High Sensitivity Characterization of Transparency Films Using High Speed DSC

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Introduction

Differential scanning calorimetry (DSC) is widely used for the characterization of thermophysical properties of materials. This includes the glass transition temperature (Tg), melting points, crystallization temperatures, heat setting temperatures, polymorphic melts and heats of transitions. Samples are generally heated at rates of 10 or 20 C/min when performing DSC experiments. However, the ability of Power Compensation DSC to achieve much faster linear heating and cooling rates permits real-life DSC experiments to be conducted at rates of 50 to 400 C/min. The application of high heating or cooling rates has been presented in the literature by Pijpers and Mathot [1,2] and is known as High Performance DSC or High Speed DSC.

The advantages of the use of high heating or cooling rates for performing DSC experiments are:

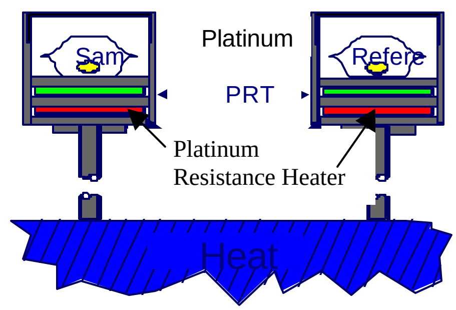
- Significantly higher sensitivity since the DSC sensitivity is proportional to the applied heating rate.
- Faster experimental turnaround times where DSC experiments can be conducted in several minutes using the High Speed DSC approach.
- Better simulation or mimicking of processing conditions experienced by a material during production.

In the latter case, materials may experience ballistic heating conditions (microwave heating or laser heating) and High Speed DSC can better mimic the real-life conditions experienced by the material.

Power Compensation DSC

The use of the High Speed DSC technique requires a DSC instrument with an extremely fast response time and very high resolution. The one DSC that meets the requirements of the High Speed approach is the Power Compensation DSC from PerkinElmer Instruments. Power Compensation DSC uses the Thermal Null principle to apply or remove power from two independently controlled furnaces (sample and reference sides). The Thermal Null approach is true 'temperature zero' where the sample and reference are maintained at the same identical temperature. The Thermal Null feedback system adjusts power to the furnaces to provide this temperature null condition. Power Compensation DSC measures true power or heat flow, Q, rather than a temperature differential via thermocouples.

The Power Compensation DSC employs ultra lightweight furnaces (mass of 1 g) which yields very low thermal inertia and the fastest possible DSC response time. The fast responsiveness of the Power Compensation DSC translates into the ability to obtain very fast linear or controlled heating and cooling ramps (up to 500 C/min). This also provides very high resolution or high definition of DSC transitions.



Power Compensation DSC Cell Design

In marked contrast, most heat flux DSC devices using a single, larger mass furnace, which has higher thermal inertia and provides a much more sluggish DSC response. This yields slower heating and cooling rates and poorer resolution or definition of thermal events. The High Speed DSC approach is not practical or possible using the heat flux DSC instruments.

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In this study, the properties of a transparency film (3M Transparency Film for HP Ink Jet Printers) were characterized using the High Speed DSC approach. Transparency films consist of a thin crosslinked polymeric coating on a PET substrate. The detection of the coating by DSC is very difficult or even impossible due to the nature of the coating and its low mass relative to that of the PET substrate.

Experimental

The following conditions were used to characterize the transparency film

Experimental Conditions

Instrument	Pyris Power Compensation DSC
Technique	High Speed DSC
Heating rate	50 C/min
Temperature range	-20 to 300 C
Sample mass	10 mg
Sample pan	Crimped aluminum pan
Cooling	Intracooler II
Purge gas	Nitrogen

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

Results

One key aspect of performing DSC experiments at fast heating rates is the stability of the DSC baseline. The changes in the baseline response become amplified or more pronounced at the faster heating rates, so a DSC capable of providing stable performance is necessary.

A series of baseline experiments were performed on the Pyris Power Compensation DSC at a heating rate of 50 C/min. Two empty pans were used to better simulate real sample running conditions.

Displayed in Figure 1 are the results obtained for 10 baseline DSC experiments at the very fast heating rate of 50 C/min over a temperature range of –50 to 300 C. As these results demonstrate, the Pyris Power Compensation DSC provides excellent baseline stability which is critical for the application of the High Speed DSC approach.

A 10 mg sample of the transparency film was then loaded into the DSC and heated under High Speed conditions at a rate of 50 C/min between -20 and 300 C. The experiment only took 6 minutes to complete.

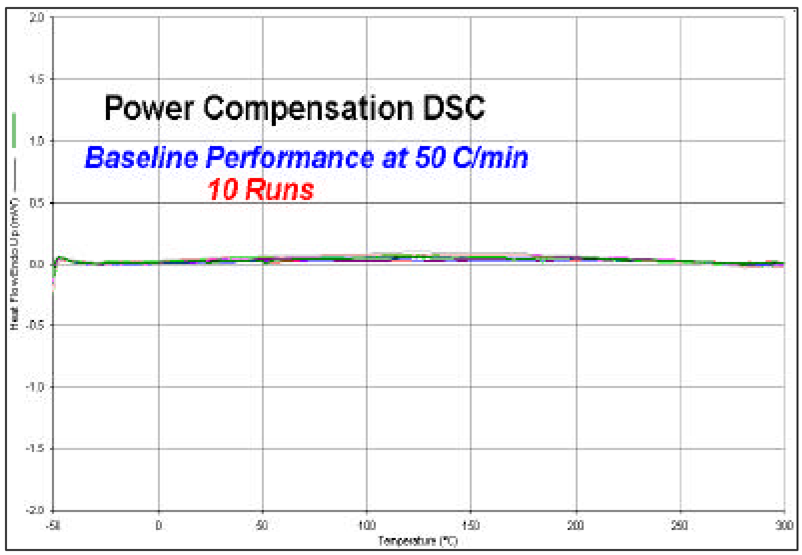

Figure 1. Ten (10) baseline experiments performed on Pyris Power Compensation DSC at a heating rate of 50 C/min

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Displayed in Figure 2 are the High Speed DSC results generated for the 3M transparency film sample. The normally hard to detect Tg of the coating is clearly evident at a temperature of 57 C. The higher inherent sensitivity provided by the High Speed DSC approach makes the detection of the Tg of the very thin, crosslinked coating possible. The Tg of the PET substrate is obtained at 87 C. The Tg of the PET substrate is higher than the usual 75 C and this reflects the high crystallinity and/or orientation of the substrate material used for the transparency application.

A fresh sample of the transparency film was analyzed using the High Speed DSC technique to ensure reproducibility and an overlay of the duplicate experiments obtained on the sample is displayed in Figure 3.

The High Speed DSC approach yields excellent reproducibility as the results shown in Figure 3 demonstrates.

After heating through the melting point of the PET substrate, the film sample was quench cooled to generate an amorphous material. The quench cooled sample was then heated at a rate of 50 C/min using the High Speed DSC approach and these results are presented in Figure 4.

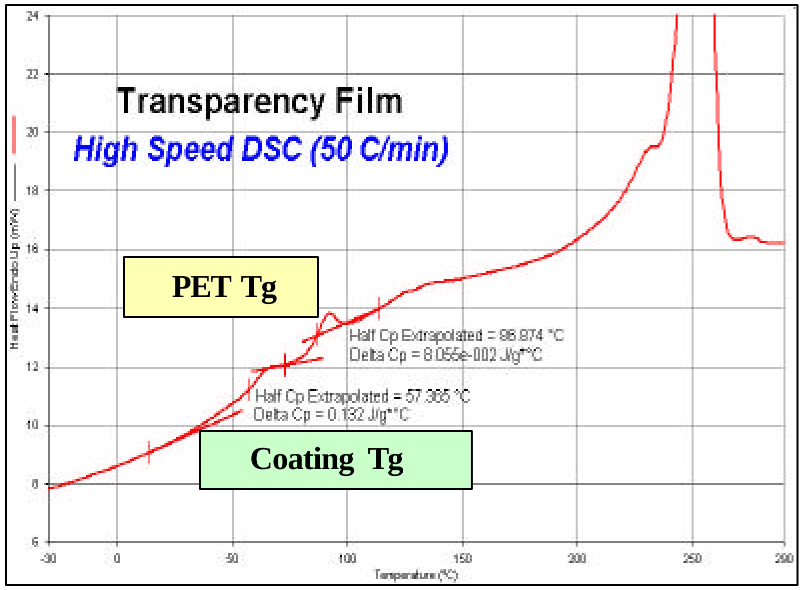

Figure 2. High Speed DSC results obtained on as-received 3M transparency film

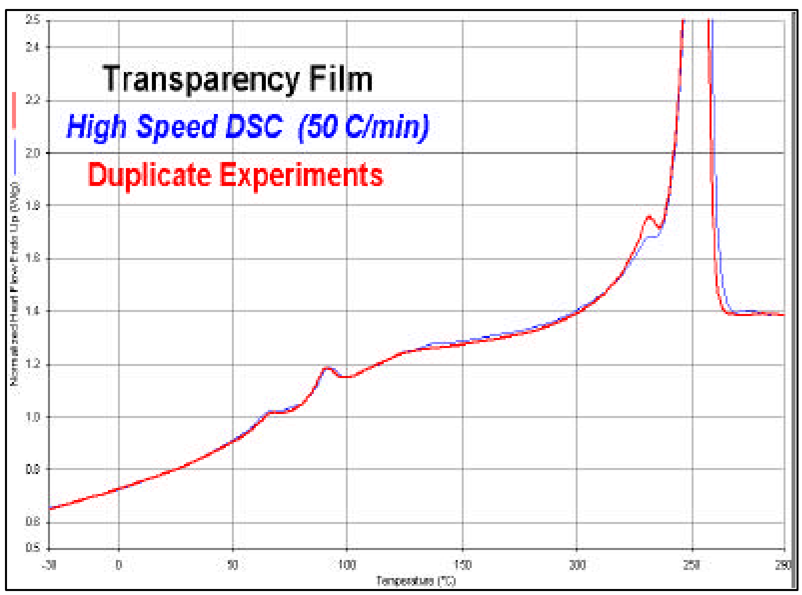

Figure 3. Overlay of duplicate High Speed DSC results generated on transparency film

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The quenched cooled sample exhibits the properties of an amorphous PET material with a pronounced Tg at 75 C, cold crystallization at 135 C and melting (of equal magnitude) at 253 C. Even at the very fast rate of 50 C/min, the Power Compensation DSC provides outstanding peak resolution or definition. The integration of the DSC sample baseline response below and above the melt yields a combined heat of transitions (crystallization and melt) of 0.08 J/g or 0% crystallinity. This is entirely consistent with a completely amorphous sample.

An enlarged or magnified view of the DSC results between 0 and 120 C is displayed in Figure 5. The Tg of the coating of the quench cooled film is still very evident and is now observed at 50 C. The lower of the measured Tg's of the as-received and quench cooled film reflects the differences in the morphologies of the sample as a result of different thermal histories.

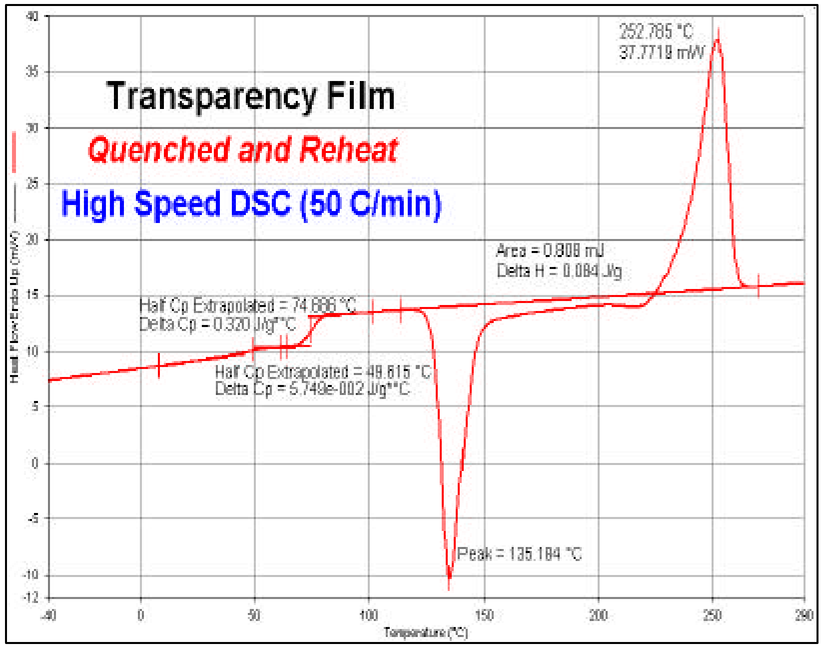

Figure 4. High Speed DSC results obtained on quench cooled transparency film

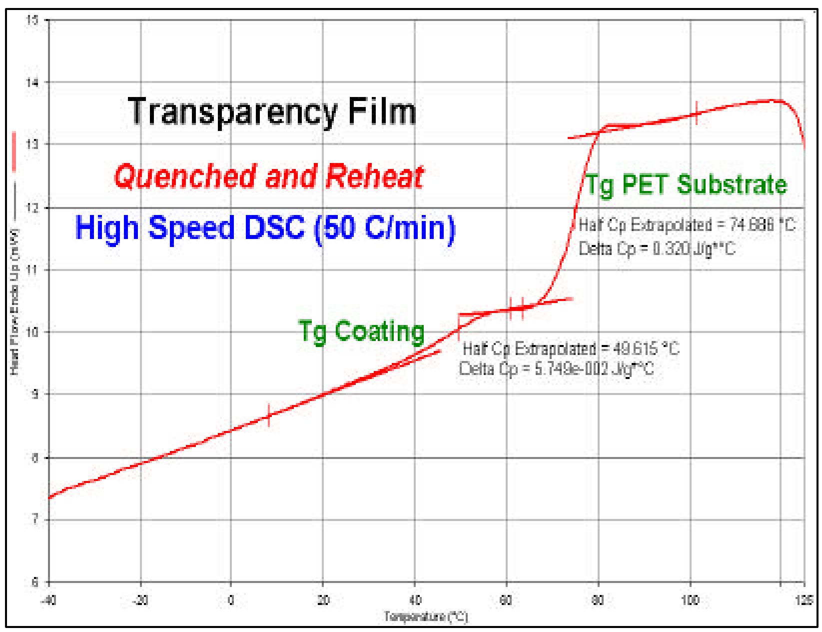

Figure 5. Enlarged view of Tg region obtained via High Speed DSC on quench cooled transparency film

Summary

The PerkinElmer high performance Pyris Power Compensation DSC provides the necessary thermal responsiveness to permit High Speed DSC measurements. This is the application of a linear heating or cooling rate which is much faster (50 to 400 C/min) than normal (10 to 20 C/min). The High Speed DSC approach provides higher real-life sensitivity making it possible to detect transitions which are extremely difficult or 'impossible'. Only the Pyris Power Compensation DSC can perform the High Speed DSC measurements because of its

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use of ultra light weight furnaces which yields fast responsiveness and the best possible resolution or peak definition. The Power Compensation DSC uses the Thermal Null principle to extract the highest quality calorimetric results. The High Speed DSC approach is not possible or practical with heat flux DSC instruments because of their use of a much greater furnace mass.

References

1. T. F.J. Pijpers, V.B.F. Mathot, B. Goderis and E. van der Vegte, The Proceedings of the 28th North American Thermal Analysis Society Conference, Orlando, pp. 32-37, 2000.
2. T.F.J. Pijpers, V. Mathot, B. Cassel, The Proceedings of the 28th North American Thermal Analysis Society Conference, Orlando, pp. 860, 2000.

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