APPLICATION NOTE

Differential Scanning Calorimetry

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Measurement of Tg of Polypropylene Using the Double-Furnace DSC

Introduction

Polypropylene is one of the most commonly used thermoplastic because of its versatility. The polymer exhibits excellent chemical resistance, low density, high tensile strength and relatively high melting point, especially in comparison to its counterpart, polyethylene. Polypropylene finds widespread use for a variety of applications including fibers, packaging and capacitor films, food containers, home appliances, automotive components, telecommunication cables, injection molded products, and more recently as the recommended material for COVID-19 mask filters.

As with all thermoplastics, it is important to characterize the thermophysical properties of polypropylene, including melting temperature, percent crystallinity, crystallization when cooling from the melt, and the glass transition temperature, Tg. Different grades of the polypropylene will result in different physical properties and for process control and optimization, it is important to characterize the polypropylene material. Additionally, it is essential to analyze the thermophysical properties of the end product for quality assurance purposes.

PerkinElmer Double Furnace (Power Compensation) DSC 8500

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For the Better

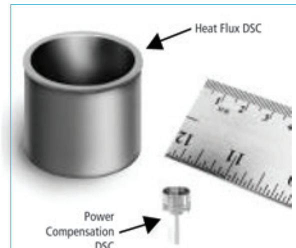
Thermal analysis provides an ideal means of characterizing the properties of polymers, including polypropylene. Differential Scanning Calorimetry (DSC) is a particularly useful technique for the characterization of polypropylene.

The measurement of the glass transition event, Tg, of polypropylene is generally considered difficult by DSC given that the transition is weak. However, a DSC with high sensitivity and flat and reproducible baseline is able to detect the weak Tg associated with polypropylene. The high performance Double Furnace (Power Compensation) DSC 8500 from PerkinElmer® can readily detect the Tg of polypropylene.

Power Compensation DSC

The double-furnace DSC uses the exclusive Power Compensation approach which applies or removes power (or energy) to two independently controlled furnaces (sample and reference). While other, more conventional DSC instruments, employ the heat flux DSC approach (single, high mass furnace), the Power Compensation DSC uses two very lightweight furnaces with a mass of only 1 g. This provides exceptionally nimble performance in terms of rapid equilibration and the ability to heat and cool at ultra fast rates (up to 750 ˚C/min).

In contrast, some of the heat flux DSC devices employ a large, high mass silver block (150 g), which then yields a sluggish response by virtue of its high thermal inertia. The physical difference in masses between the heat flux and Power Compensation DSC furnaces is displayed in the following figure.



The Power Compensation DSC uses new technology which combines ultra fast reponsiveness with high stability.

This provides the highest performance of any DSC on the market.

In this study, the physical properties of polypropylene were studied using the Double Furnace Power Compensation DSC.

Experimental

The following conditions were utilized to characterize a sample of polypropylene (high density, isotactic polypropylene film).

Experimental Conditions	
Instrument	Power Compensation DSC
Heating rate	20 ˚C/min
Sample mass	Approximately 10 mg
Sample pan	Crimped standard aluminum pan
Purge gas	Nitrogen
Cooling system	Intracooler II
Temperature range	-50 to 200 °C

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

The baseline response of the Power Compensation DSC was highly linear, such that no baseline subtractions were necessary.

Results

Displayed in Figure 1 are the DSC results generated on the as-received polypropylene film sample. The polymer exhibits a number of melting transitions (due to processing and thermal history factors). The main melting peak is observed at 168 ˚C with other processing-induced peaks occurring at 163 and 78 ˚C. The heat of melting is found to be 107.0 J/g for the as-received film sample. The rate of heating is a very important characteristic of thermoplastics as it is related to the percent crystallinity of the material. The heat of melting can be used to determine the percent crystallinity using the following simple relationship.

$$\%\ \text{Xtal} = (\Delta Hm/\Delta Hm°) \cdot 100\%$$

In this expression, ΔHm is the measured heat of melting by DSC and $\Delta Hm°$ is the reference value for the heat of melting. For polypropylene, this reference value is 207 J/g. This yields an estimated percent crystallinity of 51.7% for the as-received polypropylene film.

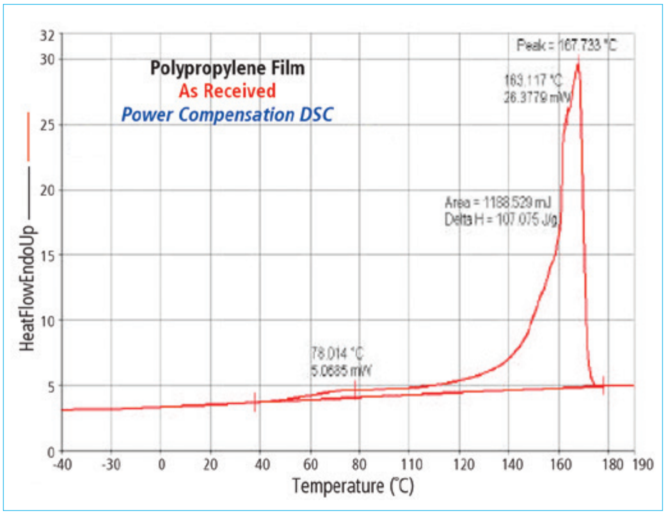


Figure 1: DSC results on as received polypropylene film sample showing multiple melting peaks.

The as-received polypropylene film also has a glass transition event, Tg. Although this is very weak, due to the highly crystalline and oriented nature of the film sample, the Power Compensation DSC has the necessary high degree of sensitivity to be able to detect the Tg. This may be seen in Figure 2, which is an enlarged view of the heat flow response in the regions below the main melting transition.

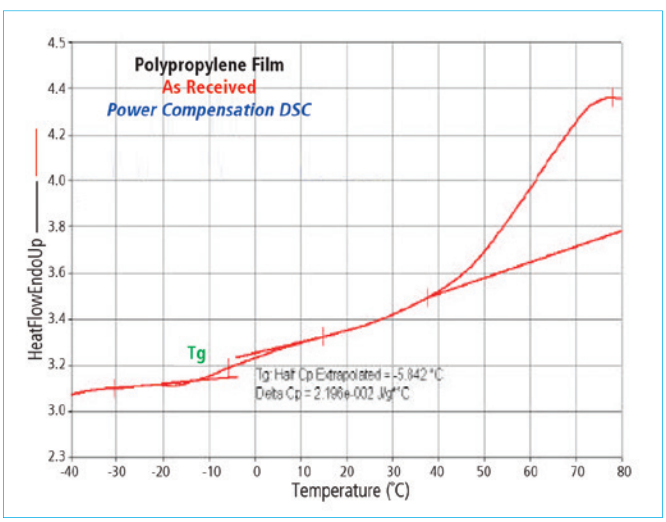


Figure 2: Enlarged view of Tg of as received polypropylene film sample.

The Tg of the as-received, oriented film is observed at -6 ˚C as a small, stepwise change in the heat flow response. Although this Tg is exceedingly weak, the Power Compensation DSC has the very high degree of sensitivity that permits its detection.

The polypropylene sample was cooled back to -50 ˚C and reheated at a rate of 20 ˚C/min to demonstrate the effects of thermal history. Shown in Figure 3 is an overlay of the DSC results from four (4) reheat experiments performed on the polypropylene material over the complete temperature interval. These results demonstrate the outstanding reproducibility of the Power Compensation DSC instrument as the different data sets are virtually indistinguishable.

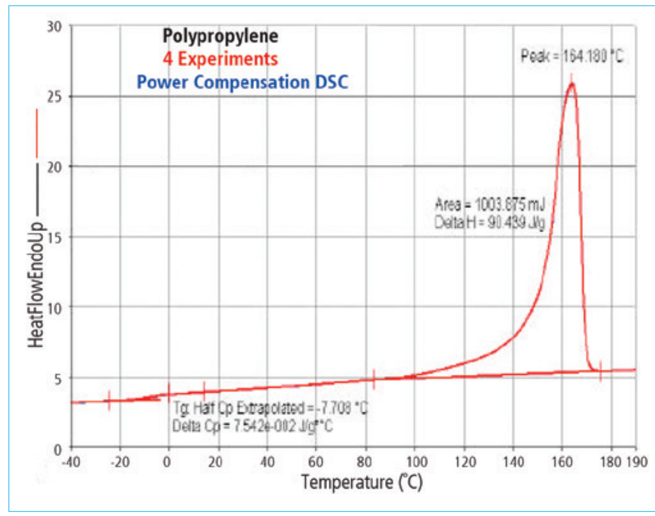


Figure 3: Overlay of four (4) reheat experiments performed on polypropylene sample.

After the polypropylene film specimen is melted, cooled and reheated, only a single melting peak is obtained at 164.2 ˚C. The heating of melting is 90.5 J/g, which yields a percent crystallinity of 43.7%. This is significantly less than the crystallinity value of the as-received film sample, which is attributable to the differences in thermal histories. The Tg of the reheat polypropylene sample is observed at -7.7 ˚C and is more readily observable as compared to the original, as-received film sample.

The high quality results obtained for the Tg of the polypropylene sample may be seen in Figure 4. The figure shows an overlay of the Tg results generated for the four separate experiments on the reheat polypropylene sample. The data is all the more remarkable considering that it was generated *without* the need for baseline subtraction. This demonstrates the very high performance level of the Power Compensation DSC. Although the detection of the Tg of polypropylene by DSC is normally considered difficult, the Power Compensation DSC is readily able to handle this particular measurement.

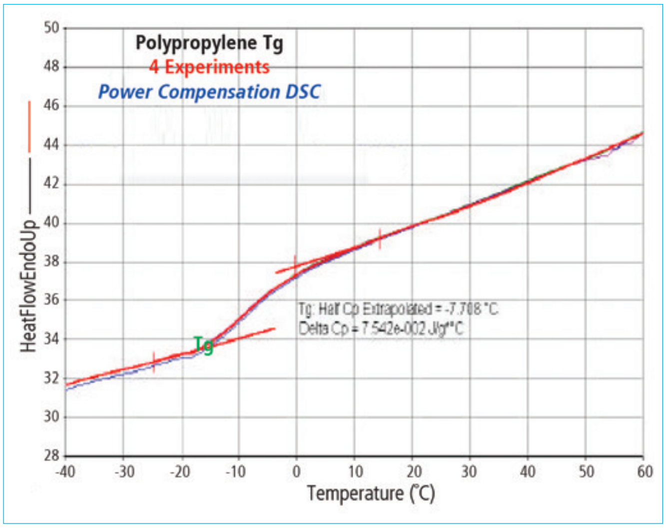


Figure 4: Reproducibility of Tg of reheat polypropylene sample showing overlay of four (4) DSC experiments.

The differences in the thermophysical properties between the as-received and reheat polypropylene samples may be seen in Figure 5. These results are a direct overlay of the two different sets of DSC data. These overlay type of data presentations are highly useful for comparative purposes. It may be seen that the given thermal history has a major effect upon the thermal characteristics of the polypropylene material. The high resolution response of the Power Compensation DSC makes these differences evident.

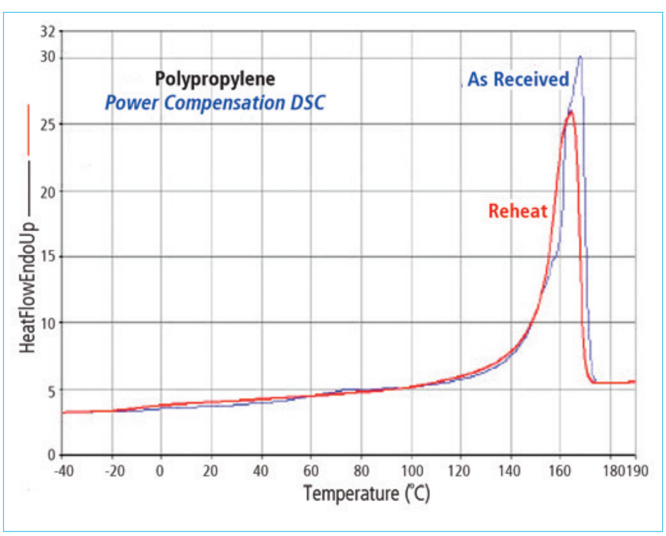


Figure 5: Overlay of DSC results for as received polypropylene film and melt-cool-reheat sample.

Summary

The Power Compensation DSC provides an ultra high level of performance. This is exemplified by the results generated on a polypropylene film sample. The Power Compensation DSC is able to detect the weak Tg of the melt-cooled resin as well as the very weak Tg of the highly crystalline and oriented film sample. The outstanding calorimetric response of the Power Compensation DSC yields outstanding reproducibility for both the melting as well as the Tg of the polypropylene material. The Power Compensation DSC provides the highest research-grade performance of any DSC on the market.

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