Insight — Application Note 3.21

Measuring Degree of Cure With Dielectric Cure Monitoring

Dependence of ion viscosity on temperature and cure state

When temperature is constant, it is easy to understand how dielectric measurements indicate cure state—only the degree of cure affects the ion viscosity of a thermoset or composite. However, ion viscosity actually depends on *both* degree of cure *and* temperature, and accounting for temperature is necessary to correctly interpret non-isothermal tests. Two rules can sum up the behavior of ion viscosity:

1. At constant degree of cure, increasing (or decreasing) temperature decreases (or increases) ion viscosity

2. At constant temperature, increasing (or decreasing) degree of cure increases (or decreases) ion viscosity

Because these rules have opposite effects, the net result depends on which dominates at a particular moment. Figure 21-1 plots data from the cure of an epoxy-fiberglass prepreg.

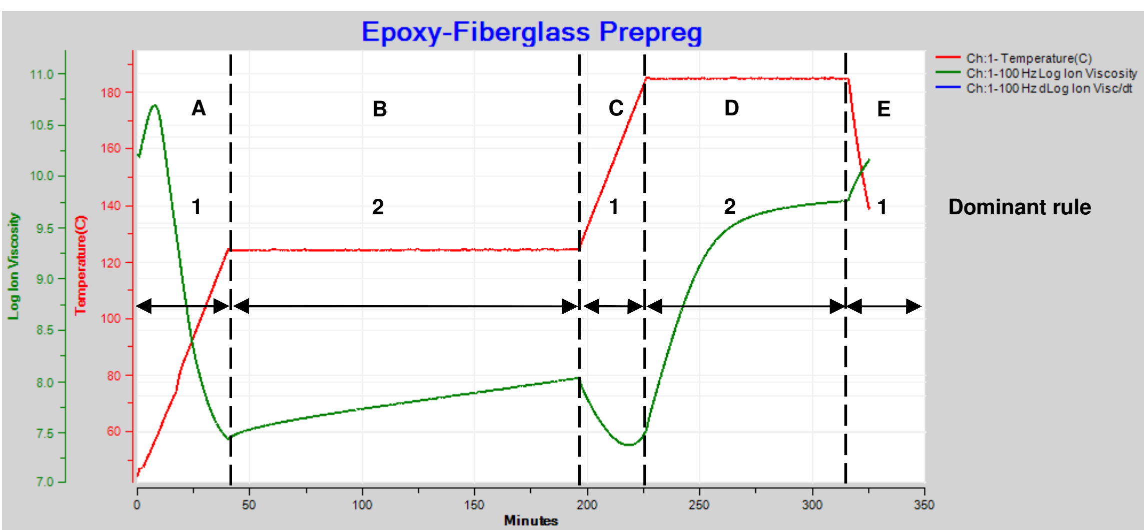

Figure 21-1
Epoxy-fiberglass prepreg cure with ramps and holds

Here ion viscosity changes as temperature goes through two ramp and hold steps then a final cooling:

A. Temperature increases but is too low to initiate significant reaction, so degree of cure is essentially constant and ion viscosity decreases (Rule 1 dominates).

B. Temperature is constant and the slow reaction slightly increases degree of cure, accompanied by a small increase in ion viscosity (Rule 2 dominates).

C. Temperature increases but is still too low for significant reaction or change in degree of cure, and ion viscosity decreases (Rule 1 dominates).

D. At this higher constant temperature, the reaction and degree of cure increase significantly, causing a large increase in ion viscosity (Rule 2 dominates).

E. Temperature decreases. Cure is complete by this time, degree of cure is constant and ion viscosity increases (Rule 1 dominates).

Sometimes the changing temperature and cure rate create a more complex ion viscosity curve, as shown in Figure 21-2. Why does ion viscosity rise then fall between 90 and 150 minutes? Shouldn't the reaction be accelerating because temperature is increasing during this time? Or is the cure somehow reversing?

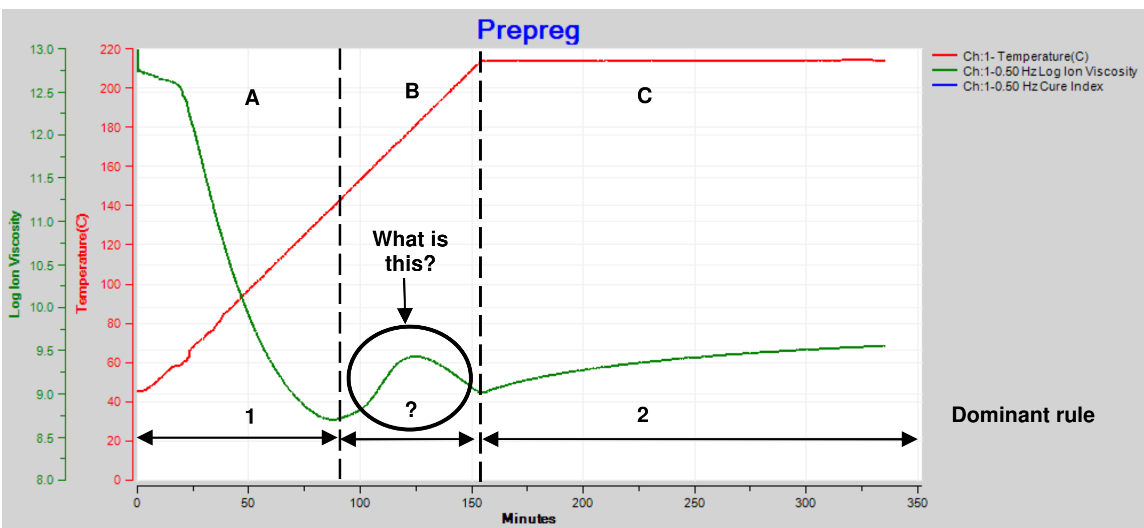

Figure 21-2
Epoxy-fiberglass prepreg cure with ramp and hold

Cure Index

For more insight, a parameter called *Cure Index* accounts for the effect of temperature and is closely related to degree of cure. Calculation of Cure Index requires two baselines that are characteristic of the material: one for the temperature dependence of ion viscosity at 0% cure and the second at 100% cure.

Any measurement of ion viscosity and the associated temperature now exists as a point between these baselines, as shown in Figure 21-3. Cure Index is the vertical distance between this point and the 0% baseline, expressed as a proportion of the vertical distance between the two baselines.

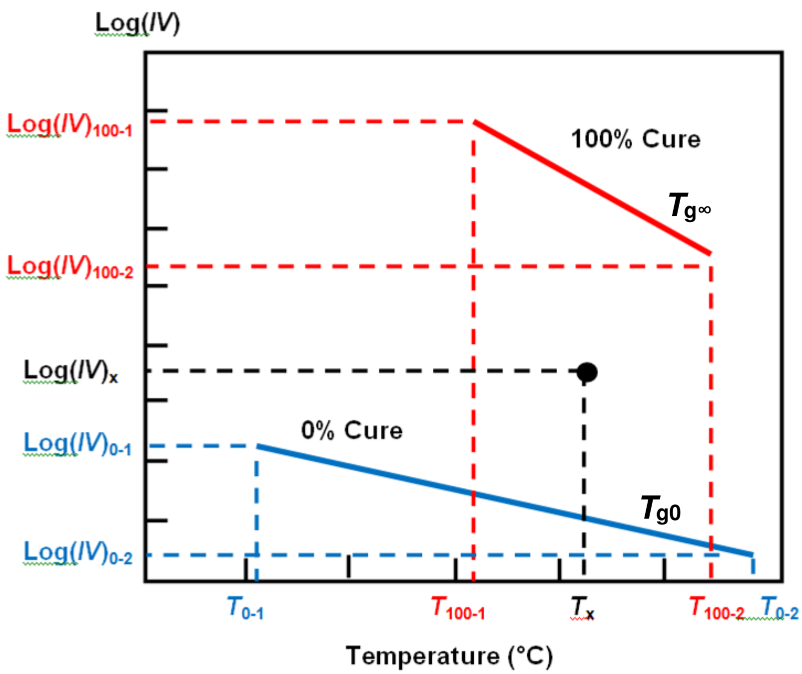

Figure 21-3
Cure Index baselines with ion viscosity-temperature data point

The 0% and 100% baselines are determined by measuring ion viscosity at different temperatures for uncured and fully cured material, respectively. Figure 21-4 shows the baselines obtained in this way for the prepreg of Figure 21-2. The ion viscosity-temperature data are plotted between them. The resulting Cure Index curve for this prepreg is shown in Figure 21-5 along with the original ion viscosity.

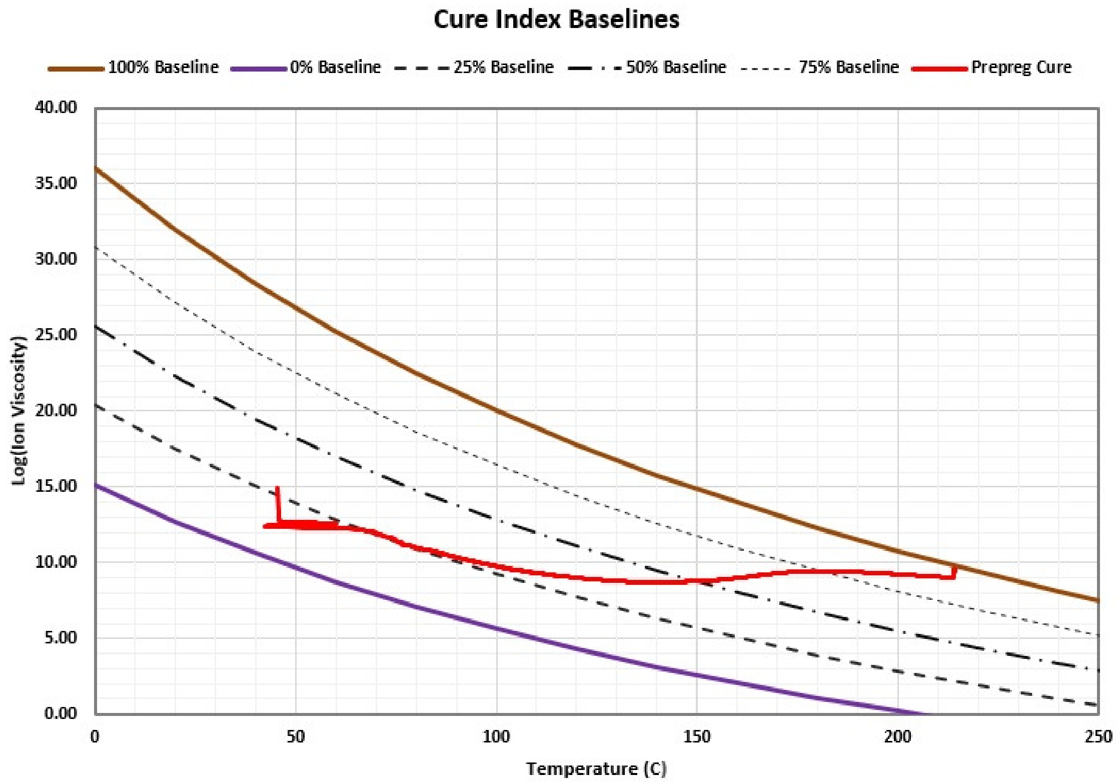

Figure 21-4
Prepreg data between Cure Index baselines

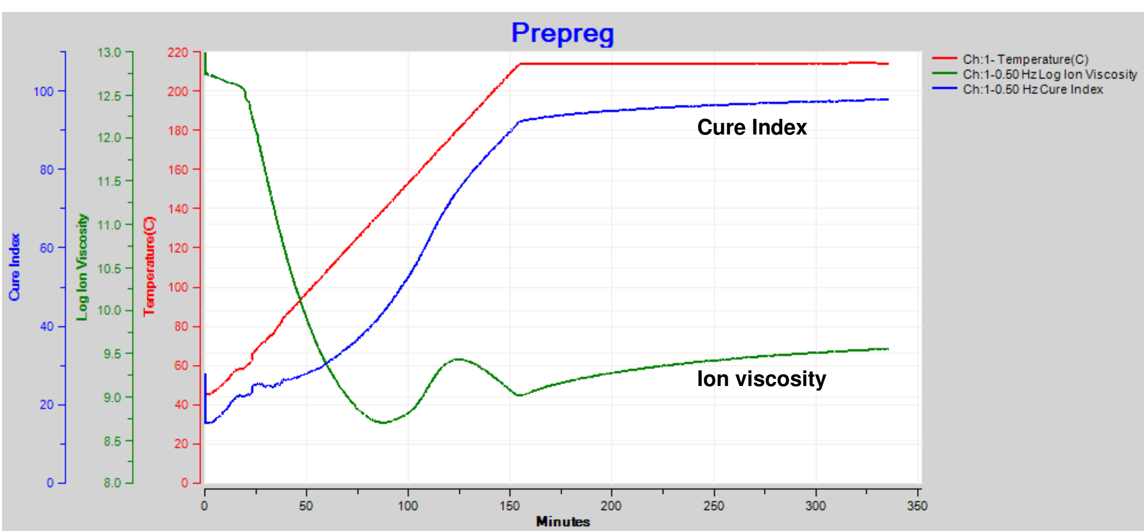

Figure 21-5
Epoxy-fiberglass prepreg ion viscosity and Cure Index

The reaction that drives polymerization is irreversible and the degree of cure always increases with time. The Cure Index of this prepreg shows a continuous increase, consistent with irreversibility, even though ion viscosity peaks and falls between 90 and 150 minutes.

Cure Index reveals this behavior is simply the effect of curing dominating heating between about 90 and 125 minutes, then heating dominating curing between 125 and 150 minutes. To understand the bump in ion viscosity, consider these segments as two separate responses: a) resin during cure as shown in Figure 21-6 and b) resin after end of cure as shown in Figure 21-7.

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, as shown in Figure 21-6.

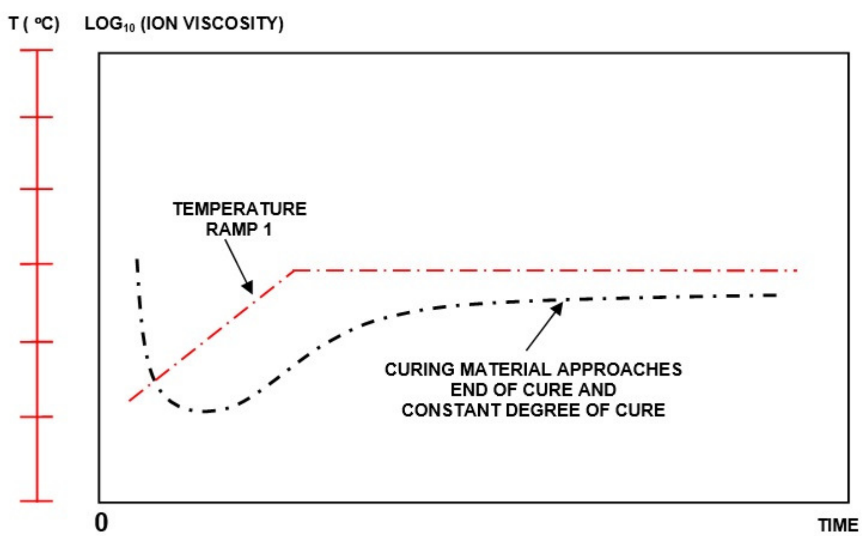

Figure 21-6
Ion viscosity during cure

The degree of cure is constant after the reaction has stopped, and under this condition Figure 21-7 shows ion viscosity remains constant during the first isothermal hold stage. When temperature increases during Ramp 2, ion viscosity decreases according to Rule 1: *At constant degree of cure, increasing (or decreasing) temperature decreases (or increases) ion viscosity*. Finally, during the second isothermal hold stage, ion viscosity again becomes constant because both degree of cure and temperature are constant.

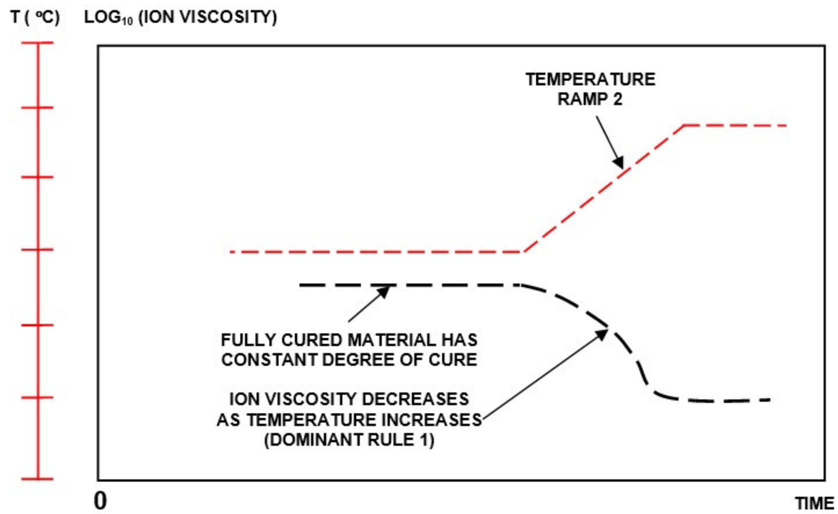

Figure 21-7
Ion viscosity during temperature ramp after end of cure

The behaviors of Figures 21-6 and 21-7 can be combined in Figure 21-8 to show how ion viscosity changes in response to two ramps and holds.

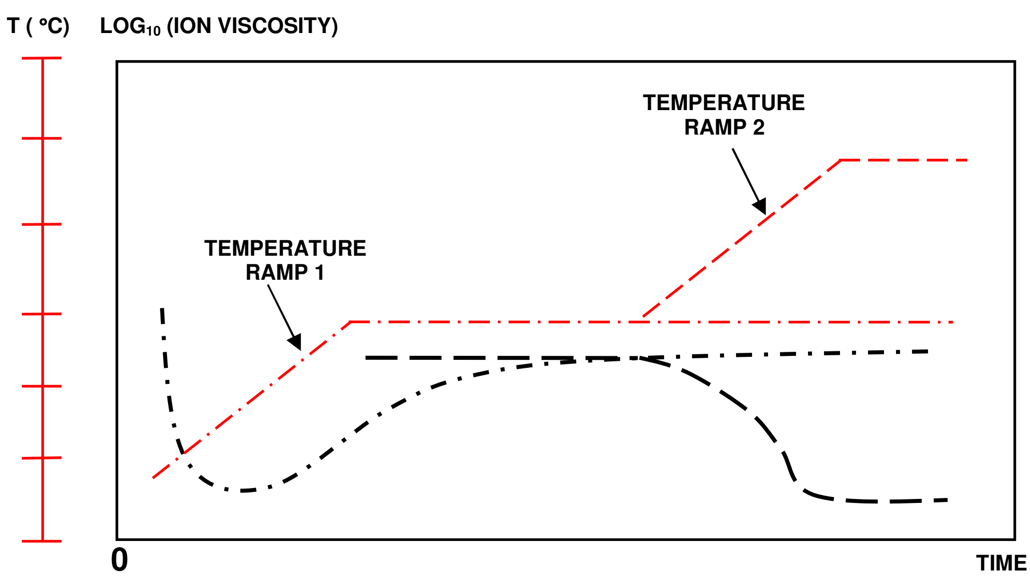

Figure 21-8
Ion viscosity response to two ramp and hold stages

If the time decreases between the two temperature ramps, the result looks like Figure 21-9.

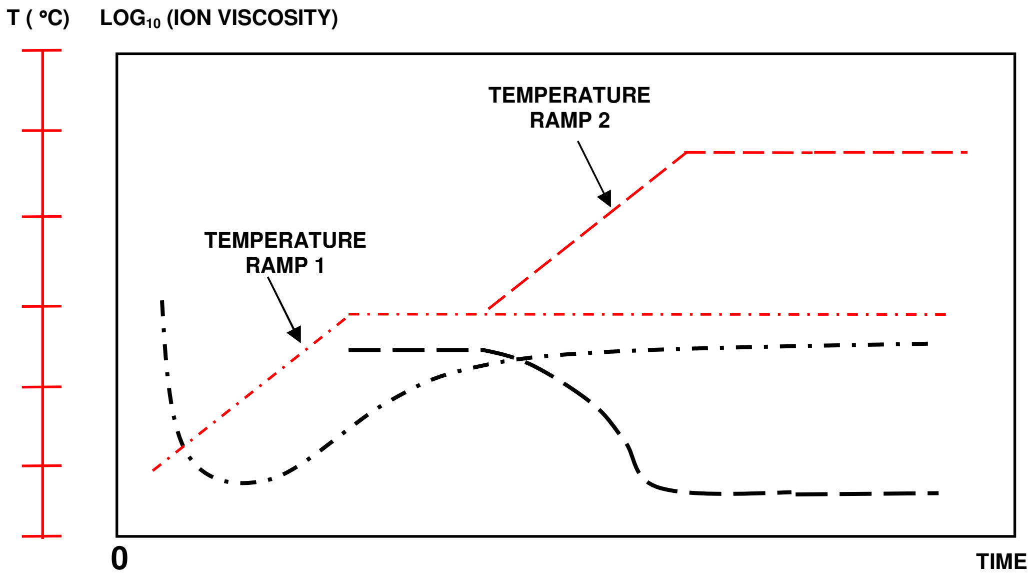

Figure 21-9
Ion viscosity response to two ramp and hold stages

Finally, with a single ramp of sufficient duration and magnitude, the combined behavior of ion viscosity produces the curve shown in Figure 21-10.

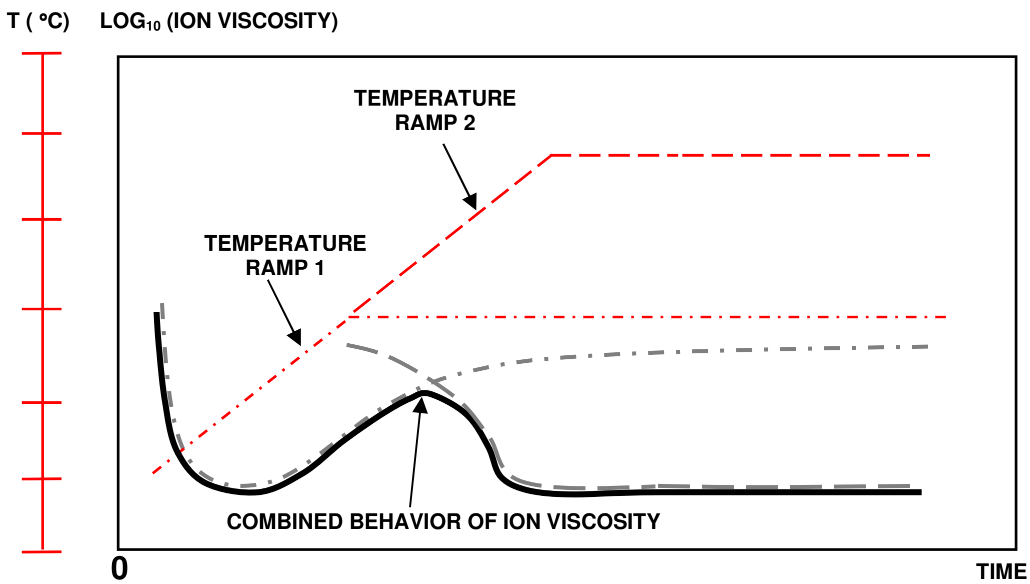

Figure 21-10
Ion viscosity response to a single ramp and hold step

When both cure state and temperature vary during thermoset processing, the progress of cure may not be clear and straightforward. Even worse, ion viscosity may present confusing behavior. Use of Cure Index can account for the effect of temperature on ion viscosity to yield a reproducible indicator of cure state. In fact, Cure Index is physically related to degree of cure and can be a valuable way to interpret the results of dielectric cure monitoring.

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