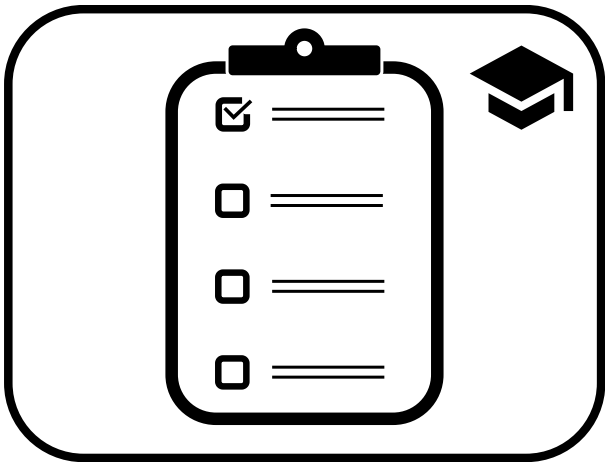
M100

How to measure curing time and degree of cure

Foundational knowledge method



Document Type	Method
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Themes	• Thermal management
Relevant Class	Material
Tags	• Method • Chemical properties • Cure and crystallization • Material characterization • Outcome parameters • Thermoset polymers
Prerequisites	• Degree of cure • How to measure gel time

Scope[edit | edit source]

This page outlines several methods that can be used to measure curing time and the degree of cure (DOC) of a composite part made of a thermoset resin, such as an epoxy or polyester. The discussed methods are of varying complexities, with each providing different levels of resin cure information that can be obtained. The choice of method may be influenced by the equipment that the user has available, the time involved, and the extent of detailed information that is required by the user.

Significance[edit | edit source]

Knowledge of a resin's curing time and degree of cure is significant for ensuring that the intended and maximum mechanical properties of the thermoset polymer matrix resin is achieved. The further the degree of cure has progressed towards fully cured, the higher the mechanical properties of the resin.

Knowledge of the degree of cure is also important for intermediate-processing steps such as deposition, demoulding or machining. For example, if demolding takes place prior the resin has

reached vitrification, and so before a specific degree of cure, structural robustness throughout this intermediate processing steps cannot be confidently ensured and the part might deform during it.

Prerequisites[edit | edit source]

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

- Degree of cure
- How to measure gel time

Overview[edit | edit source]

Provided on this page are several test methods that either directly measure or indirectly measure the degree of cure of a thermoset resin. The table briefly summarizes each method with the level of complexity involved, any specialized equipment necessary, and general comments about the test methods. The table is meant to be an initial guide, where it is recommended that each method be reviewed in detail in order to determine the most appropriate method for your particular use.

	Test Method	Necessary Equipment	General Comments:
Simple	**Heat Measurement** Using: 100 grams of resin	• Plastic or paper cups, glass jars • Thermocouple and multimeter	Method does not actually quantify the degree of cure, but is used to approximate curing time. It is a simple test to perform and can be used in conjunction with other methods to characterize the resin system's cure kinetics.
Moderate	**Resin Hardness Measurement** Using: Barcol Impressor	• Barcol hardness impressor	Method allows for tracking of the degree of cure evolution with time, however, only at a qualitative level as not absolute DOC values are measured.
Detailed	**Heat Measurement** Using: Differential Scanning Calorimetry (DSC)	• DSC instrument (laboratory)	Method quantifies the degree of cure of a thermoset resin sample. If a modulated DSC (MDSC) instrument is used, the resin's heat capacity and glass transition temperature can also be simultaneously determined during testing.

Heat Measurement (100g-Sample)
Resin Hardness Measurement (Barcol Impressor)
Heat Measurement (Differential Scanning Calorimeter)

Scope[edit | edit source]

Measuring the peak exothermic temperature and the time at which it occurs for a 100g sample of resin, is a common industrial practice. This information is often reported on the material data sheets for liquid thermoset resin systems.

While the simple detection of this heat generation does not in itself quantify the resin’s degree of cure, it is useful in providing a rough guide to the curing time of the resin. This can be determined as the peak exotherm occurs near the same time that the resin curing accelerates and a rapid rise in the DOC index takes place. Furthermore, these two measurements can qualitatively identify cure

kinetics changes brought on by resin modifications.

The described curing resin heat measurement test is not an industry standardized test, although as mentioned, recording 100g exotherm temperature and the time is a common industry practice for both polyesters and epoxies. The steps outlined here are largely adopted from a procedure provided in the Polynt Composites – Composites Applications Guide [1]. It is one procedure of such a test, other similar tests with slightly differing parameters may exist elsewhere. A similar test is described in the no longer active ASTM standard D2471 [2]. Using the peak exotherm is described in Epoxyworks literature (Gougeon Brothers, Inc. – WEST SYSTEM Epoxy) as a pragmatic approach to qualitatively assess resin cure kinetics to compare between formulations [3].

Setup[edit | edit source]

Equipment[edit | edit source]

- Stopwatch
- Scale to weigh sample
- Cups/containers: suitable containers include – 250mL (8 oz.) paper cups, wide mouth mason jars, etc.
- Thermocouple and a temperature reading device such as a thermocouple compatible multimeter or computer data acquisition setup
- (Optional for heated test) Water bath setup

The choice of sample container size and shape is an important consideration and consistent use of similar sample containers between tests should be insured. The Polynt guide recommends using cups or jars for curing the 100g resin sample. Casting thin resin samples for exotherm measurement should be avoided (minimal and difficult to detect exotherm). See the analysis section for further details on the sensitivity of sample amount, and container geometry on the exotherm temperature measurement.

Test Specimen[edit | edit source]

- 100g of freshly mixed sample.

The 100g amount of resin is an accepted industry practice, but it is not standardized. While a different amount of resin can be used, the use of 100g is recommended. Avoid using greater amounts of resin as excessive exothermic heat generation and thermal run-away can occur, with the potential for burn or fire danger. Conversely, using too little sample can result in a minimal or no temperature increase that is measurable.

Procedure[edit | edit source]

The following procedure steps are a summary of those found in the Polynt Composites – Composites Applications Guide [1]:

1. Start stopwatch once catalyzation or resin mixing (two part resin system) has commenced.
2. Weigh 100 grams of freshly mixed resin poured into the sample container.
3. Place thermocouple into the resin while it is still liquid, or in a soft gel state. Ensure that the thermocouple is centred both vertically and horizontally in the resin sample.
4. Insulate the sample container as best as possible from the bench top or room environment.

Failing to do so may affect the temperature recorded.
5. Record peak temperature and the time elapsed.

Analysis[edit | edit source]

Resin reaction kinetics[edit | edit source]

Changes in the resin reaction behaviour are reflected in changes to both the measured exothermic temperature and time for it to take place. As general rule, slower reacting resin systems exhibit both a lower peak exotherm temperature, and a longer time to reach this point [3]. Qualitative comparison of these two measured values between samples of different resin formulations (e.g. comparing different hardening agents for curing of the same base resin), a sense for any corresponding changes to the reaction cure kinetics behaviour can be established.

Sample mass sensitivity[edit | edit source]

Maintaining consistency in the amount of sample between individual tests is imperative for the effectiveness of this heat measurement method. The resin's exothermic behaviour is very sensitive to the amount of reacting sample. In general, the more sample that is reacting, the greater the exothermic temperature rise. This is due to a combination of an increase in resin thermal mass and the thermal insulating properties of the resin (poor heat dissipation). Therefore, consistency in resin quantity between samples is critical if these measurements are to be used for any comparative evaluation. 100g of resin is standard industry practice.

Sample container sensitivity[edit | edit source]

In addition to the amount of sample reacting, careful choice of an appropriate sample container must also be made. The exothermic temperature rise generated from the thermoset polymer reaction is very sensitive to the surface area -to- volume ratio of the resin sample used for the measurement.

When the curing resin is spread out thin, the large surface area facilitates heat dissipation resulting in minimal exothermic heat build up within the sample. If the same volume of resin is instead cured in a narrower and taller container, the reaction heat is generated faster than the rate that the heat can migrate to the resin surfaces and out of the sample – resulting in a greater peak exotherm temperature rise.

Careful choice of sample containers, and consistent usage of the same container geometry between tests must be insured.

Limitations[edit | edit source]

The described 100g resin test only provides the time from catalyzation or resin/curing agent mixing until the thermoset cross-linking chemical reaction is happening at an accelerated rate. On its own, the measurements do not provide detailed information for the resin degree of cure (quantitatively how far the curing process has progressed). However, when performed along with gelation timer test and the Barcol hardness test, a fairly complete characterization of the curing behaviour for the resin system can be obtained.

Scope[edit | edit source]

This method uses resin hardness as a proxy to track the degree of cure (DOC) evolution for a curing thermoset resin. The method is based on the principle that increases in resin hardness correspond to increases in the resin degree of cure as chemical cross-links are formed, increasing the rigidity of the polymer.

While hardness can be measured by a variety of devices, the Barcol impressor (hardness tester) is recommended by ASTM (D2583) as appropriate for both reinforced and non-reinforced rigid plastics [4]. It is a relatively simple method to carry out, and requires minimal equipment.

The procedure description provided here is adopted from the Barcol Hardness test procedure in the Polynt Composites - Composites Applications Guide [1]. Fundamentally, this procedure is a derivation on ASTM D2583 – Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor [4] – that is used to measure the hardness of cured polymers.

Setup[edit | edit source]

Equipment[edit | edit source]

Two separate Barcol hardness impressors are required to measure hardness for rigid plastics that are commonly used as polymer matrices. Switching between the Barcol impressors is dictated by the hardness of the material at the time it is being indented.

- Barcol 935 (softer materials)
- Barcol 934 (harder materials) - used when resin hardness is scale 75 and greater

Test Specimen[edit | edit source]

The hardness measurements can be made on production parts, as well as on purposely produced quality control laboratory samples. Barcol hardness measurements are not valid for gel coats as the specimen thickness is insufficient – inadvertently measuring the hardness of the material under the gel coat.

Minimum thickness: 0.8mm (1/32") - according to the Polynt [1] procedure, 1.5mm (1/16") - according to ASTM D2583 [4].

Measurement locations: Sample measurements should be made at positions at least 3mm away from the sample edges, and the test area should be smooth. If measuring a composite material containing fibre reinforcement, the measurement location ideally should be in an area of neat resin to avoid unwanted measurement of the fibre hardness.

Number of sample measurements: For a fully cured polymer, ASTM D2583 recommends at least 10 measurements [4] to be made to determine the resin hardness. However, taking hardness measurements while the resin is still curing (and hardening) to provide a 'snap-shot in time' requires that measurements be taken in quick succession, making this number of measurements difficult. The Polynt guide [1] specifies a minimum of 3 measurements. As a general rule of thumb, more variation is observed and therefore more measurements are required for softer material.

Procedure[edit | edit source]

The following procedure steps are a summary of those found in the Polynt Composites – Composites Applications Guide [1]:

1. Calibrate the Barcol impressor according to the manufacturer's instructions.
2. Note the time of catalyzation or resin mixing (part A + part B, e.g. two part epoxy).
3. Weigh the amount of resin used.
4. After the sample has gelled: check the sample every 5 minutes with a pencil performing pencil indentation. When the resin is no longer able to be "pencil dented", measurement with the Barcol 935 meter can begin. Ensure the needle assembly is perpendicular to the surface and take a reading with the Barcol 935 impressor, reporting the average of the readings.
5. Perform measurements every 5 minutes until the Barcol 935 reaches a measurement of 60-70. When this occurs, switch to the Barcol 934 impressor and continue measuring. During the initial switch to Barcol 934, the needle impressor reading may fade to 0 during the initial readings, make note of this. In the hardness transition range, measurements with both Barcol 935 and Barcol 934 meters should be made (see example analysis).
6. If any resin sticks to the needle, remove and wash the needle to prevent impressor blockage.

Analysis[edit | edit source]

Sample data from the Polynt Composites - Composites Applications Guide [1]:

	Time (min.)	Barcol 935	Barcol 934
Catalyzed (polyester)	0	-	-
Gelled	15	-	-
	20-25	-	-
	30	5	-
	35	15	-
	40	50-60	0
	45	70	0-5
	50	80	15
	55	80	20-30
	60	80	40

Limitations[edit | edit source]

The described hardness test method does not directly quantify the resin degree of cure as it is defined (see degree of cure page and its definition). The method only provides qualitative information regarding the cure progression with time. If hardness values for the fully cured resin are known ahead of time (or measured previously), the method can provide the user with a quick reference to the resin's relative degree of cure. Otherwise, hardness measurements should be carried out until hardness values plateau as a determination that the resin curing is nearing completion.

The nature of the measurements involved in this test method are best suited for room temperature cure resin systems.

Scope[edit | edit source]

Differential Scanning Calorimetry (DSC) laboratory testing instrument.

Determining the degree of cure (DOC) of a thermoset sample by differential scanning calorimetry (DSC) measurements is the most exact and precise of the methods described on this page. It is achieved by using a DSC laboratory instrument to measure the residual heat of reaction from a sample of the matrix resin to complete any remaining reaction, and comparing it to the resin system's total heat of reaction for complete curing from the uncured state.

The residual heat of reaction is typically measured by subjecting the sample to a constant linear heating rate, from a low temperature (e.g. -90°C) to a high temperature (e.g. 200°C). Heating is carried out to a sufficiently high enough temperature to ensure complete curing of the sample by the end of the test.

Dynamic tests can be performed in Standard or Modulated mode (if using a modulated DSC instrument - MDSC). The modulated mode adds a sinusoidal heating profile to a linear ramp. The sample undergoes an average increase in temperature but experiences periods of instantaneous heating and cooling. For modulated testing, relatively slow heating rates (e.g. 2-8°C/min) are typically used to allow for sufficient modulations during a thermal event. The modulated mode allows to measure not only the degree of cure but also the glass transition temperature.

Please see the catalogue volume for a list of suppliers selling DSC equipment.

Setup[edit | edit source]

Equipment[edit | edit source]

- Differential Scanning Calorimetry (DSC) laboratory instrument
- Required DSC sample pans, lids, and crimping tool
- High precision scale suitable for measuring 20mg or less of sample (5-10mg of sample is typical)

Test Specimen[edit | edit source]

- Resin sample to be evaluated. DSC sample sizes are small, in the milligram (mg) range. Typically, 5-10mg of resin sample is suitable
- Uncured sample to measure the total heat of reaction

Procedure[edit | edit source]

1. Weigh matrix resin test sample to be evaluated on a high precision scale. Typically, this is in the mg range (5-10mg is typical) for polymer resins. Follow the appropriate scale procedures.
2. Prepare test sample in DSC test pan, place on lid and crimp closed according to DSC manufacturer's instructions.
3. Perform dynamic heating test on DSC instrument according to the DSC manufacturer's operating procedure. A standard heating test, or a modulated test can be performed (see Analysis section for discussion).

Analysis[edit | edit source]

If no peak exotherm is recorded by the DSC, it means that the sample was fully cured.

If an exothermic peak was measured by the DSC – determine the heat of reaction by integrating under the obtained curve. Integration of the exothermic peak curve is usually directly offered by the DSC's software. Alternatively, any suitable mathematics solving computer program can be used. This energy represents the residual heat of reaction, or the remaining uncured portion in the sample prior to DSC testing.

If a modulated dynamic test was performed, the curve to be integrated is the kinetic component of the total heat flow, sometimes referred to as the non-reversing heat flow curve. An advantage of performing a modulated test is that additionally, the resin heat capacity and glass transition temperature can also be simultaneously measured. Modulated testing can only be performed on a modulated DSC (MDSC) instrument, not all DSC instruments have the ability.

The degree of cure of the sample is determined from the following equation\[x=1-\frac{H_{res}}{H_R}\]

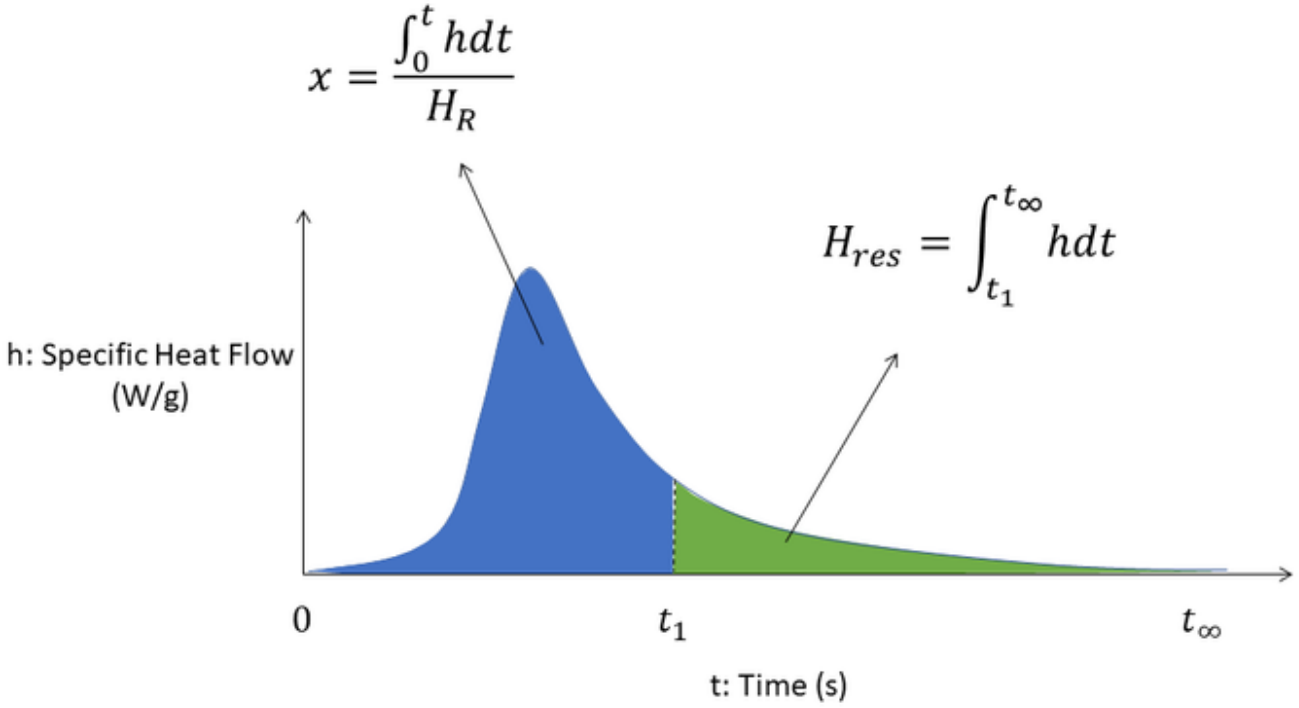
Where,

\(x=\) Degree of cure

\(H_R=\) Heat of reaction - total [J/g]

\(H_{res}=\) Heat of reaction - residual [J/g]

Visually, from a DSC characterization of the specific heat flow curve:



By measuring the residual heat of reaction against the total heat of reaction by DSC characterization, the degree of cure can be determined.

To determine the total heat of reaction of the resin system, a dynamic heating test must be performed on an uncured sample of the resin.

Limitations[edit | edit source]

Differential scanning calorimetry (DSC) is a specialized piece of laboratory equipment that may not be accessible to all practitioners. In such cases, measurement and analysis will have to be sub-contracted out to specialist laboratory. Please see the KPC resource guide for a list of laboratories.

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 • Foundational method documents - A153 • 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 • How to measure reinforcement content (and corresponding matrix content) - M109 • Tensile Testing - M117
Foundational Knowledge Worked Examples	
Systems Knowledge Articles	• Systems knowledge method documents - A191
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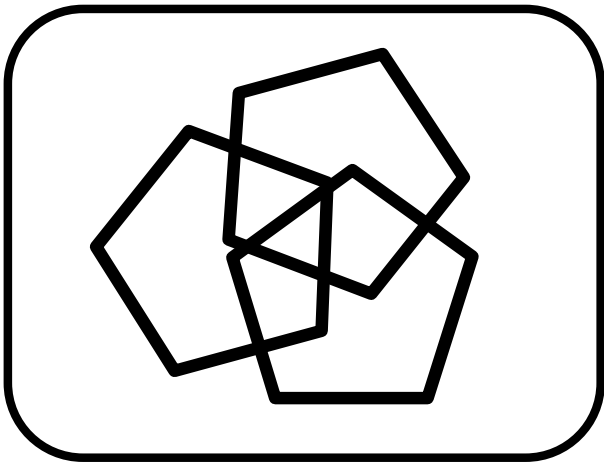
Practice Documents	• Decreasing Cure Cycle Time - P121 • Practice for developing a thermal transformation process step - P105 • Troubleshooting scale-up issues from thin to thick parts - P140 • Troubleshooting scaling-up issues from coupons to parts - P134
Case Studies	• Troubleshooting of room temperature processes for large recreational and industrial parts - C100

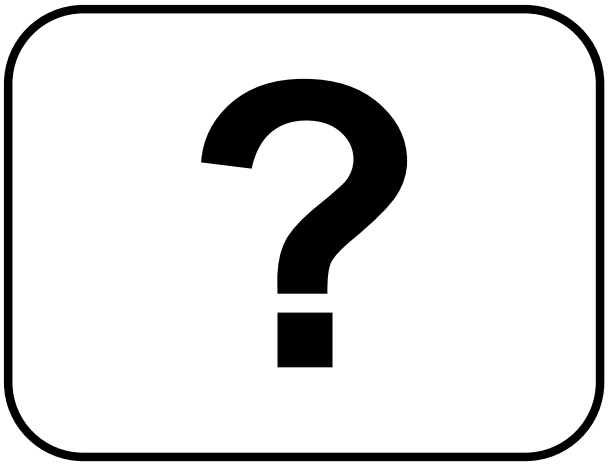
Perspectives Articles	• Composite materials engineering webinar session 3 - Constituent materials - Resin - A122 • Composite materials engineering webinar session 4 - Thermal management and resin cure - A123 • Composite materials engineering webinar session 5 - Manufacturing processes - Introduction - 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 • Parameters for Structural Analysis of Composites - A247 • 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. ↑ [1.0] [1.1] [1.2] [1.3] [1.4] [1.5] [1.6] [Ref] Polynt Composites USA Inc. (2015), *Composites Applications Guide*, Polynt Composites USA Inc.
2. ↑ [Ref] ASTM International (1999), *ASTM D2471-99, Standard Test Method for Gel Time and Peak Exothermic Temperature of Reacting Thermosetting Resins (Withdrawn 2008)*, ASTM International, doi:10.1520/D2471-99
3. ↑ [3.0] [3.1] [Ref] Barnard, Mike. "Controlling Exotherm". Retrieved 21 January 2021.
4. ↑ [4.0] [4.1] [4.2] [4.3] [Ref] ASTM International (2013), *ASTM D2583 - 13a, Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor*, ASTM International, doi:10.1520/D2583-13A



About



Help

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.

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.

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.

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.

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

Differential Scanning Calorimetry (DSC).

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.

Any manufacturing and/or decision making activity that occurs during any stage of the development design cycle (e.g. conceptual design to production).

In the context of Knowledge in Practice, practice refers to the systematic use of science based knowledge to reduce composites manufacturing risk, cost, and development time.

Polymerization of thermoset resins is an exothermic reaction and heat is generated during the curing process. A thermosetting resin has the potential to release a certain amount of energy while curing. This is called the total heat of reaction, H_R, with a unit of J/g (SI units).

The heat of reaction during polymerization is measured using a Differential Scanning Calorimeter (DSC) equipment measuring much energy/heat comes out of the reaction for a small resin sample.