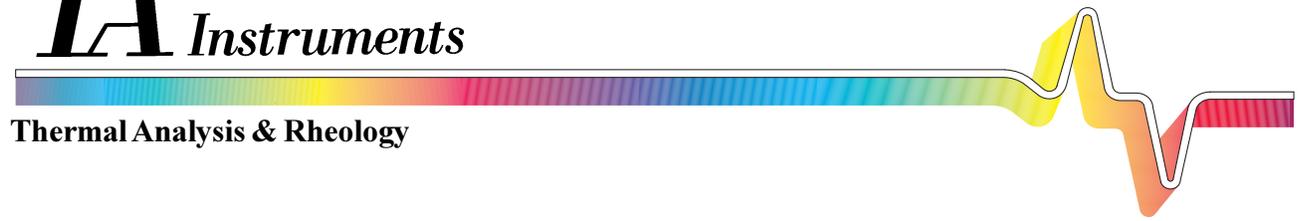


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Thermal Analysis & Rheology



CHARACTERIZATION OF A POLYCARBONATE/ POLYETHERESTER BLEND USING 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 phenomena such as the glass transition and melting, 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 polycarbonate/polyetherester (PC/PEE) blend, 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: 15 mg (nominal) in crimped aluminum pans; cut to ensure a flat side for good sample/pan contact

Purge: Helium at 25 cc/minute

Calibration:

- The heat of fusion was calibrated with Indium to 28.4 J/g
- Temperature was calibrated based on Indium melt onset at 156.6°C
- Heat capacity was calibrated with low density polyethylene to 2.57 J/g°C at 150°C (above melt) using isothermal MDSC with a (±0.424°C) amplitude and a 40 second period.

MDSC parameters (optimized for analyzing 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 40 second period was chosen in this study.

- Underlying Heating Rate

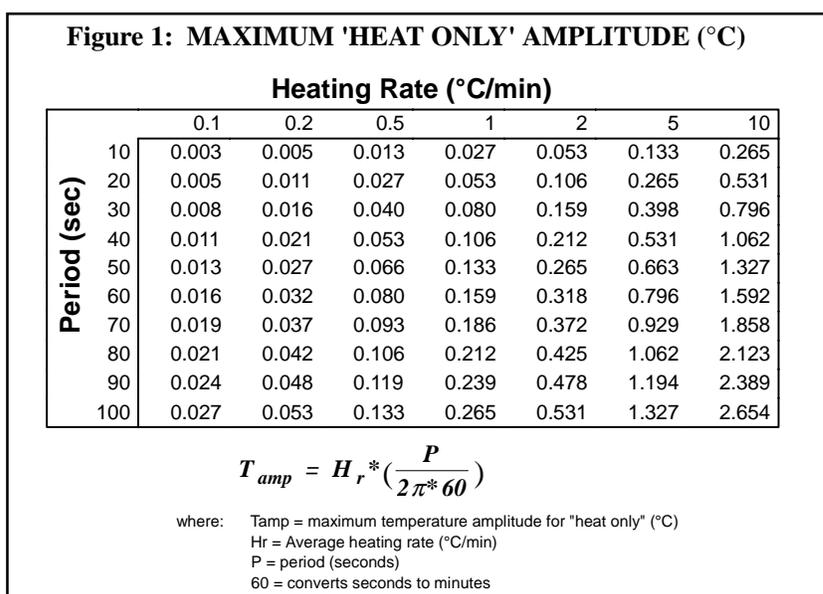
A heating rate which provides a minimum of 4-5 cycles at the half-height of the sharpest melting peak should be selected. 4°C/minute was selected in this study.

- 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 4°C/min heating rate with 40 second period is twice the value at 2°C/min ($2 \times 0.212 = \pm 0.424^\circ\text{C}$). 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 based on the classical heat flow equation shown previously. 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:

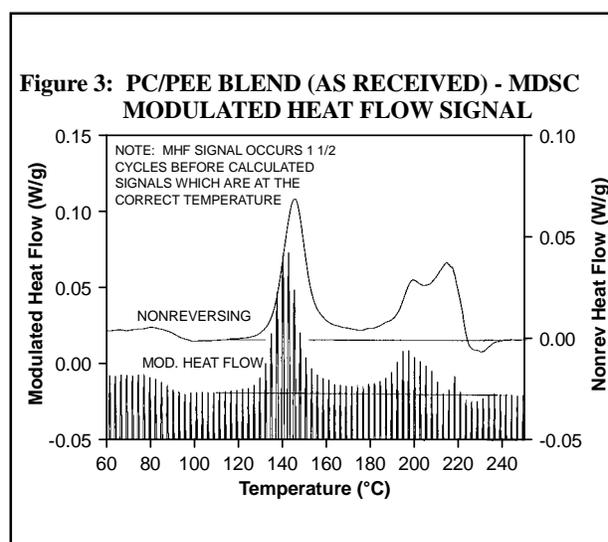
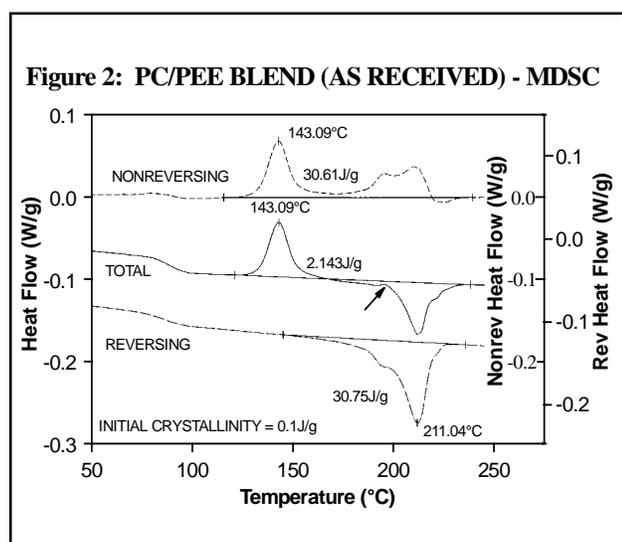
Preliminary experiments indicated that the glass transition of this blend changes as the blend is temperature cycled. Therefore, the actual results were obtained as the blend was cycled four times between -50 and 250°C. The cooling rate was kept constant at 5°C/minute to separate cooling effects from material changes. Each cycle consisted of cooling at 5°C/minute to -50°C, equilibration for 5 minutes, heating at 4°C/minute in MDSC mode to 250°C, equilibration for 5 minutes, and then repeating the cycle.



RESULTS

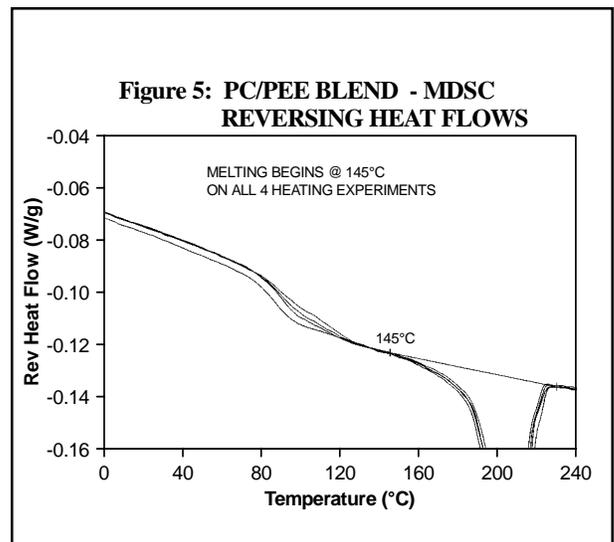
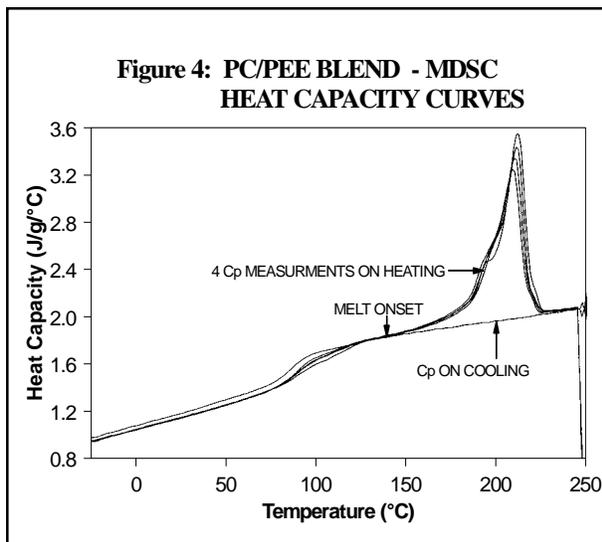
Separation of Simultaneous Melting and Crystallization/Crystalline Perfection Processes

Figure 2 shows the three primary modulated DSCTM signals for the PC/PEE blend “as-received”. The Total Heat Flow, which is qualitatively and quantitatively equivalent to the curve obtained from conventional DSC, indicates three transitions - a glass transition about 80°C, a cold crystallization peak at 143°C and a melting peak at 211°C. In addition, although there is no clear indication of a transition between the cold crystallization and the melt, the “baseline” has an apparent exothermic bump prior to the onset of melting. The reason for this bump becomes obvious once the modulated DSC reversing and nonreversing curves are evaluated. Figure 3 shows the top of the modulated heat flow curve before deconvolution. Since the experimental parameters as described earlier were set so that no cooling occurred during the modulated DSC experiment, the heat flow at the top of the modulated heat flow curve should be zero unless kinetic processes are occurring. This expanded view clearly shows that above the cold crystallization exotherm there are additional exothermic processes occurring. In the same temperature region, there are also endothermic processes occurring as seen from the reversing heat flow signal (Figure 2). These simultaneous exothermic and endothermic processes are believed to be associated with crystallization/melting/crystalline perfection prior to the onset of “bulk” melting at 211°C. Conventional DSC, which represents the sum of all thermal events occurring at any given time and temperature, cannot separate these overlapping events.



More Accurate Measurement of the Temperature Range of Melting

Using standard baseline extrapolation procedures, the onset of melting in conventional DSC for the “as received” blend is projected to be 195°C (Figure 2). Examination of the modulated DSC reversing heat flow, on the other hand, yields a significantly different result. Theory predicts that, in the absence of other phenomena, the heat flow curve prior to melting should be a linear, increasingly endothermic line with a slope directly related to heat capacity. Obviously, that is not the case for this blend. Endothermic deviation from baseline (onset of the “melting process”) actually occurs immediately after cold crystallization - about 50°C earlier than predicted by conventional DSC. Figures 4 and 5 further indicate that the onset of melting is consistent on subsequent reheating of the blend. Figure 4 shows the heat capacity results from the four heating curves overlaid with the heat capacity curve during cooling. The cooling curve heat capacity is not “contaminated” by the presence of any overlapping phenomena, and hence provides the expected linear, increasingly endothermic “baseline” predicted by theory. Figure 5 shows the reversing heat flow curves from the four heating curves. The inability of conventional DSC to accurately measure the range of melting is, of course, again directly related to the inability to separate simultaneous thermal events.

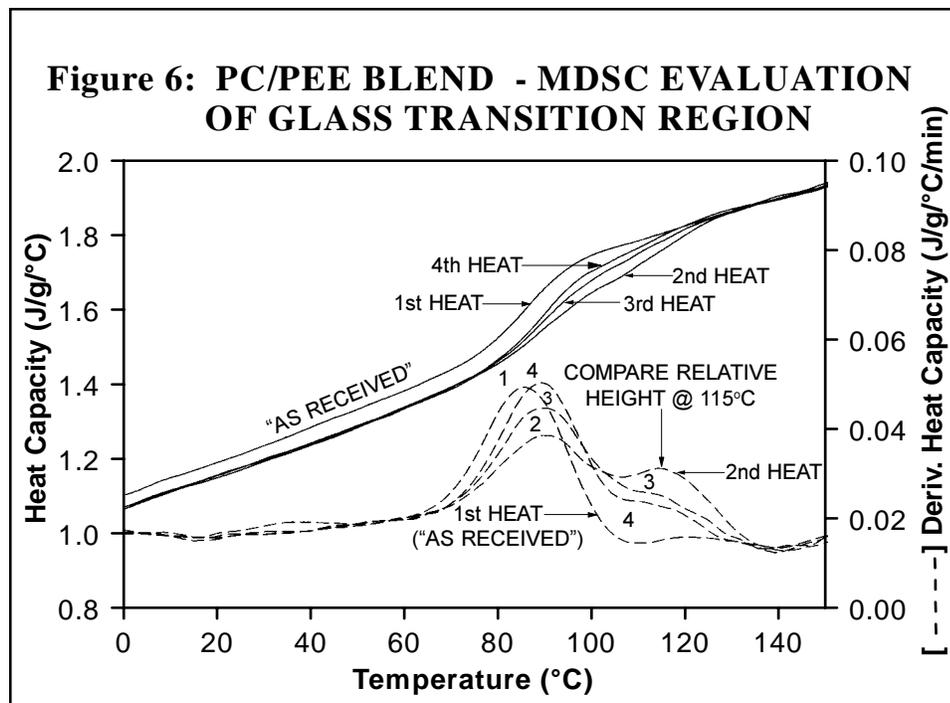


Increased Precision of Heat Capacity Measurements

The excellent precision of modulated DSC™ for measuring heat capacity is evident in Figure 4. The only deviation outside the glass transition region is seen in the initial heating of the “as-received” blend, and the higher heat capacity seen there might be expected given the material was prepared by injection molding and hence it was probably cooled at a faster rate.

In addition to having excellent precision, the heat capacity signal also has an excellent baseline because all thermal drift in the calorimeter which occurs at a different frequency, is eliminated due to the way that the signal is calculated.

The combination of excellent precision and baseline makes it possible to detect small changes in structure as seen in the glass transition of the different heating segments in Figure 6. The time-based derivative of the heat capacity signal (dashed line) is particularly useful for emphasizing differences. In this case, there are two events in the T_g region which change in size as the material is cycled. The most likely interpretation of these two events is that the higher temperature (weaker) event is associated with amorphous material trapped in crystalline regions of the polymer where molecular mobility is restricted until a higher temperature is reached. This theory, and the relative heights of the higher temperature event, is supported by the initial crystallinity results described in the next section.



More Accurate Measurement of Initial Crystallinity

Conventional DSC has been widely used to assess the initial crystallinity of polymers based on comparison of the enthalpies associated with crystallization and melting. However, because the cold crystallization process, as occurs here, often overlaps the melting range, it is difficult to make accurate initial crystallinity measurements with conventional DSC [1,2]. The only reasonable alternative, therefore, in conventional DSC is to integrate the sum of the crystallization and melting processes by drawing a single baseline between the onset of crystallization (approx 120°C) and end of melting (approx. 235°C). Using this approach yields a value which is still 2-3 J/g too high (Figure 2). On the other hand, the modulated DSC™ calculation of initial crystallinity is based on summing the reversing (melting) and nonreversing (crystallization) signals and it has the advantage that separate integration limits can be accurately defined and used. Figure 7 summarizes the results obtained from the four heating cycles on the PC/PEE blend. The modulated DSC initial crystallinity results agree well with the crystallization measured during controlled cooling between heating cycles, whereas the results from conventional DSC are too high. In addition, the initial crystallinity increases significantly between the “as received” and first heating cycle material but then decreases on each subsequent heating cycle. This agrees with the trends observed at the glass transition.

Figure 7: PC/PEE BLEND - INITIAL CRYSTALLINITY

SAMPLE	INITIAL CRYSTALLINITY (CONVENTIONAL DSC)	CRYSTALLINITY IMPARTED DURING COOLING	INITIAL CRYSTALLINITY (MDSC)
AS-RECEIVED	2.1 J/g	--	0.1 J/g
SECOND HEAT	12.5 J/g	8.2 J/g	9.8 J/g
THIRD HEAT	9.8 J/g	6.4 J/g	7.0 J/g
FOURTH HEAT	7.6 J/g	4.8 J/g	4.4 J/g

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 [3,4], evaluation of aging effects in amorphous PET [5], determination of thermal conductivity in polymers [6], evaluation of melting phenomena in polyethylene [7], and characterization of isothermal cure and vitrification in thermosets [8].

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3. TA Instruments Publication No. TS 22
4. TA Instruments Publication No. TS 24
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7. TA Instruments Publication No. TA 227
8. TA Instruments Publication No. TA 219

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