

## **Focus on Rheology**

by

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The performance of prepreg in the lamination process is continually being pushed to the limits. Circuit boards have become more intricate and material performance and reliability in the multilayer board manufacturing process is more critical than ever before. Prepregs must readily meet the new demands of today's electronic product designs. The application of prepreg rheology in the lamination cycle can help characterize prepregs to allow more performance under the increased demands of miniaturization and advanced packaging designs.

When one considers the types of computing power and speeds of just ten years ago contrasted to today, it is hard to imagine the developments we will see in the next ten years. As electronic products take on smaller sizes for speed, convenience and portability, these devices provide additional power and performance capabilities. Because of this, multilayer boards contain much finer lines and spaces as well as increased layer counts. Prepregs must fill more difficult circuit geometries than ever before. The tight requirements for dielectric thickness control must be maintained for controlled impedance applications. Prepregs must wet, fill and encapsulate very well, yet not flow so much as to create a multilayer board with the profile of an official NFL football.

In these days of tough international competition and shortened development cycles, our productivity must constantly increase so we can remain competitive and profitable in the marketplace. The lamination press can not be a bottleneck. Deliveries must be just-in-time and products must work right the first time. Stack heights are being increased and cycle times decreased to improve manufacturing throughput. In addition, new prepreg and laminate materials with higher performance properties are available to help increase yields through the harsh manufacturing process of making a multilayer circuit board. Improved resins, blends, new resins and new additives come with claims of improved performance. If new manufacturing procedures are not carefully developed through Statistical Product Development, the processing window can appear to be very small or elusive.

Rheology, when applied to the multilayer lamination process, replaces some of the magic in the lamination process with the science of material deformation and fluid mechanics. An understanding of prepreg rheology can turn the lamination process away from the remnants of EVOP, SWAG or other rituals (like crossing one's fingers or mumbling a quick prayer as the press closes). This can mean the difference between a process that is robust, in the middle of its process window, or one that occasionally drifts out of control when lamination parameters do not line up exactly.

### **RHEOLOGY (BEFORE MULTILAYER ELECTRONICS)**

Rheology is the science of material deformation and flow. It relates to the relationship between stress, strain and time. It is a material response we can readily relate to in less technical terms in everyday life. We would commonly use the words lubricate, spread, squeeze, as non-technical examples of rheological responses.

As force is applied to an object it can do one of several things: It can cause the object to be strained or ruptured, or it can make the object move, flow or accelerate. Rheology describes material response to the forces of deformation.

When we look through recorded history, the origins of Rheology can be traced back to a Pre-Socratic

Greek metaphysician named Heraclitus. In the 5th Century B.C., Heraclitus was noted for documenting: "παντα ρει" or more simply, "Everything Flows."

At the turn of the 17th century, renowned English mathematician and theologian Sir Isaac Newton started to define rheology as a formal science. Newton developed the basic relationship as shear stress being equal to a proportionality constant times the shear rate<sup>1</sup> or:

$$F/A = u * (V/L)$$

F/A is the Shear Stress or Force per Unit Area u is a proportionality constant V/L is the velocity per thickness of layer or Shear Rate

From this relationship, it did not take very long to define viscosity as the ratio of the Shear Stress (Force per unit area) divided by the Shear Rate.

Today the structural composites industry and the electronics business rely heavily upon rheological testing for existing product improvement as well as new product process development.

## **VISCOSITY**

The definition of the relationship, along with Newton and Baron von Leibniz' independent development of Calculus, accelerated developments in the science of rheology and measurement of fluid viscosity. There are many different ways to measure viscosity, depending on the type of material being studied and the viscosity range of the fluid under consideration. This article will not attempt to describe them all. A good source for information on rheology basics as well as instrument types for polymer melts would be: "Polymer Melt Rheology - A Guide For Industrial Practice" by F.N. Cogswell, 1981 published by Halsted Press, a Division of John Wiley & Sons, NY.

The coefficient of viscosity (or simply viscosity), is the measure of resistance to an applied force, or the resistance to flow. In Figure 1, this is illustrated by a model of two plates separated by a fluid. One plate is stationary, while the other is moving at a constant speed, maintaining a constant distance from the stationary plane. When such a force is applied, the layer of fluid immediately adjacent to the moving plane moves nearly at the speed of the moving plane, while subsequent layers, closer to the stationary plane move more slowly. This establishes a velocity gradient between the plates<sup>2</sup>.

When a fluid more effectively transfers its momentum to adjacent layers, there would be less of a velocity gradient, and the observation in our plate model is that the fluid layer has a high viscosity. When a fluid does not effectively transfer its momentum to adjacent fluid layers in our plate model, the velocity gradient is more pronounced and the fluid has a low viscosity.

This sets up the basis for a rheometer. When the shearing plates are of a known geometry and at a fixed distance, a calibrated strain can be applied to the plate. A transducer, attached to the stationary plate, can measure the induced stress in the test sample. By determining the ratio of the shear force (force per unit area) to the shear rate (velocity gradient), the flow resistance, or viscosity is derived.

## **FACTORS AFFECTING VISCOSITY**

In the realm of polymer processing, it is important to consider the factors that affect viscosity. These are:

## A: Temperature Effects.

The presence or absence of heat determines how active molecules are in a fluid. As solids and liquids increase in temperature, molecules become more active, and less likely to remain entangled, so it is not surprising that the viscosity tends to decrease as temperature increases. In our shear plate model, the molecules are less likely to remain entangled when heated, so the velocity gradient will be more pronounced, resulting in a lower viscosity.

## B: Concentration Effects.

High viscosity polymers can be lowered in viscosity by dilution with low molecular weight polymers. The low molecular weight polymers can act as a "slippage plane" in our simple shear plate example- where the fluid has a more pronounced velocity gradient between the plates. Low viscosity components can act as lubricants or plasticizers for the larger molecules, to keep the larger molecules from entangling. (Moisture in prepreg can lower the apparent melt viscosity because it acts like a plasticizer)

## C: Molecular Weight & Distribution Effects.

Molecular size can affect the intrinsic viscosity of materials. Smaller molecules tend to have lower viscosities. As the size of a molecule increases and the molecular weight increases, the tendency will be towards higher viscosities.

## D: Molecular Branching & Chain Diameter Effects.

As molecules increase in branching and chain diameter, the more likely they are to entangle to distribute shear stress in our shear plate model. This results in a higher observed viscosity.

## E: Shear Effects.

### Newtonian Fluids

Fluids are considered Newtonian when the coefficient of viscosity remains constant over changes in shear stress. This means the viscosity remains constant, regardless of the applied shear stress.

### Non-Newtonian Fluids

Fluids that exhibit a change in viscosity with a change in the shear rate are known as Non-Newtonian fluids (Figure 2.) To be meaningful, viscosity values should be reported with the shear rate used when measurements are reported.

## **OTHER RESPONSES TO SHEAR STRESS**

It is useful to be aware of the various types of response to shear stress. As seen in Figure 3, the following types of response<sup>1</sup> can occur when a plastic or fluid is subjected to shear stress:

1. A Bingham plastic or "true plastic", flows only after a certain yield point has been exceeded as the shear stress is increased. (Chewing gum is an example of a Bingham plastic).
2. Pseudoplastic materials appear to have a yield stress where flow increases dramatically with increases

in shear stress. (Paper pulp is an example of a pseudoplastic material).

3. Dilatant materials show high flow under very low shear stresses, but further increases in shear rate result in lower flow. These are also referred to as shear thickening or inverted plastics. (Quicksand is an example of a dilatant substance).

4. Thixotropic materials are the opposite of dilatant materials. These materials will increase in flow rate with increases in agitation or increases in shear stress. When agitation or shear stress is stopped, hysteresis occurs. Generally, the material will thicken, but less shear stress is required to create a given flow compared to the first application of shear stress. (Paint for example, flows when brushed, yet does not sag afterwards).

5. Rheopectic substances are materials that when periodically sheared will "set" or build in viscosity rapidly. The apparent viscosity of a rheopectic substance will increase with time under a constant shear stress. (Gypsum or bentonite solutions exhibit rheopectic behavior).

## **MEASUREMENT OF PREPREG MELT VISCOSITY**

Prepreg rheology is most commonly characterized by parallel plate rheometer. It is an instrument that has been widely used in one form or another since the 1950's<sup>3</sup>. The instrument can be envisioned as a set of parallel plates contained within a programmable oven. The oven is used to provide either an isothermal (steady state) or programmed heat ramp. This makes the instrument ideal for characterizing a dynamic manufacturing process such as a multilayer board lamination cycle rather than a quick isothermal test such as a flow or gel test.

The operator programs the heating profile, test frequency and strain into the instrument. The sample (prepreg dust that has been removed from the reinforcement and sifted to remove reinforcement fibers) is tested without reinforcement because within the parallel plates, fabric reinforcements result in strange, often unrepeatable results.

The bottom plate is attached to a motor which oscillates the plate at the programmed strain (displacement angle) and frequency (speed), to produce a stress within the sample. Since the prepreg melt is viscoelastic, the stress contains both a storage modulus (the elastic component) as well as a loss modulus (viscous component).

The upper plate is attached to a transducer. This transducer measures the torque resulting from the strain upon the sample. The system computer compares the material stress to the input strain and determines the tan delta or phase angle along with the storage and loss modulus components.

The torque is separated into the in-phase component (storage modulus) or elastic component and the out-of-phase component (loss modulus) or viscous components. These are used to mathematically derive the complex viscosity. (Figure 4).

## **THE MULTILAYER RELAMINATION CYCLE**

Isothermal tests are sometimes not sensitive enough to show what is actually occurring in the manufacturing process. For example, the "Resin Flow of Prepreg" test (per IPC-TM-650 method 2.3.17 Rev B), is performed on a 4 inch by 4 inch layup of 4 plies of prepreg at 200 psi at 171 C. When considering the Resin Flow Parameter<sup>4</sup>:

$$F = C * \frac{P}{A} \int \left( \frac{1}{\mu} \right) dt$$

F= Resin Flow Parameter

C= Geometry Constant

P= Pressure

A= Area

$\mu$ = melt viscosity

t= time

resin flow is proportional to the pressure to area ratio of the lamination cycle. The pressure to area ratio is the basis for the scaled flow test method. By scaling down the pressure to area of a lamination process as a quick incoming flow test, more meaningful information can be determined about how the resin will flow and the final thickness it can yield in the lamination process. For many prepreg users, the scaled flow test is a better way to specify lamination prepreg.

For the Resin Flow test, the pressure to area ratio is 12.5! The Resin Flow Parameter for this test method is very large, which is why the test does not correlate well with production scale lamination. In Figure 5, the pressure to area ratio of 12.5 has been modelled to show the lamination pressures required to obtain the same flow parameter. For a 12 inch by 18 inch panel, this equates to a lamination pressure of 2700 psi. From this, it is easy to understand why the Resin Flow test does not relate well to production results in the press.

In Figure 6, the Scaled Flow Test (IPC-TM-650 method 2.4.38), a pressure to area ratio of 0.805, more closely equates to actual lamination pressure profiles. The Scaled Flow test equates to a pressure profile of 174 psi for a 12 inch by 18 inch panel. The scaled flow test more closely indicates the kind of flow, fill and thickness likely to be yielded by a prepreg in a "standard" press cycle.

The rheology of prepreg is a critical part of processing B-stage during lamination. Prepregs undergo a series of changes during lamination. Prepregs are partially advanced B-stage materials. When heated, the resin system, which has been advanced to a controlled state of partial cure, starts to melt from a solid into a viscoelastic melt. This means that the prepreg responds to the stresses of lamination with both a viscous and an elastic response (Since part of the prepreg response is elastic, lamination stresses can be locked in. Such stresses could result in failures during soldering or other final fabrication steps.)

As the lamination cycle continues, the prepreg temperature increases and there are opposing effects. The rising temperature in the press acts to lower the prepreg melt viscosity, while at the same time, the rising temperature increases the reaction rate (cross-linking) to the point of gelation and final cure of the resin. The dilemma for the lamination engineer is how to take into account all the variables in the multilayer board design and to provide the proper heating rate and pressure profile to ensure complete encapsulation of the inner layer circuitry while maintaining good control of the multilayer board final thickness.

Over the years, the lamination process has been experimentally determined from both empirical observation as well as experimental design to balance the press cycle into a good, forgiving process.

Some of the empirical observations over the years include:

-When prepregs are heated more quickly, they become "juicier" or more fluid during melt. (Figure 7)

This is utilized to provide more flow during lamination. When taken to extreme, there can be so much flow or uneven flow in a multilayer package so as to induce the appearance of dryness (resin starved glass), voids (gel occurs too rapidly) or thickness tolerance problems.

-When prepregs are heated more slowly, they become less fluid. This is done to reduce the amount of flow and flash during lamination. If the heating rate is too slow, there may be voiding or incomplete encapsulation of traces, or poor adhesion to inner layer circuitry.

These observations are readily explainable. In considering the two opposing activities- resin melt vs resin gelation, a slower heat rate provides resin time to orient, react and advance its molecular weight at elevated temperatures, before having had a chance to reach full melt and reach a critical reaction temperature. The resin has more time to "age" at higher temperature before it reaches its minimum melt viscosity. When taken to an extreme (too slow a heating rate), the prepreg might even reach a state where it is "dead" before it reaches its minimum melt viscosity.

With faster heating rates, there is considerably less thermal aging of the prepreg, so there is less time for cross-linking before the prepreg reaches its minimum melt viscosity. The lower molecular weight of the prepreg results in lower melt viscosity. At faster heating rates, material is brought through melt faster and to the gel point faster so the increased fluidity is offset by decreased working time. The relative advantages and disadvantages of these press cycle extremes are summarized in (Fig. 8).

## APPLICATION OF RHEOLOGY TO THE LAMINATION PROCESS

When considering the flow parameter equation, the lamination press can be considered to be a rheometer of sorts. While the lamination press does not provide actual units of viscosity measurement, lamination does provide flash around the edge of the laminate. By quantifying the type and amount of flow, the lamination press can provide quick rheological information about the press cycle. Inspection of the flash will reveal whether there is enough flow, excessive flow or inadequate resin flow. As a qualitative instrument, the edge flash from lamination can be used to determine whether the press cycle is providing a consistent resin flow.

When the flow is excessive, it can be from too much pressure or too fast a heating rate. It can result in resin flowing onto the press platens and encapsulation of the parts and caul plates. In addition to spending unproductive time chipping away to clean the press and plates, this can result in parts that are too thin or severely tapered. The press cycle needs to be adjusted to provide less flow. This can be done with adjustments to either heating rate or lamination pressure. Generally, a slower heating rate with increased pressure can decrease flow, and result in a flatter laminate.

When the flow bead is too small, there is usually evidence of dry corners and edges or even voiding in low pressure areas. Boards can exhibit poor interlaminar shear strength. Faster heating rates can help eliminate voiding in low pressure areas, and higher pressures can ensure proper flow of resin to the corners of the laminate.

In the process of lamination, it is important to understand the various stages that the prepreg goes through. The first is the softening point of the resin. It is the region where the resin starts to soften and flow as an elastic material. From this point, the material drops through several decades of viscosity (from about 10<sup>7</sup> poise down to 10<sup>0</sup> to 5000 poise). Minimum viscosity occurs at the temperature where the material is most fluid, and reaction rates start to increase as viscosity starts to build as the resin starts to gel. The gel point is defined as the point where the tan delta is one, or the point where the storage and loss modulus have the same value.

By restating the Resin Flow Parameter Equation, it can be seen that Flow is proportional to the inverse viscosity. The inverse viscosity is defined as Fluidity<sup>5</sup>, so flow is proportional to Fluidity. The fluidity curve provides meaningful information in terms of defining the temperatures for the onset of fluidity, maximum fluidity (minimum viscosity), and gel point.

In Figure 9, the fluidity curves illustrate the differences between epoxy and polyimide materials. For epoxy, the resin starts to become fluid around 180 F to 200 F, while polyimide becomes fluid around 250 F. Epoxy reaches peak fluidity at about 280°F. and polyimide around 350°F. The gel points for epoxy occur at about 320° F, and polyimide around 400°F.

For polyimide, the higher temperature of fluidity also happens where the temperature difference between product and platen temperature is smaller, so it is on a slower heating rate portion of the temperature profile. (This also explains why slightly higher heating rates are specified for some polyimides- the heating rate needs to be faster to get a similar viscosity profile).

A quick process tool to increase heating rate might be to increase the initial platen temperature rather than remove press padding which might change the heat and pressure distribution through the stack. The higher starting temperature increases the heating rate through the critical fluidity region of the press cycle.

When using a kiss cycle, where high pressure application is delayed until 190 to 210°F (product temperature) for epoxy, and 265°F for traditional polyimide, the fluidity profiles support these traditional choices for delayed pressure application. Full pressure is applied just as the resin becomes fluid, before the resin reaches its minimum melt viscosity and starts to gel. If full pressure is applied at a higher temperature, working time is lost, so dryness might result. If pressure is applied sooner, before melt, more elastic stresses might be locked into the laminate.

Kiss cycles reduce lamination stress by waiting until the resin melts to apply full pressure. This does several things. By waiting until the resin is more fluid, there is less shear stress induced during the elastic region of melt, so there is less stretching of the glass reinforcement. This results in less "snap back" when parts are cooled and pressure is removed. Registration is improved. Use of kiss pressure also allows the resin to work and wet in a more laminar flow, to provide better filling of details with reduced hydraulic force and turbulent flow. It reduces shear upon copper oxide bonding surfaces, and may improve bond strength.

Use of Fluidity curves can be a valuable tool in characterizing new prepreg systems. By looking at the fluidity profile, one can determine the temperature range that a resin becomes fluid, and better predict a pressure application temperature for a kiss cycle.

An understanding of the temperatures where a resin flows and gels helps to define the working window for the lamination process. It also helps to know the temperature delta profile (center to edge and outside to inside temperature differences) when deciding to use delayed pressure application, so that part of the package is not making the transition to final pressure when it might be too late for flow (near or after gel). Consult your prepreg supplier for recommendations because different resin systems may have different fluidity profiles.

The fluidity curve can also be integrated to derive a Fluidity time integral or Integrated Flow<sup>6</sup>.

This integral has been used to compare prepreps and different press cycles.

Experimental work has shown that plateau cycles can be used when a particularly difficult configuration requires a lot of fill (heavy opposing copper planes), where excess resin flow results in poor dielectric thickness control and crushed or deformed inner layers. In Figure 10, the concept behind a plateau temperature is to quickly heat the package to a chosen temperature, slightly shy of the resin system minimum melt viscosity. This provides the advantage of a lower minimum viscosity than is provided by a slower heating rate. By choosing a plateau temperature that is slightly lower than the minimum melt viscosity, the lower rate of reaction of the melt will result in a longer time to gelation. This plateau is usually 15 to 25 minutes long to extend resin flow. The press cycle then continues on to the final cure temperature.

Since the plateau cycle takes the advantages of both the fast heating rate cycle as well as the slow heating rate cycle, wetting is improved, yet uniform resin retention is achieved for thickness control.

## **SUMMARY**

Prepreg rheology offers several perspectives to the lamination engineer. The parallel plate rheometer offers the advantage of observing the effects of an actual process on the instrument. Modelling can be done on a lab instrument without having to put expensive product at risk. More educated process changes can be made with rheological information.

An understanding of the critical rheological parameters of a given resin system will allow for a robust lamination process. As circuit configurations change, an understanding of resin rheology can be used to counterbalance rheological effects. Pressure application temperatures (kiss cycles) and plateau cycles can be used to push prepreg to new performance limits.

1. Considine, Douglas M; Considine, Glenn D., Encyclopedia of Chemistry, Fourth Edition, Van Nostrand Reinhold, N.Y., 1984
2. Binder, Stephen, Fluid Mechanics, Fourth Edition, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1962
3. Marshall, D.I., Measuring Viscosity by Thermosetting Resins by Parallel Plate Plastometry
4. Bartlett, C.J.; Bloechle, D.P.; & Mazeika, W.A., The Use of Scaled Flow Testing For B-Stage Prepreg, IPC Technical Paper IPC-TP-281, IPC 22nd Annual Meeting, April, 1979
5. Van Black, L.H., Elements of Materials, Science & Engineering, Addison-Wesley Publishing Company, Reading, MA, 1975
6. Galgoci, E.C., Pigneri, Young, G.C., Tait, R.A., Jackson, R.J., Rheological Indexing of Prepreg Resin, 3rd International SAMPE Electronics Conference Proceedings, June 1989 ( Vol 3, Pp1224-1233)