Insight — Technical Overview 2.02
Equipment for Dielectric Cure Monitoring

Dielectric Cure Monitors

Dielectric cure monitors measure the dielectric properties of material at a single frequency or across a range of frequencies, selectively revealing the influence of mobile ions and dipole rotation. Ion viscosity of a material is frequency *independent* resistivity (ρ_{DC}) and is often proportional to the change in mechanical viscosity before gelation and proportional to the change in modulus after gelation. Consequently, ion viscosity is a useful probe of material state through the entire cure.

Characteristics of thermoset cure

A thermoset cures because monomers react to form polymer chains, then crosslink to form a network. Often this process is exothermic—generating heat—or is driven by the heat of a press or oven. Typically, mechanical viscosity initially decreases as temperature increases; the material melts or flows. Resistivity also decreases as mobile ions experience less resistance to movement. At this point the reaction is still slow but eventually accelerates until it dominates the system. Mechanical viscosity reaches a minimum then increases as the material becomes more viscous, gels then becomes rigid. Ion viscosity similarly reaches a minimum then increases due to the lengthening chains, which present greater and greater impediment to the flow of ions.

Eventually the reaction slows and mechanical viscosity becomes immeasurable. At this point ion viscosity is no longer proportional to mechanical viscosity. Ion viscosity continues to change, but more and more slowly, approaching a limit at the end of cure. Figures 1 and 2 show the behavior of a typical thermoset with one temperature ramp step and one temperature hold step.

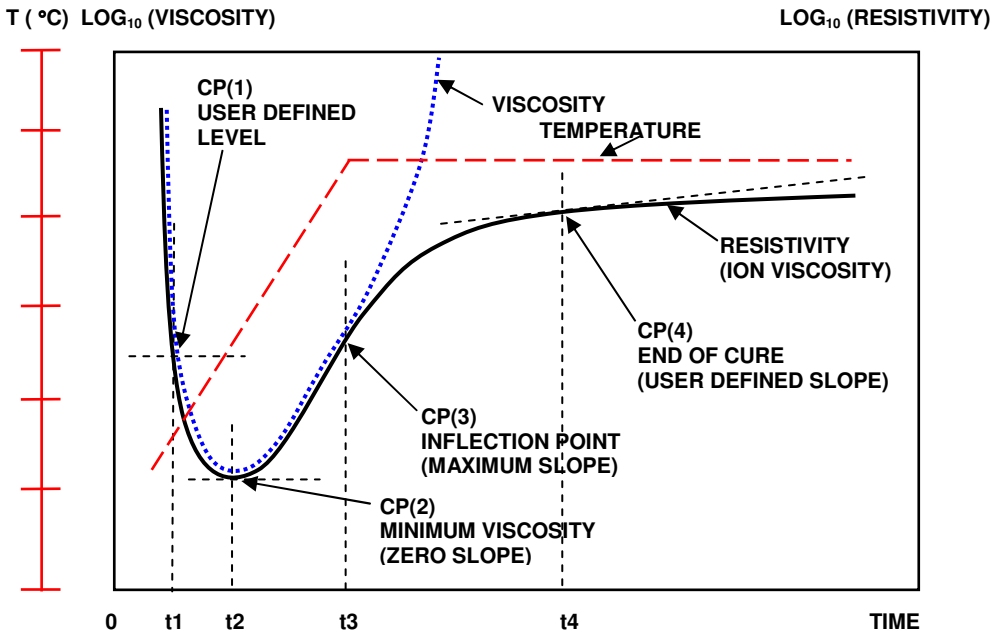


Figure 1
Ion viscosity and mechanical viscosity in a curing thermoset

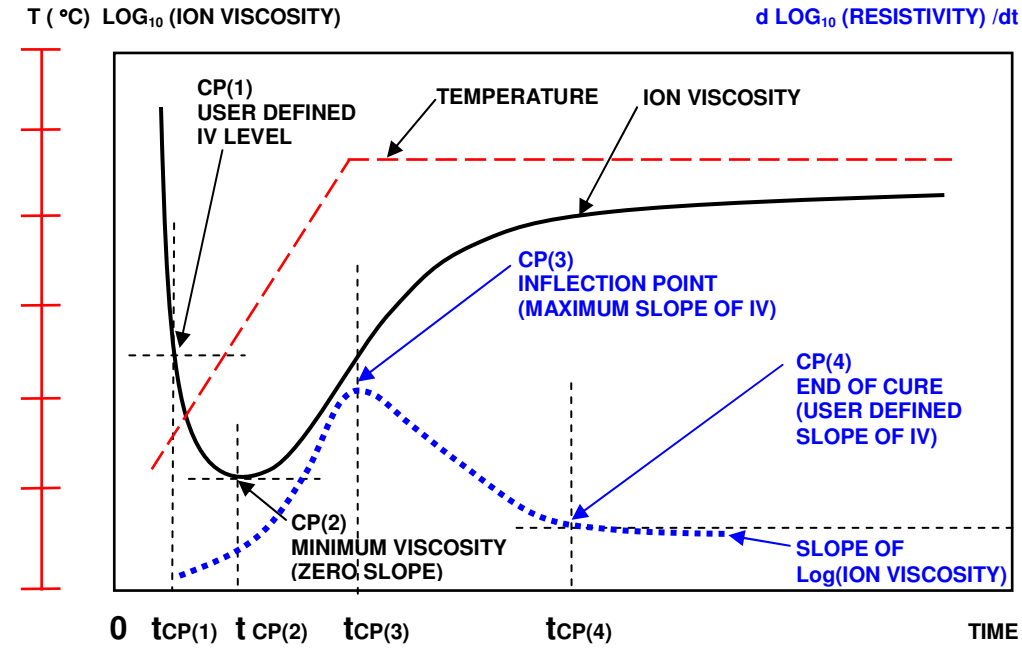


Figure 2
Ion viscosity, slope and Critical Points in a curing material

The dielectric cure curve is characterized by four Critical Points:

- **CP(1)—Onset of flow:** a user defined level of ion viscosity, which identifies when material reaches the sensor at the beginning of cure.
- **CP(2)—Ion viscosity minimum:** closely corresponding to the mechanical viscosity minimum, which indicates when the accelerating reaction dominates material behavior.
- **CP(3)—Inflection point:** the point of maximum reaction rate, after which the reaction begins to slow; it can be associated with gelation but does not indicate gelation.
- **CP(4)—Critical slope:** a user defined slope of ion viscosity that can identify end of cure. The decreasing slope corresponds to the decreasing reaction rate. Note that dielectric cure monitoring continues to reveal changes in material state past the point when measurement of mechanical viscosity is not possible.

Dielectric/Conductivity Sensors

Dielectric cure monitors measure the resistance (*R*) and capacitance (*C*) of material between a pair of electrodes, which can be modeled as a resistance in parallel with a capacitance, as shown in Figure 3.

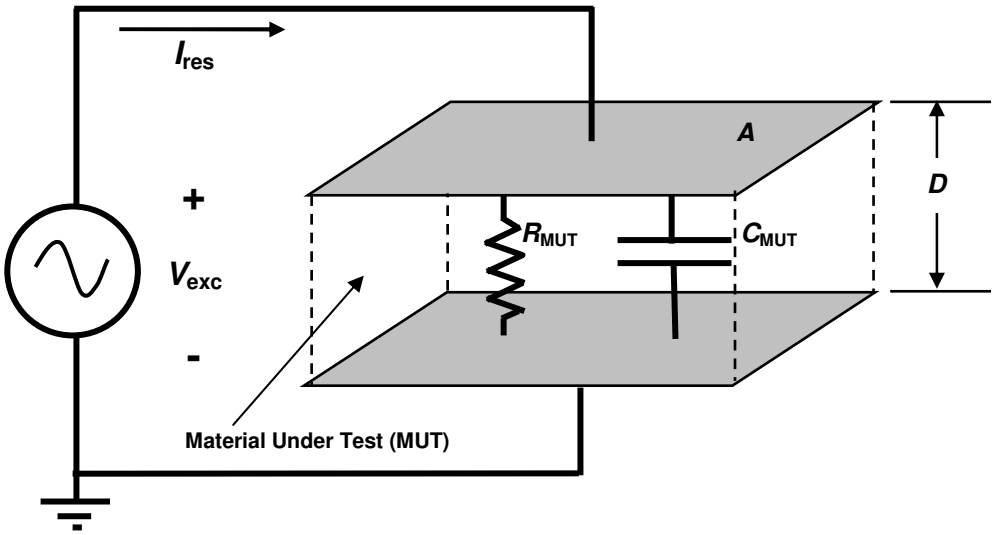


Figure 3
Dielectric model of a Material Under Test

Simple parallel plate electrodes, shown in Figure 4, are often used for this purpose. The ratio of electrode area *A* and the distance *D* between them—the *A*/*D* ratio—is a figure of merit. A larger *A*/*D* ratio corresponds to greater sensor sensitivity. The *A*/*D* ratio is also the scaling factor for calculating resistivity from resistance, and permittivity from capacitance. Unfortunately, distance *D* can change with pressure, or with expansion and contraction of the material, causing inaccurate results.

An alternative is the interdigitated electrode, also shown in Figure 4. A rigid substrate supports the electrodes and resulting the planar structure does not change with pressure, or expansion and contraction of the material under test (MUT). While the parallel plate sensor makes a bulk measurement, an interdigitated sensor makes a surface measurement. As a rule of thumb, interdigitated electrodes, with the same width and separation, measure to a depth approximately equal to the electrode width. The parameter of *A*/*D* ratio also applies to interdigitated electrodes as a figure of merit and is the scaling factor for calculating resistivity and permittivity.

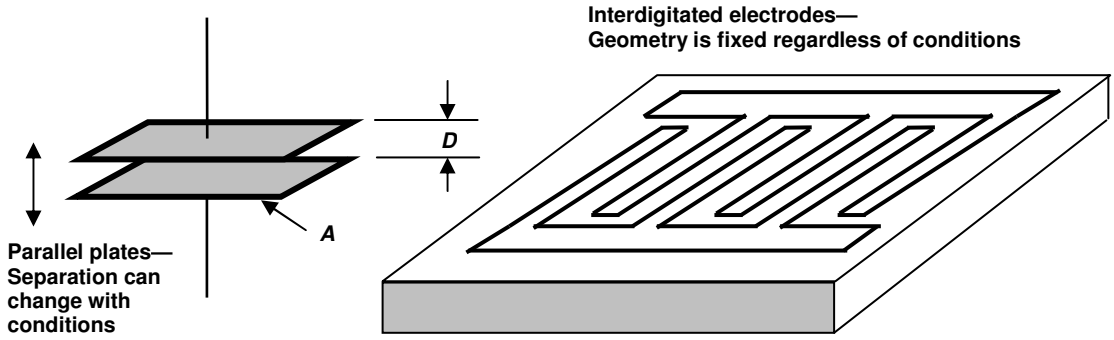


Figure 4
Comparison of parallel plate and interdigitated electrodes

Figure 5 shows a typical disposable dielectric/conductivity sensor with interdigitated electrodes 100 microns wide. Constructed as a Kapton® flex circuit, this sensor is thin enough to be inserted between the plys of a laminate and may be discarded after use. The narrow electrodes, too small to be visible in the figure, result in a large A/D = 160, with correspondingly great sensitivity. The

trade-off is the measurement of dielectric properties only within 100 microns of the surface.

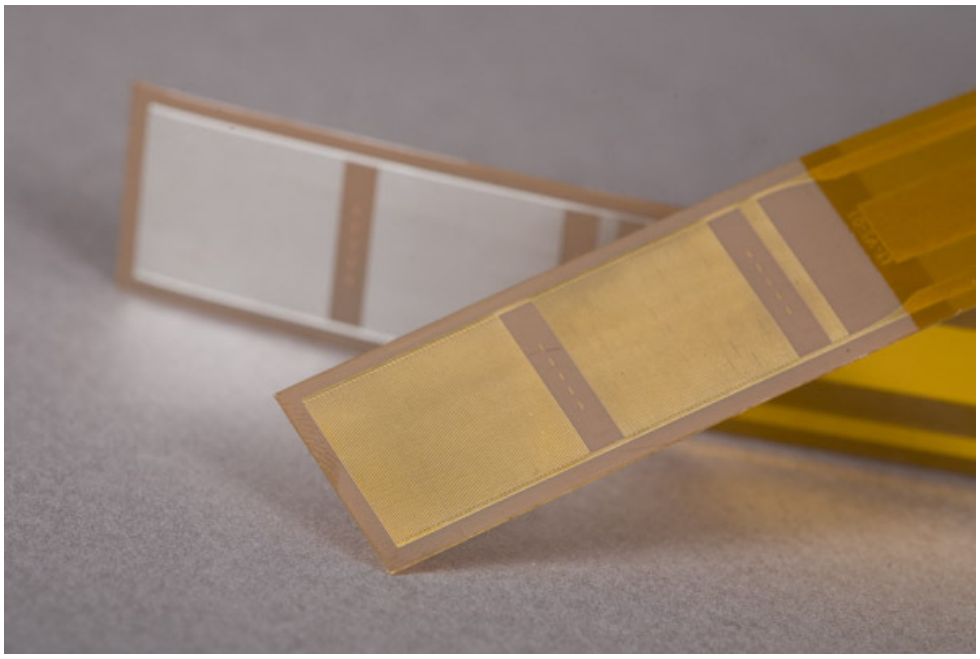


Figure 5
Disposable dielectric/conductivity sensor on polyimide flex circuit

Figure 6 shows a reusable dielectric/conductivity sensor embedded in a platen for a small press. This sensor is constructed with interdigitated electrodes embedded in ceramic and has an A/D = 10. When mounted as shown, it is possible to place a sample in the press, then heat and compress it and simultaneously make dielectric measurements to monitor cure. Afterward the sample can be removed from the sensor and the process can be repeated.

Reusable sensors are convenient for applications such as Quality Assurance/Quality Control (QA/QC), which involve repetitive testing. Note the wider electrodes, visible in Figure 6. This sensor is able to measure more deeply into the material, with the trade off of decreased sensitivity because of the smaller A/D ratio.

Figure 6
Reusable dielectric/conductivity sensor embedded in press platen

AC vs. DC Measurements

Interestingly, it is often *not* useful to measure ρ_{DC} using DC signals. The phenomenon of electrode polarization can create a blocking layer across sensor electrodes during early cure, when material is most conductive. This blocking layer acts like a capacitor and prevents the passage of DC current. In the presence of electrode polarization, dielectric data from very low excitation frequencies are distorted, as shown in Figure 7 for the cure of a graphite-epoxy prepreg.

Note the flattening of the loss peak at 10 Hz and the *dip in place of the loss peak* at 1 Hz. This distortion becomes worse at lower and lower frequencies, and with DC signals a conductive material can even appear *non-conductive*.

Besides avoiding distorted data from blocking layers, AC signals can also make measurements through a release film, which is a very thin layer of material used to prevent material from adhering to a mold or platen.

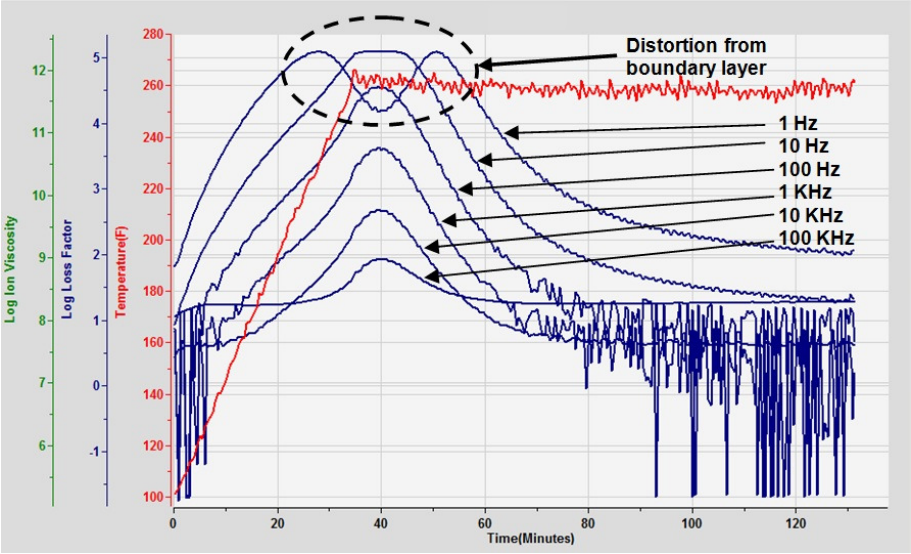


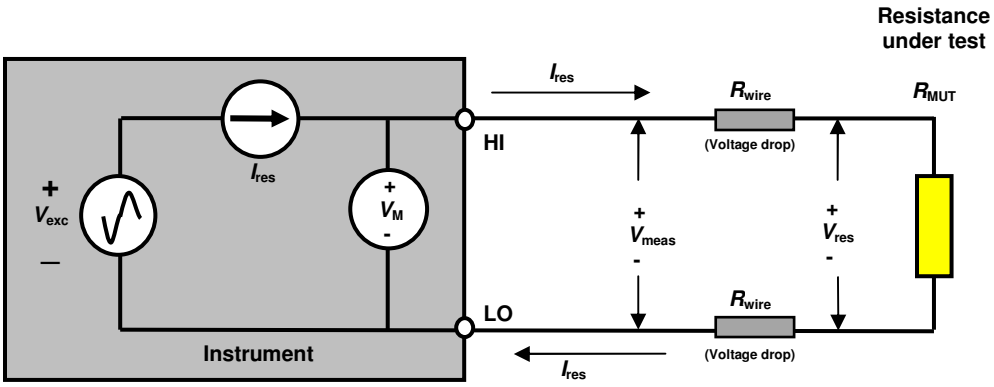
Figure 7
Distortion in loss factor data from a blocking layer

AC signals have significant advantages over DC signals. For dielectric cure monitoring, the optimum range of frequencies depends on the material and application. Extremely low frequency data require long acquisition times and are subject to distortion from electrode polarization. For most thermosets 0.1 Hz to 10 Hz is a reasonable lower limit. High frequency data tends to be dominated by dipolar rotation, which masks ion viscosity at the end of cure. For most thermosets 10 kHz to 100 kHz is a good upper frequency limit that still allows studies of dipole response.

LCR Meters and Four-Wire Connections

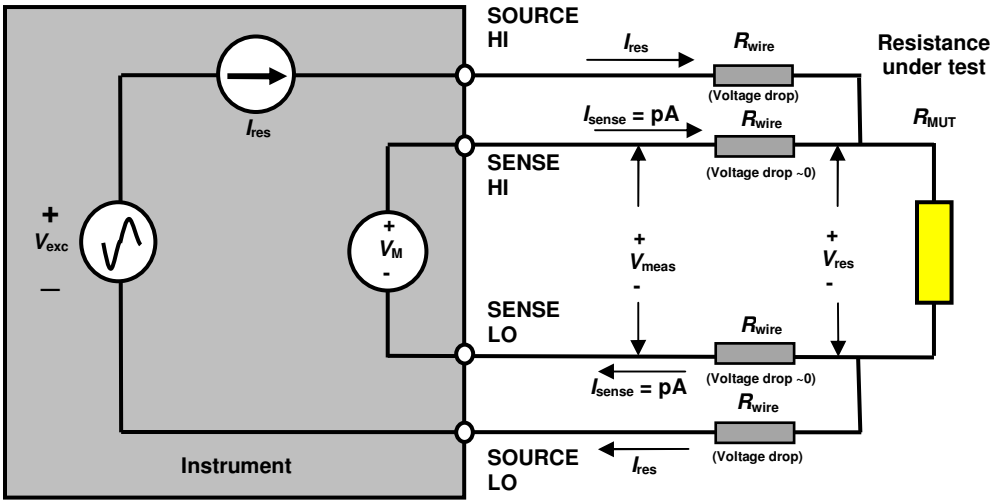
Many researchers make their own dielectric cure monitors with LCR (Inductance-Capacitance-Resistance) meters, which measure resistance and capacitance across a range of frequencies. Typical LCR meters use a four-wire, or Kelvin, connection to eliminate the effect of cable resistances, as shown in Figure 8.

Bulkier and more complex than a two wire connection, a four-wire connection is useful when the resistance under test is small (less than 10 Ω) and comparable to lead wire resistances. However, the resistances encountered with a typical sensor during thermoset cure are on the order of 10,000 Ω or more. As a result, for dielectric cure monitoring, a simpler two-wire connection may replace the cumbersome four-wire connection without loss of accuracy.



V_{meas} = Voltage measured by instrument
V_{res} = Voltage across resistor R_{MUT}
I_{res} = Current through resistor R_{MUT}

Measured resistance = $V_{meas}/I_{res} = R_{MUT} + 2(R_{wire})$



V_{meas} = Voltage measured by instrument
V_{res} = Voltage across resistor R_{MUT}
I_{res} = Current through resistor R_{MUT}

Sense current negligible so $V_{meas} = V_{res}$

Measured resistance = $V_{meas}/I_{res} = V_{res}/I_{res} = R_{MUT}$

Figure 8
Two-wire and Four-wire (Kelvin) connection for resistance measurements

Temperature Measurements

Temperature measurement, usually with a thermocouple, is an essential function for dielectric cure monitoring. At a given cure state, ion viscosity decreases as temperature increases. Knowing temperature provides additional insight into the nature of the cure and can avoid misinterpretation of data. Figure 9 shows the isothermal cure of an epoxy, in which the minimum ion viscosity occurs at time t = 0 and ion viscosity increases monotonically during cure.

In contrast, Figure 10 shows the cure of a "five-minute" epoxy, which produces an exotherm. Here temperature initially increases as curing begins, liberating heat and resulting in a decrease in ion viscosity. Eventually the reaction dominates, ion viscosity goes through a minimum then increases. Notice also how the peak exotherm occurs at the same time as the maximum slope of ion viscosity—identifying the point of maximum reaction rate. Temperature data is valuable to understanding how a material cures, and is necessary when developing a process or formulation.

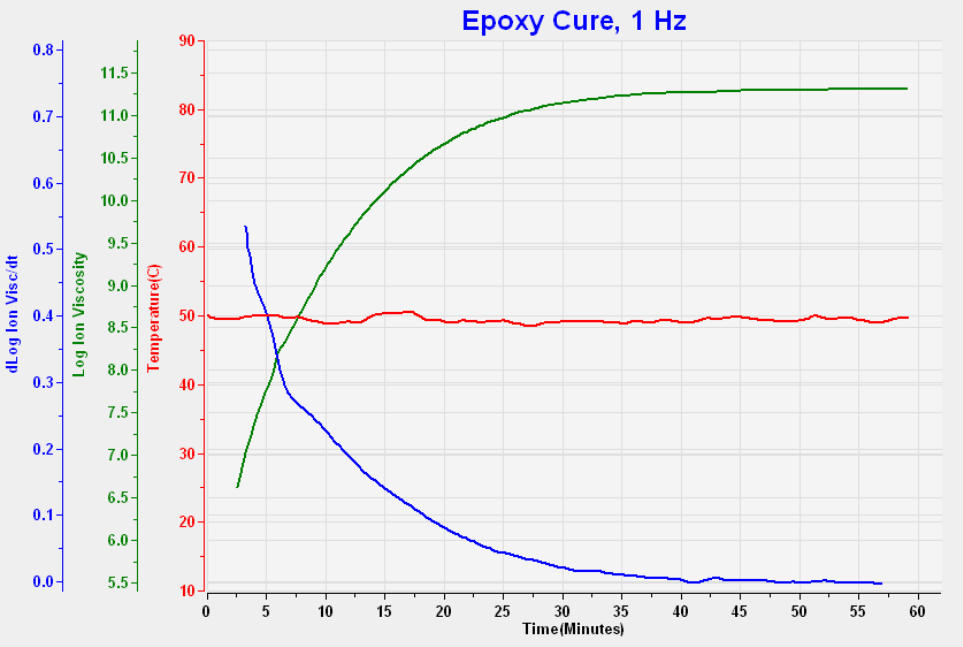


Figure 9
Isothermal epoxy cure at 50 °C

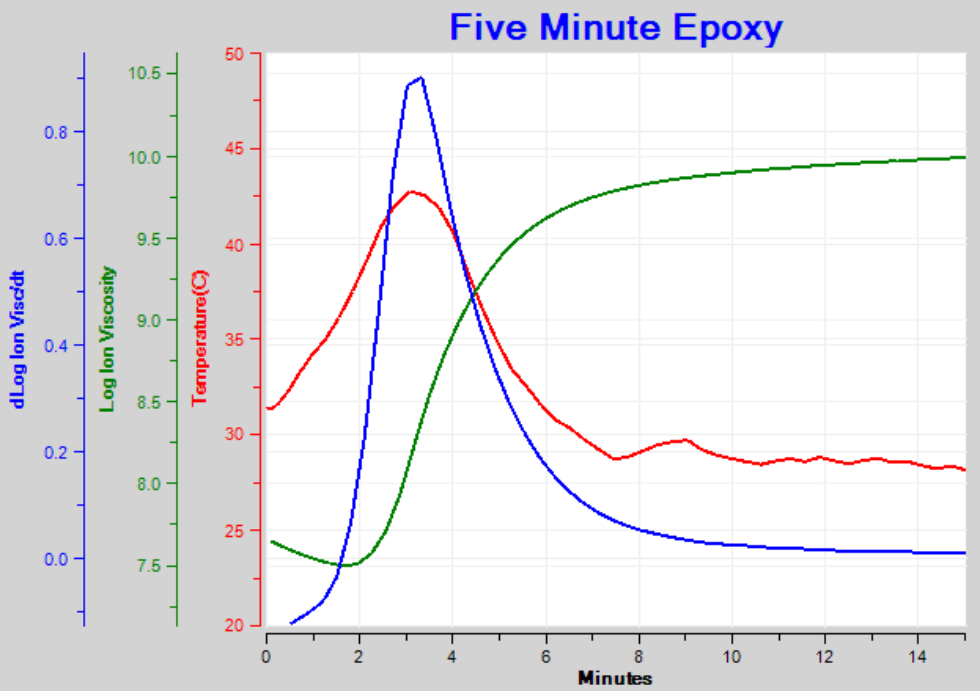


Figure 10
"Five-minute" epoxy cure with exotherm

A Dielectric Cure Monitoring System

Figure 11 shows the essential elements of a dielectric cure monitoring system. Making contact with the thermoset under test, dielectric/conductivity sensors have two general configurations, parallel plate or interdigitated electrodes. The selection of a sensor depends on the desired type of measurement, either surface or bulk, and the desired sensitivity as indicated by the *A*/*D* ratio.

Sensors connect to an instrument, and the most versatile instruments use AC signals for measurement. A wide range of excitation frequencies allow selection of an optimal frequency for observing ion viscosity, and multiple frequencies enable studies of the dipolar response. Temperature measurement is important for understanding cure, especially under non-isothermal conditions.

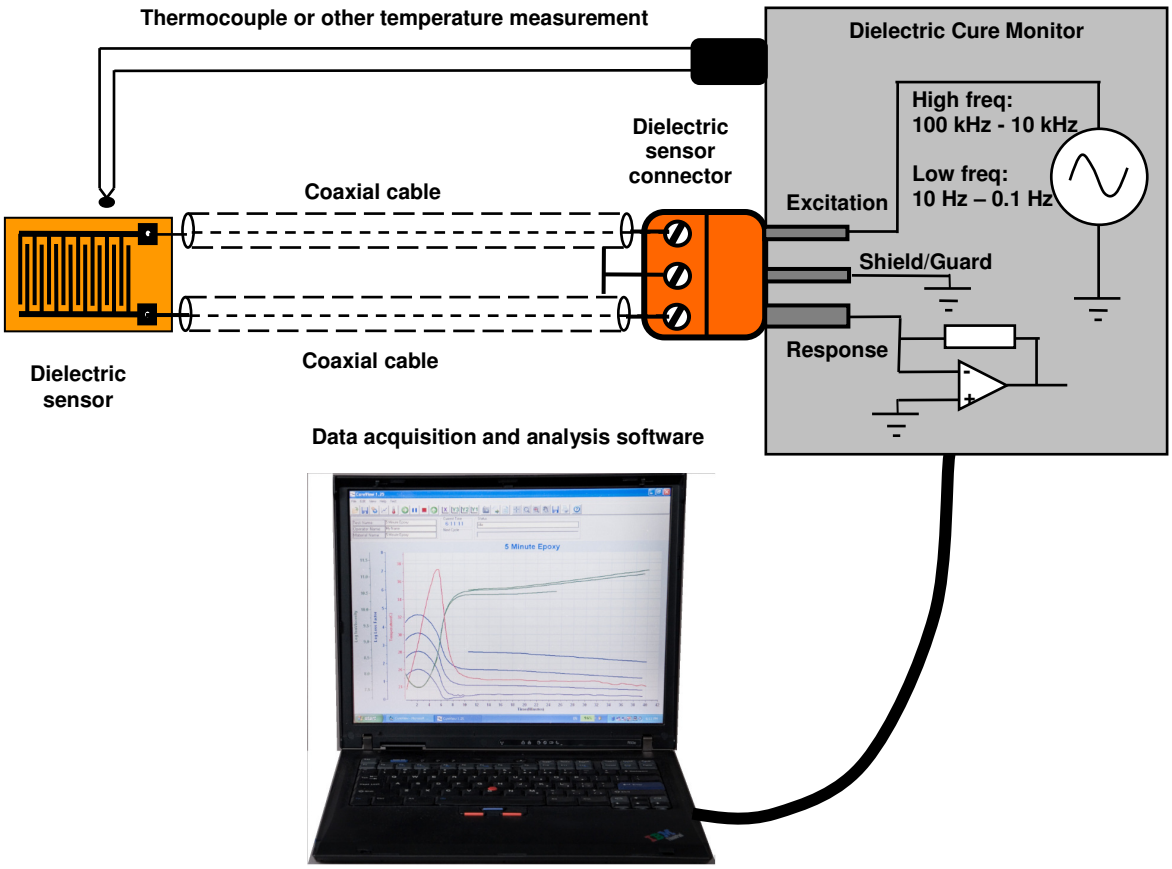


Figure 11
Essential elements of a dielectric cure monitoring system

Finally, software controls the instrument, usually through a computer connected to the dielectric cure monitor. Cure state cannot be determined from a single point measurement, but must be extracted from the change of ion viscosity and the shape of the curve over time. So software, which makes repetitive measurements, and stores and analyzes data, is crucial to the performance of the system.

Lambient Technologies LLC
649 Massachusetts Avenue, Cambridge, MA 02139
857-242-3963
www.lambient.com
info@lambient.com