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Thermal Analysis & Rheology



**CHARACTERIZATION OF MELTING PHENOMENA IN
LINEAR LOW DENSITY POLYETHYLENE BY
MODULATED DSC™**

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INTRODUCTION

Modulated DSC (MDSC™) is an analytical 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. The equation which describes heat flow in modulated DSC is:

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(T, t)$$

(TOTAL) (REVERSING) (NONREVERSING)

where:

$$\frac{dQ}{dt} = \text{total heat flow}$$

$$C_p = \text{heat capacity}$$

$$\frac{dT}{dt} = \text{heating rate}$$

$$f(T, t) = \text{heat flow dependent on absolute temperature and time}$$

Because of this ability to separate “total” heat flow into its components, modulated DSC provides unique new insights into polymer melting and related phenomena, including:

- separation of simultaneous crystallization and melting processes
- more accurate measurement of the temperature range of melting
- increased precision of heat capacity measurements
- more accurate measurement of the initial crystallinity of polymers

This paper, which describes evaluation of a linear low density polyethylene, illustrates these unique capabilities of modulated DSC.

EXPERIMENTAL

The results described here were obtained using a TA Instruments DSC 2920 with modulated DSC option and a Refrigerated Cooling System (RCS). Experimental conditions included:

Sample Size: 10 mg (nominal) in crimped aluminum pans; sample cut to ensure a flat side for good sample/pan contact

Purge: Helium at 25 mL/minute

Calibration:

- The heat of fusion was calibrated with Indium to 28.4 J/g
- Temperature was calibrated based on the melt onset of indium at 156.6°C
- Heat capacity was calibrated with low density polyethylene to 2.57 J/g°C at 150°C (above melt) using “quasi-isothermal” MDSC with a (±0.239°C) amplitude and a 60 second period.

MDSC parameters (optimized for analyzing the melting region):

- Modulation Period

A period between 40 to 100 seconds should be selected when using helium as a purge gas, and 60 to 100 seconds with a nitrogen purge. If an accurate value of heat capacity is also desired from the measurement, values greater than the minimums are recommended. Since 4-5 modulation cycles are desired at half-height of the sharpest melting peak, the longer the period, the slower the average underlying heating rate that is required. A 60 second period was chosen in this study.

- Underlying Heating Rate

A heating rate which provides a minimum of 4-5 cycles at the half-height of the sharpest melting peak should be selected. 1.5°C/minute was selected in this study.

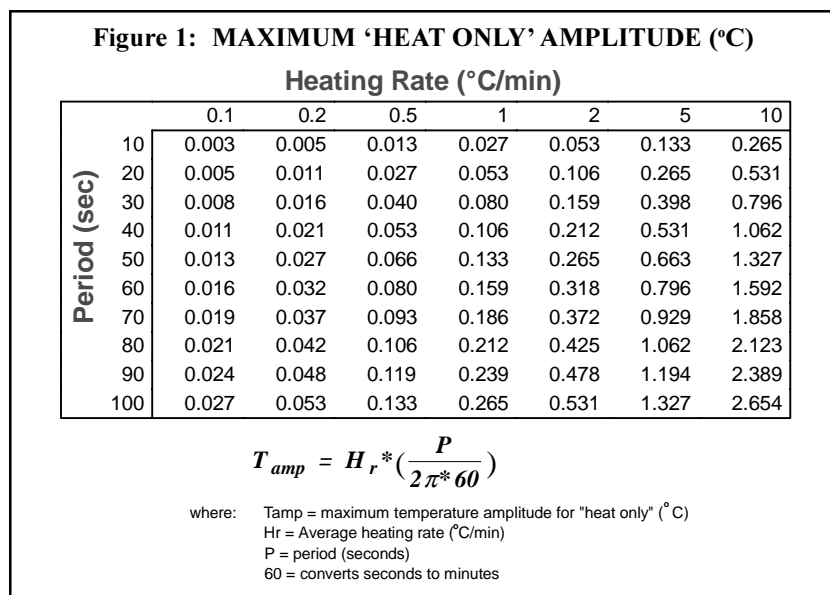
- Modulation Amplitude

An amplitude which provides cyclic heating only (no cooling) and causes the heating rate to periodically go to 0°C/min should be selected. This is done with the use of the table shown in Figure 1. The table is linear and, therefore, the desired amplitude for a 1.5°C/min heating rate with 60 second period is the sum of the value at 0.5°C/minute and 1°C/minute (0.08 + 0.159 = ±0.239°C). The primary reason for having the heating rate periodically go to 0°C/min is to periodically eliminate the contribution of heat capacity to the heat flow signal. When the heating rate ($\frac{dT}{dt}$) goes to zero, the heat capacity contribution to the total heat flow signal also goes to zero (see previous equation) and this permits continuous, time-dependent processes such as crystal perfection or crystallization to be observed in the raw, modulated heat flow signal. The heat flow at the lowest heating rate is seen along the top of the modulated heat flow signal. Hence, the top of the modulated heat flow signal should have the same shape as the Nonreversing signal, which is the calculated MDSC signal for time-dependent processes.

Thermal History:

Preliminary experiments indicated that the melting behavior in the polyethylene studied is affected by thermal history. Therefore, results were obtained from both an initial “as received” run and a second heating run after cooling at a known rate from the melt. The actual sequence was:

- Cool the “as received” polymer to -30°C at 5°C/minute and equilibrate for 5 minutes
- Heat at 1.5°C/minute to 160°C in MDSC mode and equilibrate for 5 minutes
- Cool at 5°C/minute to -30°C in conventional DSC mode and equilibrate for 5 minutes
- Heat a second time at 1.5°C/minute to 160°C in MDSC mode

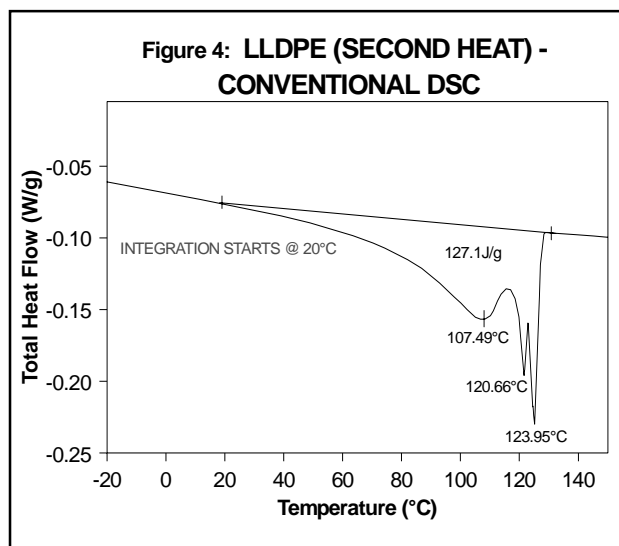
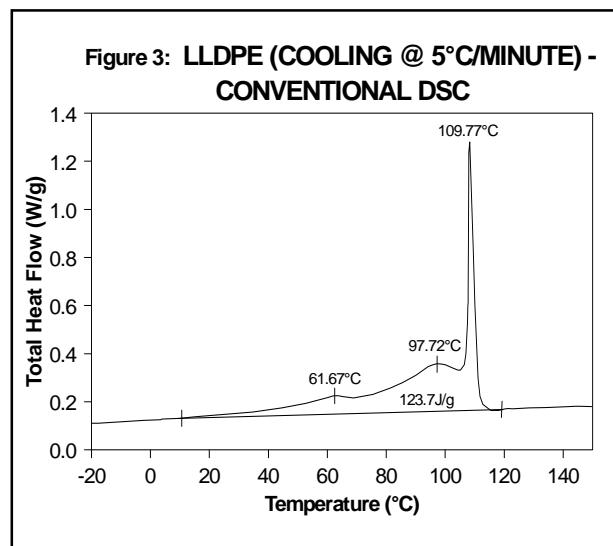
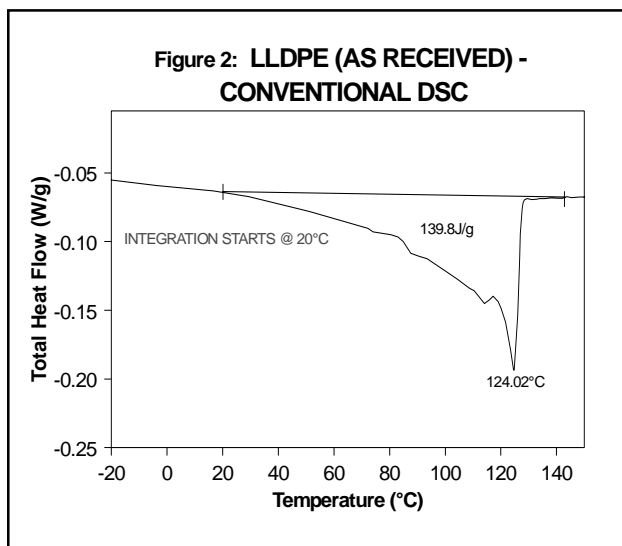


RESULTS

Figures 2-4 represent the conventional DSC results from the first heating, controlled cooling and subsequent reheating portions of the experiment. The initial heating shows a broad, somewhat noisy, melting curve with a single peak maximum at 124°C. The “noise” is thought to be caused by relaxation processes in the sample since they all occur above room temperature. The total heat of fusion associated with this peak is 140 J/g, which corresponds to 48% crystallinity based on the reported theoretical value of 293 J/g for 100% crystalline linear polyethylene [1]. The cooling curve shows crystallization peaks at 110, 98, and 62°C and a total heat of crystallization of 123.7 J/g. The second heating shows three overlapping melting peaks with maxima at 107, 121, and 124°C and a total heat of fusion and % crystallinity of 127.1 J/g and 43% respectively.

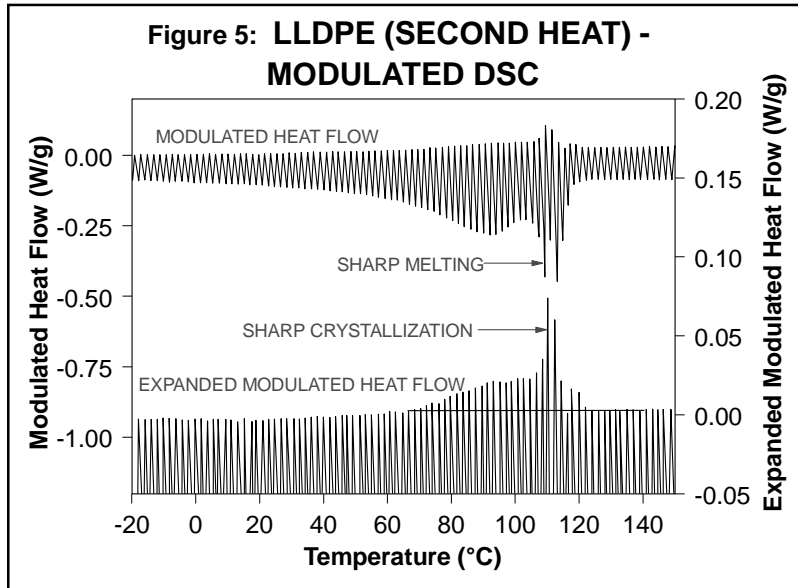
Comparison of these conventional DSC results raises several interesting questions:

- (1) Why does the cooling curve only show a single sharp crystallization peak at higher temperature and the subsequent heating curve shows two sharp melting peaks?
- (2) Why does the “as received” polymer show a higher % crystallinity based on its heating curve than the “slow cooled” polymer? This is opposite to what would be expected since the “as received” polymer came from an extrusion process where it was exposed to a higher cooling rate.



The modulated DSC results (Figures 5-11) fortunately provide answers to these questions and more.
Separation of Simultaneous Melting and Crystallization/Crystalline Perfection Processes

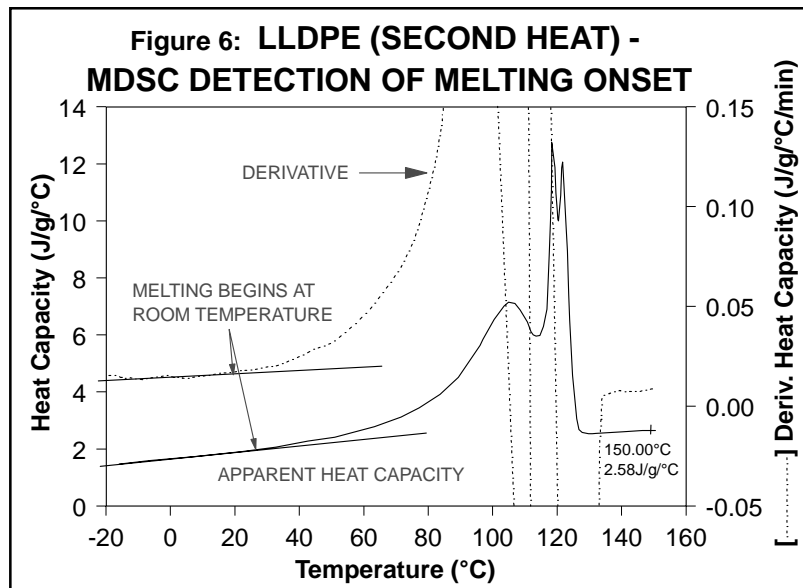
Figure 5 shows the modulated heat flow curve obtained by MDSC for the reheated polymer before deconvolution, as well as the modulated heat flow curve expanded so that the top of the curve can be examined. Since the experimental parameters as described earlier were chosen so that no cooling occurred during the MDSC experiment, the heat flow at the top of the modulated heat flow curve should be zero unless a kinetic process is occurring. This expanded view clearly shows the presence of several sharp exothermic events around 120°C, probably due to crystalline perfection processes. In the same temperature region, there are also sharp endothermic melting peaks (see the bottom of the complete modulated heat flow curve). The direct overlap of these sharp competing phenomena near 120°C makes the melt appear as two separate



melts in the total (conventional) DSC profile.

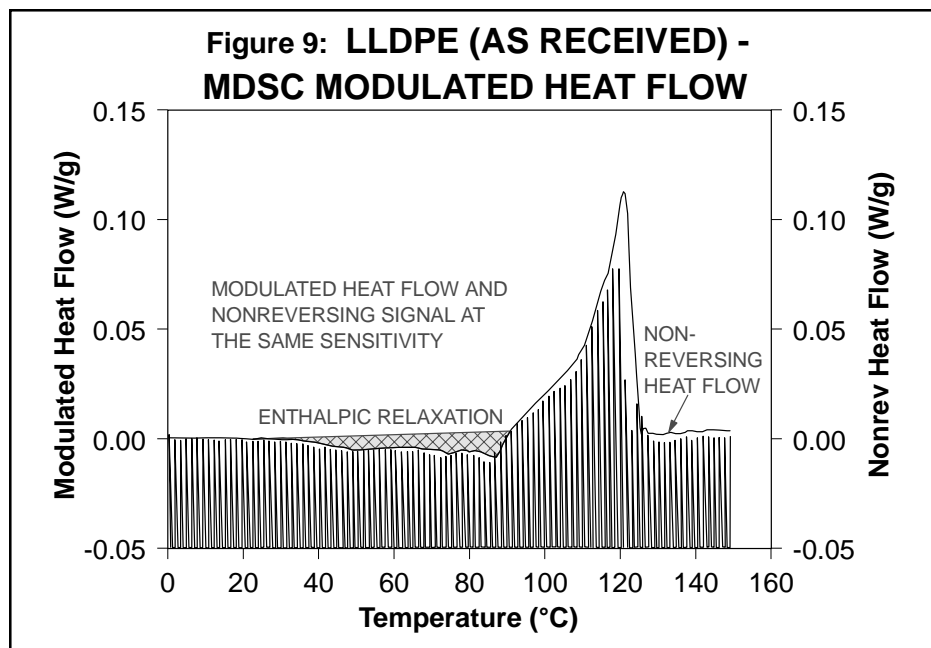
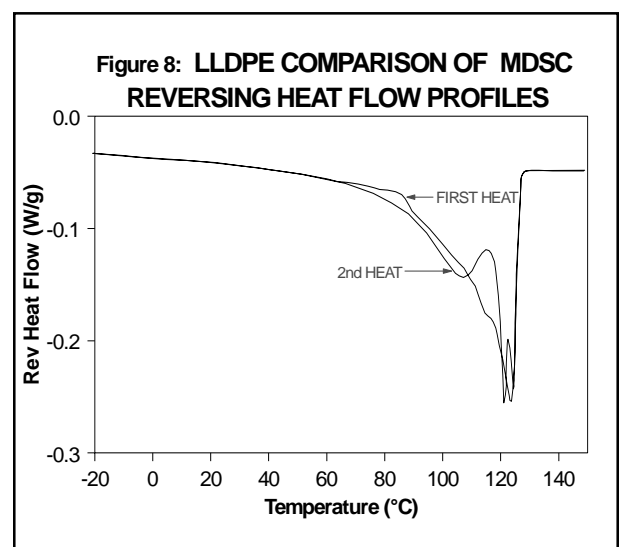
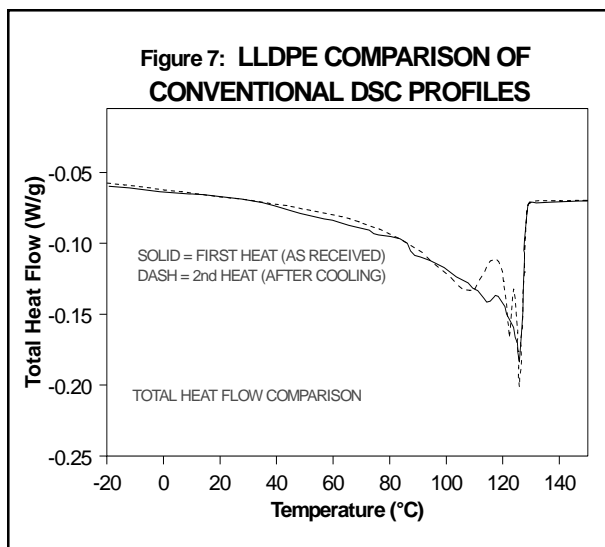
More Accurate Measurement of the Temperature Range of Melting

Using standard baseline extrapolation procedures to determine the onset of melting from the conventional DSC results (Figure 2 and 4) is extremely difficult. Using the modulated DSC heat capacity (Figure 6) or reversing heat flow curves for this determination, on the other hand, is easy and reproducible. Theory predicts that, in the absence of other phenomena (e.g. baseline drift, other thermal events), the heat flow curve prior to melting should be a linear, increasingly endothermic line with a slope directly related to heat capacity. Both the heat capacity curve and its time-based derivative clearly show that the onset of melting for this polymer actually begins around 20°C. This would be difficult to determine from Figures 2 or 4, and in fact, the modulated DSC results were actually used to decide where to draw the conventional DSC baseline.

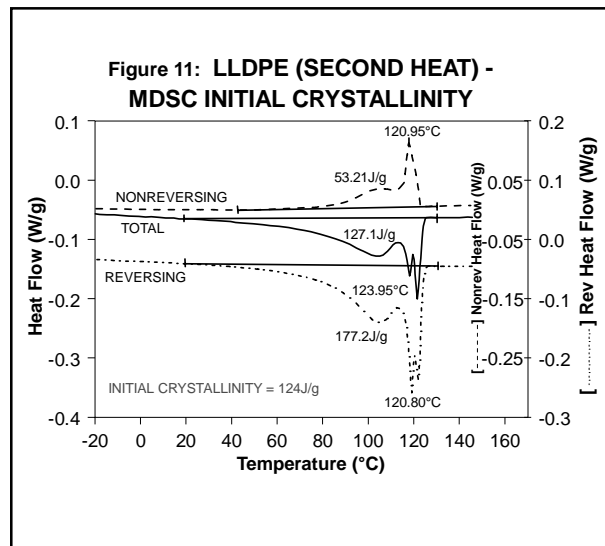
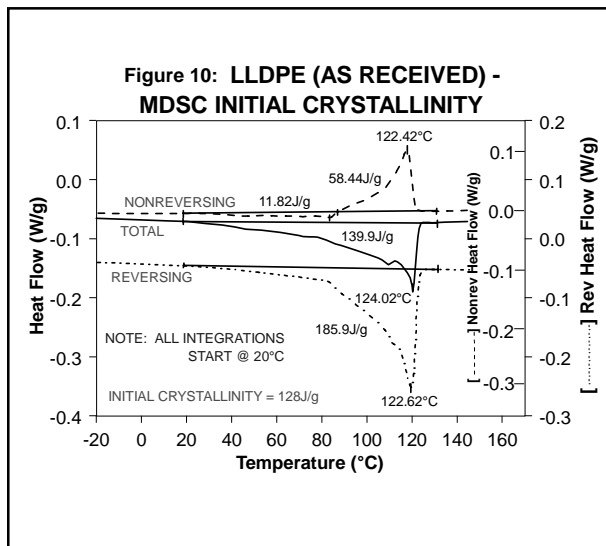


More Accurate Measurement of Initial Crystallinity

Conventional DSC has been widely used to assess the crystallinity (initial crystallinity) of polymers based on comparison of the enthalpies associated with crystallization and melting [2,3]. In LLDPE, the conventional DSC curves show no apparent exothermic crystallization/crystalline perfection processes, and hence the crystallinity is determined by measuring the melting endotherm and comparing the heat flow obtained to that for a material of known crystallinity as described earlier. The results obtained, however, are not always as expected because overlapping events such as crystalline perfection are not accounted for and adversely contribute to the measured heat flow. Figure 7, for example, shows the conventional DSC results for LLDPE “as received” and on second heating, these results imply that the “as received” polymer melts more in the range from 30 to 90°C than the reheated polymer. Modulated DSC on the other hand, shows (Figure 8) that there is no difference up to 65°C and the “as received” polymer actually has less melting prior to 100°C. Enthalpic relaxation of stresses caused by extrusion of the polymer may explain this discrepancy. If there is such an endothermic relaxation process over the temperature range of 30 to 90°C, then it would appear as melting in conventional DSC. However, if it is enthalpic relaxation, it would be visible at the top of the modulated heat flow signal and in the deconvoluted nonreversing signal. Figure 9 shows both of these MDSC signals plotted at the same sensitivity. Both clearly show a time-dependent (kinetic), endothermic event over this temperature range.



Eliminating the contribution of this relaxation from the heat associated with melting and using the sum of the MDSC reversing and nonreversing signals to calculate crystallinity (Figures 10 and 11), results in the conclusion that the polymer's crystallinity is not significantly affected by thermal history. This conclusion agrees well with published literature results and indicates that LLDPE crystallization from the melt is extremely rapid.



SUMMARY

The benefits associated with modulated DSC continue to be developed as additional materials are evaluated. Other measurements not covered in this paper which should be of interest to polymer scientists include determination of polymer blend composition [4,5], evaluation of aging effects in amorphous PET [6], determination of thermal conductivity in polymers [7], evaluation of transition phenomena in blends [8], and characterization of isothermal cure and vitrification in thermosets [9].

REFERENCES

1. V. B. F. Mathot, *Polymer*, **25**, 579-599 (1984)
2. TA Instruments Publication No. TS 20
3. TA Instruments Publication No. TS 21
4. TA Instruments Publication No. TS 22
5. TA Instruments Publication No. TS 24
6. TA Instruments Publication No. TS 25
7. TA Instruments Publication No. TA 086
8. TA Instruments Publication No. TA 226
9. TA Instruments Publication No. TA 219

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