Determination of Polymer Crystallinity by DSC

Roger L. Blaine, Ph.D.
TA Instruments, 109 Lukens Drive, New Castle DE 19720, USA

ABSTACT

Perhaps no fundamental property affects the physical properties of a polymer in so general a way as the degree of crystallinity. Differential scanning calorimetry (DSC) provides a rapid method for determining polymer crystallinity based on the heat required to melt the polymer.

INTRODUCTION

An understanding of the degree of crystallinity for a polymer is important as crystallinity affects physical properties such as storage modulus, permeability, density and melting temperature. While most of these manifestations of crystallinity can be determined, a direct measure of degree of crystallinity provides a fundamental property from which these other physical properties can be predicted.

DSC is a technique that measures heat flow into or out of a material as a function of time or temperature. Polymer crystallinity can be determined with DSC by quantifying the heat associated with melting (fusion) of the polymer. This heat is reported as Percent Crystallinity by normalizing the observed heat of fusion to that of a 100 % crystalline sample of the same polymer. As authentic samples of 100 % crystalline polymer are rare, literature values are often used for this value (*1,2*).

EXPERIMENTAL

In DSC, the sample contained in a metal pan and the reference (usually an empty pan) sit on raised platforms on the sensors. As heat is transferred through the sensor, the differential heat flow to the sample and reference is monitored by area thermocouples. A thermocouple monitors sample temperature. A preheated purge gas is present to provide additional baseline stability as well as the desired sample/atmosphere interaction.

In this study, samples of polyethylene are analyzed over the temperature range from ambient to 180 °C. A heating rate of 10 °C/min was used with a nitrogen atmosphere around the sample. Since the previous thermal history of a polymer affects the measured degree of crystallinity, these samples are evaluated both “as received” and after being subjected to a common “thermal treatment” designed to impart equivalent thermal history to all three samples. This thermal treatment consists of cooling the sample from 180 °C at 5 °C/min.

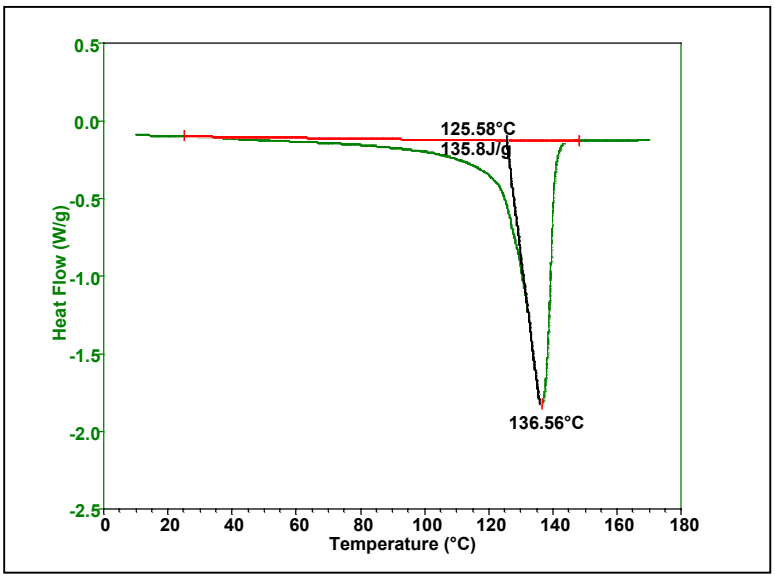

Figure 1 – "As Received" Polyethylene Sample

RESULTS

Figure 1 shows the melting endotherm for one of the polyethylene samples during the initial "as received" heating. Universal Analysis software is used to calculate Percent Crystallinity based upon 293 J/g for the 100 % crystalline material (*2*). The results for the three samples studied are summarized in Table 1.

Table 1 – "As Received" DSC Characterization of Polyethylene Samples

Sample	Melt Onset Temperature (°C)	Melt Peak Temperature (°C)	Enthalpy (J/g)	Crystallinity (%)
1	125.6	136.6	135.6	46.3
2	125.6	136.9	133.7	45.6
3	123.1	133.4	120.8	41.7

These results clearly indicate that samples 1 and 2 are identical in terms of crystallinity and melting profile, suggesting that these two polymers were previously subjected to the identical processing conditions (thermal history). Sample 3, on the other hand, has a sharper melt and lower crystallinity indicating different processing conditions and different end-use properties.

After "thermal treatment", the three polymers exhibit different crystallinities than initially obtained. These results are shown in Table 2

Table 2 – DSC Characterization of Polyethylene Samples after a Common Thermal History

Sample	Melt Onset Temperature (°C)	Melt Peak Temperature (°C)	Enthalpy (J/g)	Crystallinity (%)
1	124.9	135.7	121.4	41.4
2	124.7	134.5	128.1	43.7
3	124.6	134.8	122.6	41.8
mean	124.7	135.0	124.0	42.8
std. dev.	0.15	0.60	3.6	1.2

The results reflect elimination of earlier processing thermal history effects. It is reasonable to assume that all of these polymers would now have similar final properties. By subjecting polymer samples to different "thermal treatments" in the DSC prior to the crystallinity determinations, much may be learned about optimizing processing conditions.

SUMMARY

DSC may quickly and easily be used to determine the degree of crystallinity of thermoplastic polymers through the measurement of the enthalpy of fusion and its normalization to the enthalpy of fusion of 100 % crystalline polymer. Precision is typically a few percent.

REFERENCE

1. B. Wunderlich, *Thermal Analysis*, Academic Press, **1990**, pp. 417-431.
2. TN 48, "Polymer Heats of Fusion", TA Instruments, New Castle, DE

KEYWORDS

differential scanning calorimetry, melting, polyolefins, thermoplastic polymers