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Thermochimica Acta 260 (1995) 1-16

thermochimica
acta

A comparison of different evaluation methods in modulated temperature DSC

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Received 3 January 1995; accepted 13 February 1995

Abstract

Modulated temperature-DSC is a new method for measuring the thermal behaviour of materials. In this method, the response of the sample to a time-dependent signal (sinusoidal temperature change) is measured. Two different methods are known for the evaluation of the measured data. The first is the separation of the measured data into reversing and non-reversing components of heat flow. The second is based on the linear response theory and yields a complex heat capacity with a real part (storage heat capacity) and an imaginary part (loss heat capacity).

The theoretical basis and the possibilities of interpretation of both evaluation methods are investigated. The results of both methods are compared theoretically for the case of simple time-dependent processes. Experimental results are given for the glass transition process.

Keywords: Glass transition; Heat capacity; Modulated DSC; Time-dependent reactions

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List of symbols

A	pre-exponential factor of the Arrhenius law
a_f	slope of the function f
B	activation constant of the Arrhenius law
b_f	temperature-independent part of the function
$C(t)$	time-dependent heat capacity
C	complex heat capacity (Fourier transformed $C(t)$)
$\dot{C}$	derivative of $C(t)$
$\lvert C \rvert$	modulus of C
C'	storage heat capacity (real part of C)
C''	loss heat capacity (imaginary part of C)

SSDI 0040-6031(95)02294-5

C_p	(static) heat capacity of the sample (at constant pressure)
C_β	time-dependent heat capacity measured at the scanning rate β_0
C_∞	heat capacity at high frequencies ($\omega \rightarrow \infty$)
f	time-dependent function which describes the kinetic component of the measured signal
f_1	time-dependent function which describes the thermodynamic function of the measured signal
H	enthalpy
i	imaginary unit
Q	heat
Q_r	heat of reaction
$Q_{rp,T}$	Q_r at constant pressure and temperature
T	temperature
T_a	temperature amplitude
T_0	starting temperature
t	time
t_p	period of sinusoidal signal

Greek letters

α_Φ	linear part of the heat flow of reaction
β	temperature change
β_0	scanning rate
v	rate of reaction
$v_{p,T}$	v at constant pressure and temperature
τ	relaxation time
Φ	heat flow rate
Φ_a	amplitude of sinusoidal heat flow rate
Φ_d	dynamic (or oscillating) component of heat flow rate
Φ_{dc}	deconvoluted heat flow rate; underlying heat flow rate
Φ_{non}	non-reversing component of heat flow rate
Φ_r	reaction heat flow rate
Φ_{rev}	reversing component of heat flow rate
φ	phase shift between heat flow and temperature change
ω	angular frequency
ω_0	angular frequency of the measurement
ω_β	angular frequency of the measured thermal glass transition at the cooling rate β_0

1. Introduction

In conventional DSC, an isothermal or linear time/temperature program is used. After subtraction of the empty pan curve, correction for heat transport effects (desmearing) and calibration, one gets the curve of the heat flow rate $\Phi(t)$ into the sample versus temperature.

In modulated-temperature DSC (MT-DSC), the common temperature program is superimposed with a dynamic temperature change (sinusoidal in most cases). The measured signal is influenced by heat transfer conditions which change both the amplitude and the phase shift. After subtraction of the empty pan measurement under the same conditions and calibration, the heat flow rate into the sample $\Phi(t)$ can be calculated from the measured signal. The measured heat flow rate is usually separated into the underlying heat flow rate Φ_{dc} (this is approximately the conventional DSC curve) and the dynamic component Φ_d. There are two known methods for the determination of these curves.

In one method, published by Reading and coworkers [1–4], the reversing component of the heat flow rate Φ_{rev} is calculated from the dynamic component, whereas the so-called non-reversing component Φ_{non} is the difference between Φ_{dc} and Φ_{rev}.

The other evaluation method, published by Schawe [5], is based on the linear response theory in which the analysis of the dynamic component Φ_d yields a complex heat capacity C, with a real part C' (storage heat capacity) and an imaginary part C'' (loss heat capacity). This complex heat capacity is dependent on the frequency of the temperature modulation.

However, the results and also the interpretation are different for the two evaluation methods.

These new methods of evaluating and interpreting MT-DSC measurements require critical analysis in order to obtain a better understanding of the results and to permit a quantitative evaluation. In this paper the theoretical background to the evaluation of the measured curves is investigated, irrespective of questions concerning the calibration methods and the construction of the DSC in question.

2. Theoretical basis of the evaluation methods

2.1. The approach of separating the reversing and non-reversing components

The fundamental equations leading to the separation of reversing and non-reversing components of the MT-DSC signal have been published by Reading and coworkers [1–4]. This procedure is used commercially both in MDSC (TA-Instruments) and ODSC (Seiko Instruments) [1,6]. The theoretical part of this section is taken from Refs.[1–4].

As mentioned, a sinusoidal temperature change with angular frequency $\omega_0 = 2\pi/t_p$ (t_p is the period) and amplitude T_a is superimposed upon a conventional DSC temperature program (with constant scanning rate β_0 and starting temperature T_0)

$$T(t) = T_0 + \beta_0 t + T_a \sin \omega_0 t \tag{1}$$

It is postulated that for the heat flow rate into the sample $\Phi(t)$, the following equation is valid [2–4]

$$\Phi(t) = \frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t, T) \tag{2a}$$

From Ref. [1]

$$\Phi(t)=\frac{\mathrm{d}Q}{\mathrm{d}t}=(C_p+f_1(t,T))\frac{\mathrm{d}T}{\mathrm{d}t}+f(t,T) \tag{2b}$$

where C_p is the heat capacity of the sample and $f(t, T)$ describes the kinetic component of the heat flow rate. In Eq. (2b) the heat capacity is supplemented by an additional time-dependent function $f_1(t, T)$ to describe the thermodynamic heat flow component. To obtain the results, which are published in Refs. [2–4], the function $f(t, T)$ in Eq. (2a) must be linear with temperature

$$f(t,T)=a_f(t)T+b_f(t) \tag{3}$$

Inserting Eqs. (1) and (3) into Eq. (2a), we obtain

$$\Phi(T(t))=C_p(\beta_0+T_a\omega_0\cos(\omega_0 t))+a_f T_a\sin(\omega_0 t)+f(t,T) \tag{4}$$

with

$$f(t,T)=a_f(t)(T_0+\beta_0 t)+b_f(t) \tag{5}$$

If Eq. (2b) is used instead of Eq. (2a), and $f_1(t, T)$ treated as in Eq. (3), we obtain a result with the same structure and information as Eq. (4). Elementary transformations of Eq. (4) yield

$$\Phi(T(t))=\Phi_{dc}(T(t))+\Phi_a(T(t))\cos(\omega_0 t-\varphi) \tag{6}$$

where φ is the phase shift, Φ_a the cyclic component, and Φ_{dc} the underlying heat flow; Φ_a is then

$$\Phi_a=T_a\sqrt{C_p^2\omega_0^2+a_f^2} \tag{7}$$

We obtain the reversing component of the heat flow from

$$\Phi_{rev}(T(t))=\frac{\Phi_a(T(t))}{T_a\omega_0}\beta_0 \tag{8}$$

The kinetic component (the non-reversing component) is then

$$\Phi_{non}(T(t))=\Phi_{dc}(T(t))-\Phi_{rev}(T(t)) \tag{9}$$

We will now discuss some results obtained using this approach. If no physical or chemical transformations occur in the sample, the function $f(t,T)$ in Eq. (2) and its derivative a_f (see Eq. (3)) are both zero. In this case a comparison of Eqs. (7) and (8) shows that the reversing component Φ_{rev} corresponds to the heat capacity. Then the heat capacity of the sample can be determined directly from the amplitude of the measured heat flow rate. This method is discussed in Refs. [7] and [8]. In the case of time-dependent thermal events in the sample, a_f in Eq. (7) cannot be neglected. The problem is then to distinguish between the influence of C_p and a_f on Φ_a and to interpret a_f.

As will be shown in the next section, this method of evaluating MT-DSC measurement results represents a special case, which is valid only for time-independent events in the sample or in the case of isothermal measurements ($\beta_0 = 0$). If the events in the sample are time-dependent (as for instance in glass transitions), this method of evaluation develops interpretation problems.

2.2. The complex heat capacity approach

A more detailed discussion of the theoretical basis of this evaluation method is given in Ref. [5], which can be summarized as follows.

If a physical system is in equilibrium, classical thermodynamics describes it by time-independent potential functions. The connection between the enthalpy and temperature is then

$$\partial H(T) = C(T)\partial T \tag{10}$$

where the heat capacity $C(T)$ describes the behaviour of the material. In the case of a constant heating rate β_0, the heat flow rate into the sample is

$$\Phi(T) = C(T)\beta_0 \tag{11}$$

If a thermal event depends on time, we may describe this phenomenon with the aid of a time-dependent heat capacity $C(t)$.

If the disturbances in the system during the measurement are sufficiently small-scale, and the system is close to a local equilibrium, a description using the linear response theory is possible.

The relationship between the (time-dependent) enthalpy and the temperature is then given by the convolution product

$$\partial H(t) = \int_{-\infty}^{t} \dot{C}(t-t')\partial T(t')\mathrm{d}t' \tag{12}$$

with

$$\dot{C}(t) = \frac{\mathrm{d}C(t)}{\mathrm{d}t} \tag{13}$$

After Fourier transformation, Eq. (12) reads as a normal algebraic product

$$H(\omega) = C(\omega)T(\omega) \tag{14}$$

with a frequency-dependent complex heat capacity

$$C(\omega) = C'(\omega) - iC''(\omega) \tag{15}$$

which is connected to $C(t)$ (caused by time-dependent molecular movements) by Fourier transformation

$$C(\omega) = C_\infty + i\omega\int_0^t (C(t) - C_\infty)\mathrm{e}^{-i\omega t}\mathrm{d}t \tag{16a}$$

or

$$C(\omega) = C_\infty + \int_0^t \dot{C}(t)\mathrm{e}^{-i\omega t}\mathrm{d}t \tag{16b}$$

(i, imaginary unit; ω, angular frequency)

The real part of the heat capacity, C', describes molecular motions and corresponds to the heat capacity in the case of equilibrium C_p. The imaginary part C'' is linked to dissipation processes.

In DSC measurements, the heat flow rate into the sample

$$\Phi = \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_p = \frac{\mathrm{d}H}{\mathrm{d}t} \tag{17}$$

is the measured quantity.

By inserting Eq. (17) into Eq. (12), one obtains the following for the measurement signal

$$\Phi(t) = \int_0^t \dot{C}(t-t')\beta(t')\mathrm{d}t' \tag{18}$$

where

$$\beta(t) = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{19}$$

In the case of MT-DSC, a sinusoidal temperature change is superimposed on a linear one and, from Eq.(1)

$$\beta(t) = \beta_0 + \omega_0 T_a \cos(\omega_0 t) \tag{20}$$

Insertion of Eq. (20) into Eq. (18) yields

$$\Phi(T(t)) = C_\beta(T)\beta_0 + \omega_0 T_a |C(T, \omega_0)| \cos(\omega_0 t - \varphi) \tag{21}$$

with

$$|C| = \sqrt{C'^2 + C''^2} \tag{22}$$

In the case of time-dependent phenomena, C_β corresponds to the heat capacity which, in a conventional DSC measurement, should be determined at a constant heating rate β_0. C_β is different from the static heat capacity C_p at equilibrium. The constant scanning rate β_0 can be connected to a certain average frequency ω_β. An example of such a phenomenon is the dependence of the glass transition temperature T_g on the cooling rate [9].

If the underlying scanning rate β_0 is slow then the following is valid

$$\omega_\beta \ll \omega_0 \tag{23}$$

and

$$C_\beta(T) \simeq |C(T, \omega_\beta)| \tag{24}$$

These results must now be interpreted.

The assumption was that the experiment took place at a sufficiently small underlying scanning rate β_0 and a sufficiently small temperature amplitude T_a. In this case the measured curve may be considered as a superposition of two independent signals, an underlying heat flow Φ_{dc} (equal to the conventional DSC signal) and an oscillating heat flow. If we take Φ_a as the amplitude of the oscillating part of Eq. (21), we obtain the modulus of the complex heat capacity

$$|C(T,\omega_0)| = \frac{\Phi_a(T,\omega_0)}{T_a\omega_0} \tag{25}$$

From this value, and the phase shift φ between the oscillating heat flow signal and the temperature change, the real and imaginary parts of the heat capacity can be calculated

$$C'(\omega_0) = |C(\omega_0)|\cos\varphi \tag{26}$$

and

$$C''(\omega_0) = |C(\omega_0)|\sin\varphi \tag{27}$$

In general both components are dependent on the measurement frequency ω_0.

In the case of time-dependent processes, the heat capacity from the underlying signal C_β and that from the oscillating signal $|C(\omega_0)|$ are indeed different. Only in the case of measurements without a time-dependent thermal event are C_β, $|C(\omega_0)|$ and $C'(\omega_0)$ identical, and $C''(\omega_0) = 0$.

3. Differences between the evaluation methods

Comparison of the heat flow rate formulae of the two methods (Eqs. (6) and (21)) shows that these relationships look alike. In both cases the measured heat flow is a superposition of an underlying heat flow and an oscillating heat flow. But the interpretation of these quantities is different. The differences are listed in Table 1.

Reading's separation method [1–4] has an empirical basis: consequently the equations and quantities contain little information. Our evaluation method [5] is based on the well-known linear response theory and we have the relaxation theory and irreversible thermodynamics at our disposal for interpretation of the measured quantities.

Table 1

Comparison of the different interpretation of the resulting quantities from MT-DSC measurements (Eqs. (6) and (21)). Method 1 (separation of "reversing" and "non-reversing" component) is described by Reading et al. [1–4]; method 2 (evaluation of a complex heat capacity) is described in Ref. [5]

	Method 1	Method 2
Underlying heat flow	The same information as the conventional DSC curve	The same information as the conventional DSC curve
Amplitude of the oscillating heat flow	Relative complex connection between the time-independent heat capacity C_p and the derivative of time-dependent function f (Eq. (7)). A separation of these two values is not easy	Includes the information on the modulus of the complex heat capacity. An additional term is not necessary for the interpretation
Phase shift of the oscillating heat flow	Not used	Necessary for the calculation of storage and loss heat capacity

3.1. Differences in theoretical foundations

This section compares the fundamental basis of the two evaluation methods. To make this clear, a general description of a linear time-dependent reaction under non-isothermal conditions is given.

The fundamental relationship in the evaluation method of Reading et al. [2–4] is Eq. (2). The time-dependent behaviour is described by the kinetic function $f(T, t)$. In the case of reactions, this equals the reaction heat flow rate $\Phi_r(t)$. If a time-dependent reaction takes place under isothermal conditions, then the following is valid

$$\Phi_r(t) = \left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{p,T} = -Q_{rp,T} v_{p,T}(t) \tag{28}$$

where $Q_{r\ p,T}$ is the heat of reaction and $v_{p,T}$ is the rate of reaction [10]. In Eq. (28), $Q_{rp,T}$ and $v_{p,T}$ are independent of temperature (isothermal reactions). This is not valid in general. If $Q_{rp,T}$ and $v_{p,T}$ are temperature functions, then it is not correct to use Eqs. (2) or (28) for non-isothermal processes. We demonstrate this by calculating the heat flow rate into the sample for a simple non-isothermal example. To simplify, we assume that the temperature dependence of the heat capacity may be neglected. We consider a linear process with a step-shaped heating program. At the initial temperature T_0, a heat flow rate

$$\Phi(t, T) = \Phi(t, T_0) = C_p \beta_0 + \Phi_r(t, T_0) \tag{29}$$

is measured. If the heat flow rate at a certain time t_1 has not vanished and the temperature is raised by $\mathrm{d}T$, it follows that

$$\begin{aligned} \Phi(t,T) &= \Phi(t, T_0) + \Phi_r(t - t_1, T_0 + \mathrm{d}T) \\ &= \Phi(t, T_0) + \Phi_r(t - t_1, T_0) + \alpha_\Phi(t - t_1)\mathrm{d}T \end{aligned} \tag{30}$$

with

$$\alpha_\Phi = \frac{\mathrm{d}\Phi_r}{\mathrm{d}T} \tag{31}$$

From the superposition principle, it follows that the resulting heat flow rate is the sum of the signal for $t < t_1$ and the heat flow rate, which is caused in addition by the step change in temperature.

If we assume that $\Phi(t, T_0) = 0$ and that a transition is a sequence of infinitely small temperature steps (continuous heating), then

$$\Phi(t, T) = \int_0^t \alpha_\Phi(t - t')\beta(t')\mathrm{d}t' \tag{32}$$

This is the well-known Boltzmann superposition principle and is described in detail in Ref. [11]. It can be seen that Eq. (32) corresponds to Eq. (18). Such processes can be described with the complex heat capacity approach [5]. But this basic relationship is not considered in the approach of reversing and non-reversing components [2–4].

However, Eq. (2) may be used to evaluate time-dependent processes if the reaction runs isothermally (see Eq. (28)).

For isothermal processes, Eq. (2) is as a special case of Eqs. (32) and (17). Otherwise the step from Eq. (2) to Eq. (4), and, accordingly, the methods of separation and interpretation for non-isothermally modulated DSC measurements recommended in Refs. [2–4], are not correct. They are valid only for time-independent processes. But in this case the non-reversing component is always zero.

3.2. The reversing and non-reversing components in the case of a simple dynamic model

This section discusses the connections and differences between the reversing and non-reversing components on the one hand and the complex heat capacity on the other. For the reversing component, this connection is given by Eqs. (8) and (21). The heat capacity, which is calculated from the reversing component is identical to the modulus of the complex heat capacity. To demonstrate the information contained in the non-reversing component, we shall discuss the simplest model of a dynamic system, namely, an exponential time-dependent heat capacity

$$C(t) = (C_p - C_\infty)(1 - e^{-t/\tau}) + C_\infty \tag{33}$$

For the complex heat capacity (see Eq. (16) or Ref. [11]) we get

$$C(\omega) = \frac{C_p - C_\infty}{1 + i\omega\tau} + C_\infty \tag{34}$$

with

$$C'(\omega) = \frac{C_p - C_\infty}{1 + \omega^2\tau^2} + C_\infty \tag{34a}$$

and

$$C''(\omega) = \frac{(C_p - C_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{34b}$$

C_p is the static heat capacity at equilibrium ($\omega \to 0$). C_∞ is the heat capacity for $\omega \to \infty$ (in the case of glass transition, this is the heat capacity of the glassy state), and τ is the relaxation time of the system. The connection between τ and the temperature may be described by an exponential function (Arrhenius law) as the simplest model [12]:

$$\tau = A \exp(B/T) \tag{35}$$

From the amplitude of the oscillating component, we determine the modulus of the heat capacity (see Eq. (25)). To obtain the non-reversing heat flow Φ_{non}, $|C|$ must be subtracted from C_p (compare Eqs. (9) and (21)).

Because of these calculations, $\omega\tau$ is eliminated from Eq. (34) and we get

$$\left(C' - \frac{C_p + C_\infty}{2}\right)^2 + C''^2 = \left(\frac{C_p - C_\infty}{2}\right)^2 \tag{36}$$

After elementary transformations we obtain

$$|C|^2 = C'^2 + C''^2 = C'(C_p + C_\infty) - C_p C_\infty \tag{37}$$

Assuming that

$$C_p C_\infty \simeq C' C_\infty \tag{38}$$

we find for the reversing and non-reversing components

$$\Phi_{rev}(T, \omega_0) = |C(T, \omega_0)|\beta_0 \approx \sqrt{C_p(T) C'(T, \omega_0)}\beta_0 \tag{39}$$

$$\Phi_{non}(T, \omega_0) = (C_\beta(T, \omega_\beta) - |C(T, \omega_0)|)\beta_0 \approx (C_\beta(T, \omega_\beta) - \sqrt{C_p(T) C'(T, \omega_0)})\beta_0 \tag{40}$$

None of these signals contain any information from the imaginary part C''.

In fact the non-reversing component is determined by subtracting two logically different quantities which were obtained under dissimilar measurement conditions and that are not directly comparable. This is illustrated in Fig. 1, in which the functions of C_β and $|C(\omega)|$, calculated from Eqs. (34) and (35), as well as the difference, the non-reversing component, are plotted. In using the evaluation method we propose that C' and C'' are determined directly from the amplitude of the modulated heat flow and from the phase shift. These values are amenable to an interpretation in terms of a linear response.

4. Experimental check

In this section we demonstrate the difference between the evaluation methods by experimental verification.

4.1. The measuring device

All measurements were carried out on a modified Perkin-Elmer DSC 7. In this special calorimeter, the programmed temperature is modulated with a sinusoidal temperature change. The temperature of the sample furnace is measured in addition to the usual quantities. A complete description of this device will be given elsewhere [13]. The measured raw heat-flow rate data are calibrated using a procedure based on phase and amplitude [14]. Then the underlying heat flow rate and the amplitude and phase shift of the oscillating component of this signal are determined. Then, according to Eq. (21), C_β is calculated from the underlying heat flow. A Fourier analysis of the oscillating component yields C' and C''.

To compare the evaluation methods, the results of Reading's evaluation method [2–4] are also calculated from the complex heat capacity and C_β. Thus, $|C|$ (the reversing component) is determined according to Eq. (22). The non-reversing component is $C_\beta - |C|$.

At present, heat flux DSCs are mostly used for MT-DSC measurements. For these types of calorimeters, a theoretical description of this method is given in Ref. [7]. The

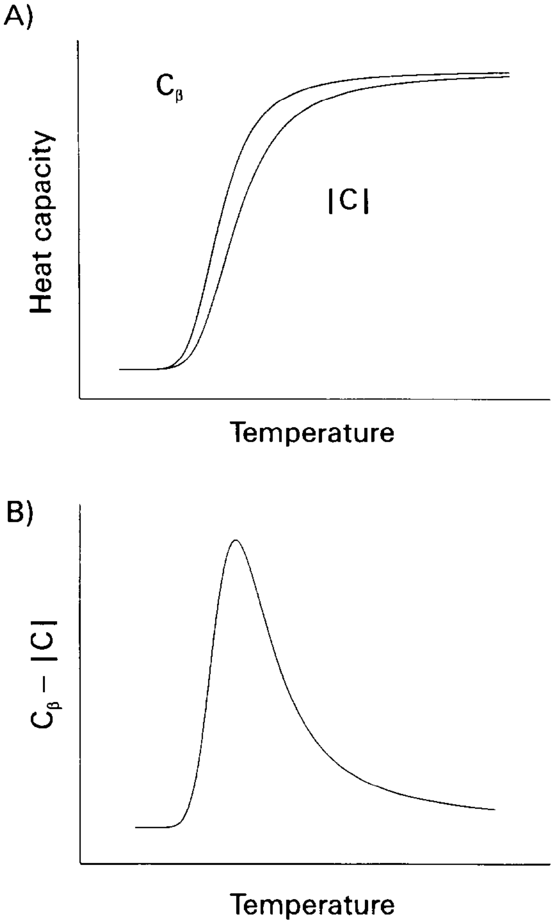

Fig. 1. Curves calculated from Eqs. (34) and (35). A. Curves of the underlying heat capacity C_β and the reversing component C. B. Curve of the non-reversing component.

DSC-7, however, is a power-compensated DSC. The differences between these two types of calorimeter are discussed in the relevant textbooks (e.g. Ref. [15]). In principle, all linear systems may be used for scanning and modulated measurements. In Refs. [16–19] it is shown that a power-compensated DSC is a linear system and thus suitable. The comparison of experimental results both from heat flux and power-compensated DSC in modulated temperature mode supports this thesis.

In Fig. 2, the measured curves of poly(ethylene-terephthalate) (PET) are given. Curves A are taken from the literature [3]; curves B are measured on the modified DSC-7. These curves will not be discussed in detail; however the curves A and B generally agree for the three different reactions (glass transition, cold crystallization, and melting). Differences between the two sets of results appear only in the temperature range of cold crystallization and in the absolute values of the specific heat capacity. The

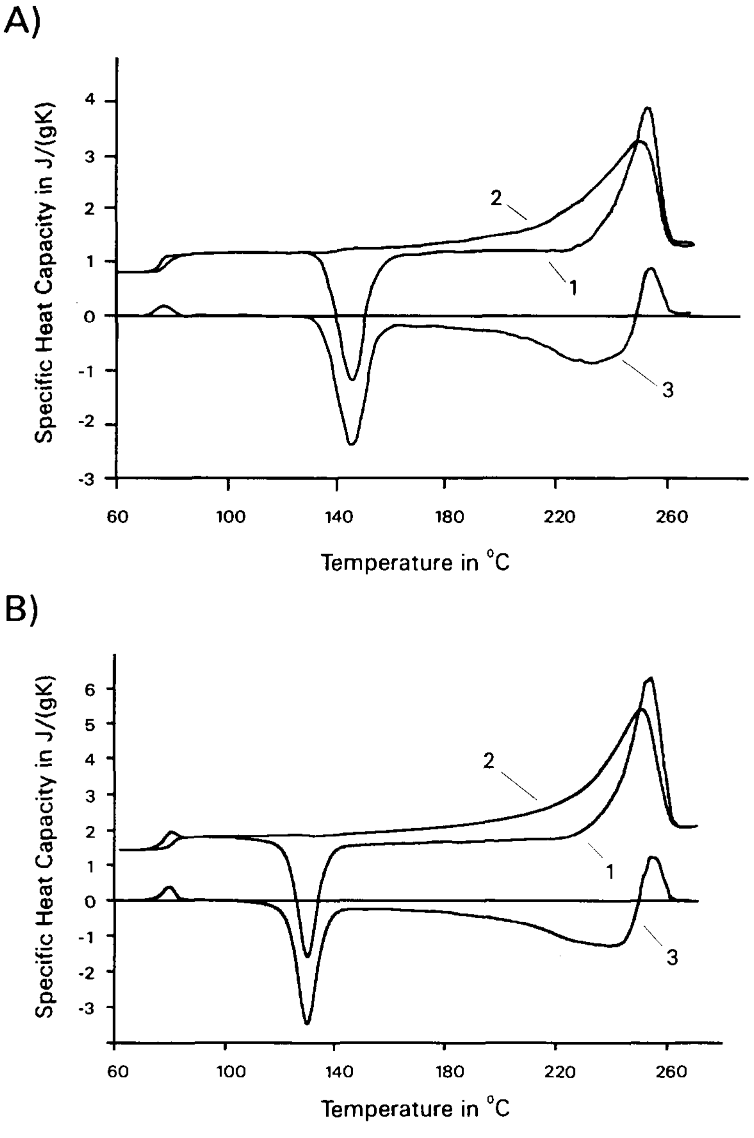

Fig. 2. Measured curves of PET ($\beta_0 = 5\,\mathrm{K\,min^{-1}}$, $T_a = 1\,\mathrm{K}$, $t_p = 30\,\mathrm{s}$). A. Measured with a heat flux DSC [15]. B. Measured with a modified Perkin-Elmer DSC-7. Calculated from: 1, the underlying heat flow; 2, reversing component; 3, non-reversing component.

difference in the cold crystallization results from a different sample material (more athermal nuclides). The other difference is caused by an incorrect calibration of the MT-DSC in question [3]. The specific heat capacity of the PET in the glassy state at 60°C is never smaller than $1\,\mathrm{J\,g^{-1}\,K^{-1}}$.

Because the theoretical understanding of the MT-DSC measured curves in the case of relaxations is relative clear [9], the glass transition behaviour of polystyrene (PS) NIST GM-754 is used as an example to discuss the different results.

4.2. *The different evaluation methods*

To test the theoretical understanding of the MT-DSC results, we chose the glass transition process of polystyrene (PS), which is well understood from the point of view of the relaxation.

PS ($m = 17.45\,\mathrm{mg}$) was cooled from 150 to 70°C with a cooling rate $\beta_0 = -1\,\mathrm{K\,min^{-1}}$ superimposed by a sinusoidal temperature change with a period $t_p = 100\,\mathrm{s}$ and an amplitude $T_a = 1$ K. Fig. 3 shows the curves which correspond to Reading's evaluation method [2]. Fig. 4 shows the complex heat capacity ($C'$and C'') and C_β. A direct comparison of the two is made in Fig. 5. The results are as expected from the simple exponential model analysis (see Fig. 1).

The curves $C_\beta(T)$ and $|C|(T)$ belong to different frequencies, and are thus different. As a consequence the non-reversing signal is the difference between two curves measured under different conditions. In Ref. [3] the peak of the non-reversing curve in the glass transition region is discussed as the enthalpy relaxation component of the heat

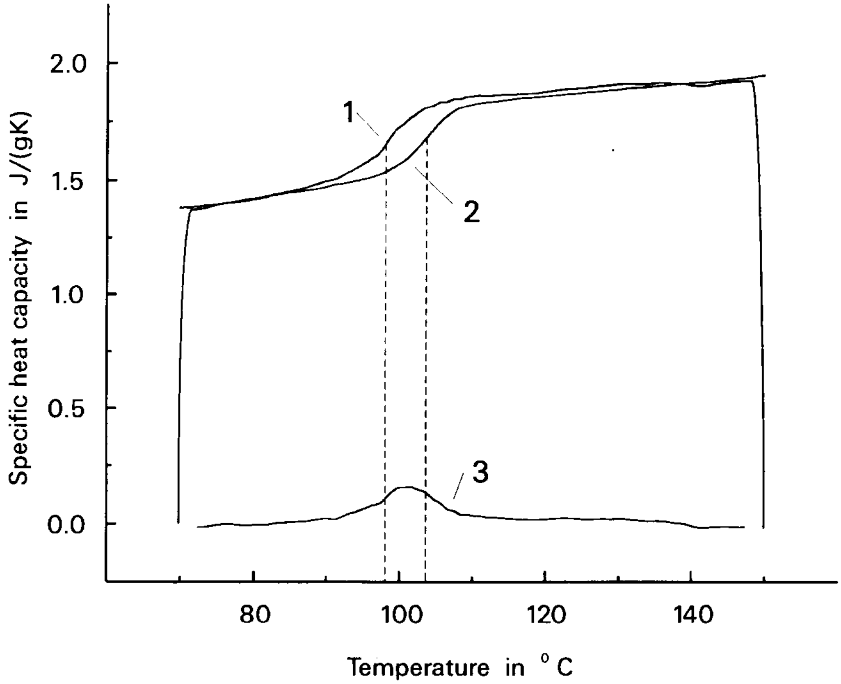

Fig. 3. Glass transition curves of PS measured in cooling mode ($\beta_0 = -1\,\mathrm{K\,min^{-1}}$, $T_a = 1$ K, $t_p = 100$ s): 1, C_β; 2, reversing component $|C|$; 3, non-reversing component.

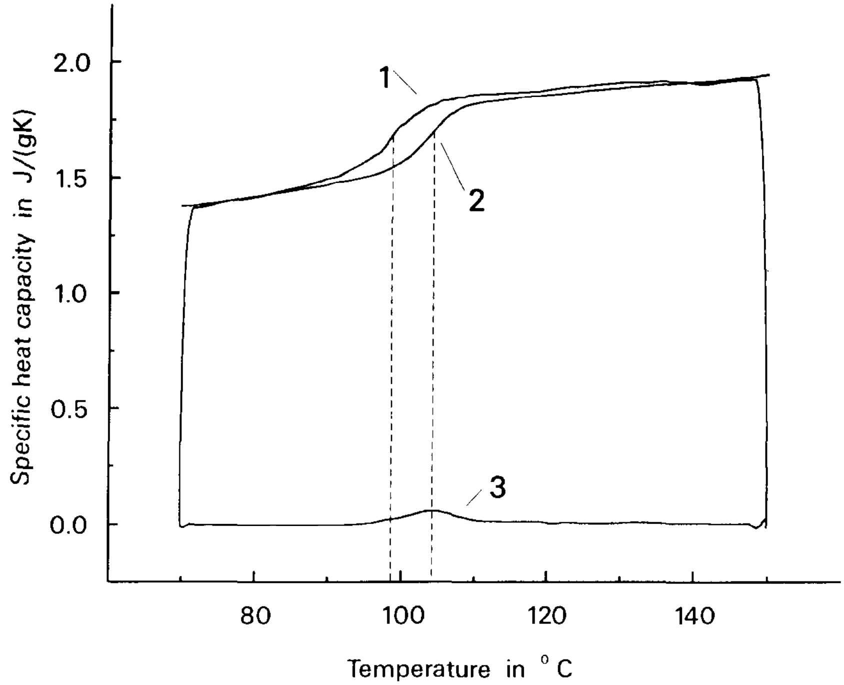

Fig. 4. Same measurements as in Fig. 3 but with: 1, C_β; 2, C'; 3, C''.

flow rate. In a cooling experiment, such an interpretation is impossible as an enthalpy relaxation does not exist in this mode. However, the enthalpy relaxation in the heating curve cannot be separated from the molecular motions on transition from non-equilibrium (glassy state) to equilibrium (liquid state). This is a result of the relaxation theory of glass transition [9, 20, 21].

One experimental result which shows this effect is published by Boller et al. [22]. In their study, the glass transition of PS after annealing was investigated in heating mode with an MDSC. The non-reversing component also shows a peak in the glass transition region on annealing above the glass transition. Because enthalpy relaxation does not exist, under such conditions the interpretation in Ref. [3] is incorrect, whereas the result is easy to understand as the difference between two measurements under different conditions.

However, interpretation in terms of the complex heat capacity approach is straightforward. The real part of the heat capacity C' exhibits a step-shaped change during the glass transition, whereas C'' has a peak. The glass transition observed in C_β occurs at a lower temperature than that of C', because the transition in C_β is generated by the successive freezing of modes of cooperative molecular motion. In the case of a modulated measurement at ω_0, the characteristic behaviour of the complex heat capacity is determined by the cooperative modes which cannot follow the temperature change. The modes which have the greatest actual influence on the relaxation behaviour at ω_0 are still not frozen.

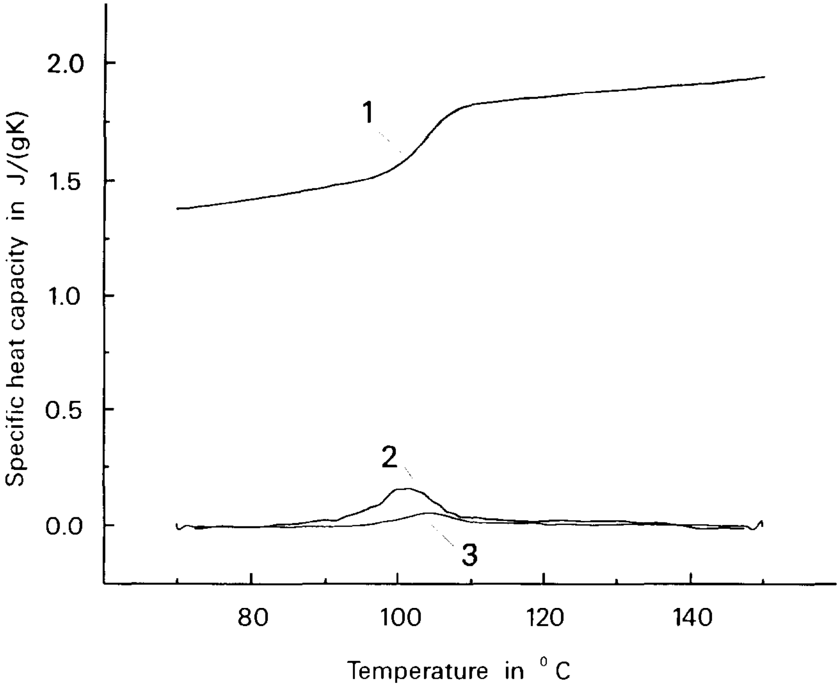

Fig. 5. Same measurements as in Fig. 3 but with: 1, $|C|$ and C' together; 2, non-reversing component; 3, C''.

5. Summary

In order to improve our understanding of the measurements obtained with the modulated or MT-DSC, two methods of evaluation were analysed.

In the algorithm separating components into reversing and non-reversing, only the amplitude of the oscillating component was used in the evaluation. The phase shift information is neglected. It has been shown that the fundamental evaluation equation represents a special case, which is valid only for time-independent thermal events (classical thermodynamics) or for isothermal measurements. This yields problems in interpretation of the measured curves. The non-reversing component is only the difference between two different results, which are measured under different conditions.

The other evaluation method is based on the linear response theory. Both the phase shift and the amplitude of the dynamic component are used for the calculation of a complex (frequency-dependent) heat capacity. These quantities can be interpreted in the context of the relaxation theory or irreversible thermodynamics. A comparison of the two evaluation methods shows that the reversing component is connected with the modulus of the complex heat capacity.

Acknowledgements

The author gratefully acknowledges discussions with Dr. Marcel Margulies, Dr. Bruce Cassel (Perkin-Elmer Corporation) and Dr. Guenther Höhne (University of Ulm). The investigations were supported by the Perkin-Elmer Corporation. Parts of this work were performed in the Research and Development Laboratories of the Perkin-Elmer Corporation in Norwalk, CT.

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