



Insight — Application Note 2.27

Dielectric Cure Monitoring of Polyurethane

Introduction

Lambient Technologies studied room temperature cures of a polyurethane resin with three different catalysts. An LT-451 Dielectric Cure Monitor made measurements during each test at excitation frequencies from 0.1 Hz to 100 kHz for 24 to 36 hours.

The change in ion viscosity, which is frequency independent resistivity, is often proportional to mechanical viscosity before gelation and proportional to modulus after gelation. Used properly, ion viscosity is a useful probe of cure state. Ion viscosity at room temperature is relatively low, however, and the effects of dipole rotation dominate the dielectric response for much of these cures over a range of frequencies. Therefore, it is important to know when valid ion viscosity may be extracted from dielectric data.

When dipole loss peaks are visible in the data, it is feasible to use dipole relaxation times to assess cure state.

Tests showed both the change of $\log(\text{ion viscosity})$ and the change of $\log(\text{dipole relaxation time})$ increase proportionally with $\log(\text{cure time})$, allowing:

- Measurement of cure rate by the slope of $\log(\text{ion viscosity})$ vs. $\log(\text{time})$
- Measurement of cure rate by the slope of $\log(\text{dipole relaxation time})$ vs. $\log(\text{time})$
- Prediction of isothermal cure state by using cure rate information

Definitions

This report presents and discusses *loss factor* (ϵ''), which is defined as:

$$\text{(eq. 1)} \quad \epsilon'' = \sigma / \epsilon_0 \omega \quad \text{(unitless)}$$

Where:

σ = conductivity ($\text{ohm}^{-1} - \text{cm}^{-1}$)

ϵ_0 = permittivity of free space = 8.85×10^{-14} F/cm

ω = angular frequency = $2\pi f$ (radians/sec)

f = excitation frequency (Hz)

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 add as expressed below:

$$(eq. 2) \quad \sigma = \sigma_{DC} + \sigma_{AC} \quad (\text{ohm}^{-1} - \text{cm}^{-1})$$

Consequently, loss factor has components due to mobile ions (frequency *independent* conductivity) and dipole rotation (frequency *dependent* conductivity):

$$(eq. 3) \quad \epsilon'' = (\sigma_{DC} / \epsilon_0 \omega) + (\sigma_{AC} / \epsilon_0 \omega)$$

Dipole rotation has a relaxation time τ , which is a measure of polymer chain length and crosslink density. The frequency of a peak in loss factor determines the dipole relaxation time, given by:

$$(eq. 4) \quad \tau = 1/\omega \quad (\text{sec})$$

Where:

ω = angular frequency of loss peak = $2\pi f$ (radians/sec)

f = excitation frequency of loss peak

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

$$(eq. 5) \quad \rho = 1/\sigma \quad (\text{ohm-cm})$$

From its relationship to conductivity, resistivity also has both frequency independent (ρ_{DC}) and frequency dependent (ρ_{AC}) components. Polymer chain length and crosslink density, which determine degree of cure, affect both mechanical viscosity and the movement of ions. Therefore degree of cure influences 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:

$$(eq. 6) \quad IV = \rho_{DC} \quad (\text{ohm-cm})$$

Procedure

For each test the polyurethane resin and selected catalyst were mixed in a 1:1 ratio by weight and poured on a Mini-Varicon sensor and a type J thermocouple. An LT-451 Dielectric Cure Monitor measured dielectric properties and temperature at 30 second intervals for 24 to 36 hours using 0.1, 1 Hz, 10 Hz,

100 Hz, 1 kHz, 10 kHz and 100 kHz excitation frequencies. Lambient Technology's CureView software acquired and stored the data, and performed post-analysis and presentation of the data.

Results

The ion viscosity of a thermoset, which is frequency independent resistivity, is often very low for much of a cure at room temperature. Dipole relaxation may dominate the dielectric response over a range of frequencies in the later stages, as shown in the 10 Hz-100 kHz resistivity curves of Figure 1. Tests show that for this polyurethane with all three catalysts, ion viscosity dominates throughout the cure only for measurements at 1 Hz or lower. So ion viscosity can probe cure state only with excitation frequencies of 1 Hz or lower.

When dipole effects dominate, loss factor data presents an alternate means of determining cure state. By equation 3, total loss factor is a simple sum of factors with frequency independent and frequency dependent conductivity. Therefore, distinguishing the effects of ion mobility and dipolar rotation is easier when examining loss factor.

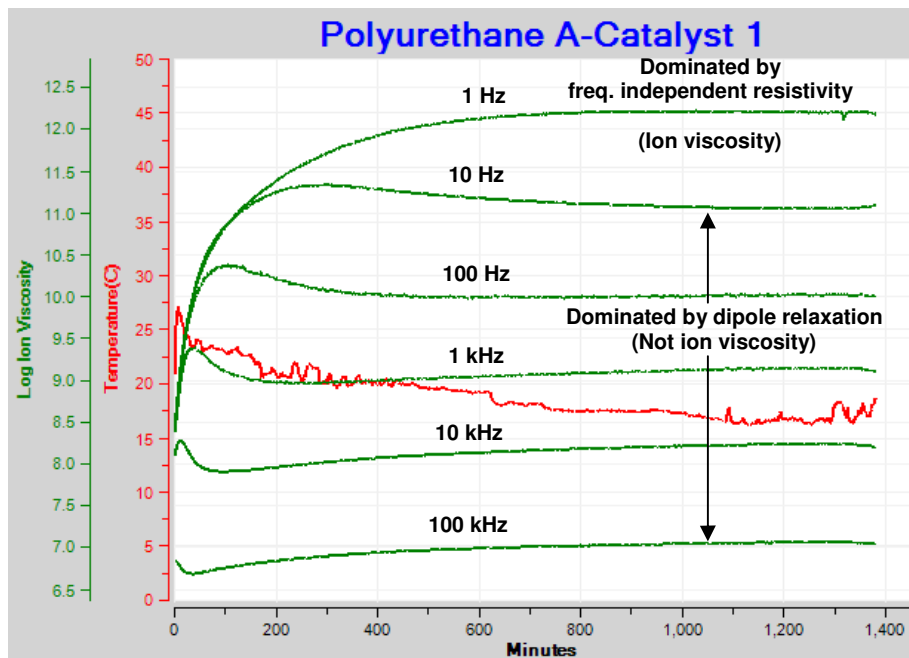


Figure 1
Resistivity of PU resin A (plotted against log(ion viscosity) axis)

Figures 2, 3 and 4 show loss factor curves for polyurethane resin A and three different catalysts. Close examination of these data reveals differences in cure rate among the tests.

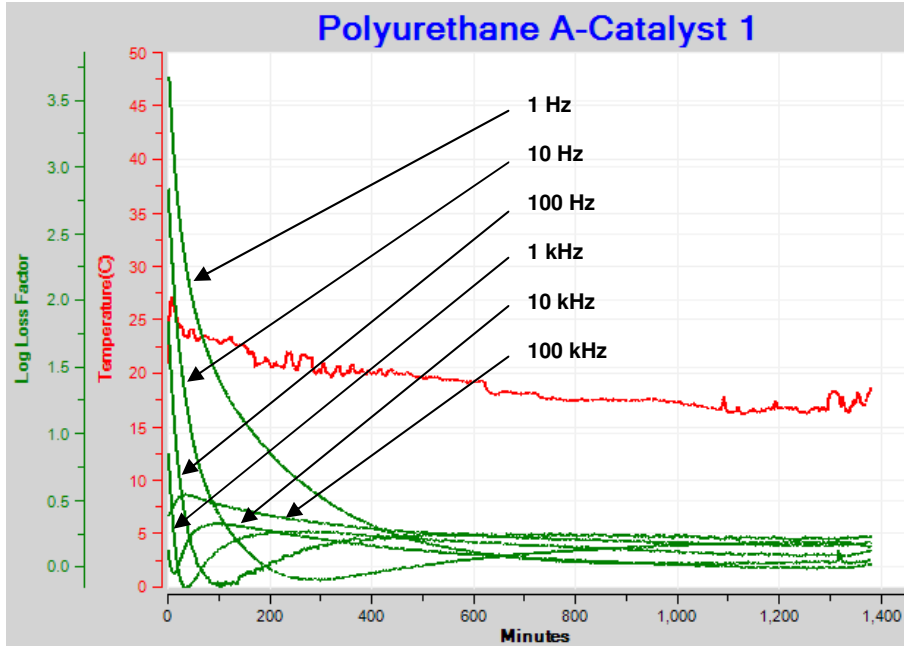


Figure 2
Loss factor of resin A-catalyst 1

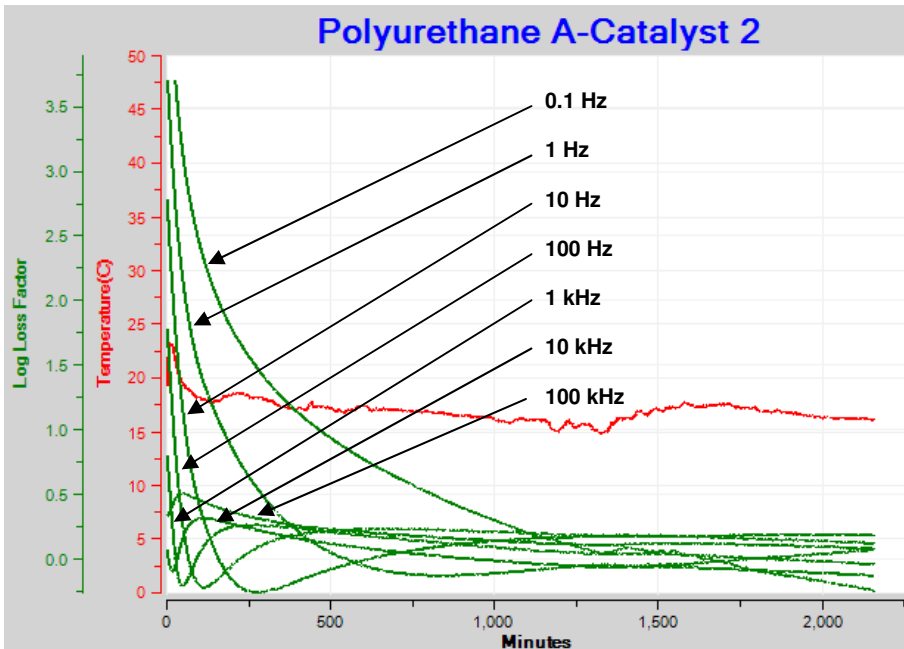


Figure 3
Loss factor of resin A-catalyst 2

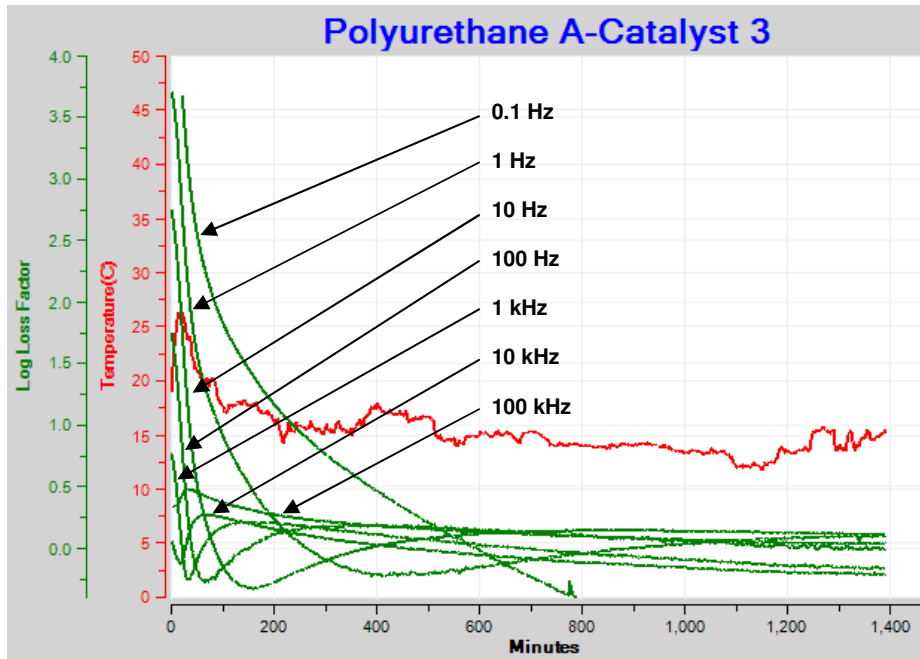


Figure 4
Loss factor of resin A-catalyst 3

Figure 5 shows ion viscosity vs. cure time for these tests. Ion viscosity was extracted from 1 Hz loss factor data. $\log(\text{ion viscosity})$ plotted against $\log(\text{cure time})$ has a linear relationship that indicates a simple kinetic model governs the cures.

Plots deviate from straight lines when dipole relaxation dominates the dielectric response—ion viscosity does not dominate and cannot reveal cure state after this point. It is possible to extract valid ion viscosity (frequency independent resistivity, ρ_{DC}) from dielectric properties at a lower excitation frequency, but at the expense of much longer measurement times.

Figure 6 shows dipole relaxation time vs. cure time for the same tests. Increasing crosslink density affects both ion mobility and dipole rotation, so it is not surprising to also see a linear relationship in $\log(\text{relaxation time})$ when plotted against $\log(\text{cure time})$.

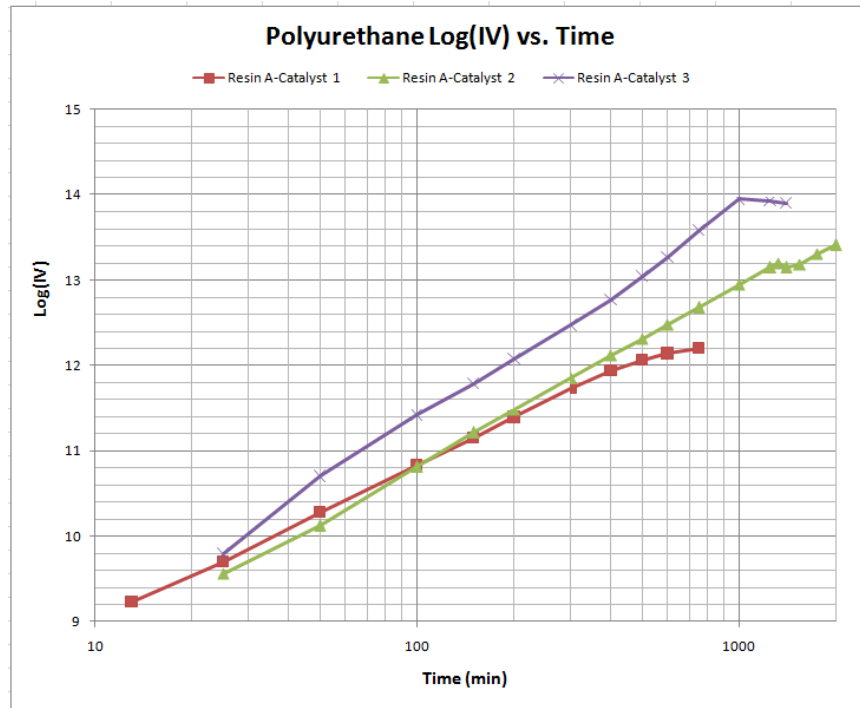


Figure 5
Ion viscosity vs. time for PU resin A and catalysts 1, 2 and 3

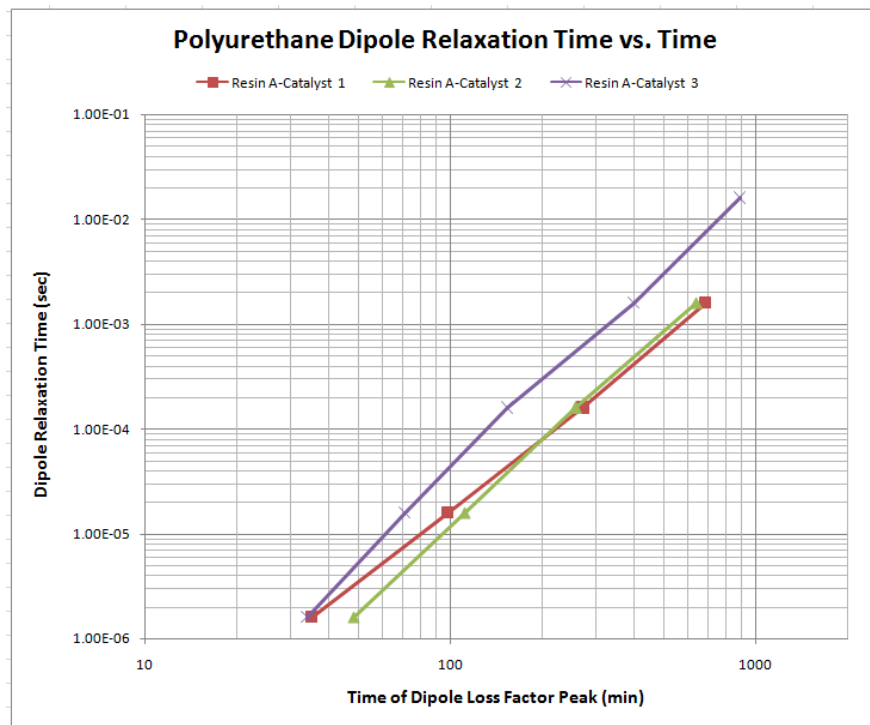


Figure 6
Dipole relaxation time vs. time for PU resin A and catalysts 1, 2 and 3

Table 1 lists slopes for the data of Figures 5 and 6, showing clear differences among the three cures with different catalysts. Figure 7 plots the data of Table 1 and shows the correlation between the slope of $\log(\text{ion viscosity})$ and the slope of $\log(\text{relaxation time})$. Note that the slope of $\log(\text{ion viscosity})$ increases with the slope of $\log(\text{dipole relaxation time})$. This relationship is expected if cure state simultaneously affects *both* ion mobility and dipole rotation.

Table 1
Ion viscosity slope and dipole relaxation time slope

	X	Y
	Log(IV) Slope	Dipole Slope
Resin A-Catalyst 1	1.785	2.322
Resin A-Catalyst 2	2.113	2.665
Resin A-Catalyst 3	2.498	2.802

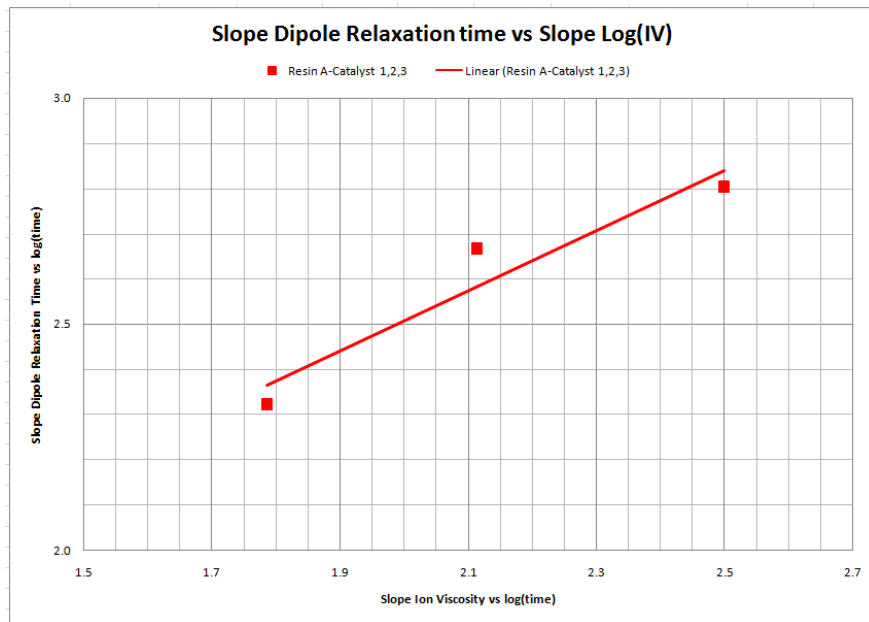


Figure 7
Correlation between slope of dipole relaxation time change and ion viscosity change

Conclusion

Tests of a polyurethane resin with three different catalysts showed that both the change of log(ion viscosity) and the change of log(relaxation time) increase proportionally with log(cure time). As a result, it is possible to:

- Measure cure rate by the slope of log(ion viscosity) vs. log(time)
- Measure cure rate by the slope of log(relaxation time) vs. log(time)
- Predict isothermal cure state by using cure rate information

Dielectric cure monitoring can measure cure state over the entire cure. The ion viscosity and dipole relaxation time give real time information about reaction kinetics that no other thermal analysis method, such as DMA or DSC, can provide.



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