Characterization of Photocopier Toners by DSC for Forensic Applications

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Introduction

Crime laboratories must often work with small samples in order to determine the type of material and its possible manufacturer for investigatory and evidence purposes. An example would be in the analysis of a photocopied document for the identification of the particular type of toner used in the generation of the document. Different toners have different physical properties, which can help in the tracking down of the origin of the document.

Thermal analysis, and in particular differential scanning calorimetry (DSC), is useful for characterizing photocopier toners and this is typically done on the toner itself before photocopying. When a document is photocopied, small amounts of the polymeric toner are attracted to the electrically charged surface of the paper and the toner binds itself to the paper. The level of toner on a photocopied document is low in relationship to the paper substrate. The toner typically comprises only about 10% of the total mass of the photocopied document. It therefore becomes difficult to analyze the toner used on a photocopied document by DSC for its particular thermal characteristics as the paper tends to greatly diminish the heat flow signal from the toner itself. For this application, a DSC instrument with a high level of sensitivity and performance is required.

The PerkinElmer Pyris 1 DSC offers the necessary high performance required for the characterization of photocopied toners as well as for other demanding forensic applications:

- Use of low mass (1 g) individual sample and reference furnaces for rapid response times
- Ability to heat and cool very quickly (500 C/min)
- Ability to achieve isothermal conditions rapidly
- Measurement of true heat flow rather than temperature differential for more accurate calorimetric determinations
- Use of PRT or platinum resistance thermometers, rather than thermocouples, for the most accurate and precise measurement of sample temperature
- Outstanding resolution
- Very high sensitivity for detection of weak or low energy transitions
- StepScan DSC for the separation of 'fast' and 'slow' thermal events (on the time scale of the DSC experiment). This provides for better data interpretation and for a clearer measurement of the glass transition event (Tg).

In this study, two different photocopied documents (labeled as 1 and 2) were analyzed using the Pyris 1 DSC to characterize or 'fingerprint' the thermal properties of the toners used to generate the documents.

Experimental

Small disks were cut from the photocopied documents to get a test specimen containing toner on paper. The total mass of the sample was about 14 mg. In order to make the DSC measurements more sensitive to the properties of the toner, blank paper cut from the document in regions where no toner was present was used for the reference.

The following experimental conditions were utilized to characterize the photocopied documents:

Instrument:	Power compensated DSC
Pans:	Standard crimped aluminum pans
Sample mass:	Approximately 14 mg (total mass of paper with toner)
Reference:	Blank paper (no toner) with mass of approximately 13 mg
Heating rate:	10 C/min
Initial temperature:	25 C
Final temperature:	150 C
Purge gas:	Nitrogen at a flow rate of 25 mL/min

The photocopied document were heated as received (1st heat), then cooled back to 25 C and then reheated (2nd heat). This heat-cool-reheat helps in the interpretation of the results and provides more characterization information as to the nature and identity of the given toner.

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Figure 1. DSC results for first heat of photocopied document 1.

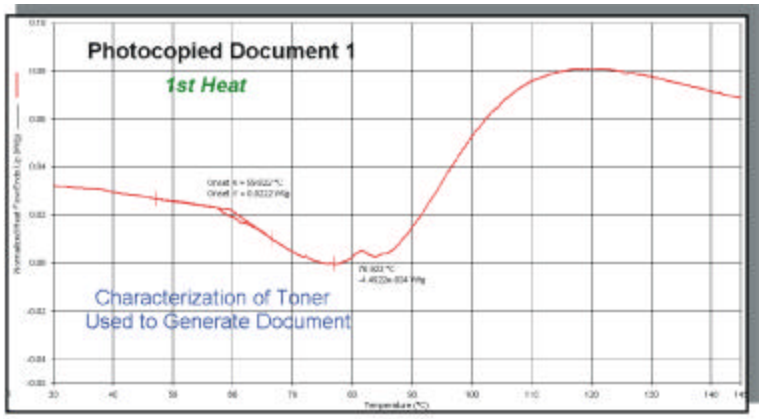


Figure 2. DSC results on second heat for photocopied document 1.

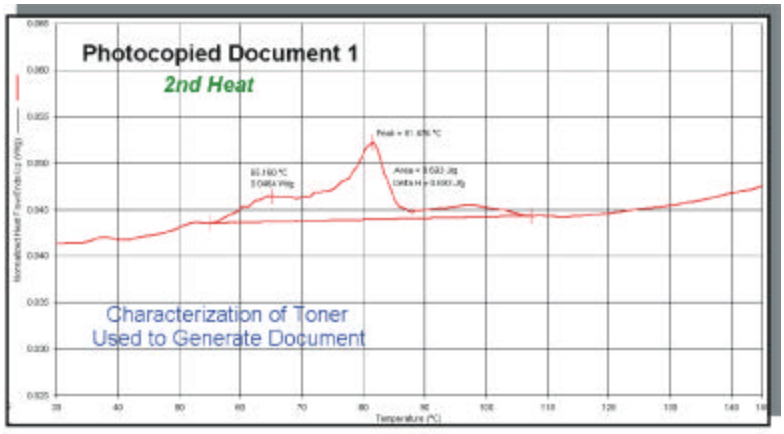
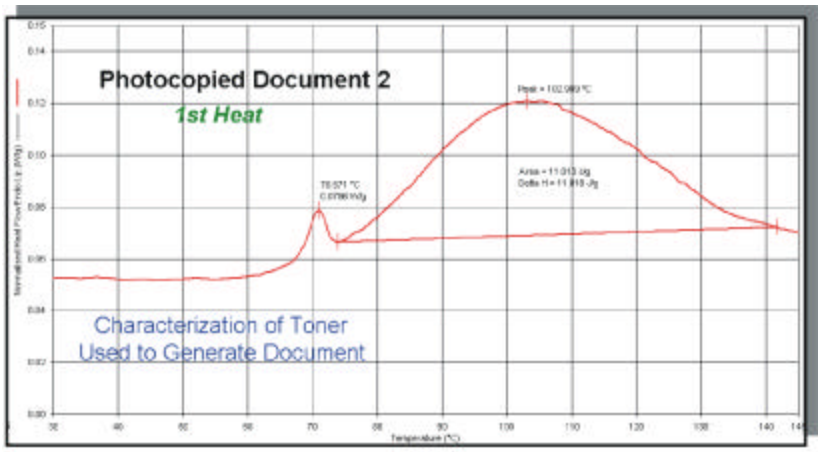


Figure 3. DSC results for first heat of photocopied document 2.



Results

Displayed in Figure 1 are the DSC results obtained during the 1st heating segment on photocopied document 1. The plot shows the DSC normalized heat flow (mW/mg) as a function of the sample temperature and an endothermic response is oriented upward. The results on document 1 shows that the toner undergoes some sort of exothermic transition with an onset temperature of 59.6 C and a peak temperature of 58.8 C.

The sample was cooled back to room temperature and then reheated up to 150 C and these results are displayed in Figure 2. The DSC results during the reheat are clearly different from those obtained during the first heating segment.

The reheat results show that the toner undergoes melting, as reflected by the endothermic response, with peak temperatures of 65.1 and 81.5 C. The total heating of melting is 0.69 J/g . The DSC results obtained during the first and second heating segments for this document help in the identification of the toner used in the generation of the document based on its particular DSC 'signature'.

The second photocopied document (2) was analyzed in the same manner as 1 and the DSC results for the first heating segment are displayed in Figure 3.

Sample 2 yields a small endothermic event at 71.0 C followed by a large endothermic response at 103 C. A comparison of the DSC results in Figures 1 and 3 demonstrates that the two different photocopied documents yield very distinctly different results, due to differences in toners.

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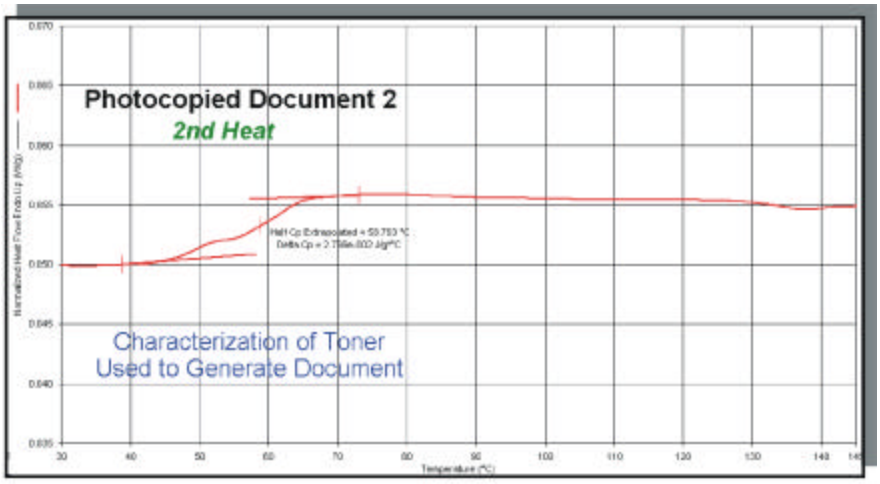
Figure 4. DSC results obtained on second heating of photocopied document 2.



Sample 2 was cooled back to room temperature and reheated to 150 C and these results are displayed in Figure 4.

The toner associated with document 2 now exhibits the characteristics of a glass transition event with Tg occurring at 58.8 C. A comparison of Figure 2 and 4 shows that the two toners yield distinctly DSC characteristics during the second heating segment. The DSC traces are useful and instructive in highlighting distinctions between the two different toners. Clearly, different toners with very different properties were used in the generation of the photocopied documents.

Summary

The PerkinElmer Pyris 1 DSC was used to examine the characteristics of toners used in the generation of photocopied documents. Although the mass of the toner was small relative to that of the paper substrate, the Pyris 1 DSC had the high degree of sensitivity to detect the thermal transitions associated with the toners. Two different photocopied documents were tested and the DSC was able to show clear and unambiguous differences between the two toners. The DSC 'signature' can be used for forensic applications to help identify the toners used in the generation of photocopied documents.

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