Insight — Application Note 2.12

Dielectric Measurements During Post-Cure

Introduction

Large composite structures such as an airplane wing are processed in autoclaves or molds that apply pressure to form the part until it has cured. The need to maximize use of this equipment may require cycling material through it as quickly as possible, and often a part is removed as soon as it has hardened enough to retain its shape. Afterwards, it may undergo post-cure in an oven for several hours to several days. During this time cure continues at elevated temperature until the composite material has hardened further or achieved other desired properties.

Dielectric measurements can determine the state of the thermoset during post-cure and corroborate when it has reached a specified condition. Because ion viscosity depends on both the degree of cure *and* temperature, conventional dielectric cure monitoring is used under isothermal conditions to eliminate the temperature variable. During post-cure, however, oven temperature may fluctuate significantly, complicating dielectric measurements. Nevertheless, it is possible to take advantage of these fluctuations to get useful information.

Definitions

This application note presents and discusses data for *log(ion viscosity)*, which indicates the state of cure. For brevity, log(ion viscosity) will be called *log(IV)*.

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. 12-1) $$\sigma = \sigma_{DC} + \sigma_{AC} \qquad (ohm^{-1} - cm^{-1})$$

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

(eq. 12-2) $$\rho = 1/\sigma \qquad (ohm\text{-}cm)$$

From its relationship to conductivity, resistivity also has both frequency independent (ρ_{DC}) and frequency dependent (ρ_{AC}) components. Crosslink density, which is a measure of cure state, affects both mechanical viscosity and the movement of ions, and therefore 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. 12-3) $$IV = \rho_{DC} \qquad \text{(ohm-cm)}$$

Ion viscosity change during post-cure

As a material cures, the increase of ion viscosity with time is easily visible in an isothermal environment, where only the ongoing cure changes dielectric properties. In an environment where temperature also changes, isolating the effect of varying temperature is necessary to determine the effect of continuing cure. Figure 12-1 illustrates the post-cure of a thermoset in an oven. A thermocouple measures the temperature of the sample. Attached to opposite sides of the sample, electrodes form a parallel plate sensor that measures dielectric properties. For other situations, an interdigitated dielectric sensor may be coated with resin or be embedded in the material under test (MUT).

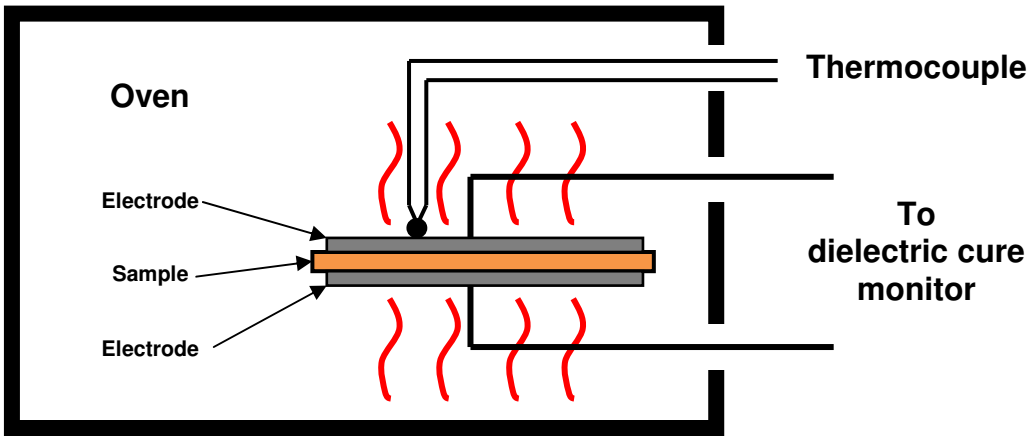

Figure 12-1
Post-cure of a thermoset in an oven

Figure 12-2 shows the ion viscosity of a silicone tube measured with parallel plate electrodes in an oven. For this sample, as for thermoset materials in general, higher temperature decreases ion viscosity and lower temperature increases ion viscosity (See Application Note 2.06—Ion Viscosity and Temperature).

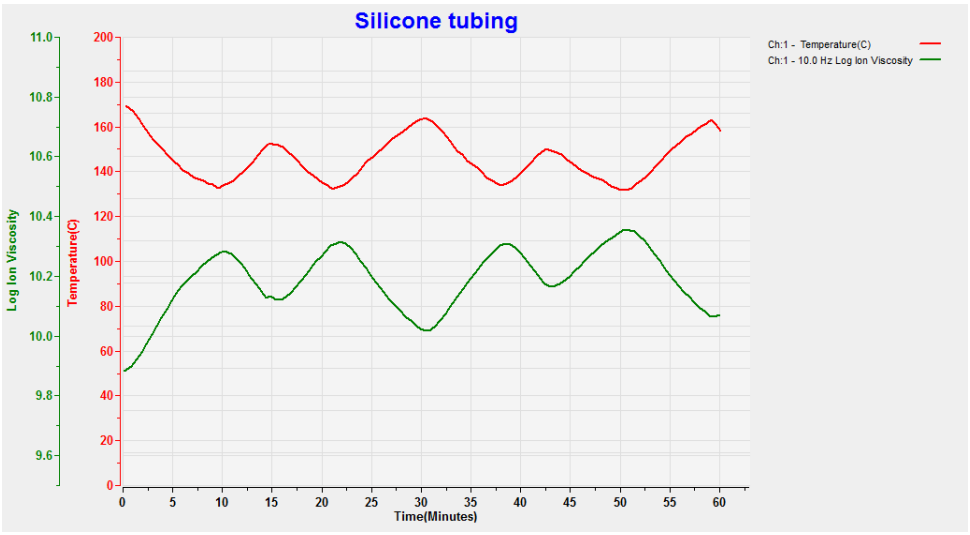

Figure 12-2
Post-cure of a silicone in oven with temperature fluctuation

Plotting ion viscosity against temperature presents the data as a series of "orbits" as shown in Figure 12-3. The shape of the orbit indicates whether cure is present. In the absence of cure, the orbit traces the same trajectory as temperature changes repetitively. Ongoing cure causes the orbit to change with time as ion viscosity increases.

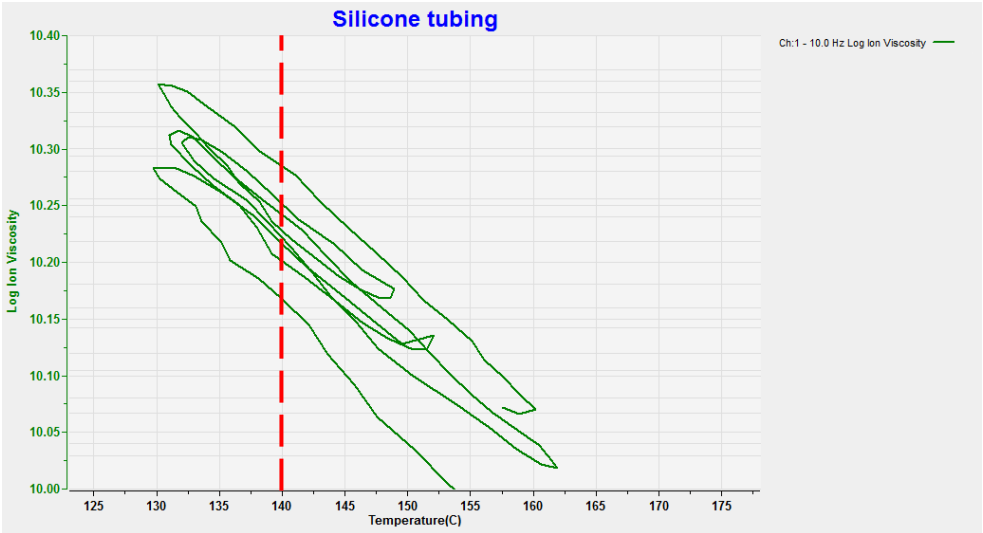

Figure 12-3
Log(*IV*) of silicone tubing sample vs. temperature

When oven temperature increases, thermal lag may cause the bulk of the sample to be slightly cooler than the surface, resulting in ion viscosity measurements that are higher than expected. Conversely, when oven temperature decreases, the bulk of the sample may be slightly warmer than the surface, resulting in ion viscosity measurements that are lower than expected. Other factors such as the exact nature of the thermal contact between the thermocouple and the sample, the sample's thermal conductivity and the location of the heating source may affect this relationship. To account for thermal lag, the average log(*IV*) from rising and falling temperatures should give a value that better represents the actual ion viscosity.

Figure 12-4 shows log(*IV*) of the silicone tubing at 140 °C. The log(*IV*) data has been normalized to a value of 1.0 at time t = 0. From the slope of the curves, it is clear that ion viscosity increased during this time, indicating that the silicone continued to cure.

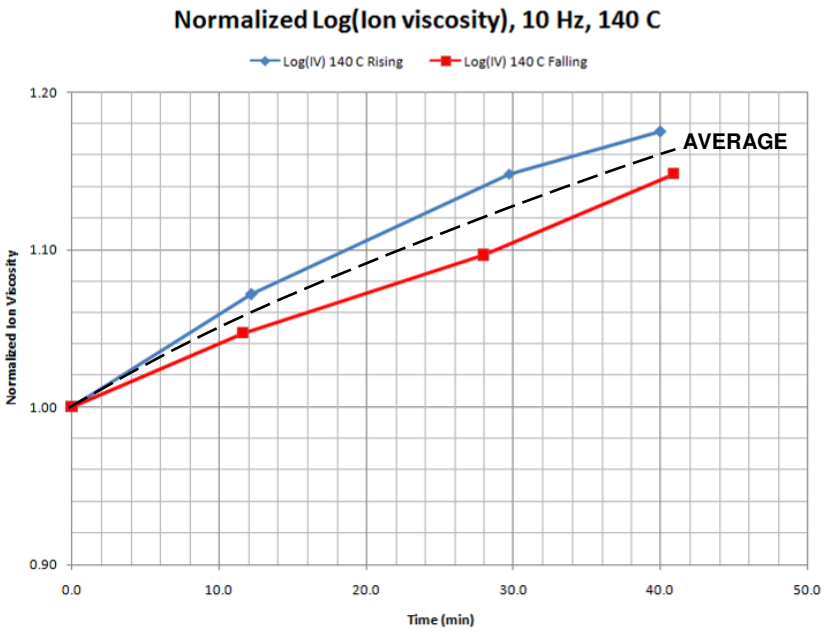

Figure 12-4
Log(*IV*) at 140 °C, normalized (data from Figure 11-2)

Post-cure of an epoxy resin

For the fabrication of large structures, the manufacturer of an epoxy resin recommends initial cure at temperatures of 40 °C to 50 °C. Processed at these relatively low temperatures, the epoxy has a low degree of cure, and physical properties such as hardness and glass transition temperature (T_g) are inadequate for the finished product. Consequently, the manufacturer also specifies post-cure at elevated temperature to advance the degree of cure and increase T_g and hardness.

Figure 12-5 shows the ion viscosity of this epoxy, measured with a 1 Hz excitation by a dielectric sensor. After 60 minutes at 50 °C, the degree of cure has reached the maximum amount possible for this temperature. The reaction has essentially stopped, indicated by the near zero slope of ion viscosity. The glass transition temperature is still relatively low and the epoxy is solid but distinctly rubbery at room temperature.

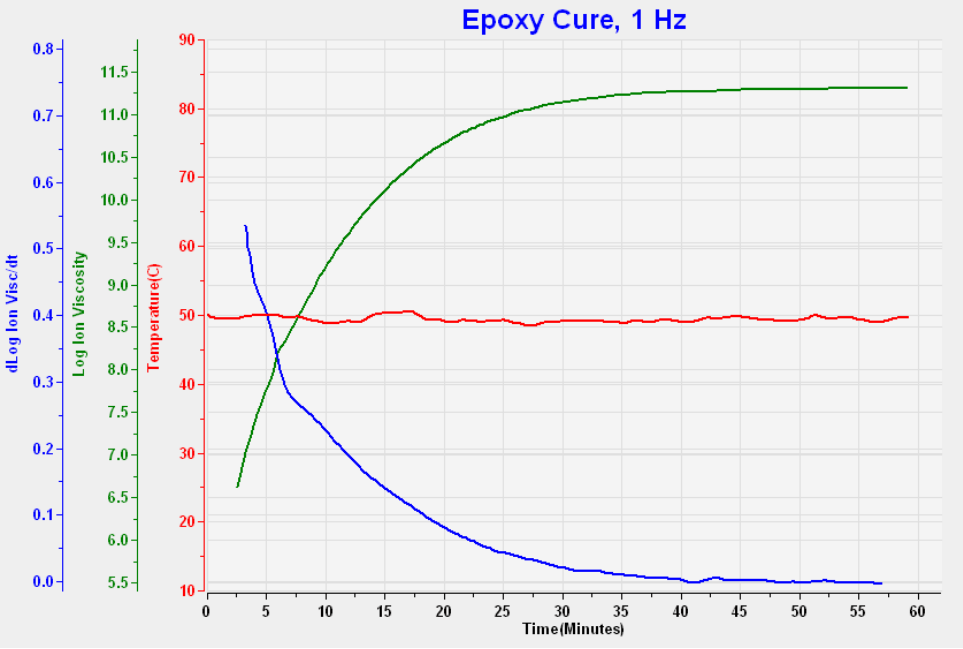

Figure 12-5
Cure of an epoxy at 50 °C

Figure 12-6 shows the temperature and ion viscosity of this epoxy during post-cure. Although the oven was nominally set to 70 °C, the actual temperature of the sample varied greatly and ion viscosity varied in turn. It is possible to identify additional cure by an increase in ion viscosity at points of constant temperature. Figure 12-7 shows the result at 67 °C, which was chosen to provide data over as much time as possible. The ion viscosity increased at first then

became constant after about 100 minutes. After this time the epoxy did not cure any further.

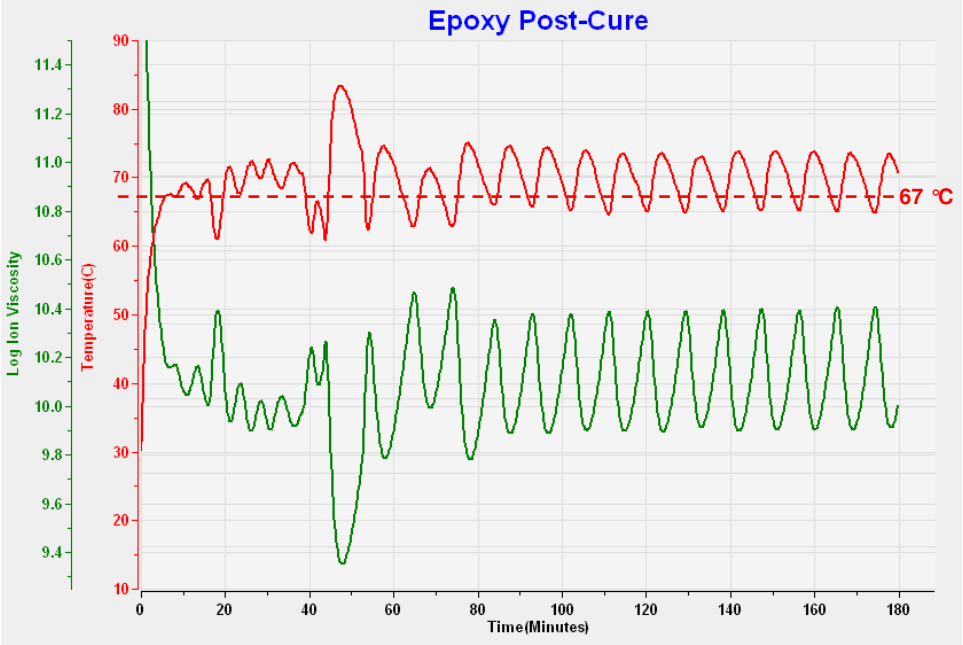

Figure 12-6
Post-cure of an epoxy in oven with fluctuating temperature

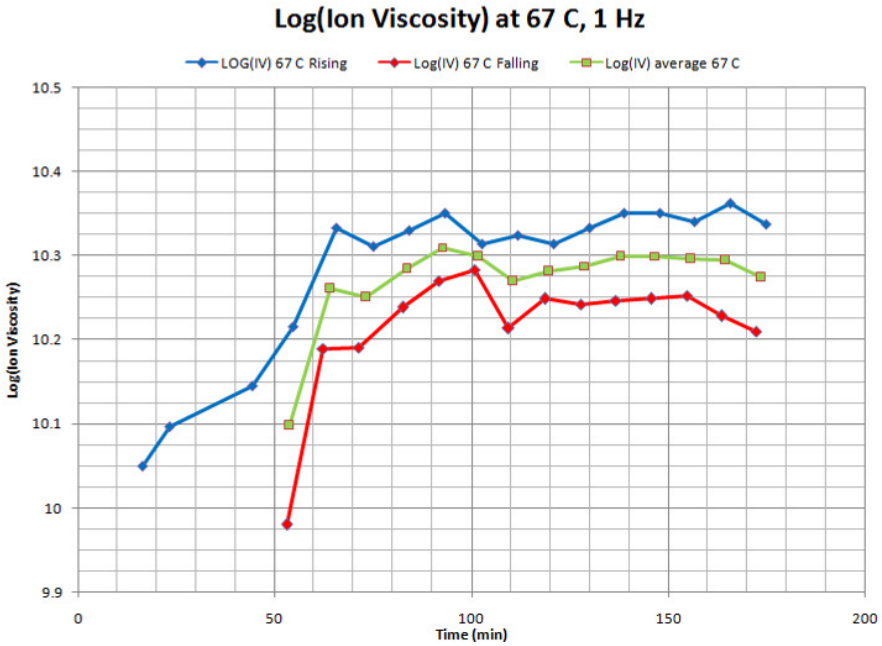

Figure 12-7
Log(*IV*) at fixed temperature

Conclusion

Dielectric cure monitoring is effective for determining the cure state of a thermoset. When temperature varies, care must be taken to observe the behavior of ion viscosity at times of fixed temperature. Using this procedure during post-cure, it is possible to monitor the change in degree of cure. By identifying when additional cure has ended, a part can be removed from post-cure as soon as possible, increasing throughput during manufacturing.

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