

MODULATED DSC AS A TOOL FOR POLYETHYLENE STRUCTURE CHARACTERIZATION

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The Modulated Differential Scanning Calorimeter (MDSC) technique, using TA Q1000 instrument, has been applied as a tool to study the reversible and non-reversible heat flow characteristics of a wide range of polyethylenes. It was found that the heat flow characteristic is dependent upon the heating rates and modulation period used in the test. By using a set of standard test conditions, MDSC was found to be useful in studying the effect of previous thermal processing conditions, additive effects, and also the density, MI, type of comonomer, and molecular architecture.

Keywords: characterization, heat flow, MDSC, polyethylene, structure

Introduction

Modulated DSC or MDSC™ is used to describe the technology invented by Dr. Mike Reading of ICI (Slough, UK) and patented by TA Instruments [1]. Although this technique has been shown to be useful in many areas (cold crystallization of PET, glass transition dependency on rate, thermal conductivity, specific heat, initial crystallinity and others), the application to the melting phenomenon proved to be controversial [2]. The technique has been adapted in the mode known as ‘Quasi-Isothermal Modulation’ by Professor Bernhard Wunderlich (Oak Ridge National Lab, University of Tennessee) [3]. The most recent work attempted to apply this technique to compare precisely synthesized lengths of crystallizable units to a homopolymer and a random copolymer to obtain a new insight into the nature of crystallization, melting, and the decoupling of sequences [4]. Although the coupling and decoupling of segment of macromolecules from the bulk of the molecules in the crystalline and amorphous states is a relatively new concept and has not been widely accepted, and no direct application of this concept to establish firmly correlation between structure to properties has been developed, this may be a useful concept to correlate back to another concept of tie-chain molecules. A new method of applying the Raman technique of 3-phase characterization in correlating the inter-phase to the tie chain has recently been established [5].

There were several recent works of MDSC by Cser *et al.* [6–10], which demonstrated the importance of this technique for polyethylene structure characterization. We have attempted to apply the modulated DSC technique in characterizing the mo-

lecular architecture of different polyethylenes by studying the response of reversible and irreversible heat flow for this semi-crystalline polymer.

Following the recommendation of TA Instruments, the ramp rate and modulation period and amplitude are obtained from the half width of the peak melting event at the standard 10°C min⁻¹ ramp rate. Since the melting peak characteristics are different for different resins, the optimum test conditions may not be the same. Hence for the initial method development work, an arbitrary fixed conditions of underlying heating rate of 1.25°C min⁻¹ and a modulation period of 60 s were adopted, and the modulation amplitude was then automatically computed by the TA software. While this approach may be satisfactory when studying the MDSC behavior of resins of similar melting endotherm, the fixed conditions may not be universally applied. Hence further study was carried out to investigate the various factors that may affect the MDSC behavior with respect to polyethylene resins that differ in MI, density, and molecular architecture.

Experimental

Two series of experiments were carried out using different MDSC conditions to investigate the correlations between modulation period and resin molecular architecture.

Effect of modulation period

The Quasi-Isothermal TMDSC technique used by the Wunderlich group [3, 4] appeared to be an attempt to

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address the effect of the underlying heating ramp. However this technique is time-consuming and quantitative interpretation is also difficult. Hence it was decided to adopt a fixed underlying heating ramp, and alter the modulation period in this study.

The effect of changing the modulation period was studied using LLDPE-2 as the candidate. The test conditions were given in Table 1 as follow:

Table 1 Modulated DSC test conditions

Ramp/ °C min ⁻¹	Modulating amplitude/ ±°C	Modulating period/ s
2.00	0.05	10
2.00	0.11	20
2.00	0.16	30
2.00	0.21	40
2.00	0.27	50
2.00	0.32	60
2.00	0.42	80

Effect of MDSC on resin molecular architecture

The following resins, Table 2, were selected for the study:

Table 2 Properties of polyethylene resins

Resin	Melt index, I_2	Density/g mL ⁻¹	Comonomer
MDPE-2	113	0.931	C4
HDPE-1	4.9	0.960	–
HDPE-2	0.41	0.957	C4
LLDPE-2	1.0	0.920	C8
LLDPE-3	1.0	0.922	C8
LLDPE-4	1.0	0.920	C8
LLDPE-5	1.0	0.917	C8
HDPE-3	0.30	0.955	C6
HDPE-4	8.50*	0.945	C6
MDPE-1	150	0.932	C8
LDPE-1	2.3	0.918	–
LLDPE-6	1.0	0.918	C6

*Flow rate, I_{21}

All resins were subjected to the same thermal processing history of 10°C min⁻¹ cooling from 200°C and the MDSC test was run using an underlying ramp rate of 2°C min⁻¹ and a modulating period of 50 s as the test conditions. Two specimens were prepared for each resin, one of the specimens was subjected to duplicate test. The results for the average of the three tests were used.

Results and discussion

Effect of modulation period

Modulated DSC is very similar to step scan DSC, and it also has some similarity to the SSA technique [11]. In the case of step scan DSC and SSA, the objective is to thermally fractionate the sample, whereas in the case of MDSC, the idea is to use the superimposed oscillation thermal program to enable the heat flow data to be separated into the reversible and non-reversible components. In fact, a combination of TMDSC and thermal fractionation has been used to investigate the situation where crystallization was achieved at near to equilibrium conditions [12].

Comparison of the total heat flow of MDSC with the standard normal DSC run is shown in Fig. 1 for two modulation periods of 20 and 60 s. For the standard DSC curve for LLDPE-2, the behavior is characterized by a broad low temperature endotherm peak around 109°C, and a sharp melting peak at around 119°C, the characteristic curve for a linear low density polyethylene. Careful study of this normal DSC curve also reveals the presence of a high temperature shoulder at around 123°C. In the case of MDSC, the same lower broad temperature peak at around 109°C and a sharp melting peak at 119°C are also observed. However, with decreasing modulation period, the high temperature shoulder started to emerge as a distinct high temperature peak!

Hence it can be seen that imposing the modulating temperature program effectively is similar to adding on a step scan or SSA mode of fractionation. This allows separation of different crystallizing species which normally is not detected or clearly identified using a normal scan rate of 10°C min⁻¹. Low modulating period (high frequency) appeared to enhance the separation.

The overlay plots for different modulation period are shown in Figs 2, 3 and 4.

By studying the change in profile of the non-reversible heat flow (Fig. 4), it can be seen that there are

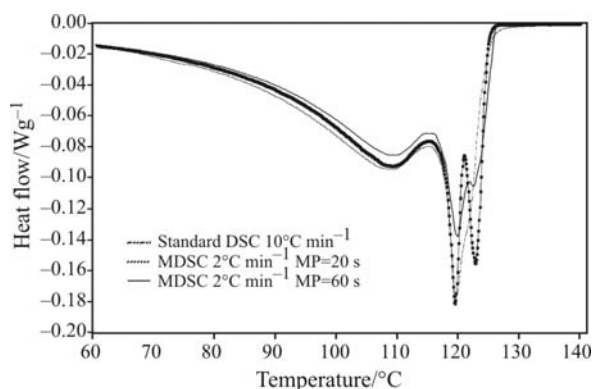


Fig. 1 Standard and modulated DSC comparison – total heat flow

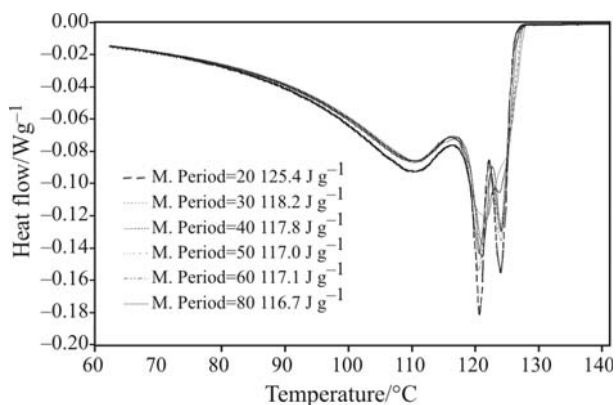


Fig. 2 Modulated DSC – total heat flow

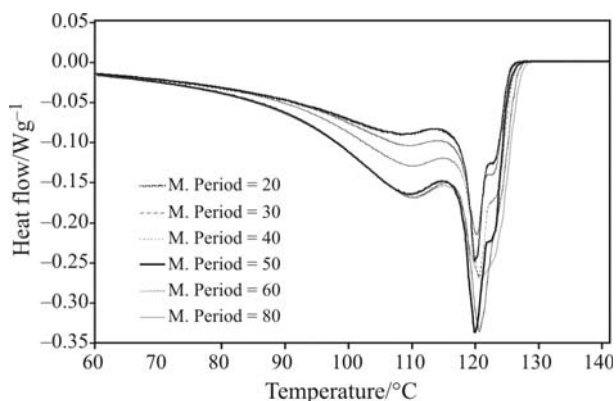


Fig. 3 Modulated DSC – reversible heat flow

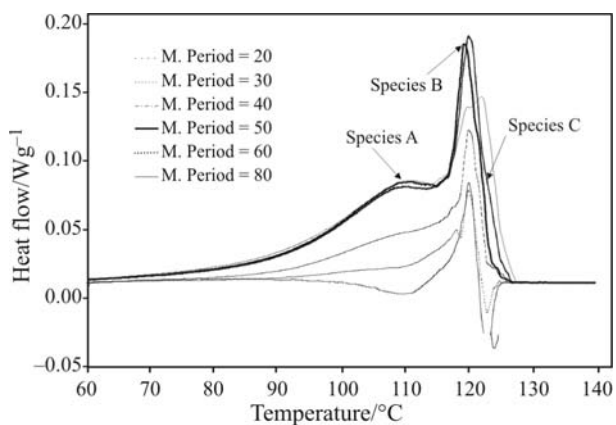


Fig. 4 Modulated DSC – non-reversible heat flow

three distinct crystallizing species, A, B, and C that respond differently to the modulation period. Species A (broad peak around 109°C) exhibited exothermic characteristics for modulation period greater than 20 s, and became endothermic at and below 20 s. Species B (peak around 120°C) remain exothermic throughout the entire modulation period used, remaining exothermic at the lowest modulation period of 20 s. Species C (shoulder at around 124°C) became endothermic for modulation period equal and smaller than 30 s.

From the plot of total heat flow (Fig. 2), the three different crystallizing species can be easily discerned for modulation period up to 60 s. However by looking at all the three plots, the different response towards modulation period is shown clearer, and this could then explain the strange positive up and negative down peaks observed for modulation period of 20 and 30 s in the case of the non-reversible heat flow between 110 and 130°C.

In the case of polymer crystallization and melting process, it has been postulated that [12]:

- The reversible heat flow is associated with (a) thermodynamic heat capacity, (b) heat capacity due to conformational motions, and (c) reversible melting.
- The non-reversible heat flow is associated with (a) crystal perfection, (b) secondary crystallization, and (c) primary crystallization.

The presence of non-reversible heat flow indicates the presence of the process of recrystallization and/or annealing during the heating process in the test. This was postulated to be due to the presence of metastable crystallites formed in the previous thermal and processing history, and in the above case, the 10°C min⁻¹ cooling history, the pre-treatment given to the sample. These metastable crystallites are dependent on the molecular architecture, for example, in the case of LLDPE-2; we can identify three different species. Each of these species will then form metastable crystallites that respond differently to the modulation period when tested under the same underlying heating rate.

The melting enthalpy for the three different heat flow as a function of modulating period is shown in Fig. 5. The non-reversible enthalpy appeared to approach zero at modulation period of lower than 20 s for this resin LLDPE-2.

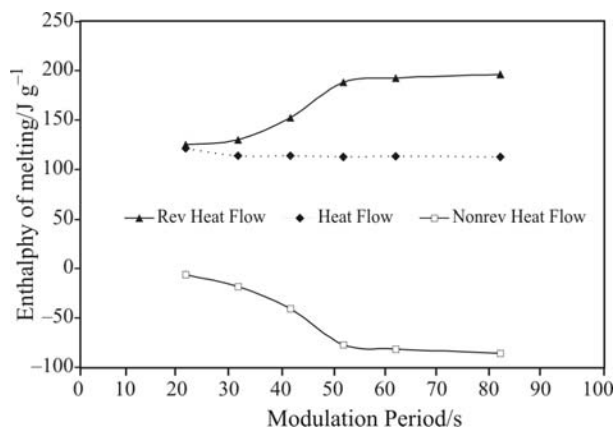


Fig. 5 Modulated DSC – effect of modulation period

Resin molecular architecture

The effect of resin molecular architecture on the thermal behavior under a ramp rate of 2°C min⁻¹ and a

Table 3 Summary of modulated DSC results

Product	MDPE-2	HDPE-1	HDPE-2	LLDPE-2	LLDPE-3	LLDPE-4	LLDPE-5	HDPE-3	HDPE-4	MDPE-1	LDPE-1	LLDPE-1
Density/g mL ⁻¹	0.9310	0.9600	0.9570	0.9200	0.9221	0.9200	0.9170	0.9550	0.9450	0.9320	0.9180	0.9175
M _w /g mol ⁻¹	32000	71900	169200	107700	110400	101800	100300	119700	168000	27600	94800	110900
Reversible heat	193.9	118.5	140.6	195.2	180.7	174.5	177.7	133.7	164.5	197.4	150.8	158.1
	180.0	135.3	155.6	184.9	171.7	182.8	182.6	157.5	154.4	200.8	143.0	158.4
	213.6	125.3	143.8	179.1	179.6	181.8	174.1	162.8	159.8	190.7	153.9	175.3
Mean	195.8	126.4	146.7	186.4	177.3	179.7	178.1	151.3	159.6	196.3	149.2	163.9
St _{dev}	16.9	8.5	7.9	8.2	4.9	4.5	4.3	15.5	5.1	5.1	5.6	9.8
Non reversible heat	45.9	-88.7	-55.3	70.7	58.4	56.4	58.7	-65.8	-16.0	41.2	34.3	37.3
	35.7	-74.5	-40.7	58.6	56.2	65.2	71.9	-39.2	-27.5	55.1	35.4	34.8
	55.5	-86.8	-57.6	67.3	56.2	58.9	57.4	-37.6	-23.5	32.5	40.5	49.1
Mean	45.7	-83.4	-51.2	65.5	56.9	60.2	62.7	-47.5	-22.3	42.9	36.7	40.4
St _{dev}	9.9	7.7	9.1	6.3	1.2	4.5	8.0	15.8	5.8	11.4	3.3	7.6
Total heat flow	148.0	207.2	195.9	124.5	122.3	118.1	119.0	199.5	180.5	156.2	116.5	120.9
	144.3	209.9	196.4	126.3	115.5	117.6	110.7	196.7	181.9	145.7	107.6	123.6
	158.1	212.1	201.3	111.8	123.4	122.9	116.7	200.8	183.3	158.2	113.4	126.3
Mean	150.2	209.7	197.9	120.9	120.4	119.5	115.5	199.0	181.9	153.4	112.5	123.6
St _{dev}	7.1	2.5	3.0	7.9	4.3	2.9	4.3	2.1	1.4	6.7	4.5	2.7

modulation period of 50 s was studied. Table 3 below summarizes the heat flow data.

The standard deviation for the total heat flow is generally good. However, in the case of reversible and non-reversible heat flow, occasionally a wider spread of results is observed.

Looking at the non-reversible heat flow MDSC (Fig. 6) for the high-density polyethylene (HDPE-1, HDPE-2, HDPE-3 and HDPE-4), it is clear that for polyethylene with no or a very small amount of branching, the non-reversible heat component is totally endothermic at this heating rate and modulation period. The absence of exothermic heat indicated that for HDPE, there was very little recrystallization and/or annealing taking place when heating a sample previously cooled at 10°C min⁻¹. Hence a thermal cooling history of 10°C min⁻¹ for HDPE basically generated crystalline morphology of near to equilibrium state. The magnitude of the non-reversible endothermic heat appeared to be a function of density, increasing with increase in density as shown in the Table 4 below.

Molecular mass (mass average) appeared to have no or very small effect on the magnitude of the non-reversible heat component. The total heat also indicated some dependency on the density, although the trend is not as clear as in the case of non-reversible heat component, especially looking at HDPE-2 and HDPE-3.

When we compared the MDSC for the similar density octene-LLDPE made with Ziegler-Natta

(LLDPE-2 and LLDPE-4) and single site catalyst (LLDPE-3 and LLDPE-5), a completely different behavior was obtained (Figs 7a-c).

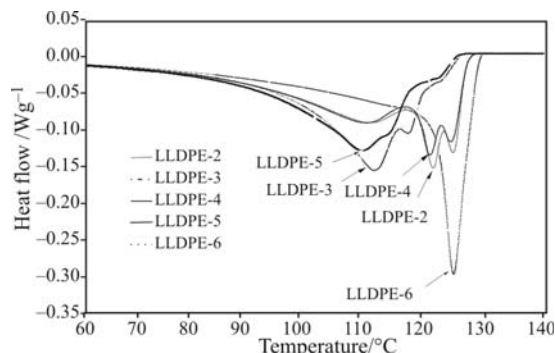


Fig. 7a MDSC total heat

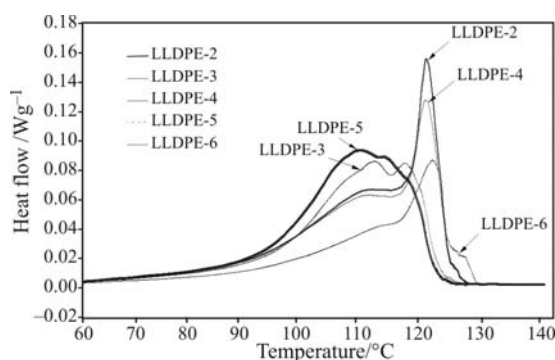


Fig. 7b MDSC non-reversible heat flow

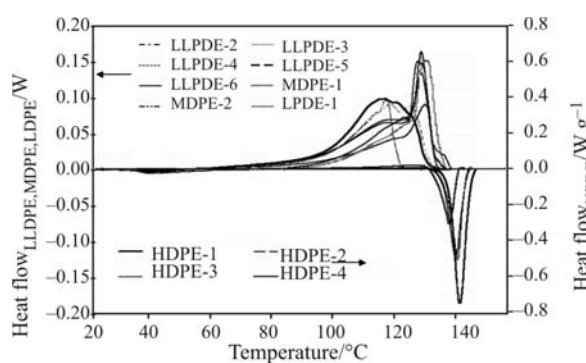


Fig. 6 MDSC non-reversible heat flow

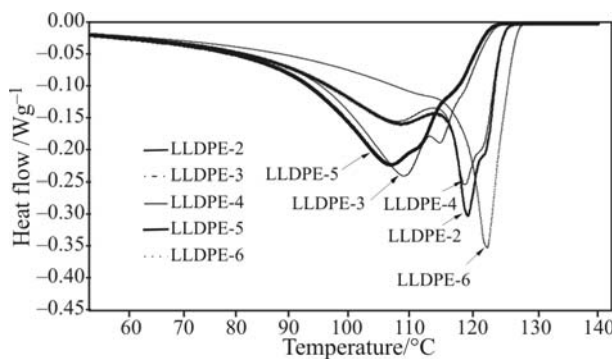


Fig. 7c MDSC reversible heat flow

Table 4 Molecular and thermal properties of high density polyethylenes

Product	HDPE-1	HDPE-2	HDPE-3	HDPE-4
Density/g mL ⁻¹	0.9600	0.9570	0.9550	0.9450
M _w /g mol ⁻¹	71900	169200	119700	168000
MWD (polydispersity)	3	13	9	15
Reversible heat flow	126.4	146.7	151.3	159.6
Non-reversible heat flow	-83.4	-51.2	-47.5	-22.3
Total heat flow	209.7	197.9	199.0	181.9

In the total heat flow, for the single site catalyst LLDPE (LLDPE-3 and LLDPE-5), we observed a much larger low temperature high comonomer peak (around 109°C), and the high temperature peak at around 120°C was much reduced in size. The 123°C peak was absent, and instead, we observed a shoulder at around 115°C. The gas phase ZN hexene-LLDPE (LLDPE-6), on the other hand exhibited very broad high comonomer low melting peak, and a single high temperature peak at 123°C.

The non-reversible heat flow of the single site LLDPE (Fig. 7b) appeared to show the presence of two crystallizing species, and the species appeared to have different peaks for LLDPE-3 and LLDPE-4. This could be due to the polymerization process of the dual reactors system. For the hexene-LLDPE (LLDPE-6), the non-reversible heat flow appeared to indicate the presence of a relatively high temperature shoulder at 127°C.

The MDSC for LDPE-1 appeared to show single species for reversible heat flow (Fig. 8) and possibly also for the non-reversible heat flow, indicating the homogeneity in the crystallizing species in LDPE-1.

In the standard DSC run, for LDPE and LLDPE, a very small peak is usually observed around 40°C, and is usually absent in the case of HDPE. This was also seen in the total heat flow in the MDSC (Fig. 9).

When we look at the non-reversible heat flow plot (Fig. 10), it is clear that this low temperature characteristic is real, and is giving rise to an endothermic melting of a species of very low melting point. Only the HDPE-4 (with the lowest density among the four HDPEs) shows a possible presence of this low temperature endothermic melting peak, whereas the other three HDPEs appeared to have no distinct endothermic event at this low temperature range. In the case of reversible heat flow, there was no peak at 40°C for all polyethylenes studied. It is postulated that this could be the interfacial semicrystalline structure. Further study is required to identify the structures that contribute towards this low temperature

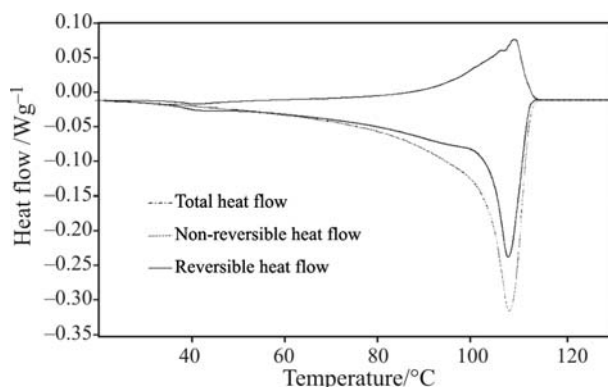


Fig. 8 Modulated DSC of low density polyethylene

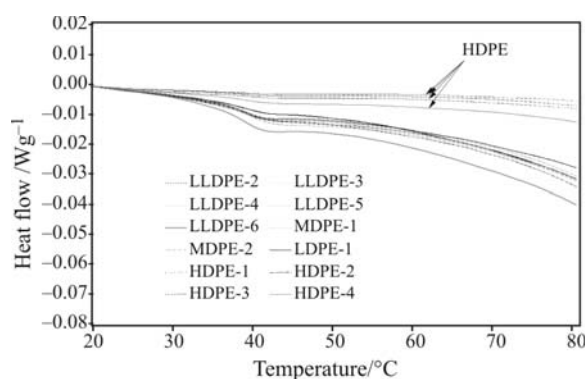


Fig. 9 Modulated DSC – total heat

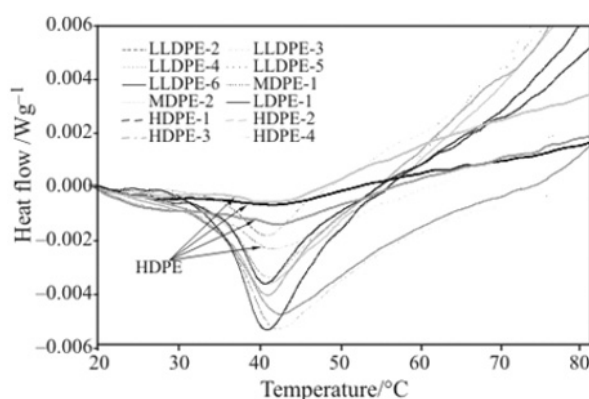


Fig. 10 Modulated DSC – non-reversible heat flow

non-reversible endothermic characteristic, which may arise from the short chain branching or comonomer branching.

Conclusions

In summary, MDSC offers a number of advantages over conventional DSC for studying blends and semi-crystalline polymers. This technique is a powerful new tool for a more complete characterization of polymer systems by calorimetry. However, special care should be given to the experimental conditions, as the separation of total signal into heat capacity and kinetic components changes significantly around the melting region whenever MDSC experimental conditions are changed.

Despite the concerns of applying MDSC to the understanding of the polymer melting process and crystalline morphology, correlations have been established between the effect of modulation period and resin molecular architecture. MDSC experiments can be used to investigate the effect of the presence of high-density component and processing effect [13]. By applying the same experimental conditions on twelve NOVA Chemicals resins with a range of

density, the magnitude of the non-reversible endothermic heat appeared to be a function of density, increasing with increase in density. The results for HDPE samples indicated that all three heat flows were endothermic. Also, the non-reversible heat flow was much lower in the case of less branched samples. The total heat flow also indicated the presence of a small peak at about 40°C for LDPE and LLDPE resins but not for HDPE.

The major advantage of MDSC is its increased sensitivity to detect small differences in crystalline structure (as illustrated in sample LLDPE-2). This is an analogue to fractionation technology in step scan DSC or SSA. This is postulated to be due to the presence of metastable crystallites formed in the previous thermal and processing history, or any pre-treatment given to the sample. The formation of these metastable crystallites is dependent on the molecular architecture, which can then give rise to a possible simple characterization technique to identify different species within a sample. Each of these species may form meta-stable crystallites that respond differently to the modulation period when tested under the same underlying heating rate.

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References

- 1 L.C. Thomas, 'Characterization of Melting Phenomena in Linear Low Density Polyethylene by Modulated DSCTM', TA Instruments, TA-227.
- 2 Mike Reading, 'Modulated Temperature DSC (MTDSC); Basic Theory, Operation, Applications and Comparison to Traditional DSC', Advanced Thermal Analysis Short Course: August 5–6, 2006, NATAS 34th Annual Conference.
- 3 B. Wunderlich, 'Quantitative Temperature-Modulated Calorimetry', NATAS Notes, Vol. 35 No. 3, Fall 2003.
- 4 W. Qiu, J. Sworen, M. Pyda, E. Nowak-Pyda, A. Habenschuss, K. B. Wagener and B. Wunderlich, 'Effect of the Precise Branching of Polyethylene at Each 21st CH₂ Group on Its Phase Transition, Crystal Structure, and Morphology', *Macromolecules* 2006, 39, 204–217.
- 5 X. C. (Alan) Wang, M. Weber, H. Hay and M. Cossar, 'Single-Site Catalysts and Dual Reactor Technology Create More Freedom in PE Rotomolding Resin and Product Design', ANTEC 2005.
- 6 F. Cser, F. Rasoul and E. Kosior, *J. Thermal Anal.*, 50 (1997) 727.
- 7 F. Cser, F. Rasoul and E. Kosior, *J. Therm. Anal. Cal.*, 52 (1998) 293.
- 8 F. Cser, J. Hopewell and E. Kosior, *J. Therm. Anal. Cal.*, 53 (1998) 493.
- 9 F. Cser, J. L. Hopewell and R. A. Shanks, *J. Therm. Anal. Cal.*, 54 (1998) 707.
- 10 F. Cser, J. L. Hopewell, K. Tajne and R. A. Shanks, *J. Therm. Anal. Cal.*, 61 (2000) 687.
- 11 J. Chau and J. Teh, *J. Therm. Anal. Cal.*, 81 (2005) 217.
- 12 G. Amarasinghe and R.A. Shanks, *J. Therm. Anal. Cal.*, 78 (2004) 349.
- 13 Unpublished results, NOVA Chemicals.

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