

OBTAINING MODULATED TEMPERATURE DSC CURVES THROUGH A NON-CONVENTIONAL DSC METHOD

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Abstract

The DSC curve obtained in conventional equipment usually only shows the resultant thermal effect due to simultaneous phenomena, which may occur during isothermal or dynamic analyses. This does not allow one to identify the processes properly and may cause an erroneous interpretation of the resulting curves.

Modulated DSC equipment enhances the operating conditions and the analysis capacity of conventional DSC by superimposing a sinusoidal temperature modulation on the linear temperature control. Thus reversing and non-reversing heat flow curves are obtained, which are, respectively, the heat capacity and kinetic components of the DSC curve. Therefore, events that are related to these components can be separately analyzed.

A method to obtain curves similar to the MDSC reversing and non-reversing components was developed using conventional DSC equipment in a non-conventional way. It was applied to analyze samples of poly(ethylene terephthalate) (PET) taken from bottles of mineral water. The second PET crystallization step that occurs during its melting was quantified and an apparent initial crystallinity was obtained from the resulting data.

Keywords: modulated temperature DSC (mt-DSC), non-conventional DSC, poly(ethylene terephthalate), PET crystallization

Introduction

The DSC curves obtained using conventional equipment usually only show the resultant thermal effect due to simultaneous events, which can occur during isothermal or dynamic analyses. This does not allow one to identify the processes properly and may cause erroneous interpretation of the resulting curves.

Modulated DSC equipment, which was introduced in the early 90's [1, 2], enhanced the operating conditions and the analysis capacity of conventional DSC by adding a sinusoidal modulation term to the linear temperature control function with constant heating rate. Besides producing a plot of total heat flow, which is equivalent

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to the conventional DSC curve, mt-DSC can produce so-called 'reversing' and 'non-reversing' heat flow curves [3], which show, respectively, the heat capacity and kinetic components of the total curve. As a consequence, the events that are related to those components can be separately analyzed. This solves some of the interpretation problems of complex systems, as well as contributes to more precise thermal characterization of the materials being studied [4].

Modulated temperature differential scanning calorimetry (mt-DSC) [5] has been used in many applications, including the direct measurement of heat capacity [6], the study of the glass-transition kinetics of polymers [7], physical aging of sugar glasses [7], cure of isothermal and non-isothermal thermosetting systems [8–10], evaluation of polymer blends [11, 12], and characterization of melting phenomena of linear low-density polyethylene (LLDPE) [13] and poly(ethylene terephthalate) (PET) [3].

Conventional DSC curves of poly(ethylene terephthalate) samples usually show a glass transition, followed by a crystallization exotherm (when the sample was formerly quenched) and a separate melting endotherm occurs at higher temperature ranges. If the same quenched sample is analyzed by modulated DSC, the non-reversing heat flow curve shows that a second exothermic crystallization peak occurs during melting. The reversing heat flow curve in turn, shows a bigger melting peak than obtained in a conventional DSC curve [3], which represents the resulting difference between the respective thermal effects.

A method was developed to obtain curves similar to the mt-MDSC reversing and non-reversing components by using conventional DSC equipment in a non-conventional way. The method was applied to analyze samples of PET taken from bottles of mineral water. The second PET crystallization step that occurs during melting can be seen and quantified and an apparent initial crystallinity can be obtained from the resulting heat flux components.

Modulated temperature DSC

The theory and the discussion of the operating variables and conditions of mt-DSC have been extensively presented and discussed in the literature [1–3].

In mt-DSC analysis, the programmed temperature (T) can be expressed as follows [2]:

$$T(t)=T_0+bt+B\sin(\omega t) \quad (1)$$

where T_0 is the starting temperature, b the heating rate, t the analysis time, B the amplitude of the temperature modulation and ω the frequency, which is equal to $2\pi/P$, where P is the period of the modulation. As a consequence, the heating rate is expressed as:

$$dT/dt=b+B\omega \cos(\omega t) \quad (2)$$

In Eq. (1), the first two terms represent the programmed temperature function used in conventional DSC, which usually uses a constant heating rate β . The equation which describes the resultant heat flow is:

$$dQ/dt = C_p dT/dt + f(t, T) \quad (3)$$

where the first term depends on the sample heat capacity (C_p) and the second, on any kinetic process which may occur as a function of the temperature during the analysis. These terms are named, respectively, as the reversing and non-reversing components of the total heat flow.

Because the heating rate in mt-DSC is a periodic function, as can be seen by Eq. (2), the measured heat flow is a periodic function as well, and both have their respective amplitude of modulation.

If it is assumed [2] that the temperature modulation is small and that, over this interval, the response of the rate of the kinetic process to the temperature can be approximated as linear, the resulting heat flow can be expressed as:

$$dQ/dt = C_p (b + B\omega \cos(\omega t)) + f'(t, T) + C \sin(\omega t) \quad (4)$$

where $f'(t, T)$ is the average underlying kinetic function, once the effect of the sine wave modulation has been subtracted, and C is the amplitude of the kinetic response to this modulation.

As can be seen, the measured heating rate and total heat flow signals are cyclic functions that depend on the chosen operating variables. This permits the heat capacity of the sample (C_p) to be calculated continuously, by dividing the modulated heat flow amplitude by the modulated heating rate amplitude [4]. Thus, the reversing heat flow component of Eq. (3) is obtained by multiplying C_p by the underlying heating rate β .

Using a discrete Fourier transform (DFT) algorithm [2], the corresponding underlying heat flow signals at any time t , may be used to reconstitute the result of a conventional DSC heat flow curve, which is the left-hand term of Eq. (3). The non-reversing heat flow component is calculated by subtracting the reversing one from the underlying heat flow at the same time.

The non-conventional DSC method

Using a conventional TA Instruments DSC, model 2010, a non-conventional method was developed in order to produce heat flow curves similar to those obtained in an mt-DSC. The method includes two different type of analysis for each sample and a software for processing the data, as described below.

In the first analysis, two different constant heating (or cooling) rates (β_1 and β_2) are applied consecutively for the same period of time to a sample, and this is repeated over the desired temperature range. Thus, a resulting cyclic heating rate curve may be induced, which oscillates between or very close to β_1 and β_2 , depending on these values, the sample material and mass and the period programmed for each constant rate application. This results in a cyclic heat flow curve, which also shows a modulated

heat flow amplitude as a function of time and temperature, similar to the one obtained in an mt-DSC. This analysis, with a heating rate modulation in a conventional DSC equipment, will be referred to in the text as DSCM.

As a second step, a conventional DSC analysis is performed with the same original sample at a heating rate β , such that β is equal to the arithmetic mean of β_1 and β_2 . The resulting heat flux curve will represent, practically, the underlying curve that would be obtained in an mt-DSC, with an underlying heating rate β and the same heating rate amplitude and frequency.

The second analysis gives the total heat flow curve. Applying the same procedure as described for the mt-DSC to the data resulting from both analyses, using software developed by the author for that purpose, curves similar to the reversing and non-reversing heat flow curves can be obtained as below described.

mt-DSC equipment has appropriate hardware and software to do many modulations over the course of any observed transition. Conventional DSC equipment has limitations on the number of heating rate modulations it can perform over a large temperature range, because it is not designed for that purpose. When there are no transitions within a temperature range, a few modulations are sufficient to obtain a reliable total heat flux curve, which is, in this case, a straight line representing the average of the corresponding values at a given time t (or temperature) of the points taken from the straight lines passing through the maximum and minimum values, respectively, of the modulating heat flux.

For temperature ranges where transitions occur, using the same approach, non-linear functions may be obtained by applying numerical methods to the maximum and minimum points of the modulated heat flux. However, the limitations of conventional DSC, described above, may result in erroneous estimations of the total heat flux and, consequently, incorrectly calculated modulation amplitudes, which are not constant during transitions. Errors may be avoided by using many multiple modulating steps applied to shorter subsequent temperature ranges, but this procedure would be too time-consuming.

The second conventional DSC analysis performed in the present method is necessary to bypass this difficulty and to have a correct and continuous total heat flux measurement at any desired temperature. Thus, the amplitudes of the heat flux modulation, which are used for the calculation of the heat capacity, as done in mt-DSC, are obtained from the moduli of the differences between the maximum and minimum values of the modulating heat flux produced and the corresponding DSC heat flux, at a given time or temperature. From these initial values, the amplitude of the heating flux at any temperature is calculated by applying numerical methods.

The amplitude of the heating rate at a given temperature is obtained from linear interpolation of the nearest maximum and minimum points of the resulting modulating heating rate curve produced by the DSC equipment. Thus, the points corresponding to the heat capacity of the sample (C_p) at desired temperatures, and those of the reversible and non-reversible heat flow curves are obtained as calculated in mt-DSC.

Materials and methods

The non-conventional DSC method was applied to two samples of PET, taken from two different brands of mineral water bottles, named A and B. After being melted at 300°C in sealed aluminum pans, samples of about 6 mg of each type, were quenched with blowing air, as well as slowly cooled to ambient temperatures, in order to have A and B samples with different resulting crystallinities before the analysis.

The reversing and non-reversing heat flux curves show, respectively, the melting endotherm and crystallization exotherm(s) occurring during the analyses. The lower the initial crystallinity of a PET sample is, the lower will be the difference ($M-C_i$) [13], where M is the area of the melting peak per unit mass and C_i is the total area of the crystallization peak(s) per unit mass (first and/or second stages, when this is the case). C_i represents the total enthalpy of crystallization and M , the enthalpy of fusion. The area of each peak, delimited by a straight line joining the adjacent points of the baseline and the respective peak curve, was measured by applying a numerical integration method and the corresponding enthalpies were obtained in J g^{-1} .

The heat of fusion varies as a function of temperature and the first crystallization step, when observed, usually occurs at lower temperature ranges than melting. On the other hand, the difference between the heat of crystallization of PET samples and the corresponding heat of fusion is about 2 J g^{-1} [3]. This is of the same order as the precision in the measurement of the heat of fusion, so we lump it in with the experimental imprecision. Therefore, the initial crystallinity of the samples was compared by using a non-dimensional parameter, which was named 'apparent initial crystallinity' (AIC), obtained by Eq. (5).

$$\text{AIC}=100((M-C_i)/M) \quad (5)$$

It must be noted that the AIC, which may be obtained from MDSC or DSCM data, is calculated on the basis of the heat of fusion measured from the reversible heat flux curve and not on the 'true' or 'absolute' heat of fusion of the polymer.

The standard calibration procedure of the heat flux signal, as recommended by the manufacturer, was performed with indium, at the same underlying heating rate as that for the analyses. The mass of each sample was measured with a precision of 10^{-6} g and the difference between the mass of any sample pan and that of the reference was always less than $2 \cdot 10^{-5} \text{ g}$.

All the analyses using the non-conventional DSC procedure, described previously, were performed using 45 ml min^{-1} of nitrogen as the purge gas. The analysis with the modulation step (DSCM) was done by programming alternating 4 and 6°C min^{-1} constant heating rates, applied for a period of 60 s each. The heating rate modulation was started at 110 and ended at 290°C, which is the range where usually the first crystallization, melting and the second crystallization of PET occur. Before and after the modulation range, a constant heating rate of 5°C min^{-1} was used, as done in the second non-modulated conventional DSC analysis, to have a reference baseline.

Results and discussion

Typical plots of the raw heat flow curves obtained for a slowly cooled sample A of PET, are shown in Fig. 1. The conventional DSC curve, which represents the total heat flow during the modulated analysis, does not show a crystallization step. This was expected because it had already occurred during the slow cooling step before the analysis. The modulated heat flow curve shows a variable amplitude which is due to the events which can only be seen in Fig. 2, which shows the reversing and non-reversing components of the total heat flow, in the temperature range where the heating

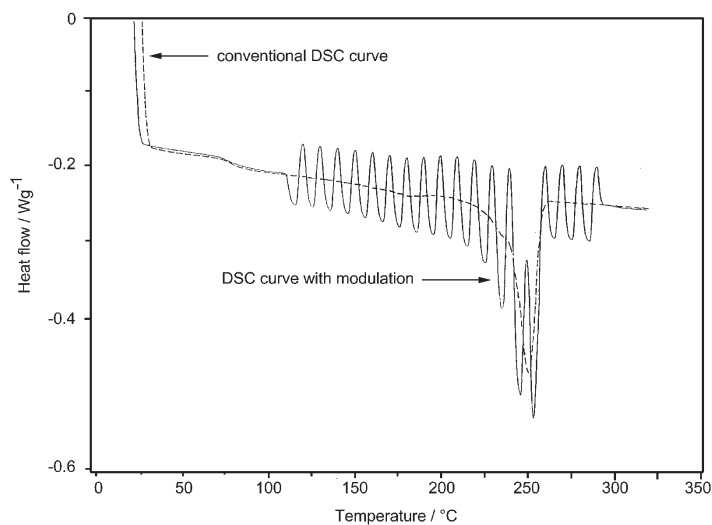


Fig. 1 Typical conventional DSC and DSCM raw heat flow curves for slowly cooled A sample

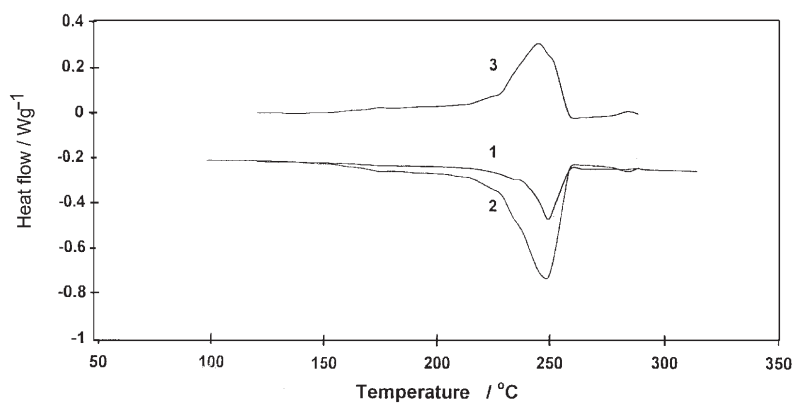


Fig. 2 Heat flow curves obtained by the non-conventional DSC method for slowly cooled A sample. (1 – total, 2 – reversing, 3 – non-reversing)

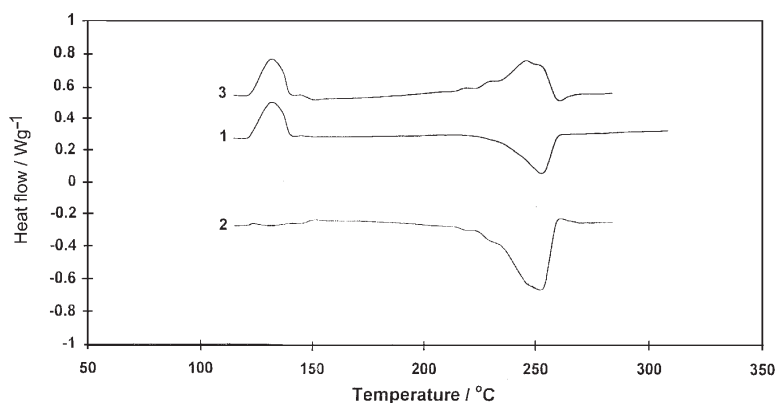


Fig. 3 Heat flow curves obtained by the non-conventional DSC method for quench cooled A sample. (1 – total, 2 – reversing, 3 – non-reversing)

rate modulation was applied. A crystallization step begins at about 150°C, simultaneously with the beginning of PET melting, which actually has a much higher melting peak than the one shown in the conventional DSC curve. This occurs because the latter is the resulting difference between the real endothermic melting peak shown in the reversing component and the exothermic crystallization peak shown by the non-reversing component.

Figure 3 shows the results for sample A after quench cooling. It is clear that, in this case, a first crystallization step occurs between 120 and 140°C. The reversible curve does not show any other significant simultaneous event in that temperature range. The conventional DSC curve also shows practically the same peak. Again a crystallization step occurs during melting, which can only be quantified by the non-reversing component of the total heat flow.

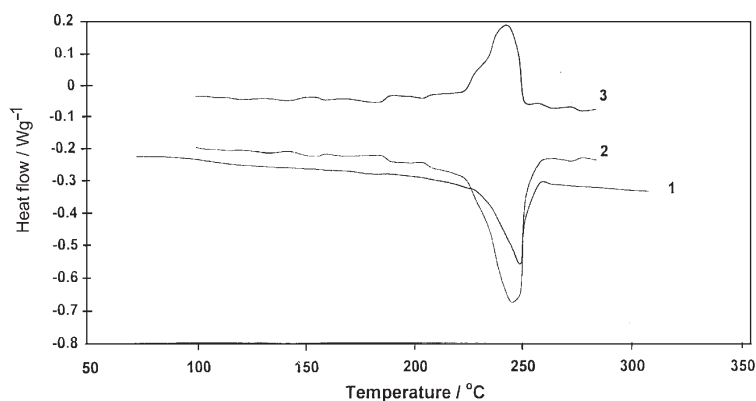


Fig. 4 Heat flow curves obtained by the non-conventional DSC method for slowly cooled B sample. (1 – total, 2 – reversing, 3 – non-reversing)

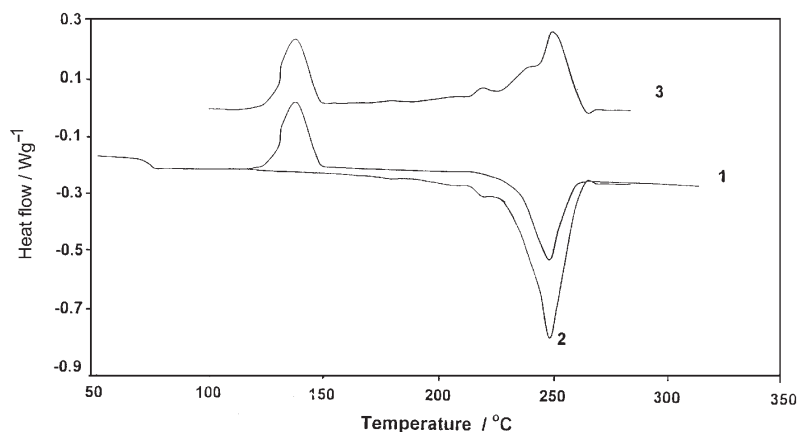


Fig. 5 Heat flow curves obtained by the non-conventional DSC method for quench cooled B sample. (1 – total, 2 – reversing, 3 – non-reversing)

Similar occurrences can be seen in Figs 4 and 5, which show, respectively, the analyses of the slowly cooled and quenched B samples.

Table 1 Crystallization and melting data obtained for PET samples using non-conventional DSC method

Sample	Type of cooling	Crystallization enthalpy/ J g^{-1}			Melting enthalpy/ J g^{-1}	Apparent initial crystallinity/%
		1st	2nd	total		
A	slow	0	-100.7	-100.7	142.7	29.4±1.4
A	quench	-28.0	-72.6	-100.5	116.3	13.6±1.7
B	slow	0	-65.7	-65.7	110.4	40.5±1.8
B	quench	-34.8	-78.7	-113.6	126.2	10.0±1.6

The estimated enthalpies obtained from the corresponding areas of crystallization and melting peaks of each sample are shown in Table 1, as well as the estimated AIC with their respective estimated deviations, considering experimental errors in heat flow measurements. As expected, the slowly cooled samples show a higher initial crystallinity than those which were quenched. Although the initial crystallinities of the quenched samples are low, the results show that quenching only to ambient temperature, simulating a fast cooling in blowing air of a melted piece of PET, is not sufficient to avoid some crystallization.

Conclusions

When two different constant heating (or cooling) rates are alternately applied to a sample in a conventional DSC equipment, a resulting cyclic heating rate, as well as a cyclic heat flow may be effectively induced, similar to those occurring in temperature modulated DSC.

When a conventional DSC is run using the same underlying heating rate as for an mt-DSC analysis, the resulting DSC curve is equivalent to the total heat flow obtained in the mt-DSC analysis.

Using a non-conventional method in a conventional DSC equipment, with the above steps and a proper processing of the resulting data, it is possible to obtain curves similar to the reversing and non-reversing heat flow components of an mt-DSC.

From the resulting data, an apparent initial crystallinity may be calculated on the basis of the heat of fusion measured from the reversible heat flux curve.

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