Insight — Application Note 3.03

Basics of Thermoset Cure

Stages of thermoset cure

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 3-1.

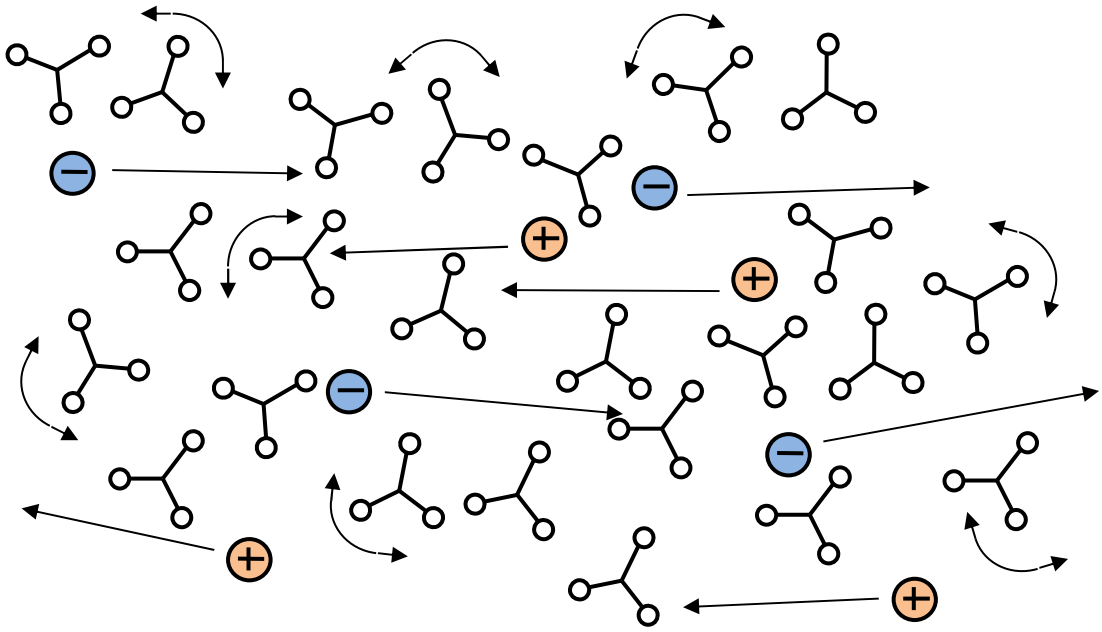

Figure 3-1
A-Stage thermoset (uncured)

Characteristics of A-Stage thermoset

Physical

- Fluidity measured by viscosity
- Viscosity low
- Glass transition temperature T_g low
- Mean free path long
- Diffusion coefficient large
- Free ion mobility high
- Dipole rotation large

Chemical

- Monomers unreacted
- Molecular weight low
- Degree of cure α low
- No network formation

Electrical

- Conductivity at maximum (resistivity at minimum)
- Dielectric constant at maximum

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 3-2. 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.

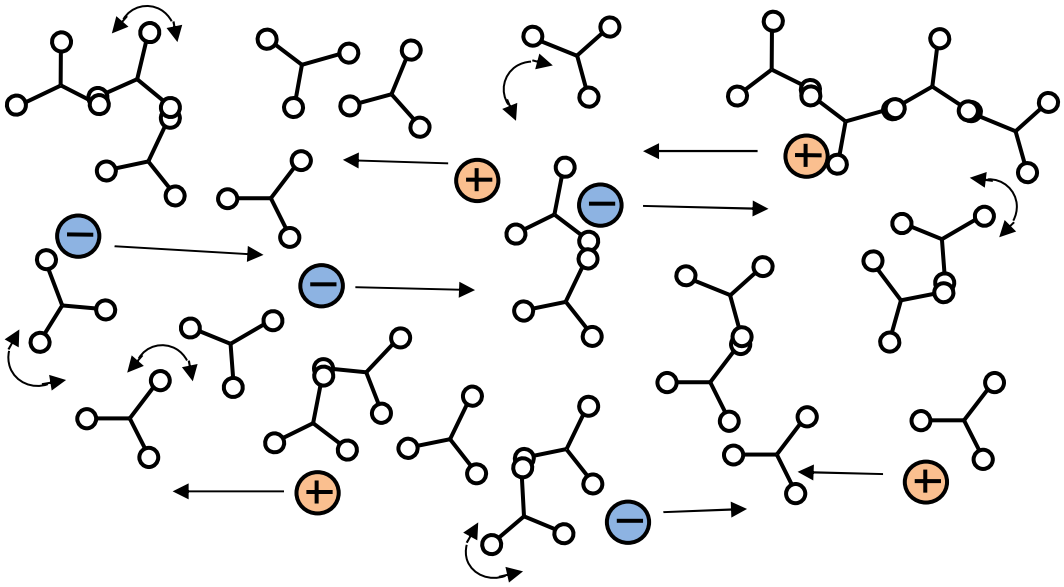

Figure 3-2
B-Stage thermoset (partial curing, before gel point)

Characteristics of B-Stage thermoset

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

Chemical

- Monomers reacting and molecular chains lengthening
- Molecular weight increasing
- Degree of cure α increasing
- Little network formation

Electrical

- Conductivity decreasing (resistivity increasing)
- Dielectric constant decreasing

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 3-3. Crosslinks restrict the movement of polymer chains and the thermoset's viscosity increases rapidly.

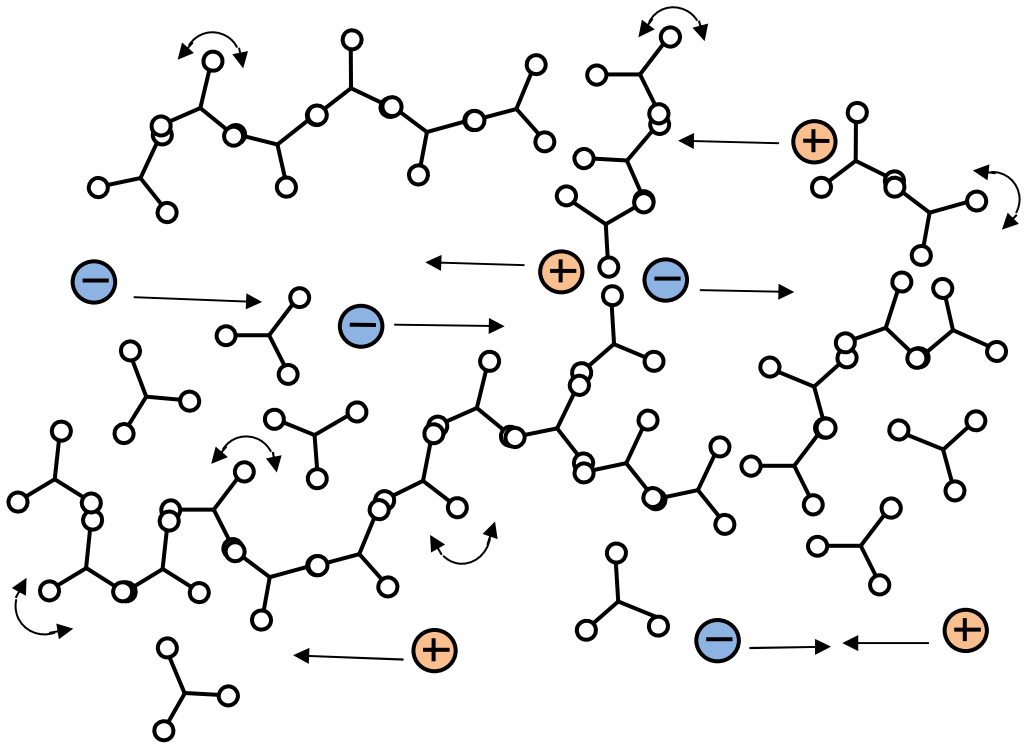

Figure 3-3
Gel point (start of infinite network)

Characteristics of thermoset at gel point

Physical

- Viscosity increasing rapidly to infinity
- Rigidity measured by modulus
- Modulus low
- Glass temperature T_g increasing
- Mean free path shortening
- Diffusion coefficient decreasing
- Free ion mobility decreasing
- Dipole rotation decreasing

Chemical

- Monomers reacting, molecular chains lengthening and branching
- Molecular weight increasing
- Degree of cure α increasing
- Beginning of infinite network formation

Electrical

- Conductivity decreasing (resistivity increasing)
- Dielectric constant decreasing
- No sudden change in dielectric properties

At some point the network essentially becomes a single molecule of infinite molecular weight, and the beginning of infinite network formation is called *gelation* or the *gel* point—the material changes from a viscous liquid that can flow to a gel or rubber that cannot.

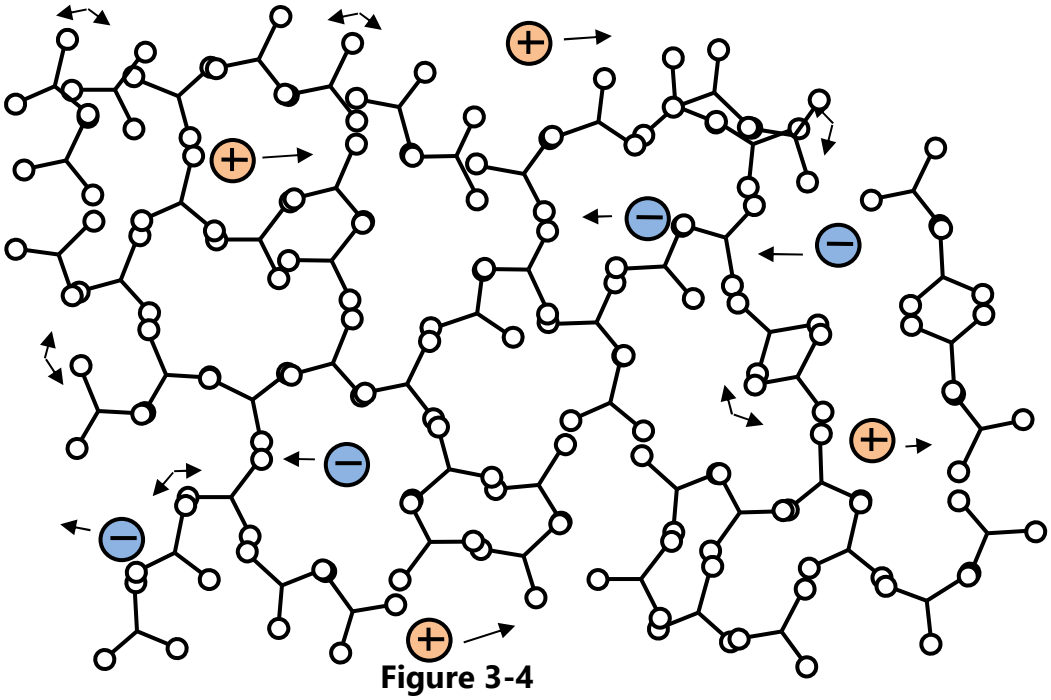

Figure 3-4
C-Stage resin (end of cure)

Characteristics of C-Stage thermoset

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

Chemical

- Reaction approaching end of cure
- Molecular chains lengthening and branching
- Molecular weight approaching infinity
- Degree of cure α approaching maximum for cure temperature
- Infinite network approaching maximum

Electrical

- Conductivity reaching minimum (resistivity reaching maximum)
- Dielectric constant reaching minimum

Note that gelation is a mechanical condition that does not cause a corresponding 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 3-4.

At constant temperature, as a thermoset cures from A-Stage to B-Stage to C-Stage, both free ion mobility and the amount of dipole rotation decrease continuously. Ion mobility and dipole rotation vary with temperature as well as cure state, however, and their behavior is more complex if these factors change at the same time.

The electrical quantities of resistivity and permittivity depend on free ion mobility and dipole rotation, respectively. As a result, these dielectric properties correlate with viscosity before gelation, and with rigidity or modulus after gelation.

Degree of cure and glass transition temperature

The degree of cure α 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. 3-1) $$\alpha = \Delta H \,/\, \Delta H_R$$

Where:

ΔH = Total heat released
ΔH_R = Heat of reaction

The degree of cure also correlates with *crosslink density*; α 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. 3-2)
$$\frac{(T_g - T_{g0})}{(T_{g\infty} - T_{g0})} = \frac{\lambda\,\alpha}{(1 - (1 - \lambda)\,\alpha)}$$

Where:

T_g = Glass transition temperature (K or °C)
T_{g0} = Glass transition temperature at α = 0 (uncured)
$T_{g\infty}$ = Glass transition temperature at α = 1 (fully cured)
λ = Adjustable parameter

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.

Lambient Technologies, LLC
649 Massachusetts Ave., Cambridge MA 02139, USA
(857) 242-3963
https://lambient.com
info@lambient.com

