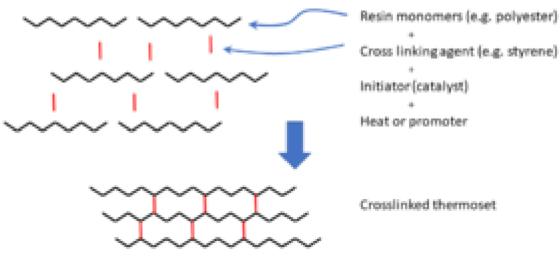
A105

Thermoset polymers

Foundational knowledge article



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Prerequisites	• Matrix

Introduction[edit | edit source]

Thermoset or thermosetting polymers are one of the two groups of polymers (the other being thermoplastics). They are characterized by the molecular crosslink covalent bonds that are formed between adjacent primary polymer chains. Thermosets undergo polymerization and crosslinking during a curing stage, which in many cases occurs with the aid of a hardening agent and heating or promoter.

Thermoset precursor materials may be of low molecular weight, and some after mixing will flow and crosslink at room temperature [1] – allowing for relative ease to process. However, many thermosets require the input of heat to complete the curing (crosslinking) process.

Scope[edit | edit source]

This page provides a brief overview to the family of polymers classified as thermoset or thermosetting polymers. It briefly covers their molecular structure, their material forms, and an introduction to the thermoset curing process and their post-cured properties.

Significance[edit | edit source]

Thermosets are a popular polymer matrix material for fibre reinforced composites. Common examples include polyesters and epoxies. They are the most predominant type of matrix system, particularly in the aerospace market segment. Thermoset matrix composites are more widely used than thermoplastic matrix composites due to their lower viscosity at relatively low temperatures (less than 100°C), which better facilitates the resin/fibre wetting process [2].

Prerequisites[edit | edit source]

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

- Systems Catalogue: Matrix materials

Overview[edit | edit source]

Thermoset or thermosetting polymers are one of the two groups of polymers (the other being thermoplastics). Thermosets undergo polymerization and crosslinking during a curing stage, which in many cases occurs 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). As a result, thermoset polymers are considered single use materials as they cannot be reprocessed.

Crosslink Structure[edit | edit source]

Thermosets are characterized by their molecular crosslink structure, where adjacent linear polymer chains are joined together by covalent bonds. Often, the crosslink structure is accomplished by additive atoms and molecules that are covalently bonded to the chains [3]. It is these bonds that form between the chains that give the crosslink structure its name.

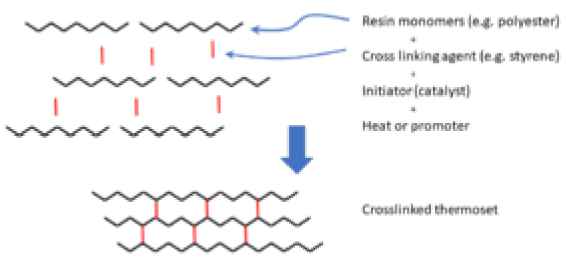


Illustration of the molecular crosslink formation for a thermoset polymer.

Thermoset resins often come in two parts: part A (resin) and B (crosslinking curing agent, or sometimes referred to as hardener). The ‘curing reaction’ (curing process) is the physical synthesis between these two substances by a chemical reaction.

Material Forms[edit | edit source]

Uncured thermoset polymers often come in the form of a liquid resin that is to be combined with reinforcement fibres in either a hand lay-up or liquid composite moulding composite manufacturing process. They can also be provided in a partially-cured and tacky almost solid-like state in the form of a resin film that is to be used in resin film infusion processes. Extending the latter form, another popular handling form for thermosets is to be pre-combined with reinforcement fibres as a B-stage prepreg material.

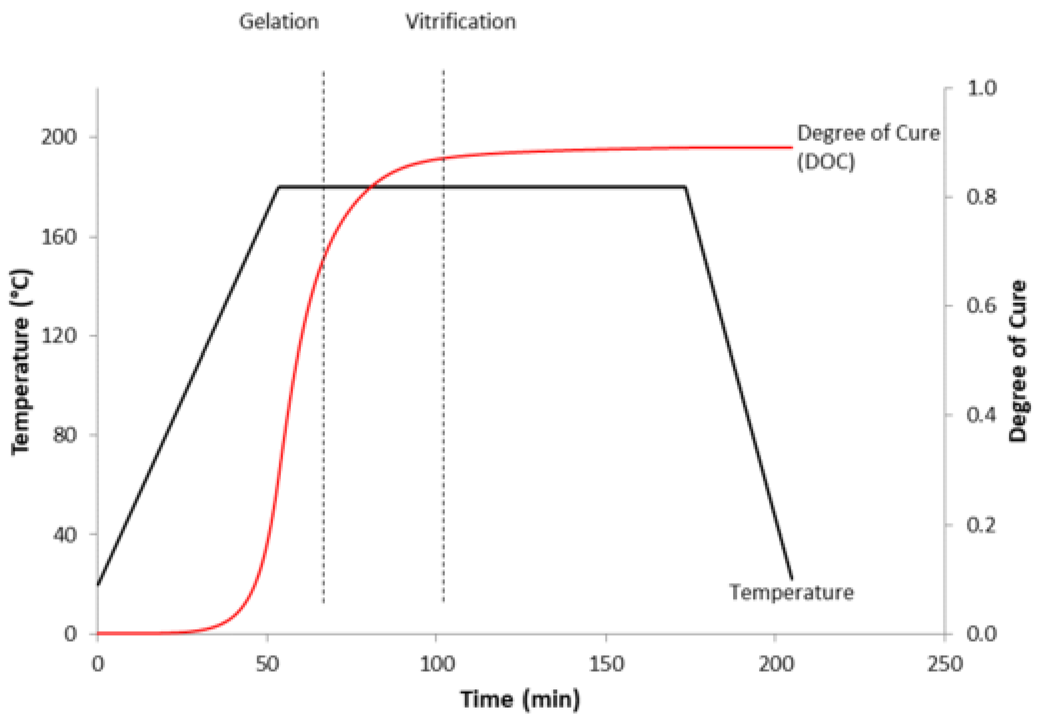
Please see the systems catalogue for more information regarding thermoset resin material forms (Thermoset Polymers - Systems Catalogue page).

Curing and Final Properties[edit | edit source]

Link to main Curing of Thermosetting Polymers page

A curing process is necessary to polymerize the thermoset polymer and form the molecular crosslink structure responsible for their desired properties. During this process, the thermoset polymer transforms from a flowing liquid resin into a rigid polymer. Curing can be initiated by various means depending on the particular polymer system; heat, radiation, chemical additives, etc., or a combination of these.

Heat is often employed as part of this process to fully cure the polymer. An example of a cure process temperature profile and the evolution of the crosslinking process (represented as degree of cure) is shown below.

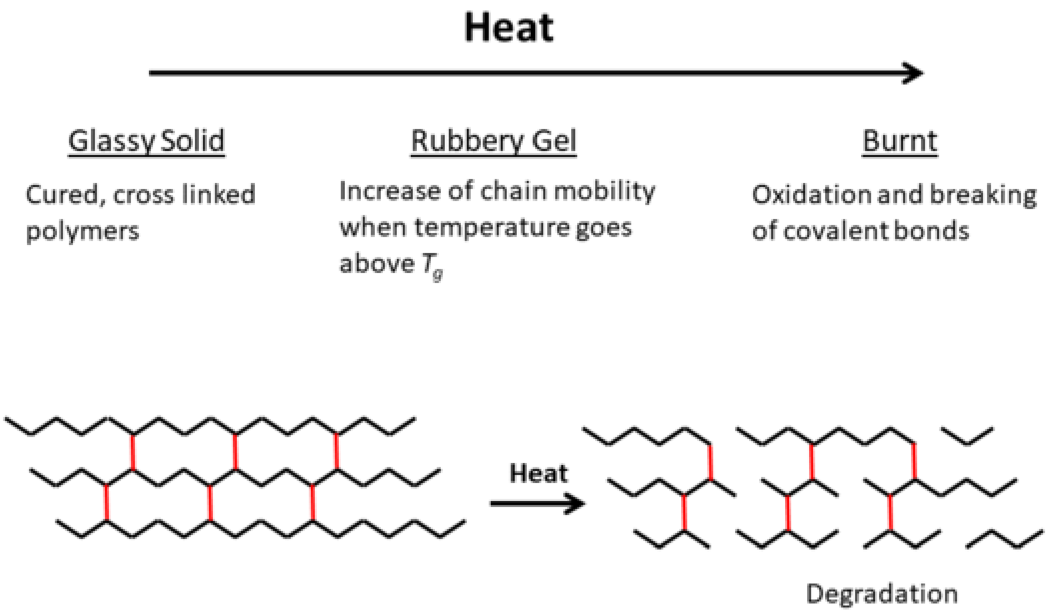


Example of a thermoset polymer heated cure cycle process showing the crosslink development (degree of cure). .

Once curing is complete, fully cured thermosets exhibit the following [4]:

- Excellent environmental resistance
- Excellent solvent resistance
- High mechanical strength and stiffness
- Low toughness (downside)

After curing, if heated to very high temperatures, thermosets chemically breakdown.



Thermoset polymer breakdown if subjected to high thermal breakdown temperatures.

1. Initially softening
2. After time, transforming into char

Example Thermoset Materials[edit | edit source]

Examples of popular thermosets used as polymers matrices include:

- Polyesters
- Vinyl esters
- Epoxies
- Phenolics
- Bismaleimides

For more information on popular thermoset matrix materials, see the catalogue volume thermoset matrix page.

Related pages

Page type	Links
Introduction to Composites Articles	
Foundational Knowledge Articles	• Basic Definitions of Material Properties - A211 • Composite properties - A214 • Cure of thermosetting polymers - A162 • Degree of cure - A104 • Glass transition temperature (Tg) - A210 • Heat of reaction - A114 • Material properties - A150 • Polymer properties - A212 • Reinforcement properties - A213 • 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	
Systems Catalogue Objects – Shape	
Systems Catalogue Objects – Tooling and consumables	
Systems Catalogue Objects – Equipment	
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 • Dr. Anoush Poursartip's cdmHUB global composites expert webinar - A136 • 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] McCrum, N. G. et al. (1997). *Principles of Polymer Engineering*. Oxford University Press. ISBN 978-0-198565-26-0.
2. ↑ [Ref] Hoa, S V (2018). *Principles of the Manufacturing of Composite Materials*. DEStech Publications, Incorporated. ISBN 9781605954219.
3. ↑ [Ref] Callister, William D. (2003). *Materials Science and Engineering: An Introduction*. John Wiley & Sons, Inc. ISBN 0-471-13576-3.
4. ↑ [Ref] Pilato, Louis A.; Michno, Michael J. (1994). *Advanced Composite Materials*. Springer-Verlag Berlin Heidelberg. doi:10.1007/978-3-662-35356-1. ISBN 978-3-540-57563-4.

About **Help**

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

A class of polymer, some common examples include polypropylene and polyethylene.

They soften and melt upon heating (i.e. potentially recyclable), high viscosity when melted, therefore difficult to saturate fibres. Usually needs a lot of pressure and heat to process.

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.

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.

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.

Pre-impregnated (prepreg) material refers to fibre that is already combined with resin. It is the most common material form used in aerospace.

During prepreg production, (e.g. fibres are run through a resin bath), prepreg is heated and partially cured to B Stage (< 5 % degree of cure). Thermoset prepregs (e.g. epoxy prepreg) have to be kept in a freezer at around -20 °C. At room temperature, the epoxy starts to cure.

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.