

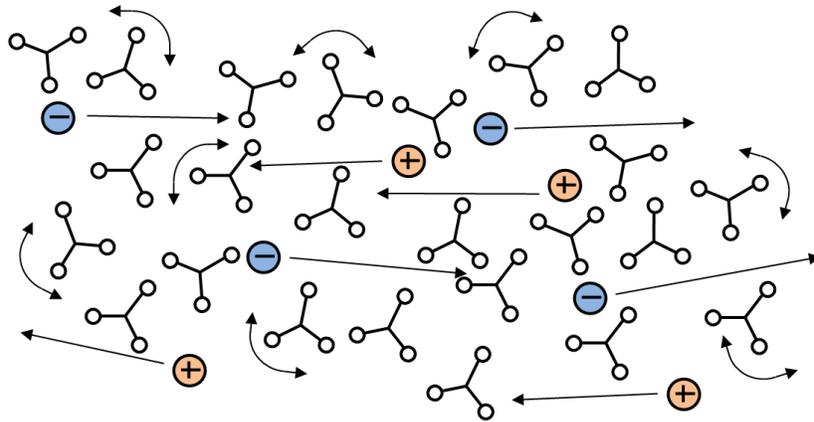


## Insight — Application Note 2.02

### Basics of Thermoset Cure and Dielectric Measurements

#### The thermoset cure process

Thermosets are an important class of materials used for adhesives, coatings and composites. They include epoxies, (poly)urethanes, acrylics, phenolics, vinyl esters, silicones and many other compounds. Uncured thermosets, or *A-stage* materials, are composed of small molecules called monomers, as shown in Figure 2-1.

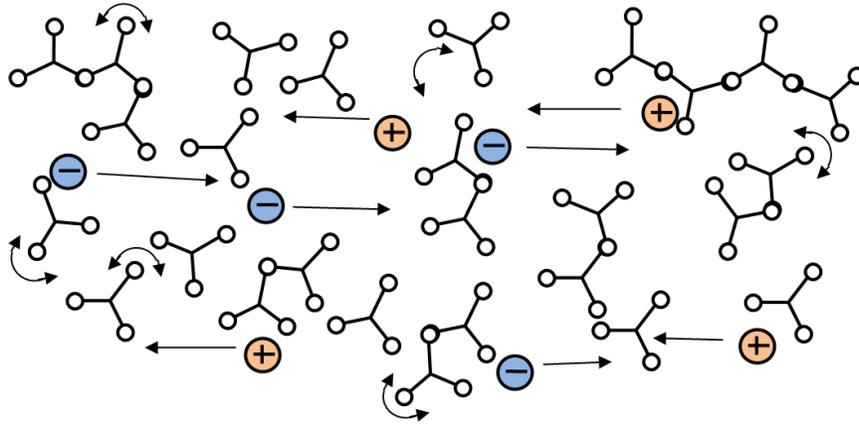


Characteristics of A-Stage thermoset:

- Chemical
  - Monomers unreacted
  - Molecular weight low
  - Degree of cure  $\alpha = 0$
  - No network formation
- Physical
  - Fluidity measured by viscosity
  - Viscosity at minimum
  - Glass transition temperature  $T_g$  low
  - Mean free path long
  - Diffusion coefficient large
  - Free ion mobility high
  - Dipole rotation large
- Electrical
  - Conductivity at maximum (resistivity at minimum)
  - Dielectric constant at maximum

**Figure 2-1**  
**A-Stage thermoset (uncured)**

With the application of a catalyst, hardener, or energy such as heat or light, these monomers react and bond to one another to form longer and longer chains called polymers. Once curing begins, but while still fluid, the thermoset is a *B-Stage* material, represented in Figure 2-2. During this period the number of molecules decreases while their molecular weight increases. The thermoset's viscosity also increases, as does its resistance to the flow of mobile ions in an electric field. Dipoles in the polymer can rotate in response to an oscillating electric field, and this ability to rotate also decreases as cure advances.

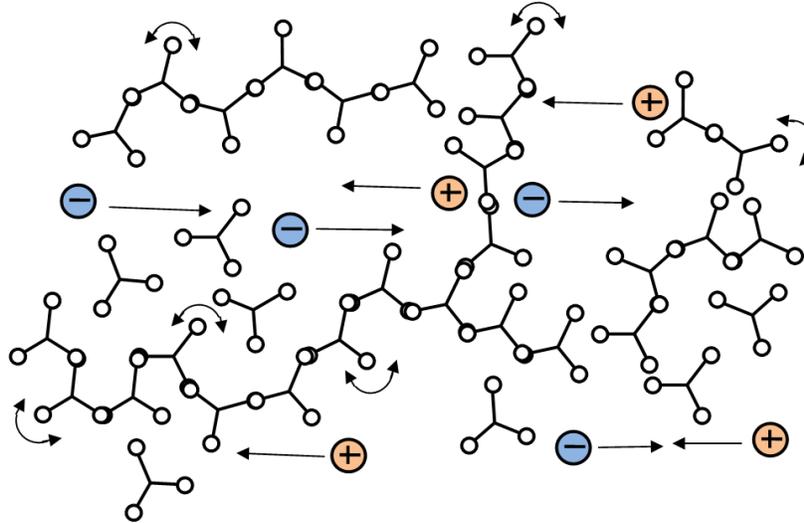


Characteristics of B-Stage thermoset:

- Chemical
  - Monomers reacting and molecular chains lengthening
  - Molecular weight increasing
  - Degree of cure  $\alpha$  increasing
  - Little network formation
- Physical
  - Fluidity measured by viscosity
  - Viscosity increasing
  - Glass transition temperature  $T_g$  increasing
  - Mean free path shortening
  - Diffusion coefficient decreasing
  - Free ion mobility decreasing
  - Dipole rotation decreasing
- Electrical
  - Conductivity decreasing (resistivity increasing)
  - Dielectric constant decreasing

**Figure 2-2**  
**B-Stage thermoset (partial curing, before gel point)**

Through the process of crosslinking, which is the formation of bonds that link one polymer chain to another, an extended branching network appears as shown in Figure 2-3. Crosslinks limit the movement of polymer chains and the thermoset's viscosity increases rapidly.



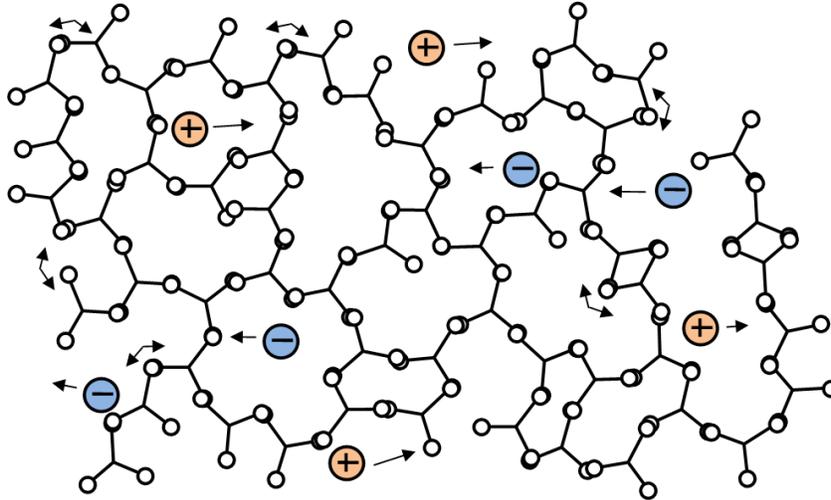
Characteristics of thermoset at gel point:

- Chemical
  - Monomers reacting, molecular chains lengthening and branching
  - Molecular weight increasing
  - Degree of cure  $\alpha$  increasing
  - Beginning of infinite network formation
- Physical
  - Viscosity increasing rapidly to infinity
  - Rigidity measured by modulus
  - Modulus at minimum
  - Glass temperature  $T_g$  increasing
  - Mean free path shortening
  - Diffusion coefficient decreasing
  - Free ion mobility decreasing
  - Dipole rotation decreasing
- Electrical
  - Conductivity decreasing (resistivity increasing)
  - Dielectric constant decreasing
  - No sudden change in dielectric properties

**Figure 2-3**  
**Gel point (start of infinite network)**

At some point the network essentially becomes a single molecule of infinite molecular weight, and the moment of its appearance is called *gelation* or the *gel point*—the material changes from a viscous liquid that can flow to a gel or rubber that cannot. Note that gelation is a mechanical condition that does not cause a corresponding sudden change in electrical properties.

After gelation the thermoset hardens into a solid. Upon full cure the thermoset is a *C-Stage* material as shown in Figure 2-4.



Characteristics of C-Stage thermoset:

- Chemical
  - Reaction approaching end of cure
  - Molecular chains lengthening and branching
  - Molecular weight approaching infinity
  - Degree of cure  $\alpha$  approaching maximum for cure temperature
  - Infinite network approaching maximum
- Physical
  - Rigidity measured by modulus
  - Modulus increasing to maximum for cure temperature
  - Glass transition temperature  $T_g$  reaching maximum for cure temperature
  - Mean free path shortening
  - Diffusion coefficient decreasing
  - Free ion mobility decreasing
  - Dipole rotation decreasing
- Electrical
  - Conductivity reaching minimum (resistivity reaching maximum)
  - Dielectric constant reaching minimum

**Figure 2-4**  
**C-Stage resin (end of cure)**

Throughout the cure, from A-Stage to B-Stage to C-Stage, both free ion mobility and the amount of dipole rotation decrease continuously. Resistivity depends on free ion mobility and permittivity depends on dipole rotation. As a result these dielectric properties vary with viscosity before gelation, and with rigidity or modulus after gelation.

The degree of cure  $\alpha$  is a measure of the amount of reaction for the thermoset. Each bond releases a fixed amount of heat, and the degree of cure is defined as:

$$(eq. 2-1) \quad \alpha = \Delta H / \Delta H_R$$

where:

$$\begin{aligned} \Delta H &= \text{Total heat released} \\ \Delta H_R &= \text{Heat of reaction} \end{aligned}$$

The degree of cure also correlates with *crosslink density* and  $\alpha$  therefore is useful for indicating physical state.

A material undergoes a glass transition when it changes from a glassy and relatively brittle solid to one that is rubbery and relatively soft. Above the glass transition temperature  $T_g$  (actually a range of temperature) a polymer is rubbery because sufficient thermal energy is available to increase the flexibility of crosslinks. Below  $T_g$  the polymer vitrifies and is rigid. Like degree of cure, glass transition temperature increases with crosslink density, increases as cure progresses and is a measure of cure state. The DiBenedetto model, below, is often used to relate degree of cure to glass transition temperature.

$$(eq. 2-2) \quad \frac{(T_g - T_{g0})}{(T_{g\infty} - T_{g0})} = \frac{\lambda \alpha}{(1 - (1 - \lambda) \alpha)}$$

where:

$$\begin{aligned} T_g &= \text{Glass transition temperature (K or } ^\circ\text{C)} \\ T_{g0} &= \text{Glass transition temperature at } \alpha = 0 \text{ (uncured)} \\ T_{g\infty} &= \text{Glass transition temperature at } \alpha = 1 \text{ (fully cured)} \\ \lambda &= \text{Adjustable parameter} \end{aligned}$$

The relationships among degree of cure, glass transition temperature and electrical properties of the thermoset are the basis for dielectric cure monitoring, which uses electrical measurements to measure cure.

### **ASTM standard for dielectric measurements**

The ASTM standard E 2039-04 **Standard Test Methods for Determining and Reporting Dynamic Dielectric Properties** describes general configurations of sensors, circuits and instruments. Although withdrawn in 2009 without replacement, this standard still provides useful background and guidance for making dielectric measurements.

Section 4.1 of E 2039-04, cited below, recognizes that the dielectric properties of material between two electrodes are determined by measuring the current passing through the material along with the voltage driving that current between the electrodes.

#### **4. Summary of Practice**

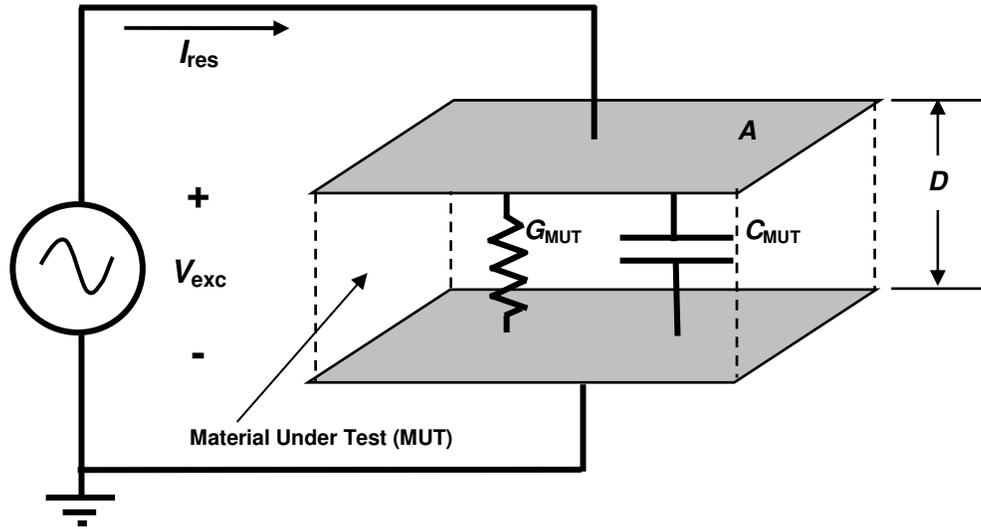
4.1 An oscillatory electric potential (voltage) is applied to a test specimen by means of an electrode of known geometry. An electric current is measured at a sensing electrode separated from the transmitting electrode by the specimen under test. From the amplitude and phase shift of the measured current relative to the applied voltage and from known geometrical constants, such as electrode spacing and electrode arrangement, desired dielectric properties of the specimen under test may be obtained. Such properties include conductivity, dielectric constant, dielectric dissipation factor, dielectric loss angle, dipole relaxation time, dissipation factor, relative permittivity, loss factor, and tangent delta. The desired dielectric properties may be obtained as a function of frequency, temperature, or time by varying and measuring these independent parameters during the course of the experiment.

NOTE 1—The particular method for measurement of amplitude and phase shift depends upon the operating principle of the instrument used.

**(From ASTM 2039-04, withdrawn without replacement in 2009)**

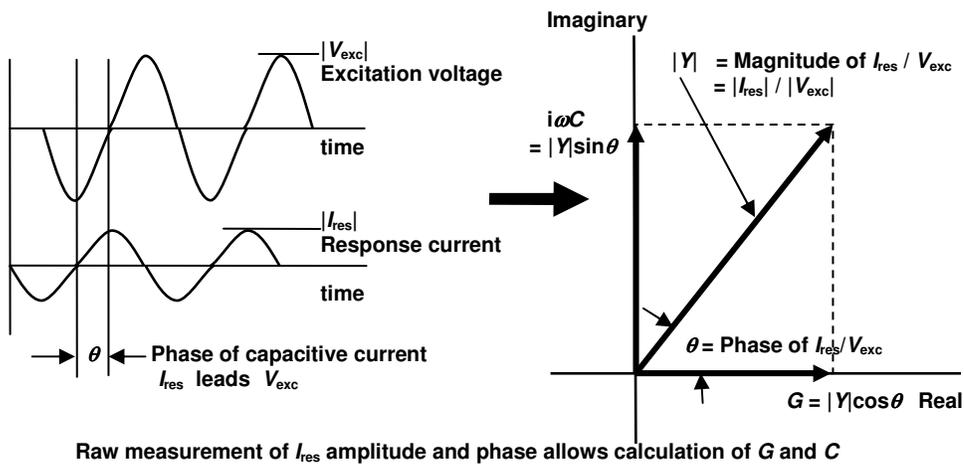
### Electrical model of Material Under Test (MUT)

Dielectric instrumentation measures the conductance  $G$  (or resistance  $R$ ) and capacitance  $C$  between a pair of electrodes at a given frequency. The Material Under Test (MUT) between these electrodes can be modeled as a conductance in parallel with a capacitance, as shown in Figure 2-5.



**Figure 2-5**  
**Electrical model of dielectric Material Under Test**

An AC excitation voltage  $V_{exc}$  applied between a pair of parallel plate electrodes, drives response current  $I_{res}$  through the MUT. The amplitude of this current and the phase relationship between  $V_{exc}$  and  $I_{res}$  provide the information to calculate admittance  $Y$ , as shown in Figure 2-6.



**Figure 2-6**  
**Signal relationships for the admittance of Material Under Test**

Admittance  $Y$ , and therefore conductance  $G$  and capacitance  $C$ , of the MUT are defined by equation 2-3:

$$(eq. 2-3) \quad Y_{MUT} = G_{MUT} + i\omega C_{MUT} = I_{res} / V_{exc}$$

where:

- $I_{res}$  = AC current through MUT (a complex number, amps)
- $V_{exc}$  = AC voltage across MUT (a complex number, volts)
- $C_{MUT}$  = Capacitance of MUT (a real number, Farads)
- $G_{MUT}$  = Conductance of MUT (a real number, ohms<sup>-1</sup>)
- $f$  = Excitation frequency (Hz)
- $\omega$  =  $2\pi f$  (angular frequency, radians/sec)

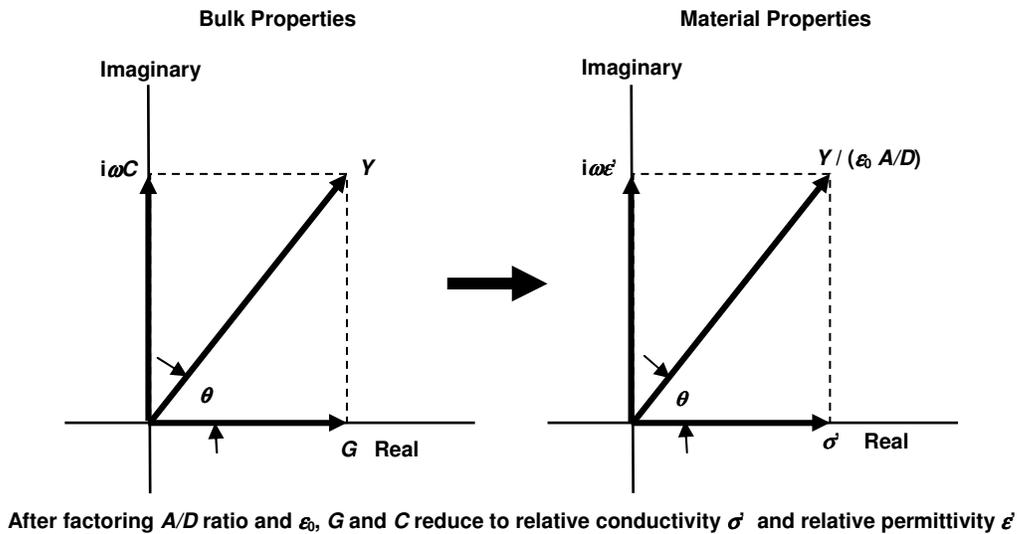
The material properties of relative conductivity  $\sigma'$ , and relative permittivity  $\epsilon'$ , can be calculated from equations 2-4 and 2-5, as shown in Figure 2-7.

$$(eq. 2-4) \quad \sigma' = G / (\epsilon_0 A/D) \quad (\text{relative conductivity})$$

$$(eq. 2-5) \quad \epsilon' = C / (\epsilon_0 A/D) \quad (\text{relative permittivity})$$

where:

- $\epsilon_0 = 8.86 \times 10^{-14}$  F/cm
- $A$  = Electrode area (cm<sup>2</sup>)
- $D$  = Distance between electrodes (cm)



**Figure 2-7**  
**Converting bulk properties to material properties**

It is preferable to obtain relative permittivity  $\epsilon'$ , and relative conductivity  $\sigma'$  (or conductivity  $\sigma$ ) because they are fundamental material properties, which do not depend on the quantity of material being measured.



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