Insight — Application Note 2.11

Measuring Degree of Cure with DEA

Introduction

Data from dielectric cure monitoring (DEA) correlate with glass transition temperatures (T_g) obtained from differential scanning calorimetry (DSC). In many cases a linear relationship exists between log(ion viscosity) and T_g. Dielectric measurements can be converted to *Cure Index*, which is a reproducible indicator of the state of cure. For some materials, Cure Index closely follows the degree of cure, α, calculated by the DiBenedetto equation, which uses glass transition temperature 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. 11-1) $$\sigma = \sigma_{DC} + \sigma_{AC} \qquad (\text{ohm}^{-1} - \text{cm}^{-1})$$

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

(eq. 11-2) $$\rho = 1/\sigma \qquad (\text{ohm-cm})$$

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. 11-3) $$IV = \rho_{DC} \quad \text{(ohm-cm)}$$

Ion viscosity and degree of cure

For thermoset cure, the degree of cure, α, is a measure of the amount of reaction. Each bond releases a fixed amount of heat, and the degree of cure is defined as:

(eq. 11-4) $$\alpha = \Delta H \,/\, \Delta H_R$$

Where:

ΔH = Total heat released
ΔH_R = Heat of reaction

The degree of cure measures the total amount of bond formation, which is the *crosslink density*, and α therefore is useful for indicating physical state.

During cure, log(*IV*) increases with crosslink density, which in turn is related to glass transition temperature. Ueberreiter and Kanig[1] reported that crosslink density is directly proportional to the change in T_g. Furthermore, the DiBenedetto[2] equation, below, relates T_g to the extent of conversion, or degree of cure:

(eq. 11-5) $$\frac{(T_g - T_{g0})}{(T_{g\infty} - T_{g0})} = \frac{\lambda \alpha}{(1 - (1 - \lambda)\, \alpha)}$$

Where:

T_g = glass transition temperature
T_{g0} = glass transition temperature at 0% cure
$T_{g\infty}$ = glass transition temperature at 100% cure
λ = experimentally derived parameter
α = extent of conversion or degree of cure

This chain of relationships implies a correlation between log(*IV*) and degree of cure. Published data of an isothermal epoxy cure shows the overlap between log(resistivity) and T_g. In this test, T_g increased in proportion with log(resistivity), which is also log(*IV*), as shown in Figure 11-1.

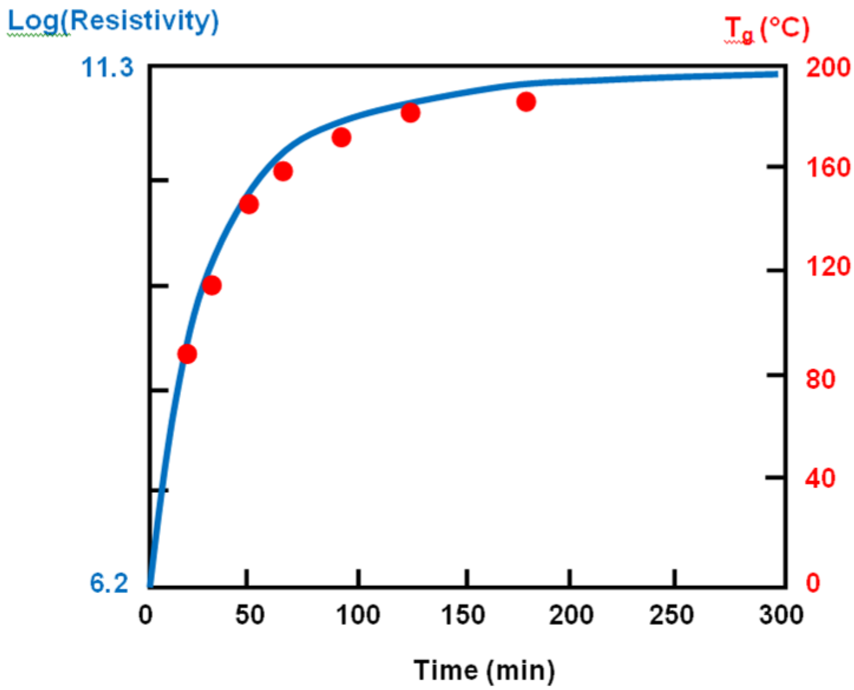

Figure 11-1
T_g and log(resistivity) vs. time during an epoxy cure (200 °C)[3]

For isothermal processing, over limited degrees of reaction, the following expression often applies between degree of cure, α, and ρ_{DC} (or ion viscosity):

(eq. 11-6) $$\alpha = k \log(\rho_{DC}) + C$$

In equation 11-6 both k and C are constants, and determining the degree of cure at a constant temperature is straightforward. For non-isothermal conditions, however, equation 11-6 cannot apply because resistivity decreases as temperature increases, even at a fixed degree of cure.

Figure 11-2 shows how resistivity varies with temperature for a particular epoxy resin. The dashed lines represent percentage degree of cure as determined by DSC. The solid lines approximate baselines for 0% and 100% degrees of cure.

Figure 11-3 shows the baselines alone, which can be used to determine glass transition temperature by linear interpolation of dielectric data.

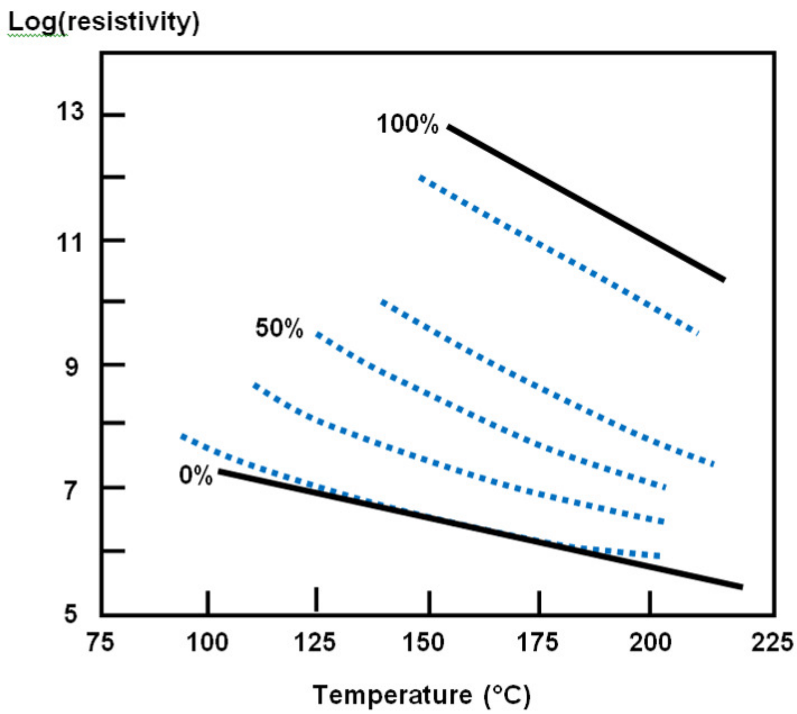

Figure 11-2
Variation in log(resistivity) with temperature for an epoxy[3]

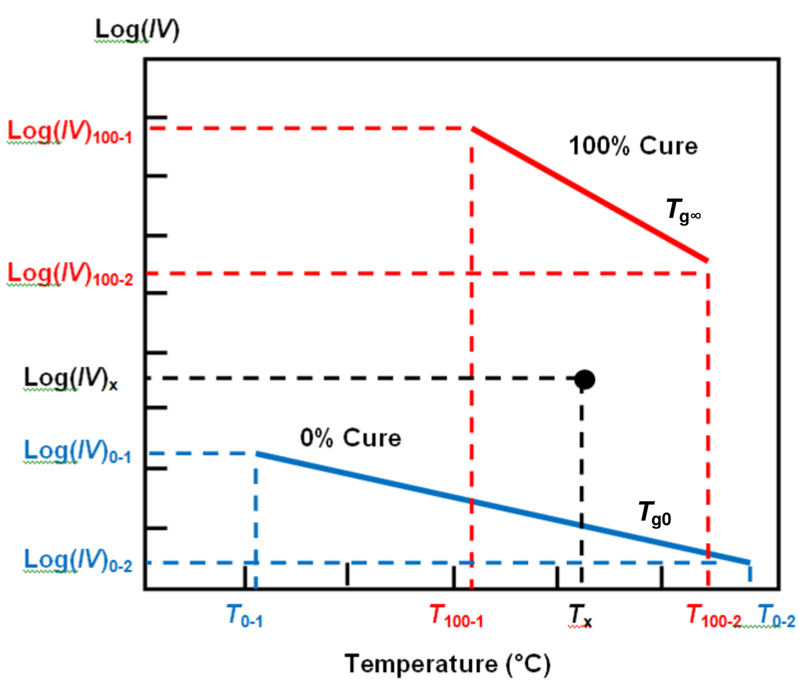

Figure 11-3
Baselines for determining T_g during non-isothermal cure

The 0% and 100% cure baselines are determined experimentally. Assuming a linear relationship between T_g and log(*IV*), the glass transition temperature, as a function of T_x and $\text{Log}(IV)_x$, is given by equation 11-7:

(eq. 11-7)
$$T_g = T_{g0} + \frac{\text{Log}(IV)_x - \text{Log}(IV_0(T_x))}{\text{Log}(IV_{100}(T_x)) - \text{Log}(IV_0(T_x))}[T_{g\infty} - T_{g0}]$$

Where:

$\text{Log}(IV_0(T_x)) = m_0\, T_x + b_0$ (eq. of 0% baseline)

$\text{Log}(IV_{100}(T_x)) = m_{100}\, T_x + b_{100}$ (eq. of 100% baseline)

$m_0 = (\text{Log}(IV)_{0\text{-}1} - \text{Log}(IV)_{0\text{-}2}) / (T_{0\text{-}1} - T_{0\text{-}2})$ (slope, 0% cure)

$m_{100} = (\text{Log}(IV)_{100\text{-}1} - \text{Log}(IV)_{100\text{-}2}) / (T_{100\text{-}1} - T_{100\text{-}2})$ (slope, 100% cure)

$b_0 = \text{Log}(IV)_{0\text{-}1} - m_0\, T_{0\text{-}1}$ (y-intercept, 0% cure)

$b_{100} = \text{Log}(IV)_{100\text{-}1} - m_{100}\, T_{100\text{-}1}$ (y-intercept, 100% cure)

Using Figure 11-2 as a linear model for T_g, interpolation of dielectric data for non-isothermal cure of the epoxy results in calculated glass transition temperatures as shown in Figure 11-4.

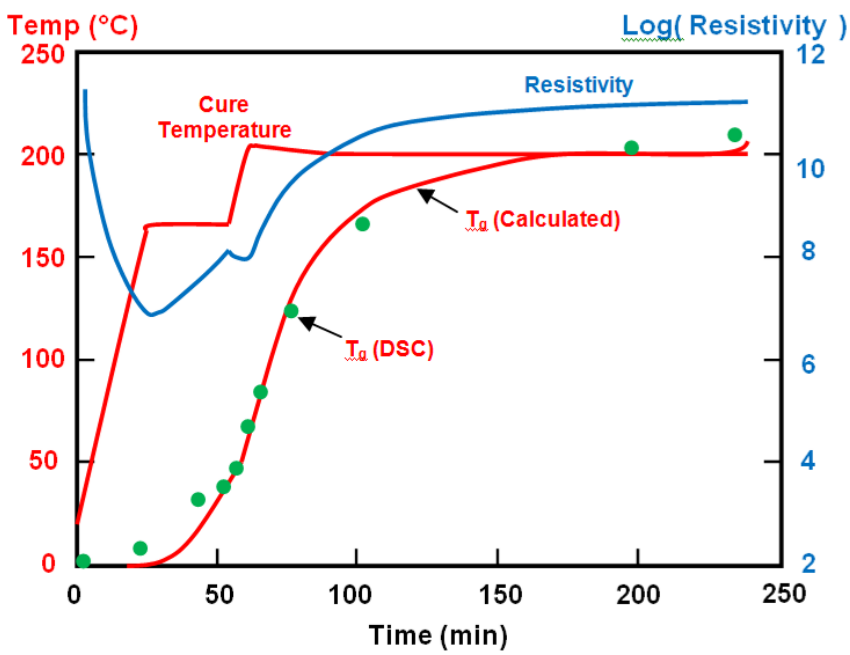

Figure 11-4
Calculated T_g during non-isothermal cure with linear T_g model[3]

For this particular material, glass transition temperatures measured by DSC show good agreement with values calculated from the linear T_g model.

Note that this model may not apply in the presence of multiple reactions, loss of reaction products or loss of solvents. Results also may not be consistent from sample to sample of the same material if variations in background ion level are too great. For most commercial or industrial thermosets, product composition is well controlled and differences in background ion concentration are typically not an issue.

Equation 11-7 may be rearranged to calculate *Cure Index*, which is a reproducible indicator of cure state that does not rely on information about glass transition temperature.

(eq. 11-8)
$$\text{Cure Index} = \frac{[T_{g\infty} - T_{g0}]}{[T_g - T_{g0}]} = \frac{\text{Log}(IV)_x - \text{Log}(IV_0(T_x))}{\text{Log}(IV_{100}(T_x)) - \text{Log}(IV_0(T_x))}$$

Figure 11-5 below shows the percentage Cure Index for the data of Figure 11-4.

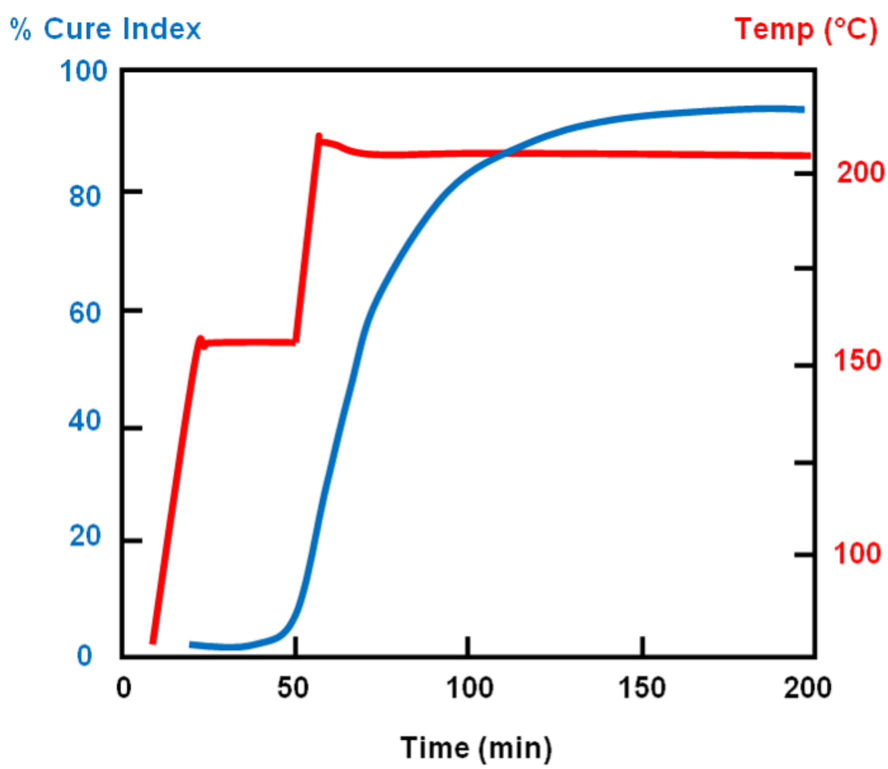

Figure 11-5
Percent Cure Index during non-isothermal cure with linear T_g model[3]

The DiBenedetto equation requires glass transition temperature information to determine degree of cure. If the experimental parameter λ = 1 for the DiBenedetto equation, then the expression reduces to equation 11-9.

(eq. 11-9)
$$\frac{[T_{g\infty} - T_{g0}]}{[T_g - T_{g0}]} = \alpha$$

In this case the degree of cure, α, expressed by equation 11-9 equals the Cure Index of equation 11-8. The term *Cure Index* was coined by D. R. Day[4] to distinguish it from *degree of cure*. Cure Index is a reproducible measure of cure state, although it may not exactly equal the degree of cure, depending on the value of λ. Nevertheless, Cure Index may still be sufficiently close to α to serve as a substitute to first order.

Conclusion

Dielectric cure monitoring, or DEA, can infer T_g during cure by using temperature and ion viscosity data with baseline information about glass transition temperatures. The resulting T_g can then be used in the DiBendetto equation to determine the degree of cure. *Cure Index* is a simpler method that can yield the same degree of cure as the DeBenedetto equation in the case of λ = 1. Even though Cure Index may not always equal degree of cure, Cure Index is a convenient alternative measure of cure state that does not require glass transition temperature information.

References

1. K. Ueberreiter, G. Kanig, *J. Chem. Phys.*, **18**, 399 (1950)

2. "Glass transition Temperature vs. Conversion Relationships for Thermosetting Polymers," Pascault, J.P. and Williams, R.J.J., *J. of Polymer Science, Part B:Polymer Physics*, **28**, 85-95 (1990)

3. "Dielectric Properties of Polymeric Materials," D.R. Day, Micromet Instruments, 1987
(Figures have been redrawn for clarity)

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

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