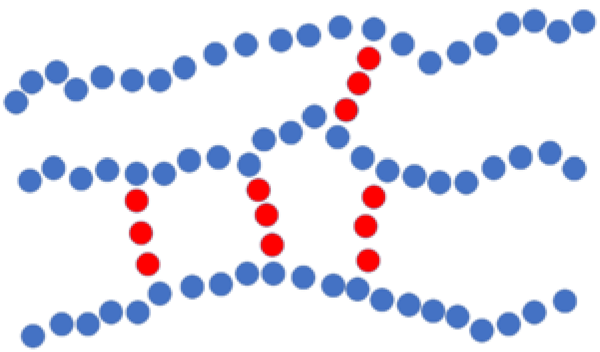
A162

Cure of thermosetting polymers
Foundational knowledge article



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Prerequisites	• Thermoset polymers • Degree of cure • Matrix

Introduction[edit | edit source]

For thermosetting polymers, the manufacturing process step of curing is necessary to transform the viscous polymer resin into a rigid solid. During this process, chemical reactions take place that result in the formation of molecular bonds that set the polymer into shape.

Scope[edit | edit source]

This page provides an overview of the curing process for thermosetting polymers. It covers a brief overview of the chemical curing reaction, physical changes experienced during the curing process, and measurement and monitoring techniques.

Significance[edit | edit source]

The curing process for thermoset polymers is responsible for their polymerization and the formation of the molecular crosslink network of bonds that give thermosets their desirable mechanical properties. This process solidifies the polymer matrix, thereby locking the composite part into its desired shape. Completion of the curing process (complete chemical reaction) is critical for obtaining the full mechanical properties of the polymer.

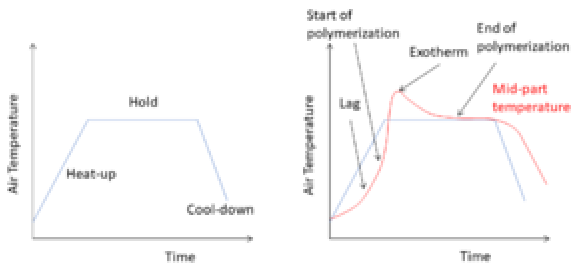
Prerequisites[edit | edit source]

Recommended documents to review before, or in parallel with this document:

- Thermoset polymers
- Degree of cure
- Systems Catalogue: Matrix materials

Overview[edit | edit source]

Thermoset polymers are synthesized during the curing process. Polymer chains link together by means of the short crosslink structures, creating a connected rigid network of linked polymer chains. It is this resulting structure that give thermoset polymers their unique mechanical characteristic traits, making thermosets such as epoxy or polyester desirable for use as the matrix component in composite materials.

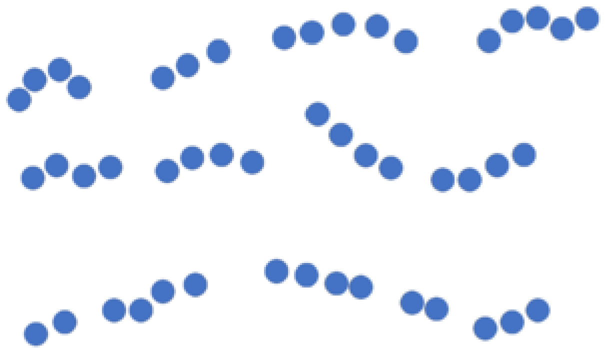


Example of a 1-step cure cycle temperature-time profile used to cure a thermoset polymer.

In the curing process, the thermoset polymer transforms from a flowing liquid resin into a rigid polymer. The timing and control of the curing process is a critical process step within the composite manufacturing process, as once the polymer takes on its rigid form, the composite part shape is locked into place and cannot be reshaped. During this transformation process, the thermoset polymer undergoes a series of chemical reactions and physical changes. Full completion of the chemical reactions is necessary for the polymer to acquire its desired properties, particularly its mechanical properties.

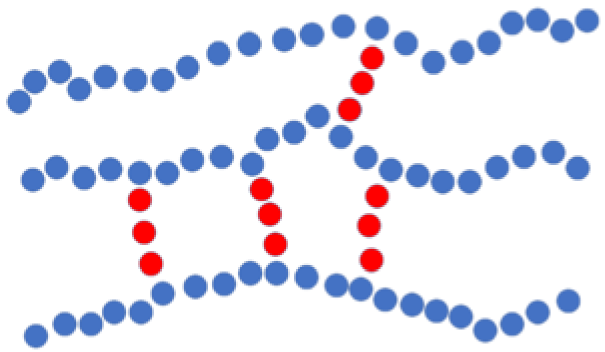
For some thermoset polymers, the curing reaction can occur to completion at room temperature, while many other thermoset polymers require a substantial amount of energy in the form of external heat input (e.g. oven or press process) to initiate and complete the process. An initiator (catalyst) may also be involved to initiate and accelerate the polymerization reactions.

Chemical Reaction (Polymerization)[edit | edit source]



Simplified schematic of monomers pre-polymerization, prior to their formation of long linear polymer chain structures.

During the curing process, the thermoset polymer undergoes polymerization and transitions from a flowing liquid resin into a rigid polymer.



Simplified schematic of crosslinked polymer chains. Crosslinks (shown in red) bridge between the main linear polymer chains.

Two polymerization reactions are taking place in this process:

1. Linear polymer chains form and grow with the joining together of short monomers
2. Crosslinks form between the linear polymer chains

With passing reaction time, this occurs throughout the polymer forming a linked rigid network of polymer molecules. The specific chemical reactions that take place are dependent on the thermoset polymer system resin and hardener.

For some specific examples of these reactions, please see:

- Epoxy page - Systems Catalogue
- Polyester page - Systems Catalogue

Polymer Chain Growth[edit | edit source]

The initial resin state prior to curing consists of short unreacted monomers. These are short repeating molecule units that when reacted together form longer linear polymer chains. This occurs in a variety of methods depending on the thermoset polymer. It can happen by homopolymerization with the input of heat, or through addition reactions where polymer chains are formed by joining the resin monomers to the curing agent molecule to form a co-polymer chain.

The short monomer lengths prior to curing provides the thermoset polymer resin with a low viscosity state as a liquid at room temperature, or at only moderately elevated temperatures (e.g. 100°C). This allows for relative ease of processing into composite materials when compared to thermoplastics [1]. The longer polymer chain length present with thermoplastics, requires high temperature processing for resin flow and processing into composite materials.

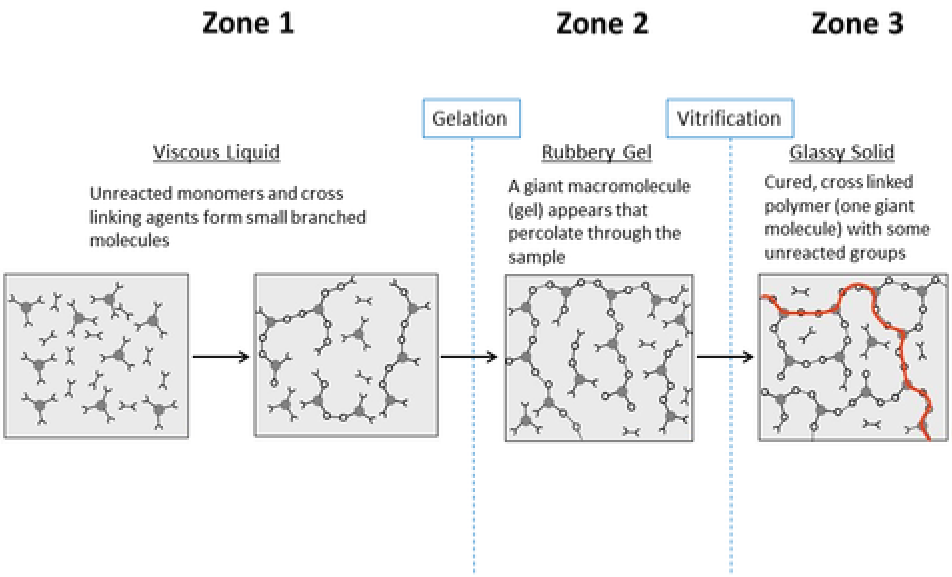
Crosslink Reaction[edit | edit source]

Thermoset polymers used in composites are most often are synthesized by a chemical reaction between two substances: resin and the hardener (crosslinking agent). In these cases, crosslinks between the resin polymer chains are created by addition reaction of the crosslinking agent. The crosslinking agent itself is a short molecule that has reactive sites that react and covalently bond to reactive sites on adjacent polymer chains. In a simple analogy, these short crosslinks bridge the linear polymer chains together. As the crosslink reaction continues, an interconnected three-dimensional network of linked polymer chains is formed that give the thermoset polymer its rigidity.

The frequency of the crosslinks along the linear polymer chain is known as the crosslink density. Increased crosslink density provides the thermoset polymer added rigidity, higher temperature stability (through a higher glass transition temperature), improved resistance to chemical attack, but with increased brittleness.

Physical Changes During the Curing Process[edit | edit source]

During the curing process as polymerization and crosslinking formation takes place, the thermoset polymer goes through several distinct transformation phases.



Thermoset polymer phase transformations during the curing process.

Behavioural stages of a thermoset polymer as it cures:

1. Initially the polymer is a flowing viscous liquid
2. At gelation, the polymer changes from a viscous liquid to a rubbery gel
3. As the curing advances, the rubbery gel transforms into glassy solid at vitrification

Zone 1 - Viscous Liquid Zone, before gelation[edit | edit source]

At room temperature, the resin is highly viscous. As the temperature is increased, the viscosity drops drastically. The reduction of viscosity with temperature continues until curing starts due to the external heat, which causes an increase in molecular weight and thereby viscosity. The viscosity increases rapidly with increasing degree of cure until the resin gels and the resin effectively transforms from a liquid to a solid.

Zone 2 - Rubbery Gel Zone, after gelation and before vitrification[edit | edit source]

As the curing process advances with time and temperature, at a certain degree of cure, a giant macromolecule is formed which spans the material and the material gels. For typical epoxies, gelation occurs at a degree of cure of 0.5 to 0.6. At gelation, the viscosity increases from a finite value to infinity and an insoluble macromolecule (gel) appears in the system. The resin now starts to develop modulus and exhibit viscoelastic properties. As the degree of cure advances, modulus is increased and viscoelastic properties evolved. During this stage, with the advancement of polymerization, the relaxation time and storage modulus of the material increases while loss modulus of the material decreases.

Zone 3 - Glass Solid Zone, after vitrification[edit | edit source]

As the cure advances, the glass transition temperature also advances. Further curing also reduces the free volume in the material (cure shrinkage) and hence the polymer chain mobility. Over a critical free volume range, the chain mobility is hindered and the polymer transforms from a rubbery to a glassy state. This transition, does not occur at a specific temperature but over a temperature range. Glass transition (Tg) + 25°C is usually mentioned in the literature as the threshold for this transition. Past this transition to the glassy state, due to the low chain mobility, the curing rate drops significantly and consequently modulus development slows down. As a simplification, the material in this stage is usually assumed to behave like an elastic material because the relaxation times are sufficiently long. Most resins never achieve a degree of cure of one (i.e. DOC =1). The final degree of cure is generally 0.85-0.95 for most commercial epoxy systems.

Measuring and Monitoring Cure[edit | edit source]

The crosslinking reaction is exothermic (heat releasing) allowing it to be measured in the laboratory using different methods at various degrees of accuracy to indirectly assess the curing progress. Numerically, the extent of the curing reaction that has occurred in a thermoset polymer can be represented by the degree of cure (DOC) index. It indicates what percentage of the crosslinking reaction has taken place in the polymer.

- See here to learn more about the degree of cure
- See here to learn how to measure the degree of cure

Other methods that may be used to monitor curing, depending on the thermoset system include:

- Rheological methods
- Dielectric methods
- Spectroscopy (e.g. FTIR) methods

Related pages

Page type	Links
Introduction to Composites Articles	
Foundational Knowledge Articles	• Cure of thermosetting polymers - A162 • Degree of cure - A104 • Glass transition temperature (Tg) - A210 • Heat of reaction - A114 • Thermal phase transitions of polymers - A102 • Thermoplastic polymers - A161 • Thermoset polymers - A105 • Viscosity (resin) - A203
Foundational Knowledge Method Documents	• How to measure curing time and degree of cure - M100 • How to measure gel time - M101
Foundational Knowledge Worked Examples	
Systems Knowledge Articles	
Systems Knowledge Method Documents	
Systems Knowledge Worked Examples	
Systems Catalogue Articles	
Systems Catalogue Objects – Material	

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Practice Documents	• Practice for developing a thermal transformation process step - P105 • Troubleshooting scale-up issues from thin to thick parts - P140 • Troubleshooting scaling-up issues from coupons to parts - P134
Case Studies	• Troubleshooting of room temperature processes for large recreational and industrial parts - C100
Perspectives Articles	• Composite materials engineering webinar session 1 - Introduction - A120 • Composite materials engineering webinar session 3 - Constituent materials - Resin - A122 • Composite materials engineering webinar session 4 - Thermal management and resin cure - A123 • Composite materials engineering webinar session 5 - Manufacturing processes - Introduction - A124 • Composites Process Simulation: A Review of the State of the Art for Product Development - A283 • Effect of cure on mechanical properties of a composite (Part 1 of 2) - A319 • Effect of cure on mechanical properties of a composite (Part 2 of 2) - A320 • Heat Transfer in Composites Processing - A321 • Introduction to the processing of thermoplastic composites - A322 • Resin Behaviour During Processing: What are the key resin properties to consider when developing a manufacturing process? - A257 • Understanding Polyester Resin Processing: The Effect of Ambient Temperature on the Final Part - A286

References

1. ↑ [Ref] Hoa, S V (2018). *Principles of the Manufacturing of Composite Materials*. DEStech Publications, Incorporated. ISBN 9781605954219.

For polymer matrix composites (PMCs), resin refers to the matrix; the continuous material phase that binds the reinforcement together, maintains shape, and transfers load. Resins are divided into two main groups: thermosets and thermoplastics.

Thermosets are a class of polymer that undergo polymerization and crosslinking during curing with the aid of a hardening agent and heating or promoter. Initially they behave like a viscous fluid. During curing, they change from viscous fluid to rubbery gel (viscoelastic material) and finally glassy solid.

If heated after curing, initially they become soft and rubbery at high temperatures. If further heated, they do not melt but decompose (burn)

Comes in two parts: part A (resin) and B (hardener). When mixed, curing reaction starts and is not reversible.

Examples include epoxy or polyester.

The continuous material phase that binds the reinforcement together, maintains shape, transfers load, protects the reinforcement from environment and damage, and provides the composite support in compression.

Desirable characteristics:

- Moisture/chemical resistance
- Low density
- Processability

Engineered materials (designed to have specific properties) made from two or more constituent materials with different physical or chemical properties. The constituents remain separate and distinct on a macroscopic level within the finished structure.

In composites processing, viscosity is an indicator of how easily the resin matrix will mix with the reinforcement and how well it will stay in place during processing. The lower the viscosity, the more easily resin flows. Resin viscosity ranges considerably across chemistries and formulations.

By scientific definition, viscosity is a measure of a material's resistance to deformation. For liquids, it is in response to imposed shear stresses.

Degree of cure (DOC) is an indication of how far the chemical curing reaction (crosslinking process) has advanced in a thermoset resin.

DOC is defined with a number between 0 and 1 (or 0% and 100%) where 100% is a fully cured resin. It does not have to fully reach 100% for the resin to become solid or the part to be used. In some aerospace applications, resins are only cured to about 90%. Higher the degree of cure, higher the mechanical properties.

The glass transition temperature (T_g) is the temperature region where the polymer transitions from a hard, glassy material to a soft, rubbery material. It is one of the most important properties of any amorphous polymer.