Insight — Application Note 3.32

Real-Time Monitoring of H.B. Fuller U3345 UV-Cured Adhesive

Abstract

High speed dielectric cure monitoring (DEA) has the unique ability to measure cure in real-time under actual process conditions, which is valuable for studying materials that polymerize in seconds, such as H.B. Fuller U3345[1], a UV curable, modified acrylate adhesive. Under UV irradiation, U3345 reacts rapidly and exhibits dynamic behavior that would be difficult or impossible to see with other methods. The utility of dielectric cure monitoring allows the study of degree of cure and the response of UV-curable materials to irradiance and exposure.

Dielectric cure monitoring

Dielectric cure monitoring, also known as *Dielectric Analysis* (DEA), measures a polymer's resistivity (ρ) and permittivity (ε'), which are a material's dielectric properties. Resistivity itself has a frequency independent (ρ_{DC}) component due to the flow of mobile ions and a frequency dependent (ρ_{AC}) component due to the rotation of stationary dipoles.

Although often called DC resistivity, frequency independent resistivity actually extends across a range of frequencies that includes DC (0 Hz). Because a thermoset's degree of cure affects both mechanical viscosity and frequency independent resistivity, the term *ion viscosity* was coined to emphasize the relationship between the two. Ion viscosity (*IV*) is therefore defined as:

(eq. 1) $$IV = \rho_{DC} \quad \text{(ohm-cm)}$$

This paper presents and discusses data for log(ion viscosity), which will be called *log(IV)* for brevity. Because ion viscosity correlates with cure state, it is a useful material probe of epoxies, polyurethanes, polystyrenes and especially UV-cured resins.

Dielectric 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. A common configuration is the interdigitated electrode, such as the example of Figure 1, the Quarto-Varicon[2] dielectric sensor used in this study. This sensor is constructed as a thin polyimide flex circuit with an electrode width and separation of 100 microns.

As a rule of thumb, interdigitated electrodes with the same width and separation measure to a depth approximately equal to the electrode width. Consequently, the sensor used in this study makes a very localized measurement only 100 microns into the sample.
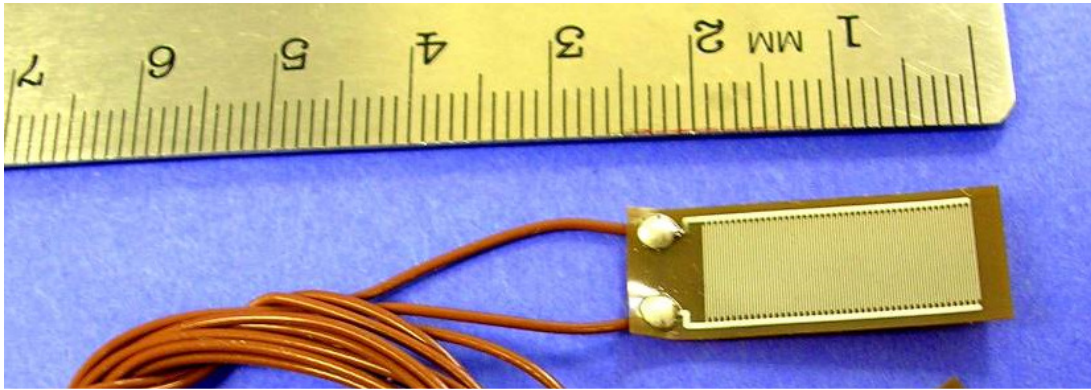
Figure 1
Dielectric sensor with interdigitated electrodes

For UV curing, interdigitated sensors may be placed within a sample and away from the surface to avoid any confounding effects from oxygen inhibition, which prevents cure at the interface with the atmosphere.

Ultraviolet light source

The SunSpot 2 UV/Visible Light Curing System[3] was the UV source for this study. The high-power output from its arc lamp is wide-band and intensity at the end of the light guide is typically >18,000 mW/cm^2 in UVA (320-390 nm), with adjustable settings from I = 0 to I = 10 for intensity values ranging from 61% to 100%, respectively.

This UV source uses both a dichroic filter and mirror to greatly reduce IR transmission through the light guide. Absorption of radiation in the remaining visible/UVA/UVB/UVC wavelengths nevertheless can produce considerable heating of samples at high intensities.

Procedure

The experimental set-up is shown in Figure 2. At the end of the light guide, a collimator concentrated the light and projected it onto a platform for the sample. Each test used a standoff of 15 cm, 20 cm, 38 cm or 48 cm between the collimator and platform. UV source intensity was set to I = 0, 5 or 10, corresponding to 61%, 83% or 100% of full intensity, respectively. This combination of standoffs and settings allowed an 18:1 range of irradiance at the sensor.
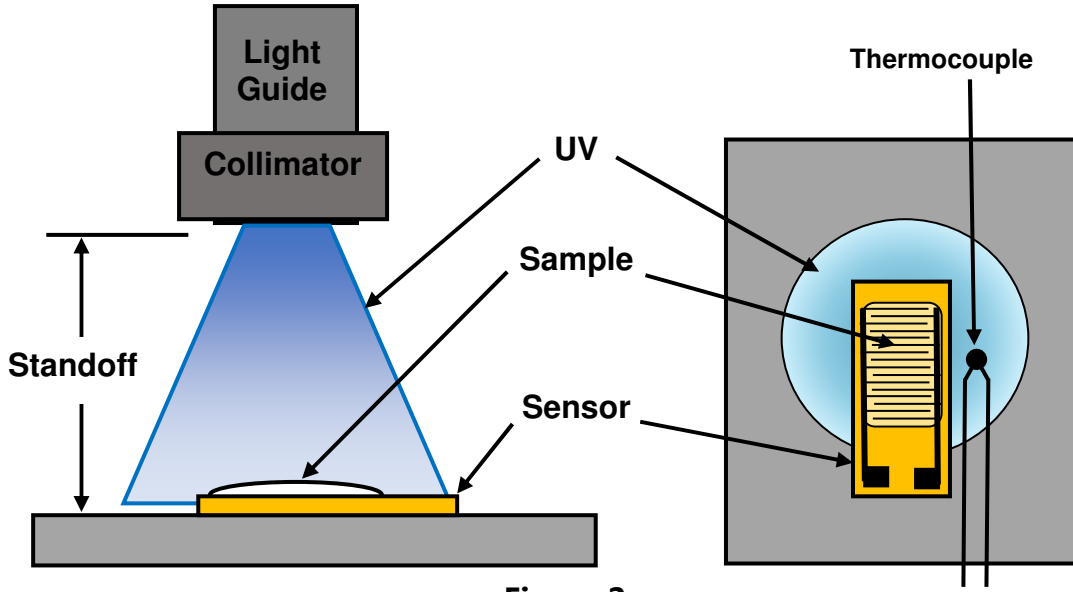
Figure 2
Test set-up for UV cure

For each test, U3345 UV-curable adhesive was applied to a new dielectric sensor, resulting in a sample 7 mm x 20 mm in area and approximately 1 mm thick. The sample was placed on the platform at the estimated center of the irradiance profile. A thermocouple beside the sensor enabled temperature measurements during and after exposure.

Lack of a UV meter prevented direct measurement of irradiance, so it was estimated from the rising and falling temperature profile during a test. These data were used to model a hypothetical thermal source for each exposure. The temperature of this hypothetical source was assumed to be proportional to actual irradiance at the sample, and was used to derive the relative irradiances of Table 1. Without absolute UV power measurements, irradiance during a test is given a relative value from Table 1 to enable comparisons among results.

Table 1
Relative irradiance

Standoff	UV Source Intensity Setting		
	I = 0 (61%)	I = 5 (83%)	I = 10 (100%)
15 cm	10.9	14.8	17.8
20 cm	9.3	12.7	15.3
38 cm	2.1	2.9	3.4
48 cm	1.0	1.4	1.6

An LT-631 High-Speed Dielectric Cure Monitor[4] measured ion viscosity at a rate of 50 ms/data point with an excitation frequency of 100 Hz. To ensure capture of the entire cure, the UV source was turned on five seconds after the start of data acquisition.

Cure from a single, low intensity exposure

After a single exposure of U3345 to brief, low intensity UV, the ion viscosity and temperature were measured for 60 seconds. Standoff was 48 cm and the UV source intensity setting was I = 0 with an exposure time of one second. From Table 1 the relative irradiance = 1.0.
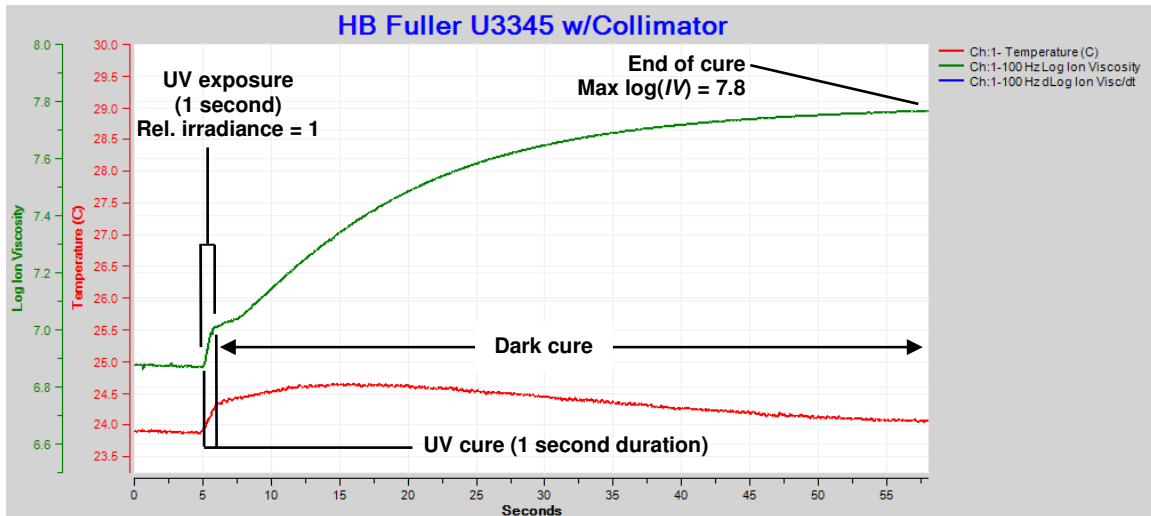
Figure 3
Ion viscosity of U3345, single exposure

Ion viscosity data from this test, shown in Figure 3, reveals three events:

1. UV cure during exposure: At constant or near-constant temperature, ion viscosity (*IV*) increases as degree of cure increases. Furthermore, the change in log(*IV*) often has a linear or near-linear relationship with the change in degree of cure as measured by glass transition temperature.[5,6,7] Before irradiation the U3345 is at 0% degree of cure and the initial log(*IV*) = 6.9.

During the one-second exposure, ion viscosity suddenly increases in response to the activated photoinitiators, which start the curing process. Temperature also increases slightly due to absorption of light.

2. Dark cure after exposure: The activated photoinitiators continue to drive cure, indicated by the increase in ion viscosity for a considerable time after UV exposure ends. As the photoinitiators are consumed, the cure process slows and ion viscosity asymptotically approaches a constant value.

3. End of cure: The asymptotic value of log(*IV*) = 7.8 at the end of cure, which occurs at approximately 60 seconds after exposure.

Cure from cumulative exposures

To investigate the effect of successive exposures, three samples of U3345 at different standoffs were exposed for one second at a time, with UV source intensity = 0, at one-minute intervals. The samples, which had standoffs of 48 cm, 38 cm and 20 cm, have relative irradiances of 1.0, 2.1 and 9.3, respectively, with each exposure. The results are shown in Figure 4.
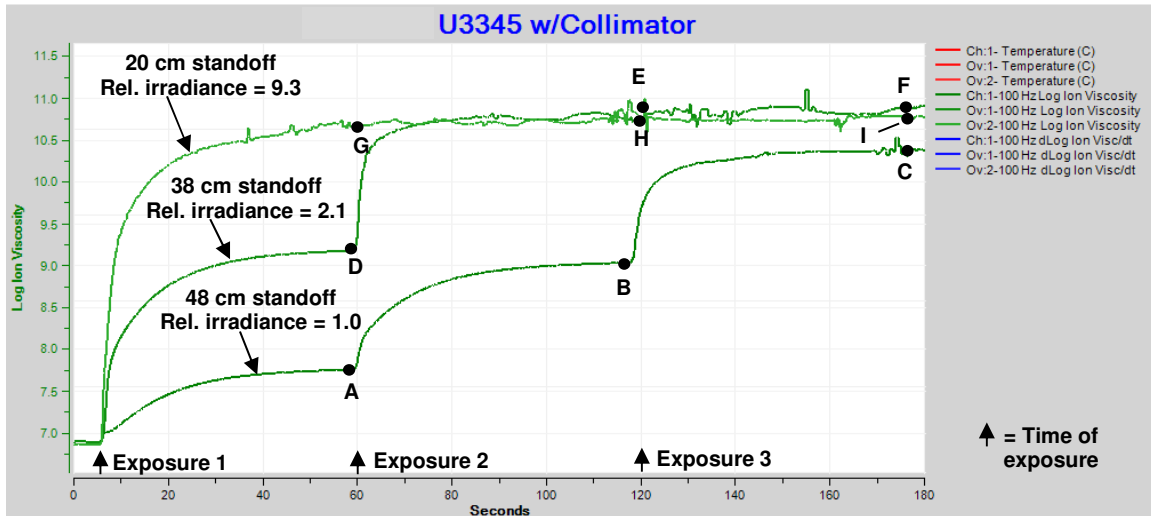
Figure 4
Ion viscosity of U3345, multiple exposures of one second each

The plot of Figure 3 is actually the first minute of the data in Figure 4 for a 48 cm standoff. Although the reaction in Figure 3 essentially ends after about 60 seconds, it is clear from Figure 4 that cure is incomplete at this point. Furthermore, the data show that maximum log(*IV*) after each incremental cure is proportional to the cumulative exposure. In each case, higher ion viscosity also corresponds to higher degree of cure.

The data show that two exposures at relative irradiance = 2.1 are sufficient to reach a plateau of log(*IV*) ~10.8, while only one exposure at relative irradiance = 9.3 is necessary. Also, once the plateau is reached, additional exposures do not change the ion viscosity level, indicating the U3345 has reached 100% degree of cure.

Table 2 lists the relative irradiances and cumulative relative exposures for each test. Max log(*IV*) is the value at the end of cure following each exposure and is indicated in Figure 4 as well as listed in Table 2. Figure 5 plots maximum log(*IV*) versus cumulative relative exposure.

Table 2
Standoff distances, relative irradiances and relative exposures

Standoff	Exposure Number	Relative Irradiance at Sensor	Cumulative Relative Exposure	Max Log(*IV*)	Degree of Cure	Point
48 cm	1	1.0	1.0	7.75	20%	A
48 cm	2	1.0	2.0	9.04	55%	B
48 cm	3	1.0	3.0	10.37	90%	C
38 cm	1	2.1	2.1	9.18	58%	D
38 cm	2	2.1	4.2	10.87	100%	E
38 cm	3	2.1	6.3	10.87	100%	F
20 cm	1	9.3	9.3	10.79	100%	G
20 cm	2	9.3	18.6	10.79	100%	H
20 cm	3	9.3	27.9	10.79	100%	I
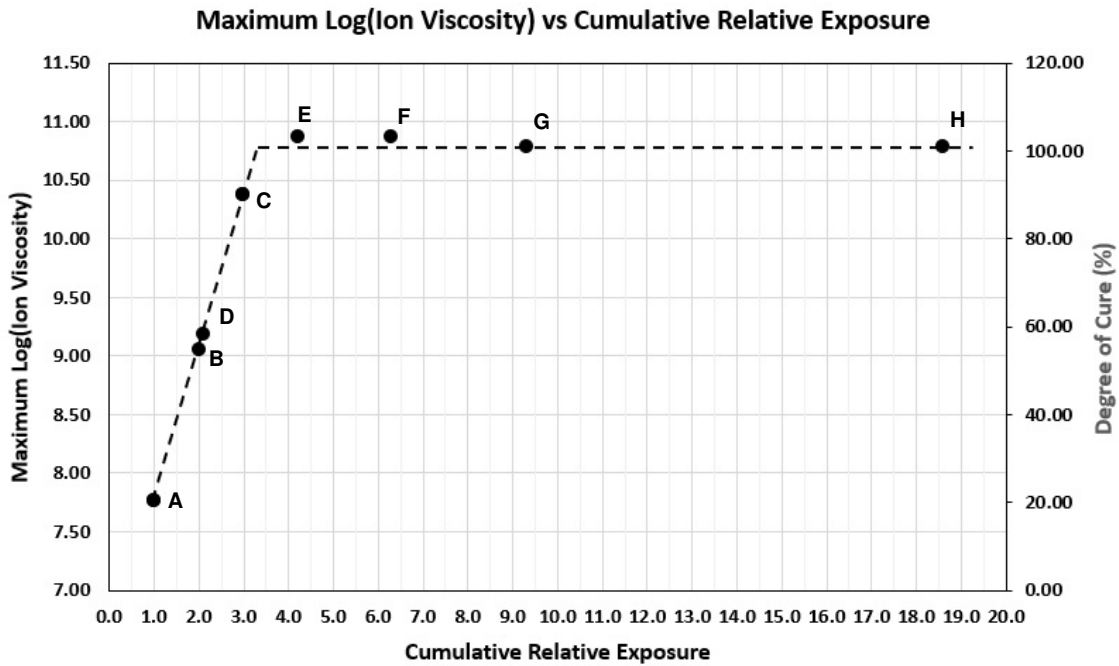
Figure 5
**Max. ion viscosity of U3345 vs. cumulative relative exposure**

Uncured resin with 0% degree of cure has a log(*IV*) = 6.9 and fully cured resin, presumed to be 100% degree of cure, has a log(*IV*) ~10.8. For many thermosets and polymers, the change in log(*IV*) is proportional to the change in

degree of cure, therefore by interpolation it is possible to correlate cumulative relative exposure with both an ion viscosity and a degree of cure.

Figure 5 shows log(*IV*) and degree of cure increase in proportion to the cumulative exposure, until reaching a maximum value that corresponds to complete cure. This result is expected because the total amount of activated photoinitiator is proportional to the total irradiation, and the amount of activated photoinitiator in turn determines the extent of polymerization. If absolute irradiance could be measured at the sample, then it would be possible to relate cumulative exposure with the resulting degree of cure.

Cure inhibition from long exposures

Figure 6 shows that curing behavior with longer exposures may have significantly different dynamics compared to very brief exposures.
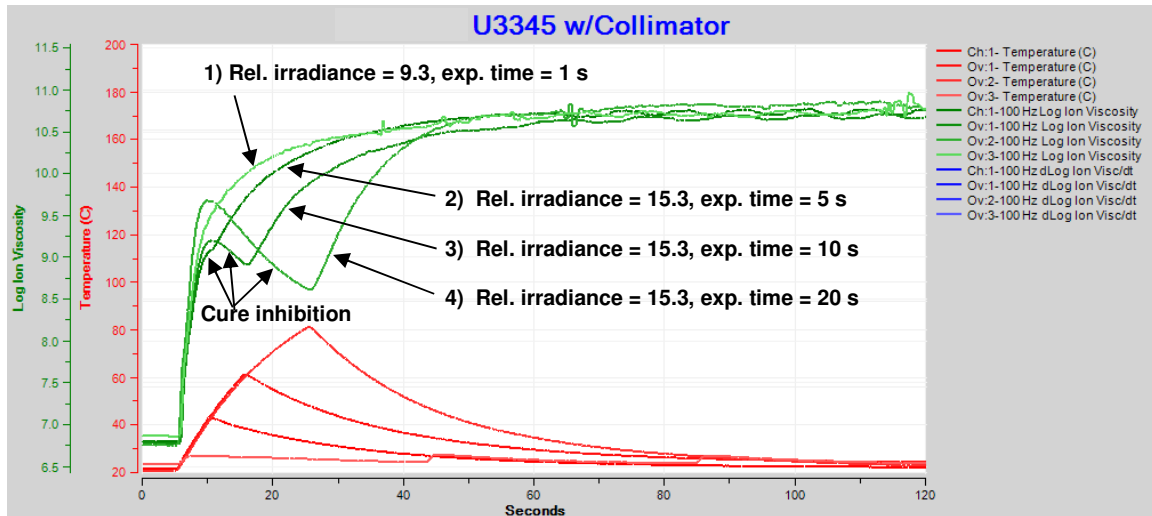
Figure 6
Ion viscosity of U3345, showing cure inhibition

Figure 6 plots ion viscosity for four curves with increasing exposure times:

1) Relative irradiance = 9.3, exposure time = 1 s: Ion viscosity increases normally and monotonically through UV and dark cure to the plateau of log(*IV*) ~10.8, indicating a typical approach to 100% degree of cure.

2) Relative irradiance = 15.3, exposure time = 5 s: Ion viscosity shows a very slight knee at about 9 s (4 s after start of exposure) then a typical approach to 100% degree of cure.

3) and 4) Relative irradiance = 15.3, exposure time = 10 s and 20 s: Ion viscosity shows a pronounced knee at about 9 s (4 s after start of exposure) while temperature continues to increase significantly due to the intense light. Log(*IV*) decreases until the end of exposure at 10 s for curve 3, and 20 s for curve 4.

Subsequently, dark cure proceeds to the ion viscosity plateau and 100% degree of cure.

This "bump" in ion viscosity has been observed in thermally cured resins (thermosets) if cure ends during an increasing temperature ramp.[8] Ion viscosity is determined by both degree of cure and temperature, and has two basic behaviors:

- At constant temperature, ion viscosity increases as degree of cure increases

- At constant degree of cure, ion viscosity decreases (increases) as temperature increases (decreases)

Normally, $\log(IV)$ increases as cure advances, and in most cases this response dominates even as temperature increases. However, if cure stops while temperature continues to increase, then the degree of cure is constant and ion viscosity decreases, resulting in the "bump."

Similarly, for U3345, the knee in $\log(IV)$, slightly visible for curve 2, prominent in curve 3 and even more prominent in curve 4, indicates that polymerization has stopped. In fact, cure has only been temporarily inhibited, because ion viscosity increases again after irradiation ceases and the U3345 undergoes dark cure.

Since ion viscosity in Figure 6 reaches the maximum value of ~10.8 (100% degree of cure) for each of the four curves, the U3345 has experienced only a delayed time to end of cure for the 5, 10 and 20 second exposures. This cure inhibition may be a general phenomenon because it has been observed in all UV-cured resins examined to date.

Cure inhibition cannot be due to the depletion of photoinitiators because dark cure after the end of exposure indicates their continued presence. Although the cause is not yet known, it is possible cure inhibition results from the competition between two factors:

- UV absorption by photoinitiators, which become activated, causing cure

- UV absorption by monomers, which become too energetic to polymerize, inhibiting cure

Although they have low concentration by weight, photoinitiators have significant effect and normally dominate during exposure, with overall increase in degree of cure. Furthermore, by absorbing UV photons, photoinitiators at least partially screen monomers from the irradiation.

The quantity of photoinitiators diminishes as a material polymerizes. If their concentration decreases sufficiently, the remaining photoinitiators may no

longer adequately screen monomers from UV photons. At this point, perhaps relatively more monomers absorb UV light and become too energetic to bond, resulting in overall inhibition of cure.

It is difficult to determine a precise time for the start of cure inhibition, but it can be estimated by the intersection of asymptotes on either side of the knee, as shown in Figure 7. *Cure inhibition time* is defined as the difference between the start of exposure, and the start of cure inhibition. Figure 8 plots the cure inhibition times for several tests at different relative irradiances and exposure times.
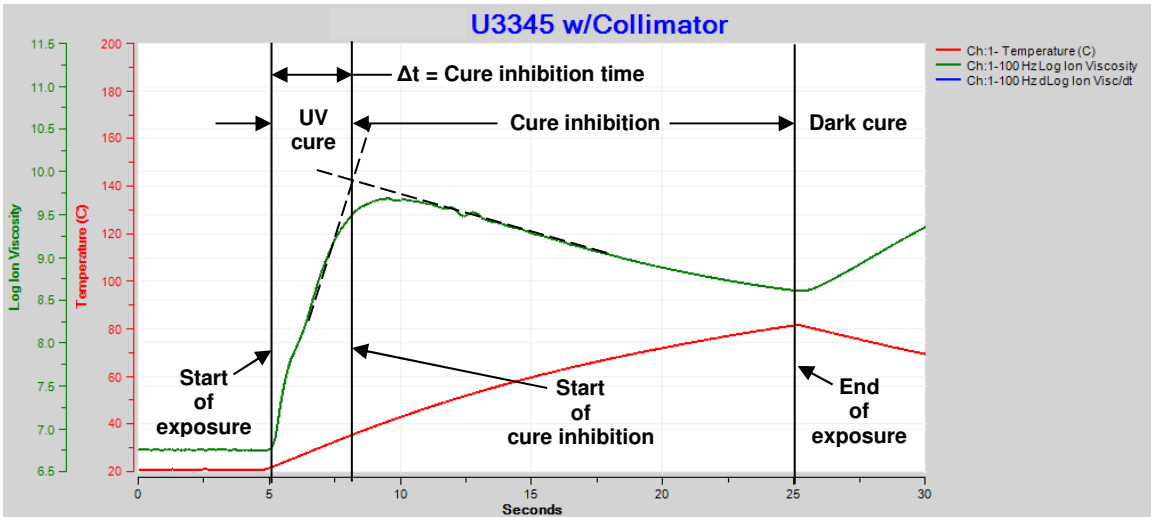
Figure 7
Determination of cure inhibition time
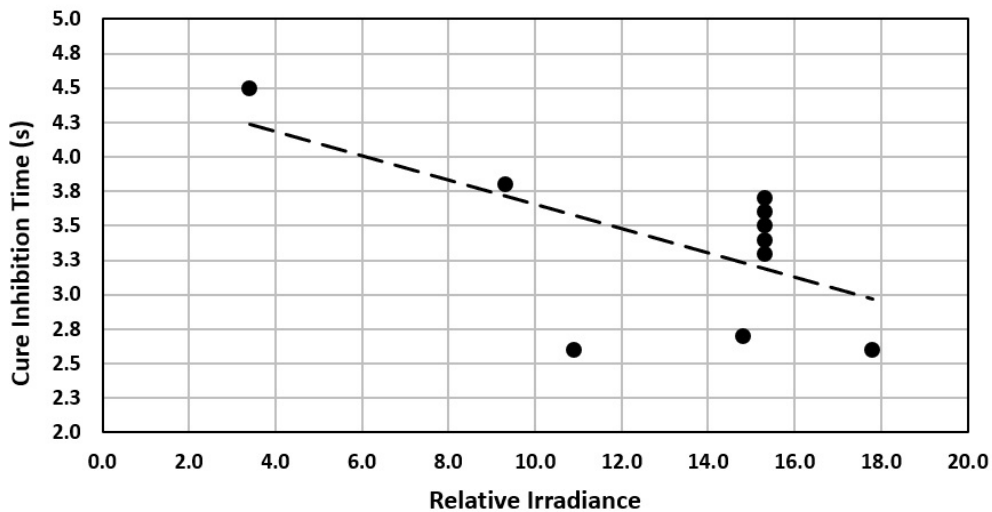
Figure 8
Cure inhibition time as a function of relative irradiance

The trend line shows increasing relative irradiances correspond with shorter inhibition times. This result is consistent with the supposition that greater irradiance reduces photoinitiator concentration more quickly, until the level reaches a point that allows cure inhibition.

**Cure degradation from long exposures**

Long exposures with high irradiances risk over-cure and degradation of a UV-cured adhesive. Figure 9 shows the progression over four tests of increasing irradiance with an exposure time of 30 seconds.

1) Relative irradiance = 2.1, exposure time = 30 s: Normal cure but total energy is only sufficient to achieve final $\log(IV)$ = 10.2 and degree of cure = 85%

2) Relative irradiance = 2.9, exposure time = 30 s: Normal cure and total energy sufficient to achieve final $\log(IV)$ = 10.7 and degree of cure ~100%

3) Relative irradiance = 3.4, exposure time = 30 s: Cure shows cure inhibition and over-cure from excessive total energy, resulting in reduced final $\log(IV)$ = 10.1 and degradation

4) Relative irradiance = 15.3, exposure time = 30 s: Cure shows cure inhibition and severe over-cure from excessive total energy, resulting in reduced final $\log(IV)$ = 8.8 and degradation
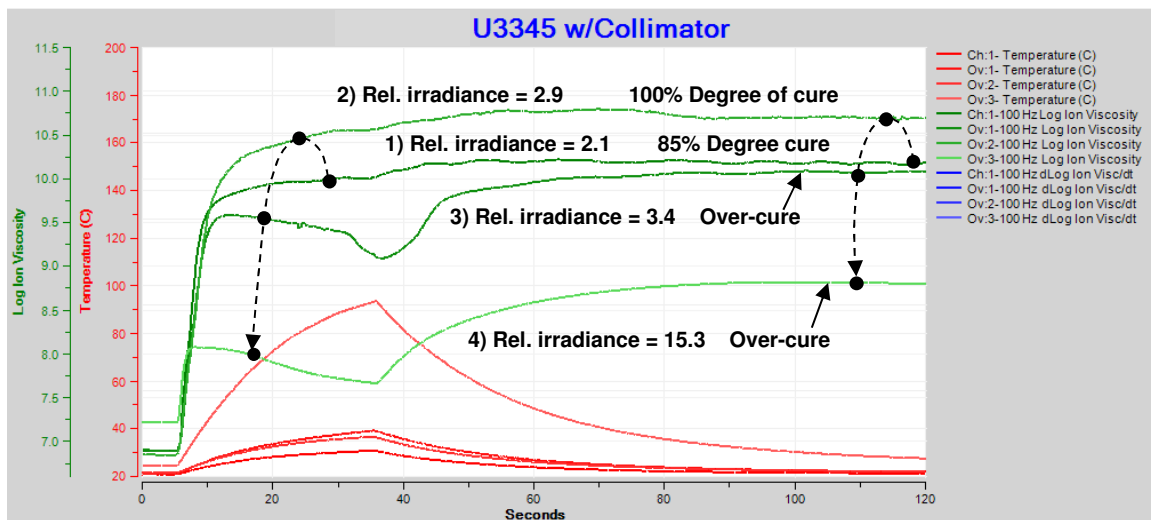
Figure 9
Ion viscosity of U3345, exposure time = 30 s

Compared to the value at 100% degree of cure, a reduction in final ion viscosity indicates the presence of damage. Lower ion viscosity is the result of greater conductivity (lower resistivity) due to degradation by-products and broken bonds. A greater decrease in final ion viscosity, as in curve 4 relative to

curve 3, indicates a greater amount of over-cure. In UV-cured materials degradation is visible as yellowing or discoloration, which may be faint or subjective. Dielectric measurements, however, can provide a supplemental, objective measure of damage caused by over-exposure.

Conclusions

Real-time dielectric cure monitoring (DEA) of UV-cured resins can complement traditional laboratory tests to relate degree of cure and exposure energy, measure the effect of formulation on cure and identify degradation from over-exposure. The ability of dielectric cure monitoring to capture events in real-time allows observation of transient phenomena such as cure inhibition, which appears to be a response of UV-cured resins in general to very long exposures.

References:

1. U3345™ UV-curable adhesive, manufactured by H.B. Fuller Company, Batavia, IL USA. www.cyberbond1.com

2. Quarto-Varicon™ sensor, manufactured by Lambient Technologies, Cambridge, MA USA. https://lambient.com

3. SunSpot 2™, manufactured by Uvitron International, Inc., West Springfield, MA USA. www.uvitron.com

4. LT-631™ High Speed Dielectric Cure Monitor, manufactured by Lambient Technologies, Cambridge, MA USA

5. Application Note 3.22, "Cure Index and Degree of Cure," Lambient Technologies, Cambridge, MA USA.

6. J.H. Chen, M.A. Octeau, M. Hojjati and A. Yousefpour, "Cure Cycle Optimization for Composite Panels Fabricated by RTM Using Dielectric Sensors," National Research Council Canada, Institute for Aerospace Research, ICCM International Conferences on Composite Materials (2009)

7. Day, D.R., "Dielectric Determination of Cure State During Non-Isothermal Cure," *Polymer Engineering and Science*; 29(5):334-338, (August 2004).

8. Application Note 3.21, "Measuring Degree of Cure with Dielectric Cure Monitoring," Lambient Technologies, Cambridge, MA USA.

Acknowledgements