Insight — Application Note 2.32

Cure Index Analysis of Five-Minute Epoxy

Introduction

Lambient Technologies tested a generic "Five-Minute Epoxy" to observe the effect of different thermal conditions on the progress of cure. For isothermal tests, ion viscosity measurements easily reveal cure state because temperature is not a variable; however, five-minute epoxy can generate a significant exotherm, making the typical reaction *non*-isothermal.

In this case, because ion viscosity depends on both cure state *and* temperature, reaction rate and degree of cure are not clear when analyzing ion viscosity alone. With Cure Index analysis, which accounts for the effect of temperature, dielectric measurements clearly show how cure time decreases and how degree of cure increases with greater peak exotherms, as expected for thermally driven reactions.

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. 32.1) $$\sigma = \sigma_{DC} + \sigma_{AC} \qquad (\text{ohm}^{-1} - \text{cm}^{-1})$$

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

(eq. 32.2) $$\rho = 1/\sigma \qquad (\text{ohm-cm})$$

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. 32.3) $IV = \rho_{DC}$ (ohm-cm)

Procedure

The epoxy resin and catalyst were mixed according to the manufacturer's directions and placed on a Mini-Varicon sensor, shown in Figure 32-1.

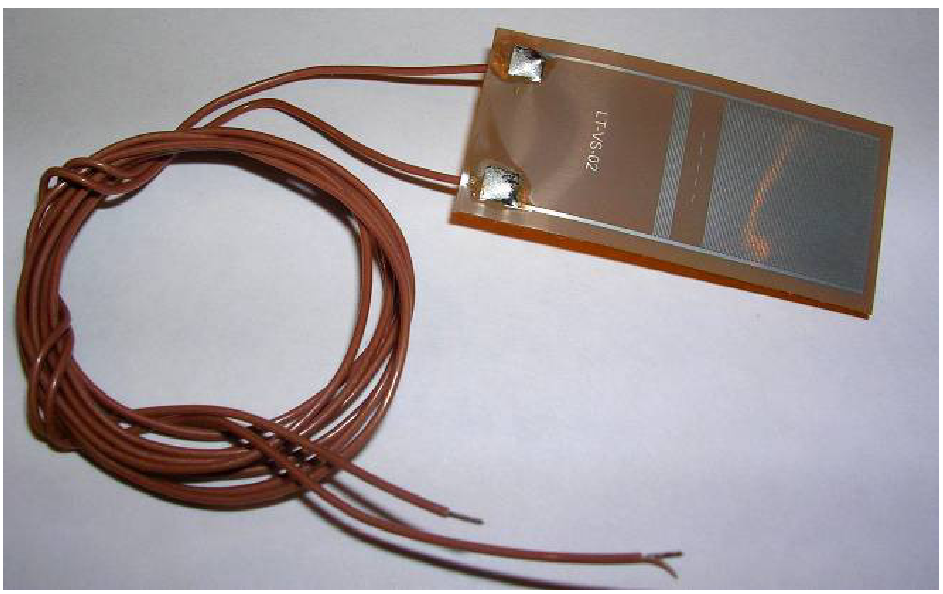

Figure 32-1
Mini-Varicon sensor

Three tests were performed under the following conditions:

Test Name	Amount Epoxy	Thermal Environment	Exotherm Peak
Cure 1	Thin Layer	Sensor on aluminum plate	28 °C
Cure 2	Medium Layer	Sensor on cardboard sheet	55 °C
Cure 3	Thick Layer	Sensor on cardboard sheet	80 °C

The Mini-Varicon sensor was trimmed to use the smaller electrode array, allowing ion viscosity measurements to remain in the optimal measurement range of the LT-451 Dielectric Cure Monitor that was used for the tests.

The aluminum plate acted as a heat sink, which reduced the exotherm for Cure 1 to only 28 °C. In contrast, the cardboard sheet was a thermal insulator, which resulted in greater exotherms for Cure 2 and Cure 3. Thicker layers of epoxy also generated more heat and higher peak exotherms because of the greater volume of reacting material.

The LT-451 Dielectric Cure Monitor measured dielectric properties using 10 Hz, 100 Hz, 1.0 kHz and 10 kHz for 20 minutes. Later it was determined that 10 Hz was the optimum frequency because frequency independent resistivity—that is, ion viscosity—dominated the dielectric response during the entire test. Lambient Technology's CureView software acquired and stored the data, and performed post-analysis and presentation of the data.

Cure Index Analysis

Cure Index analysis[1] plots ion viscosity in relation to temperature between baselines representing 0% and 100% degrees of cure and proceeds with the following steps:

- Determine 0% Cure baseline
- Determine 100% Cure baseline
- Locate temperature – ion viscosity point between baselines
- Determine Cure Index by interpolating data location between baselines

Only two measurements of ion viscosity at different temperatures are required to define a baseline. CureView has a Cure Index parameter window for entering this information.

- To access the Cure Index parameter window, click **Edit** on the main menu bar. Then click the **Cure Index** tab in the **Data Parameters** window.

1. For more information about Cure Index, see application note AN2.11, "Measuring Degree of Cure with DEA" and Chapter 11 of *The Handbook of Dielectric Analysis and Cure Monitoring*.

Determine 0% Cure baseline

Depending on whether the MUT initially reacts slowly or quickly, determine the 0% Cure baseline with one of the following procedures.

Scenario 1—Preferred method if possible:

- Freshly mixed resin-catalyst does not cure significantly during parameter measurements at chosen temperatures
- More accurate to measure ion viscosity-temperature data on mix

1. Measure log(*IV*) for the mix of resin and catalyst at a known temperature
2. Measure log(*IV*) for the same mix at a different temperature
3. Enter the same temperature and *log*(*IV*) data for **Resin 0% Cure** and **Catalyst 0% Cure**, as shown in the example of Figure 32-2
4. Enter 50 for **Percent Resin** and 50 for **Percent Catalyst**
5. Enter 0.0 for **0% Baseline Offset**—this value may be adjusted later as necessary during Cure Index analysis

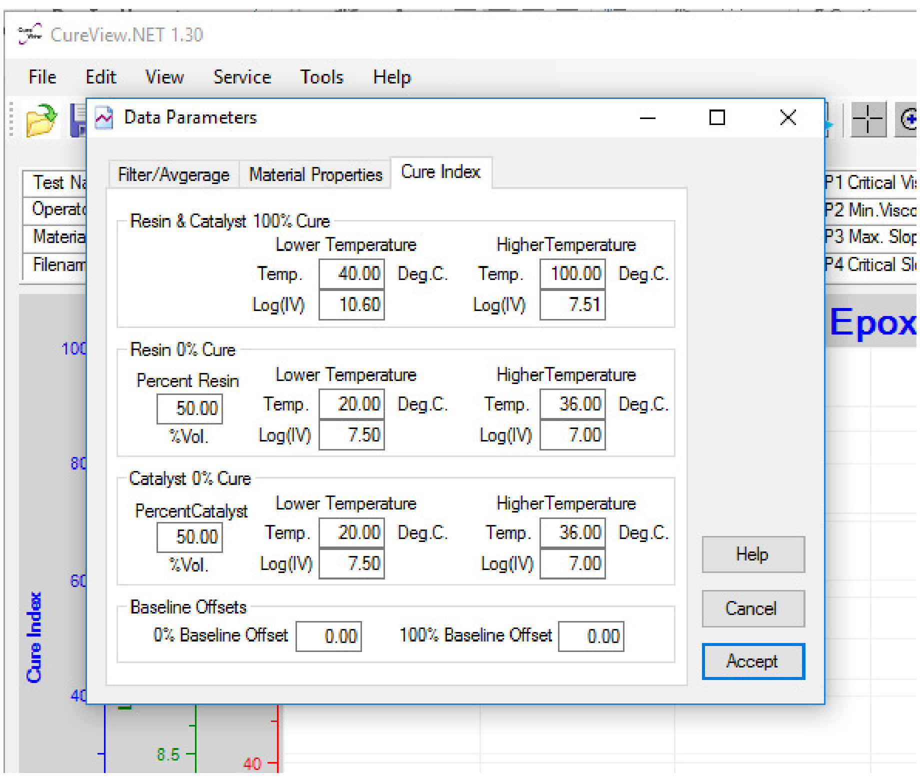

Figure 32-2
Cure Index parameter window
Example for resin-catalyst mix for 0% Cure baseline

Scenario 2—Alternative method

- Freshly mixed resin-catalyst would cure significantly during parameter measurements at chosen temperatures
- To avoid reaction, measure ion viscosity and temperature for resin and catalyst separately

1. Measure log(*IV*) for the resin at a known temperature
2. Measure log(*IV*) for the resin at a different temperature
3. Measure log(*IV*) for the catalyst at a known temperature
4. Measure log(*IV*) for the catalyst at a different temperature
5. Enter temperature-log(*IV*) data for **Resin 0% Cure** and **Catalyst 0% Cure**, as shown in the example of Figure 32-3
6. Enter **Percent Resin** and **Percent Catalyst** by volume
7. Enter 0.0 for **0% Baseline Offset**—this value may be adjusted later as necessary during Cure Index analysis

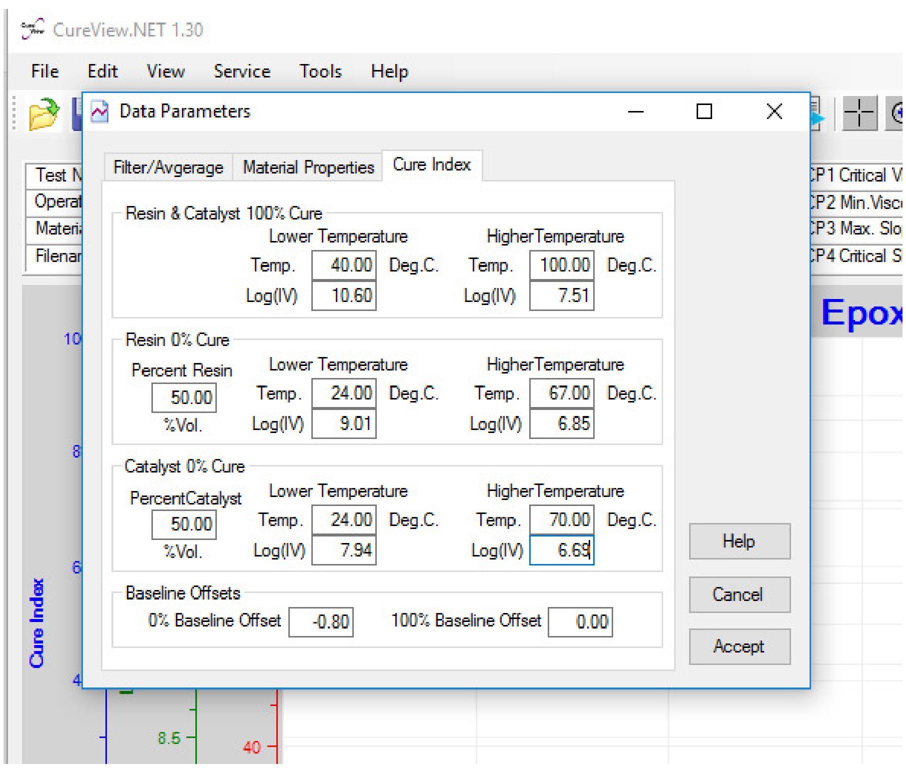

Figure 32-3
Cure Index parameter window
Example for separate resin and catalyst measurements for 0% Cure baseline

Determine 100% Cure baseline

- Maximum degree of cure at a process temperature increases as temperature increases but is not necessarily 100% Cure
- Prepare the MUT by curing at elevated temperature to ensure material has reached 100% Cure

1. Measure log(*IV*) for the fully cured MUT at a known temperature
2. Measure log(*IV*) for the fully cured MUT at a different temperature
3. Enter the temperature and log(*IV*) data for **Resin & Catalyst 100% Cure**, as shown in the examples of Figure 32-2 or Figure 32-3
4. Enter 0.0 for **100% Baseline Offset**—this value may be adjusted later as necessary during Cure Index analysis

When plotted against log(*IV*) and temperature axes, the 0% Cure and 100% Cure baselines for these examples appear as shown in Figure 32-4.

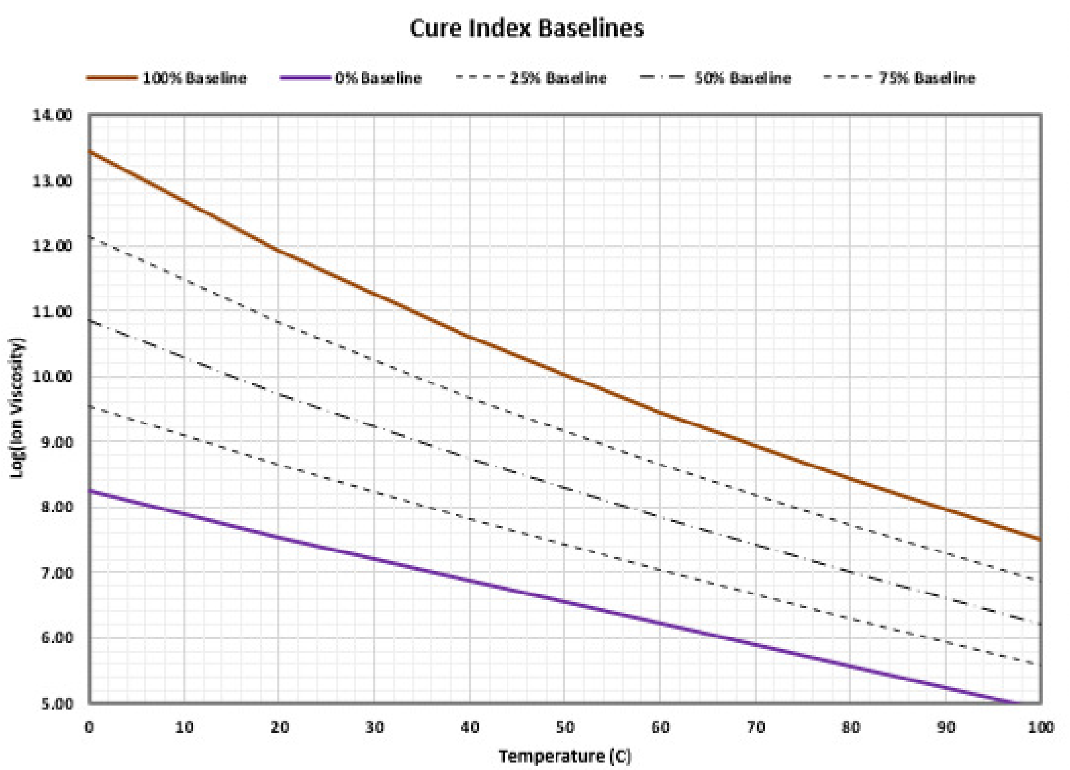

Figure 32-4
Cure Index baselines (Not displayed in CureView)

Locate temperature-ion viscosity point between baselines

Figure 32-5 shows 10 Hz ion viscosity and temperature during test *Cure 2*. The data trace the progress of a typical thermoset cure, with ion viscosity initially decreasing as temperature rises due to the exotherm. An ion viscosity minimum occurs when the viscosity increase due to accelerating cure dominates the viscosity decrease due to rising temperature.

At one point the exotherm peaks at about 55 °C then the reaction begins to slow and temperature decreases. In turn ion viscosity starts to level, eventually becoming flat over time when the reaction ends.

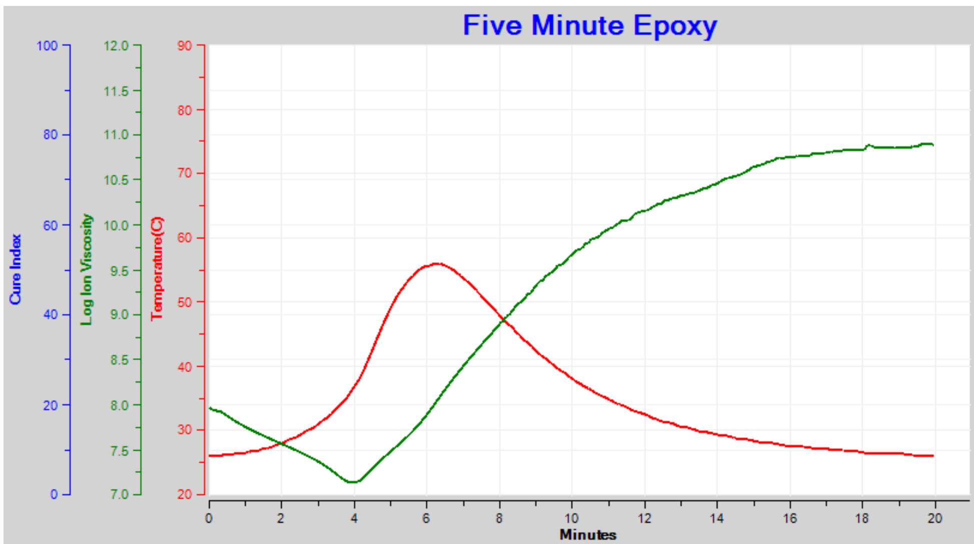

Figure 32-5
10 Hz ion viscosity and temperature for *Cure 2* of 5-minute epoxy

Figure 32-6 shows data for *Cure 2* plotted between the 0% and 100% baselines.

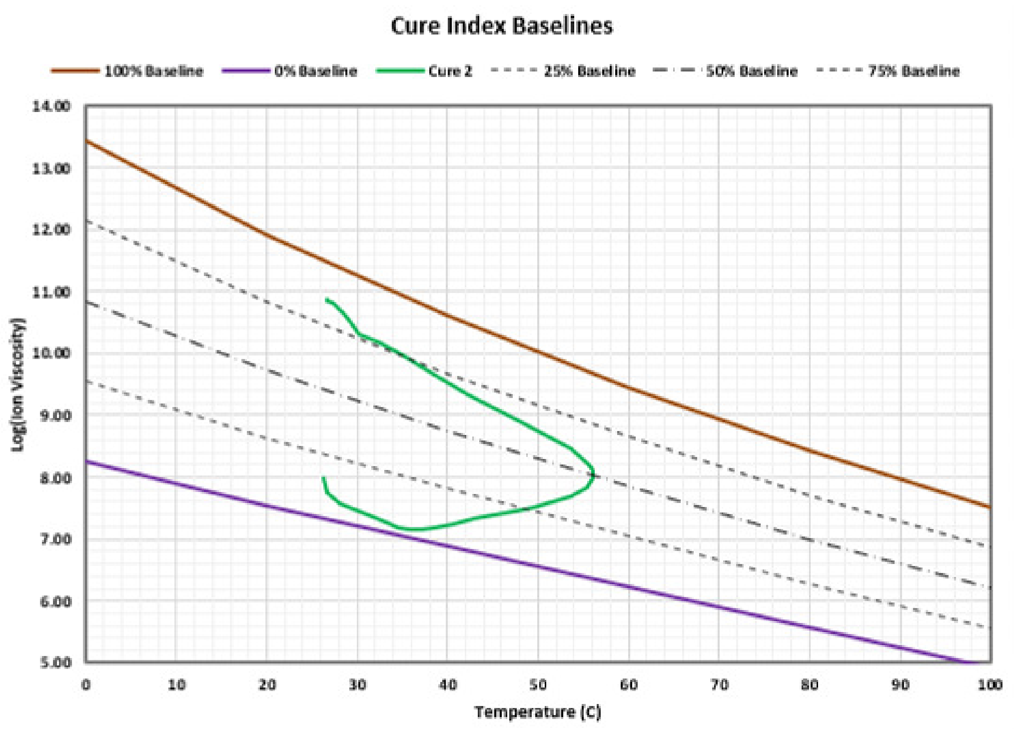

Figure 32-6
10 Hz ion viscosity and temperature for *Cure 2* plotted between baselines

Determine Cure Index by interpolating data location between baselines

For the example of *Cure 2*, interpolation of any ion viscosity-temperature point between the baselines determines Cure Index for that point. To perform Cure Index analysis on a data file, select the *Chart Configuration* icon as shown in Figure 32-7.

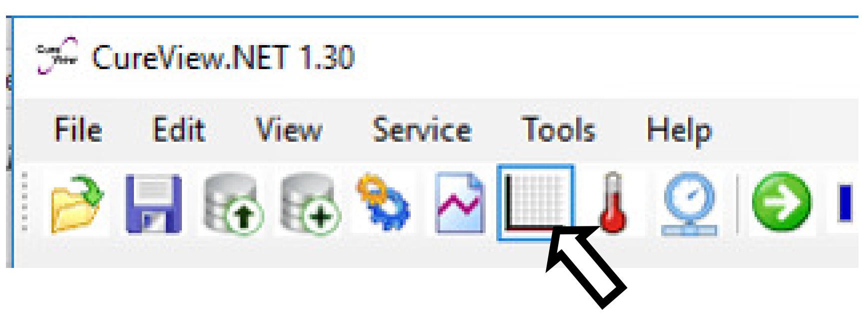

Figure 32-7
Select *Chart Configuration* icon for accessing Cure Index analysis

Then select *Cure Index* for the desired axis of the data plot as shown in Figure 32-8.

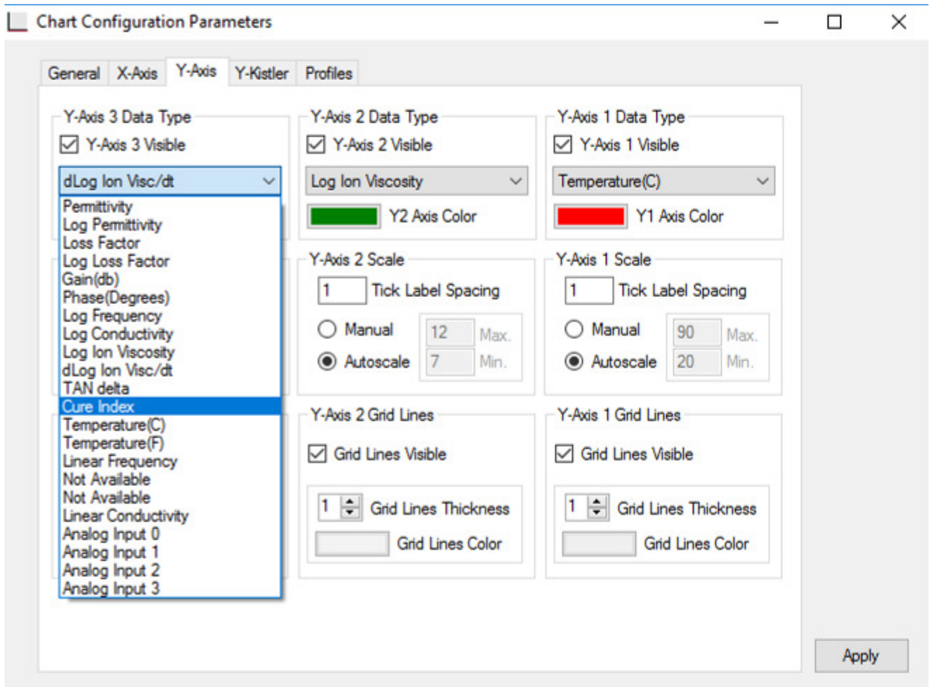

Figure 32-8
Select *Cure Index* plotting axis

After selection of the *Cure Index* axis, CureView plots Cure Index as shown in Figure 32-9.

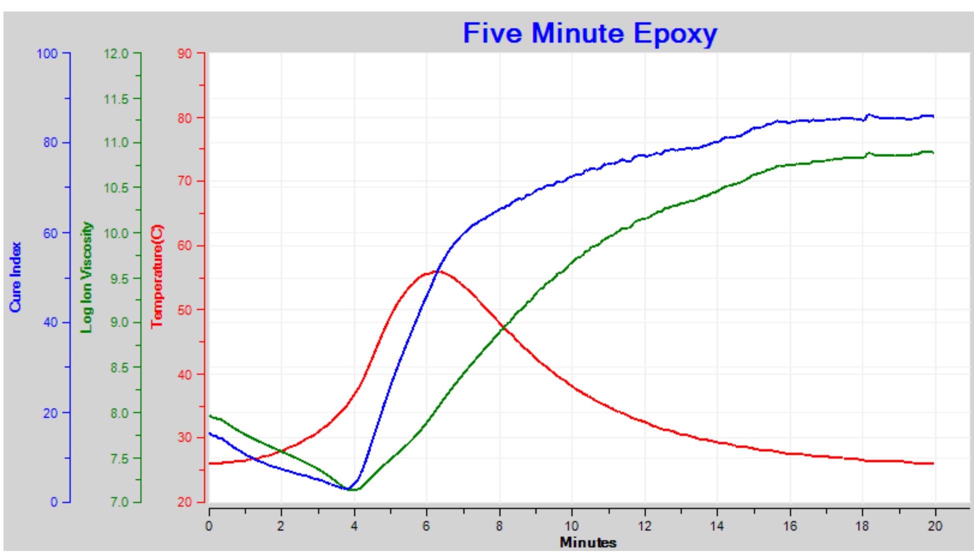

Figure 32-9
Cure Index, 10 Hz ion viscosity and temperature for *Cure 2*

Results

The term *Cure Index* was coined to distinguish it from *degree of cure*. Degree of cure has a formal definition based on the heat of reaction and is usually determined by glass transition temperatures (T_g). Cure Index is a reproducible measure of cure state that, depending on the material under test, can correlate very well with T_G. In many cases Cure Index can be a substitute for degree of cure even in the absence of glass transition temperature information.

Cure is an irreversible process, so Cure Index ideally increases continuously with time. The progress of Cure Index depends on the thermal environment but in general it takes the form shown in Figure 32-10. Curing and Cure Index are both minimal at sufficiently low temperatures. When temperature rises above a value that depends on resin chemistry, sufficient heat energy is available to drive the reaction and cure rate increases significantly.

As the reaction ends, the degree of cure and Cure Index reach a maximum value that depends on process temperature. Higher temperatures result in higher maximum degrees of cure. *Ultimate degree of cure* is the greatest amount of cure possible for the material under test and may be defined as 100% degree of cure or 100% Cure Index.

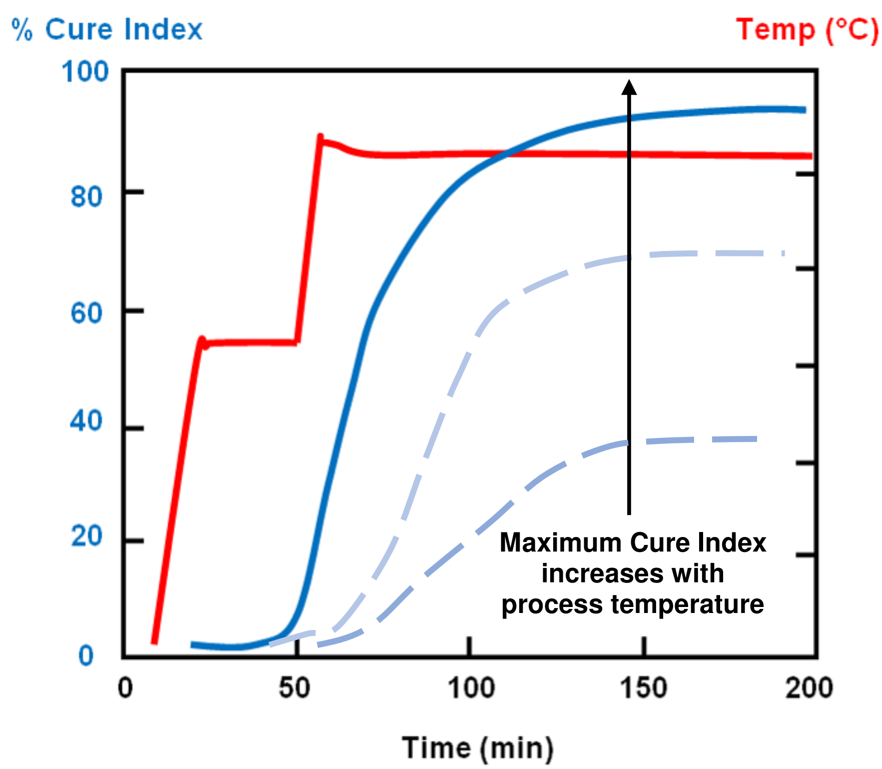

Figure 32-10
General profile of Cure Index during cure

Note that Cure Index data for *Cure 2* decreases between 0 and 4 minutes—unlike the expected continual increase. This behavior occurs because the viscous resin traps air bubbles during mixing with the catalyst. These fine air pockets refract light and turn the epoxy white as shown in the photo on the bottom left of Figure 32-11. The trapped air also increases the volume of the sample. As a result, resistivity and ion viscosity increase compared to material without air.

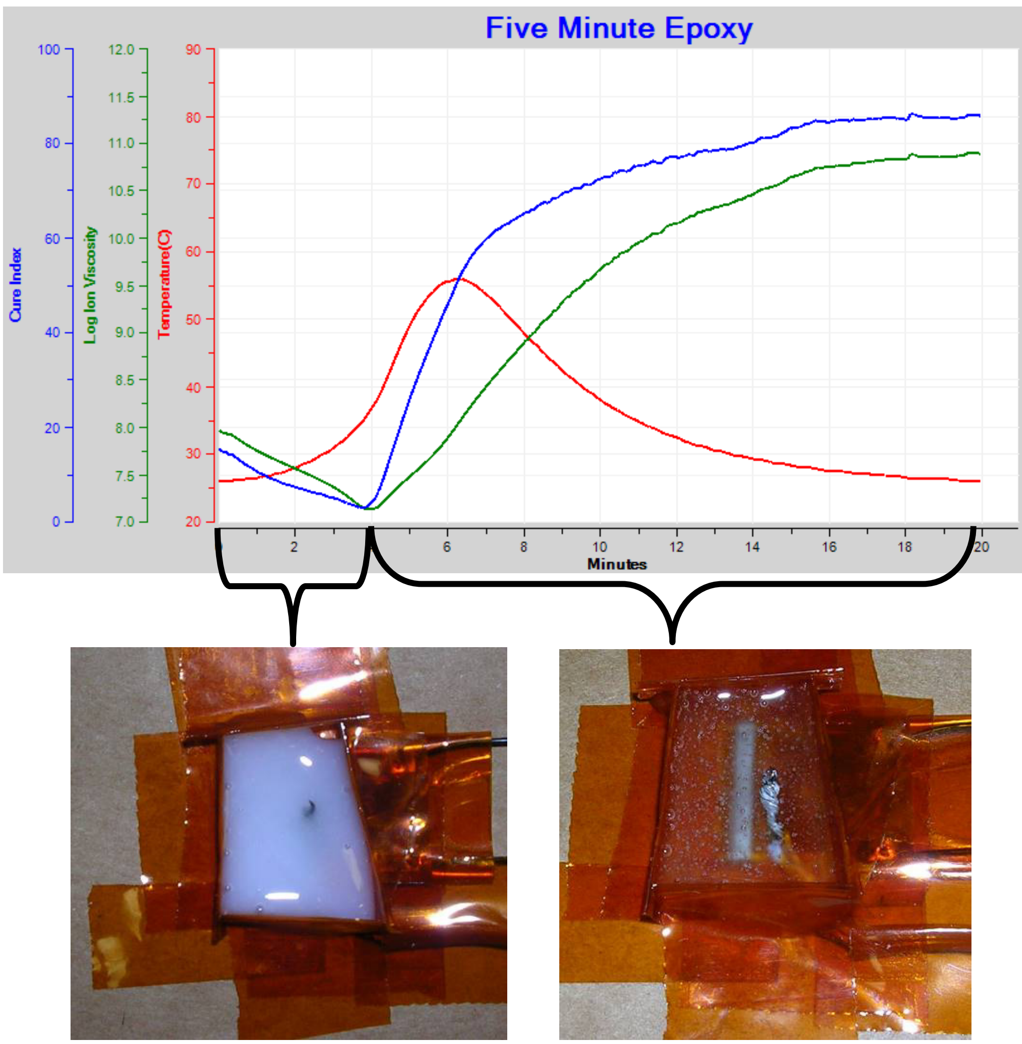

Figure 32-11
Appearance of 5-minute epoxy during *Cure 2*

During early cure the epoxy gradually absorbs the air bubbles and becomes transparent, as shown in the photo on the bottom right of Figure 32-11. Volume also decreases, causing ion viscosity to decrease. At about 4 minutes the ion viscosity increase due to accelerating cure dominates the ion viscosity decrease due to air absorption, and the dielectric response shows an ion viscosity minimum.

Because volume changes during early cure, Cure Index data artificially decreases. *Therefore,* ***for this 5-minute epoxy, Cure Index information should be disregarded before the ion viscosity minimum***. After the ion viscosity minimum, Cure Index rises continuously as expected and reaches a maximum of about 87% for *Cure 2*.

Figure 32-12 shows ion viscosity and temperature data for *Cure 1*, *Cure 2* and *Cure 3*. Based on ion viscosity alone, it is not clear that *Cure 3* is significantly different from *Cure 2*, because the ion viscosity curves for both are very similar—even though their temperature profiles are very different.

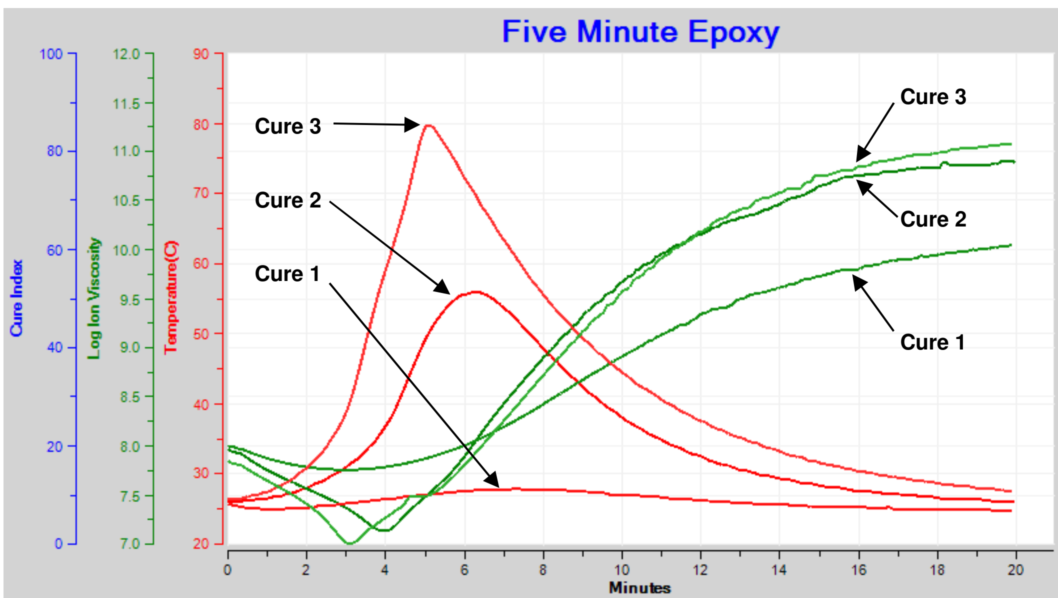

Figure 32-12
10 Hz ion viscosity and temperature for *Cure 1, Cure 2 and Cure 3*

Cures with higher exotherms should result in higher maximum degrees of cure and therefore higher maximum Cure Indexes. Figure 32-13 with the Cure Index analysis of these three tests shows this relationship is correct.

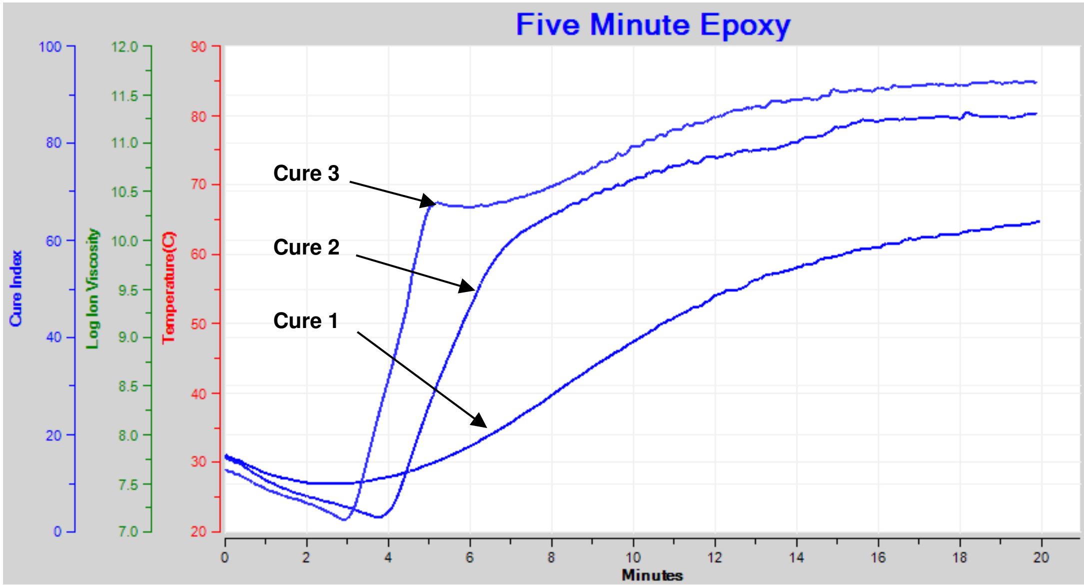

Figure 32-13
Cure Index for *Cure 1, Cure 2 and Cure 3*

Maximum Cure Index for the three tests of 5-minute epoxy is shown below:

Test Name	Amount Epoxy	Thermal Environment	Exotherm Peak	Maximum Cure Index
Cure 1	Thin Layer	Sensor on aluminum plate	28 °C	64%
Cure 2	Medium Layer	Sensor on cardboard sheet	55 °C	87%
Cure 3	Thick Layer	Sensor on cardboard sheet	80 °C	92%

Conclusion

Ion viscosity depends on both cure state and temperature, and when used alone may provide uncertain information about degree of cure. Cure Index analysis accounts for the effect of temperature and allows greater insight into the cure state of materials under test, especially during non-isothermal conditions.

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