

## Tricks of the Trade

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### Characterization of Thermosetting Polymers How to Get More Out of Your Rheometer

#### Introduction

Characterizing thermosetting polymers poses an interesting challenge to the thermal analyst. Many processing applications require the polymer to flow into a mold or consolidate during lamination, and concurrently undergo a chemical reaction to develop a fully cross-linked network. Because of the complexity of thermosetting polymer processing, the ability to understand the changing material properties during processing is required. The technique described here allows;

- Characterize the curing of a reactive polymer using differential scanning calorimetry (DSC) and oscillatory parallel plate rheometry
- Measure the viscosity, the glass transition temperature ( $T_g$ ), and the conversion during either isothermal or non-isothermal curing conditions.
- Measure the viscosity and the dielectric loss factor during either isothermal or non-isothermal curing conditions.

A simple modification of a parallel plate rheometer allows the thermal analyst to study the chemorheology of a curing resin system (1). Commercial rheometers can easily be outfitted with disposable aluminum plates to aid in the separation of the fixtures after the sample has cured. The use of disposable plates allows a small disposable dielectric sensor to be embedded in the lower plate, thus permitting dielectric data to be obtained simultaneously with viscosity data (2).

#### Experimental Description

Rheological experiments were conducted using a Rheometrics System Four rheometer with a forced-convection nitrogen purged oven. The experiments were performed in the oscillatory parallel plate geometry. Measurements were made every 30 seconds with a 2% strain amplitude at a frequency of 6.3 radians/sec (1Hz). The bottom plate was machined to accommodate a thermocouple (allowing direct measurement of the sample temperature) and a disposable dielectric sensor (Micromet Instruments).

Disposable plates with only the embedded thermocouple were used to study the relationship between the conversion,  $T_g$ , and the viscosity. Nonisothermal experiments were conducted by equilibrating the sample at 30° C and heating the sample at various heating rates to a final temperature of 175° C. At specified time intervals, the experiment was stopped, the oven opened, the disposable plates were quickly unclamped, and both the plates/sample were quenched in liquid nitrogen, stopping the chemical reaction. Thermal analysis can be performed on the quenched samples using a wide variety of commercially available DSC modules.

To correlate the viscosity and dielectric properties during curing, a disposable sensor was placed in a machined slot in the lower disposable plate. Additionally, a small slot was machined to accommodate a thermocouple. The non-isothermal rheometer runs were made in a similar manner as described above. To ensure good coverage of the interdigitated comb electrodes in the dielectric sensor, a small amount of powdered resin (at the same extent of reaction as the sample) was placed over the sensor area prior to placing the molded sample disk between the plates in the rheometer. The sample was pre-molded using a 2.54 diameter compression molding device. Powdered resin could be compacted into a solid disk without changing the degree of advancement using careful molding conditions (need to be determined for each type of resin or prepreg used in the experiments). The experimental set-up is schematically shown in Figure 1.

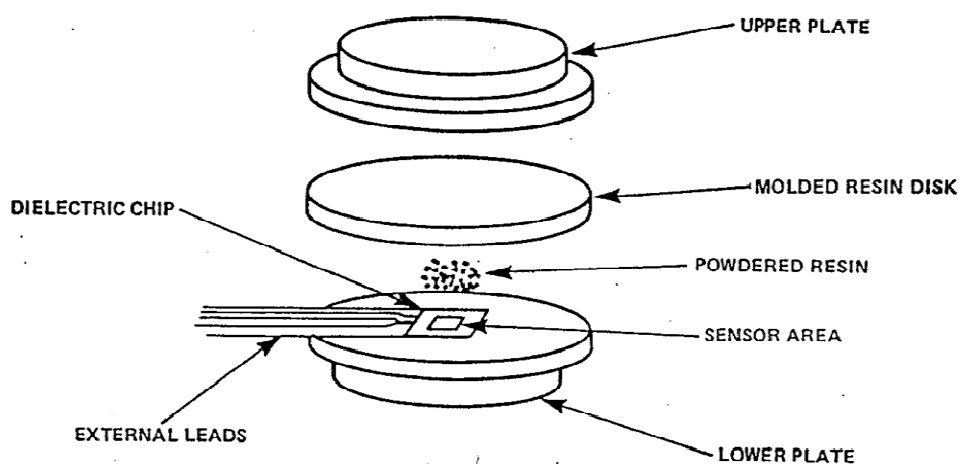


Figure 1. Disposable plates showing the placement of a disposable remote dielectric sensor in the lower plate.

Examples

### Non-isothermal curing

To correlate the conversion,  $T_g$ , and viscosity during non isothermal during, the rheometer runs were aborted at specified time intervals, the samples were quenched and analyzed by

DSC. In Figure 2, the  $T_g$  and complex viscosity are plotted as a function of time for a sample heating rate of  $9.8^\circ\text{C}/\text{min}$ . During the initial softening, the viscosity decreased by approximately 2 orders of magnitude as a result of the strong temperature dependence. Although there was a large decrease in the viscosity, the  $T_g$  remained constant during the early portion of the curing. As the temperature continued to rise, the onset of rapid crosslinking caused a sharp increase in  $T_g$ , with a concurrent increase in the viscosity.

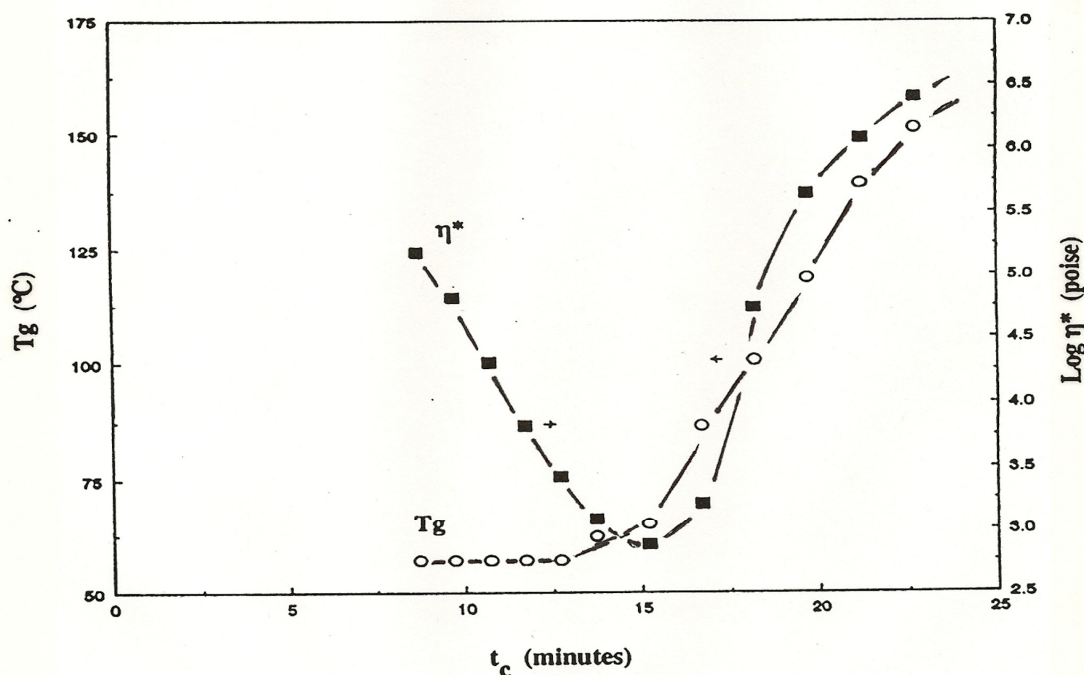


Figure 2. Complex viscosity and glass transition temperature as a function of curing time for a sample heating rate of  $9.8^\circ\text{C}/\text{min}$ .

In Figure 3, the complex viscosity and conversion are plotted as a function of curing time for a sample heating rate of  $9.8^\circ\text{C}/\text{min}$ . The initial conversion by DSC was 0.23 (This was partially reacted prepreg powder having a B-stage conversion of 23%). The conversion did not change during the initial softening of the resin. When the viscosity approached the minimum value, the conversion begins to increase. Although the conversion starts to increase, the viscosity of the growing network is more strongly governed by the temperature dependence of the viscosity. For a short time, the viscosity continues to decrease while both the  $T_g$  and the conversion are increasing. After the minimum viscosity, the network formation (crosslinking reaction) causes a rapid increase in the viscosity.

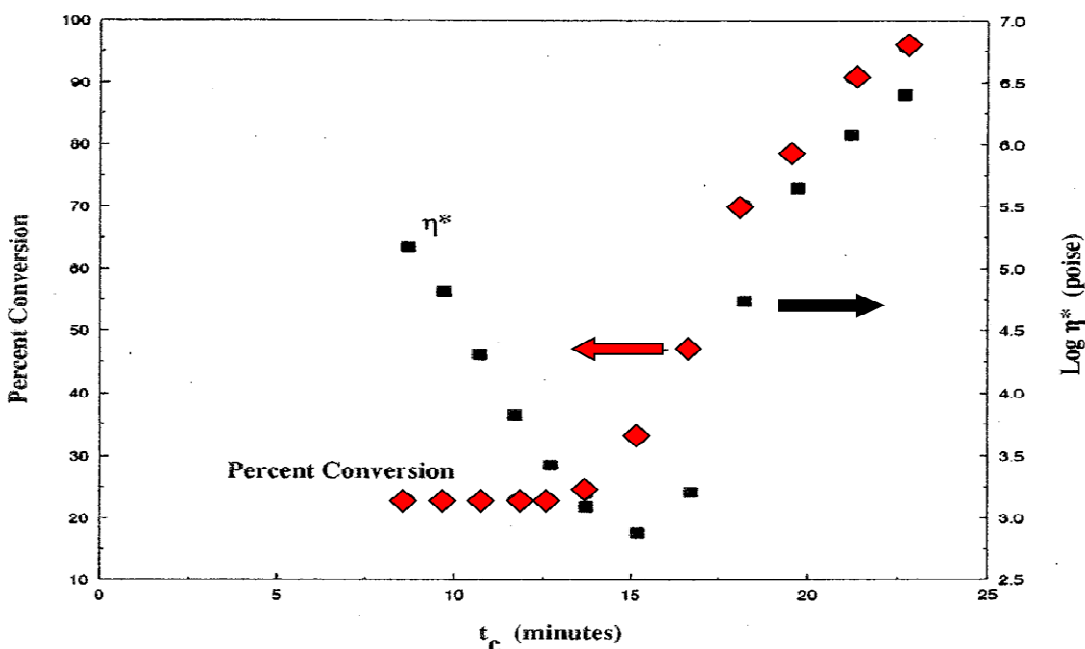


Figure 3. Complex viscosity and epoxy conversion as a function of curing time for a sample heating rate of 9.8°C/min.

### Viscosity/dielectric analysis during non-isothermal curing

During the lamination of B-staged prepregs to make printed circuit boards, the partially cured resin-impregnated glass cloth is subjected to a nonisothermal temperature profile. This causes the resin to flow over the circuit traces and chemically react forming an intractable fully cured network. The viscosity profile determines the flow window, or time when the resin is flowing. In Figure 4, the complex viscosity is plotted as a function of time for a series of heating rates to a cure temperature of 175°C. The resin system was a bis-maleimide triazine epoxy blend (3). As the temperature increases, the resin softens at the  $T_g$  of the partially cured polymer. With continued heating, the viscosity dramatically decreases. When the chemical kinetics of the crosslinking reactions are faster than the decrease in the viscosity, the viscosity reaches a minimum and subsequently increases. The curing reactions continue, the molecular weight and crosslink density increase, causing the viscosity to increase.

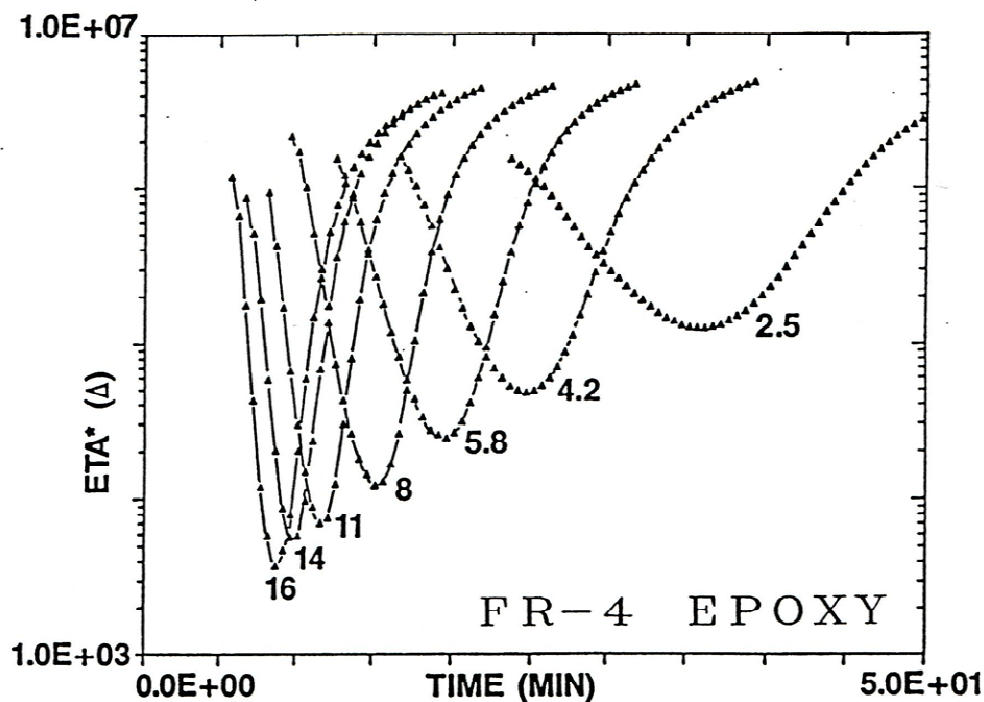


Figure 4. Complex viscosity as a function of time for various heating rates (in °C/min) to cure temperature of 175°C.

To obtain a direct correlation of the dielectric loss factor to physical changes in the resin during the curing cycle, the dielectric loss factor was measured using the embedded dielectric sensor method. Figure 5 the loss factor and complex viscosity are plotted as a function of time for a 5.8°C/min. heating rate to 175°C. This first inflection in the loss factor data corresponds to a frequency dependent dipolar relaxation (3) which occurs as the resin softens at the glass transition temperature. With continued heating, ionic conductivity begins to dominate the loss factor, with a large rise in the loss factor. The viscosity reaches a minimum value and begins to increase due to decreased segmental mobility as the crosslinking reaction increases the molecular weight. As the segmental mobility of the network decreases with crosslinking, the loss factor decreases. The resin continues to react (decrease in loss factor and increase in viscosity) at the final cure temperature until vitrification occurs, resulting in the appearance of a dipole peak and a sudden upturn in the viscosity. The vitrification event was clearly evident in the viscosity data. The rheometer oven was maintained at 175°C and data acquisition continued for a total of about 50 minutes. At about 30 minutes, the viscosity increased rapidly resulting in an input overload and the rheometer stopped taking oscillatory data, however the dielectric data acquisition continued. The diffuse shoulder on the dielectric loss factor peak at long times occurred at approximately the same time as the rapid upturn in the viscosity. The appearance of dipole peaks during isothermal curing at temperatures below the ultimate T<sub>g</sub> has been observed previously (4,5).

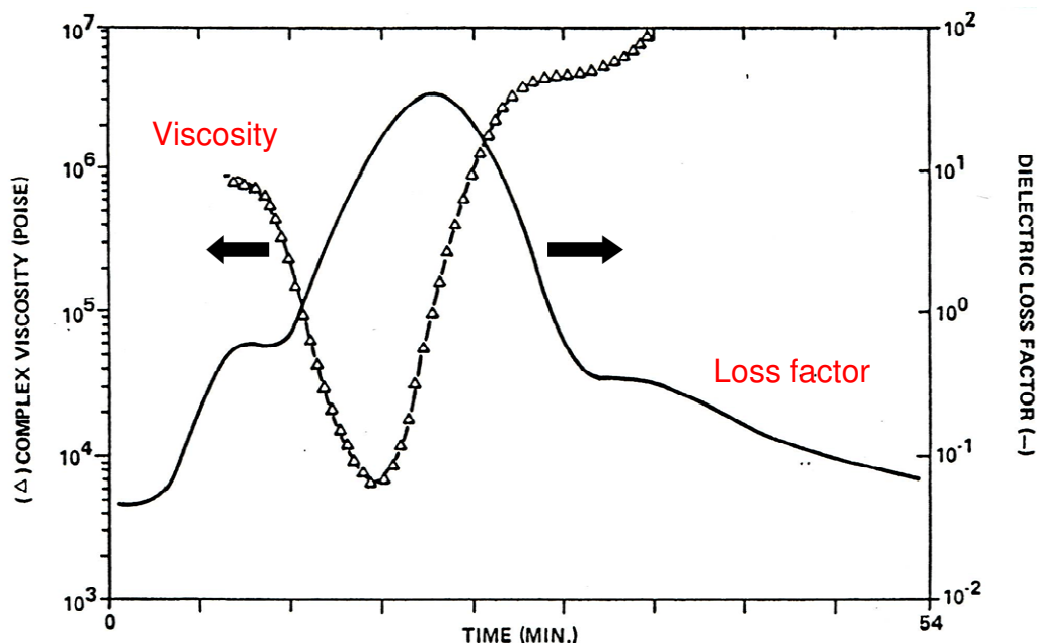


Figure 5. Complex viscosity and dielectric loss factor measured simultaneously as a function of cure time: The temperature was ramped at 5.8°C/min to a cure temperature of 175°C.

## Conclusion

A couple of examples were presented to show how the use of disposable plates in a commercial rheometer can significantly increase the amount of data and subsequent understanding on the curing of thermosetting polymers. Two nonisothermal cases were presented to demonstrate the utility of aborted rheometer runs to determine the glass transition temperature and conversion. The disposable plates also facilitate the simultaneous measurement of the viscosity and dielectric properties when a remote dielectric sensor is mounted in the bottom plate in the rheometer.

## References

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