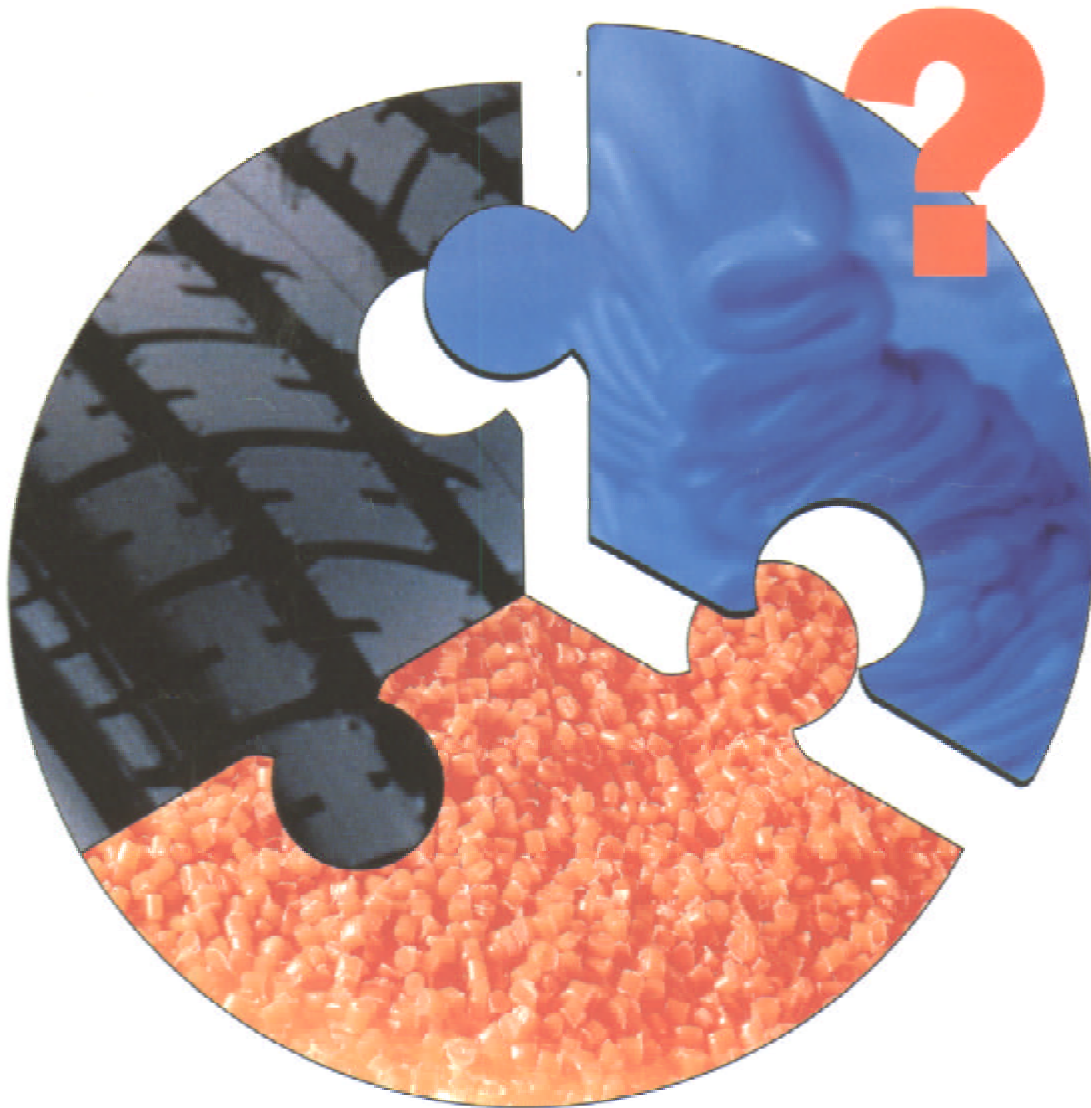




Understanding Rheology of Thermosets





Rheological Testing of Thermosetting Polymers

General Considerations

Thermoset Polymer Uses

Thermoset polymers form the matrix in filled plastics and fiber-reinforced composites used in a diversity of products. These range from consumer items and auto body panels to advanced composites for printed circuit boards (PCBs), aerospace structural components such as the Space Shuttle payload bay door and jet engine cowls and ducts, and expensive, high-performance sports equipment. Also, thermosets are used extensively as adhesives, molding compounds, and surface coatings, including protective solder masks for PCBs.

Thermosets versus Thermoplastics and Elastomers

Thermoset polymers are distinguished from elastomers and thermoplastic polymers in several ways.

Thermoplastics are processed in the molten state, their final shape and internal structure established by cooling, and they can be softened and reshaped by reapplication of heat and pressure. Also, their polymer chains, whether linear or branched, remain discrete after molding. Thermoset polymers usually go through three stages. In the A-stage, sometimes called a *resole*, the resin is still soluble and fusible. In the B-stage, thermosets are nearly insoluble, but are still thermoplastic. They can, however, spend only a relatively short time in the molten state because the temperatures that promote flow also cause the material to crosslink. The crosslinking reaction is accomplished in the final stages of polymerization – the C-stage – during molding of the product under

the controlled influence of heat and pressure over time. Thus, thermosets build their final structure during processing, forming a three-dimensional internal structural network of highly crosslinked polymer chains. And the final product is insoluble and not thermally reformable.

Elastomers share characteristics of thermoplastics and thermosets. Elastomers begin as thermoplastic polymers with discrete chains that later develop a network of covalent crosslinks. However, elastomers are distinguished from thermosets by the fact that the crosslink network is formed in a separate post-polymerization step called *vulcanization*.

Another factor distinguishing the three classes of polymers is the glass transition temperature T_g – the temperature at which polymers reversibly transmute between rubbery and glassy states. For elastomers, the glass transition temperature is below ambient temperatures; for thermoplastics and thermosets, it is substantially above ambient.

Studying the Crosslinking Reaction

The formation of a thermoset crosslinked network is shown schematically in figure 1.

Understanding of this process has been advanced substantially by use of rheological analysis – measurements of resin viscosity, shear modulus, and damping. More sensitive than even Fourier transform infrared spectroscopy for measuring extent of cure, rheological testing has become a vital supplement to DSC, chromatography, and wet chemical analysis in thermoset polymer research and development. The reasons for this reside in the na-

ture of the processes involved and the rheological changes inherent in these.

Thermoset Processing

Multistage Processing

Quite commonly, thermosetting resins are processed in two or more stages, as, for example, are those used in the production of fiber reinforced laminates.

First, a laminating varnish is produced from resin monomer, curing agent, other functional additives, and a suitable solvent. Then this varnish is applied to a reinforcing fabric made of glass fiber or other high modulus fibers, the solvent is removed, and the resin is partially reacted to form a "prepreg". At this point, the B-stage, the prepreg is a partially soluble, low-melting thermoplastic solid composed of unreacted monomer, adduct (the re-action product of a one-to-one ratio of resin and curing agent), and higher molecular weight oligomers. Some resins, particu-

larly epoxies, must be protected from moisture and refrigerated to forestall "advancement", that is, continuation of the reaction.

To fabricate a product, a multilayer sandwich of prepreg is prepared, placed in a press or autoclave, and heated to "cure". This processing step must accomplish several things: wet the fibers thoroughly with resin, consolidate the laminate to the desired thickness, remove excess resin, exhaust trapped air, moisture, and solvent to avoid porosity, and advance the cross-linking reaction to the desired level.

As the temperature is raised, the prepreg melts and its viscosity drops precipitously, then levels off and again climbs. This viscosity behavior is the consequence of the intervention of a competing circumstance: The rising temperature triggers further reaction among monomer, curing agent, and oligomers increasing the prepreg's viscosity. Because the reactants are multi-functional, crosslinks form among the polymer chains quickly in all directions.

Suddenly the system gels and flow ceases. At this point, the matrix is solid and the thickness and shape of the composite are fixed. Additional heating is needed, however, for the matrix to form the balance of its potential crosslinks and to develop, for the most part, its ultimate level of stiffness. To accomplish this, an additional out-of-mold post-cure step is generally used.

Single-stage Processing

Thermosets are also processed in a single-stage method called reaction injection molding (RIM). In use on a major scale since late in the seventies, RIM has become popular for a variety of automotive and recreational applications.

In some respects, RIM resembles thermoplastic injection molding (TIM). The key difference, however, is that RIM uses polym-

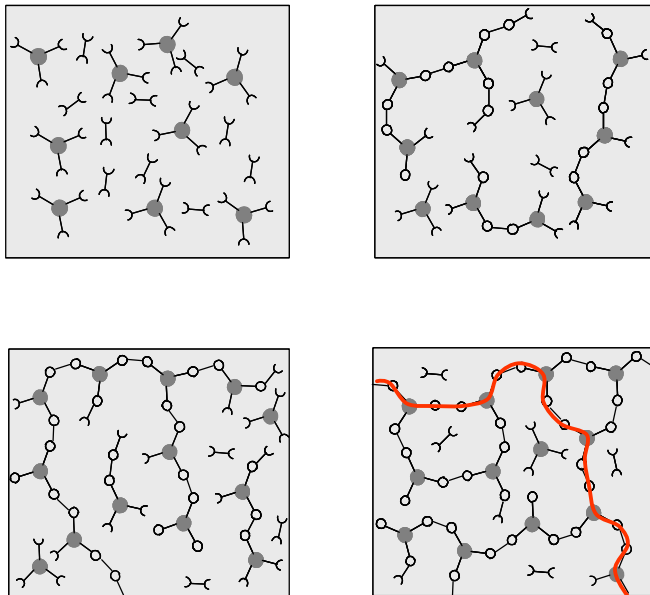


Figure 1: Schematic representation of structural development during thermoset curing: (A) unreacted monomers; (B) formation of small branched molecules; (C) the gel point: a path of covalent bonds exists across the sample; (D) the cured, crosslinked polymer with some unreacted groups and reactants.

erization in the mold rather than cooling to form a solid polymer.

Other reaction molding processes also use polymerization to solidify the molded piece; however, in thermoset injection molding, for example, reactants are heated to around 200 °C to activate the reaction. In RIM, the reactants are combined at a relatively lower temperature (about 40°C) because the reaction is activated by impingement mixing, not external heat.

In the RIM process, complex plastic parts are quickly produced directly from low viscosity reactants. Two or more liquids are impingement mixed at low temperatures and pressures as they enter the mold. Solid polymer forms by phase separation of segmented block copolymers (but structural buildup by crosslinking occurs with some urethane systems) and parts can be removed from the mold in under a minute.

Process Rheology

Thermoset structural development is accompanied by enormous rheological changes: The resin changes from a low-melting thermoplastic solid to a low viscosity liquid, to a gel, and then to a stiff solid.

Thus, the properties are vitally important to successful process-

ing. In structural laminates, resin flow influences porosity, cured part dimensional uniformity, and process economics. In multilayer printed wiring boards, resin flow properties also influence uniformity of etched circuit encapsulation, copper-to-epoxy adhesion, and final press thickness. Therefore, at each stage of the process, the rheological state should be known to employ these materials effectively and economically.

The rheology of thermosetting resins can be studied using both steady shear and dynamic oscillatory tests (sometimes referred to as dynamic mechanical analysis (DMA) or dynamic mechanical rheological testing (DMRT)). How steady shear, dynamic, and transient tests are run is described in a later section.

Steady shear measurements can characterize only the initial portion of a thermoset's viscosity range. Near the gel point the steady shear viscosity increases rapidly and becomes unmeasurable. Eventually the stiffening sample fractures or tears.

In contrast, dynamic oscillatory measurements of the resin's viscosity can be made as the reaction proceeds *through* the gel point – and beyond – until the resin becomes a stiff solid. This is possible because the measurements can be made at a strain amplitude low enough to prevent disruption of the gel structure as it is being formed. Steady shear viscosity data are compared to dynamic viscosity data for a curing epoxy resin in figure 2.

Being able to measure the viscosity throughout the thermoset curing reaction is an important capability. Still, it provides only a partial picture of the phenomenon taking place. Because the material is viscoelastic, elasticity data are needed to complete the characterization. These are obtained in a dynamic test concurrent with

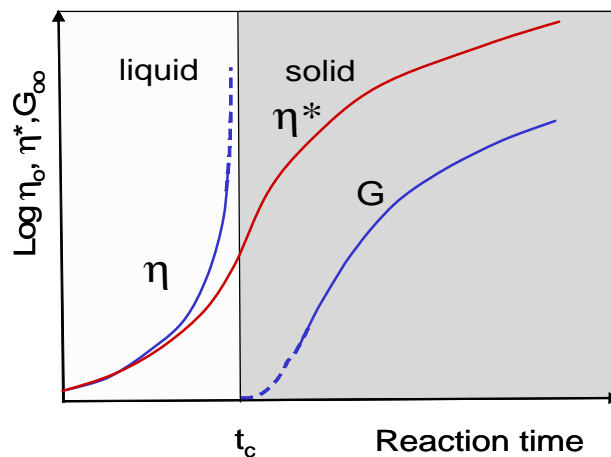


Figure 2: Measurement of the viscosity of a curing epoxy resin in

measurement of the viscosity. Figure 3 shows the storage (G') and loss (G'') moduli and complex viscosity η^* measured during an epoxy molding compound cure. Besides providing essential minimum viscosity data, the cross-over point of the two modulus curves gives an estimate of the time at which the resin begins to gel.

But this is only an approximate gel point. The problem is this: As the transient gel network structure is forming, stress relaxation is also taking place. So, unless measurements on the gelling system are made extremely rapidly, the exact time of gelation will be obscured by changes due to stress relaxation.

Recent work by H.H. Winter¹ shows that the cross-over point of the storage and loss modulus curves is not the true gel point. Rather, the instant of gelation is when the critical gel exhibits power law stress relaxation and $\tan \delta$ momentarily becomes independent of frequency. This point can be identified by making several frequency sweeps simulta-

neously, measuring $\tan \delta$ in the time scale of the developing gel.

Figure 4 shows dynamic oscillatory measurements of $\tan \delta$ made simultaneously at three frequencies on a crosslinking polydimethylsiloxane (PDMS) resin. Because $\tan \delta$ is independent of frequency at the gel point, the three curves pass through a single point and unambiguously define the instant of gelation. Such measurements are readily made using a Rheometric rheometer equipped with the MultiWave mode, described in detail in a later section.

Product Performance

To derive optimum performance from a thermoset resin, both undercure and overcure must be avoided. An undercured matrix may exhibit creep and tend to build up heat upon vibrating; an overcured matrix may experience room temperature performance problems because internal stresses build up in the glassy polymer as it cools, and stress cracks develop later.

A parameter known as the glass transition temperature T_g , often measured during DSC and TGA, has been used as an indicator of the extent of thermoset resin cure. For example, compared to a fully cured control sample of known good performance, a lower glass transition temperature indicates undercure.

But this does not necessarily mean that a higher T_g indicates overcure: The difference between complete cure and overcure cannot be detected by measuring T_g .

A higher glass transition temperature may result from exposure later to temperatures above those of cure or postcure. The glass transition temperature can be lower if the prepreg were cut and

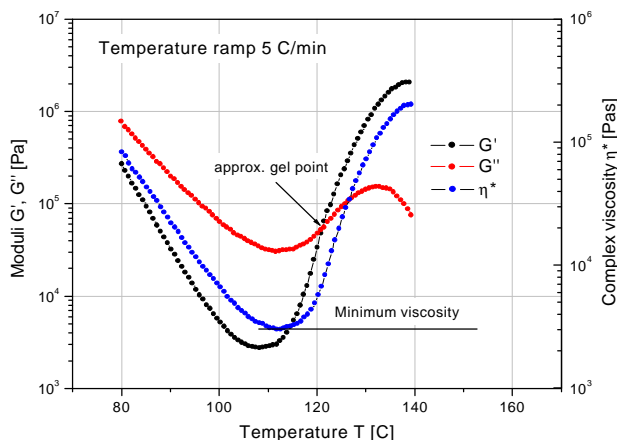


Figure 3: Measurement of the minimum viscosity and approximate gel point for a curing epoxy molding compound

¹ Fourier Transform Mechanical Spectroscopy of Viscoelastic Materials with Transient Structure E.E. Holly, S.K. Venkataraman, F. Chambon and H.H. Winter, Journal of Non-Newtonian Fluid Mechanics, 27(1988)17-26

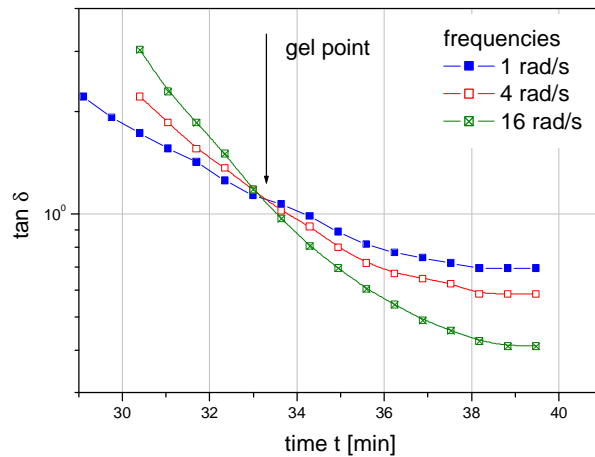


Figure 4: The precise gel point of a curing resin is identified by the intersection of $\tan \delta$ curves generated in several simultaneous frequency sweeps

laid up in a high relative humidity. (This can be verified by retesting after drying the sample, since the effect is reportedly reversible.) And formulation errors can shift the glass transition temperature up or down.

To understand the inadequacy of T_g alone as a performance gauge, what T_g is must be understood. The glass transition is a temperature-induced morphological change in a polymer between a brittle, glassy state and a viscous, rubbery state. The glass transition temperature T_g is the temperature at which this transition occurs.

Because the material experiences a substantial change in rigidity in a short span of temperatures, the glass transition is a key factor in deciding the usefulness of a polymer. So, merely knowing the temperature at which it occurs (all that DSC and TGA provide) is not enough. The modulus must be measured as a function of temperature as well. This is accomplished most effectively using dynamic mechanical rheological testing.

In the course of measuring the

moduli (G' , G'') and damping behavior ($\tan \delta$) of a polymer at a chosen oscillatory frequency over a sufficiently wide range of temperature, the effect of the glass transition can be clearly observed. The glass transition is detected as a sudden and considerable (several decades) change in the elastic modulus and an attendant peak in the $\tan \delta$ curve.

Besides being a more accurate method for measuring T_g , DMRT reveals much about the material before and after the glass transition because DMRT also measures the rubbery plateau modulus. This is important because, at high thermoset cure levels, the rubbery plateau modulus is more sensitive than is T_g itself for detecting, for example, small differences in a thermoset polymer cure level.

Also called the α transition, the glass transition is associated with crank-shaft motion of major chain segments. Other transitions, designated as β , γ , etc. in order of descending temperature of occurrence, arise from vibrations and rotations. Material toughness and impact resistance correlate with the magnitude of $\tan \delta$ at the secondary (β , γ) peaks.

For many materials, as the dynamic oscillatory frequency is increased, transitions occur at higher temperatures. Also, some transitions shift different amounts, depending on their degree of frequency dependence. This helps locate some transitions in multiphase resin systems (such as those modified by addition of elastomers or thermoplastics) if one component is more frequency-dependent than another. Shifts in the glass transition temperature and the β peak can indicate the effect of compounding or process changes on product performance. In general, the temperature of the secondary transition shifts more than does the

glass transition temperature as frequency is changed.

How dynamic mechanical testing can be employed to study the critical aspects of thermoset rheology during resin curing and solid state finished product performance is described in the following sections.

Sample Selection and Preparation

If the immediate application involves use of the neat resin, then tests should be run on material in that form. If, however, prepregs are used, then tests should be made on the staged resin mechanically extracted from the prepreg, or directly on die-cut samples of laminates (for example, a three-ply laminate of prepreg stacked with the middle and top ply oriented at 45° and 90° with respect to the fiber orientation of the bottom ply).

The die size is dictated by the diameter of the parallel plates to be used for the dynamic mechanical tests. Disposable plates, should be used for tests that cause the resin to cure since the resin can adhere strongly to the plates. The sample should be pressed (under vacuum, if possible) to reduce its bulk and hold the plies together. To avoid slippage, the test should be begun at a temperature at which the resin is tacky.

Powdered resin samples should be pulverized, dried, and pressed in a mold, forming a wafer of a size matching the test plate's diameter.

Generating Viscosity Profiles

Developing the proper cure level is perhaps the most critical step for a thermoset polymer. And both under-curing and overcuring must be avoided.

The most effective and economical way to do this is to design a thermoset cure cycle derived

from measurements of the curing resin's dynamic viscosity profile as a function of temperature and time.

Rheometers are designed to facilitate making these measurements: A time/cure mode allows test temperatures to be advanced (ramped) at rates of 1° to 5°C per minute in eight separately controlled heat zones. Each zone can be programmed for a ramp rate, final temperature, total time, measure time, and percent strain. Thus, almost any cure cycle can be conveniently simulated. And rheometers are equipped with a MultiWave mode that provides the most precise measurement of the gel point available by measuring $\tan \delta$ in several simultaneous frequency sweeps.

From a series of measurements at different temperature ramping rates (generally 1° to 5°C per minute), the storage (G') and loss (G'') moduli and the complex viscosity η^* are derived, and the following key information is obtained:

- Initial viscosity
- Minimum viscosity
- Gel point
- Optimum heating rate

Initial Viscosity

The initial viscosity, the first point of the viscosity profile, indicates the onset of matrix melting, and is not influenced by heating rate. It is a useful indicator of degree of resin advancement for quality control.

Minimum Viscosity

The minimum viscosity represents the time period and temperature range over which resistance to flow is lowest. Knowing this and the time needed to reach the minimum viscosity is critical in various processes: In laminate production, the resin viscosity must

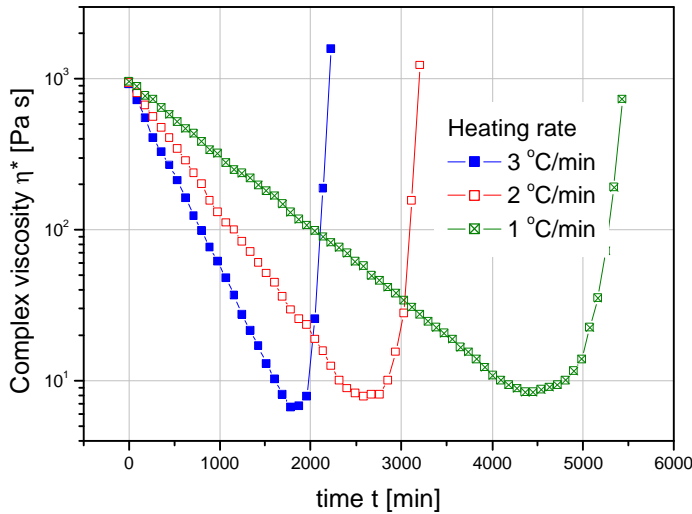


Figure 5: Measurement of the viscosity profile of a curing thermoset resin as a function of heat-up rate

be low enough to wet the embedded fibers uniformly, but not so low as to cause excessive bleeding at the laminate edges. And in the encapsulation of integrated circuits by transfer molding, the viscosity must be low enough to avoid damaging the fragile wires that connect the circuits to the frame. The time interval during which the viscosity is at or near its minimum value constitutes the processing window.

Gel Point

The gel point is the temperature or time at which the first set of covalent bonds connects across the sample (the onset of a three-dimensional network) and the molecular weight becomes infinitely large. The gel point is important in determining the time and temperature at which pressure should be applied.

Pressure is needed during lamination to squeeze the plies together, and timing is critical: Substantial pressure must not be applied until after the minimum viscosity has been reached, else the resin will bleed excessively at the edges; but it must be applied before the gel point to assure adequate compaction.

Pressure is used also to control outgassing of volatile by-products generated in some thermoset polymer reactions such as those involved in the manufacture of polyimides.

Excessive pressure must be avoided during the lamination of circuit boards that include an oxide-prepreg interfacial treatment since some oxides are fragile and can be crushed, causing delamination.

Optimum Heating Rate

The heating rate must be optimized because it affects the time needed to reach the minimum viscosity, and the time and temperature intervals over which the mini-

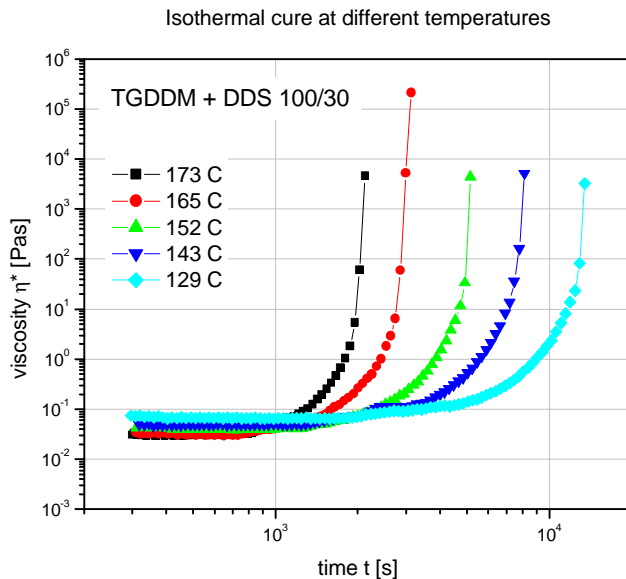


Figure 6: Isothermal scans at various temperatures are used to help decide on the time interval and temperature at which to impose isothermal holds during a thermoset resin production cure cycle

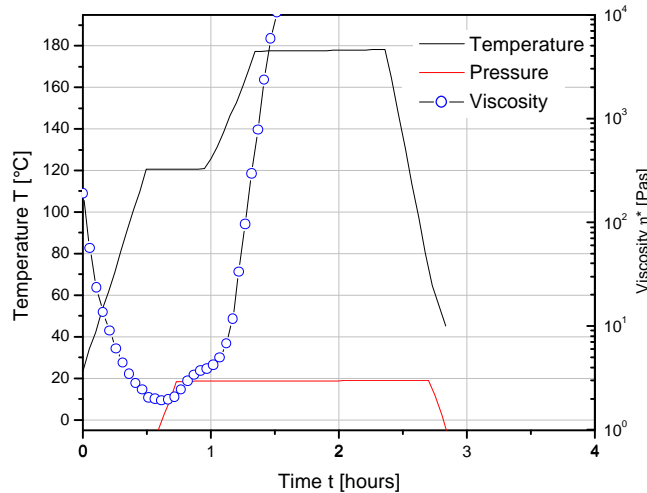


Figure 7: A thermoset resin production cure cycle in which hydraulic pressure is induced in the resin to reduce gas bubble nucleation in the cured matrix

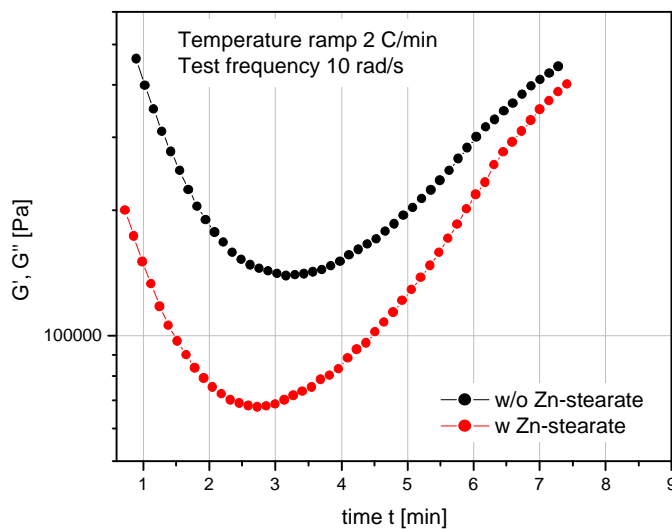


Figure 8: The addition of zinc stearate lowers resin viscosity at the injection mold barrel temperature without affecting the cure time

mum viscosity extends. Too fast a heating rate can create unwanted temperature differentials within the part, irregular curing throughout the piece, and possible porosity problems. Figure 5 shows the effect of heat-up rate on the viscosity profile.

Isothermal Scans

Once the minimum viscosity and gel point have been determined, a series of isothermal scans should be run at temperature intervals beginning with the minimum viscosity temperature and continuing up to the gel point temperature in intervals of about 10°C. These scans can be made quickly on the ARES since it can record one data point a second. This information will help in deciding the time and temperature at which to impose isothermal holds during the process. An isothermal hold at minimum viscosity extends the time the resin will remain near the minimum viscosity and determines the dimensions of the processing window.

The time at or near the minimum viscosity is a key factor in controlling overall flow and avoiding problems such as bulk porosity. A second hold near the gel point is sometimes used to eliminate surface porosity. Typical isothermal scans are shown in figure 6.

Using the Viscosity Profile

A dynamic mechanical viscosity profile offers unparalleled utility in every phase of thermoset polymer technology, including research, product development; process development and control; and quality control. Some examples follow.

Research

Dynamic mechanical testing is employed extensively in thermoset composites research to provide needed material properties for

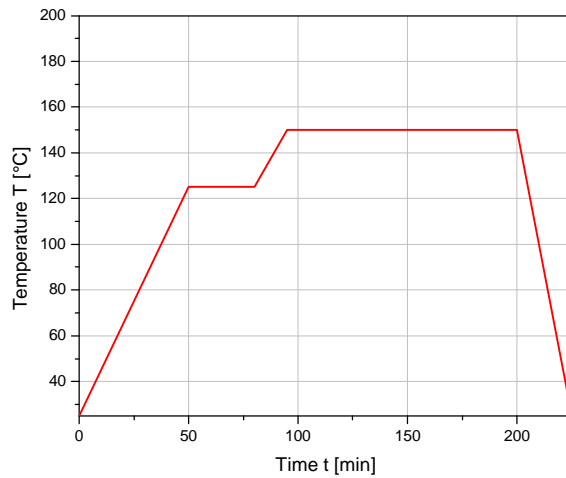


Figure 9: A graphite-epoxy production cure cycle

finite element and finite difference analyses. And dynamic viscosity profiles provide vital data for studies of cure reaction kinetics, process modeling using "expert" systems, and advanced curing concepts such as "gas diffusion control."

Diffusion control reduces gas bubble nucleation in the curing matrix by inducing hydraulic pressure in the resin during the gas volatilization stage of the cure cycle. Figure 7 shows a typical matrix resin cure cycle incorporating diffusion control, superimposed on the viscosity profile.

Product Development

Viscosity profiles are used to great advantage in thermoset product development to evaluate, for example,

- new or different resin formulations
- fiber types, finishes, and weaves
- materials from alternative suppliers; and
- functional additives

Figure 8 shows how the viscosity profile during cure has been used to evaluate, at a typical screw barrel temperature, the beneficial effect of adding 1% zinc stearate to a phenolic injection molding compound. The zinc stearate lowered the viscosity considerably at the barrel temperature without affecting cure time.

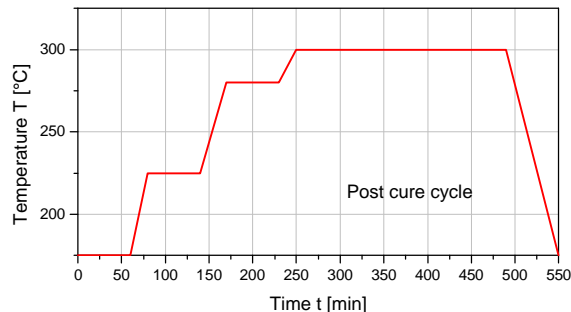
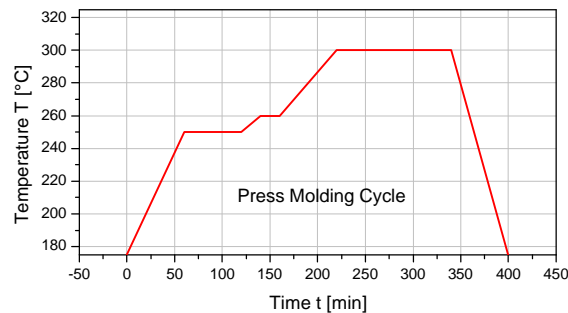


Figure 10: The cure and post-cure cycles for a polyimide resin

Process Development and Control

Developing Production Cure Cycles

A dynamic mechanical viscosity profile provides the rheological data needed to construct a production cure cycle. Figure 9 shows a typical cure cycle developed for a graphite/epoxy laminate.

Developing Post-Cure Cycles

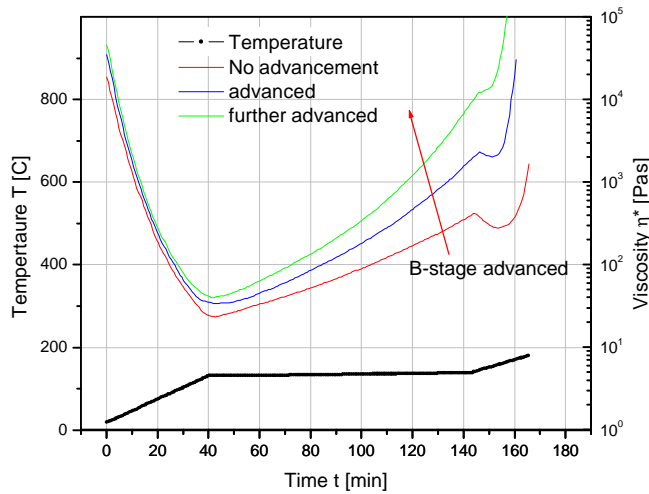


Figure 11: B-stage resin advancement alters the viscosity profile of a curing thermoset resin

In many cases, especially with bismaleimides and polyimides, a post-cure step is used. This involves heating the laminate for an extended time outside the mold to increase the crosslink density and raise the glass transition temperature of the matrix, thereby improving functional properties. A typical post-cure cycle in a circulating air oven for a polyimide resin composite used for a jet engine component is shown in figure 10.

Quality Control

The cure step is the most critical element in thermoset processing. Accordingly, maintenance of strict quality control standards on the incoming materials, the prepreg especially, is important. Two areas of major concern are degree of resin advancement and the effects of moisture.

Prepreg Advancement

Prepregs are partially re-acted by the supplier to different degrees to develop particular properties (stiffness, tack, drape) needed for a given application. The degree of reaction advancement in the B-staged prepreg is controlled mainly by stoichiometry and storage conditions, including duration, humidity, and temperature. Ideally, prepregs should be stored only a short time, and then in a cold, dry environment. Any lapses in supplier quality control or improper storage may cause the reaction to advance, changing the material's response in a standard cure cycle.

Tests on prepreg samples immediately prior to use can quickly identify advancement level differences so that adjustments can be made to the cure cycle. Figure 11 shows viscosity profiles of an epoxy resin at three different levels of minimum viscosity and the reaction rate (reflected in the slope of the viscosity curve during the isothermal hold), and the sooner gelation occurs.

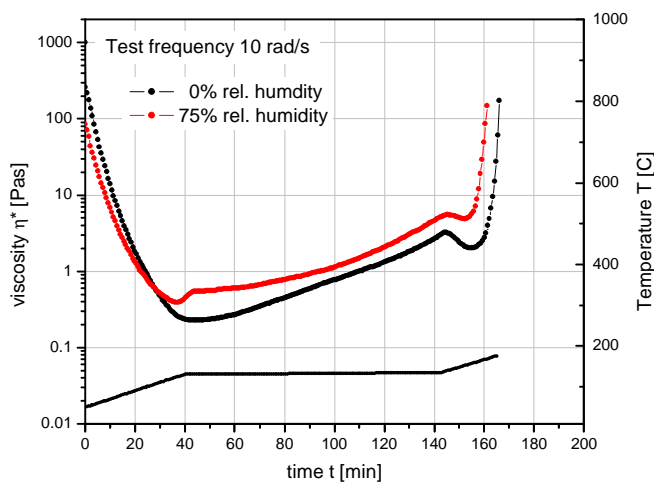


Figure 12: Viscosity profiles of a dry epoxy resin and the same resin after extended storage in a high humidity

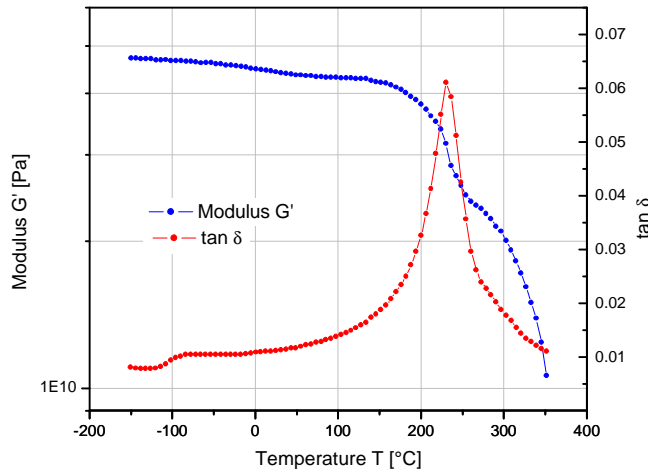


Figure 13: Temperature sweep on a cured epoxy-graphite composite. The glass transition is manifested in a sudden and considerable decrease in the storage modulus with an attendant peak in the $\tan \delta$ curve

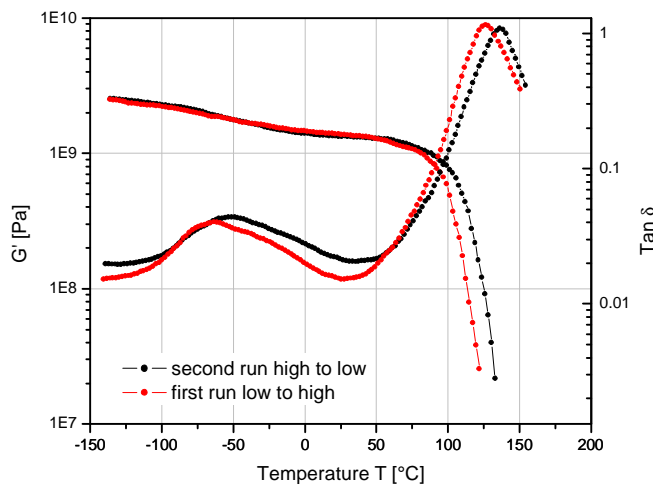


Figure 14: Different values of the glass transition temperature are obtained if the transition is approached while the sample is being cooled compared to when the sample is being heated
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Moisture Effects

Moisture adsorbed during improper storage of a prepreg can create quality problems in thermoset processing by changing reaction kinetics and thereby changing the viscosity profile of the prepreg. Also, trapped moisture can cause matrix porosity. By testing before use, moisture-related cure problems can be avoided, or at least minimized. The effects of moisture are often reversible, so the material may be salvaged by drying before curing. Figure 12 shows the viscosity profiles of a dry epoxy resin and the same resin after extended storage in a high humidity.

Evaluating Product Performance

Key factors in thermoset polymer product performance are the cured resin's modulus and glass transition temperature. The dynamic moduli (G' , G'' or E' , E'') are measured directly on solid samples with or without fiber reinforcements at a selected frequency as a function of temperature. And from these measurements $\tan \delta$ is automatically calculated. The glass transition is detected as a sudden and considerable decrease in the storage modulus and an attendant peak in the $\tan \delta$ curve. The symbol T_g denotes the temperature at which this transition occurs.

Figure 13 shows the $\tan \delta$ and storage modulus curves, the glass transition and secondary transition of an epoxy-graphite sample measured in bending on the Solids Analyzer. The glass transition temperature is not a constant, so care must be taken during its measurement to avoid generating misleading data. For example, two tests made at different heating rates can produce different values of the glass transition temperature. The slower the measurement, the lower is the glass transition temperature.

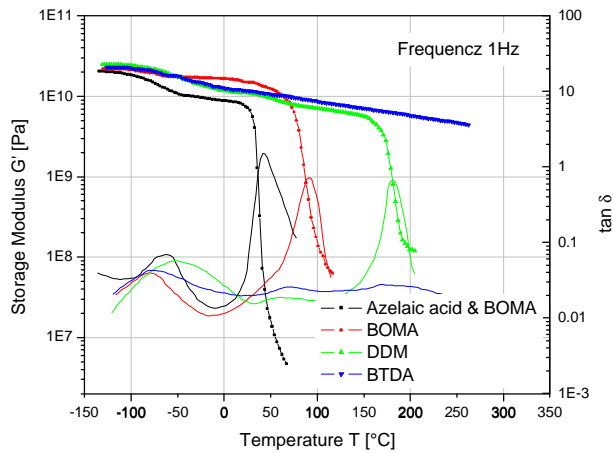


Figure 15: Temperature sweeps are an effective means for detecting the effects of different curing agents on the viscoelastic properties of thermoset resins

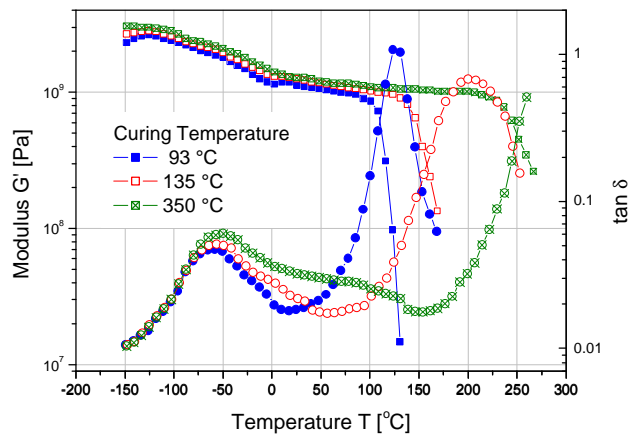


Figure 16: The cure level of a thermoset polymer as a function of cure temperature measured in torsion. Tests can also be run in compression or bending.

Also, for valid comparisons to be made, the glass transition temperature must be approached from the same direction to avoid hysteresis during the test. So, data from test samples should be compared to data from tests made under the same conditions (including oscillation frequency) on good-performing control samples.

Figure 15 shows the effect on the glass transition temperature of going from a low to high temperature and then repeating the test as the sample cools, using a cured and a cured plus postcured sample of PMR-15 polyimide.

Figure 16 shows the effects of various curing agents on the glass transition temperature of an epoxy resin.

The data in figures 14 through 16 were obtained in bending and torsion. Figure 15 shows the glass transition temperature as a function of cure level measured in tension following the procedure outlined in ASTM D5026.



Keywords: thermopsets, processing, elasticity, cure, viscosity, performance, gel point, vitrification,
glass transition