Insight — Application Note 2.35

Case Study 1: Data Processing to Reduce Noise in Dielectric Measurements

Introduction

To understand the true behavior of a curing thermoset, first examine dielectric data without averaging or filtering. Data processing is often necessary for reducing noise, especially for *slope of log(ion viscosity)*, which magnifies noise in *log(ion viscosity)*. Any numerical processing, however, introduces distortion and higher degrees of processing creates greater distortion. Therefore, it is important to reduce noise with averaging or filtering that only minimally changes the underlying response.

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. 35-1) $\sigma = \sigma_{DC} + \sigma_{AC}$ (ohm^{-1} – cm^{-1})

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

(eq. 35-2) $\rho = 1/\sigma$ (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. 35-3) $IV = \rho_{DC}$ (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.**

Characteristics of thermoset Cure

In many cases the change of *log(IV)* is proportional to the change of mechanical viscosity before gelation and continues to indicate cure state even after gelation.

A plot of Ion viscosity is a simple way to characterize the progress of cure. In simplified form, Figures 35-1 and 35-2 show the behavior of a typical thermoset with one temperature ramp step and one temperature hold step.

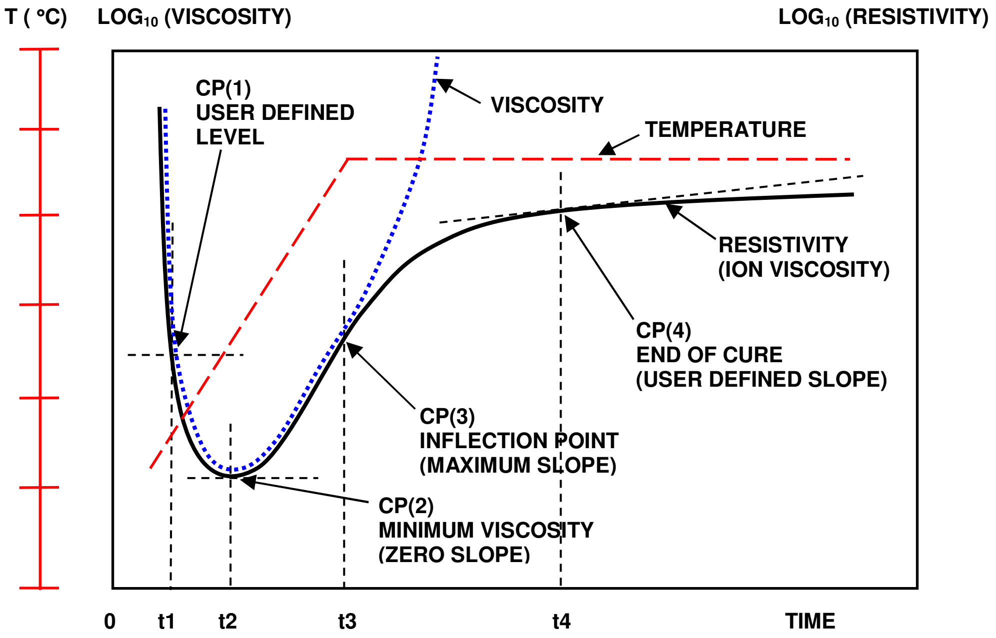


Figure 35-1
Typical ion viscosity behavior of thermoset cure during thermal ramp and hold

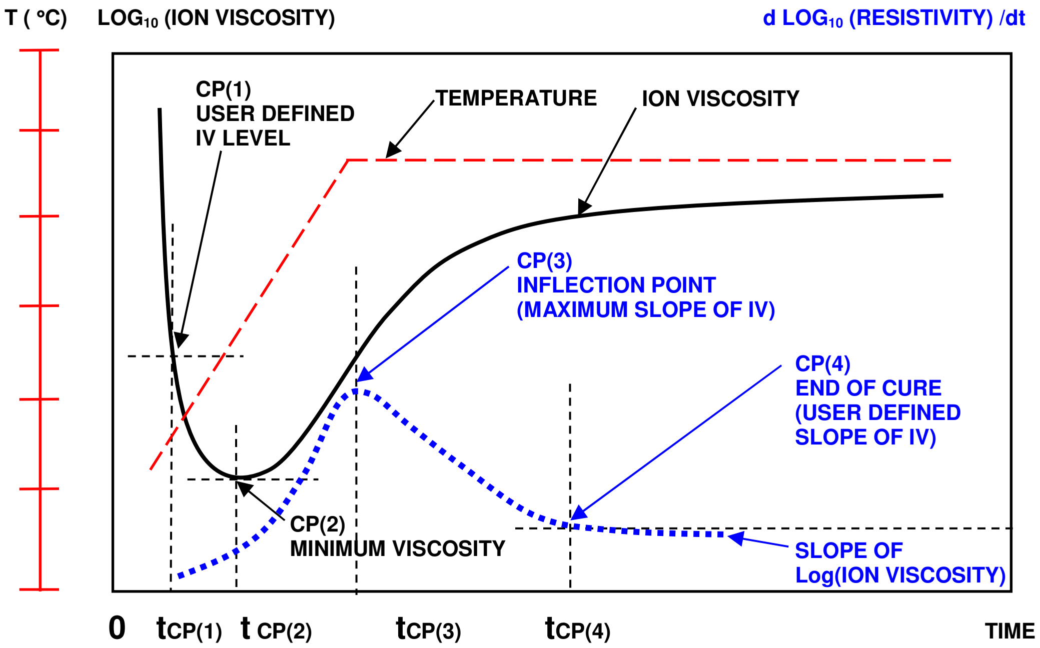


Figure 35-2
Ion viscosity curve and slope of ion viscosity of thermoset cure during thermal ramp and hold

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.

Four Critical Points characterize the dielectric cure curve:

- CP(1)—A user defined level of *log(IV)* that is typically used to identify the onset of material flow at the beginning of cure.
- CP(2)—Ion viscosity minimum, which also corresponds to the physical viscosity minimum. This Critical Point indicates the time when polymerization and the resulting increasing viscosity begin to dominate the decreasing viscosity due to heating.

- CP(3)—Inflection point, which identifies the time when the curing reaction begins to slow. CP(3) is often used as a signpost that can be associated with gelation. The height of CP(3) is a relative measure of the reaction rate.
- 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 measurement of mechanical viscosity is not possible.

Figures 35-1 and 35-2 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 35-3. In this case CP(1) either is meaningless or occurs at t = 0, immediately after the application of heat, when material flows to make contact with 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.

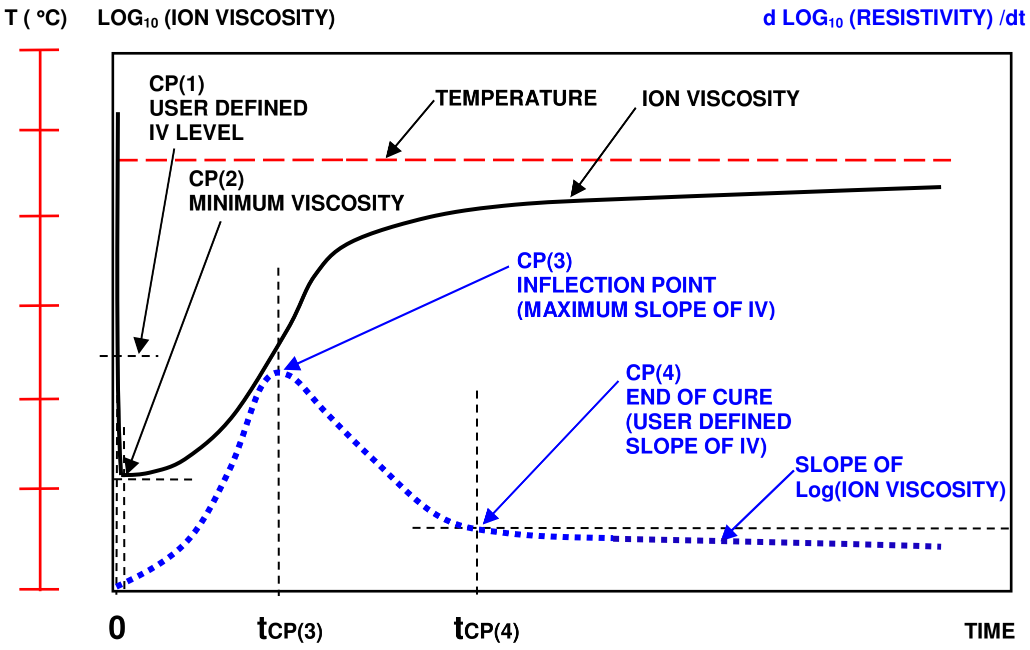


Figure 35-3
Ion viscosity curve and slope of ion viscosity of thermoset cure during isothermal processing

Distortion caused by averaging or filtering data

A sample of epoxy-fiberglass prepreg was cured at 210 °C on a Lambient Technologies Mini-Varicon sensor. A Lambient Technologies LT-451 Dielectric Cure Monitor measured the sample's dielectric properties simultaneously at several excitation frequencies. Table 35-1 lists the original noise reduction parameters.

Table 35-1
Prepreg original noise reduction parameters

Median filter	1
Sample size	3
Slope span	3
Data filter coefficient	3
Slope filter coefficient	3

The plot of *log(IV)* using these parameters is shown in Figure 35-4. *Slope* is not plotted for clarity.

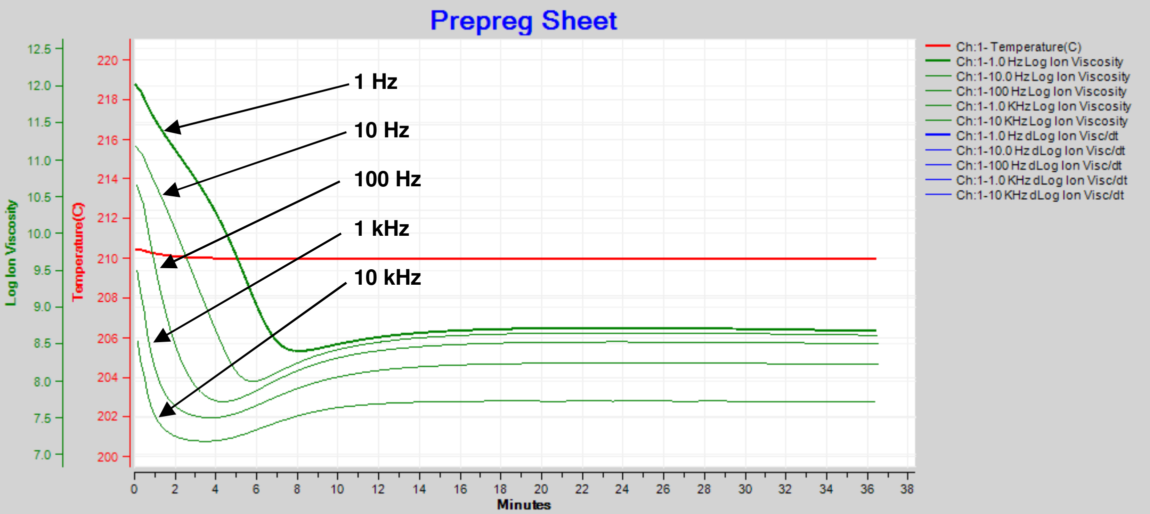


Figure 35-4
Epoxy-fiberglass prepreg cure using parameters of Table 35-1

Figure 35-4 shows 1 Hz data decreasing slowly between 0 and 8 minutes. For higher frequencies the curves show a similarly slow decrease to their respective minima but without the overlap characteristic of frequency independent resistivity in early cure. These curves do not resemble Figure 35-3, which would be expected for an isothermal cure, because excessive averaging and filtering distorted the data.

Data should first be examined without numerical processing to see the actual results, including noise. Table 35-2 lists recommended values for initial analysis.

Table 35-2
Minimal noise reduction parameters

Median filter	**1**
Sample size	**1**
Slope span	**8**
Data filter coefficient	**0**
Slope filter coefficient	**0**

Median filter = 1 disables the median filter. **Sample size** = 1 disables averaging of data, including *log(IV)*. **Slope span** = 8 is a typical value for reasonable noise reduction in the calculation of slope of *log(IV)*. **Data filter coefficient** = 0 disables filtering of data and **slope filter coefficient** = 0 disables filtering of *slope*.

The plot of data using these parameters is shown in Figure 35-5. Slope is not shown for clarity.

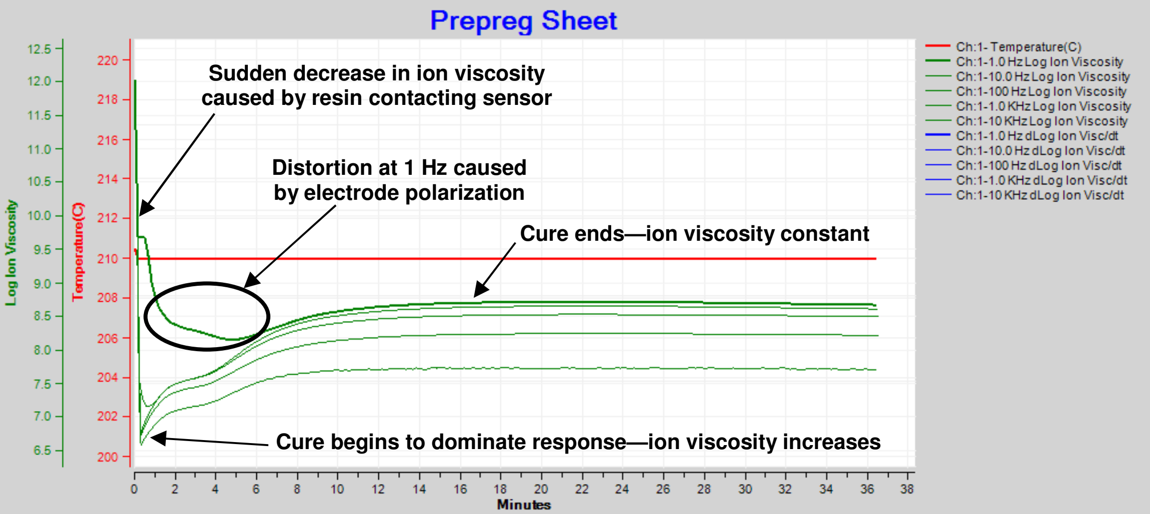
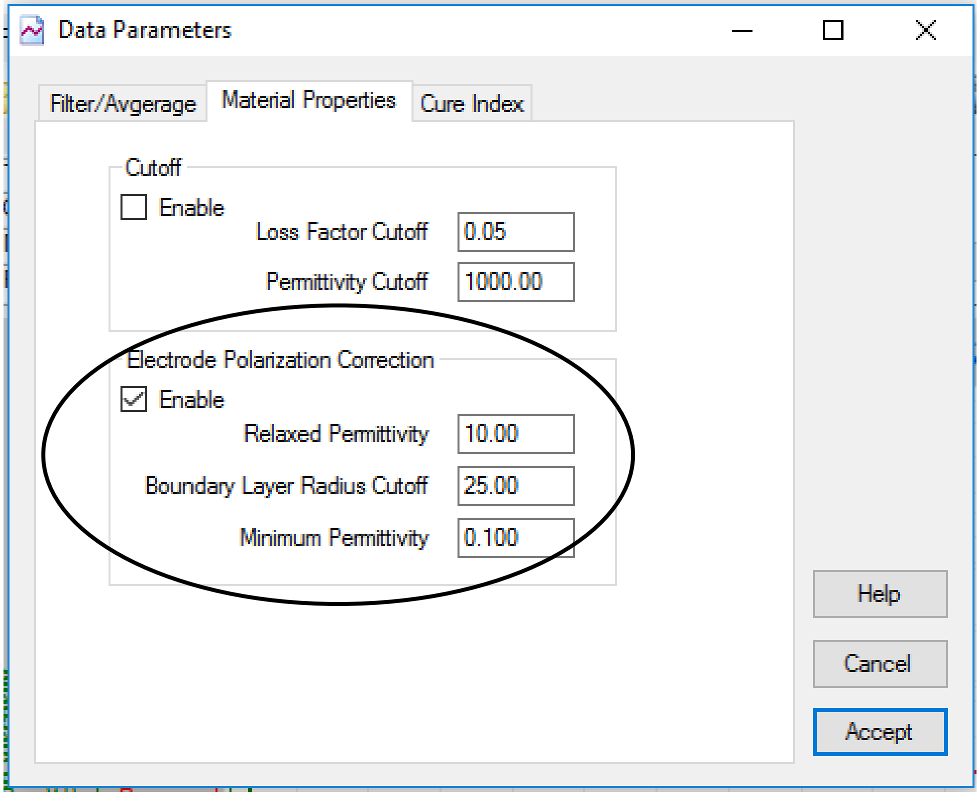


Figure 35-5
Prepreg data plotted with minimal distortion

Figure 35-5 shows the real behavior, with *log(IV)* for 10 Hz, 100 Hz, 1 kHz and 10 kHz decreasing very rapidly at the start of the test. *Log(IV)* for 1 Hz does not follow the higher frequencies because of distortion caused by electrode polarization. Electrode polarization is a common effect at low frequencies when a material is very conductive—usually around the viscosity minimum. Except for the 1 Hz data, the *log(IV)* curves now resemble Figure 35-3, as expected for an isothermal cure.

In some cases Lambient Technologies' CureView software can correct distortion caused by electrode polarization. To fix the data, check the box to enable **Electrode Polarization Correction** in the **Materials Properties** window, as shown in Figure 35-6.

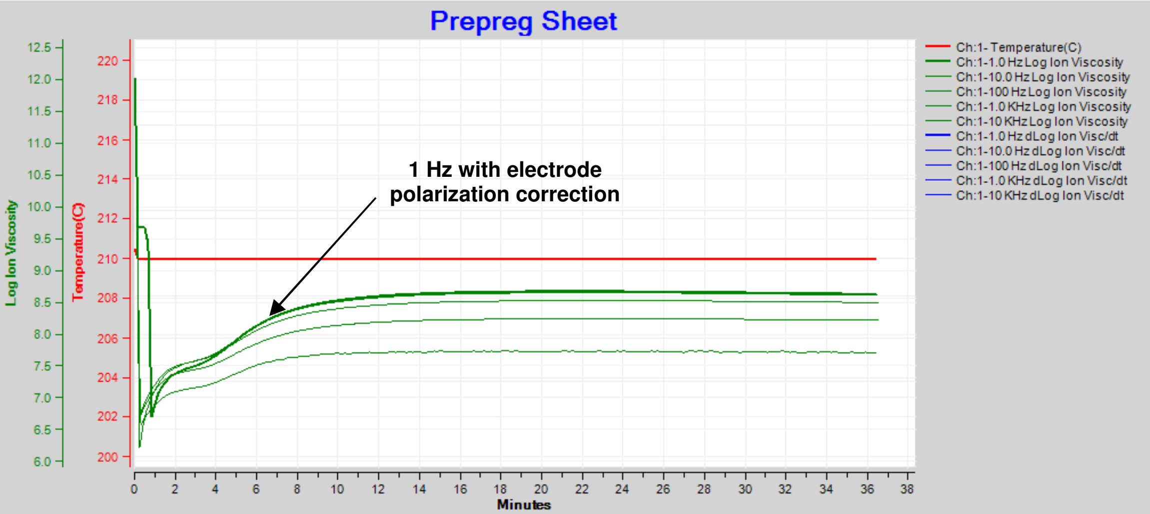


Cutoff
☐ Enable
Loss Factor Cutoff 0.05
Permittivity Cutoff 1000.00

Electrode Polarization Correction
☑ Enable
Relaxed Permittivity 10.00
Boundary Layer Radius Cutoff 25.00
Minimum Permittivity 0.100

Figure 35-6
Data Parameters window showing option for
Electrode Polarization Correction

Figure 35-7 shows the prepreg data with minimal distortion and electrode polarization correction. Note how ion viscosity during early cure for 1 Hz now follows ion viscosity for the higher frequencies.



1 Hz with electrode polarization correction

Figure 35-7
Prepreg plotted with minimal distortion and electrode polarization correction

Figure 35-7 shows the 1 Hz and 10 Hz curves closely overlap, indicating the measurement of frequency independent resistivity—which is true ion viscosity. Either 1 Hz or 10 Hz would be good frequencies for observing the cure state of this prepreg. Figure 35-8 shows the resulting 1 Hz *log(IV)* and *slope*.

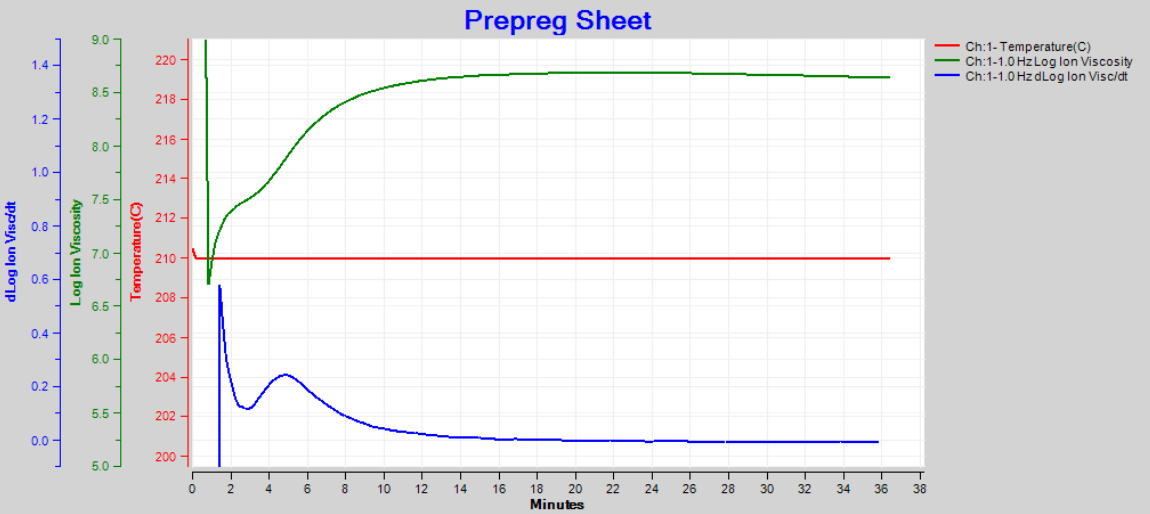
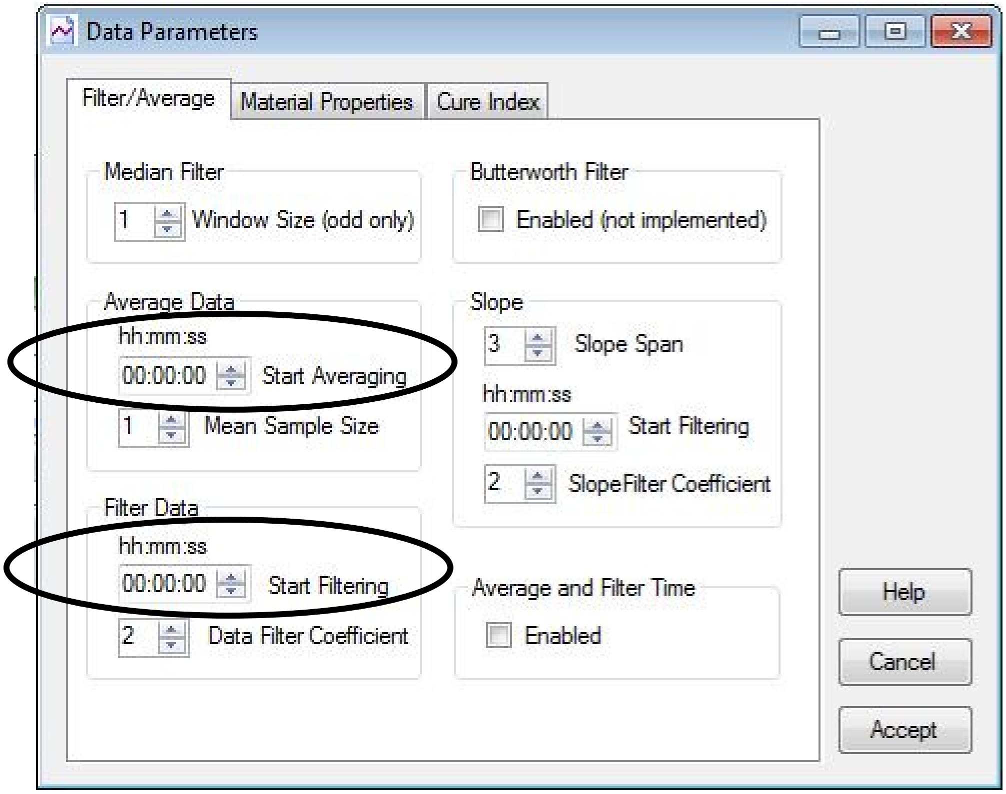


Figure 35-8
Prepreg data showing true behavior of 1 Hz *log(IV)* and slope (Rescaled for clarity)

These curves happen to have very little noise and do not require additional averaging or filtering. In the general case, if desired, processing to reduce noise may be used as long as distortion is minimized.

CureView version 1.45 and later has the option to specify the start of data averaging and filtering, as shown in Figure 35-9. This feature suspends the noise reduction algorithms until after the selected time.



Median Filter
1 Window Size (odd only)

Butterworth Filter
☐ Enabled (not implemented)

Average Data
hh:mm:ss
00:00:00 Start Averaging
1 Mean Sample Size

Slope
3 Slope Span
hh:mm:ss
00:00:00 Start Filtering
2 SlopeFilter Coefficient

Filter Data
hh:mm:ss
00:00:00 Start Filtering
2 Data Filter Coefficient

Average and Filter Time
☐ Enabled

Figure 35-9
Filter/Average parameter window showing inputs specifying averaging and filtering start times

Ion viscosity may change rapidly at the beginning of a test, as shown between 0 and 2 minutes in Figure 35-10, when material suddenly contacts the sensor or when material quickly becomes fluid from heating. Signal levels are typically high during early cure, with accompanying low noise levels. As a result, averaging or filtering is usually not necessary during this time.

As seen earlier in Figure 35-4, when *log(IV)* changes rapidly, averaging or filtering starting at $t = 0$ significantly distorts the data and may cause misinterpretation of the actual state of cure.

For this example, selecting a start time of 2 minutes for averaging or filtering avoids the distortion of Figure 35-4 while still reducing noise in later cure, when it is more likely to occur. Processing the data in this way allows a more accurate representation of how the material cures.

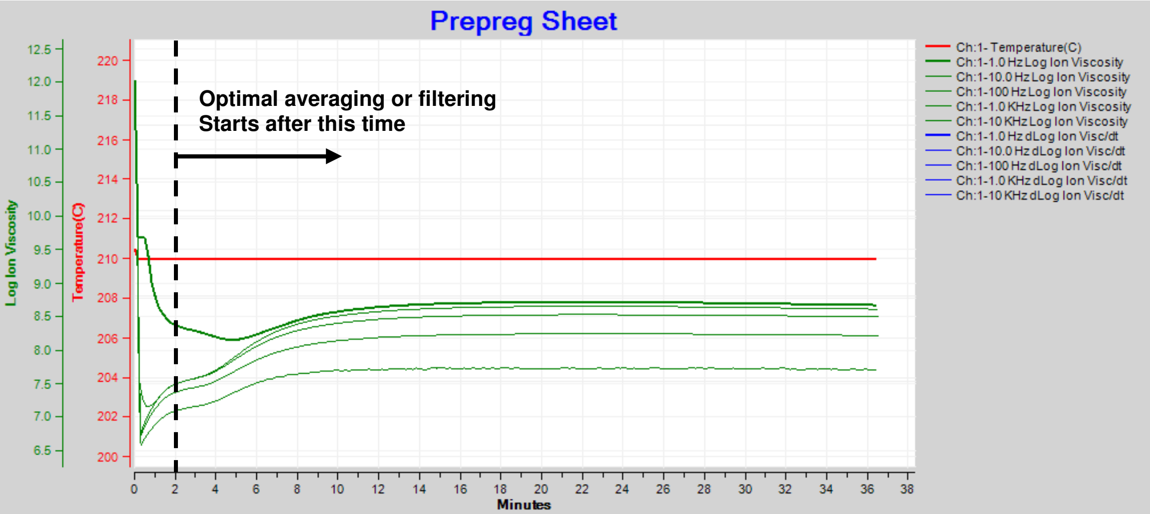


Figure 35-10

***Log(IV)* of curing prepreg, showing delayed start time for averaging and filtering to avoid distortion**

Conclusion

When raw ion viscosity data are examined before additional numerical processing, the underlying behavior of the curing material is visible. This information should be used as the reference when applying averaging or filtering to smooth the *log(IV)* and *slope* curves.

Excessive averaging or filtering can distort the ion viscosity behavior and cause misinterpretation of cure state, especially at the beginning of cure when ion viscosity may change quickly.

Conversely, appropriate use of averaging or filtering allows observation of the true progress of cure while reducing noise at the same time.

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