TA Instruments

Thermal Analysis & Rheology

THERMAL SOLUTIONS

DETECTING CRYSTALLINITY DIFFERENCES IN ENGINEERING THERMOPLASTICS

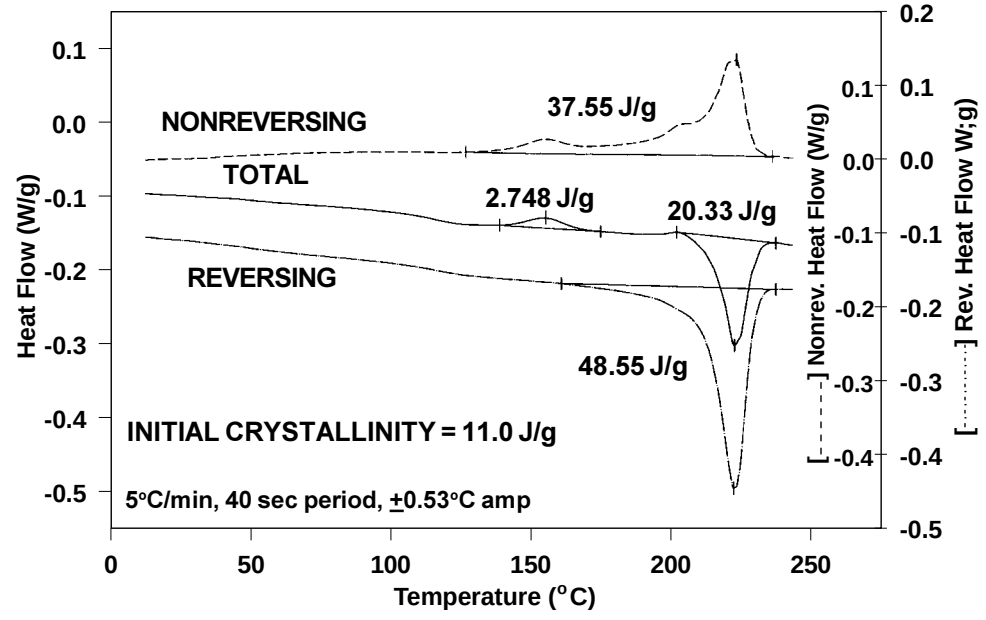
PROBLEM

In the manufacture of molded plastic parts, the crystallinity of the polymer achieved during processing often determines the final performance of the part. This crystallinity is in turn determined by the temperature of the mold and the rate of cooling as the molten polymer fills the mold. Suppliers of injection molded parts often find that the desired end-use performance (eg. toughness) of molded parts are not uniform across the part which implies that their mold temperature is not uniform. Conventional differential scanning calorimetry (DSC) evaluation of sections of these molded parts, which are expected to be more or less crystalline based on their relative position in the mold, however, does not show differences in crystallinity. Hence, it appears that another more sensitive technique is needed to detect the expected differences in crystallinity.

SOLUTION

Conventional DSC is a technique which measures the heat flow into and out of a material as a function of temperature. DSC is widely used to measure the crystallinity in polymers based on quantification of the heat associated with the melting peak. (1) Nevertheless, since polymers are known to change (anneal and develop crystalline structure) as they are heated, the suitability of conventional DSC for quantitatively determining the amount of initial (as received) crystallinity in a polymer has been questioned. Conventional DSC is suspect because it can only measure the sum of all thermal events and can not independently measure the amount of crystalline structure that is forming during heating. The thermoplastic evaluated here is an example of that limitation.

Figure 1. QUENCHED THERMOPLASTIC - INITIAL CRYSTALLINITY BY MDSC™



On the other hand, 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 (nonreversing) 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 the loss of sensitivity*
- *Measurement of heat capacity & heat flow changes from a single experiment*
- *Determination of thermal conductivity*
- *Determination of the true initial crystallinity of polymers*

The modulated DSC results for a typical engineering thermoplastic are shown in Figures 1-5. These curves represent:

Figure 1 The thermoplastic after quench cooling from the melt at a rate which is faster than the rate expected during the normal injection molding process. This "standard" sample should represent the lowest level of crystallinity achievable in processing this polymer.

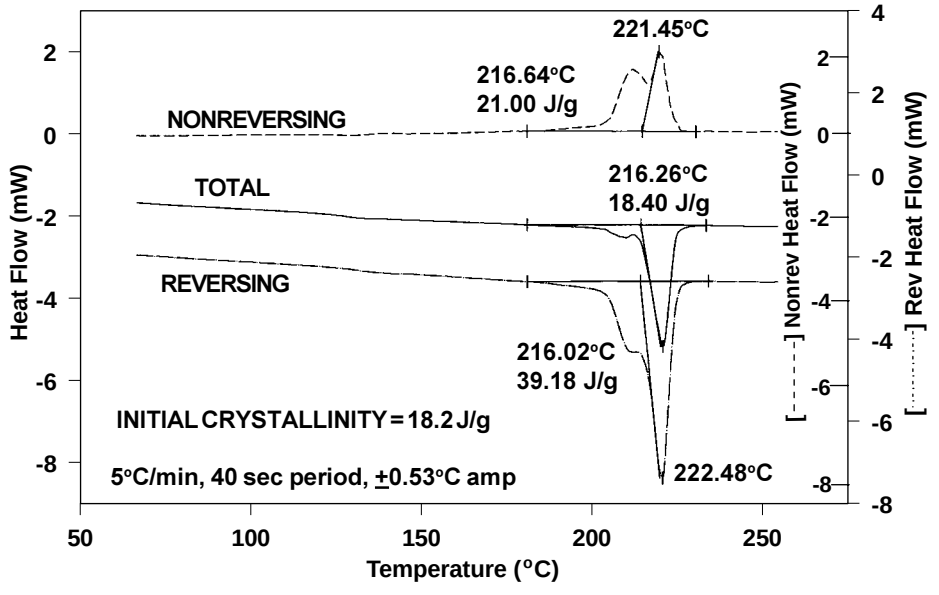
Figure 2 The thermoplastic after controlled cooling at 5°C/minute from the melt. This rate is sufficiently slow to impart the highest level of crystallinity achievable during processing of this polymer.

Figure 3 This is the cooling curve for the polymer at 5°C/minute.

Figure 4 The thermoplastic from an actual process run. This sample represents the material at the portion of the mold furtherest from the point of injection.

Figure 5 The thermoplastic from an actual process run. This sample represents the material nearest the point of injection.

Figure 2. SLOW COOLED THERMOPLASTIC - INITIAL CRYSTALLINITY BY MDSC™



Several key conclusions can be reached from these results:

(1) The MDSC™ total heat flow curves (which are equivalent to conventional DSC results) do not indicate substantial differences in the ΔH of crystallinity between the samples even though the cooling rates used to prepare them are very different. In fact, the slow cooled sample shows the lowest crystallinity (18 versus 20 J/g), which is a theoretically impossible result. The reason for this obvious anomaly is that all of the other samples have exothermic crystallization occurring prior to the melt. Since conventional DSC can not separate the total heat flow into its exothermic (crystallization) and endothermic (melting) components, it is not possible therefore to obtain an accurate melt onset and subsequent quantitation.

(2) The MDSC results, on the other hand, show differences in ΔH which agree with the expected trends. MDSC makes this measurement by summing the nonreversing (exothermic crystallization and ordering) and reversing (endothermic melting) ΔH signals. The greater the initial crystallinity, the larger the reversing signal compared to the nonreversing signal. The sum of these ΔH's for the quench cooled sample is 11.0 J/g compared to 18.2 J/g for the slow cooled sample. The latter value of 18.2 J/g agrees almost exactly with the known crystallinity of 18.5 J/g which is measured as the material is slowly cooled (Figure 3).

(3) The two real-world materials, which come from different locations in a molded part, also show consistent results when compared to each other or to the specially prepared "standard" samples. The sample from the far end of the mold has a ΔH of 13.7 J/g compared to 15.0 J/g for the sample close to the injection point in the mold. The injection point is expected to be the warmest point in the mold , and hence should cause the slowest cooling and the highest resultant crystallinity.

Another benefit of MDSC illustrated by these figures is its ability to see the presence of any multiple "crystallization" processes involved in the sample as it is heated. For example, it appears that at least three processes are present in this material. More work needs to be done before these are understood.

Figure 3. THERMOPLASTIC COOLING CURVE

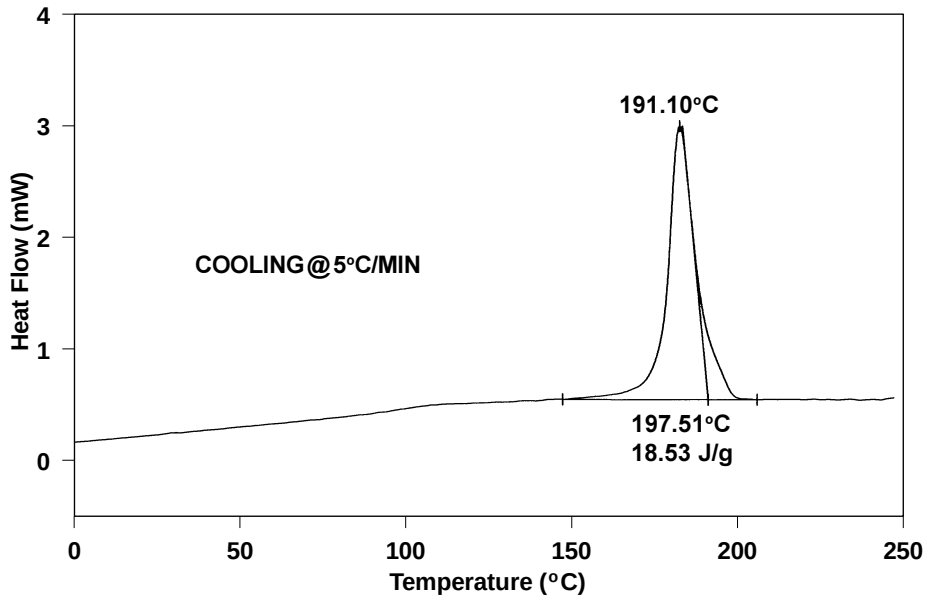


Figure 4. THERMOPLASTIC FROM FAR SIDE OF MOLD - INITIAL CRYSTALLINITY BY MDSC™

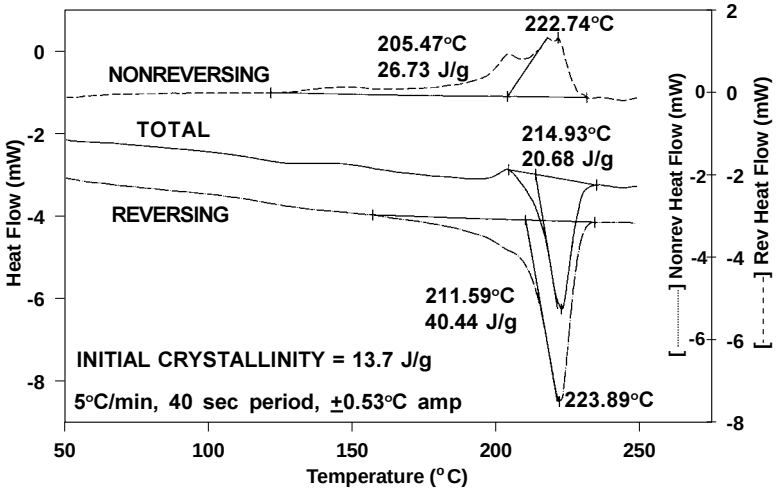
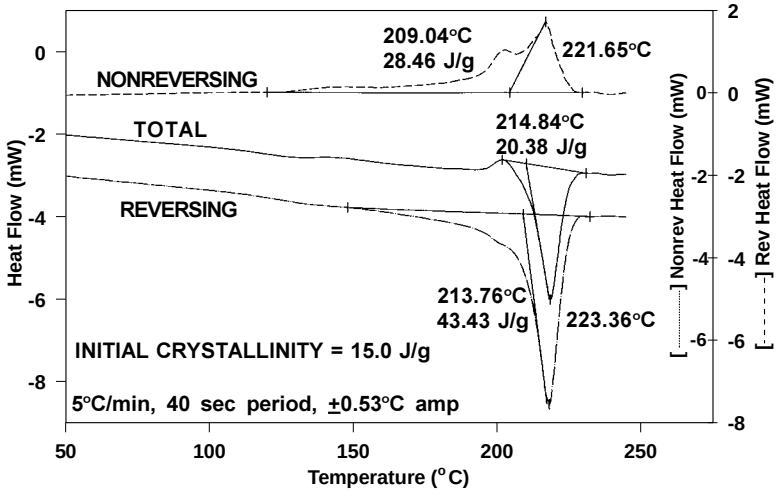


Figure 5. THERMOPLASTIC FROM NEAR INJECTION POINT - INITIAL CRYSTALLINITY BY MDSC



REFERENCES

1. TA Instruments Applications Brief TA-123.

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