Thermal Analysis Application Brief
Characterization of the Cure of High Temperature Urethane Resins by Dielectric Analysis

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SUMMARY
High temperature curing urethane - isocyanate resin systems are utilized as high performance adhesives, particularly in electronics applications. The properties of these urethane thermosetting materials in the final end-use application, as well as the economics of production, are directly related to their curing properties. Dielectric analysis (DEA) is an ideal technique for monitoring the cure of the urethane resin systems because the unreacted material (with its low viscosity) can be directly applied to the disposable sensor and continuous measurements can be made as the resin transforms from a low molecular weight liquid to a high molecular weight amorphous solid.

INTRODUCTION
Cured urethane adhesives are generated through a chemical crosslinking reaction which occurs after mixing a two-part system (e.g., urethane and isocyanate). Traditional thermal analysis methods such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) have been evaluated as means to monitor the urethane curing reaction. Success in characterizing these materials, however, has been limited. Frequently, the urethane is dissolved in a solvent, which is volatilized as the resin is heated. This volatilization of the solvent complicates the DSC analysis. Also, the heat of reaction of the urethane - isocyanate system is rather small which makes DSC analysis difficult, especially when attempting to distinguish between different batches or lots of the resin, such as for quality control purposes. DMA is difficult to use in this case because the initial resin viscosity (immediately after mixing) is so low that a support system (such as a fiberglass cloth) must be utilized to support the sample. Dielectric analysis, which measures a material’s response to an applied alternating voltage, provides a better means to evaluate thermosetting resins. DEA is more sensitive than DSC to changes in the material as cure progresses and is not adversely affected by the evolution of volatiles (such as solvents). The DEA is less affected by the material’s physical state during cure compared to DMA, and the DEA is capable of monitoring the changes which occur in a resin from the low viscosity state through the process of crosslinking and vitrification (i.e., conversion from a rubber to a glassy solid).

Dielectric analysis measures the two fundamental electrical characteristics of a material — capacitance and conductance — as a function of temperature, time, and frequency. The capacitive nature of a material is its ability to store electric charge, and this property dominates the response below the glass transition event. The conductive nature reflects the ability to transfer electric charge and this property dominates the response above the glass transition temperature. While these electrical properties are important in themselves, they have more significance when they are correlated to changes in the molecular state of a material. The actual parameters monitored using dielectric analysis are $e'$ (permittivity), which measures the degree of alignment of the molecular dipoles with the applied electrical field, and $e''$ (loss factor), which represents the energy required to align the dipoles or to move trace ions.

EXPERIMENTAL
In dielectric analysis, the sample is placed in direct contact with the sensor, or electrode array. The electrodes transmit an applied oscillating voltage to the sample and sense the response of the sample to the applied voltage. The optimum sensor arrangement for monitoring the cure reaction of thermosetting materials is the ceramic single surface sensor which contains an interdigitated array of excitation and response electrodes on
a planar surface. This sensor is easy to use and is disposable (avoiding the need for tedious clean-up procedures). The resin systems is thoroughly mixed and placed onto the sensor using a wooden rod or pipette. A platinum resistance thermometer is contained on the surface of the sensor thus providing accurate sample temperature measurements.

DEA results are affected by temperature, time and applied frequency. Dielectric analysis features a wide frequency range (from 3mHz to 100kHz) which permits the assessment of a material’s behavior over a very large range. Low frequencies (those below 30 Hz) are useful for monitoring the movement of trace ions in a resin material and provide a very sensitive means of determining the completion of cure in a thermosetting resin system.

For the urethane-isocyanate system, the sample was thoroughly mixed and then painted onto the DEA sensor at room temperature. The resin was then cooled to -75°C (to observe the glass transition event of the uncured resin) and then heated to 175°C at a rate of 3°C/min. The following frequencies were applied to the resin during the analysis: 1, 3, 10, 30, 100, 300, 1000, 3000, and 10000 Hz. The DEA cell was purged with dry nitrogen adjusted to a flow rate of 500 ml/min.

RESULTS

Displayed in Figure 1 is the data obtained by heating the uncured resin from -75 to 175°C. This plot shows the log conductivity as a function of temperature. The glass transition event of the uncured resin occurs in the region of -50°C as reflected by the series of peaks in the conductivity data. The peak temperature is dependent on the applied measurement frequency which demonstrates that this transition is a non-equilibrium, or time-dependent event, which is due to the effects of the molecular dipoles. As the measurement frequency increases, the peak temperature increases.

At temperatures near or below the glass transition temperature (Tg), the dielectric properties of the resin are dominated by the molecular dipoles (frequency dependent response). At temperatures above Tg, the conductivity data curves merge together as the resin softens (onset of flow). Above Tg, the resin viscosity becomes sufficiently low enough that the trace ions are free to move through the liquid resin and the conductivity data thus shows a frequency independent response.
The resin reaches its maximum value of conductivity at a temperature of 60°C. This maximum in the data reflects the point of minimum resin viscosity. Volatiles are evolved by the resin system beginning at this temperature and the viscosity begins to increase. The increase in the resin viscosity hinders the movement of the trace ions, and the conductivity data shows a decline. As the resin undergoes polymerization and crosslinking, a more pronounced decrease is observed in the conductivity data at approximately 100°C. The system is completely cured at a temperature of 150°C based on the observation that the conductivity data reaches a relative minimum at this point.

The conductivity data may be analyzed using the derivative of the conductivity for a more sensitive examination of the properties exhibited by the resin during heating. A plot of the derivative of the conductivity with respect to temperature is displayed in Figure 2. The glass transition event is observed as a series of peaks in the region of -50°C. The loss of the solvent from the resin system is reflected as a frequency independent peak between 50 and 70°C. The cure reaction is responsible for the peak observed between 110 and 150°C.

This data demonstrates that dielectric analysis can monitor the following major events associated with a given resin system:

- the glass transition
- onset of flow
- point of minimum viscosity
- evolution of volatiles (solvents)
- curing
- completion of cure.

In addition, dielectric analysis allows these measurements to be made continuously from the solid glassy state through the low molecular weight liquid phase, and then through the development of a crosslinked rubber.