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Development of light heating dynamic DSC II: determination of complex calibration constants[1]

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Abstract

Complex calibration constants of light heating dynamic DSC were determined experimentally. The complex calibration constants must be known to measure the phase and the amplitude of the cyclic temperature response in dynamic DSC although only real calibration constants have been estimated so far. A new mathematical equation appropriate for light heating dynamic DSC was derived and used to determine the complex calibration constants. The new equation gave results which agreed well with experimental data.

Keywords: Amplitude of cyclic temperature response; Complex calibration constants; Light heating dynamic DSC; Phase of cyclic temperature response

1. Introduction

Dynamic DSC (DDSC) is a recently developed technique for simultaneous performance of conventional DSC and ac calorimetry (ACC) [1–3]. Since a commercial apparatus was introduced extended studies have been made. The present stage of DDSC is properly described by Ozawa [4, 5], who remarked that *it is important to know what can be done and what cannot be done by this new technique.* Reading et al. have shown that endo- or exothermic peaks accompanying irreversible processes in the sample are successfully separated from the underlying heat capacity by comparing the results of DSC and ACC obtained by DDSC [1–3]. Wunderlich's group has been working on applying DDSC to measurement of the heat capacity of polymeric materials and they reported that DDSC reduces the time required for heat capacity measurement [6, 7]. On the other hand DDSC results around the first-order phase

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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transition temperature have not been fully understood. DDSC study of the first-order phase transition will be useful particularly in polymer science because heat absorption accompanying the first order phase transition of polymeric materials occurs over wide temperature range and the shape of the endothermic peak depends on state of the material. Another unsolved problem pointed out by Ozawa is linearity of the cyclic temperature response to the modulation in the temperature range of transition of the sample such as the first-order phase transition and the glass transition [4, 5].

It should be noted that separation of the endo- or exothermic peak accompanying an irreversible process and measurement of heat capacity are achieved using only the amplitude of the cyclic temperature response. To understand the results around the first-order phase transition temperature, on the other hand, the phase of the cyclic temperature response and the amplitude have to be measured. If the linearity of the cyclic temperature response is satisfied, measurement of the phase will be essential for determination of the dynamic properties of the sample. Full expression of the cyclic signal, including both the amplitude and the phase, is conveniently given by a complex number. Since heat diffusion through the furnace affects the phase as well as the amplitude, a complex expression is necessary for the machine constants. Since calibration constants depend on the complex machine constants, a complex expression is also necessary for the calibration constants. Thus determination of the complex calibration constants is necessary to answer Ozawa's problem. So far only real calibration constants have been determined. In this paper we will report determination of the complex calibration constants of our DDSC apparatus, reported in a previous paper [8], which uses light heating for modulation.

2. Experimental

The light heating DDSC apparatus constructed in our laboratory [8] is outlined here; Fig. 1 shows a schematic diagram of the system. The intensity of the light incident on the sample is modulated by two polarizers, one is rotated by a stepping motor and the other is fixed. The light intensity I is expressed as $I = I_0(1 + \sin \omega t)$ where I_0, ω and t are the amplitude of the modulation, the angular frequency and the time, respectively. Unmodulated light is incident on the reference side for thermal balance. The light incident on the sample is monitored by means of a photodiode and the monitored signal is used as a standard of the phase of the cyclic temperature response. This light heating system is combined with a commercial DSC apparatus (Rigaku DSC-8230). The light heating system used in Ref. [8] had to be removed to change the sample. The new system used in this work is fixed and the conditions of light incidence are kept constant. DDSC signal and sample temperature are input to a personal computer every 1/128 s and the DDSC signal is deconvoluted to the DSC and ACC signals.

Four kinds of sample were measured. Sample 0 was an aluminum pan only. Samples 1, 2, and 3 were aluminum pans containing one, two, and three aluminum lids, respectively. All pans were crimped. The upper surfaces of the samples were covered with carbon for light absorption. Reference material was the same as sample 0. The heating rate of the furnace was 3°C min^{-1} and the modulation frequency was 0.1 Hz.

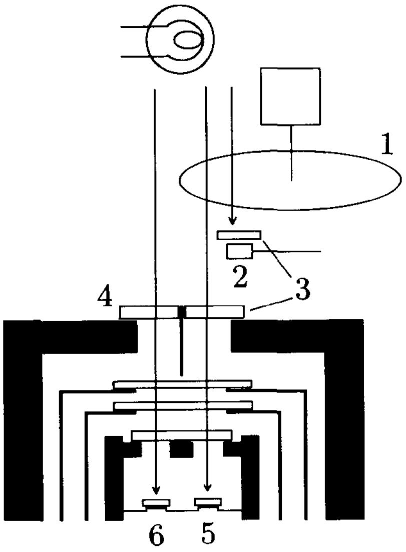

Fig. 1 Schematic diagram of the light heating system. 1: rotating polarizer. 2: photodiode. 3: fixed polarizers. 4: attenuator. 5: sample. 6: reference material.

The amplitude of the cyclic temperature response was less than 0.05°C. The modulation frequency and the amplitude of the cyclic temperature response are higher and smaller, respectively, than those of the commercial apparatus. The wide range of the modulation frequency will be useful for study of the dynamic properties of materials. The small amplitude of the cyclic temperature response will reduce smearing effects on temperature resolution.

Mathematical equations appropriate for commercial DDSC were reported by Wunderlich and co-workers [6, 7] and Hatta [9]. Those equations could not, however be used in this work because only the sample was modulated in our light heating DDSC. An equation appropriate for the light heating DDSC was deduced on the basis of equations of heat balance at the sample and the reference positions. The equations of heat balance of cyclic components are written as

$$i\omega \tilde{T}_s \tilde{C}_s = \tilde{Q} - (\tilde{K} + \tilde{L})\tilde{T}_s + \tilde{M}\tilde{T}_r \tag{1}$$

$$i\omega \tilde{T}_r \tilde{C}_r = -(\tilde{K} + \tilde{L})\tilde{T}_r + \tilde{M}\tilde{T}_s \tag{2}$$

where $\tilde{T}_x$ is the cyclic temperature response of the sample (x = s) or the reference material (x = r), and $\tilde{C}_x$ is the heat capacity of the sample (x = s) or the reference material (x = r), respectively, and its detector. A complex constant $\tilde{K}$ is an effective coefficient of heat transfer from the sample and the reference material to their surroundings. Heat exchange between the sample and the reference material is taken into account. In Eq. (1) $\tilde{L}\tilde{T}_s$ expresses heat flow out of the sample as a result of a change in the temperature of the sample. $\tilde{M}\tilde{T}_r$ expresses heat flow into the sample as a result of a change in the temperature of the reference material. $\tilde{L}$ and $\tilde{M}$ are complex constants. If the heat capacity of the furnace material between the sample and the reference sides is negligible $\tilde{L}$ and $\tilde{M}$ are real and equal to each other; we then obtain Newton's law of heat transfer. The meaning of the terms of $\tilde{L}$ and $\tilde{M}$ in Eq. (2) is the same as in Eq. (1). $i\omega\tilde{T}_x(x = s \text{ or } r)$ is equal to $d\tilde{T}_x/dt$ because the time dependence of $\tilde{T}_x$ is given by $\exp(i\omega t)$. The time dependence of $\tilde{Q}$ is also given by $\exp(i\omega t)$. From Eqs. (1) and (2) the following equations are obtained.

$$\frac{1}{\Delta\tilde{T}_{\mathrm{amp}}} = p\Delta\tilde{C} + q \qquad (3)$$

$$p = \frac{i\omega(i\omega\tilde{C}_r + \tilde{K} + \tilde{L})}{\tilde{Q}_{\mathrm{amp}}(i\omega\tilde{C}_r + \tilde{K} + \tilde{L} - \tilde{M})} \qquad (4)$$

$$q = \frac{i\omega\tilde{C}_r + \tilde{K} + \tilde{L} + \tilde{M}}{\tilde{Q}_{\mathrm{amp}}} \qquad (5)$$

In Eq. (3) $(\tilde{C}_s - \tilde{C}_r)$ is written as $\Delta\tilde{C}$. $\Delta\tilde{T}_{\mathrm{amp}}$ in Eq. (3) and Q_{amp} in Eqs. (4) and (5) are complex amplitudes of $(\tilde{T}_s - \tilde{T}_r)$ and $\tilde{Q}$. $\Delta\tilde{T}_{\mathrm{amp}}$ is the observed quantity. The calibration constants p and q depend on the complex machine constants, the intensity of the light, the modulating frequency, and the heat capacity of the reference material. Eq. (3) shows that values of $1/\Delta\tilde{T}_{\mathrm{amp}}$ plotted in the complex plane for various values of $\Delta\tilde{C}$ should be on a line. Values of the real and imaginary parts of p and q can be determined from observed values of the real and imaginary parts of $1/\Delta\tilde{T}_{\mathrm{amp}}$ obtained from standard samples.

3. Results

Fig. 2 shows the temperature-dependence of the real and imaginary parts of $1/\Delta\tilde{T}_{\mathrm{amp}}$ for sample 0. Each point in Fig. 2 was obtained from two periods of the modulation. The units of $1/\Delta\tilde{T}_{\mathrm{amp}}$ are written as 1/V because the temperature response was measured in voltage units. The curves in Fig. 2 are quadratic functions of temperature fitted by the least squares method. Experimental results for samples 1, 2 and 3 were analyzed similarly to those for sample 0. Experimental error became larger with increasing sample number — experimental error for sample 3 was five times as large as that for sample 0. One reason for the large error for sample 3 was its small temperature response because of its large heat capacity. Another possible reason was inadequate sample preparation. Even if thermal contact with the sample was good enough for conventional DSC, it might have been insufficient for DDSC because of the modulation.

Fig. 3 shows a plot of $1/\Delta\tilde{T}_{\mathrm{amp}}$ in the complex plane. Figs. 3(a), (b), (c), and (d) show results for 40, 80, 130, and 170°C, respectively. Open circles are the observed values. The numbers on the graph are the sample numbers. Real and imaginary values at each temperature were obtained from the fitted curves shown in Fig. 2. Lines in Fig. 3 are drawn by the least square method. At every temperature, positions of the open circles are close enough to the line as expected from Eq. (3).

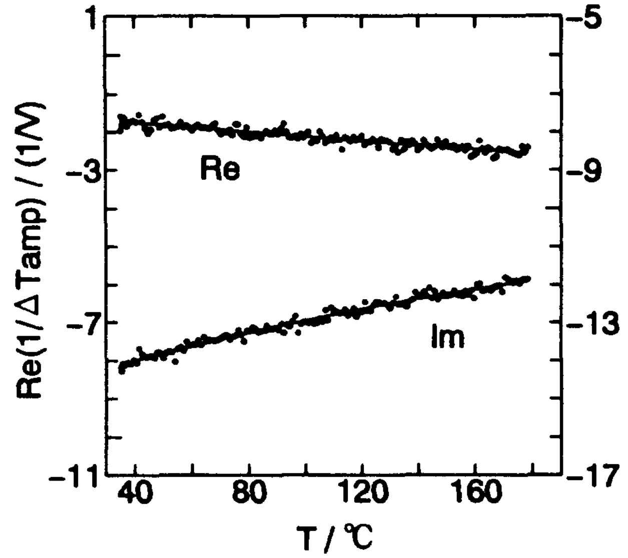

Fig. 2 Temperature-dependence of real and imaginary parts of $1/\Delta\tilde{T}_{\mathrm{amp}}$ for sample 0, with fitted curves.

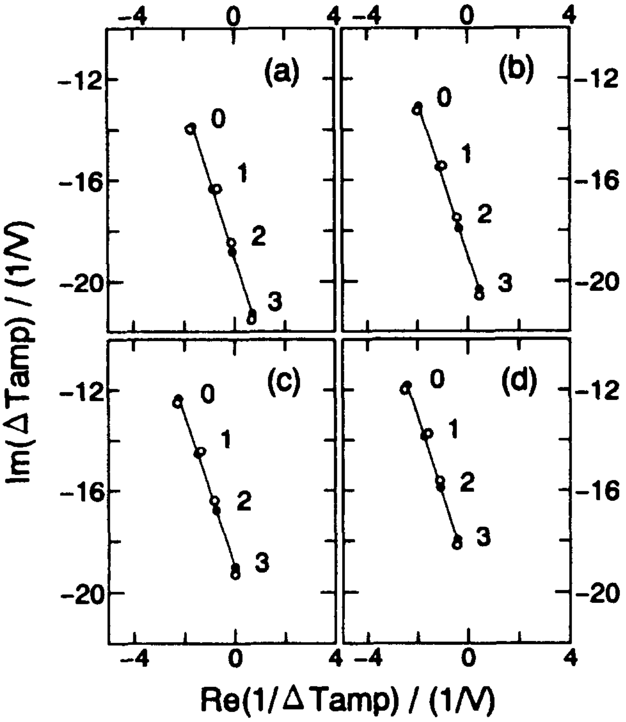

Fig. 3 Observed and calculated $1/\Delta\tilde{T}_{\mathrm{amp}}$ points plotted in the complex plane. Open and solid circles are observed and calculated points, respectively. Lines are fitted to the observed points. Numbers on the graphs are the sample numbers.

Table 1
Estimated values of the calibration constants

	p(Re, Im)/(°C/JV)	q(Re, Im)/(1/V)
40°C	$(0.181, -0.574) \times 10^3$	$(-1.64, -13.85)$
70°C	$(0.179, -0.547) \times 10^3$	$(-1.93, -13.09)$
130°C	$(0.163, -0.491) \times 10^3$	$(-2.23, -12.31)$
170°C	$(0.142, -0.441) \times 10^3$	$(-2.41, -11.82)$

Values of p and q were determined in the following way. $\tilde{C}$ of sample n ($n = 0, 1, 2, 3$) is written as $\tilde{C}_n$. $\tilde{C}_0$ is 0. $\tilde{C}_1$ is equal to the heat capacity of the aluminum lid which is 4.31 mJ °C^{-1} at 40°C, 4.39 mJ °C^{-1} at 70°C, 4.55 mJ °C^{-1} at 130°C, and 4.62 mJ °C^{-1} at 170°C. $\tilde{C}_2$ and $\tilde{C}_3$ are twice and three times as large respectively, as $\tilde{C}_1$. Substituting the values of $\tilde{C}_n$ into Eq. (3) enables the right hand side of Eq. (3) to be calculated for given values of p and q. Table 1 shows the values of p and q at each temperature which give the smallest value of the sum of the squares of the distances between the observed and the calculated points in the complex plane. The solid circles in Fig. 3 are calculated from the values in Table 1 and the above $\tilde{C}_n$ values. Agreement between the observed and the calculated point is sufficiently good at every temperature.

4. Discussion

Because the values of p and q were determined, heat capacities of other samples can be calculated from the observed values of $\Delta\tilde{T}_{amp}$. It should be noted that p and q determined above can be used if $\Delta\tilde{C}$ is complex due to a kinetic process in the sample [10]; the phase shift can be measured quantitatively. If $\Delta\tilde{C}$ is complex the point observed for $1/\Delta\tilde{T}_{amp}$ will be off the line in Fig. 3. The amount of the phase shift is equal to the angle between the line drawn in Fig. 3 and the line connecting the point observed for $1/\Delta\tilde{T}_{amp}$ and the point for sample 1, assuming that the sample is put in an aluminum pan and covered with an aluminum lid. Similar quantitative measurement of the phase shift will be possible at the first order phase transition temperature if the temperature is uniform throughout the sample. If the temperature is not uniform throughout the sample treatment is possible by a modified model instead of Eqs. (1) and (2).

As shown in Fig. 1, modulation by light heating is on the side of the sample only. To change the light heating system into the differential type is not difficult. It should, however, be noted that sensitivity range of the apparatus is determined by the DSC signal particularly at temperatures of large endo- or exotherms. If the light heating system is changed into the differential type, the cyclic temperature response will become smaller. Since the DSC signal is not affected by changing the light heating system, the smaller signal has to be measured in the same sensitivity range. One of the merits of the differential type is the possibility of measuring a small change of signal at high sensitivity by reducing the reference heat capacity from that of the sample heat capacity. The cyclic component does not have this merit.

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