Determining Percent Solid in a Polymer Blend

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ABSTRACT

When a material is melted, the heat flow to the sample produces temperature gradients in the DSC that distort the shape of the melting peak. When this peak is analyzed to determine the extent of melting as a function of temperature, the distortion produces errors in the determination of the partial areas, *i.e.*, the fraction melted and the fraction solid. Traditionally, this has been partially corrected, by post-run calculation software, such as that for the purity determination. Now, this effect has been eliminated at its source with TA Instrument's Advanced Tzero™ Technology. This effect may be demonstrated by improvement of the quality of fractional melt analysis in general, and the Percent Solid Analysis of a polymer blend in particular.

INTRODUCTION

The distortion of peak shapes by restricted heat flow across the thermal gap between the DSC cell and the encapsulated sample is well known (*1*). An earlier paper on Tzero explains how a third thermocouple junction on the Q Series™ DSC sensor is used to enable compensation for temperature gradients that occur in the sensor as a result of heat flow to the sample (*2*). Having this extra Tzero signal permits a more complete, four-term, heat flow equation to be derived and evaluated for the DSC cell heat flow measurement (*3*). With Advanced Tzero™ Technology the recorded heat flow data has removed the effects of heat flow across the thermal resistance between the DSC sensor and pan (*4*). Moreover, with Advanced Tzero, the recorded temperature is a much better indication of the actual sample temperature since thermal lag from the analyzer and pan has been removed (*5*). One place where correcting these errors is particularly important is in the calculation of the fraction melted as a function of temperature. An example of this type of DSC analysis is the calculation of the extent of melting (or Percent Solid) in plastics formulations.

In many thermoplastic formulations the processing characteristics and the end-use properties correlate with the blend ratio of compatible polymers. In other systems the molecular weight distribution or degree of branching is controlled to obtain the proper characteristics. In many of these formulations, DSC is used to obtain the melting profile to help qualify the material. The DSC peak area gives the total melting, and the running integral over this peak indicates the fraction of the material that is melted and the fraction solid, as a function of temperature. Since higher melting material imparts strength, and lower melting material imparts flexibility, the fraction melted at a specific temperature is a useful parameter to predict end-use performance. And since higher melting material crystallizes quicker when cooling during processing, this parameter is also useful for predicting the time required for a thermoplastic to achieve physical strength in the

production process. It is also useful for predicting the sealing temperatures of hot melt adhesives and the highest service temperature for finished product.

EXPERIMENTAL

The example material is a mixed polyolefin recyclate consisting of polyethylene, polypropylene and small amounts of other plastics. The specimen is a whole pellet (14 mg) encapsulated in a standard aluminum DSC pan. The material is evaluated on the second heat after an initial heat through the melting region established good thermal contact between the specimen and the pan. After melting the specimen is cooled at 10 ºC/min to establish a standardized thermal history.

A Q 1000™ DSC with Advanced Tzero Technology is used for the analysis. The use of the Tzero™ thermocouple on the DSC sensor enables the use of the complete four-term heat flow equation (*3*). The four-term heat flow equation explicitly incorporates the secondary effects caused by the asymmetries in the measuring system, including those caused by the sample. This enables the instrumental distortion to the peak shape and the thermal lag to be addressed in the output signals. The result is a more accurate determination of the fraction melted versus temperature.

As a demonstration, the Tzero signal is also used to back-calculate and *remove* all the compensation effects so as to analyze and compare the same data but without the Tzero effect. To demonstrate that the DSC calibration was identical for both these cases the same procedure was applied to a sample of indium using the same conditions as for the polymer (see Figures 1 and 2). Figure 2 shows that the four term heat flow (indicated as "T4P"), addresses the thermal lag resulting in a Percent Solid curve that is much closer to the theoretical result, *i.e.*, pure indium melts at 156.6 ºC within 0.1 ºC—not over a 1.4 ºC temperature range as would be inferred from the conventional DSC trace.

Figure 1 - Indium by Conventional DSC

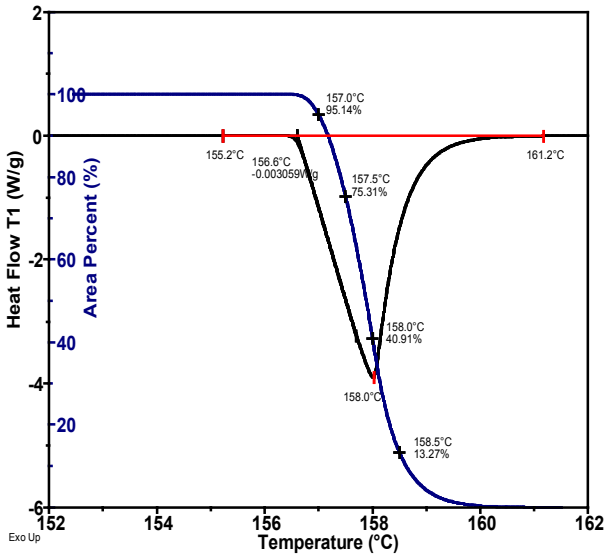
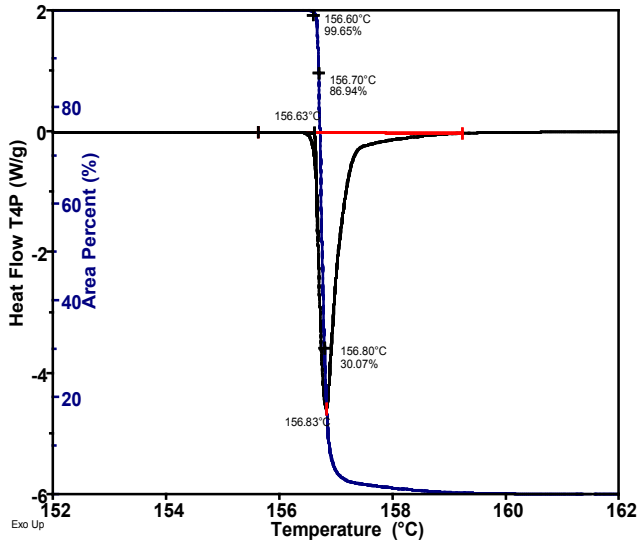
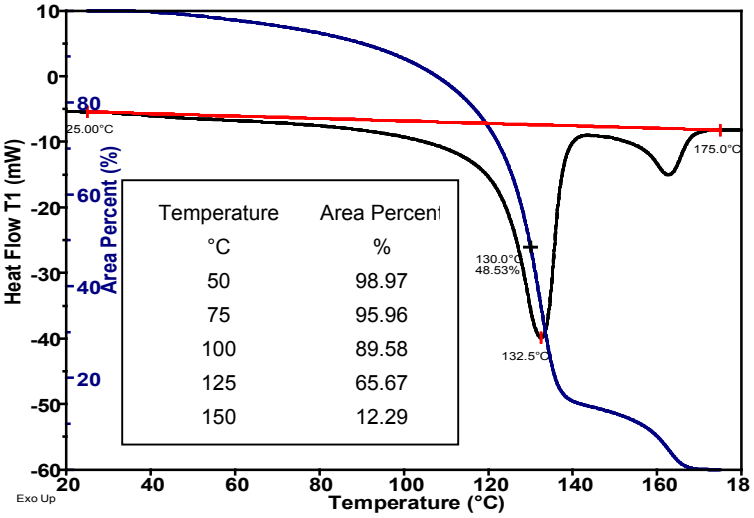


Figure 2 - Indium by Q 1000 DSC with Advanced Tzero Technology



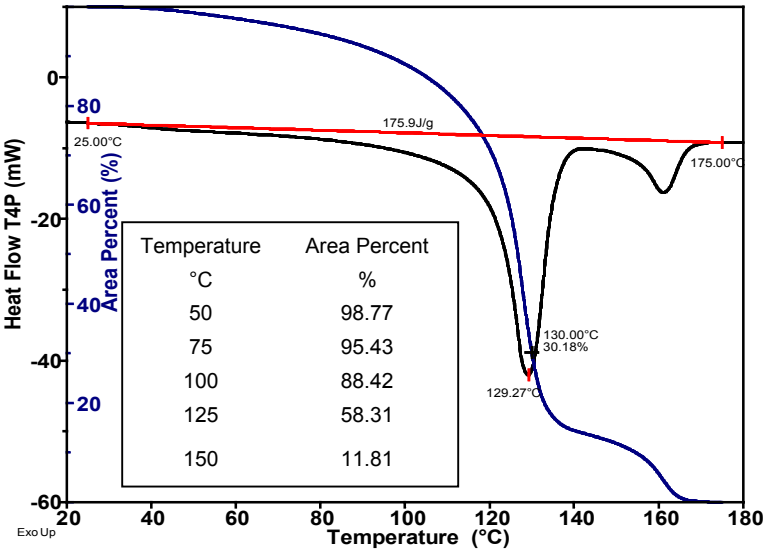
RESULTS

Figure 3 - Percent Solid by Conventional DSC



The results on the polyolefin blend (largely polyethylene) are seen in Figure 3 and 4. The two curves are qualitatively similar. The sloping baseline is due to the increasing specific heat capacity of the sample. The calculation was carried out identically on both data sets. The Area Percent curve is generated in the Universal Analysis software. The table of Percent Solid super-imposed is also generated using the standard software using a "spreadsheet view". From these tables, the differences between the two sets of results are seen. For the conventional DSC the errors in the fraction melted range from less than a percent, up to more than seven percent. The largest errors are from near the peak maximum where the thermal lag is the greatest.

Figure 4 - Percent Solid Using Advanced Tzero DSC



CONCLUSIONS

With a conventional DSC (either power compensation or heat flux types) the heat flow across the thermal resistance between the sample and the sample sensor produces errors in both the heat flow and in the sample temperature signals. Left uncorrected this result in errors in the determination of percent solid at a given temperature. These errors are more serious when using large samples, fast heating rates and/or massive, or poorly coupled, sample pans. The TA Instruments Q 1000 DSC, Advanced Tzero™ Technology addresses these effects without external, after-the-fact data manipulation.

REFERENCES

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KEYWORDS

differential scanning calorimeter, melting, thermoplastic polymers