Journal of Thermal Analysis, Vol. 50 (1997) 365-373

EXPERIMENTAL INVESTIGATION INTO THE HEAT CAPACITY MEASUREMENT USING AN MODULATED DSC

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(Received November 26, 1995, in revised form November 18, 1996)

Abstract

Experiments using a commercial modulated DSC (MDSC) for the measurement of specific heat capacity of a sample have been carried out. It is found that because the amplitude of heat flow of MDSC is a complicated non-linear function of various experimental conditions such as the modulation frequency and the heat capacities of a sample and pan, the methodology of heat capacity determination using an MDSC in a single run has not been justified. The experimental results, on the other hand, agree with the theoretical equation of one of the authors. It is therefore concluded that the capabilities of MDSC should be further examined.

Keywords: DSC, heat capacity, indium, linearity, modulated DSC

Introduction

Recently, a new DSC technique termed Modulated Differential Scanning Calorimetry (MDSC) [1–8] has been developed to permit a small sinusoidal modulation of temperature superimposed on the linearly programmed temperature changes that are used in a conventional DSC. This new MDSC technique is drawing considerable attention from researchers in the fields of thermal analysis and polymer science since DSC is the most powerful and popular technique used in these fields [1–8].

The modulation period, p, amplitude of modulation temperature, A_b, and underlying heating rate, q, of an MDSC experiment are defined in Fig. 1a and Fig. 1b illustrates an example of a raw output curve. Unlike a conventional DSC, the curve of MDSC consists of a sinusoidal heat flux curve with the same period

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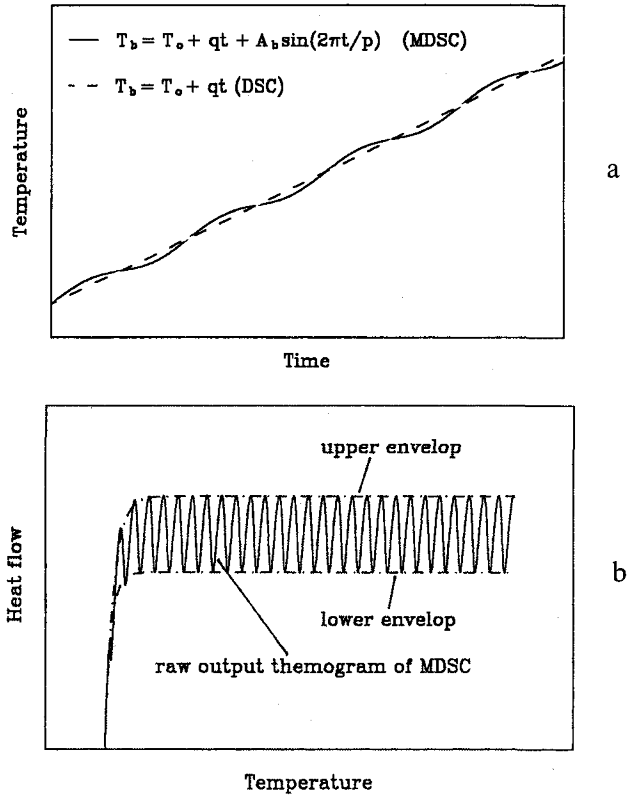

Fig. 1 Schematic illustration of a heating program (a) and heat flow output (b) of MDSC

as the modulation period. It has been believed that the upper and lower envelops of the curve represent the DSC curves of a conventional DSC corresponding to (or related to in a simple form) the highest and lowest heating rates; the former equals the sum of the underlying heating rate and the amplitude of modulation temperature ($q+A_b$); and the latter is obtained by subtracting the amplitude of modulation temperature from the underlying heating rate ($q-A_b$). This understanding invites one to believe that the heat capacity of a sample can be obtained in a single MDSC experiment [7]. In particular, it is believed that because each period of modulation in MDSC represents one measurement for the heat capacity of a sample, one can further separate "reversing" and "non-reversing" components of a thermal event. This has been achieved by subtracting the heat capacity component, determined by the amplitude of heat flow, from the total averaged or underlying heat flow [1–5]. According to this proposal, the crystallization of a quenched PET is a non-reversing thermal event, and the melting of PET is found to be a reversing thermal event under the experimental conditions adopted in those studies.

Clearly, all these understandings assume that an MDSC permits a reliable and accurate determination of the heat capacity of a sample through its amplitude of heat flow. Therefore a systematic experimental study on the heat capacity measurement using an MDSC becomes essential. The aim of this article is to provide some fundamental experimental evidence to deepen our understanding towards the capacities of MDSC.

Theoretical background

In a conventional DSC, two experiments with different heating rates for the same sample need to be carried out [9, 10]. Assuming that identical pans are used for the sample and reference, and that the reference is the empty pan only, one obtains the specific heat capacity of the sample, c_{ps} (J (g K)$^{-1}$), using Eq. (1);

$$c_{ps}=\frac{C_{ps}-C_{pr}}{m}=\frac{H_{f1}-H_{f2}}{m(q_1-q_2)} \tag{1}$$

where C_{ps} and C_{pr} (J K^{-1}) denote the heat capacities of the sample and the reference, m (g) the mass of the sample; H_f (mW) and q (K min^{-1}) represent the measured heat flow and the heating rate, respectively. The subscripts 1 and 2 indicate the experiment 1 and experiment 2.

An alternative DSC method is also available, in which two experiments with the same heating rate for two identical samples with different masses are carried out. The specific heat capacity of the sample is calculated as follows;

$$c_{ps}=\frac{H_{f1}-H_{f2}}{q(m_1-m_2)} \tag{2}$$

The major source of error of the conventional DSC technique is, perhaps, the long term stability of an instrument and the slow physico-chemical changes of the sample during two runs. The baseline could have slightly shifted during two runs due to low frequency drifting of electronics of the instrument. However, most commercial DSC instruments have solved this problem satisfactorily. On the other hand, whether there are slow changes for a sample during two DSC runs is another matter, which must be addressed case by case according to the physico-chemical nature of the sample.

In MDSC, the amplitude of heat flow of a single run is employed to determine the heat capacity of a sample to minimise the experimental errors resulting from low frequency drifting of baseline and slow changes of the sample during two runs. Wunderlich, Jin and Boller have proposed that the heat capacity can be obtained by dividing the amplitude of heat flow, A_{hf} (mW), by the product of the amplitude of modulation temperature, A_b (K) and the modulation angular frequency, ω($\omega = 2\pi/p$, where p is the modulation period) [5, 6].

$$C_{ps} = C_{pr} + mc_{ps} = K_{cp}\frac{A_{hf}}{A_b\omega} \tag{3}$$

where, C_p and c_p represent the heat capacity and specific heat capacity, respectively. The subscript r or s denotes the reference or sample, and the symbol K_{cp} represents a constant for instrumental calibration.

Moreover, the heat capacity determined according to Eq. (3) has been multiplied with the underlying heating rate to obtain so called "heat capacity component" or "reversing" component. By subtracting the "reversing" heat flow from the total underlying heat flow, one obtains so called "non-reversing" components [5–7]. This capability of separating the reversing and non-reversing components from the total underlying heat flow has been considered to be the unique feature of MDSC. It is therefore particularly important to investigate the physical meaning of the amplitude of heat flow for an MDSC experiment.

Recently, one of the authors has using mathematical analysis formulised a different theoretical expression of the amplitude of heat flow of an MDSC, A_{hf}, as follows [10, 11]

$$A_{hf} = A_b(C_{ps} - C_{pr})\lambda^2\omega\frac{\sqrt{\lambda^2\omega^2(C_{ps} + C_{pr})^2 + (C_{ps}C_{pr}\omega^2 - \lambda^2)^2}}{(C_{ps}^2\omega^2 + \lambda^2)(C_{pr}^2\omega^2 + \lambda^2)} \tag{4}$$

where, the symbol λ (J s^{-1} K^{-1}) denotes the coefficient of Newton's cooling law for an MDSC experiment, which is an indication of the intensity of thermal transfer from the heating block to a sample.

It is clear from Eq. (4) that the amplitude of heat flow of an MDSC is a complicated nonlinear function of ω, C_{ps} and C_{pr} and λ, although the relationship between the amplitude of heat flow, A_{hf}, and the amplitude of modulation temperature, A_b, is linear, and the amplitude is independent of the underlying heating rate, q.

Obviously Eqs (3) and (4) are contradictory each other. For this reason, a systematic experimental study on the heat capacity measurement using an MDSC becomes desirable.

Experimental

Pure indium was cut into thin sheets and weighed in a Perkin-Elmer micro balance with accuracy 0.001 mg. The thin indium sheets were then uniformly packed into an aluminium pan and the pan was subsequently sealed. The samples were heated to above their melting temperatures and kept isothermally for around 2 min, cooled to room temperature at a cooling rate of 20°C min^{-1} to permit the samples to form cakes intimately contacting the pans. MDSC curves were recorded as the samples were heated using a series of temperature programs.

All the MDSC experiments were carried out using a TA Instruments Inc. DSC-2920. Helium gas purge was used at a flow rate of 25 ml min^{-1}. Sample temperature and heat flow were recorded as a function of time. DSC curves were obtained by plotting the heat flow against the sample temperature.

Results and discussion

Figure 2 shows some examples of the heat flow output of an identical indium sample and an identical reference pan for various modulation periods while all other experimental conditions, shown in Table 1, were kept exactly the same. The abscissa of the plot is the sample temperature, and the ordinate denotes the heat flow output. Eight curves corresponding to the experiments with the modulation period 10, 15, 20, 30, 40, 60, 80 and 100 seconds have been plotted in one graph in order to reduce the size of this paper, also in order to avoid too many

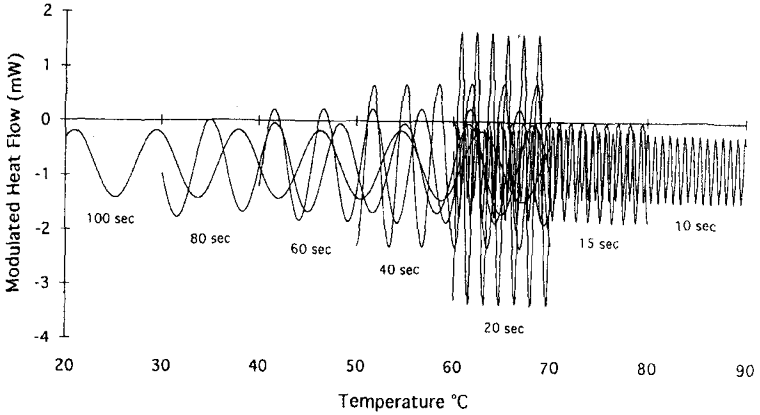

Fig. 2 The amplitude of heat flow varies with the modulation period (sample mass 37.92 mg)

Table 1 Experimental conditions employed in Figs 2, 3a, 3b and 4

Underlying heating rate	5 (°C min^{-1})
Modulation temperature	± 1°C
Mass of aluminium pan	25.1 mg (empty pan for reference)
(Heat capacity of reference, C_{pr})	(0.0251×0.900=0.0226 J K^{-1} [13])
Mass of indium	37.92 mg or 12.53 mg
(Heat capacity of sample, C_{ps})	(0.03792×0.234+0.0226=0.0315 [13]) (0.01253×0.234+0.0226=0.0255 [13])
Temperature range of measurements	0~100°C

curves overlapping each other, one part of the curve only for each curves was plotted in the figure. Sinusoidal-like heat flow curves were observed when the heat flow output were plotted against time (not presented in the article). Clearly the amplitude of heat flow is not a simple linear function of the modulation frequency.

In Fig. 3 the amplitude of heat flow is plotted against the modulation period for the two indium samples with different weights. It can be seen from the figures that the amplitude increases initially with decreasing the modulation period, reaches a maximum at a modulation period of around 20 second and then decreases on further decreasing the modulation period. This result is in contrast with Eq. (3), which essentially assumes that the amplitude of heat flow should increase linearly with the modulation period.

The modulation period dependence of the amplitude of heat flow, however, can be well interpreted using Eq. (4). By choosing different Newton's cooling coefficients, λ, which is mainly determined by the design and construction of an MDSC instrument [5, 10], and by placing the heat capacities of the reference and sample into Eq. (4), one obtains theoretical curves, also shown in Fig. 3 (solid

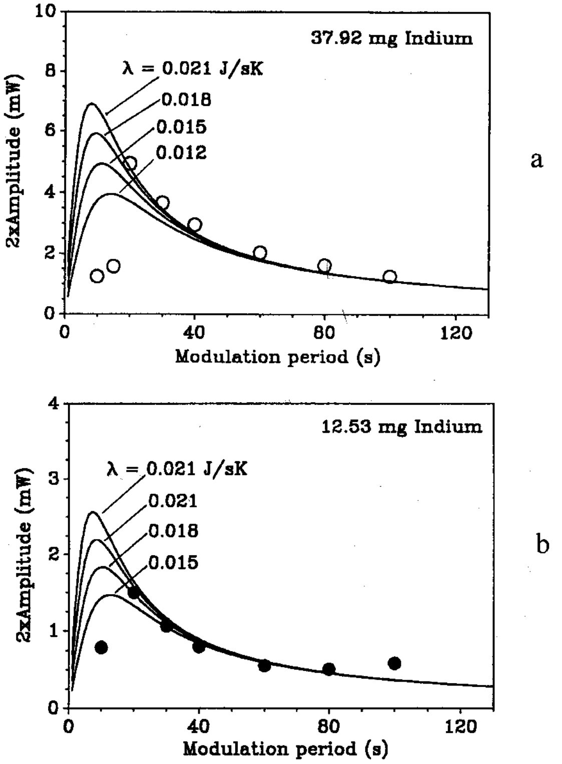

Fig. 3 Comparison between experimental results and theoretical calculations of Eq. (4)
a) sample mass 37.92 mg; b) sample mass 12.53 mg

lines). The experimental results and the theoretical curves are in reasonable agreement at the high modulation period region (>20 s). The deviation of the experimental results from the theoretical curves of Eq. (4) at the low modulation period region (<20 s) could be caused by the effect of temperature gradient in the samples at such high modulation frequencies. Another possible reason could be the deviation of temperature waveform of heating block from a true sinusoidal function at such high modulation frequencies.

The DSC curves were used to obtain the specific heat capacity of the sample using the software provided by TA Instruments Inc (no formula about how it was calculated was provided in the manual). The results for the sample of mass 37.92 mg were used as an example to plot *vs.* temperature in Fig. 4. It is seen that the obtained figure increases with the modulation period. Obviously, these results are inconsistent with each other and contradictory with the literature value of 0.234 J $(g K)^{-1}$ [13], indicating that the methodology used for the instrument to determine the specific heat capacity of a sample has not been justified and needs to be revised.

The physical meaning of the maximum amplitude of heat flow at certain modulation period is obvious. At a lower modulation period, there is no sufficient time for thermal transfer from the heating block to both the sample and reference, a smaller amplitude of heat flow will be expected. At a higher modulation period, on the other hand, both the sample and reference can catch up the temperature changes of heating block, resulting in a minimum temperature difference between the sample and reference, therefore a smaller amplitude of heat flow.

As can be seen from Eq. (4), not only the modulation period but also the heat capacity of a DSC pan would affect the amplitude of heat flow. Experiments using different DSC pans that are thought to he suitable for MDSC experiments for

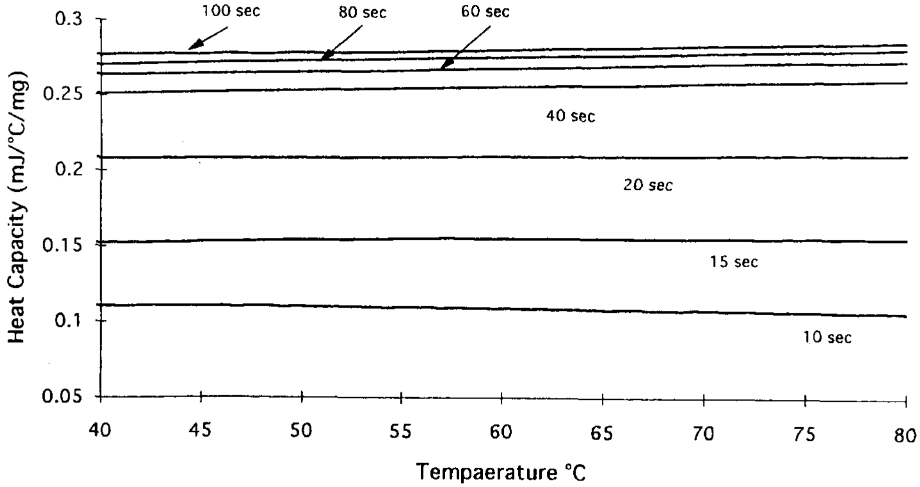

Fig. 4 Specific heat capacity of the pure indium sample calculated by using the software of the instrument for various modulation frequencies (sample mass 37.92)

Table 2 Experimental conditions employed in Fig. 5

Underlying heating rate	5 (°C min^{-1})
Mass of aluminium pan (Heat capacity of reference, C_{pr})	25.1 mg or 35.60 mg (0.0226 J K^{-1} or 0.0320 J K^{-1})
Mass of indium C_{ps}	10.05 mg ($m \times c_{ps}$=0.00235 J K^{-1}) 0.0250 J K^{-1}, 0.0344 J K^{-1}
Temperature range of measurements	0~100°C

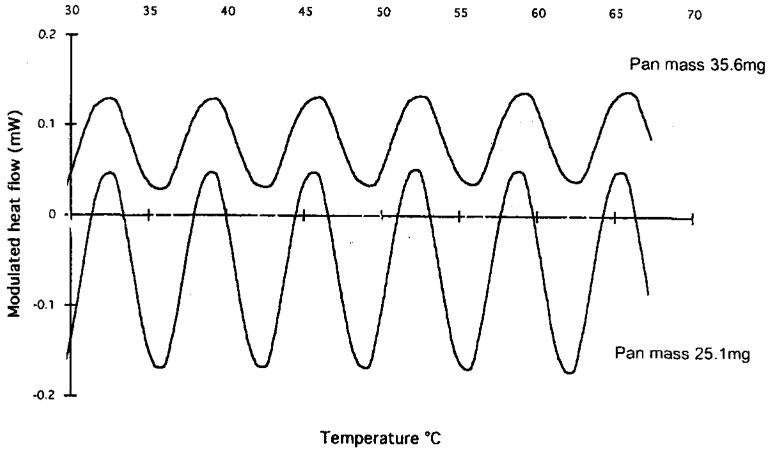

Fig. 5 An example showing the dependence of the amplitude of heat flow on DSC cell used for experiments (modulation period 80 s)

two indium samples with the same mass were then carried out, while all other experimental conditions, shown in Table 2, were maintained constant. Figure 5 shows the heat flow output of these experiments. Significant difference has been observed. This has led an inconsistent specific heat capacity value for indium obtained from the two measurements with different pans (not shown in figure). The lighter pan (smaller C_{pr} and C_{ps}) has led to a greater amplitude of heat flow, whilst Eq. (3) indicates that the amplitude should increase with the heat capacity of a pan. The experimental result in Fig. 5 is consistent with the theoretical results of Eq. (4), which suggests that the amplitude of heat flow decreases monotonically with increasing the heat capacity of pans used for sample and reference [10, 11].

Conclusion

Experiments using a commercial modulated DSC (MDSC) has been carried out to investigate the relationship between the amplitude of heat flow and the modulation frequency as well as the heat capacity of a pan used for a sample and reference. Agreement is observed between the experimental results and theoretical curves of Eq. (4) for the modulation frequency dependence of the amplitude of heat flow at low frequency region. The deviation of the experimental results from the theoretical prediction at the high frequency region, however, is considered to be caused by the temperature gradient within the sample etc. The amplitude dependence on the heat capacity of pan was also observed. Indeed, further work is required in order to fully understand the use of, and the capabilities of MDSC.

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