Pure & Appl. Chem., Vol. 69, No. 11, pp. 2315–2320, 1997.
Printed in Great Britain.

Temperature modulated differential scanning calorimetry—applicability and limitation

Takeo Ozawa

Daicel Chemical Industries, Kasumigaseki 3-2-5, Tokyo 100, Japan

Abstract: Theoretical considerations on temperature modulated differential scanning calorimetry were made taking account of linearity and non-linearity of the processes. For dynamic steady state mathematical analytical methods are applied and general solutions were obtained on some assumptions, because of its linearity. The solutions can be used for heat capcaity measurements. For glass transition like heat capacity change it was elucidated by simulation that quasi-steady state exists and the above solutions can be applied. Because transitions are non-linear processes, simulation was also applied to transitions, but complicated results were obtained including higher harmonics.

INTRODUCTION

Temperature modulated differential scanning calorimetry (tm-DSC) has drawn much interest since its publication in 1992 [1, 2], because something new can be expected. In this technique, the temperature is changed linearly with superposed sinusoidal temperature modulation, and the sample thermal response is observed in comparison with that of the thermally inert reference material. The sample thermal response in the form of temperature difference is separated into the response in-phase with the temperature modulation and the other component, and it is postulated that the in-phase response corresponds to reversible process, while the other component is due to non-reversible process [1, 2]. For the separation, Fourier transformation is applied for multiple cycles of response, and this mathematical treatment restricts tm-DSC application mainly within polymers, because sharp transitions are not suitable, and transitions for a certain temperature range suitable for this technique occurs mainly in polymers.

However, the sample thermal response is somewhat complicated, and linearity should be examined before deconvolution by Fourier transformation, as pointed out by the authors before [3, 4], because superposition principle is prerequisite for the deconvolution. In conventional DSC steady state is a linear process; it is used for heat capacity measurements and height of the base line is proportional to the heat capacity. Peak area for a transition is also proportional to the sample mass and also to the transition heat, so that peak area is linear. Electrical heat evolution in the sample cell and infrared irradiation to the sample cell are also linear processes, where the peak area and the peak height are both proportional to the energy [3, 4].

On the other hand, peak shape by sample transition is quite different, because the temperature is kept almost constant during the transition. The slope of the rising part of the peak is almost constant and not proportional to the sample mass and also not to the heat, and the peak height is also not proportional to the sample mass and the heat. Therefore, transition behavior in DSC response is non-linear in its nature. Thus, superposition principle does not hold and Fourier transformation can not be applied [3, 4].

By this reason, tm-DSC application should be severely examined before its full use [4]. However, the above-mentioned linear processes, we can apply mathematical analytical methods to elucidate relations of sample thermal properties with output signal, and we can derive useful relation for tm-DSC application [4]. For the non-linear processes simulation should be applied to reveal the sample thermal response in relation with the nature of transitions [4].

FUNDAMENTAL EQUATIONS

The heat flow in a DSC apparatus is expressed as follows [5];

$$C_s dT_s/dt + Q dx/dt = K(T_{fs} - T_s) + k(T_o - T_s) + h(T_r - T_s) \quad (1)$$

$$C_{fs} dT_{fs}/dt = K(T_s - T_{fs}) + K(T_f - T_{fs}) \quad (2)$$

$$C_r dT_r/dt = K(T_{fr} - T_r) + k(T_o - T_r) + h(T_s - T_r) \quad (3)$$

and

$$C_{fr} dT_{fr}/dt = K(T_r - T_{fr}) + K(T_f - T_{fr}) \quad (4)$$

where C, T, t, Q and dx/dt are the heat capacity, the temperature, the time, the heat of sample transformation and its rate, respectively. The subscripts, s, f, r and o indicate the sample, the heat source, the reference material and the environment, respectively, while the double subscripts, fs and fr, mean the midpoints between them, and K, k and h are the heat transfer coefficients between the indicated temperatures. The heat source temperature is controlled as follows;

$$T_f = T_b + bt + A_f \exp(i\ \omega\ t) \quad (5)$$

where b, A, i and ω are the heating rate, the amplitude of modulation, the unit of imaginary number and the angular frequency, respectively, while the subscript, b, means beginning, and

$$\exp(i\,x) = \sin x + i \cos x \text{ (Euler formula)} \quad (6)$$

DYNAMIC STEADY STATE

When the sample transformation does not occur ($Q = 0$), the dynamic steady state must establish after a certain time interval. In this steady state the temperatures other than the heat source temperature must be as follows;

$$T = T_b + bt + A^* \exp(i\ \omega\ t) + B \quad (7)$$

where A^* and B are the complex amplitude expressing the amplitude and phase shift [see Eq. (6)], and the constant temperature lag from the heat source temperature, respectively.

Introducing Eqs.(5) and (7) into the fundamental equations from (1) to (4) and comparing the coefficients, we have simultaneous equations. By solving these simultaneous equations, we can get A^*'s and B's, which describe the temperatures. However, general analytical solutions can not be obtained from these simultaneous equations [5]. When the mutual heat exchange between the sample and the reference material, h, is negligibly small and when the heat capacities of the heat paths, C_{fs} and C_{fr}, are neglected, the simultaneous equations can be solved as follows [5];

$$A_{sr} = \frac{(K/2)(K/2+k)A_f}{\omega^2 C_s^2 + (K/2+k)^2} \quad (8)$$

$$A_{si} = -\frac{(K/2)\,\omega\, C_s A_f}{\omega^2 C_s^2 + (K/2+k)^2} \quad (9)$$

$$A_{rr} = \frac{(K/2)(K/2+k)A_f}{\omega^2 C_r^2 + (K/2+k)^2} \quad (10)$$

$$A_{ri} = -\frac{(K/2)\,\omega\, C_r A_f}{\omega^2 C_r^2 + (K/2+k)^2} \quad (11)$$

where the last subscripts r and i mean the real and imaginary parts of the amplitudes, respectively.

When these neglected factors are considered, only approximate-analytical solutions can be numerically obtained by applying matrix method, and the results using parameters of the two commercial DSC apparatus estimated by the design and materials were reported [5].

HEAT CAPACITY MEASUREMENTS

By using the above general solutions, we can derive equations for heat capacity measurements, for example;

$$C_s = A_{si}(K/2+k)/\omega A_{sr} \tag{12}$$

$$\frac{A_{si}}{A_{sr}} - \frac{A_{ri}}{A_{rr}} = -\frac{\omega(C_s-C_r)}{(K/2+k)} \tag{13}$$

By further approximation, Wunderlich and his coworkers derived [6, 7]

$$C_s = KA_{dr}/(2wA_{sr}) \tag{14}$$

where A_d is amplitude of the temperature difference between the sample and the reference material.

When the above equations are used, the neglected factors, h, C_{fs} and C_{fr}, causes errors (systematic deviations from the true value). In practical heat capacity measurements by tm-DSC, the parameters in Eqs. (12) - (14) such as K and k are estimated by experiment using standard material of synthetic sapphire, and then the heat capacity of the sample is estimated by another experiment for the sample. This procedure was applied to correct values of A_{sr}, A_{si}, A_{rr} and A_{ri} obtained by the matrix method, and by using the above equations the heat capacity was calculated as thought experiments. The errors obtained by this procedure are tabulated in Table 1, where the accuracy of tm-DSC is shown [5]. As seen in the table, ballancing the heat capacity between the sandard material and the sample is essentially important to maintain high accuracy.

TABLE 1 Results of Error Percentage in Heat Capacity Measurements

(1) Eq.(13)
Model A

C_s(standard)/mJK^{-1}	20	50	70	100
C_s(sample)/mJK^{-1}				
20	0.000	0.24	0.46	0.87
50	-0.24	0.000	0.21	0.62
70	-0.46	-0.22	0.000	0.41
100	-0.87	-0.62	-0.41	0.000

Model B

C_s(standard)/mJK^{-1}	20	50	70	100
C_s(sample)/mJK^{-1}				
20	0.000	0.36	0.70	1.36
50	-0.36	0.000	0.34	0.99
70	-0.70	-0.34	0.000	0.65
100	-1.34	-0.98	-0.65	0.000

(2) Eq.(12) by present authors
Model A

C_s(standard)/mJK^{-1}	20	50	70	100
C_s(sample)/mJK^{-1}				
20	0.000	-0.26	-0.46	-0.82
50	0.26	0.000	-0.21	-0.57
70	0.47	0.21	0.000	-0.36
100	0.83	0.57	0.36	0.000

Model B

C_s(standard)/mJK^{-1}	20	50	70	100
C_s(sample)/mJK^{-1}				
20	0.000	-0.01	-0.02	-0.03
50	0.01	0.000	-0.01	-0.02
70	0.02	0.01	0.000	-0.01
100	0.03	0.02	0.01	0.000

For conventional DSC, an equation for heat capacity measurements was also derived from the above simultaneous equations without any neglected parameters, so that the accuracy is higher than that of tm-DSC. However, the sensitivity of the conventional DSC is proportionally dependent on the heating rate, while it is dependent on the modulating frequency in tm-DSC as seen in Eqs. (12) - (14). Therefore, in conventional DSC high sensitivity can be achieved with sacrifice of temperature resolution, but in tm-DSC high sensitivity can be maintained by high modulating frequency.

The precision seems to be maintained high by filtering oscillation of the modulating frequency in tm-DSC, while disturbance from the outside causes large error in the conventional DSC. In the both DSC the heat transfer coefficients, K and k, have influence on the precision, so that to keep good thermal contact between the sample cell bottom and the cell holder is essentially important.

TEMPERATURE DEPENDENT-HEAT CAPACITY

The above estimation of the accuracy was made for constant heat capacity. However, in actual measurements heat capacity changes with the temperature. Considering these situations, two cases were examined by simulation; heat capacity linearly dependent on the temperature and glass transition like heat capacity change [8].

The simulation was made by using the more sophisticated fundamental equations and finite difference method, and the simulated temperature oscillation for constant heat capacity was compared with that obtained numerically by the matrix method. The agreement between them was very good and the inaccuracy of simulation was negligibly small [8].

To examine applicability of Eqs. (12) - (14), the simulated oscillation for temperature dependent-heat capacity, such as that of synthetic sapphire, was compared with the numerical solutions by the matrix method, which are the solutions for the steady state. The difference between them was not detected, and the same agreement was also observed for heat capacity of threefold temperature dependence. Even for glass transition like heat capacity change without relaxation [9, 10], the agreement was excellent (Fig. 1) [8]. Thus, quasi-linearity holds and quasi-steady state is established in these cases; the equations for heat capacity determination [Eqs. (12) - (14)] can be applied without any additional errors [8].

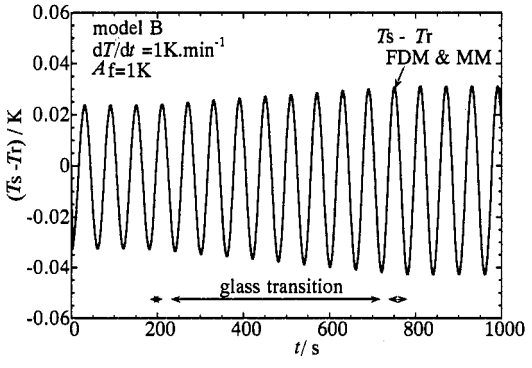

Fig. 1. Sample temperature in glass transition like heat capacity change. FDM and MM denote simulation by finite difference method and approximate-analytical solutions by matrix method.

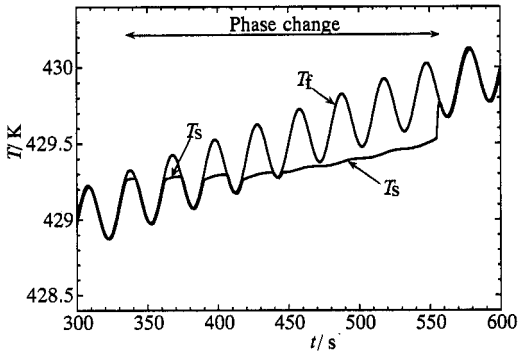

Fig. 2. Sample temperature and heat source temperature during transition by tm-DSC.

In this simulation, the heat source temperature was controlled in accordance with Eq. (5). In some tm-DSC, instead of the heat source temperature, the sample temperature is controlled as Eq. (5). However, the above conclusion on heat capacity measurements can be applied to this type of temperature control, becasue relations among the heat source temperature, the sample temperature and the reference material temperature are the same in spite of the type of temperature control in the steady state.

It can be inferred that the steady state amplitude and phase shift are changing due to temperature dependent-heat capacity and the sample thermal response is continuously approaching to this steady state oscillation with short thermal response time of order of second [8]. It is worth to note that second harmonics were detected by Wunderlich [10] in his simulation of glass transition, taking account of relaxation phenomenon. Thus, the second harmonics and non-linearity are caused by kinetics of hole concentration change in the glass transition.

TRANSITIONS

Simulation was carried out for two cases of transition, where the heat capacity changes pulsively during the transitions; in one case the process is perfectly reversible without any supercooling and in the other case the transition is non-reversible. A typical result is reproduced in Fig. 2 [11] . As seen in this figure, the sample temperature oscillation is distorted by the transition and the sample temperature is kept almost constant during the transition [11].

The usual procedure of data processing [1, 2] was applied to the simulated results. One example of the results for the transition of wide temperature range like polymer melting is reproduced in Fig. 3, where the two cases are shown [11]. It should be pointed out that there is no distinctive difference between them, and it can not be made by observing the results to distinguish a reversible transition from a non-reversible transition. Similar results were obtained by the simulation of a sharp transition.[11].

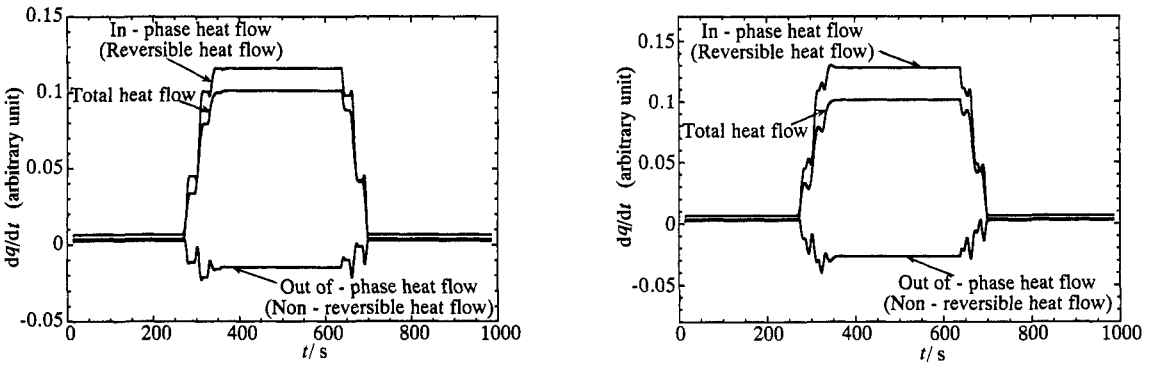

Fig. 3. "Reversible" and "Non-reversible" components.
(a) reversible trnasition (b) non-reversible transition

As pointed out in the above, the processes dealt with in this simulation are non-linear processes, so that higher harmonic oscillations must be existing [4]. To elucidate this non-linear effect, the second harmonics was searched in the simulated results, and one example is shown in Fig. 4 [11]. For the perfectly reversible transition the second harmonics was found at the beginning and the end presumably due to drastic change of the heat capacity and their duration is about 100 s. Except these interval higher harmonics were not detected and the steady state was established because of the constant heat capacity. The out-of-phase higher harmonics are quite similar. On the other hand, both of in-phase and out-of-phase second harmonics were seen in the irreversible process, because of distorted oscillation [11]. Irregular changes in the reversible and non-reversible components in Fig. 3 are presumabley due to this non-linear effect. Similar results were obtained also for the sharp transitions [11].

To observe reversibility of transitions, a new method was proposed; the temperature difference between the sample and the heat source or between the sample and the reference material is integrated and plotted against the sample temperature, as seen in Fig. 5 [11]. Because the integration corresponds to enthalpy change, irreversibility or supercooling can be detected as spikes in the plot [11].

CONCLUDING REMARKS

Tm-DSC is a powerful tool to measure heat capacity especially from practical viewpoint. It should also be pointed out that the measurements can be made even in cooling mode, which is of practical importance, for instance, for molding technology of plastics. For accurate and precise measurements, a few points shall be taken into account, as described in this paper.

For observation of transitions, especially their reversibility, separation of reversible component and non-reversible component postulated before was not proved effective but seemes erroneous, and another

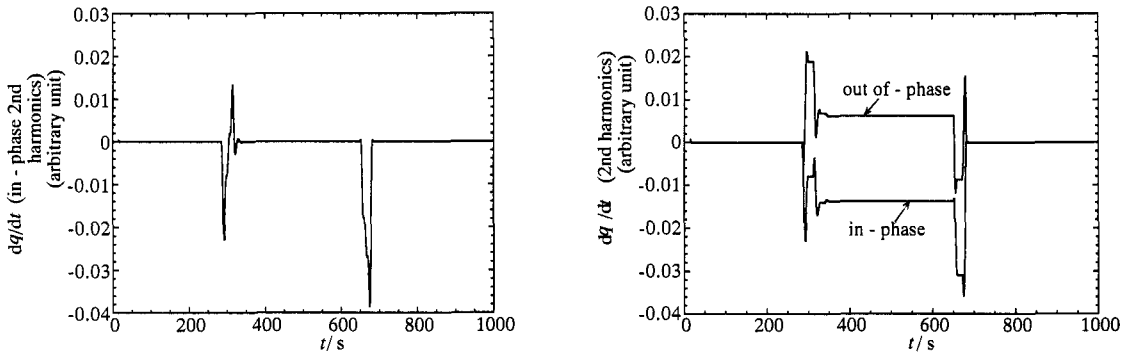

Fig. 4. Second harmonics in transition.
(a) reversible transition (b) non-reversible transition

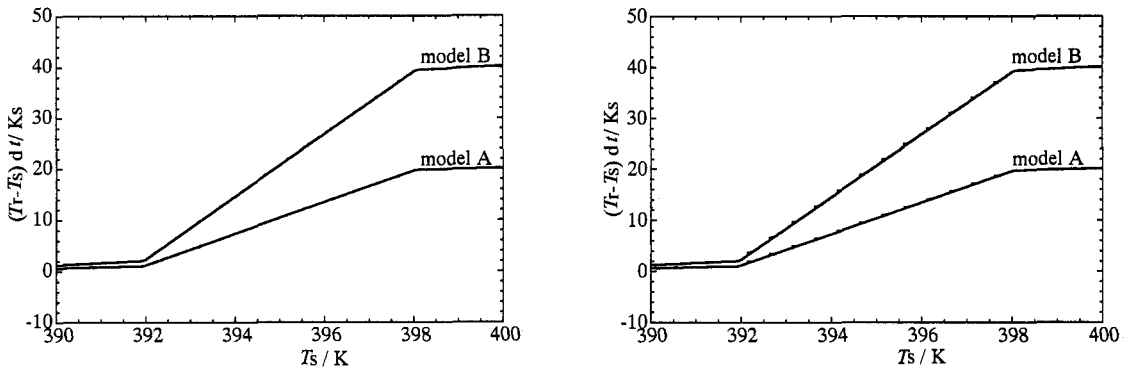

Fig. 5. Integral of temperature difference.
(a) reversible transition (b) non-reversible transition

method was set forth. In this method quantity related with enthalpy change is observed with the sample temperature change due to the modulation.

Thus tm-DSC has two aspects. One is observation of the sample thermal response to the temperature modulation in the sterady state, and it can be used for heat capacity measurements. The other is observation of enthalpy change due to alternative heating and cooling in transition region. Another characteristics and interesting application of tm-DSC is quasi-isothermal observation [9, 12-14], where the average temperature is constant (b=0), i.e., alternative heating and cooling.

Boundary of quasi-linearity has not yet been elucidated, so that range of tm-DSC applicability to heat capacity measurements is also unkown. Linearity in wide sense should also be considered [15].

REFERENCES

[1] M. Reading, D. Elliott and V. L. Hill, *J. Thermal Anal.*, **40** , 949(1993).
[2] P. S. Gill, S. R. Sauerbrunn and M. Reading, *J. Thermal Anal.*, **40,** 931(1993).
[3] T. Ozawa, *Netsu Sokutei,* **4,** 55(1977).
[4] T. Ozawa and K. Kanari, *Thermochim. Acta,* **253,** 183(1995) .
[5] T. Ozawa and K. Kanàri, *Thermochim. Acta,* **288,**39(1996).
[6] B. Wunderlich, Y. Jin and A. Boller, *Thermochim. Acta,* **238** , 277(1994).
[7] A. Boller, Y. Jin and B. Wunderlich, *J. Thermal Anal.*, **42** ,307(1994).
[8] K. Kanari and T. Ozawa, *Thermochim. Acta* (tm-DSC special issue) submitted.
[9] A. Boller, C. Schick and B. Wunderlich, *Thermochim. Acta,* 266 , 97.(1995).
[10] B. Wunderlich, In *Program Book 11th ICTAC Congress* (M. Keating ed.) 11, Philadelphia (1996).
[11] K. Kanari and T. Ozawa, *J. Thermal Anal.* (Proc. 11th ICTAC Congress) submitted.
[12] K. Ishikiriyama, A. Boller and B. Wunderlich, *J. Thermal Anal.* submitted.
[13] K. Ishikiriyama and B. Wunderlich, *J. Polym. Sci.* submitted.
[14] I. Okazaki and B. Wunderlich, *Macromolecules* submitted.
[15] B. Wunderlich, A. Boller and I. Okazaki, *Thermochim. Acta,* **282/283,**143 (1996).