High Sensitivity Measurement of Magnetic Coatings Using StepScan DSC

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Introduction

Magnetically coated materials are widely utilized for communications, home entertainment and computer applications, including videotapes, cassette tapes and floppy diskettes. They consist of a thin film of crosslinked polymeric matrix with magnetic particles and binders. This magnetic coating is then adhered to and supported by a thermoplastic substrate, generally polyethylene terephthalate (PET) film. The semi-crystalline nature of the PET substrate provides a stable support medium for the thin magnetic, data storage coating.

The thermal properties of the magnetic coating (e.g., degree of crosslinking, glass transition event, stiffness, brittleness) will have a major effect on the quality of the data storage material and can have a significant impact on its long-term performance. It is desired to be able to measure the Tg of the coating as this parameter is related to the other properties, such as long term performance.

The measurement of the Tg of the magnetic coating by differential scanning calorimetry (DSC) is difficult due to a number of factors:

- The coating is very thin (0.01 to 0.025 mm)
- The properties of the coating are diluted by the presence of the much thicker substrate
- The magnetic particles further dilute or weaken the signal obtained from the coating

What is required is a DSC instrument with high inherent sensitivity to be able to detect the very weak signal from the coating. The Pyris 1 DSC from PerkinElmer Instruments is a high performance DSC featuring the unique power compensation design.

The Pyris 1 DSC offers the following desired characteristics:

- High sensitivity
- Outstanding resolution
- Ability to heat and cooling quickly and linearly (500 C/min)
- Use of PRT (platinum resistance thermometer) for most accurate temperature measurements
- Outstanding temperature response to reach isothermal conditions quickly

In addition, the Pyris 1 DSC offers StepScan DSC, which is a member of the family of modulated temperature DSC techniques (MTDSC).

StepScan DSC

StepScan DSC is new software 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, 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 shows the StepScan DSC approach with the application of a repetitive sequence of short heating – isothermal hold segments.

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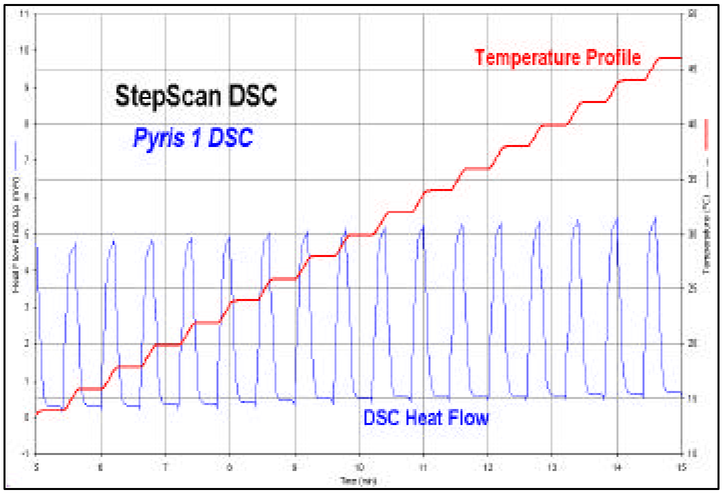

Figure 1. StepScan DSC approach showing time-temperature profile and DSC heat flow results

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' or reversible phenomenon, such as the sample's heat capacity (molecular vibrations) or Tg (molecular rotations). For example, if a sample has a Tg, 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 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 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 MTDSC (modulated temperature 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 Floppy Diskette

A floppy diskette was analyzed using the Pyris 1 DSC to determine if the Tg of the magnetic coating could be directly analyzed.

The magnetically coated film, taken from a Verbatim floppy diskette, was cut into small pieces and then placed into a standard, crimped aluminum DSC pan. The mass of the sample was approximately 18 mg. The as-received floppy diskette sample was analyzed by heating from room temperature to 300 C at a rate of 10 C/min. The DSC results obtained on the as-received floppy diskette are displayed in Figure 2.

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The floppy diskette shows an endothermic peak at 104 C and the main melting peak at 257 C. These two transitions are those of the PET substrate and the peak at 104 C is an enthalpic relaxation peak occurring at the elevated Tg. From the heat of melting, the percent crystallinity of the PET substrate can be assessed, and is found to be 40.6%. From these DSC results, the magnetic coating transition is not observed.

The sample was then quench cooled back to room temperature (using the fast cooling capability of the Pyris 1 DSC) and the sample reheated. The DSC results generated from the quenched cooled diskette sample are displayed in Figure 2. The DSC results now exhibit the characteristics of amorphous PET, with a classic Tg at 79 C, a cold crystallization exothermic peak at 136 C and a melting transition at 256 C. By integrating the combined areas under the cold crystallization and melting peaks, the total heat of initial crystallinity can be obtained. This is found to be 0.06 J/g or 0% for the quench cooled sample. This value is entirely consistent for amorphous PET.

Although the standard DSC approach provides excellent results on the PET substrate associated with the floppy diskette, it does not show the magnetic coating transition. However, with the higher inherent sensitivity of StepScan DSC, it is possible to detect the very weak coating transition.

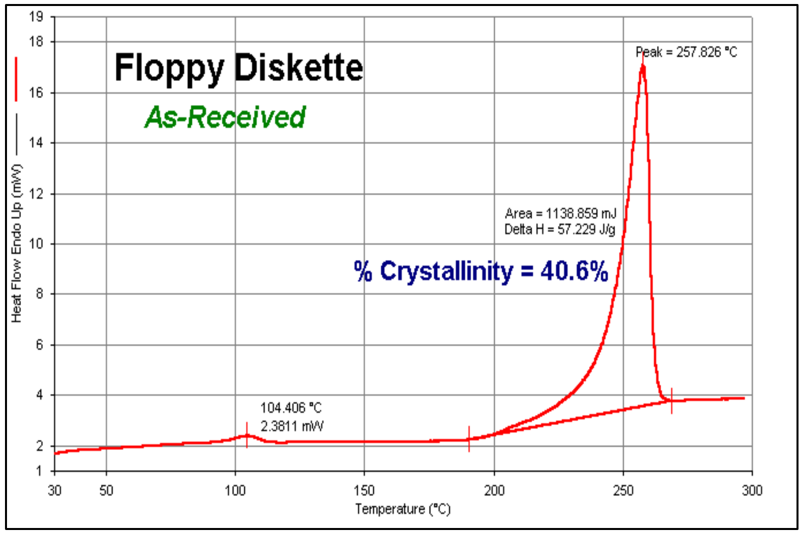

Figure 2. DSC results obtained on as-received floppy diskette.

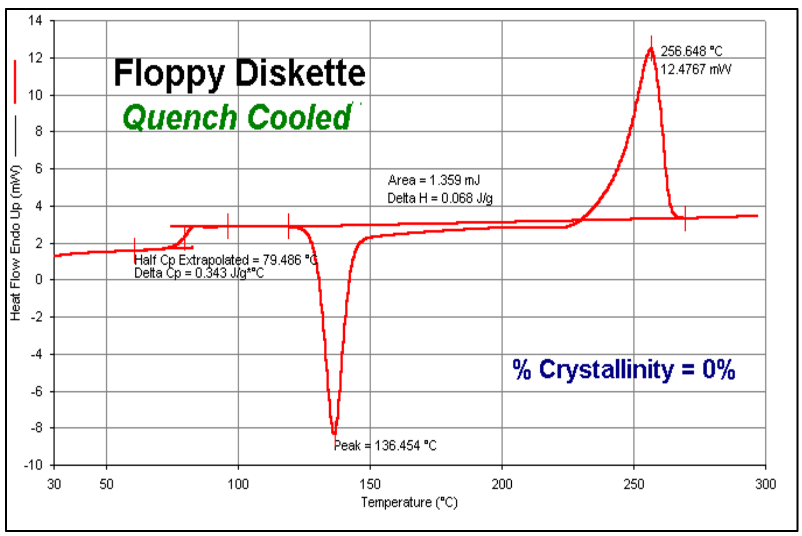

Figure 3. DSC results obtained on quench cooled floppy diskette

StepScan DSC Results on Floppy Diskette

The StepScan DSC approach was used to characterize the floppy diskette and the experimental conditions are listed in the following table.

Experimental Conditions

Instrument	Pyris 1 DSC StepScan DSC
Temperature range	0 to 270 C
Heating rate between steps	10 C/min
Isothermal hold time at step	20 seconds
Temperature increment between steps	2 C
Sample mass	18 mg
Sample pan	Crimped Al pan
Purge gas	Helium

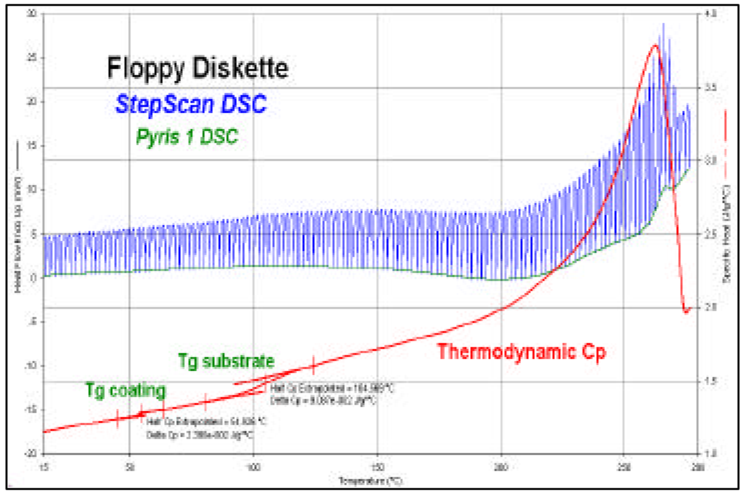

Figure 4. StepScan DSC results on as-received floppy diskette

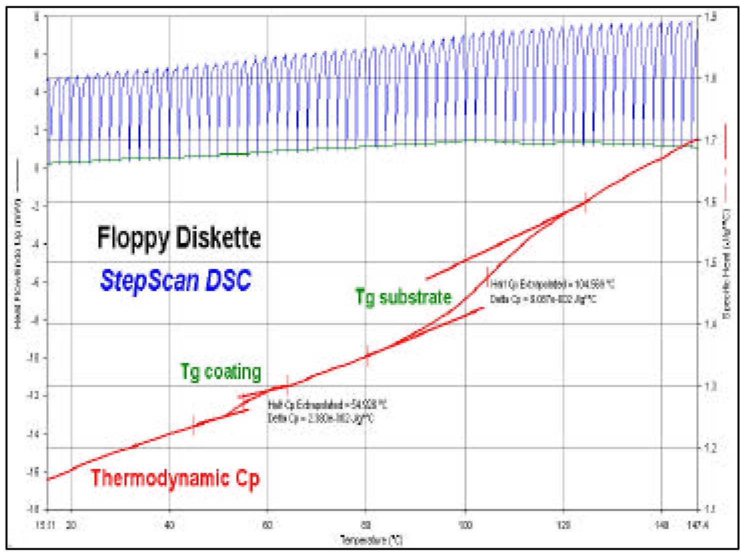

Figure 5. Magnified view of Tg's obtained on floppy diskette

Displayed in Figure 3 are the results generated on the as-received floppy diskette using StepScan DSC. The results show that the StepScan approach yields the Tg's for both the PET substrate at 104 C as well as the crucial magnetic coating Tg at 54 C. The irreversible enthalpic relaxation peak at the PET substrate Tg disappears from the reversible Thermodynamic Cp signal making it much easier to observe the Tg of the PET in its highly crystalline, as received state.

An enlarged view of the glass transition results for the as-received floppy diskette sample is displayed in Figure 4. The two Tg's are evident and are well defined. The main reason that StepScan DSC can detect the very weak Tg of the magnetic coating is that the technique provides an exceptionally flat baseline response. This allows very small changes in ΔCp to be detected.

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The floppy diskette sample was cooled back to 0 C at 200 C/min and then reheated using the StepScan DSC technique. The results on the rapidly cooled sample are displayed in Figure 6. The diskette sample now shows properties consistent with amorphous PET. The Tg of the PET substrate is observed at 82 C and is much more intense than that of the as-received floppy diskette. This change in the properties at Tg reflects the decrease in crystallinity of the PET substrate between the as-received and rapidly cooled diskette. The cold crystallization exotherm of PET appears in the IsoK (irreversible) response. The magnetic coating transition is still evident at 54 C for the rapidly cooled diskette sample.

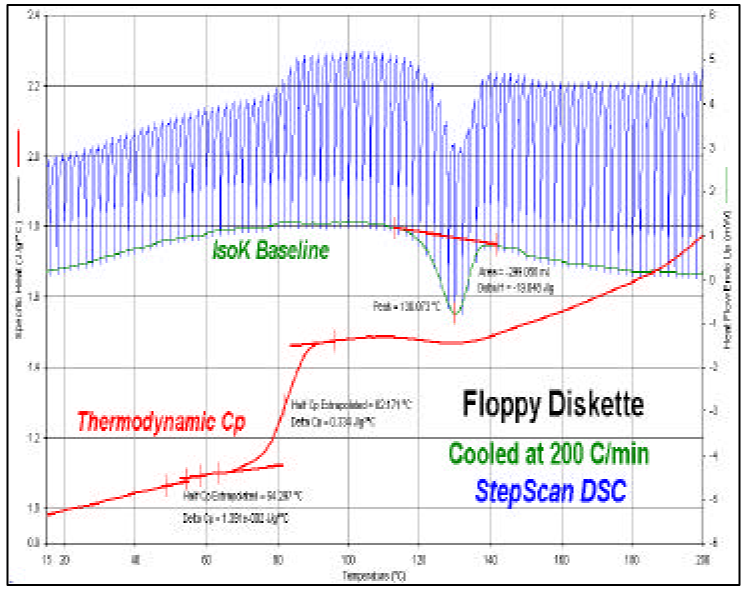

Figure 6. StepScan DSC results on rapidly cooled floppy diskette

Summary

The high performance Pyris 1 DSC provides outstanding results on magnetic coating materials, including floppy diskettes. The use of the new StepScan DSC technique yields enhanced characterization information by separating out the reversible and irreversible thermal events. The StepScan DSC approach yields increased sensitivity, for the detection of the very weak Tg of the magnetic coating, by providing an extremely fast baseline response [2].

The StepScan DSC approach offers several benefits over conventional MTDSC:

- More straightforward in that the sample is either being heated or held under pure isothermal conditions
- No deconvolution or Fourier transform analysis is required
- Faster than MTDSC (approximately 3 times faster) yielding valuable and more comprehensive results in a much shorter time perod
- More sensitive

References

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

[2] W.J. Sichina, *2000 NATAS Conference Proceedings*, Orlando, FL

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