How Tzero™ Technology Improves DSC Performance

Part I: Flat Baselines and Glass Transition Measurements

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Abstract. When a weak glass transition (Tg) is measured by DSC, instrumental baseline effects, e.g., slope, curvature and noise excursions, can adversely affect Tg analysis and assignment of the Tg parameters. By using Tzero™ Technology, the Q series DSC reduces these effects, thus providing the increased DSC sensitivity to detect the Tg.

Background. What should be the appearance of a DSC baseline in the absence of a sample? In an ideal analyzer the baseline would be a flat line of zero milliwatts (the unit of heat flow measured by DSC). Then when a sample is run, the only displacement observed is that due to the thermal characteristics of the sample. If that were the case, there would never be a need to subtract an empty pan baseline.

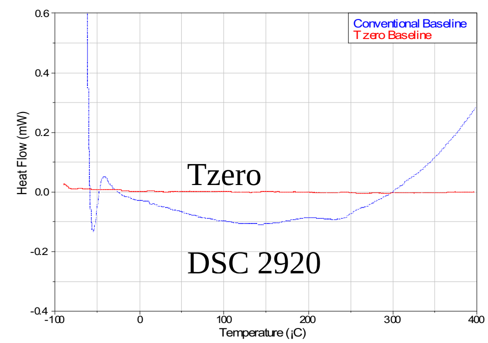
On most DSCs when a baseline is run, one sees a startup hook, offset, slope and curvature. If the baseline is reproducible then one can make duplicate runs, with and without the sample, and subtract the baseline. If these artifacts of the analyzer are *not* perfectly reproducible, then there is no way to be certain that a bump or shift observed when running a sample is due to the sample, or is just a baseline artifact. Unfortunately, these baseline artifacts are inherent in the design and manufacture of DSC instrumentation. They are caused by sample-reference side asymmetry that is not compensated for by the DSC electronics.

INSTRUMENTATION

Tzero™ Technology. TA Instruments has designed a new DSC sensor with a unique internal Tzero™ reference temperature that allows instrumental asymmetry to be detected and compensated in its measuring circuitry (1, 2). With this Tzero™ Technology the minor asymmetries of the DSC sensor, which cause the baseline artifacts, are removed by using a four-term heat flow equation, together with a unique cell calibration. The result is a heat flow signal that faithfully represents the heat flow to or from the sample specimen itself, without the superimposed influence of the instrumental system.

Baseline Performance. An example Tzero™ baseline run under demanding conditions (-80C to 400ºC @20ºC/min using standard purge) is seen in Figure 1. Along with the Tzero™ baseline, the baseline from the 2920 DSC is shown for comparison. Previous to the introduction of the new TA Instruments Q Series DSCs with Tzero™ technology, the TA Instruments 2920 DSC had the best baseline of any commercial DSC. This data dramatically illustrates how flat the baseline is with the new Q Series DSCs. With typical power compensation or heat flux devices, baseline bow can be up to 100 times worse! Tzero™ technology is available with either the Q100 or Q1000 DSC.

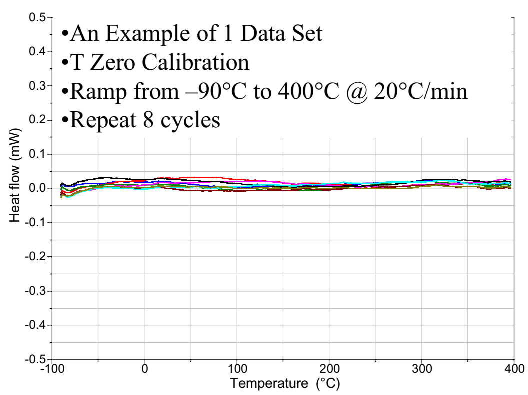
Figure 1. Instrument Baselines Using the 2920 DSC and the Q1000 DSC



Another performance feature illustrated in Figure 1 is the reduction of the "start-up hook" in the Tzero™ baseline. A start-up hook is normally seen at the beginning of a DSC scanning step and is caused by the DSC system coming to equilibrium. The start-up hook determines how far below the transition of interest a user must start. Since the start-up hook is reduced significantly with the Q Series DSCs that utilize Tzero™ technology, more of the low-end range of the DSC/cooling accessory combination can be used.

Figure 2 shows Tzero™ baseline reproducibility. Some manufacturers will emphasize baseline subtraction as a way to compensate for poor baselines. In many cases, these same instruments suffer from non-reproducible baselines that leave curvature and slope even after baseline subtraction.

Figure 2. Tzero Baseline Reproducibility

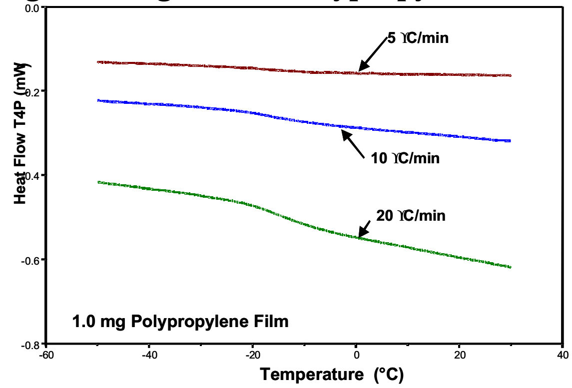


RESULTS

Glass Transition of Polypropylene. Polypropylene (PP) is a commodity thermoplastic used in a wide range of structural and packaging applications. Typically it is crystalline with only a few percent in an amorphous phase. However, this small percent amorphous PP plays an important role in preventing brittle cracking, an adverse end-use property. The amorphous content gives rise to a weak glass transition (Tg) that can sometimes be detected by the change in heat flow at Tg. By measuring the change in heat capacity (ΔCp) at Tg, the amorphous content can be determined. And from measuring the Tg temperature one can determine the temperature below which cracking will occur.

The problem with measuring a weak and broad Tg is that a small change in the position of the Tg constructs can make a large change in the calculated value for Tg and ΔCp. Figure 3 shows the clear Tg measured using the Q1000 DSC. The Tg can be detected and quantified even at the less than optimal heating rate of 5°C/min. The measurement problem for this sample is exacerbated by the small one-milligram sample size. In other instruments the baseline would have sufficient character that there would be substantial uncertainty in the position of the Tg constructs. By changing the slope of one of the constructs, a drift or curvature of only a few microwatts could shift the Tg by several degrees, and introduce considerable error in the ΔCp determination. As demonstrated here with the Q1000, the underlying baseline is sufficiently straight that it is unnecessary to rerun without a sample and subtract the baseline data before performing the calculation. This level of stability is easily achievable with the Q Series DSC, while with most DSCs it would be difficult even to detect the presence of the Tg because of baseline character.

Figure 3. Tg of Thin Polypropylene Film



Tg of a thermoset. Another application area where weak glass transitions are a measurement problem is that of highly cross-linked thermoset composites. These composites are used in the electronics industry and are specifically designed to reduce the coefficient of thermal expansion to better match the low expansion of the metallic conductors. To achieve this end the composites are highly cross-linked and highly filled. The result is a highly constrained matrix with little increase in heat capacity at the glass transition. Because of the difficulty in quantifying (or even detecting) these weak Tgs, this measurement is frequently carried out by dynamic mechanical analysis (DMA), which is more sensitive to Tg. DMA, however, is more time consuming and more operator-intensive than DSC because of the demanding sample mounting requirements. So a substantial time savings and accuracy improvement results if the Tg measurement can be made by DSC.

Figure 4. Tg of a Highly Cross-Linked Composite Using a 2920 DSC and Q100 DSC

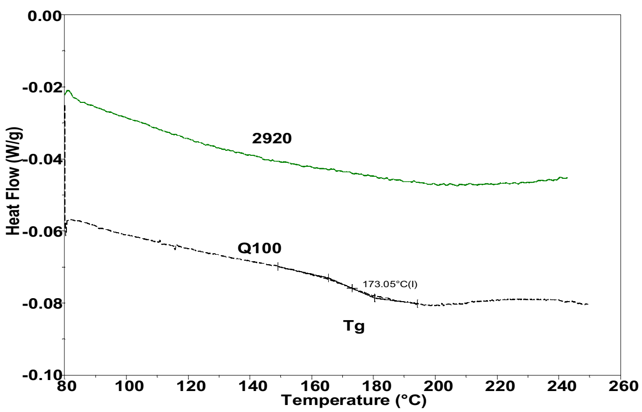


Figure 4 shows just such a sample run identically by the 2920 DSC and by the Q100 DSC, where Tzero™ Technology is used to ensure a flat baseline. While the Tg is marginally visible on the DSC 2920, the baseline curvature makes the assignment of the Tg arbitrary. It is likely that the Q100 and the Q1000 DSCs, which employ Tzero™ Technology, are the only DSCs available that could successfully analyze this weak Tg.

CONCLUSIONS

While glass transitions can be detected by most commercial DSCs, weak Tgs can only be measured *reliably* on a DSC with a *reliably* flat baseline, as ensured by Tzero™ Technology. Moreover, even strong, but broad, transitions can more accurately and reliably be measured using the flat baselines of the Q100 and Q1000 DSC.

REFERENCES

1. R. L. Danley and P. A. Caulfield, “DSC Baseline Improvements Obtained by a New Heat Flow Measurement Technique”, *Proc. 29th Conf. N. Amer. Therm. Anal. Soc.*, (2001).

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