TA Instruments

Thermal Analysis & Rheology

THERMAL SOLUTIONS

DETERMINATION OF INITIAL CRYSTALLINITY BY MODULATED DSC™

PROBLEM

Manufacturers of crystalline and semi-crystalline polymers need to have a method for quickly determining the percent crystallinity of their polymers after processing. Differential scanning calorimetry (DSC) has been widely used for this purpose based on quantifying the heat of melting. (1) However, it has long been recognized that DSC only measures the sum of all thermal events occurring in the polymer during heating. Hence, if overlapping transitions such as crystallization and melting are occurring, these individual transitions may not be seen and accurately assessed. An example of this limitation is seen in the conventional DSC data shown in Figure 1. This figure shows the heating of a sample of polyethylene terephthalate (PET) after it has been quench cooled from the melt to approximately -100°C in a few seconds. Three transitions are observed. The glass transition at about 75°C indicates the presence of some amorphous structure. It is followed by crystallization at 126°C where a fraction of this amorphous material crystallizes. Finally, at 239°C the onset of the crystalline melt occurs. Comparison of the enthalpies associated with crystallization and melting indicates that some crystalline structure is initially present after quench cooling, specifically 50.77-36.59=14.18 J/g. However, this conclusion does not agree with wide and small angle x-ray diffraction studies which show no crystalline content (2).

SOLUTION

Modulated DSC is a new technique which subjects a material to a linear heating method which has a superimposed sinusoidal temperature oscillation (modulation) resulting in a cyclic heating profile. Deconvolution of the resultant heat flow profile during this cyclic heating provides not only the "total" heat flow obtained from conventional DSC, but also separates that "total" heat flow into its heat capacity-related (reversing) and kinetic (non-reversing) components. Thus, modulated DSC provides all the same benefits as conventional DSC plus several unique benefits including:

- *Separation of complex transitions into more easily interpreted components*
- *Increased sensitivity for detection of weak transitions*
- *Increased resolution of transitions without loss in sensitivity*

Figure 1. QUENCHED PET (CONVENTIONAL DSC)

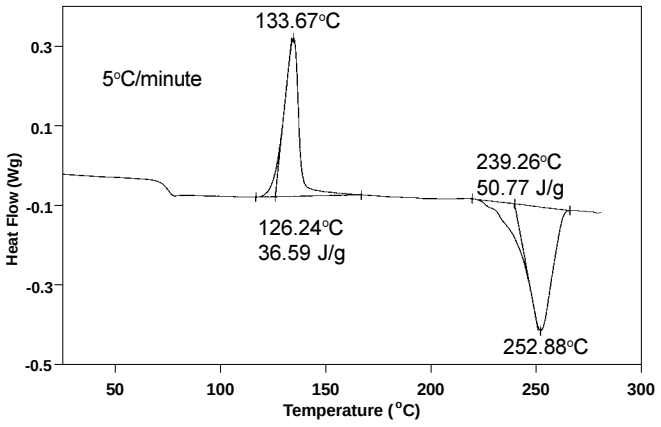
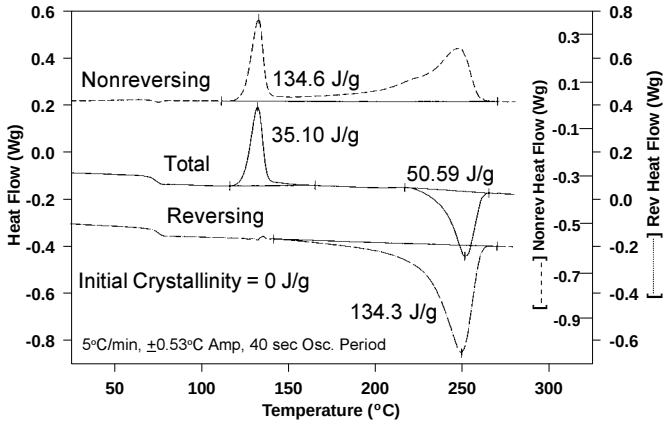


Figure 2. QUENCHED PET (MDSC™)



- *Measurement of heat capacity & heat flow from a single experiment*
- *Determination of thermal conductivity*
- *Determination of the true initial crystallinity of polymers*

The modulated DSC™ results for the same quenched PET evaluated in Figure 1 are shown in Figure 2. The modulated DSC total heat flow, which is equivalent to conventional DSC, shows the same information as seen in Figure 1. The reversing and nonreversing signals, however, show that over the temperature range of 100 - 270°C there is actually more (134 J/g) exothermic ordering/crystallization (nonreversing behavior) and more (134 J/g) endothermic melting (reversing behavior) than seen in the total heat flow. The sum of these two signals is 0 J/g, which represents the actual initial crystallinity of the sample.

To reconfirm that modulated DSC is measuring the initial crystallinity, another sample of PET was cooled at 40°C/minute from the melt. Figure 3 shows the resultant cooling curve which indicates that 48 J/g of crystallinity is developed under these conditions. Figure 4 shows the modulated DSC results for this sample on reheating. Since crystallization occurs during cooling, no cold crystallization exotherm is observed. Furthermore, both the melting total heat flow and the sum of the modulated DSC exothermic nonreversing and endothermic reversing signals agree well with this "known" crystallinity.

REFERENCES

1. TA Instruments Brief TA-123.
2. E. Turi and A. Siegmann, J. Macromol. Sci.-Phy., B10(4), 689-708 (1974).

Figure 3. PET COOLING CURVE

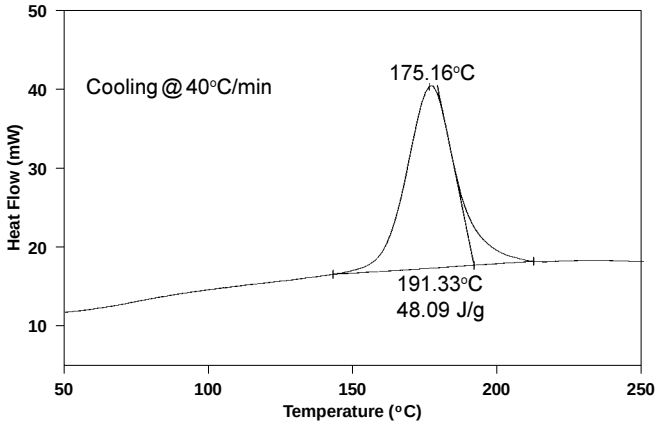
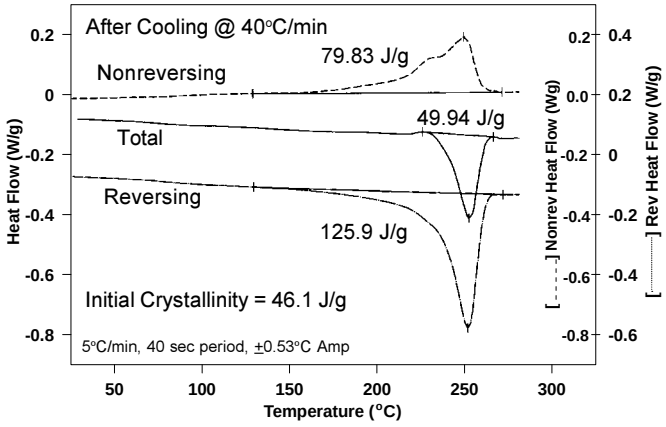


Figure 4. SLOW COOLED PET (MDSC™)



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