# AN 12–Dielectric Cure Monitoring of an Acrylic Adhesive

## Introduction

Lambient Technologies tested samples of a commercially available two-part acrylic structural adhesive with the LT-451 Dielectric Cure Monitor. Following are the results of dielectric cure monitoring at room temperature. This report presents and discusses *Log(ion viscosity)* and slope of *Log(ion viscosity)* curves, which indicate the progress of the cure. The data clearly show cure of the acrylic adhesive and characteristic features of the cure such as minimum ion viscosity, maximum slope of Log(ion viscosity) and the decreasing reaction toward end of cure.

## Definitions

Loss factor (unitless) is defined as:

$$\varepsilon'' = \sigma' / \omega \qquad \text{(eq. 1)}$$

Relative conductivity (unitless) is defined as:

$$\sigma' = \sigma / \varepsilon_0 \qquad \text{(eq. 2)}$$

Where

$\sigma$ = conductivity ($ohm^{-1} - cm^{-1}$)
$\varepsilon_0 = 8.86 \times 10^{-14}$ F/cm
$\omega = 2\pi f$ (radians/sec)
f = frequency of excitation signal (Hz)

Ion viscosity ( ohm-cm ), also known as resistivity, is defined as:

$$IV = \rho = 1/\sigma \qquad \text{(eq. 3)}$$

## Procedure

The Mini-Varicon sensor in the mid-sensitivity configuration was connected to the LT-451 Dielectric Cure Monitor. No thermocouple was used in this test, so no temperature data is available. The CureView cure monitoring software was configured to acquire data for 30 minutes using excitation frequencies 1, 10, 100, 1K, 10K and 100 KHz. Data acquisition proceeded for approximately 1.5 minutes with no material on the Mini-Varicon sensor.

After 1.5 minutes the two-part acrylic adhesive was dispensed through a static mixer onto the electrodes of the Mini-Varicon sensor. Data acquisition continued for the remainder of the 30 minute period, with ion viscosity results plotted below in Figure 1.

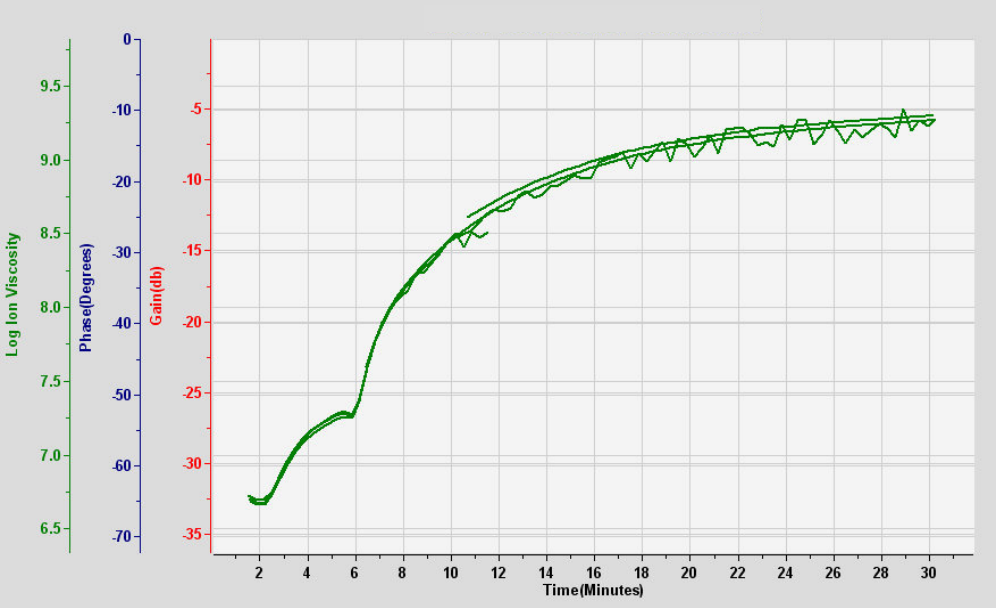


Figure 1
Ion viscosity data from cure of acrylic structural adhesive

**Results**

The mechanical viscosity of a material typically correlates with its ion viscosity up to a certain point. In addition, the progress of a curing material can be monitored by observing the ion viscosity even past the point where mechanical viscosity can no longer be measured.

Ion viscosity is the frequency independent--or DC—resistivity, ρ. As a result, dielectric data obtained at different frequencies ideally convert to the same ion viscosity and yield a single curve. In reality the curves may diverge due to the presence of additional dielectric phenomena such as dipole relaxation, boundary layer or other effects. CureView software has user selected materials parameters which allow it to determine whether derived data corresponds to frequency independent resistivity. Proper selection of these parameters results in the calculation and display of ion viscosity without confounding effects.

Figure 1 shows the ion viscosity curve derived from the curing acrylic structural adhesive. Although multiple traces exist, they are all essentially on top of one another, confirming that the plot shows frequency independent resistivity. No data exists for the first 1.5 minutes because no material was on the Mini-Varicon sensor during that time. The adhesive was dispensed onto the sensor at 1.5 minutes, which corresponds to the first point of the ion viscosity data.

After deposition of the adhesive, the magnitude of the ion viscosity decreases, typically due to an exothermic reaction causing increased material temperature as the acrylic reacts and polymerizes. Increasing temperature causes the material to become more fluid; its electrical resistivity ρ—and therefore the ion viscosity--decreases.

Eventually the polymerization process accelerates and dominates as temperature continues to rise. The material becomes stiffer and the ion viscosity starts to increase

after reaching a minimum at 2.0 minutes. Thus ion viscosity provides a direct measure of the time of minimum mechanical viscosity.

This increasing ion viscosity indicates increasing mechanical viscosity and advancing cure state. At about 3.5 minutes the *slope* of ion viscosity starts to decrease, corresponding to a decreasing reaction rate. Although the cure continues, the reaction is slowing down and eventually would stop.

At about 5.5 minutes, however, a second reaction appears to take place. The ion viscosity shows a local minimum at about 6.0 minutes. Like the minimum at 2.0 minutes, the cause is likely an increase in temperature as the new exothermic reaction begins. Ion viscosity then briefly decreases before the accelerating reaction rate dominates once again, causing further increase in ion viscosity.

After 6.0 minutes the slope of ion viscosity continuously decreases, indicating a steadily decreasing reaction rate. Ion viscosity itself continues to increase, though, indicating an ongoing reaction and a polymer network that is becoming stiffer and stiffer. During this last segment, the user may choose to define an ion viscosity slope which corresponds to a desired state at the end of cure. In this way dielectric monitoring permits measurements of the time to end of cure, as well as visibility into reaction rates and dynamics throughout the entire process.

**Critical Points during cure**

A material cures due to the crosslinking of monomers, and often this reaction is exothermic—generating heat— or is driven by the heat of a press or oven. Typically the viscosity initially decreases as the temperature increases and the material responds by simply melting and becoming more fluid. Resistivity also decreases as mobile ions experience less resistance to flow. At this point the curing reaction is still slow, but eventually it accelerates with greater temperature and then dominates the system. Viscosity reaches a minimum--a point of zero slope--and then increases as the material becomes more rigid and hardens. Resistivity similarly undergoes a minimum and then increases due to greater impediment to the flow of ions through the growing network.

Eventually the reaction slows and the viscosity becomes infinitely large. At this point the base resistivity dominates the electrical response and behavior of resistivity departs from that of viscosity. Resistivity continues to change, but more and more slowly, approaching a limit that signals the end of cure. The viscosity and resistivity (ion viscosity) typically follow curves like those of Figure AN 6-1.

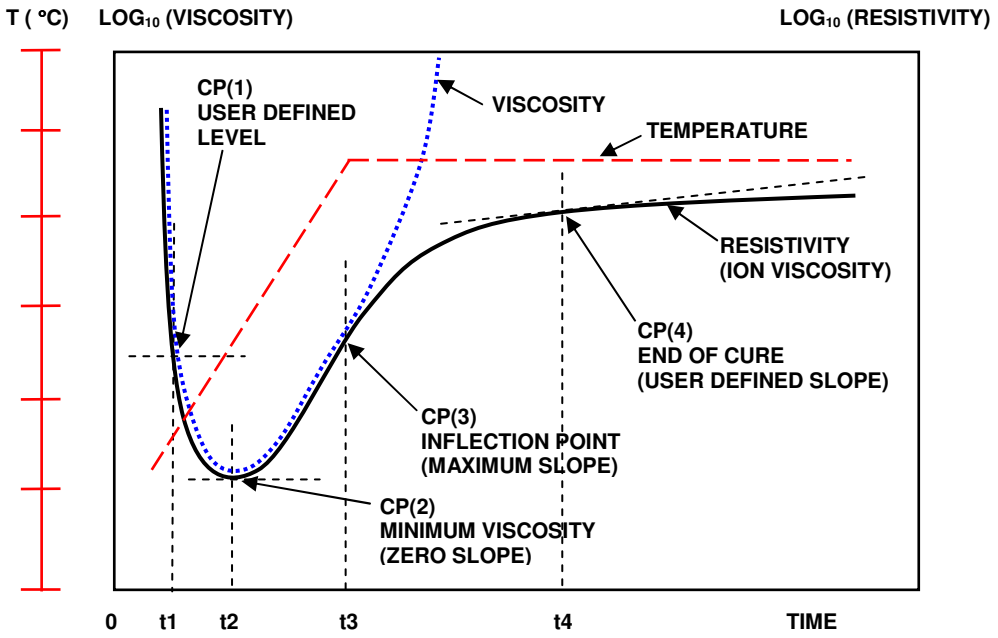


Figure AN 6-1
Viscosity and resistivity in a curing material

The dielectric cure curve is characterized by four Critical Points:

- 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 cure monitoring can provide insight into the reaction and cure of polymers, and the proportionality between ion viscosity and physical viscosity in many materials has proven to be useful in polymer processing. Furthermore, with dielectric measurements it is possible to observe the effects of different chemistries, formulations, process conditions and temperatures. Dielectric cure monitoring of the acrylic structural adhesive clearly shows dielectric events which identify:

- Time of minimum mechanical viscosity
- Rate and progress of initial polymerization reaction
- Time when a second reaction begins
- Rate and progress of second polymerization reaction

Knowing when material has reached the viscosity minimum, for example, allows optimum application of pressure to compress a laminate or to extract air bubbles from a molded part. Even after ion viscosity diverges from viscosity, the ability to observe further changes in the cure state allows the determination of an end of cure, resulting in consistent properties from part to part.