



Better Characterization of Thermosets Using StepScan DSC

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Introduction

Thermosetting resins, such as epoxies, are widely utilized for a variety of applications in the automotive, electronics, aerospace and home product industries. One powerful means of characterizing the thermal, physical and mechanical properties of thermosetting resin systems is with thermal analysis.

Thermal analysis is a sophisticated, yet easy-to-use series of analytical techniques for the characterization of thermosetting materials. It provides essential information for materials development and selection, process optimization, engineering design and prediction of end-use performance. Thermal analysis techniques include DSC for the measurement of thermophysical properties, TGA for weight loss and decomposition studies, TMA for the assessment of dimensional properties, DMA for the measurement of mechanical characteristics and thermal conductivity for the measurement of heat transfer properties.

The most widely used technique for the characterization of thermosetting materials is DSC. This technique measures critical properties such as softening or T_g, onset of cure, maximum rate of cure, completion

of cure, degree of cure and cure kinetics [1].

The information obtained by DSC on thermosetting resins can be further enhanced with StepScan DSC [2].

StepScan DSC

StepScan DSC is new software from PerkinElmer Instruments for the enhanced characterization of the thermal properties of materials. The technique permits the separation of DSC results into thermodynamic (reversible) and kinetic (irreversible) components for better interpretation. The method is straightforward and utilizes the traditional approach for measuring the heat capacity, C_p, for the highest possible reliability of results without interfering experimental problems [3,4].

The StepScan DSC approach is only possible with the design of the power compensated Pyris 1 DSC, with its very low mass sample and reference furnaces and rapid response time.

Figure 1 shows the StepScan DSC approach with the application of a repetitive sequence of short heating – isothermal hold segments.

With the application of heating (10°C/min) over small temperature increments (1.5 or 2°C), and by holding for a short time interval (e.g., 30 seconds), the heat capacity that is yielded reflects the reversible aspects of the sample. Kinetic or irreversible effects (on the time scale of the experiment) are eliminated in the *Thermodynamic C_p* data set, which reflects ‘fast’ or reversible phenomenon, such as the sample’s heat capacity (molecular vibrations) or T_g (molecular rotations).

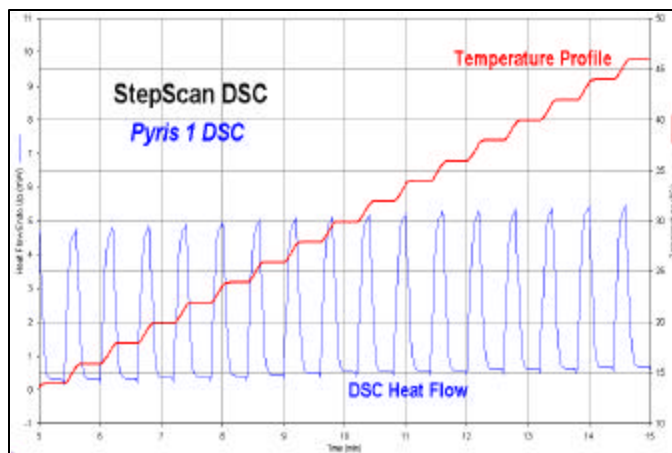


Figure 1. StepScan DSC temperature – isothermal steps

For example, if a sample has a T_g, with an overlapping enthalpic relaxation, moisture loss or crystallization event, the Thermodynamic Cp signal will show the classic, stepwise change in the heat capacity. This then makes it simple and straightforward to analyze and interpret. The StepScan DSC approach also provides the kinetic or *IsoK Baseline* data set, which is reflective of the irreversible or ‘slow’ or irreversible processes taking place during the experiment. The enthalpic relaxation event, which can occur on physically aged samples at T_g, will show up in the IsoK Baseline data set.

Because the StepScan DSC approach requires rapid DSC response times, the technique is only feasible with the power compensated DSC, which allows for fast heating and thermal equilibration. The application of the StepScan approach to a large mass furnace, heat flux DSC instrument would be difficult or technically unfeasible due to the inability to rapidly respond and equilibrate. In addition, the StepScan DSC experiments are generally faster (by a **three-fold improvement**) as compared to equivalent TMDSC results generated on a slower responding, heat flux DSC device.

In this study, the properties of a partially cured epoxy thermosetting resin were studied using StepScan DSC.

Experimental

The following table outlines the experimental conditions used to measure the reversible and irreversible properties of a powdered

epoxy resin using the StepScan DSC approach.

Experimental Conditions	
Instrument	Pyris 1 DSC with Intracooler II
Technique	StepScan DSC
Sample mass	17 mg
Sample pan	Open aluminum pan
StepScan conditions	Heat at 10 C/nib, 30 second iso hold, 2 C step increment
Temperature range	20 to 260 C
Purge gas	nitrogen

The DSC instrument was calibrated for temperature and enthalpic responses using high purity indium metal.

Results

Displayed in Figure 2 are the StepScan DSC results generated for the uncured epoxy resin. The plot shows the DSC heat flow as a function of sample temperature. The StepScan raw data shows the following features of the uncured resin: T_g, enthalpic relaxation at T_g and curing. The analysis of the StepScan DSC results provides enhanced characterization information about the resin since it separates the transitions into reversible and irreversible signals.

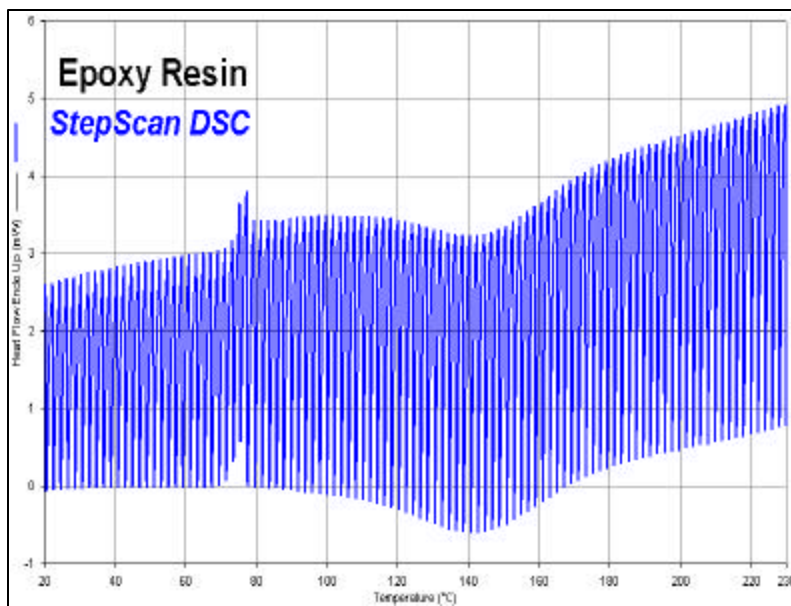


Figure 2. StepScan DSC raw data for epoxy resin

Displayed in Figure 3 are the analyzed results for the StepScan DSC data for the epoxy resin. This plot shows the reversible Thermodynamic Cp component (upper curve) and the irreversible Iso K signal (lower curve).

The Tg of the partially cured epoxy is observed as a large stepwise change in the Thermodynamic Cp signal at 74 C. Accompanying the Tg is a large enthalpic relaxation event. Since this is irreversible, on the time scale of the DSC experiment, this relaxation peak is relegated to the Iso K signal. Thus, StepScan DSC is able to separate out the reversible stepwise Tg from the simultaneous, irreversible enthalpic relaxation event. The Iso K signal allows for the quantitative analysis of this enthalpic relaxation peak ($\Delta H = 3.9 \text{ J/g}$ at 76 C). Immediately above the Tg, the epoxy resin powder starts to undergo cure as is reflected by the occurrence of an exothermic peak in the Iso K signal. This exotherm represents the cure and crosslinking of the epoxy resin and this is an irreversible transition. The total heat of cure is found to be 56 J/g.

The reversible Thermodynamic Cp signal shows the occurrence of a small transition during the crosslinking of the epoxy and this most likely reflects the revitrification of the epoxy, where the crosslinked resin converts to a glass. The high sensitivity of the power compensation DSC coupled with the extremely flat baseline produced with the StepScan DSC approach makes the detection of this very weak transition possible. This small event cannot be observed by standard DSC techniques. An enlarged view of the reversible

Thermodynamic Cp component is displayed in Figure 4 for the epoxy resin.

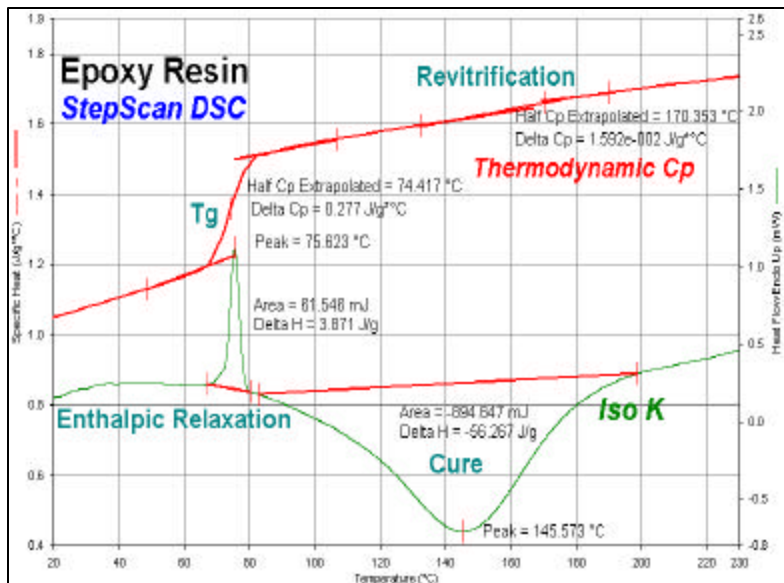


Figure 3. Analyzed StepScan DSC results (Thermodynamic Cp and Iso K signals) for partially cured epoxy resin

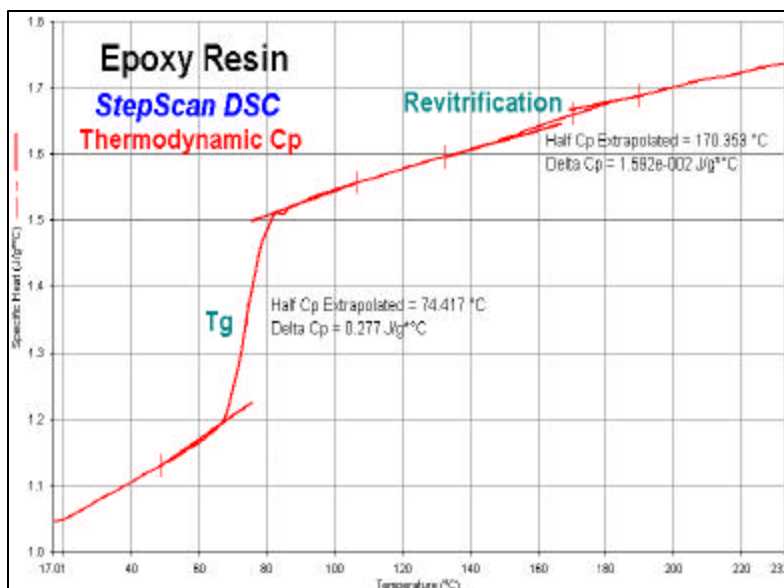


Figure 4. Enlarged view of reversible Thermodynamic Cp component for epoxy resin

The cured epoxy resin was reheated using the StepScan DSC approach and these results are displayed in Figure 5. The only transition that is observed for the cured resin is the reversible T_g at 106 C. No irreversible events, such as the enthalpic relaxation peak or a residual cure exotherm are observed for the cured resin. These results confirm that the epoxy resin was completely cured during the initial StepScan DSC experiment.

Summary

DSC yields valuable characterization information for thermosetting resins, including T_g, onset of cure, heat of cure, completion of cure, heat of cure and degree of cure. The DSC analysis of thermosetting materials, such as epoxies, is further enhanced through the use of StepScan DSC, which is a member of temperature modulated DSC (TMDSC). The StepScan DSC applies a repetitive series of ‘pure’ heating and isothermal holding steps. Using this approach, the reversible and irreversible characteristics of materials can be easily separated out, as was shown for the partially cured epoxy resin. This provides for better data interpretation. The StepScan DSC approach takes advantage of the very fast response time provided by the power compensation DSC from PerkinElmer Instruments. The StepScan DSC technique provides many advantages over conventional TMDSC approaches.

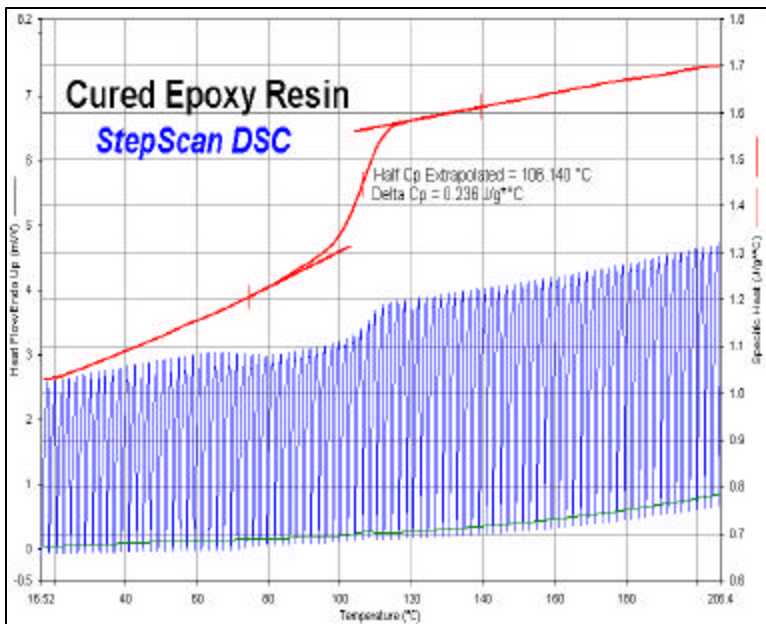


Figure 5. StepScan DSC results for cured epoxy resin

References

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- [2] B. Biyleu, W. Brostow, K. Menard, “Evaluation of the Curing Processes in a Fiber Reinforced Epoxy Composite by Temperature Modulated and StepScan DSC and DMA”, ASTM STP1402 (2001).
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