) curve reaches a minimum about 1.5 minutes after the start of the test, indicating the time of minimum mechanical viscosity.



Data dominated by dipoles (ρ_{AC})
--Not accurate for end of cure comparison

Figure 31-2
55 °C, 10 Hz data

After about 7.0 minutes the log(*IV*) data is dominated by dipoles (ρ_{AC}) because the curve displays a slight decrease in value—a characteristic of the influence of dipoles. As a result, after this time the 10 Hz data is not accurate for evaluating the state of cure. To observe log(*IV*) data dominated by ion mobility (ρ_{DC}) that characterizes cure, it is necessary to make measurements at a lower frequency such as 1 Hz.

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1. Data averaging = 2, slope span = 8, data filter = 0, slope filter = 2, slope filter start = 1 min, avg time = yes, e" cutoff = 0.00, e' cutoff = 10,000

For the 70 °C cure, in Figure 31-3, the log(*IV*) curve reaches a minimum about 1.0 minute after the start of the test, indicating that the time of minimum mechanical viscosity had occurred sooner than in the 55 °C cure. The maximum slope occurred at about 3.0 minutes, which is also reduced compared to the 55 °C cure. Both of these results are expected because the reaction rate increases with temperature.

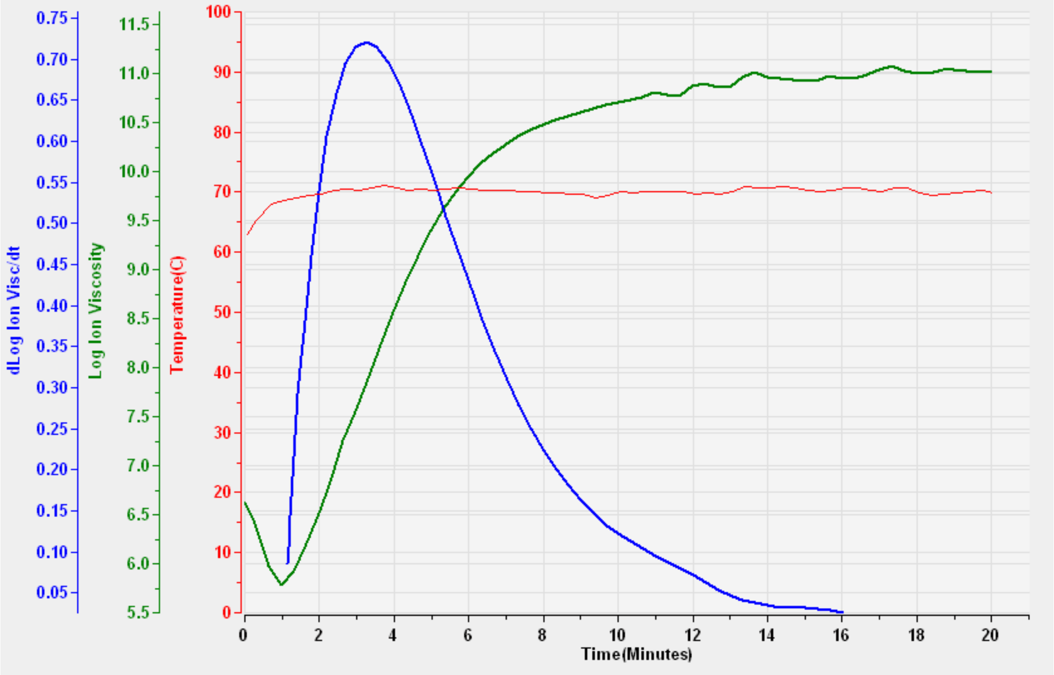

Figure 31-3
70 °C, 10 Hz data

By the end of the test the resin is still shows a definite non-zero slope, and the reaction could continue for some time after the end of data acquisition.

For the 85 °C cure, in Figure 31-4, the log(*IV*) curve does not go through a viscosity minimum point. The reaction at this temperature is very rapid, causing the resin to immediately gel. The time of maximum reaction rate occurs at the beginning of the test. By the end of the test the material is almost completely cured as indicated by the nearly zero slope.

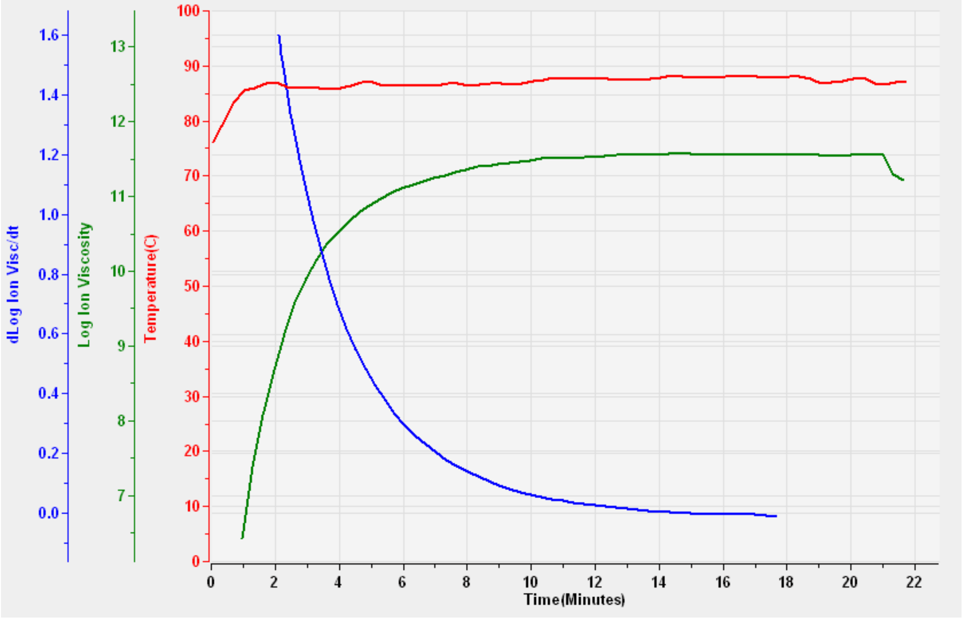

Figure 31-4
85 °C, 10 Hz data

Comparison of cures at different temperatures

Figure 31-5 shows log(*IV*) data from the three tests, allowing direct comparison of the cures at each temperature. As noted before, after seven minutes the log(*IV*) data for the 55 °C test is dominated by dipoles and is not suitable for evaluating cure state.

It is immediately obvious that the time of minimum viscosity decreases with increasing processing temperature. By the end of the test at 20 minutes, the resin at 70 °C has not reached the end of cure, but the resin at 85 °C has completed its cure.

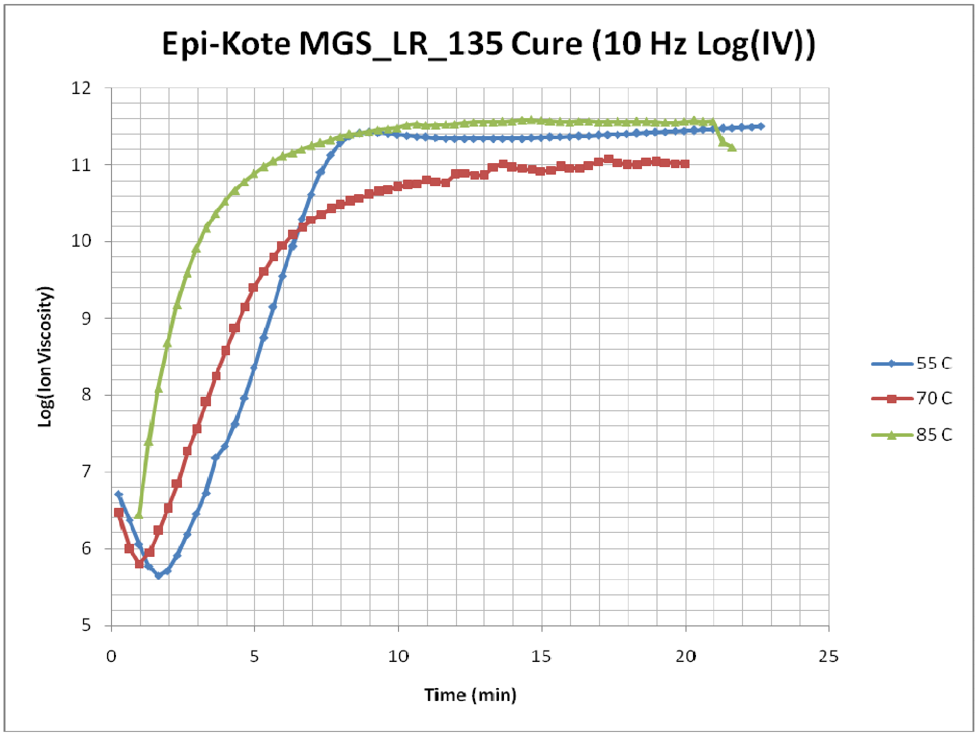

Figure 31-5
Comparison of Log(*IV*) data

Figure 31-6 compares slope data from the three cures. The time of maximum slope, which indicates the time of maximum reaction rate, decreases with increasing processing temperature.

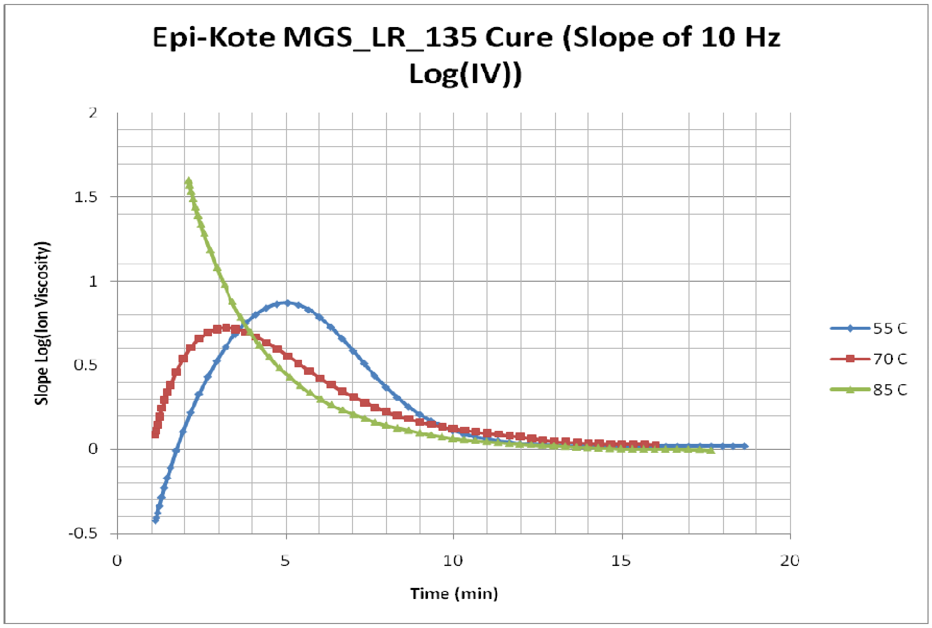

Figure 31-6
Comparison of slope data

A user defined slope can indicate the time to end of cure. If the end of cure is arbitrarily chosen at a slope of 0.03, then end of cure occurs at about 16 minutes for the 70 °C test and at about 12 minutes for the 85 °C test. Figure 31-7 shows an expanded view of the slope data at the end of cure for the tests at these two temperatures. ***The actual slope to define end of cure depends on the requirements of the application and is usually selected to correlate with other tests, such as DMA or DSC***.

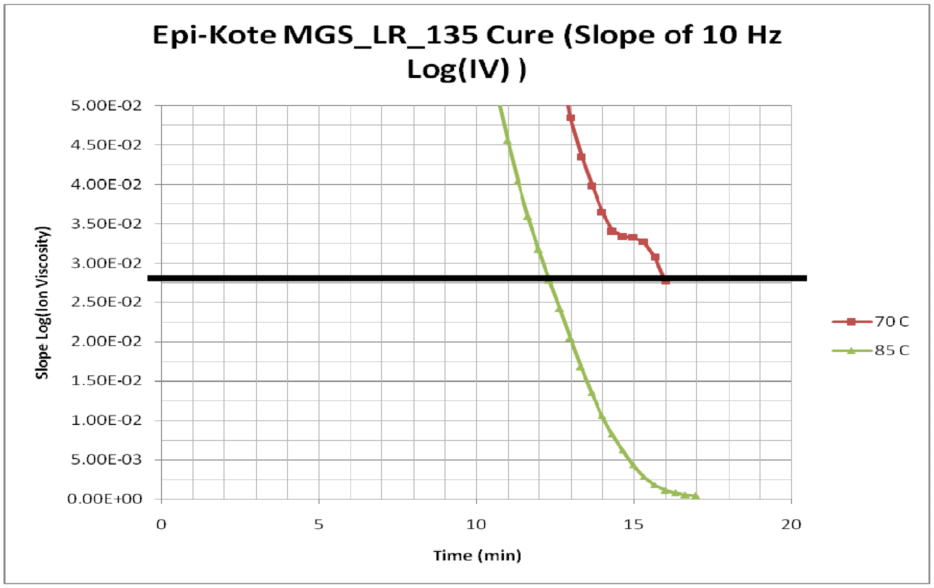

Figure 31-7
Expanded slope data for 70 °C and 85 °C

Characteristics of a thermoset Cure

Ion viscosity is defined as the frequency independent resistivity, ρ_{DC}. In many cases ion viscosity correlates with mechanical viscosity before gelation and with modulus after gelation, and therefore is a sensitive probe of cure state.

Ion viscosity produces a curve that characterizes the progress of cure. In simplified form, Figures 31-8 and 31-9 show the behavior of a typical thermoset with one temperature ramp step and one temperature hold step.

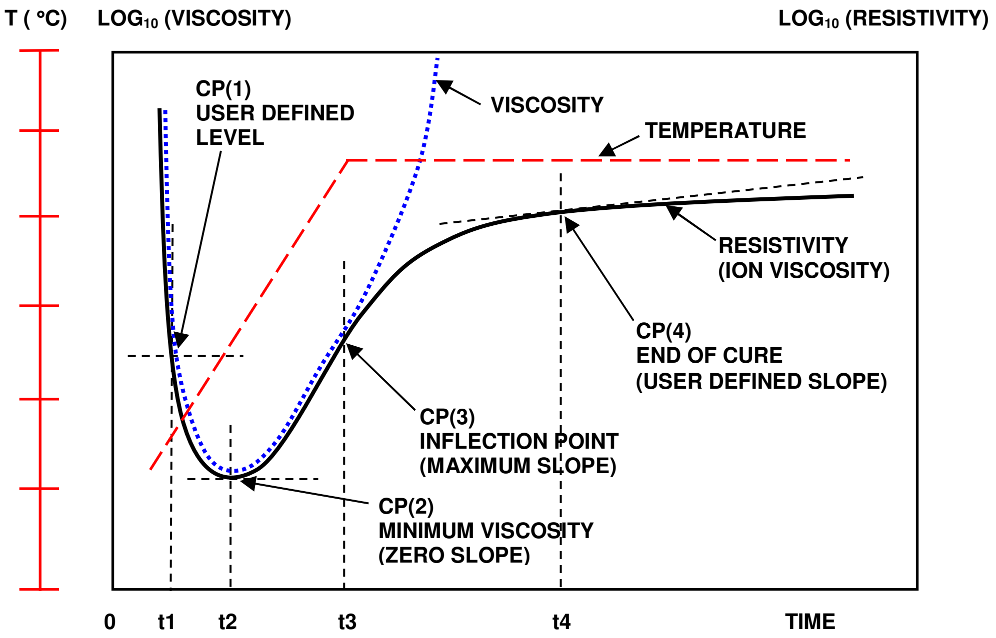

Figure 31-8
Typical ion viscosity behavior of a curing thermoset

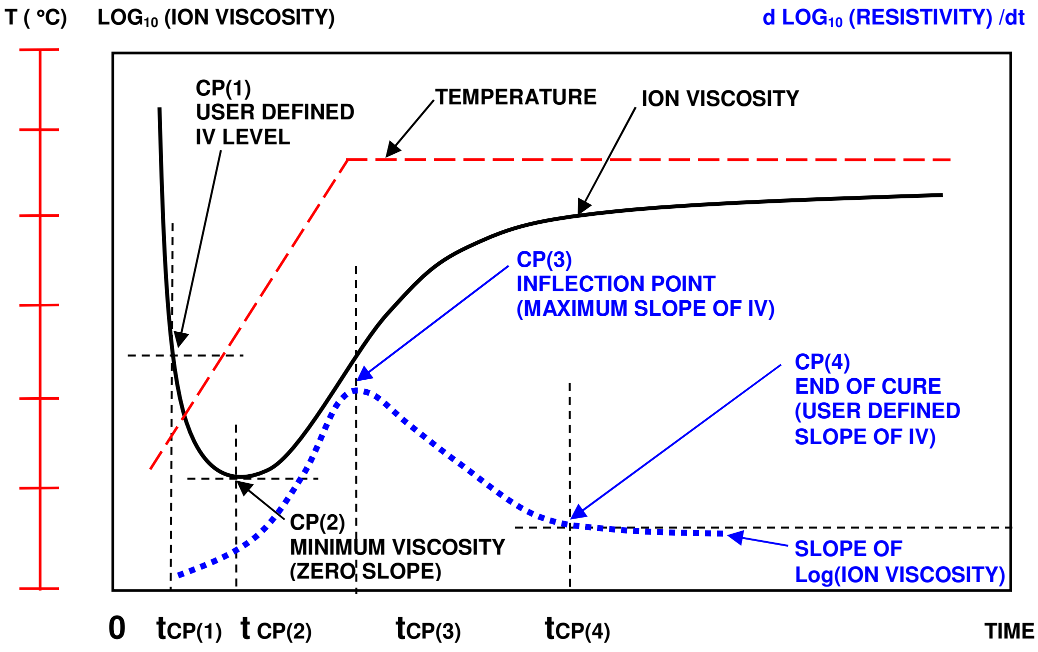

Figure 31-9
Ion viscosity curve and slope of ion viscosity of a curing thermoset

At first, as temperature increases, ion viscosity decreases because the thermoset is 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 polymerization overcomes the decrease in ion viscosity due to rising 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.

Conclusion

Dielectric measurements allow observation of thermoset cure in real time, and the extraction of Critical Points quantify the characteristics of the reaction. Dielectric cure monitoring of Epi-Kote MGS LR 135 resin with Epi-Kure MGS LN 134 catalyst over the range of temperatures from 55 °C to 85 °C clearly indicates the direct correlation between temperature and cure rate.

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