ELSEVIER

Thermochimica Acta 310 (1998) 47–51

thermochimica acta

Finite-element calculations on the behaviour of a DSC in temperature-modulated mode[1]

G.W.H. Höhne*, N.B. Shenogina

Universität Ulm, Sektion für Kalorimetrie, Albert-Einstein-Alle 11, 89081 Ulm, Germany

Received 16 June 1997; accepted 19 June 1997

Abstract

The influence of changes of sample properties on the amplitude and phase shift of the differential-temperature signal as well as the influence of frequency changes has been calculated for a one-dimensional model of a temperature-modulated DSC (TMDSC) using a computer program for finite-element-method (FEM) calculations. Amplitude and phase shift of the measured signal ΔT (which is proportional to the differential heat-flow rate) is strongly influenced by the heat capacity of the sample. The connection is only linear for rather small heat capacities. The influence of the heat-transfer coefficient between sample and sample pan on amplitude and phase shift of the signal is not so large and linear (within the framework of our calculations). The influence of the heat-transfer coefficient between sample and sample pan on amplitude and phase shift of the signal is not so large and linear (within the framework of our calculations). For precise measurements, a very careful ''calibration'' is needed, which must take all the aforementioned influences into account. © 1998 Elsevier Science B.V.

Keywords: DSC; Finite-element method; Model calculations; Temperature modulation; TMDSC

1. Introduction

Temperature-modulated differential scanning calorimetry (TMDSC), which is commercially available for some years now, has become a widely used method in characterizing materials, in particular polymers. Nevertheless, the theoretical background of this method is not fully understood and the different approaches discussed in literature [1–3] are somewhat controversial. In addition, the influences of the apparatus, of its heat-transport properties and of those of the sample on the measured quantities were not, in our opinion, sufficiently precisely investigated to allow the user to consider his results critically. Anyway, such results, if they exist, have not been published yet. The manufacturers, on the other hand, have no great interest in publishing data showing the limits of their apparatus. The same is true for the ''calibration'' procedures, necessary to eliminate these influences.

These reasons have induced us to carry out model calculations to simulate the influence of apparatus properties on the amplitude and phase of the measured heat flow-rate signal. The results of these calculations may enable the user to distinguish, and to separate a possible influence of the apparatus from that of the sample reaction in question. A precise knowledge of such an influence is necessary to be able to ''calibrate it away'' correctly. The influence of different sample

*Corresponding author.

[1]Presented at the Twelfth Ulm-Freiberg Conference, Freiberg, Germany, 19–21 March 1997

PII S0040-6031(97)00384-5

reactions on the measured flow-rate signals were determined from model calculations as well; the results have been published elsewhere [4].

For reasons of simplification, we constructed a one-dimensional model (Fig. 1) of the essential parts of the heat-flow pathway in a real DSC (DSC-7, Perkin–Elmer). This model was used together with commercial finite-element-method (FEM) software (Ansys) to solve the heat-transport problems in a DSC in temperature-modulated mode. We proceeded as follows: the temperature of the heater was forced to follow the set temperature due to the time function:

$$T(t) = T_0 + \beta t + T_A \sin(\omega_0 t) \quad (1)$$

with T_0 the initial temperature, β the underlying heating rate, T_A the temperature amplitude and ω_0 the angular frequency. The temperature difference ΔT, between the thermometers on the sample and reference side of the model, was calculated at every moment and taken as the measure for the differential heat flow-rate ϕ. In normal DSC, ΔT is usually thought to be proportional to the latter:

$$\phi(t) = K\Delta T(t) \quad (2)$$

K being the calibration factor of the DSC. For TMDSC, the oscillating part of the flow-rate signal reads (in the absence of any time-dependent process in the sample) as follows [5]:

$$\tilde{\phi}(t) = mc_p\omega_0 T_A \cos(\omega_0 t - \varphi) \quad (3)$$

with m the mass and c_p the specific heat capacity. This model simulates the function of a heat-flux type DSC. From the calculated $\Delta T(t)$ function both, the amplitude and the phase shift (compared to $T(t)$) can be determined easily.

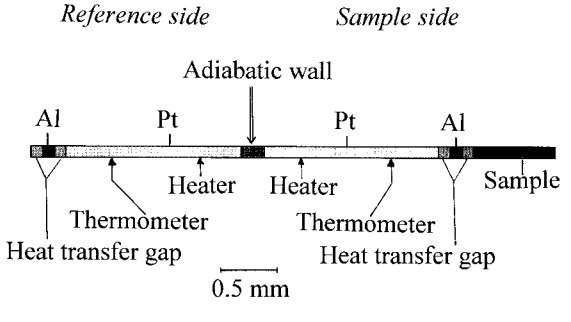

Fig. 1. Linear model of a DSC used for FEM calculations.

Power compensation could be simulated in our model too by controlling the power output of the sample as well as the reference heater proportional to the difference between the set temperature (1) and the actual temperature of the sample and the reference, respectively. The proportionality constant was selected in such a way, that the measured ΔT signal drops to ca. 10% of its value measured without power compensation (which fits rather well to experiences with the real apparatus).

2. Results

The following standard values have been used for the simulation calculations of TMDSC measurements: sample size and properties as of an indium sample of 10 mg mass, underlying heating rate β=1 K min^{-1}, modulated temperature amplitude T_A=1 K and a frequency of 50 mHz (ω=0.314 s^{-1}). The transient calculations of the temperature and heat-flow fields have always been continued until steady-state condition was reached. The amplitude and phase shift of the $\Delta T(t)$ signal was calculated from results within the steady-state region.

During real DSC measurements both, the heat capacity and the heat-transfer coefficient between sample and crucible can change during a run. This is obvious if a phase transition (e.g. melting) takes place in the sample, but may occur even during other events.

2.1. Influence of sample heat-capacity change

We started with the calculation of the influence of a change of the specific heat capacity of the sample, which was varied from 0.235 to 2.35 Jg^{-1} K^{-1}. The sample size and all other parameters (heat conductivity and density) were kept constant. The results are shown in Fig. 2. Both, the amplitude and the phase shift of the ΔT signal increase with increasing specific heat capacity of the sample. The connection is, however, not linear, as it should be from the theoretical point of view (Eq. (3)). This demand is fulfilled for small heat capacities only. For larger heat capacities both, amplitude and phase do not change any more, the temperature of the ''big'' sample is not able to follow the temperature changes of the furnace because of the

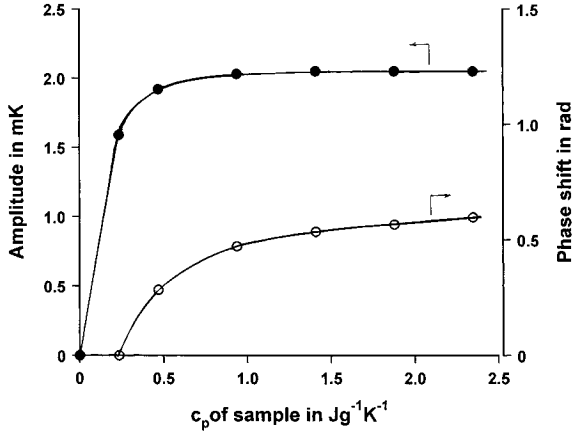

Fig. 2. Influence of the specific heat capacity on (●) amplitude and (○) phase of the ΔT-signal of the model (Fig. 1); T_A – 1 K, β – 1 K min^{-1} and f – 50 mHz.

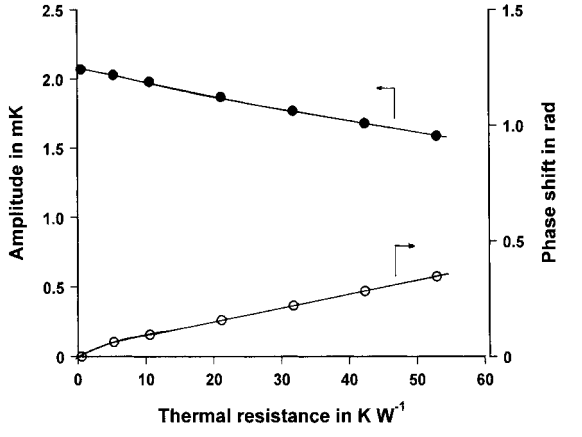

Fig. 3. Influence of the thermal resistance between sample and pan on amplitude (●) and phase (○) of the ΔT-signal of the model (Fig. 1); T_A: 1 K, β: 1 Kmin^{-1}, f: 50 mHz.

limited thermal conductivity between them. This follows from the phase shift (ca $\pi/2$) too. The thermal diffusivity of the sample is inversely proportional to the specific heat capacity, as both, density and thermal conductivity were kept constant during these calculations. Real measurements, with sample masses below 10 mg, are almost all on the left-hand side of Fig. 2, where a linear behaviour is found.

2.2. Influence of sample heat-transfer change

Next, we studied the influence of changes of the coefficient of heat transfer between sample and crucible on the properties of interest. This was done by changing the thermal conductivity of the "gap" material in our model, rather than by changing the dimension of the gap, which would have required the construction of a new model for every calculation. From the physical point of view both methods are equivalent. The thermal conductivity was chosen in such a way, that it reflects gap dimensions of 1–100 μm. Again, all other parameters, from the set of standard values of the model, were kept constant.

We found an almost linear relationship (Fig. 3) between amplitude as well as phase shift and the gap width, at least within the chosen range of variation, which seems to be reasonable from the practitioners point of view.

This behaviour is as expected, the gap acts as a thermal resistor (in series with others) along the heat-flow pathway. Every thermal resistor must reduce the temperature amplitude of the sample and cause a phase shift because of the limited speed of heat conduction. Such an influence of a thermal resistor can be described by a complex calibration factor $\tilde{K}$ between the oscillating parts of the heat-flow rate and the ΔT signal, in analogy to Eq. (2). The rather small deviations from strict linearity (see Fig. 3) should, however, be borne in mind, as this may influence the precision of measurements (or calibration).

2.3. Influence of frequency changes

Lastly, we changed the frequency ω_0 of the modulated temperature and calculated its influence on the amplitude of the ΔT signal (Fig. 4). From Eq. (3), a proportional behaviour should be expected. This is, however, only true for low frequencies. For higher frequencies, the behaviour of the TMDSC looks like that of a low-pass filter. This is because of the time constant of the response of the DSC signal on temperature changes of the heater. From the transfer theory it follows that ω_{max} (at the maximum of the $\Delta T(\omega)$ curve) is approximately reciprocal to the time constant ($\tau=1/\omega_{max}$). In our case, we get (from Fig. 4) $\omega_{max}\equiv 2\pi\nu_{max}=0.6\ s^{-1}$ and $\tau=1.65$ s, which corre-

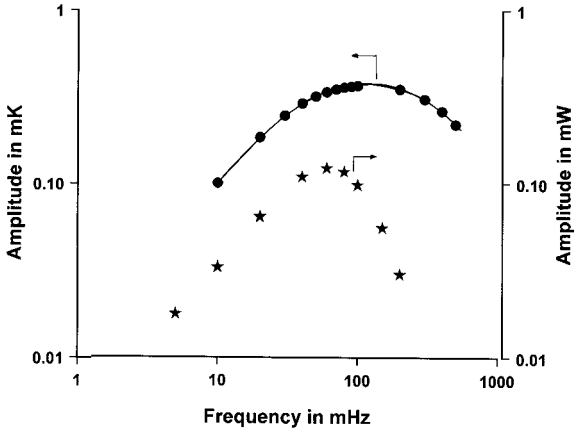

Fig. 4. Influence of the frequency of the temperature modulation on (●) amplitude of the ΔT-signal of the model (Fig. 1). For comparison, measured values (*) from a real DSC are added.

sponds to the measured value for such a type of DSC.

The fast decrease of the amplitude both, for lower and higher frequencies limits the frequency bandwidth of the DSC to a rather narrow region. If we restrict ourselves to a measuring range, where the signal-to-noise ratio does not change more than 1 : 10, we come to a frequency range of ca. 2.5 decades around ν_{max}.

To show the quality of our calculations, we have added measured values from a real DSC (DSC-7, Perkin–Elmer, in isothermal mode) which was loaded with a sample of 24 mg aluminium (Fig. 4, stars). The results from measurements and calculations coincide rather well, the very simple linear model seems to describe reality sufficiently closely. The faster decrease of the measured values at the high frequency side, compared with those of the calculations, is due to an additional time constant of the electronics (additional low-pass filter), which has not been taken into account in the FEM calculations.

2.4. *Influence of the power compensation*

All calculations presented so far have been carried out, including the power compensation control. The respective results are the same, beside the magnitudes of the calculated signals, which decrease 90%. This is as expected, because the power-compensation controller is a proportional controller which is a linear device, and influences the results only in a linear manner.

3. Conclusions

The model calculations, though starting from a very simple one-dimensional model, yield some results which are essential for the practice of TMDSC:

1. Amplitude and phase shift of the measured signal ΔT (which is proportional to the differential flow rate) is strongly influenced by the heat capacity of the sample. The connection is only linear for rather small heat capacities, at least for the modulation parameters (T_A and β) used in our calculations, which, however, are taken from real TMDSC measurements from literature.
2. The influence of the heat-transfer coefficient between sample and sample pan on amplitude and phase shift of the signal is not so large and linear (within the framework of our calculations). Nevertheless, this must been taken into consideration, especially if the heat-transfer conditions change during the measurement.
3. The influence of the modulation frequency on the amplitude of the signal restricts the frequency range of the TMDSC to a maximum of two-and-a-half decades. The centre of this range is determined by the reciprocal time constant of the apparatus in question. Again, the connection between frequency and amplitude is strongly non-linear.

To sum up:

For precise measurements a very careful ‘‘calibration’’ is needed, which must take all the aforementioned influences into account. In addition, the calibration substance, used for that purpose, should have the same heat capacity, thermal conductivity and heat-transfer coefficient (between sample and pan) to give reliable results.

To simply subtract an ‘‘empty-pan run’’ from the sample run, as is done in normal DSC to exclude apparatus influences, seems not to be of value in case of temperature-modulated DSC, because of the rather complex (often non-linear) influence of apparatus and sample properties on the measured signal in question.

References

[1] M. Reading, Trends in Polym. Sci. 8 (1993) 248.
[2] J.E.K. Schawe, Thermochim. Acta 260 (1995) 1.
[3] B. Wunderlich, A. Boller, I. Okazaki, S. Kreitmeier, J. Therm. Anal. 47 (1996) 1013.
[4] G.W.H. Höhne, Thermochim. Acta 304/305 (1997) 209.
[5] J.E.K. Schawe, Thermochim. Acta 271 (1996) 127.