Better Characterization of Coatings, Pigments and Inks Using Stepscan DSC

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Introduction

For many polymeric samples, including coatings, pigments and inks, the interpretation of DSC results can be difficult as the transitions may not be obvious or they may be masked by a concurrent or simultaneous event. In particular, the assessment of the glass transition event (Tg), where an amorphous or partially amorphous sample changes from a hard solid to a flexible liquid, can be complicated by the simultaneous occurrence of enthalpic relaxation, stress relief, hysteresis or other factors. It is possible to mistake a glass transition for a melting transition or some other transformation because of the different thermal manifestations that can take place in the regions near Tg.

What is desired is a straightforward means of improving sample characterization or interpretation of DSC results. A valuable new tool in this regard is StepScan DSC as developed by PerkinElmer.

StepScan DSC

StepScan DSC is new software for the enhanced characterization of the thermal properties of materials. The method is straightforward and utilizes the traditional approach for measuring the heat capacity, Cp, for the highest possible reliability of results without interfering experimental problems [1]. 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. StepScan DSC results showing repetitive heat-isothermal hold segments.

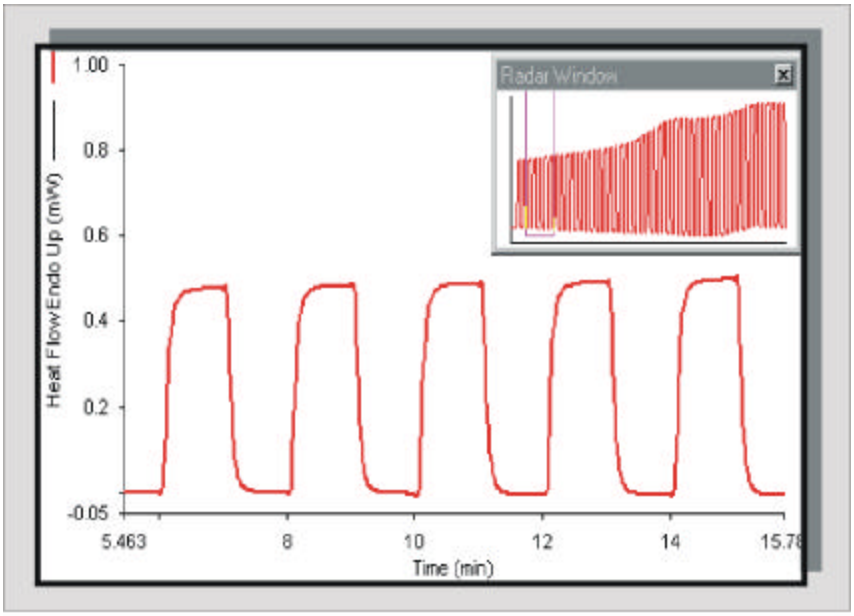

Figure 1 shows the StepScan DSC approach with the application of a repetitive sequence of short heating – isothermal hold segments.

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 Cp*** data set, which reflects 'fast' phenomenon, such as the sample's heat capacity (molecular vibrations) or Tg (molecular rotations). For example, if a sample has a glass transition, Tg, which has an overlapping enthalpic relaxation, moisture loss or crystallization event, the Thermodynamic Cp signal will show the classic, stepwise change in the heat capacity, which 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' processes taking place during the experiment. The enthalpic relaxation event, which can occur on physically aged samples at Tg, 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

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Figure 2. Standard DSC results on pigment sample S2-T.

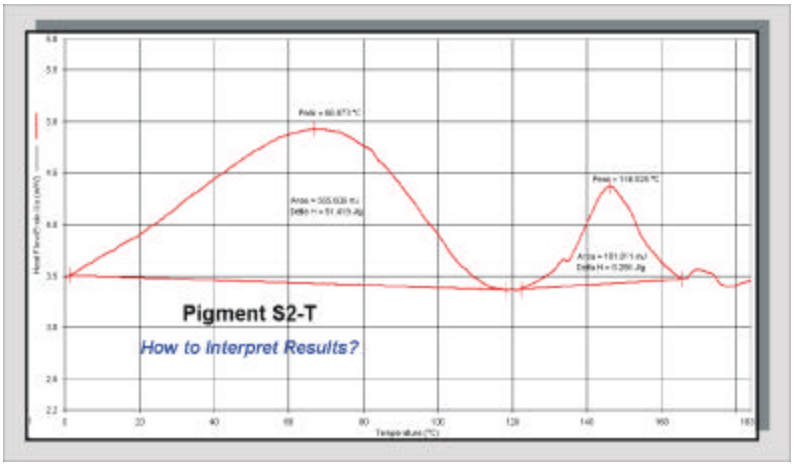
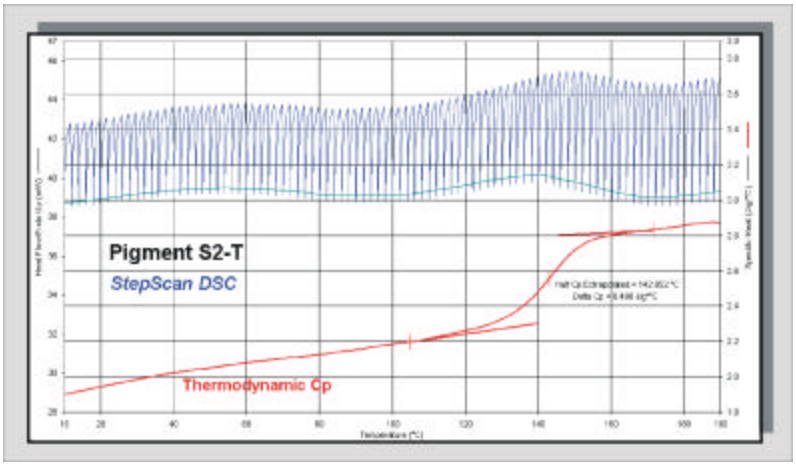


Figure 3. StepScan DSC results on pigment S2-T.



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. The other advantage of the StepScan DSC approach is that it provides a direct heat capacity measurement using the traditional and time-proven means without the need for deconvolution or the extraction of sine wave amplitudes. Other techniques, such as TMDSC (temperature modulated DSC), as applied to a large mass, heat flux furnace, oftentimes have problems due to distorted sine waves and phase lag. Because of the direct nature of the StepScan DSC experimental approach for assessing the thermodynamic heat capacities, the results are not plagued with these experimental difficulties.

DSC Results on Paper Pigments

Displayed in Figure 2 are the DSC generated on a polymeric pigment material (sample S2-T) used to generate letterheads. The sample was analyzed by heating about 11 mg of pigment in a crimped aluminum pan at a rate of 10 C/min.

The pigment material yields two main transitions including a broad endothermic event at about 66 C and a peak at 146 C. The question becomes how to interpret these DSC results for the pigment sample.

The following are reasonable interpretations based on the results presented in Figure 2:

There are two melting transitions at approximately 60 and 146 C

The sample yields volatiles at about 65 C and undergoes melting at 146 C.

The second option seems more likely given the shapes of the DSC curves. A very broad endothermic event near or below 100 C is generally indicative of the loss of volatiles. And the symmetrical shape of the transition at 146 C would seem to be indicative of the melting of the resin. However, it is desired to be more certain of this interpretation, and this can be accomplished with Step Scan DSC.

StepScan DSC Results on Pigments

Pigment S2-T was re-analyzed using the StepScan DSC approach. The following conditions were utilized:

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Figure 4. StepScan DSC results on pigment S2-T showing Thermodynamic Cp and IsoK baseline signals.

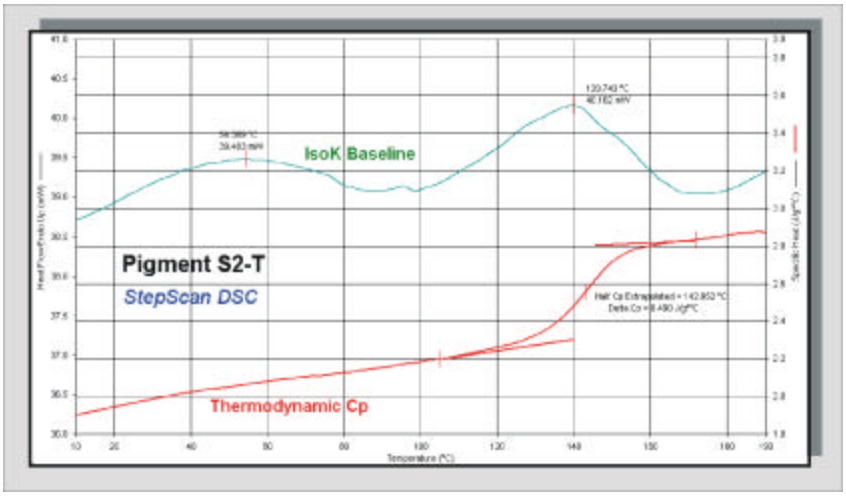
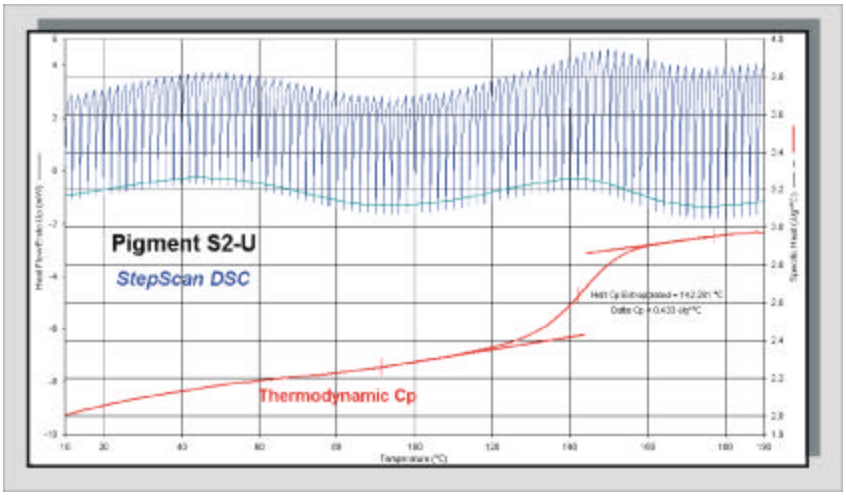


Figure 5. StepScan DSC results on different pigment batch, S2-U.



Instrument:	Power compensated Pyris 1 DSC
Mode of operation:	StepScan DSC
Heating rate between steps:	10 C/min
Isothermal hold step time:	0.4 minute

Temperature increment:	2 C/min
Sample mass:	Approximately 11 mg
Sample pan:	Crimped aluminum pan
Initial temperature:	0 C
Final temperature:	190 C

The StepScan DSC results obtained on pigment S2-T are displayed in Figure 3. In the figure the blue (uppermost) curve is the 'raw' StepScan DSC data, the green curve (center) is the IsoK baseline response (slow) and the red curve (bottom) is that of the Thermodynamic Cp (fast).

The StepScan DSC results obtained show that the pigment is actually an amorphous polymer as is evidenced by the well-defined glass transition event at 142.9 C in the Thermodynamic Cp data set. The Tg is accompanied by a large simultaneous enthalpic relaxation event, which is irreversible in nature and thus is relegated to the IsoK baseline response. This enthalpic relaxation peak dominates the response of the sample near 140 C and is easily mistaken as a melting transition by standard DSC. However, the ability of StepScan DSC to separate out the slow and fast thermal events makes it easily understood that there is actually a Tg with a simultaneous relaxation event. Having this information by StepScan DSC makes the interpretation much clearer and allows for a better understanding of the properties of the resin.

Displayed in Figure 4 are the StepScan DSC results generated on pigment S2-T showing the Thermodynamic Cp and the IsoK baseline responses (without the raw data).

The IsoK baseline response confirms that the transition near 60 C is not a melting event, but is irreversible in nature and most likely is due to the evolution of volatiles from the sample. The sample was weighed after the completion of the DSC experiment, and it was found that the mass had decreased by about 5%, giving credence to the assignment of the peak at 60 C as corresponding to the loss of water or other volatiles. The PerkinElmer TGA could be used to directly measure the mass loss of the sample to absolutely confirm this. The endothermic peak observed in the IsoK baseline signal confirms that the Tg,

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Figure 6. StepScan DSC results on 'good' pigment specimen (R7-N).

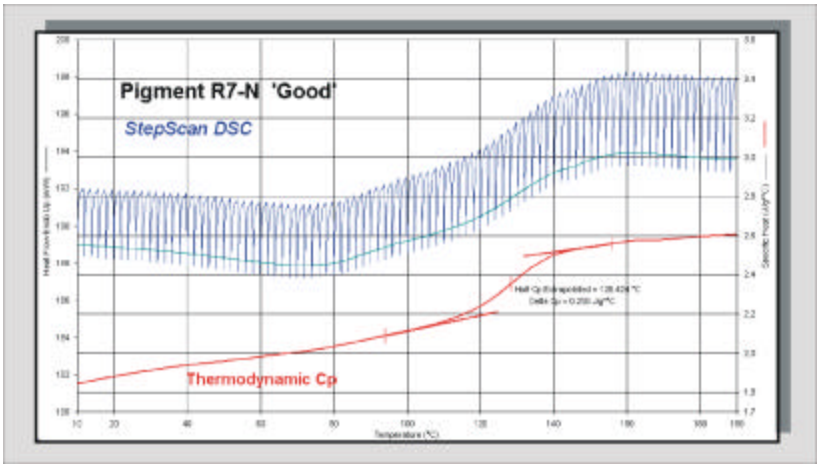
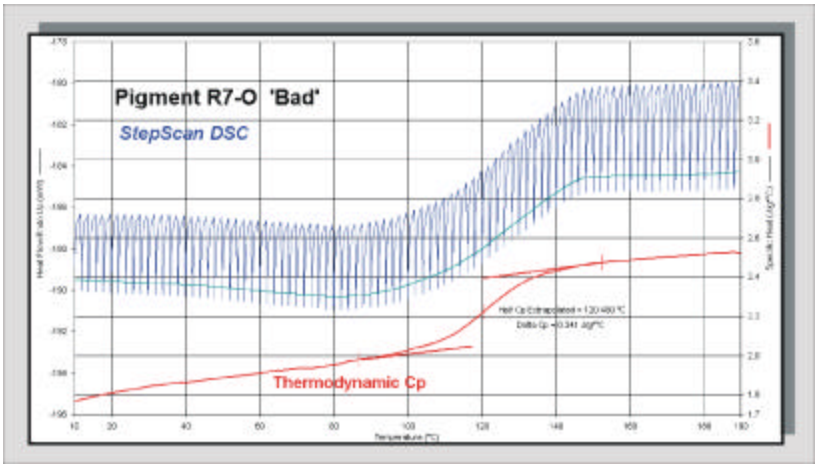


Figure 7. StepScan DSC results on 'bad' pigment specimen (R7-O).



identified in the Thermodynamic Cp signal, is accompanied an irreversible process, most likely enthalpic relaxation. The StepScan DSC results clearly demonstrate that the key properties of the pigment (and its subsequent processibility) are governed by a glass transition event rather than a melting transition. Knowing this tremendously helps for quality assurance and for processing and product uniformity considerations.

As an example, the lab manager at the pigment production facility was concerned that two different batches of the S2 pigment were perhaps significantly different based on the standard DSC results. However, the problem was that the company was interpreting the results incorrectly and was assuming that the pigments underwent melting rather than having a Tg and were basing their conclusions upon the 'melting' peaks and heats. Displayed in Figure 5 are the StepScan DSC results obtained on a different batch of the pigment, S2-U.

These StepScan DSC results show that the Tg of pigment S2-U (142.3 C) is essentially identical to that of pigment S2-T. The glass transition temperature primarily governs the flow of the pigment; and, therefore, pigments S2-T and S2-U are nearly identical. The subsequent processibility of the two pigments showed that this was indeed the case. However, the standard DSC results showed significant differences between the two different batches. But, this was due to inconsequential differences in the enthalpic relaxation events. The StepScan DSC results were far more definitive at providing true processing information for these pigment resins based on the detection of the resin's Tg.

Two different batches of another letterhead pigment (R7-N and R7-O) were analyzed using the StepScan DSC technique. The two batches behaved differently during subsequent processing and one pigment (R7-N) flowed satisfactorily and gave good response while the other (R7-O) had poor flow characteristics, with too much flow, and did not yield satisfactory letterheads. The StepScan DSC results for the good pigment are displayed in Figure 6.

The Thermodynamic Cp signal reveals that this pigment has a well-defined glass transition event at 128.4 C accompanied with a small enthalpic relaxation event.

Displayed in Figure 7 are the StepScan DSC results generated on the poorly performing pigment, R7-O.

These DSC results reveal that this resin has a significant lower Tg (120.5 C) as compared to the other pigment batch with its Tg of 128.4 C. The lower Tg of pigment of batch R7-O is consistent with the fact that this resin had a lower viscosity and exhibits too much flow for satisfactory adherence to the paper in the generation of letterheads. The clear and unambiguous measurement of the resin's Tg makes the interpretation and

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characterization of the pigments much easier. The StepScan DSC data makes it possible to better understand the suitability of the pigments for subsequent processing.

Summary

The characterization by DSC of polymeric materials, including coatings, pigments and inks, can be difficult due to the occurrence of overlapping or simultaneous irreversible phenomenon. The StepScan DSC approach, as developed by PerkinElmer, greatly aids in the interpretation and characterization of coatings, inks and pigments through the separation of 'fast' and 'slow' events, such as Tg (fast) and loss of volatiles, stress relief effects and enthalpic relaxation (slow). The Thermodynamic Cp data set, obtained from StepScan DSC, showed that the properties of the pigments tested were governed not by melting, as was originally believed using standard DSC; but by the glass transition event, Tg. One of the primary benefits of StepScan DSC is its ability to greatly enhance the detection and analysis of glass transition events making the interpretation and analysis much easier.

The StepScan DSC approach is possible with the power compensated Pyris 1 DSC given the fast response time of the instrument. This is in distinct contrast to the TMDSC as applied to the much slower responding heat flux DSC device. The fast response time of the Pyris 1 DSC and StepScan DSC results in significantly shorter experimental times, over a given temperature range, as compared to TMDSC. For many materials, StepScan DSC experiments can be performed 3 times faster as compared to TMDSC.

Reference

[1] R.B. Cassel, The Pittsburgh Conference, 1974.

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