

# AN INTRODUCTION TO THERMOSETS

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Thermosets are network-forming polymers. They include epoxy, phenolic, unsaturated polyester, polyurethane, dicyanate, bismaleimide, acrylate and many others. Unlike thermoplastics, chemical reactions are involved in their use. As a result of these reactions the materials first increase in viscosity and eventually cross-link and become *set*, and as a result they can no longer flow or dissolve. Cure is most often thermally activated, which gives rise to the term *thermoset*, but network-forming materials whose cure is light activated are also considered to be thermosets. Some thermosetting adhesives cross-link by a dual cure mechanism, that is by either heat or light activation. The reader interested in more detailed discussion of thermosets and their behavior is directed to Prime (1), Pascault et al. (2), Van Mele et al. (3), and Gotro and Prime (4).

In the uncured state thermosets are mixtures of small reactive molecules, often monomers. Catalysts are often added to accelerate cure. Most thermosets incorporate particulate fillers or fiber reinforcement to reduce cost, to modify physical properties, to reduce shrinkage during cure, or to improve flame retardance. Thermosets generally possess good dimensional stability, thermal stability, chemical resistance and electrical properties. Because of these attributes, they find widespread use in several applications such as adhesives; primary and secondary structural members in aerospace; countertops and floors for manufacturing facilities and homes; printed circuit boards, conductive polymer elements, and encapsulation materials for electronic applications; dental materials, especially adhesives; and recreational products such as tennis racquets, bicycle frames, golf clubs and fishing rods.

Unlike thermoplastic polymers the processing of thermosets includes the chemical reactions of cure. As illustrated in Fig. 1 cure begins by the growth and branching of chains. As the reaction proceeds, the increase in molecular weight accelerates, causing an increase in viscosity, illustrated in Fig. 2, and reduction in the total number of molecules. Eventually several chains become linked together into a network of infinite molecular

weight. The abrupt and irreversible transformation from a viscous liquid to an elastic gel or rubber is called the gel point. The gel point of a chemically cross-linking system can be defined as the instant at which the weight average molecular weight diverges to infinity (5).

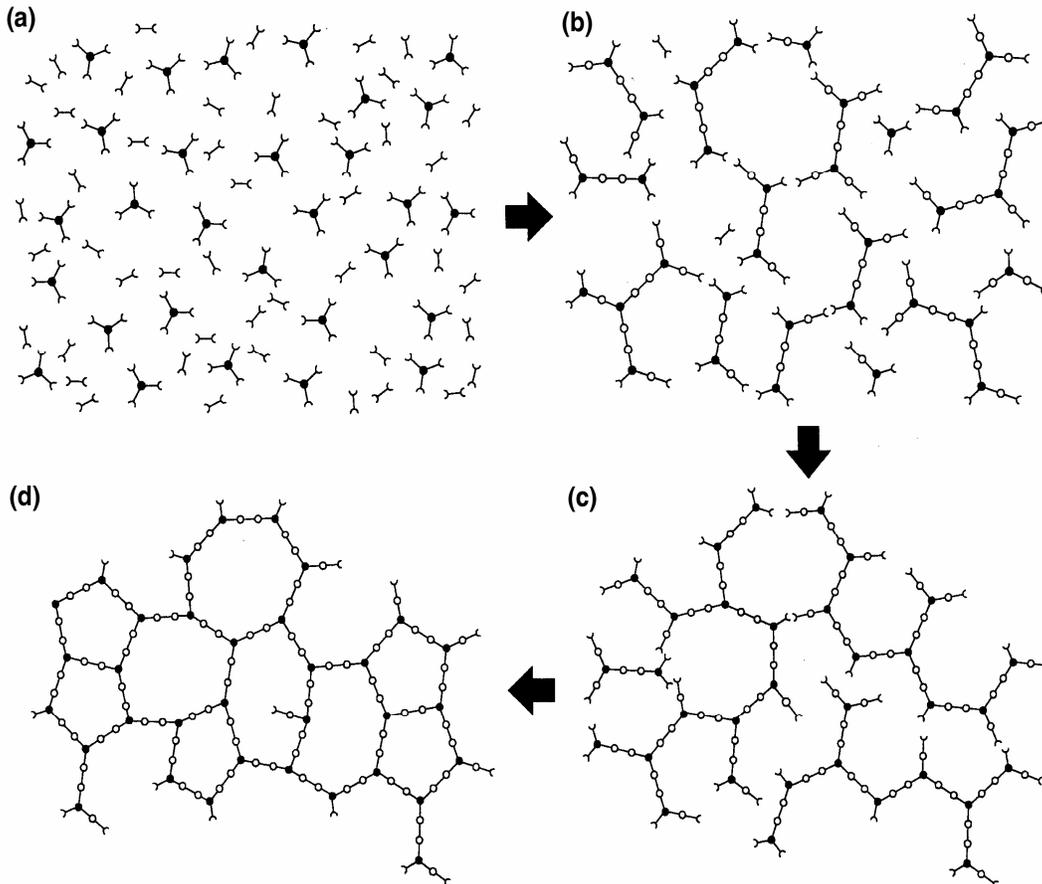


Figure 1. Schematic, two-dimensional representation of thermoset cure. For simplicity difunctional and trifunctional co-reactants are considered. Cure starts with A-stage or uncured monomers and oligomers(a); proceeds via simultaneous linear growth and branching to an increasingly more viscous B-stage material below the gel point (b); continues with formation of a gelled but incompletely cross-linked network (c); and ends with the fully cured, C-stage thermoset (d). From Ref. 1.

The macroscopic progress of cure is illustrated in Fig. 2. In the early stages of cure the thermoset can be characterized by an increase in its viscosity  $\eta$ . The gel point coincides with the first appearance of an equilibrium (or time-independent) modulus as

shown. Reaction continues beyond the gel point to complete the network formation, where physical properties such as modulus build to levels characteristic of a fully developed network.

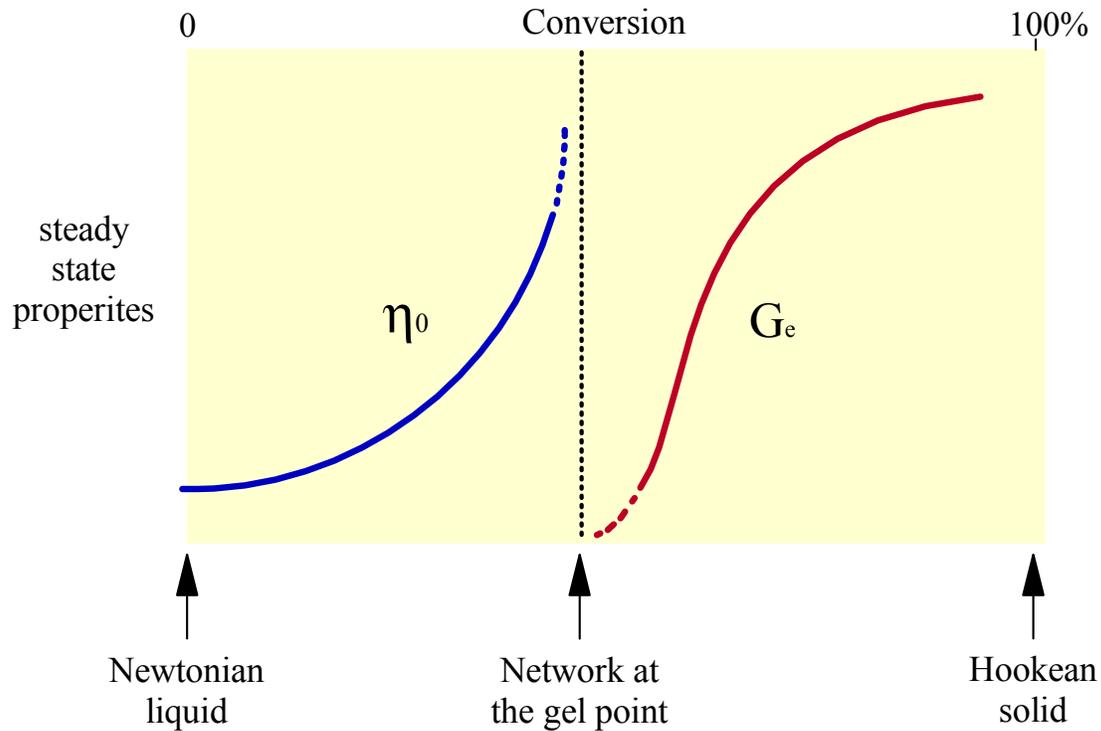


Figure 2. Macroscopic development of rheological and mechanical properties during network formation, illustrating the increase in viscosity  $\eta$ , which tends toward infinity at the gel point; the first appearance of an equilibrium modulus  $G_e$  at the gel point; and the increase in modulus with completion of the network. From Ref. 6.

Gelation is the incipient formation of a cross-linked network, and it is the most distinguishing characteristic of a thermoset. A thermoset loses its ability to flow and is no longer processable above the gel point, and therefore gelation defines the upper limit of the work life. As an example, for a *Five Minute Epoxy*, which can be found in any hardware store, the five minutes refers to the gel point. After the two parts are mixed the user must form an adhesive joint within five minutes before the material becomes rubbery, and then keep the repaired part fixtured, usually for several hours until cure is sufficiently complete. A distinction may be drawn between the phenomenon of molecular gelation and its consequence, macroscopic gelation. Molecular gelation occurs at a well-

defined stage of the chemical reaction, provided the reaction mechanism is independent of temperature and free of non-cross-linking side reactions (7-9). It is dependent on the functionality, reactivity and stoichiometry of the reactants. Macroscopic consequences of gelation include a rapid approach toward infinite viscosity and development of elastic properties not present in the pregel resin. The gel point may be calculated if the chemistry is known (7, 8). Molecular gelation may be detected as the point at which the reacting resin just becomes insoluble, or as the point where the mechanical loss tangent becomes frequency independent (5, 10). Macroscopic means to approximate gelation include the time to reach a specific viscosity, the  $G' = G''$  crossover in a dynamic rheology measurement, and a series of frequency-independent damping peaks accompanied by a small increase in storage modulus in a dynamic mechanical measurement. Gelation in condensation systems typically occurs between 50 and 80% conversion (degree of cure  $\alpha = 0.5 - 0.8$ ). For high functionality and free-radical initiated systems, gelation may occur at much lower conversions. The degree of conversion at the gel point  $\alpha_{gel}$  is constant for a given thermoset, independent of cure temperature, i.e. gelation is iso-conversional. For this reason the time to gel versus temperature can be used to measure the activation energy for cure. Gelation does not usually inhibit cure (e.g., the reaction rate remains unchanged), and it cannot be detected by techniques sensitive only to the chemical reaction, such as differential scanning calorimetry (DSC). Beyond the gel point, reaction proceeds toward the formation of one infinite network with substantial increases in cross-link density, glass transition temperature and ultimate physical properties. In the case of the *Five Minute Epoxy* completion of cure may take ten or more hours at ambient temperature but a much shorter time at 40°C.

Vitrification, a completely distinct phenomenon from gelation, may or may not occur during cure depending on the cure temperature relative to the  $T_g$  for full cure. Vitrification is glass formation due to  $T_g$  increasing from below  $T_{cure}$  to above  $T_{cure}$  as a result of the cure reaction, and is defined as the point where  $T_g = T_{cure}$  (11). Vitrification can occur at any stage during the reaction to form either an ungelled glass or a gelled glass. It can be avoided by curing at or above  $T_{g\infty}$ , the glass transition temperature for the fully cured network. In the glassy state, the rate of reaction will usually undergo a significant decrease and fall below the chemical reaction rate as the reaction becomes

controlled by the diffusion of reactants. It is common for complete vitrification to result in a decrease in the rate of reaction by 2 – 3 orders of magnitude. Unlike gelation, vitrification is reversible by heating, and chemical control of cure may be reestablished by heating to devitrify the partially cured thermoset. Vitrification may be detected by a step increase in heat capacity by modulated-temperature DSC (MTDSC) and by dynamic mechanical analysis (DMA) as a frequency-dependent transition resulting in a glassy modulus typically >1 GPa. The shift from chemical control to diffusion control of the reaction may be observed by a decay of the reaction rate, which is often observed when  $T_g$  reaches 10 – 15°C above  $T_{cure}$ . It is possible for diffusion to control the cure kinetics prior to vitrification; it is also possible for sluggish reactions to remain under chemical control well into the glassy state (see Refs. 1-4).

**Table I. Glossary of Characteristic Cure Parameters**

$\alpha$	chemical conversion (e.g., of epoxide groups), degree of cure
$\alpha_{gel}$	$\alpha$ at the gel point
$t_{gel}$	time to gelation, gel time
$t_{vit}$	time to vitrification
$T_{cure}$	cure temperature, a process parameter
$T_g$	glass transition temperature, a material property
$T_{g0}$	$T_g$ for uncured thermoset with degree of conversion $\alpha = 0$
$_{gel}T_g$	$T_g$ for thermoset with degree of conversion $\alpha_{gel}$
$T_{g\infty}$	$T_g$ for fully cured thermoset with degree of conversion $\alpha = 1$

Table I lists some characteristic thermoset cure parameters and their definitions. Note that some authors use  $x$  rather than  $\alpha$  to denote conversion.

Isothermal time-temperature-transformation (TTT) cure diagrams, as illustrated in Fig. 3., are a useful tool for illustrating the phenomenological changes that take place during cure, such as gelation, vitrification, complete cure and degradation (11, 12). Three critical temperatures are marked on the temperature axis of the TTT cure diagram:  $T_{g0}$ ,

the glass transition temperature of the completely unreacted thermoset;  $_{gel}T_g$ , the temperature at which gelation and vitrification coincide; and  $T_{g\infty}$ , the glass transition temperature of the fully cured network (see Table I). On this generalized diagram, the times to gelation and the times to vitrification are plotted as functions of the cure temperature. At temperatures below  $T_{g0}$ , reaction takes place in the glassy state and is therefore slow to occur.  $T_{g0}$  serves to define storage temperatures for unreacted systems, e.g., for premixed and frozen adhesives; 30 – 50°C below  $T_{g0}$ , i.e. deep into the glassy state, is recommended to effectively quench the reaction. Between  $T_{g0}$  and  $_{gel}T_g$ , the liquid resin will react without gelation until its continuously rising glass transition temperature becomes coincidental with the cure temperature, at which stage vitrification begins and the reaction may become diffusion controlled. Note that  $_{gel}T_g$  is the temperature at which gelation and vitrification occur simultaneously.

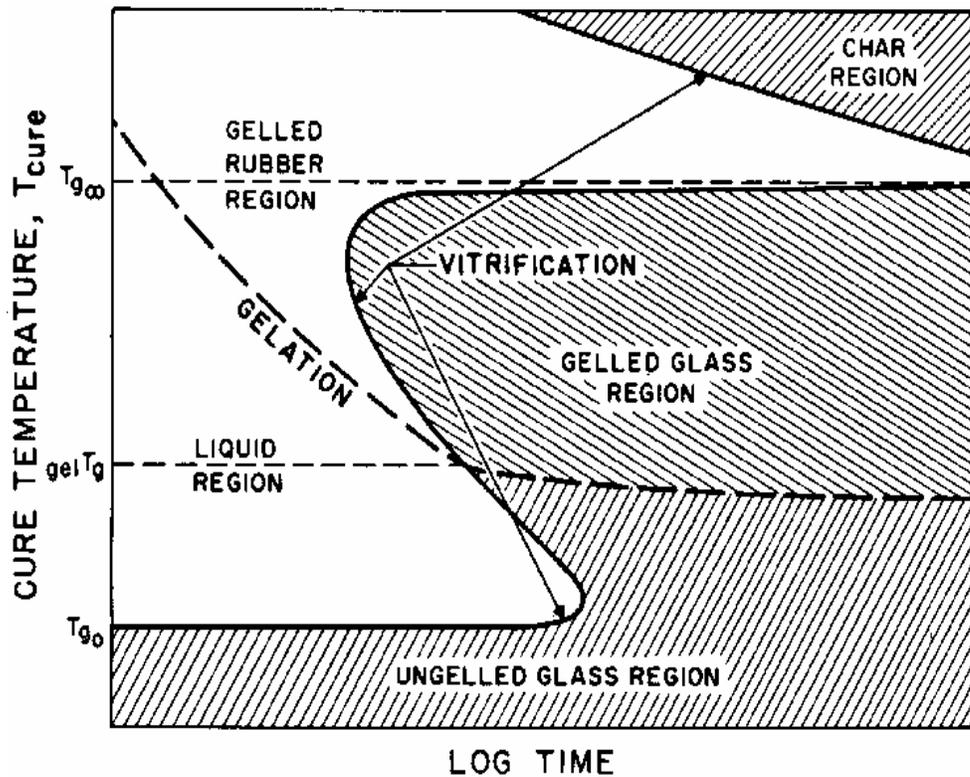


Figure 3. Generalized time-temperature-transformation (TTT) cure diagram. A plot of the times to gelation and vitrification during isothermal cure versus temperature delineates the regions of four distinct states of matter: liquid, gelled rubber, gelled glass, and ungelled glass. From Ref. 12.

At temperatures between  $T_{gel}$  and  $T_{g\infty}$ , the viscous liquid changes to a viscoelastic fluid, then to a rubber, and finally to a glass. Gelation precedes vitrification, and a cross-linked rubbery network forms and grows until the glass transition temperature coincides with the cure temperature, where the reaction may become diffusion controlled. At temperatures above  $T_{g\infty}$ , the network remains in the rubbery state after gelation unless other reactions occur, such as thermal degradation or oxidative cross-linking. Note that in the manufacture of carbon-carbon composites, network degradation is part of the process.

The handling and processing of thermosets are very much dependent on gelation and vitrification. For example, thermosets are often identified at three stages of cure: A, B, and C. A-stage refers to an unreacted resin; B-stage to a partially reacted and usually vitrified system, below the gel point, which, upon heating to devitrify, may be processed and cured; and C-stage to the completely cured network. Thus, to B-stage a thermoset requires vitrification prior to gelation, and this can be accomplished by maintaining the reaction temperature below  $T_{gel}$ . B-staging often provides systems that are optimized for processing. In general, thermosets that need to be solid during processing, e.g. powder coatings, will be B-staged to  $T_g > T_{process}$ , while thermosets that need to have some flow or tack during processing, e.g. prepregs, will be B-staged to  $T_g \leq T_{process}$ . To avoid vitrification and achieve complete cure in a reasonable time generally necessitates cure at temperatures close to or greater than  $T_{g\infty}$ .

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