



Insight — Application Note 3.18

Real-Time Monitoring of Ultraviolet Cure Quad-Cure™ 1933

Quad-Cure™ 1933 ultraviolet curing bonder

Quad-Cure™ 1933¹ is a urethane acrylate glass-metal bonder that may be cured with UV, visible, LED light and heat. Under UV irradiation, this resin reacts rapidly and exhibits dynamic behavior that would be difficult or impossible to see with differential scanning calorimetry (DSC), the conventional method of studying cure state. In contrast, dielectric cure monitoring (DEA) has the unique ability to measure cure in real-time, which is valuable for studying materials that polymerize in seconds like Quad-Cure™ 1933.

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:

$$\text{(eq. 18-1)} \quad \sigma = \sigma_{DC} + \sigma_{AC} \quad (\text{ohm}^{-1} - \text{cm}^{-1})$$

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

$$\text{(eq. 18-2)} \quad \rho = 1/\sigma \quad (\text{ohm-cm})$$

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

$$(eq. 18-3) \quad IV = \rho_{DC} \quad (\text{ohm-cm})$$

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.**

Procedure

The SunSpot 2 UV/Visible Light Curing System² was the UV source for this study. The output from its arc lamp is wide-band and intensity at the end of the light guide is typically $>18,000 \text{ mW/cm}^2$ in UVA (320-390 nm), adjustable from 25% to 100%.

As natural consequence of the optics, light intensity varied radially across the projected spot and approximately uniform illumination was only possible with a small area. Consequently, resin was applied on half of a Quatro-Varicon³ dielectric sensor, resulting in a sample approximately 7 mm x 10 mm in area. The set-up is shown in Figure 18-1.

The SunSpot 2 uses both a dichroic filter and mirror to nearly eliminate IR transmission through the light guide. Absorption of high intensity radiation in the remaining visible/UVA/UVB/UVC wavelengths nevertheless produces considerable heating, which can damage a sample.

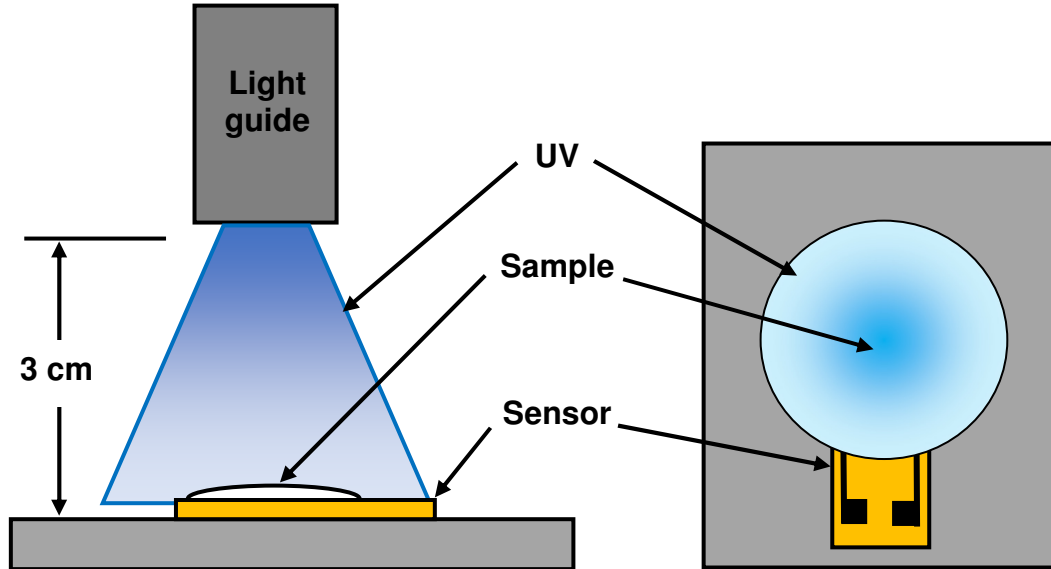


Figure 18-1
Test setup for UV cure

Before the tests, a thermocouple measured temperature at the center of the light spot for a 20 second exposure at 60% intensity. Peak temperature as shown in Figure 18-2 was just over 150 °C. The manufacturer recommends a maximum temperature of 120 °C for Quad-Cure™ 1933 to avoid thermal damage.

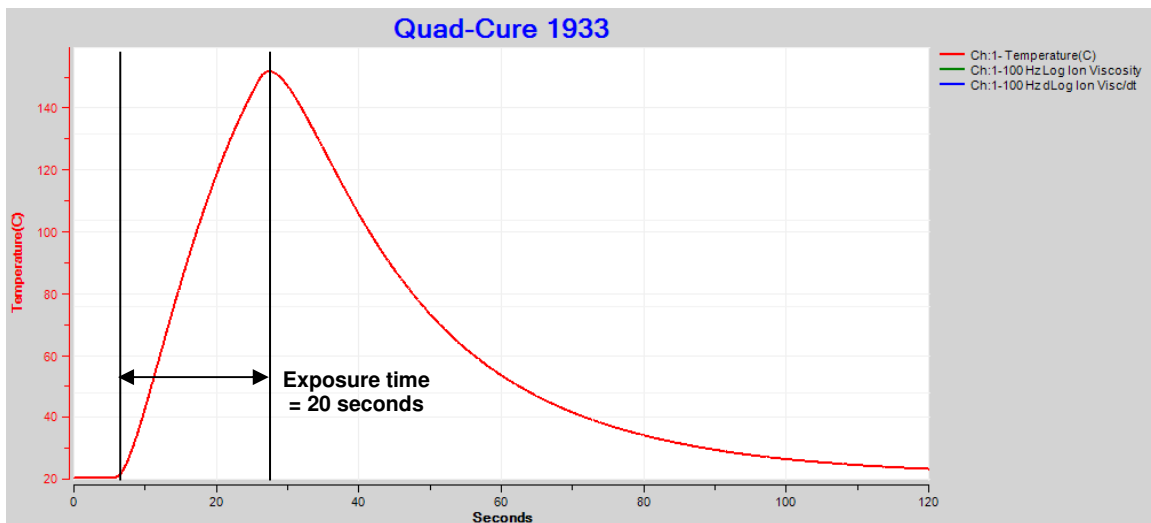


Figure 18-2
Thermocouple temperature, exposure time = 20 seconds, intensity = 60%

An LT-631 High-Speed Dielectric Cure Monitor⁴ measured ion viscosity at a rate of 50 ms/data point. The first test used UV irradiation at 60% intensity for 20 seconds to observe the effects of severe over-exposure.

Results

Figure 18-3 shows ion viscosity data with five distinct events:

1. Initial decrease in ion viscosity due to temperature increase
2. UV cure
3. Cure plateau
4. Post-exposure heat cure
5. End of cure

Cure reaches a plateau between ~17 and 27 seconds, possibly from an equilibrium between UV polymerization and UV breakdown of bonds. The slight decrease in ion viscosity during this time is caused by increased conductivity from the continually rising temperature shown in Figure 18-2.

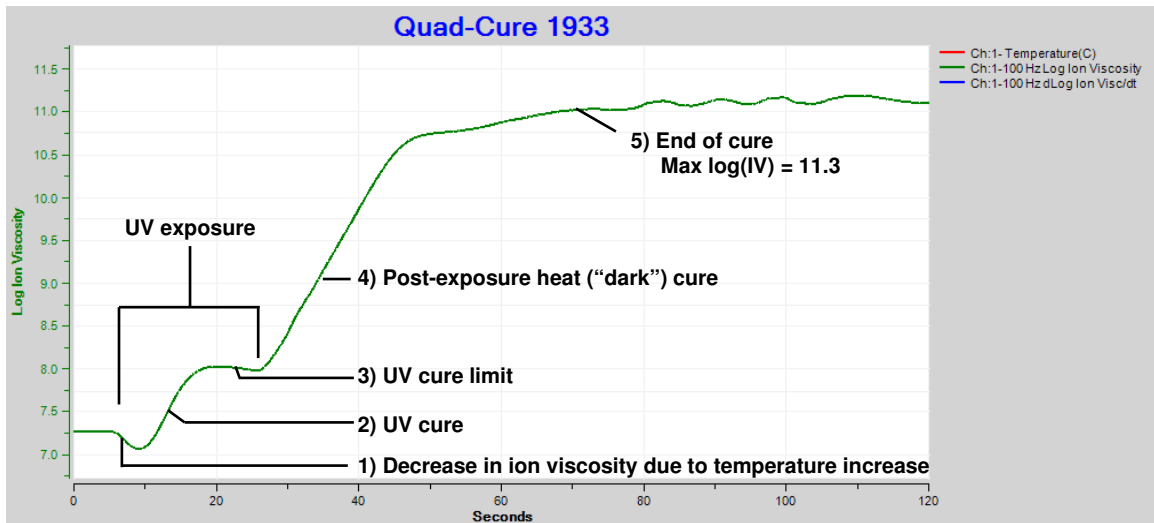


Figure 18-3

Ion viscosity of Quad-Cure™ 1933, exposure intensity = 60%, time = 20 sec.

Figure 18-4 shows a) correct exposure, b) slight over-exposure and c) significant over-exposure.

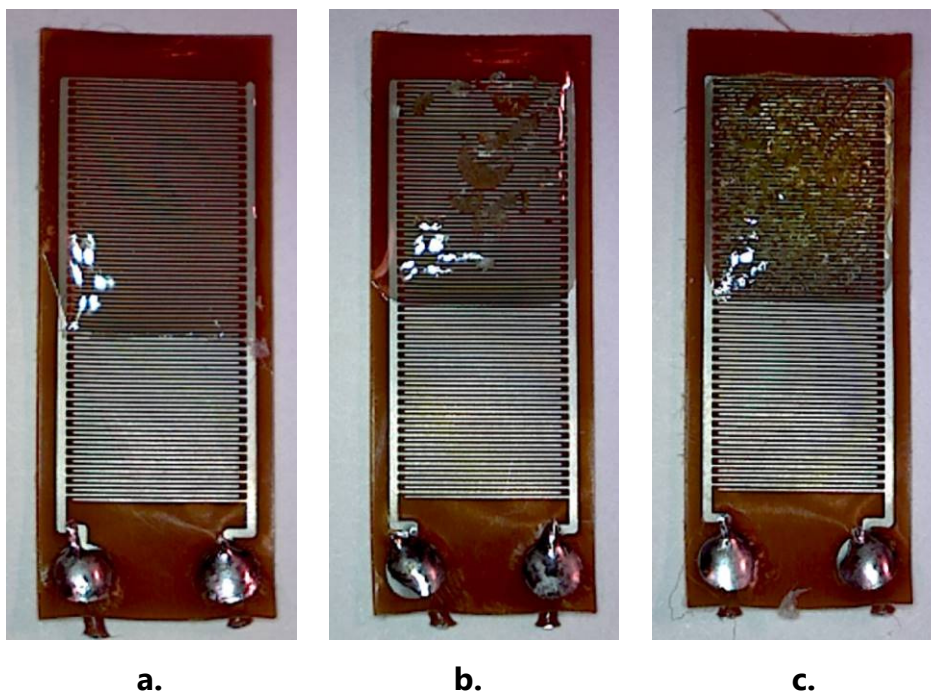


Figure 18-4

Correctly exposed (a), slightly (b) and significantly (c) over-exposed samples

As a result of over-exposure, excessive UV energy causes yellowing of the material and excessive heat creates bubbles and brittleness. The sample of this first test is significantly over-exposed and looks like Figure 18-4.c.

After UV exposure ends, the activated photoinitiators persist and accelerate polymerization driven by heat. This post-exposure, or "dark," cure continues for nearly 70 seconds.

Thermal damage is undesirable and the irradiation time should be shortened to reduce overall heating of the sample. Figure 18-5 compares cure with 10 and 20 second exposures. Even though 10 second irradiation eliminates the plateau, the sample still exhibits bubbling from excessive heat, like Figure 18 4.c.

Final ion viscosity after 10 seconds of UV illumination is significantly less than after 20 seconds. A direct relationship exists between degree of cure and ion viscosity; consequently, the shorter exposure, which produces fewer activated photoinitiators, results in less cure and a lower maximum ion viscosity.

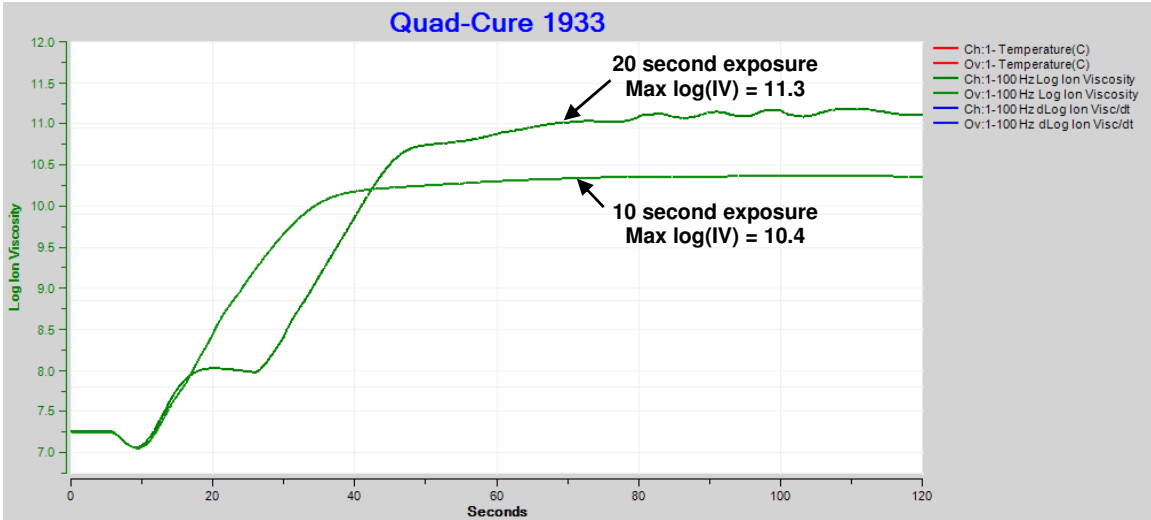


Figure 18-5
**Ion viscosity of Quad-Cure 1933, exposure intensity = 60%,
comparison of exposure time = 10 sec. and 20 sec.**

Figure 18-6 shows how higher exposure energy results in higher ion viscosity at the end of cure, which in turn indicates a greater degree of cure. Note that a single exposure was used for each test and that exposure energy is the product of intensity and exposure time. Although not apparent from the ion viscosity data, the exposure at the highest energy also damaged the sample from excessive heat.

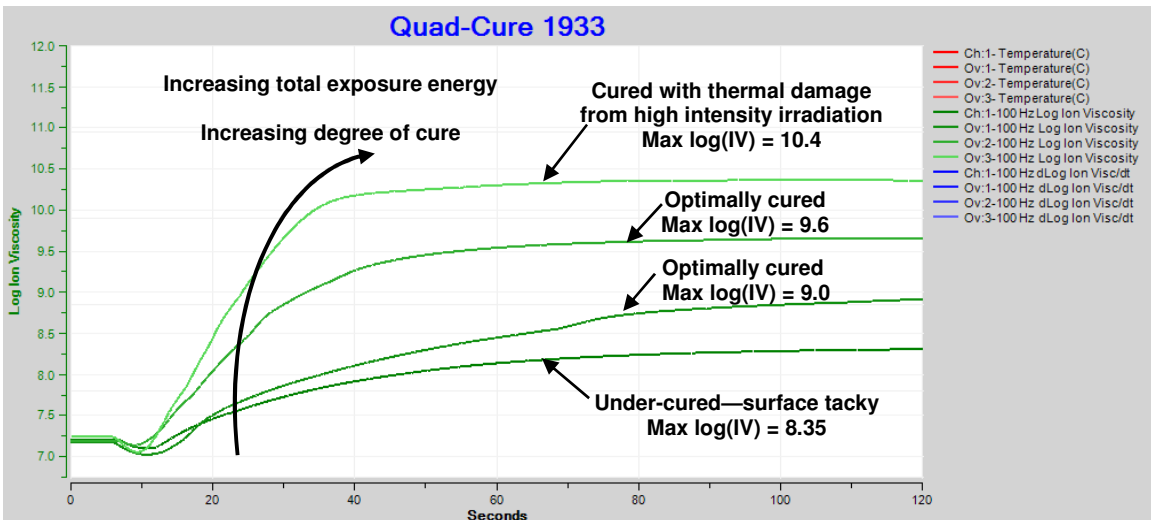


Figure 18-6
**Comparison: Ion viscosity of Quad-Cure™ 1933,
single exposures with increasing total energies**

The results may be summarized as follows:

- Values of $\log(IV) < \sim 9$ are associated with surface tackiness and indicate under-cure
- Values of $\log(IV)$ between ~ 9.0 and ~ 9.6 correspond to optimum cure, which produces a “sleek” surface without damage
- Values of $\log(IV) > \sim 10$ accompany brittleness and thermal damage from the excessive exposure to high intensity light

Instead of a single high-intensity exposure, multiple low-intensity exposures can drive cure to higher degrees without the damage from excessive heating. How would the relationship between ion viscosity and final material state change in this case? For quickly reacting resins like those used in UV curing, the value of dielectric cure monitoring lies in its ability to gather real-time information and answer questions like this in ways not possible with other methods.

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 $\log(\text{ion viscosity})$ is a simple way to characterize the progress of cure and Figure 18-7 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.

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.

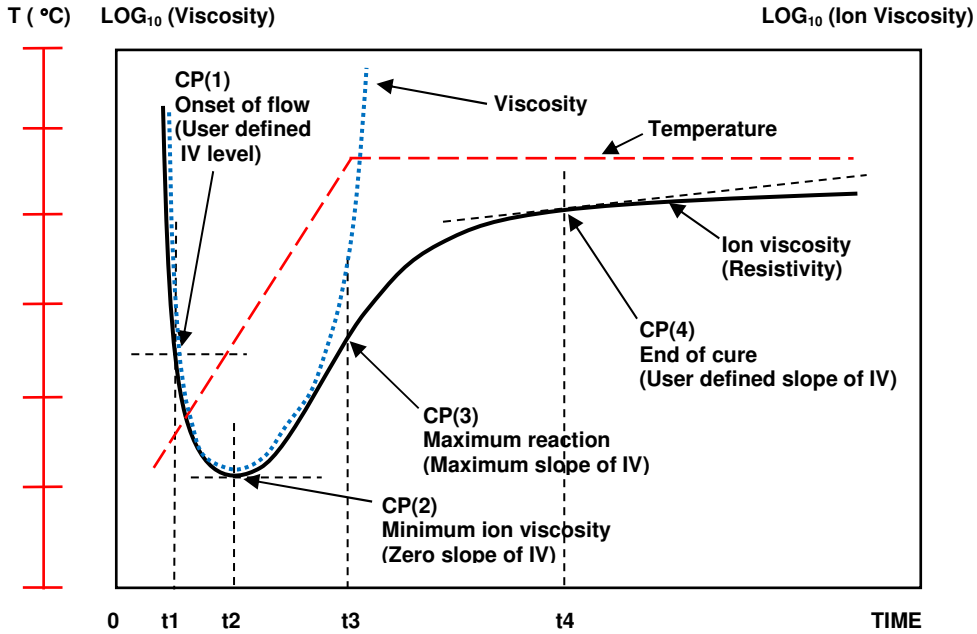


Figure 18-7
Typical ion viscosity behavior of thermoset cure
during thermal ramp and hold

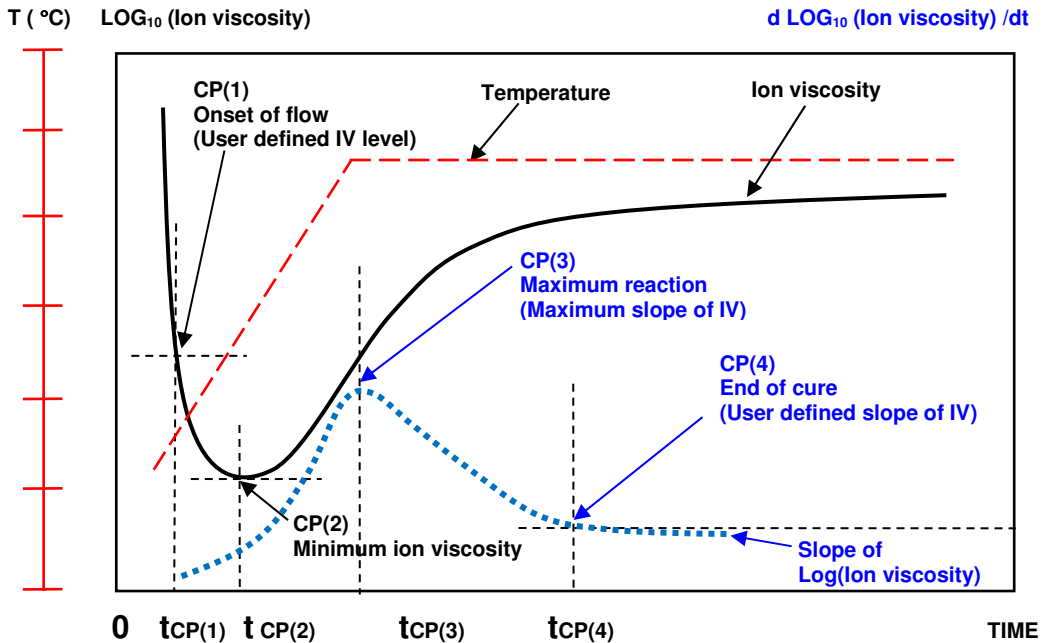


Figure 18-8
Ion viscosity curve and slope of ion viscosity of thermoset cure
during thermal ramp and hold

As shown in Figure 18-8, 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 18-7 and 18-8 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 18-9.

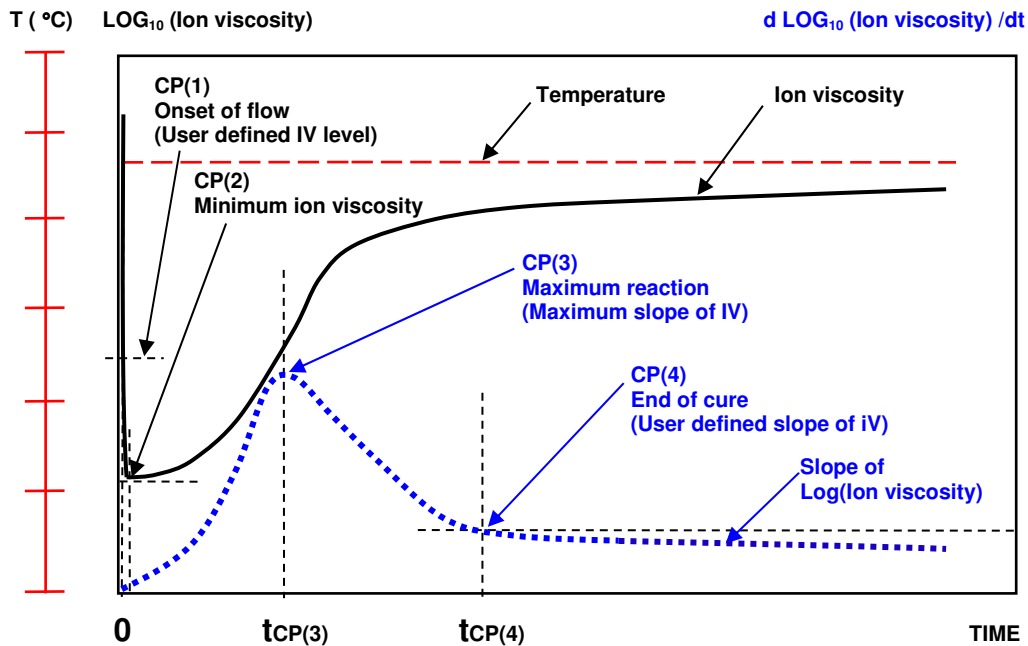


Figure 18-9
Ion viscosity curve and slope of ion viscosity of thermoset cure
during isothermal processing

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. Quad-Cure 1933™, manufactured by Incure, Inc., New Britain, CT USA. www.uv-incure.com
2. SunSpot 2™, manufactured by Uvitron International, Inc., West Springfield, MA USA. www.uvitron.com
3. Quarto-Varicon sensor, manufactured by Lambient Technologies, Cambridge, MA USA. <https://lambient.com>
4. LT-631 High Speed Dielectric Cure Monitor, manufactured by Lambient Technologies, Cambridge, MA USA



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