Thermosets and Structural Adhesives

Keywords: hot melts, structural adhesives, thermosets, cure, Tg., cure cycle, gel point

RH007

INTRODUCTION

Structural adhesives are usually thermosetting polymers. Generally applied to the surface as low viscosity, reactive liquids, their viscosities increase rapidly as they polymerize and crosslink in the joint to form a rigid, high strength bond. Therefore, knowing the viscosity as a function of cure time and cure temperature is important for establishing optimum cure conditions.

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, aerospace structural components, and expensive, high-performance sports equipment.

THE CROSSLINKING REACTION

In order to build a chemical network, one of the monomers has to be two-functional and one three-functional (figure 1). The formation of a crosslinked network can be followed, measuring the viscosity as a function of time and temperature as shown in figure 2. As the network structure builds, the viscosity increases due to the growing resistance to the flow. Near the gel point, the steady viscosity increases rapidly and becomes unmeasurable – eventually the stiffening sample breaks. In contrast an oscillatory measurement 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.

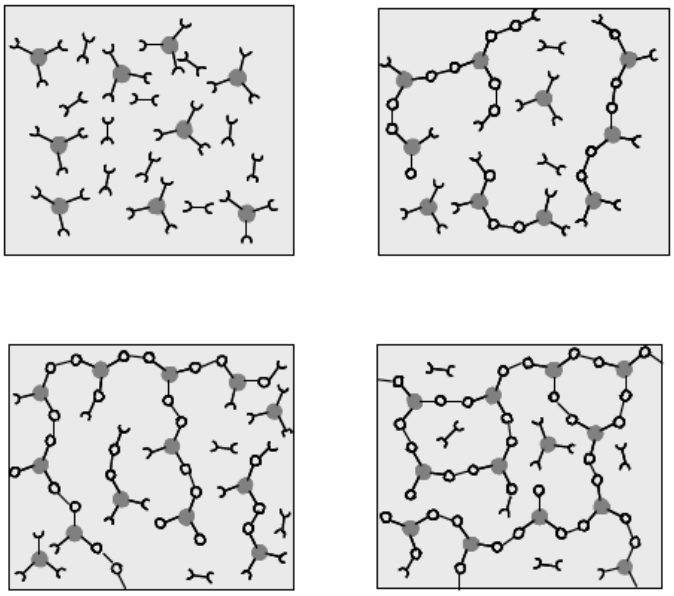

Figure 1. Schematical representation of structural development during thermoset curing for the reaction of a dimer with a trimer

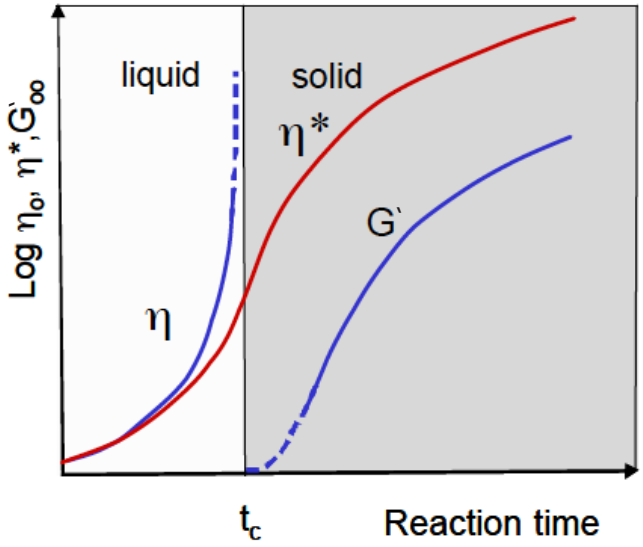

Figure 2. Measurement of the viscosity of a curing resin in a steady shear and a dynamic oscillatory test

The time/cure mode is an efficient way to generate viscosity profiles of a curing thermoset polymer. The viscosity profile yields the initial viscosity, minimum viscosity, approximate gel point, and optimum heating rate of a thermoset during curing. Data obtained on a curing epoxy compound are shown in figure 3. This information can then be used to develop a production cure cycle.

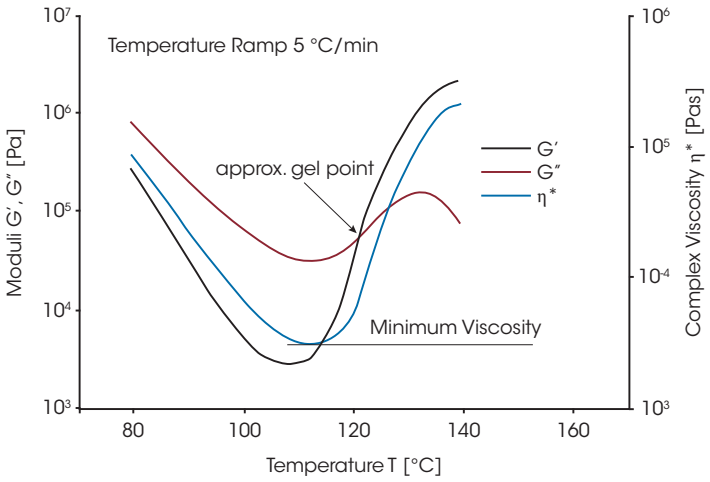

Figure 3. Measurement of the minimum viscosity and approximate gel point for a curing epoxy compound

The crossover point of the storage and loss modulus curves (Figure 3) is a good estimate of the gel point of a curing thermoset. But it is only an estimate, because, as the gel network structure forms, the modulus changes. So unless measurements on the gelling system are made fast enough, the exact gel point will be obscured by changes in the modulus. The reason is, that the instant of gelation the modulus of the critical gel exhibits power law behavior and tan δ becomes frequency independent for a brief moment ($G' \sim G'' \sim a\omega^n$). This point can be found by making several simultaneous frequency measurements to obtain tan δ in the time scale of the developing gel (figure 4). Because tan δ is independent of frequency at the gel point, the curves pass through a single point and unambiguously define the instant the gel forms as shown in figure 5.

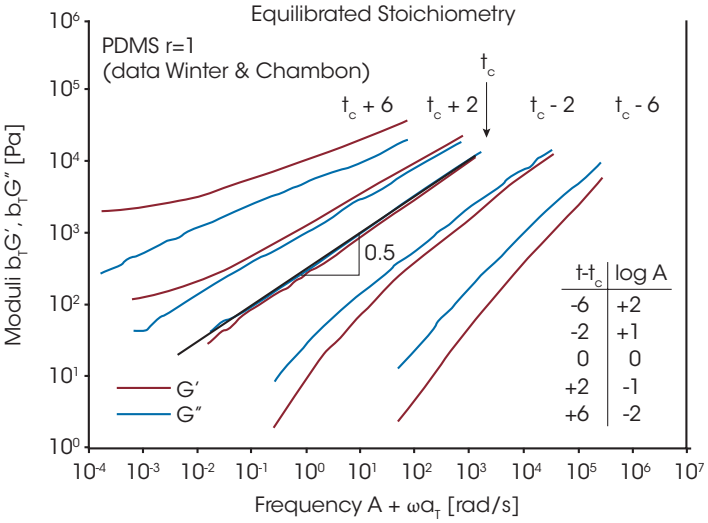

Figure 4. Frequency sweeps measuring G′ and G″ at any point in time during cure

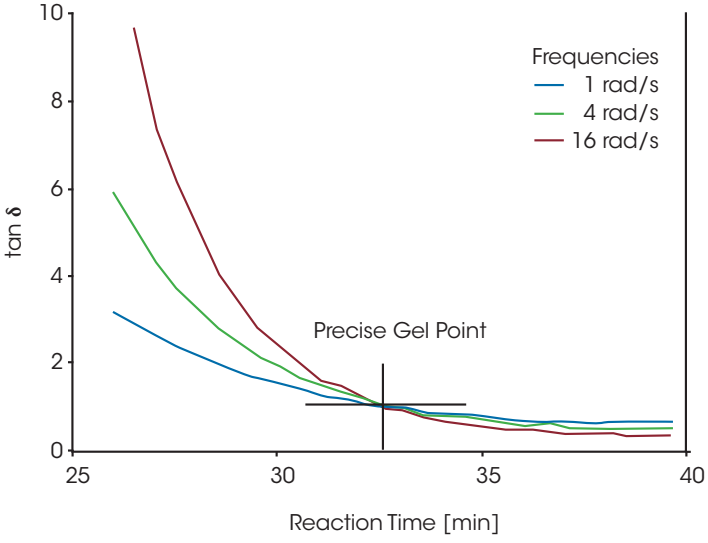

Figure 5. The gel point identified by the intersection of tan δ curves generated from the simultaneous frequency sweeps

EFFECT OF HEATING RATE

Figure 6 shows viscosity versus reaction time at several heating rates for a typical epoxy structural adhesive. With increasing rate, the viscosity minimum does not only occur earlier, it is also lower. This is significant – for example in a lamination process, the resin viscosity must be low enough to wet the embedded fibres uniformly, but not so low to cause excessive bleeding at the laminate edges or in the en-capsulation of integrated circuits by transfer-molding. The viscosity must not be too high to damage the fragile fibers.

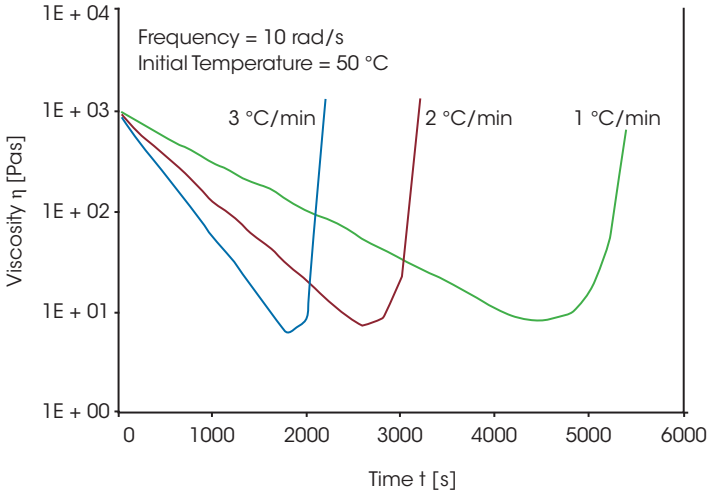

Figure 6. Measurement of the viscosity profile of an epoxy resin as a function of the heat-up rate

EFFECT OF MOISTURE

Excessive water content in an epoxy resin can cause a plasticizing effect, lubricating the polymer and causing a decrease in viscosity. Figure 7 shows a comparison of the viscosities measured during cure for both a good and a bad performing resin sample during impregnation of a woven glass cloth. The bad resin did not adhere to the cloth but instead was flowing through the weave. The results show that the bad resin's viscosity peaked at approximately 100 °C but then decreased to a minimum which was below that of the good resin.

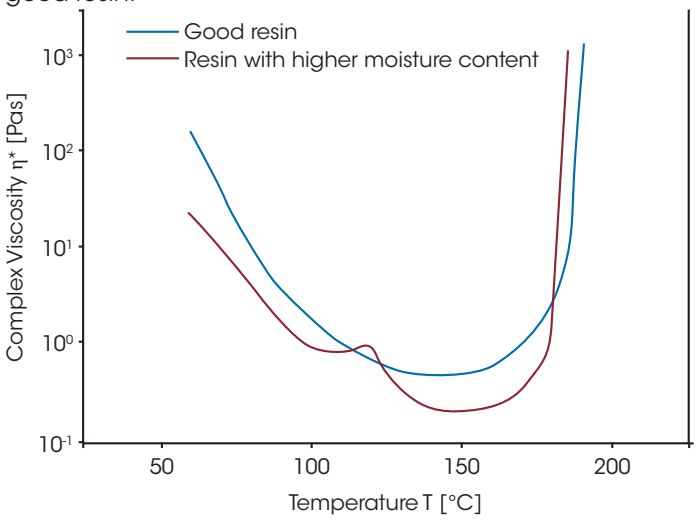

Figure 7. Viscosity as a function of temperature for a good and a bad (excess moisture) sample

At the boiling point of water, some of the excess moisture evaporated, leaving voids in the material and causing the resin's viscosity to rise. But as the temperature increased further, the remaining excess water acts briefly as a plasticizer and the viscosity decreased to a lower minimum than that of the good resin, which was drier. When pressure was applied to the resin during impregnation of the glass cloth, the low viscosity resulted in resin migration and poor adhesion of the resin to the cloth.

Moisture, even in low concentration, causes large changes in the rheological and chemical behavior of adhesives. Figure 7 shows the change in the reaction profile due to moisture. This data can be used to predict, for example, bond layer thickness and cycle times in printed circuit board laminations.

EFFECT OF CURE TEMPERATURE

Beyond the gel point, the modulus increases to give the adhesive its ultimate strength. Adhesive strength is evaluated from dynamic modulus measurements as a function of frequency and temperature. Figure 8 shows the dynamic elastic modulus G' and tan δ versus temperature. For three different cure temperatures of 93, 135 and 350 °C, the Tg of the cured epoxy resin shifted from 130 °C to over 250 °C.

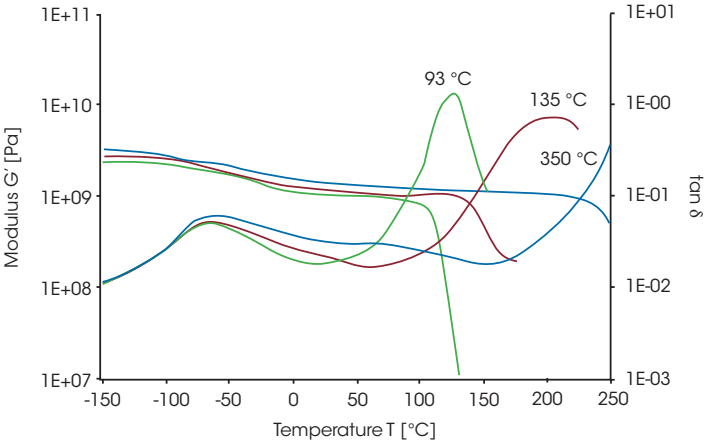

Figure 8. The extent of the cure of a thermoset as a function of the curing temperature shows in Tg

EFFECT OF ADDITIVES

The ideal injection molding thermoset (RIM) needs to be highly stable at a low viscosity level at the screw barrel temperature, yet cure rapidly upon entering the mold.

Figure 9 shows a simulation of the cure behavior of two phenolic compounds at two different temperatures, the barrel and the mold temperature. Compound A showed fast curing in the mold and made a good final part, but had too high a viscosity at the barrel temperature. The compound B injected well with low shear heating, but cured slower. The addition of 1% of Zn stearate to compound A lowered the viscosity at the barrel temperature compared to coumpound B, but without significantly affecting the cure time.

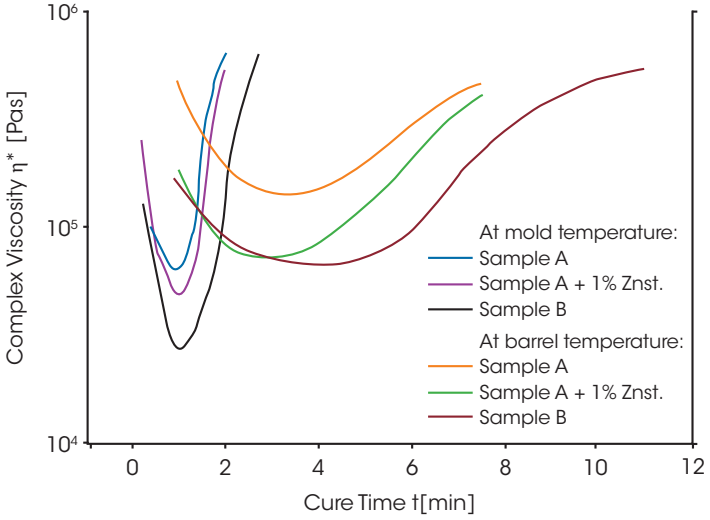

Figure 9. Effect of Zn stearate on the viscosity profile during cure at barrel and mold temperature

Simulations of the viscosity under various cure conditions provides the necessary data in process design: barrel temperature, nozzle size and effect of shear heating.

EFFECTS OF VARIOUS CURING AGENTS ON EPOXY RESIN

Epoxy resin used in printed circuit boards (PCB's) requires sufficient rigidity during exposure to high end-use temperatures (approximately 140 °C), and soldering temperatures (approximately 250 °C). When exposed to high operating temperatures, the PCB's may became dimensionally unstable, resulting in a defective product and material waste when not formulated correctly.

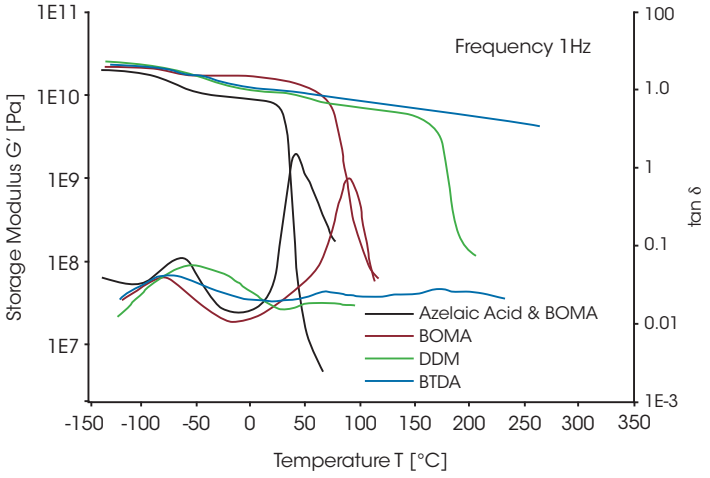

Figure 10. Effect of different curing agents on the mechanical properties of the final product

Using different curing agent, an increase of the maximum continuous use temperature by increasing the glass transition (Tg) was obtained under the same curing conditions. DMA measurements as a function of temperature (ASTM D 4065), shown in Figure 10, were performed on the final samples. Sample 4 (BTDA) was found to be the most efficient, increasing the Tg to over 270 °C, higher than both the end-use temperature and the soldering temperature. The peak in tan δ or glass transition temperature (Tg) can be evaluated

to determine the degree of cure. The storage modulus, G' (amount of energy stored in a material), is a measure of each sample's stiffness. Curing agents not only affect the rate of change of the polymer's viscosity, but also it's physical properties by increasing the crosslinking density and as such the performance of the final product.

CURE BEHAVIOR OF COMPOSITE PREPREGS

The resin in many structural adhesives is also used as matrix material in fiber reinforced composites. Dynamic mechanical testing is a valuable characterization technique for composite matrix resins. Rheological analysis of the neat resin to predict processing characteristics of glass and graphite reinforced composites has become a standard procedure in product development of advanced composites.

Figure 11 compares results for the cure of a graphite prepreg and neat resin using parallel plate fixtures in a oscillatory rotational rheometer. Note that, although there are large differences in minimum viscosity, cure times are identical.

CONCLUSIONS

Dynamic mechanical measurements of thermosetting adhesives can give valuable information about their curing behavior, including minimum viscosity and gel point, glass transition temperature and degree of crosslinking.

A more comprehensive discussion of this topic is available from TAI in "Understanding Rheological Testing—Thermosets."

ACKNOWLEDGEMENT

Revised by A. Franck, TA Instruments

For more information or to place an order, go to http://www.tainstruments.com/ to locate your local sales office information.

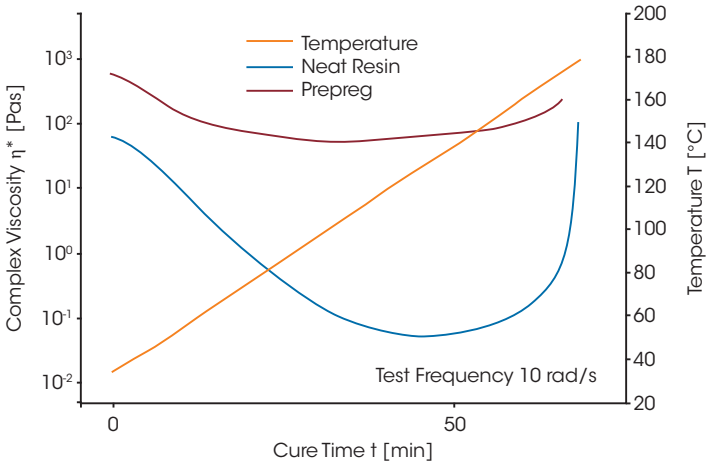

Figure 11. Viscosity profile of composite (prepreg) and the neat resin during cure