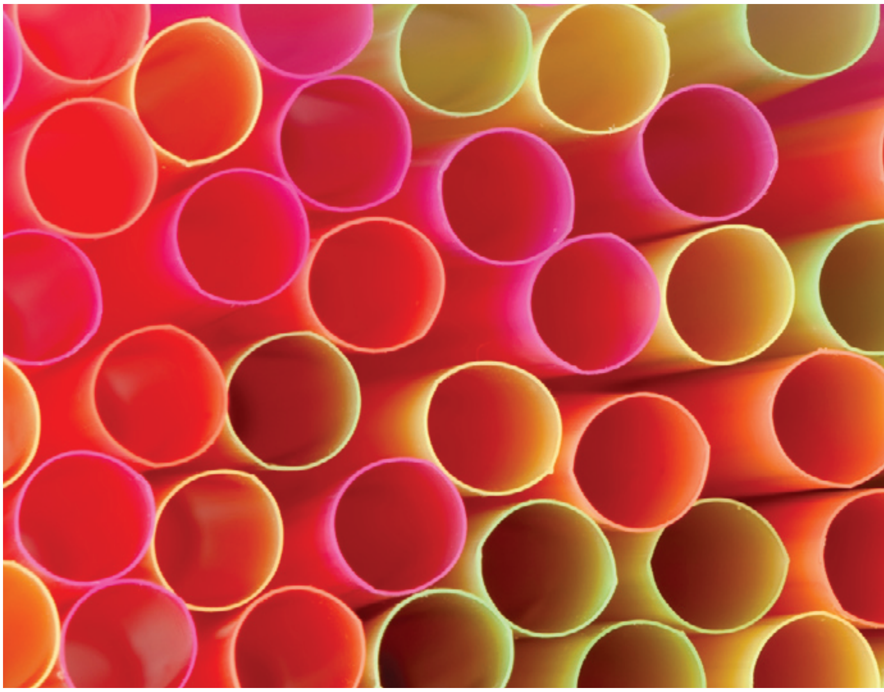

APPLICATION NOTE

Thermal Analysis

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Differential Scanning Calorimetry of Epoxy Curing Using DSC 6000

Introduction

When testing materials using DSC, scientists often utilize multiple techniques to study their samples. When presented with a sample which exhibits multiple and/or overlapping thermal events, separation and identification of the transitions become important. One of the more obvious questions is whether the events are thermo-dynamic or kinetically controlled. A couple of examples of thermodynamic events would be the melting point and the glass transition of materials. An example of a kinetic transition would be a thermal event, which involves a change in the material such as cross-linking, and decomposition. It is not uncommon to find kinetic events close to (if not overlapping) thermodynamic transitions, such as enthalpic relaxation and the glass transition or melting and decomposition. The two most common techniques used to assist when studying these types of materials is HyperDSC® or MT-DSC. HyperDSC can be utilized to suppress kinetic events, and MT-DSC to separate kinetic from thermodynamic events.

A commonly studied sample by DSC is thermoset epoxy materials where the sample is heated to an elevated temperature, at which point it starts to cross-link.When studying these types of materials, multiple transitions are typically sought after:

- Initial glass transition T_{gi}
- Peak cure temperature
- Cure onset temperature
- Cure heat
- Final glass transition T_{gf}
- Specific heat of the final material
- Percent cure

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For the Better

PerkinElmer's DSC 6000 is an excellent tool for measuring these thermal events, not only in the typical testing methods, but also thanks to the expanded StepScan (MT-DSC) capability of the instrument.

- PerkinElmer's new compact, single furnace DSC, the DSC 6000, provides a solution for a wide range of routine applications in the academic, polymer and pharmaceutical markets.
- The DSC 6000 has the option of a 45-position autosampler. The DSC 6000 gives you all of the advantages of a standard Heat Flux DSC and includes Modulated Temperature DSC (MT-DSC) technology for easier data interpretation and additional capabilities for product development and troubleshooting.

Figure 1. PerkinElmer's DSC 6000.

Experimental

A DSC 6000 was used for the experiments and was optimized for the below settings:

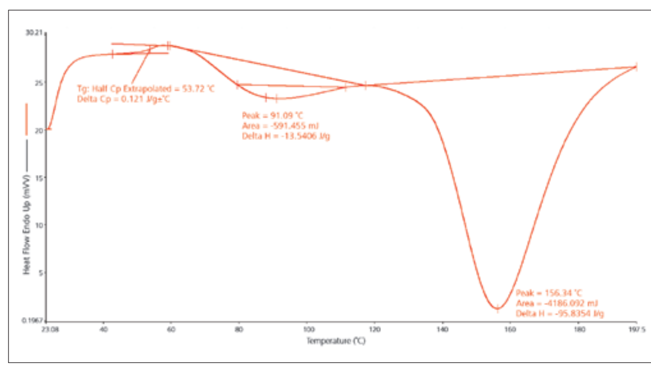
- Purge gas was nitrogen at 20 mL/min.
- A two point calibration was performed with indium and zinc.
- A 2P cooling device was installed on the DSC.

Two experimental techniques were performed, each of which consisted of multiple steps. Both techniques were applied to fresh samples from the same batch, to minimize error.

- Standard DSC experiment
  - Heat from 25-200 ˚C at 10 ˚C/min.
  - Hold isothermal at 200 ˚C for 10 min.
- StepScan method
  - Heat from 25-200 ˚C
  - Step size 1 ˚C
  - Step time 2 min.
  - Criterion 0.01 mW
  - Hold isothermal for 10 min at 200 ˚C
  - Heating rate is 5 ˚C/min.
- To verify maximum cure
  - The StepScan cured sample was rested utilizing first heat parameters.
  - The standard DSC cured sample was retested utilizing first heat parameters.

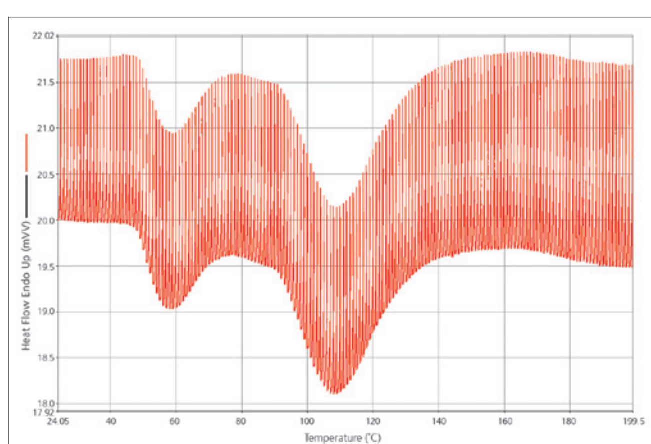
Results

Standard DSC method at 10 ˚C/min.

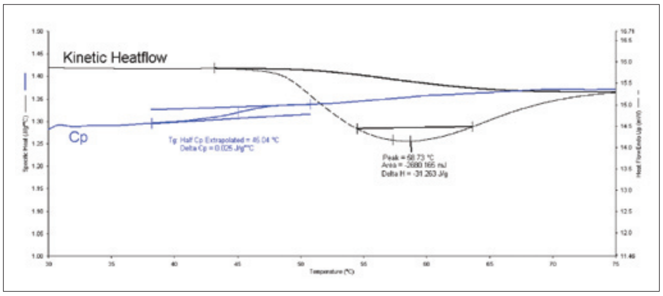


- On the first heat we see a glass transition around 53 ˚C and two exothermic peaks at 91 ˚C and 156 ˚C.
- Note that T_{gi} is difficult to measure since it is in close proximity to the onset of the cure.

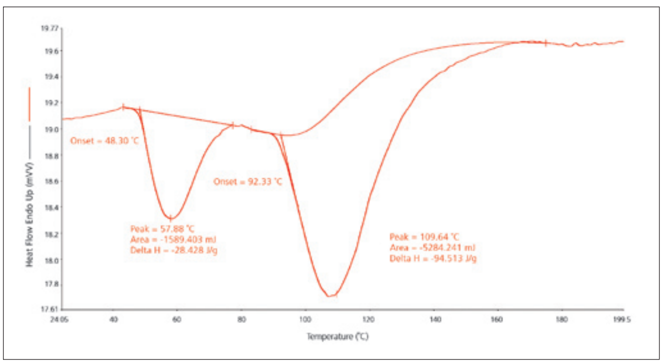
StepScan DSC (Base data file)



StepScan Calculation of the Glass transition region



– Notice how we are able to clearly pick out the glass transition (45.0 ˚C) in the Cp curve without overlap of the first exothermic peak at 58.7 ˚C.

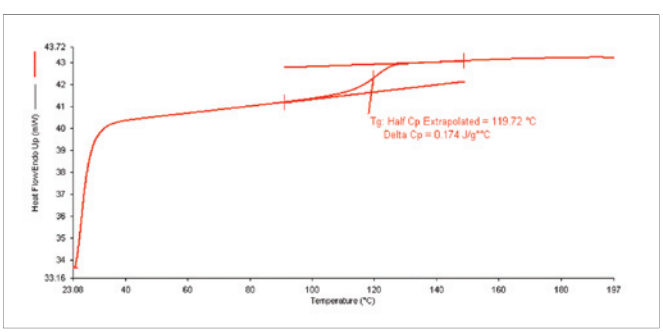


– The exothermic peaks only show up in the Iso-K curve and have shifted to lower temperatures due to the removal of the effect of heating rate on the kinetic events (58 ˚C and 109 ˚C in comparison to 91 ˚C and 156 ˚C).

Verifying the Cure

Standard DSC 10 ˚C/min

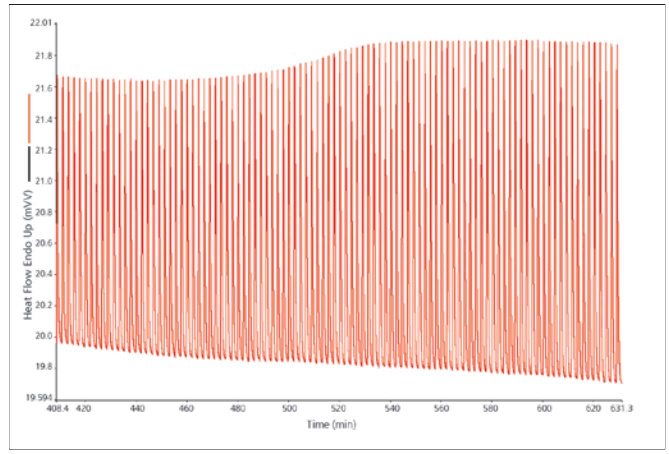
Second Heating at 10 ˚C/min



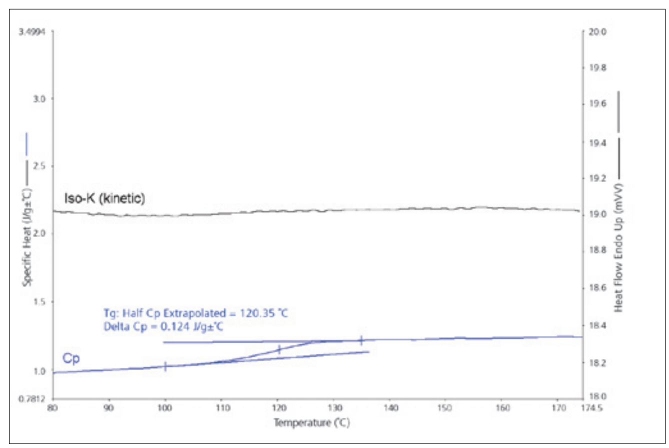
– Note the T_{gf} of the cured material (120 ˚C) and that no exotherm is present in the second heat suggesting the maximum cure was achieved.

StepScan DSC

StepScan (Base file)



StepScan Calculation of the glass transition region



– We were able to detect the glass transition in the Cp curve with limited effect from the heating rate (120 ˚C).

– Sample was retested after the StepScan measurement to verify maximum cure had occurred (note the absence of any exothermic events in the Iso-K curve).

Conclusions

PerkinElmer's DSC 6000 is capable of observing the cure profile of epoxy materials to determine the more commonly desired experimental parameters. It achieves this through both standard DSC techniques as well as through StepScan. The highlights are easy detection of T_{gi}, T_{gf}, and percent cure.

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