Journal of Thermal Analysis, Vol. 46 (1996) 1047-1059

Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

A STUDY OF PBT/PC BLENDS BY MODULATED DSC AND CONVENTIONAL DSC

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Abstract

Two poly(butylene terephthalate)/polycarbonate (PBT/PC) blends with different formulations were analyzed by modulated DSC (MDSC) and conventional DSC to determine differences in crystallization behavior. A significant difference (30°C in cold crystallization temperature) between the two samples was detectable by MDSC while no significant difference was seen by conventional DSC. That indicates *the total heat flow from MDSC is not always equivalent to the heat flow from conventional DSC* as we have assumed or seen before. The reason has not been fully understood, but may be related to unusual nucleation and crystallization induced by modulation. Alternative conventional DSC methods were developed and compared to the MDSC results.

Keywords: conventional DSC, crystallization, glass transition, modulated DSC, PBT/PC blend

Introduction

Melt blends of polys(butylene terephthalate) (PBT) and polycarbonate (PC) are widely used engineering plastics for automotive, business machines, appliances and other industries [1–8]. These blends offer toughness, good chemical resistance, and excellent molding characteristics.

Due to possible reaction between PBT and PC, the glass transition and crystallization behavior of various blends can depend on the formulation and processing conditions [8]. DSC is widely used to monitor these variations in the blends [7–8]. Because of differences in miscibility in PBT/PC blends which may have T_g's that overlap with T_c, it is quite difficult to quantitatively analyze those blends.

Modulated Differential Scanning Calorimetry (MDSC) is a recent extension of conventional Differential Scanning Calorimetry (DSC) [9]. It provides many benefits which overcome some of the limitations of conventional DSC, including the separation of complex, overlapping transitions into more easily inter-

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preted components [10]. A wide variety of applications have been reported since MDSC was first introduced in 1992 [9–14]. It has been assumed that the total heat flow from MDSC is equal to the heat flow from conventional DSC and it has been shown for slowly cooled PET and annealed PEEK that the heat flow curves from MDSC and conventional DSC are virtually indistinguishable [12].

In this paper, two PBT/PC blends with different formulations were characterized by MDSC and conventional DSC to distinguish differences in crystallization behaviour. The different results between MDSC and DSC were compared. The effects of melting and quenching conditions on MDSC results were investigated. The results from alternative conventional DSC methods were also compared.

Experimental

Samples

Two samples, designated A and B with different melt and processability characteristics, consisting of 40/60 blends of polycarbonate (PC)/poly(butylene terephthalate) (PBT) with a small amount of additives (impact modifier, stabilizer, pigment, etc.), were used for MDSC and DSC studies. Pellets were cut into 2–4 pieces, each weighing 5 to 10 mg. These were then sealed in aluminum pans. For MDSC analysis, each sample was treated as follows: After heating the sample in the DSC cell at a chosen temperature (270 or 290°C) for various intervals (3–15 min), the pan with the sample was quickly transferred to one of the following cold surfaces for quenching: 1) liquid nitrogen chilled aluminum plate (LNC) at about 0°C; 2) a Perkin Elmer DSC cold plate maintained at about −100°C by a Mechanical Cooling Accessory (MCA); 3) liquid nitrogen boiled aluminum plate (LNB) which was just taken out from liquid nitrogen below −170°C. MDSC was used to measure the cold crystallization temperature (T_c) from non-reversing heat flow and glass transition temperature (T_g) from reversing heat flow.

Instrumentation

MDSC experiments were carried out on the TA Instruments Thermal Analysts 2100 System with a 2920 Modulated DSC^{TM}, a DSC Autosampler and an autofilled Liquid Nitrogen Cooling Accessory (LNCA). The LNCA can provide consistent coolant for the noted modulation conditions and allow the experimental series to run continuously. Unless indicated, all experiments were set up to ramp from 0 to 250°C at a heating rate of 3°C min^{-1} with a modulation amplitude of ±2°C and a period of 60 seconds. The DSC cell was purged with 99.999% helium at a flow rate of 20 ml min^{-1} throughout the analysis. In some cases, samples were treated a 2nd or 3rd time, and then the MDSC experiments was run again. Data were analyzed by TA Instruments MDSC Analysis software Version 1.1A^{TM} and reported as glass transition temperature (T_g) from the reversing heat flow curve, cold-crystallization temperature (T_c) and heat of crystallization (ΔH_c) from the non-reversing heat flow curve, melting temperature (T_m) and heat of fusion (ΔH_m) from the total heat flow curve.

Conventional DSC experiments were carried out on a Perkin Elmer DSC-7 equipped with a Robotic System and Mechanical Cooling Accessory (MCA). The DSC cell was purged with dried in-house nitrogen at a flow rate of 20 ml min^{-1} throughout the analysis. Three methods were used:

Isothermal crystallization

Heat from 40 to 290°C at 20°C min^{-1}, hold at 290°C for 15 min and then rapidly cool (320°C min^{-1}) to 203°C for a minimum of 60 min isothermal crystallization. The crystallization peak was integrated and the fractional crystallinities at time intervals were analyzed by the Avrami method [13] using an Excel® worksheet. The Avrami index (n), rate constant (Z) and half-time of crystallization ($t_{1/2}$) were obtained.

Partial isothermal crystallization and melting

Heat from 40 to 290°C at 20°C min^{-1}, hold at 290°C for 15 min and then rapidly cool (320°C min^{-1}) to 203°C for 12 min isothermal crystallization followed by an immediate heating from 203 to 290 at 5°C min^{-1}. The heat of fusion was calculated based on the final DSC heating curve.

Multi-Cycle DSC

1st cycle – Heat from 40 to 290°C at 40°C min^{-1}, hold at 290°C for 3 min, cool from 290 to 40°C at 40°C min^{-1}, 2nd cycle – heat from 40 to 290°C at 40°C min^{-1} again, hold at 290°C for 5 min, cool from 290 to 40°C at 40°C min^{-1}; 3rd cycle – repeat second cycle. The crystallization temperatures were obtained from each cooling cycle (T_{c1}, T_{c2} and T_{c3}).

Results and discussion

MDSC results

One of the benefits of MDSC for polymer blends is its capability to separate the reversing glass transition from the non-reversing transition(s) [9–11]. Figures 1 and 2 are typical MDSC curves for PBT/PC blend samples with one and two glass transitions, respectively. The figures contain three curves: total heat flow on the top (similar to heat flow in normal DSC), reversing heat flow in the middle (for glass transition) and non-reversing heat flow on the bottom (for crystallization). For a totally miscible system, it only shows one T_g at 75°C

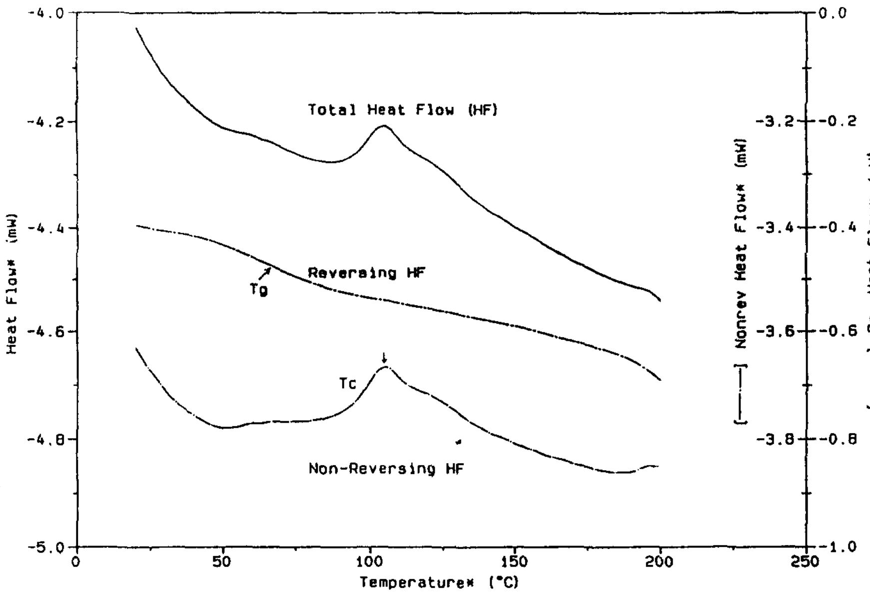

Fig. 1 MDSC curves for PBT/PC blend with one T_g in reversing heat flow and one T_c in non-reversing heat flow

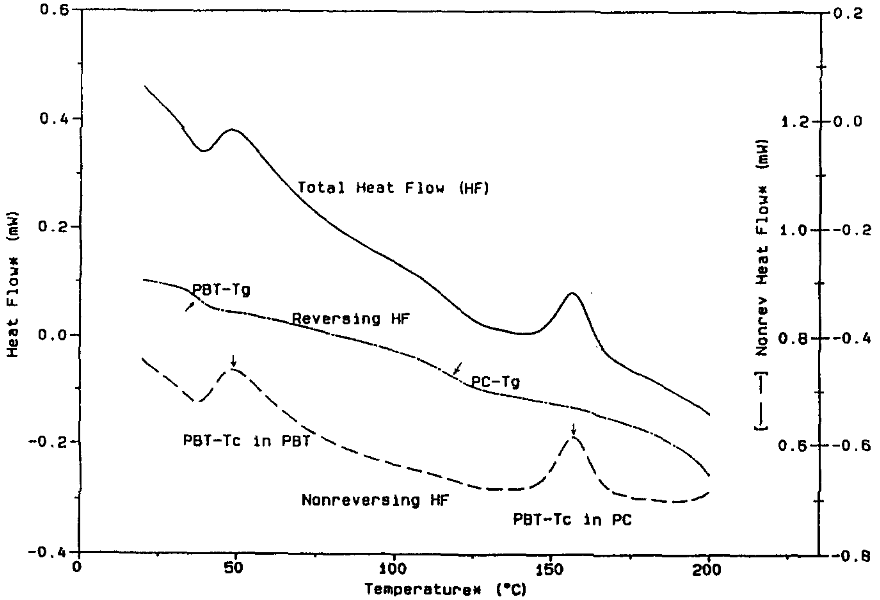

Fig. 2 MDSC curves for PBT/PC blend with two T_g's in reversing heat flow and two T_c's in non-reversing heat flow

(Fig. 1) while for a less miscible system, it shows two T_g's, one at 40°C for PBT and other at 120°C for PC, in reversing heat flow (middle curve) and two cold-crystallization processes, one at 50°C for PBT in the PBT rich-phase and other at 160°C for PBT in the PC rich-phase, in the non-reversing heat flow (bottom curve) as we expected (Fig. 2). Clearly, MDSC provides more and better information about glass transition temperatures and crystallization temperatures since it can distinguish between the heat flow associated with the reversible glass transition and the heat flow associated with the non-reversing crystallization process. Using conventional DSC, it is difficult or impossible to extract T_g values from the interfering cold-crystallization exotherm, expecially for the material with two glass transitions.

The reproducibility of MDSC results was checked by running six samples from 3 pellets, each cut into 2 pieces. Results indicate that the standard deviation for T_g, T_c and T_m is quite low (about 1°C) and similar to conventional DSC.

Comparison between MDSC and conventional DSC

It has been assumed in all previous MDSC measurements that the total heat flow from MDSC, which is an average of the modulated heat flow, is equivalent to the heat flow from conventional DSC [9–12]. In most cases, this has generally been shown to be true. However, it appears not to be the case with cold-crystallization of the PBT/PC blend. Figure 3 shows the MDSC curves for sample A and B after being treated at 290°C for 15 min and quenched using the LNC method (described in the Experimental section). Clearly, the two samples show significant differences in T_c (105°C for A with standard deviation of 0.8 and 135°C for B with standard deviation of 2.0°C based on 4 repeat runs). When we ran the same sample by conventional DSC at 5°C min^{-1}, surprisingly, we found there is no difference between sample A and B (T_c=120.0°C for A with a standard deviation of 0.6°C and T_c=121.8°C for B with a standard deviation of 1.1°C based on 4 repeated runs). Further study of same sample A was carried on the identical MDSC instrument with regular modulation and without modulation (i.e. setting amplitude zero) which was acting then like a DSC. Results are shown in Fig. 4. Clearly, they are not the same. The curve with no modulation (DSC mode) is relatively sharper than the curve with the modulation (MDSC mode). That suggests that *the total heat flow from MDSC is not always equivalent to the heat flow from conventional DSC*. The reason for the difference is not fully understood. It may be caused by instrument data analysis or connected to the temperature modulation which may induce nucleation and recrystallization behavior and lead to a T_c for sample A at a much lower temperature than for sample B.

Effect of melting and quenching conditions on T_c

In order to determine the effects of melting and quenching conditions on MDSC results and optimize the MDSC experimental conditions for best results,

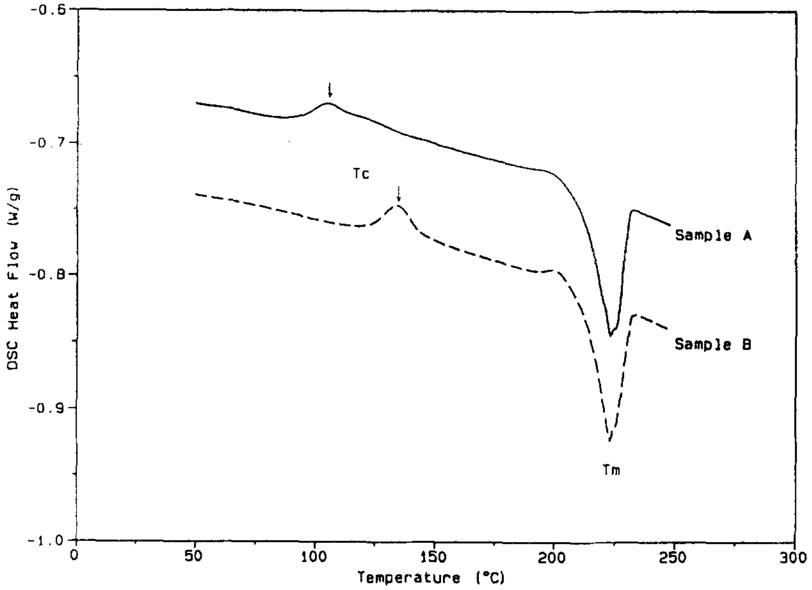

Fig. 3 MDSC total heat flow curves for sample A and B after being treated at 290°C for 15 min and quenched

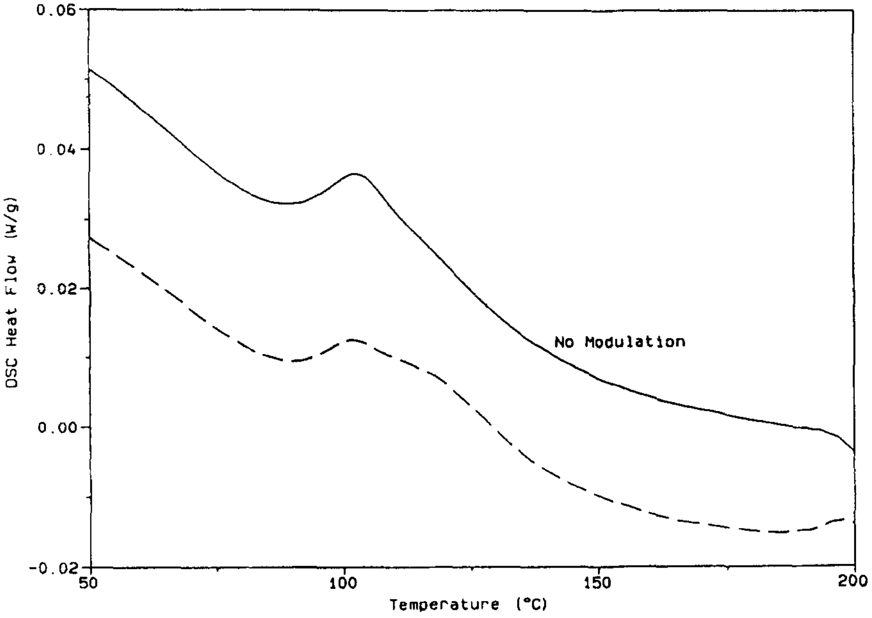

Fig. 4 Total heat flow of MDSC and DSC results for sample A. (dashed line: MDSC; solid line: DSC)

a variety of thermal conditions were applied. Two different melting temperatures (270 and 290°C), four different melting times (3, 5, 10 and 15 min) and three different quenching conditions (described in the Experimental section) were used to study the effect of different quenching rates and melting conditions on the glass transition, crystallization and melting behavior. The results, which are listed in Table 1, show the glass transition and crystallization data for samples A and B after being treated at 290°C for 3, 5, 10 and 15 min. At short hold times (3, 5, or 10 min), samples A and B show no significant difference in T_g, T_c and ΔH_c, while at longer hold times (15 min), sample A shows an about a 40°C shift to lower temperatures for T_g and T_c, and a more than doubling of the ΔH_c (from 6.5 to 16.3 J g^{-1}). Sample B shows only about a 10°C shift to lower temperatures for T_g and T_c, and less than half of the increase in ΔH_c (from 6.3 to 9.2 J g^{-1}). In addition, the difference between T_c and T_g is fairly consistent, about 40°C for both samples, which gives us the ability to estimate the T_g (which is very difficult to determine in the PBT/PC blend system by conventional DSC) from T_c values (which are relatively easy to determine by conventional DSC) based on the constant relationship between T_g and T_c. After a 2nd or 3rd melt treatment, MDSC results indicate there is no difference again between samples A and B. Both samples reach a certain limit and behave the same.

Table 1 MDSC results for sample A and B melted at 290°C for 3, 5, 10 and 15 min

Sample	Temp./Time	T_g /°C	T_c /°C	ΔH_c /J g^{-1}	T_c–T_g /°C
A	290°C/3 min	114.5	156.3	5.3	41.8
B	290°C/3 min	116.3	156.4	4.6	40.1
A	290°C/5 min	112.5	154.7	4.7	42.2
B	290°C/5 min	112.0	153.5	5.3	41.5
A	290°C/10 min	102.8	145.2	6.5	42.4
B	290°C/10 min	106.8	145.5	6.3	38.7
A	290°C/15 min (1st)	66.6	105.4	16.3	38.8
B	290°C/15 min (1st)	94.0	134.8	9.2	40.8
A	290°C/15 min (2nd)	70.3	100.7	19.8	30.4
B	290°C/15 min (2nd)	71.2	100.4	19.9	29.2
A	290°C/15 min (3rd)	69.2	100.2	19.5	30.0
B	290°C/15 min (3rd)	69.5	99.3	19.3	29.8

Figure 5 shows the effect of the hold temperature and time on T_c for samples A and B which were held at 270 or 290°C for different times and then quenched using the MCA. At 270°C, there is no significant difference between samples A and B, while at 290°C, the difference is quite significant at hold times shorter than 10 min. The effect of different quenching conditions on T_c was also stud-

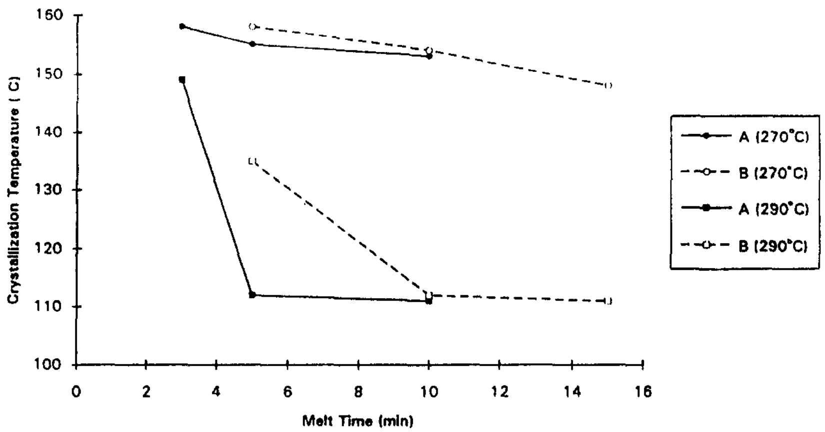

Fig. 5 Effect of the hold temperature in the melt on the cold-crystallization temperature (T_c)

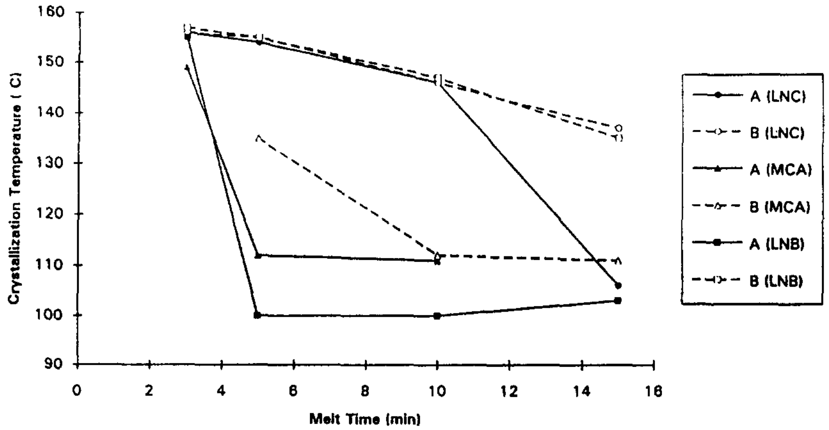

Fig. 6 Effect of different thermal quenching conditions on T_c

ied. Results are shown in Fig. 6. Using the liquid nitrogen chilled aluminum plate (LNC), no differences are seen between samples A and B if heated for less 10 min while more than a 30°C difference is seen between samples A and B after being heated for 15 min. Using the faster quench rates afforded by the aluminum plate boiled in liquid nitrogen (LNB) and the Perkin-Elmer DSC cold plate (MCA), differences between samples A and B can be seen in samples heat treated for only 5 min.

It appears that the reaction between PBT and PC takes place during heat treatment in both samples. For samples with a various degrees of reaction, one expects those with a low degree of reaction to crystallize, under quench conditions, more quickly, resulting in a relatively low amorphous phase content. The corresponding materials with a high degree of reaction will behave in a contrary fashion. On reheating, materials with a low amorphous phase content are expected to have a higher cold crystallization temperature (T_c) and lower heat of crystallization than those with a high amorphous phase content. The trends in T_c and ΔH_c of sample A and B, when reheated after identical heat and quench treatments, suggests that the reaction between PBT and PC occurs to a greater extent in sample A. NMR results supported this conclusion [16].

Alternative methods by conventional DSC

MDSC provides not only a better way to interpret DSC data by resolving overlapping glass transition and crystallization, but also gives unique information about differences in cold crystallization behavior which are not revealed by conventional DSC. However, MDSC is a relatively new technique which is still not widely available. In addition, the test turnaround time is limited by the slower heating rate of 3°C min^{-1} compared to the more usual 20°C min^{-1} in conventional DSC. Additional sample preparation (melting and quenching) steps may also introduce some experimental error. In today's industrial environment or QA laboratory, it is desirable to use existing conventional DSC instruments for quick determination of classes of material. We have attempted to test the feasibility of developing different conventional DSC approaches with fast cycle time, good reproducibility and easy operation. Based on the differences in crystallization rate for these samples, the following alternative methods were developed.

Isothermal crystallization

Isothermal crystallization by DSC is a commonly used method to study crystallization rates of materials. The principles and application have been discussed in many papers and books, e.g. Ref. [15]. Figure 6 shows isothermal DSC curves for sample A and B at 203°C. After data analysis based on the Avrami equation, the Avrami parameters are listed in Table 2 for sample A and B with 4 repeat runs each. The half-time of crystallization ($t_{1/2}$) at 203°C is 17.7 min for A with a standard deviation of 0.6 min and 12.3 min for B with a standard deviation of 0.8 min. The difference is quite significant. But as we know, the isothermal crystallization method can take a long time for the completion of crystallization, requires very good instrument baseline, and a carefully selected crystallization temperature. It also requires extra time and effort to do the data analysis based on the Avrami equation. There is currently no commercial software available for this analysis. An easier, quicker and more simple way to distinguish the differences in crystallization behavior is desirable in the industrial laboratory.

Table 2 Avrami parameters for isothermal crystallization at 203°C*

No.	Sample A			Sample B		
	n	Z	$t_{1/2}$	n	Z	$t_{1/2}$
#1	2.4	4.1E–08	17.1	2.4	8.2E–08	12.8
#2	2.6	9.9E–09	17.3	2.6	2.1E–08	13.0
#3	2.7	4.2E–09	18.4	2.5	4.8E–08	12.2
#4	2.7	4.6E–09	17.8	2.7	1.6E–08	11.2
Average	2.6	1.5E–08	17.7	2.6	4.2E–08	12.3
Std	0.1	1.8E–08	0.6	0.1	3.0E–08	0.8

*Note: linear regression based on first 70%.

Partial isothermal crystallization melting

From Fig. 7, if samples were partially crystallized at 203°C for 12 min, due to the difference in crystallization rates, the two samples should reach different degrees of crystallinity. If the samples is then heated immediately through the melt, one would expect differences in the heat of fusion. Figure 8 shows melting curves of a partially isothermally crystallized samples A and B. Clearly, they show distinct differences in ΔH_m, 1.0 J g^{-1} for A and 12.5 J g^{-1} for B, respectively. It is much easier to analyze the heat of fusion than to analyze isothermal crystallization data using the Avrami method. This procedure also requires less experimental time since the long isothermal hold time is limited. Although the partial isothermal crystallization/melting method provides an easy way to differentiate the crystallization rate, one still needs to carry out primary testing to determine the appropriate isothermal temperature and crystallization time to provide optimum results.

Multi-Cycle DSC

As we have seen from Fig. 5, if sample A and B were heated at 290°C for short times, both of them show higher T_c values while for longer times, both of them will show lower T_c values. This has been verified by reheating the same sample again and measuring T_c which is very close for sample A and B after the 2nd or 3rd heat treatment. In order to observe the difference between A and B, it is important to select proper time or temperature conditions. Because of the ability to react in the melt state of PBT/PC blends, a Multi-Cycle DSC method was used to monitor the change of crystallization from the melt after being treated at 290°C for 3 min, then an additional 5 min, and finally another 5 min (Fig. 9). Clearly, on first cooling, sample A and B do not show any differences in crystallization behavior; on second cooling, sample A seems to change more than sample B; finally, on third cooling, sample A exhibits a much lower T_c and a broad crystallization peak. Obviously, this approach is easier to carry out

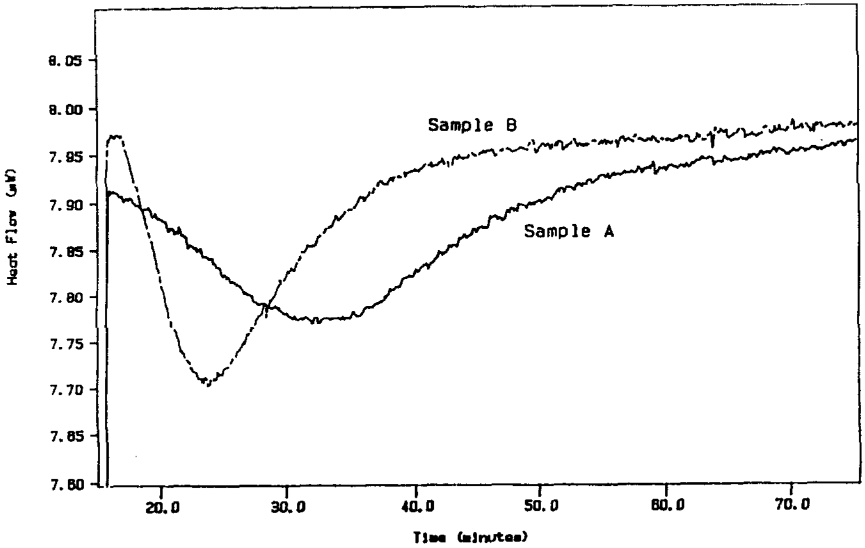

Fig. 7 Isothermal crystallization of sample A and B at 203°C

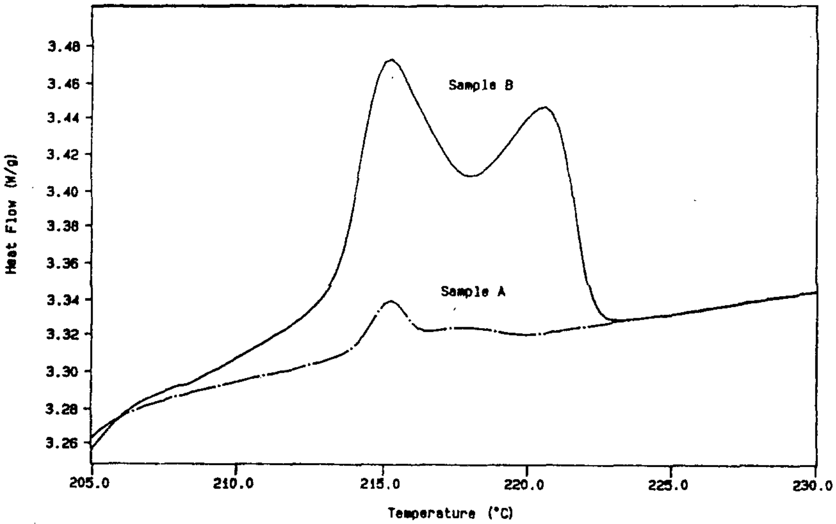

Fig. 8 DSC melting curves of sample A and B at 5°C min^{-1} after being partially crystallized at 203°C for 12 min

compared to the MDSC method which has to treat the samples identically every time and run at relatively slow heating rate. However, the T_c difference between sample A and B by conventional DSC is much smaller than those by MDSC and the differences in peak shape are not easily described quantitatively. In other words, the MDSC method is much more sensitive than other methods.

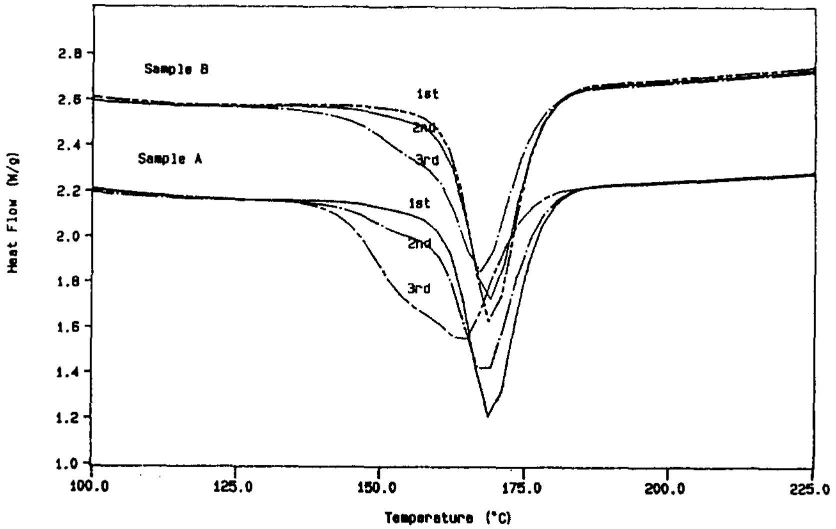

Fig. 9 Multi-Cycle DSC cooling curves for sample A and B after being treated at 290°C for different times

Conclusions

1. The total heat flow in MDSC may not be equal to the heat flow in conventional DSC when nucleating and crystallization processes are involved.
2. MDSC results for PBT/PC blends are strongly dependent on the prior heat treatment of the sample (melting and quenching conditions).
3. The MDSC method is still much more sensitive than other conventional DSC methods, but one may also use conventional DSC to characterize the difference in crystallization by selecting proper methodology.

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The authors like to thank Drs. Bernhard Wunderlich and Robert Gallucci for helpful discussion, David Shaker and Mary Parsonage for some DSC experiments. Technical support from TA Instruments is also greatly appreciated.

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