Insight — Application Note 2.06

Ion Viscosity and Temperature

Introduction

For the measurement of mechanical viscosity and cure state, ion viscosity (DC resistivity) provides valuable information from a simple electrical measurement. Ion viscosity depends on the mobility of free ions under the influence of an electric field, but also varies with temperature. Therefore, correct interpretation of ion viscosity requires knowledge of temperature at the time of measurement and an understanding of how temperature influences the data. For brevity, ion viscosity will alternatively be called *IV*.

Temperature dependence of ion viscosity

At a constant cure state, which is a fixed crosslink density in a thermoset, ion viscosity decreases as temperature rises because the mobility increases. Ion viscosity is another term for DC resistivity, ρ_{DC}, which is given by equation 6-1.

(eq. 6-1) $$\rho_{DC} = 1 / (q\ \mu\ n)$$

Where:
q = charge of free ions (coulombs)
μ = free ion mobility (cm^2 / (V-s))
n = free ion concentration (cm^{-3})

Free ion mobility determines the rate of ionic diffusion through a medium, and is given by the Einstein relationship of equation 6-2:

(eq. 6-2) $$\mu = q\ D / (k\ T) \qquad (cm^2 / (V\text{-}s))$$

Where:
D = diffusion coefficient (cm^2 / s)
k = Boltzmann's constant (eV / K)
T = temperature in degrees Kelvin (K)

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The diffusion coefficient itself is exponentially temperature dependent:

(eq. 6-3) $$D = D_0 \, e^{-Q/kT} \qquad (cm^2 / s)$$

Where: D_0 = Maximum value of diffusion coefficient (cm^2 / s)
Q = Activation energy (eV)

The maximum value of the diffusion coefficient D_0 is constant with temperature, but decreases as cure progresses because greater crosslink densities reduce the mean free path of a mobile ion. Combining equations 6-1, 6-2 and 6-3 results in the following expression for DC resistivity:

(eq. 6-4) $$\rho_{DC} = (k / (q^2 \, n \, D_0)) \, T \, e^{Q/kT}$$

The logarithm of ion viscosity (DC resistivity) then becomes:

(eq. 6-5) $$\log_{10}(IV) = \log_{10}(k / (q^2 \, n \, D_0)) + \log_{10}(T) + (Q / (kT \ln(10)))$$

which may be expressed as:

(eq. 6-6) $$\log_{10}(IV) = A + \log_{10}(T) + B \, (1 / T)$$

Where: $A = \log_{10}[k / (q^2 \, n \, D_0)]$
$B = Q / (k \ln(10))$

At a given cure state, D_0 is constant and coefficients A and B are also both constants. The 1 / T term of equation 6-6 dominates the response because it varies more with temperature than $\log_{10}(T)$. As a result, for a fixed cure state, ion viscosity decreases as temperature increases.

Figure 6-1 shows how ion viscosity changes with temperature for an epoxy resin with catalyst. Figure 6-2 shows how ion viscosity changes for a thermoplastic polyimide.[1]

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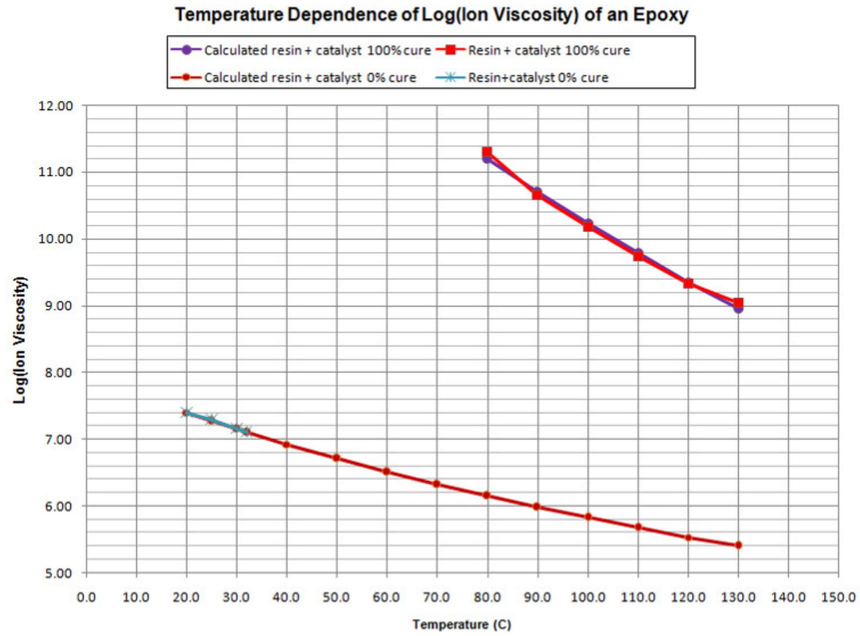

Figure 6-1

Variation in log(*IV*) with temperature for an epoxy resin

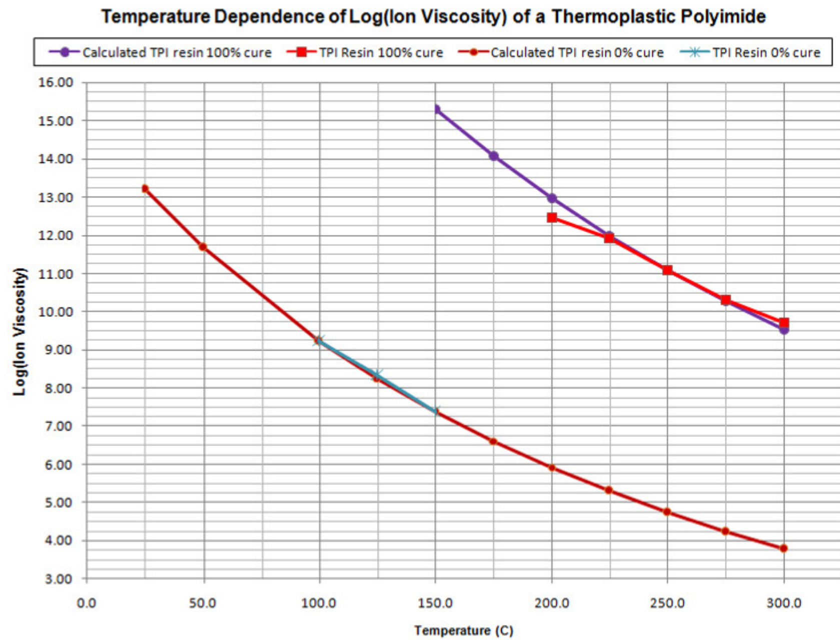

Figure 6-2

Variation in log(*IV*) with temperature for a thermoplastic polyimide[1]

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Overlaid on the data are results from equation 6-6, where coefficients *A* and *B* are determined for best fit. The good correspondence between equation 6-6 and the data validates this model of ion viscosity temperature response. As the cure state advances, D_0 decreases, causing the offset between calculated lines for 0% and 100% cure.

As seen in Figures 6-1 and 6-2, the activation energy *Q*, which largely determines the slope of each calculated line, may vary with degree of cure.

Prepreg processing

A common temperature schedule for vacuum bag curing of prepregs begins with an initial ramp-and-hold step, called the *B-Stage*. During the B-Stage, volatiles and reaction by-products are free to escape as the resin heats and melts. After the B-Stage a second ramp-and-hold heats the prepreg to high temperature for final curing. Pressure is applied during this second step to compress together the laminates of prepreg and consolidate the part. At this time any residual volatiles are unable to escape.

Figure 6-3 shows dielectric and viscosity data from the cure of an epoxy resin with two ramp-and-hold steps. Here the first minimum in ion viscosity (*IV*) occurs at 50 minutes. At this time the increase in *IV* due to the accelerating reaction dominates the decrease in *IV* caused by the temperature rise. After the second temperature ramp begins, *IV* again decreases as temperature increases. In this case the second decrease in mechanical viscosity may cause resin to flow excessively under the application of pressure, causing undesirable loss of resin and producing dry fibers and voids in the laminate. Eventually the thermally driven cure dominates once more and ion viscosity rises again.

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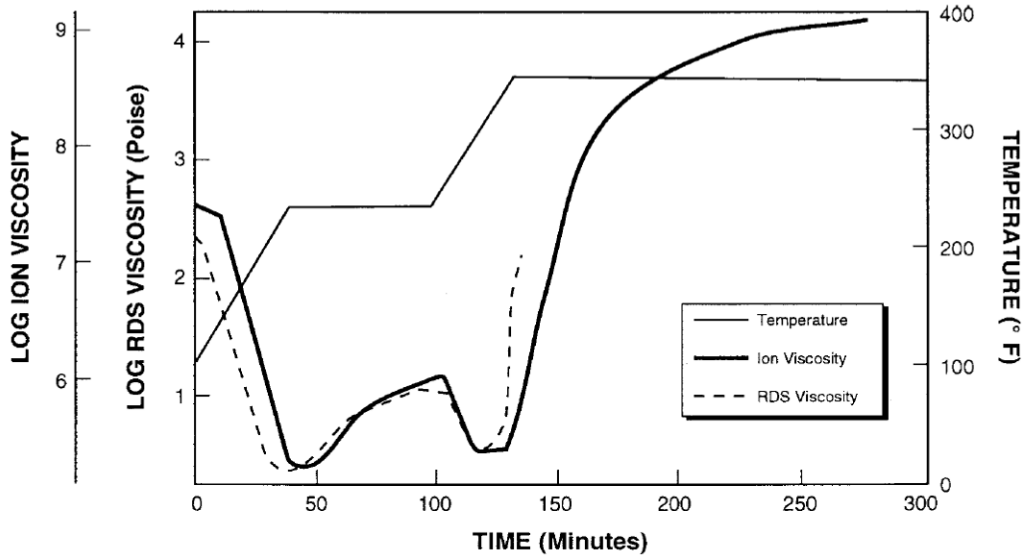

Figure 6-3
Ion viscosity for an epoxy resin cure with two ramp-and-hold steps[2]

Dielectric cure monitoring is uniquely able to observe thermoset material state in real time, and can provide valuable information for process development and process control. The ability of dielectric cure monitoring to infer mechanical viscosity during a process allows adjustment of temperature and pressure to avoid excessive flow of resin and reduce the occurrence of voids that can cause delamination of the finished part.

References

1. Proprietary thermoplastic polyimide adhesive, derived from its FM901 polyamic-acid polymer solution, provided by Fraivillig Technologies Company.

2. *Cure Monitoring of Thermosetting Resins Utilizing Dielectric Sensors*, David Shepard, Holometrix-Micromet

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