GREATER INSIGHT INTO THE MTDSC TECHNIQUE INVOLVING FUNDAMENTAL SINUSOIDAL HEAT FLOW EQUATIONS

I. MacDonald, S. Clarke, R. Pillar, M. Ginic-Markovic and J. Matisons*

Nanomaterials Research Group, Flinders University, South Australia, 5042, Australia

Modulated temperature DSC was investigated, comparing data found experimentally to that derived from theory. Deviation from theory was found with regard to the amplitude of the modulated heat flow signal when large modulation amplitudes were employed in the experiment. These deviations were determined to be dependent on the absolute temperature and it was concluded that further investigation of the heat flow signal obtained during MTDSC experiments is required.

Keywords: *DSC, heat capacity, indium, modulated DSC, modulated heat flow, theory of MTDSC, tin*

Introduction

Modulated temperature DSC (MTDSC) was originally conceived by Reading [1–4] and the mathematical theory has been extensively studied by many researchers, including Wunderlich [5–9], Cao [10–12] and Thomas [13–15]. MTDSC not only provides the same data as conventional DSC; it also provides additional information not available from conventional DSC, thus enabling the user to analyse complex transitions. MTDSC also enhances the sensitivity and resolution of the heat flow signal. The use of a modulated signal in MTDSC allows direct and continuous measurement of heat capacity, enabling the user to separate the reversing and non-reversing heat flow components that make up total heat flow. This provides the user with a greater understanding of the sample properties being tested, hence making MTDSC an invaluable technique for polymer analysis. Some examples of research conducted using MTDSC include studies on the kinetics of polymer crystallisation [7, 16], the analysis of polymer melting [9, 17, 18] and various studies examining the glass transition [1, 19].

Conflicting views regarding the theory of MTDSC have recently arisen, particularly with respect to the determination of heat capacity as shown by Wunderlich [8]. Cao and Shanks [10] produced a paper that purported to show that Wunderlich's mathematical determination of heat capacity in Eq. (1) from the MTDSC experiment was incorrect. In Wunderlich's work, a relationship for the heat capacities of the sample and reference pans (C_{ps} and C_{pr}), the amplitudes of modulated heat flow (A_{HF}) and sample temperature (A_{TS}) and the heat transfer coefficient (λ) was derived from Newton's law of cooling. This relationship is shown in Eq. (1) where ω is the modulation frequency.

$$C_{ps}-C_{pr}=\frac{A_{HF}}{A_{TS}\lambda}\sqrt{\left(\frac{\lambda}{\omega}\right)^2+C_{pr}^2} \tag{1}$$

In order to more effectively utilise the MTDSC technique, the underlying mathematics must be fully understood. Temperature modulation is added to the system by modulating the temperature of the heating block in accordance with Eq. (2), where $T_b(t)$ is the heating block temperature, T_0 is the initial temperature, A_b is the modulated block amplitude and t is time in seconds.

$$T_b(t)=T_0+\beta t+A_b\sin(\omega t) \tag{2}$$

Combining Eq. (2) with Newton's law of cooling and the equation for heat capacity, Cao [10] was able to derive an equation for the sample temperature, T_s. Equation (3) fully describes the temperature signal in MTDSC.

$$T_s=K_s e^{\frac{-\lambda_t}{C_{ps}}}+T_0+\beta\left(t-\frac{C_{ps}}{\lambda}\right)+\frac{A_b\lambda}{C_{ps}}\left[\frac{\lambda\sin\frac{\omega t}{C_{ps}}-\omega\cos\omega t}{\omega^2+\left(\frac{\lambda}{C_{ps}}\right)^2}\right] \tag{3}$$

$$H_{f(T)}=\lambda\left[K_r e^{\frac{-\lambda t}{C_{pr}}}-K_s e^{\frac{-\lambda t}{C_{ps}}}\right]+\beta(C_{ps}-C_{pr})+H_{f(t)}^{m} \tag{4}$$

* Author for correspondence: ian.macdonald@flinders.edu.au

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

$$H^{\mathrm{m}}_{\mathrm{f(t)}} = \left[A_{\mathrm{b}}(C_{\mathrm{ps}} - C_{\mathrm{pr}})\lambda^2\omega \frac{\sqrt{\lambda^2\omega^2(C_{\mathrm{ps}} + C_{\mathrm{pr}})^2 + (C_{\mathrm{psS}}C_{\mathrm{pr}}\omega^2 - \lambda^2)^2}}{(C^2_{\mathrm{ps}}\omega^2 + \lambda^2)(C^2_{\mathrm{pr}}\omega^2 + \lambda^2)} \right] \sin(\omega t - \delta) \tag{5}$$

where

$$H^{\mathrm{m}}_{\mathrm{f(t)}} = [A_{\mathrm{HF}}]\sin(\omega t - \delta) \tag{5a}$$

A similar equation can then be derived for the temperature determined at the reference thermocouple in the cell, and by substituting these equations into the heat flow equation, the total heat flow given by Eq. (4) is obtained. The total heat flow of this new temperature regime combines the linear heat flow with Eq. (5), the modulated component of heat flow, $H^{\mathrm{m}}_{\mathrm{f(t)}}$. In Eq. (4) K_{r} and K_{s} are integration constants and δ is the phase lag between the sample and reference thermocouples, that arises from the modulated heating signal.

Since Eq. (5a) is a product of the amplitude of modulated heat flow and a wave function given by sin (ωt–δ), the amplitude function in Eq. (5) can be simplified to Eq. (6). A non-linearity exists between modulated heat flow and C_{ps} in Eq. (5). Cao [10] assumed this to represent an error in the MTDSC technique. However MTDSC measures the ratio between the modulated heat flow amplitude (given by Eq. (6)) and the amplitude of the modulated temperature signal. Our earlier work [20] clearly indicated that for this ratio a linear relationship with C_{ps} exists, similar to that obtained by Wunderlich in his pseudo-isothermal mathematical evaluation. Our earlier derivation also verified that a linear relationship exists even under ramped modulated conditions [20].

$$A_{\mathrm{HF}} = \frac{A_{\mathrm{b}}(C_{\mathrm{ps}} - C_{\mathrm{pr}})\lambda^2\omega}{\sqrt{(C^2_{\mathrm{ps}}\omega^2 + \lambda^2)(C^2_{\mathrm{pr}}\omega^2 + \lambda^2)}} \tag{6}$$

Cao and Shanks [10] incorrectly assumed the relevant temperature signal to use was the modulated *block* temperature (A_{b}). A_{b} can essentially be taken as constant. However, for heat capacity determination, it is the amplitude of the modulated *sample* temperature (A_{TS}) which is used, and this is certainly not constant. The amplitude of the sample temperature is given by Eq. (7), which then describes mathematically how modulation frequency and amplitude affect these signals.

$$A_{\mathrm{TS}} = \frac{A_{\mathrm{b}}\lambda}{\sqrt{C^2_{\mathrm{ps}}\omega^2 + \lambda^2}} \tag{7}$$

There has been a number of experimental studies [9, 13, 18, 21–24] performed on the technique itself, as a reasonable number of variables can be altered in any experiment. Cao [11, 12] performed experimental studies using MTDSC, whereby the amplitude of the modulated heat flow signal was shown to change with the modulation frequency in a non-linear fashion. Such a change in frequency was also shown to change the recorded value of the heat capacity. Other researchers [21, 22] have also obtained similar results, and so shown that the heat capacity changes when the underlying heating rate is increased.

Despite the number of studies on the technique, there is still little understanding of how the changes in variables affect the results of MTDSC experiments, and how this compares to the expected theoretical results. MTDSC has become a widely accepted technique for thermal analysis since its inception in 1993, and the results have proven to be highly useful, both in academic and industrial laboratories. This highlights the need for a better understanding of the influences of MTDSC variables on the resultant data.

This research represents our initial effort at developing a greater insight into the effect of experimental variables on MTDSC experimental results and relating them to the expected theoretical MTDSC data. As this technique is now so widely used, we believe that the theoretical aspects of MTDSC must be fully understood. There has been significant research into the effects of some variables such as modulation period and heating rate [8, 10, 13, 18, 21–24], however the effect of changing the modulation amplitude on heat flow signals, specifically the change in the modulated heat flow has not been examined. This work was conducted to determine how the experimental output of MTDSC compares to the theory defining these signals.

Experimental

MTDSC runs were performed using a TA Instruments 2920 DSC. Calibrations for baseline, cell constant and heat capacity constant were performed in accordance with the TA instruments manual. High purity tin and indium were obtained from TA Instruments and enclosed in sealed hermetic pans for the experimental runs.

Experiments were established to compare experimental and theoretical modulated heat flow data for indium and tin, each run at a heating rate of 2 K min^{-1}. The modulation periods used were 30 and 60 s. Nitrogen purged the cell at a flow rate of 50 mL min^{-1}. A range of modulation amplitudes from ±0.106 to ±3.18°C (Table 1) were used, and the signal was observed from 40°C before the melt of the metal.

The results from this experimental work were compared to theoretical results obtained from solving

Table 1 Modulation amplitudes used for experimental work and theoretical calculations

Modulated heat flow	Heating only amplitudes	Tangential amplitudes	Heating and cooling amplitudes
period 30 s	0.106, 0.15, 0.18	0.212	0.318, 0.424, 0.636, 1.0, 2.12
period 60 s	0.159, 0.212, 0.28	0.318	0.424, 0.636, 1.0, 0.318

the equations for the amplitude of modulated sample temperature (A_{TS}) and the amplitude of modulated heat flow (A_{HF}). The combined heat capacity of the sample plus aluminium pan was calculated to be 0.0534 J K^{-1} for both metals. The heat capacity of the aluminium reference pan was 0.0505 J K^{-1}. The heat transfer coefficient, λ, was arbitrarily assigned values between 10 and 0.001. The theoretically determined values of A_{HF} and A_{TS} were determined using the same modulation amplitudes and frequencies used in Experimental.

Results and discussion

Initially, we sought to evaluate the effect of the heat transfer coefficient, λ on the amplitudes of the modulated heat flow, A_{HF} and the modulated sample temperature A_{TS}. The theoretical values of A_{HF} and A_{TS} have been plotted in Figs 1–3. From Fig. 1 it can be seen that the theoretical value of A_{HF} remains relatively constant above a λ value of 0.01. Significant variation in the results calculated for A_{HF} was observed when λ was less than 0.01, where the calculated value of A_{HF} decreased quickly to zero in a logarithmic fashion. In Fig. 2, there is a linear increase in A_{TS} with increasing λ. At a λ value of 1.0, the theoretical A_{TS} results closely matched the experimentally obtained values. In Fig. 3, theoretical results for A_{TS} *vs*. block amplitude were plotted for values of λ varying from 0.0001 to 1, using a constant period of 30 s. Figure 3 also contains the experimental values of A_{TS} for indium metal measured with a 30 s period. It can be seen that when λ=1, the experimental data closely matches the theoretically derived results, up to a block amplitude of 1°C.

Similarly, Fig. 4 shows a close match in theoretically derived A_{TS} with experimental data for both indium and tin when λ=1, the period is 30 s and a block amplitude of up to 1°C is used. In Fig. 5 when a 60 s period is used, both indium and tin experimental data match theoretical data for λ=1 at all the block amplitudes tested up to 2.5°C. Prior to this research, other researchers [10, 11] had used λ values of around 0.01 for their work, which is the point where deviations between experimental and theoretical results commence. These results show that a λ value of 1 produces theoretical results closest to that obtained experimentally for A_{TS} and A_{HF}. It should be noted however, that A_{HF} is calculated from the difference in T_S

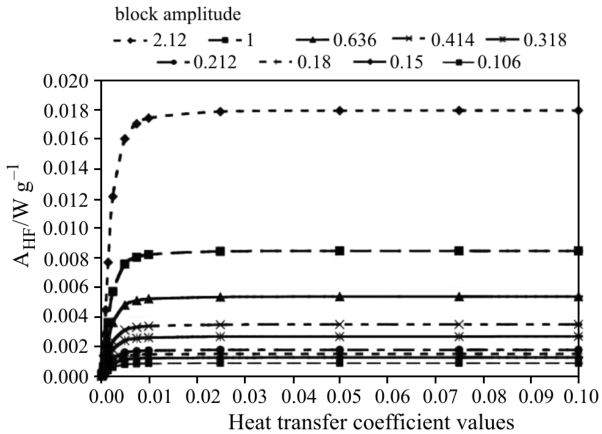

Fig. 1 Amplitude of modulated heat flow for indium at a modulation period of 30 s

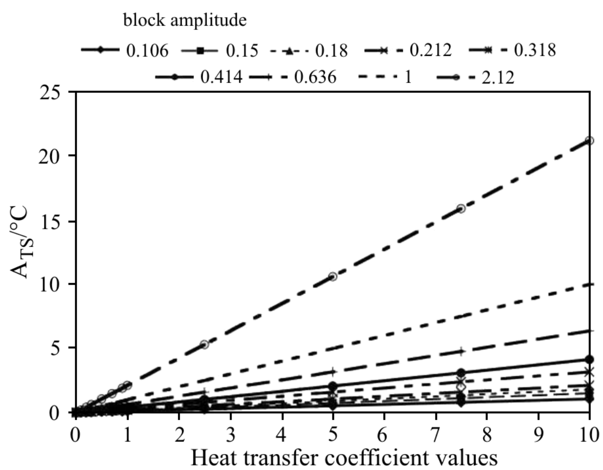

Fig. 2 Teoretical A_{TS} with changing values of the heat transfer coefficient for 30 s modulation period

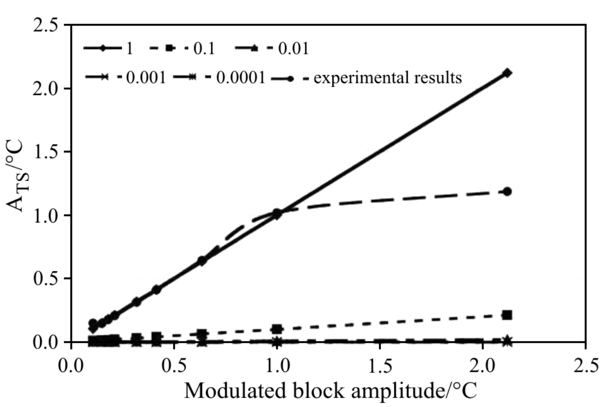

Fig. 3 Amplitude of modulated sample temperature *vs*. block amplitude for various values of λ (30 s period)

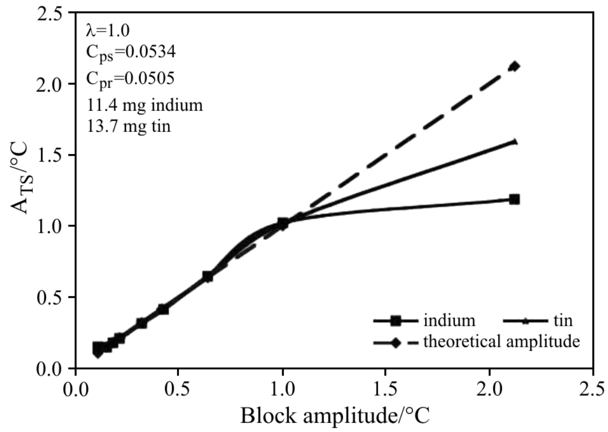

Fig. 4 Amplitude of sample temperature: period 30 s

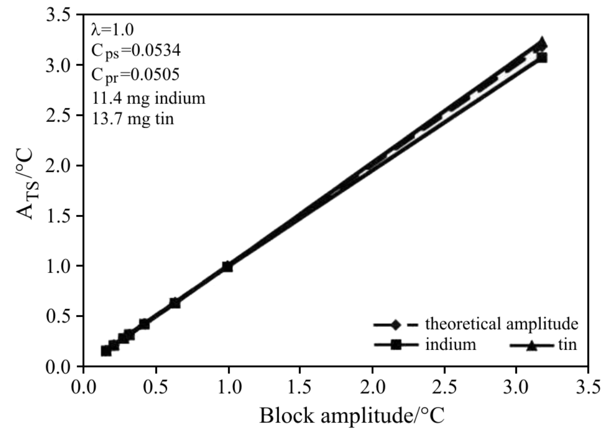

Fig. 5 Amplitude of sample temperature: period 60 s

and T_R data collected by the instrument. The fact that theoretical calculations for A_{TS} were so accurately predicted by theory is pleasing. Yet the experimental A_{HF} results were much greater for each metal tested than those calculated theoretically. This suggests that the A_{HF} calculation, using the difference of two potentially similar signals (T_S and T_R), still has errors. Further work is required to assess such errors in conventional MTDSC analysis.

Figure 4 depicts the modulated sample temperature amplitude A_{TS} *vs*. the modulated block amplitude A_b. In Fig. 1, the experimental results for A_{TS} showed an excellent linear correlation to the theoretical values. The A_{TS} did however drop below its theoretical value by almost 1°C for both samples (with a modulation period of 30 s). It was thought that there may have been some distortions in the heat flow signal due to the larger amplitude, but this was seen not to be the case. The heat capacity determination described by Wunderlich [8], is inversely proportional to the amplitude of the sample temperature, therefore the A_{TS} deviation is expected to increase the heat capacity value then determined by the technique. The experimental results are close enough to the theoretical description to validate this analysis; however care must be taken in the selection of experimental parameters so that an accurate determination of the heat capacity is realised.

In Fig. 5, the A_{TS} is plotted *vs*. the A_b results for samples run with a 60 s period. These results are much more stable, with only a slight 0.1°C deviation at the highest modulation amplitude. It appears that the 30 s period poses difficulties in maintaining steady instrumental control over the required temperature range. As Eq. (7) shows, A_{TS} is directly proportional to the block amplitude so a linear relationship between the two exists. This was confirmed experimentally over short temperature spans being careful to examine only temperature regions where no thermal transition occurs, so that the sample heat capacity remains effectively constant. Some deviations was observed for amplitudes above ±1.0°C when compared to theoretical values. The degree to which the experimental results agree with the theoretical values highlight the accuracy of the apparatus in measuring and controlling the temperature signal.

Equation (7) describes the amplitude of the modulated sample temperature, which is only dependent on the frequency of the modulation applied by the DSC and the amplitude of the block modulation, as all other values are constants. The variation in modulation frequency is currently the subject of an ongoing investigation. Figure 6 reveals the effect of modulation amplitude on the modulated heat flow signals for indium. It can be seen that for indium, increasing the modulation amplitude also increases the modulated heat flow signal. A_{HF} was examined for each run and it was determined that there was a linear relationship with the block amplitude, when the frequency is held constant. Such a linear relationship is consistent with theoretical expectations inherent in our earlier derivation of Eq. (7) [20].

Figure 7 shows the amplitudes of the modulated heat flow signal (A_{HF}) as a function of block amplitude. Theory predicts that A_{HF} should also increase linearly with the block amplitude. As shown in Fig. 7, the runs

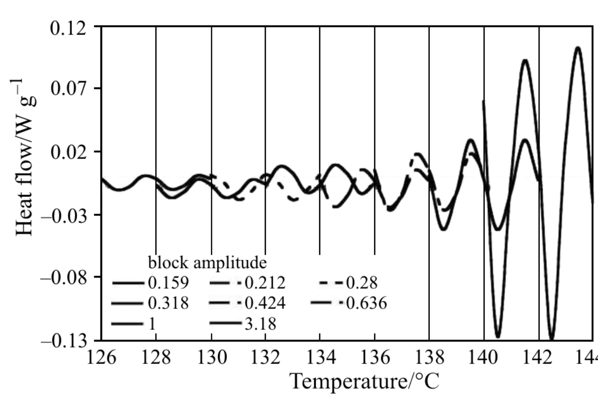

Fig. 6 Indium modulated heat flow (period 60 s)

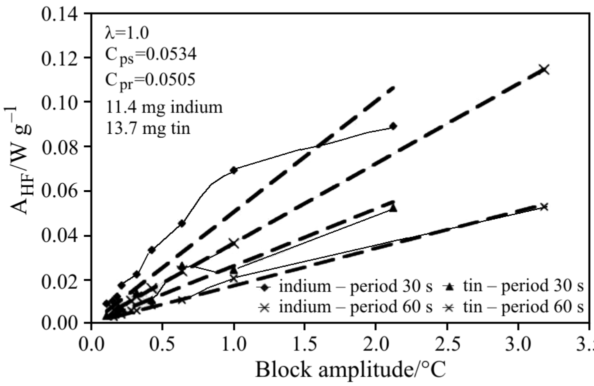

Fig. 7 Modulated heat flow amplitude experimental results

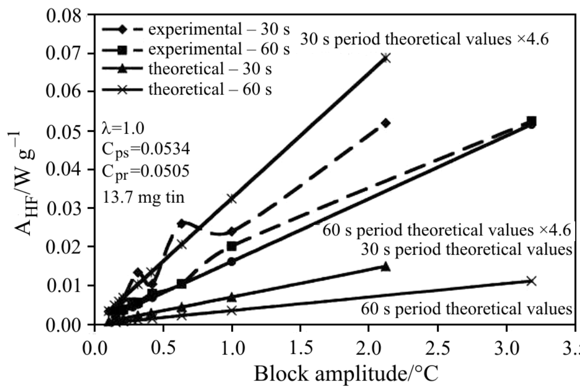

Fig. 8 Modulated heat flow amplitude: experimental and theoretical results for tin

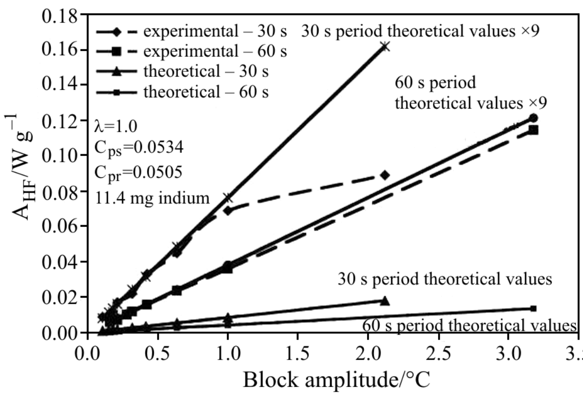

Fig. 9 Modulated heat flow amplitude: experimental and theoretical results for indium

performed at a modulation period of 60 s increased linearly with a small deviation at the highest block amplitude. The experimentally determined points for runs performed at 30 s periods showed some deviation at the larger amplitudes away from linearity and so had a greater standard deviation.

These experiments agree with Eq. (6), where A_{HF} is directly proportional to the modulated block amplitude (when the sample heat capacity remains relatively constant over short temperature spans). Using Eq. (6), the theoretical values of A_{HF} were calculated for the different block amplitudes using λ=1.0 (which produced data that closely matched the experimental results for tin and indium at 30 and 60 s periods). While these calculated values did not match the experimental results exactly, a definite similarity was observed. A linear trend occurred in the experimental results as predicted by theory, however the slopes of these lines did not fit the theoretical results. By multiplying the experimental results by a constant, the theoretical result can be made to match the experimental result. It should also be noted that the indium and tin masses used in the work gave the same heat capacity (in J °C^{-1}) so that the theoretical A_{TS} and A_{HF} should remain constant for each metal sample.

Figures 8 and 9 show the comparison between the theoretical and experimental results, as well as indicating the effect of multiplying the experimental results by a constant. The multiplication factor in Fig. 9 was estimated by dividing the slope of the experimental results by the theoretical result. The theoretical indium results, when multiplied by a factor of 9 matched for the experimental results. Similarly the experimental data for tin, when multiplied by a correcting factor of 4.6 matched the theoretical data. The exact nature of these correction factors, and their underlying fundamental cause, at this stage are not known. Radial symmetry is needed in the construction of the DSC cell and any contact resistance between the thermocouple and pans is not considered in the MTDSC equations. Lacey *et al*. [4] established that significant thermal resistance between the pans and thermocouple can result in the measured sample and reference temperatures being different to the actual sample and reference temperatures. This could account for the differences noted between the two metals.

The cell constant calibration determines a multiplying factor required to convert the electrical output signal to heat flow, and possibly the use of the modulated heating signal could require some modification of this value. The multiplication factor was not the same for the two metals used in this study, so there could be either a temperature or thermal resistance effect reflected in the determination of this value. The poor correlation between theoretical and experimental modulated heat flow amplitudes is a result of using highly conductive metals. Research currently being performed using organic materials with a much lower thermal conductivity, may influence the theoretical and experimental difference to a much lesser extent.

From these results, it would appear that Eq. (1) could more correctly be written as:

$$C_{ps} - C_{pr} = \frac{A_{HF}}{A_{TS}}\left(\frac{K}{\lambda}\right)\sqrt{\left(\frac{\lambda}{\omega}\right)^2 + C_{pr}^2}$$

where K is a correction factor that depends on the heat flow through the sample. An investigation of how this factor is determined and its effects on heat capacity measurements are the subject of ongoing investigations.

Conclusions

The purpose of this study was to examine the effect of experimental variables on MTDSC data and correlating these results to the expected theoretical results from the established MTDSC equations. The modulated block amplitude matches the modulated sample temperature as described by theoretical equations established in our previous study. There did appear to be some deviation from the theoretical results when using larger amplitudes and a 30 s modulation period, but this was ascribed to difficulties in instrumental control of the temperature regime. The comparison of the experimentally determined modulated heat flow signal amplitude with the theoretical results showed similar trends but not exactly matching results. There was some correction factor required for both results to match exactly. These results were obtained using metals that have a high thermal conductivity, so now a similar comparison using samples with lower thermal conductivities has commenced.

References

1 M. Reading and R. Luyt, J. Therm. Anal. Cal., 54 (1998) 535.
2 M. Reading, TRIP Vol. 1, 8 (1993) 248.
3 P. S. Gill, S. R. Sauerbrunn and M. Reading, J. Thermal Anal., 40 (1993) 931.
4 A. A. Lacey, C. Nikolopoulos and M. Reading, J. Therm. Anal. Cal., 50 (1997) 279.
5 A. Boller, B. Wunderlich and Y. Jin, J. Thermal Anal., 42 (1994) 307.
6 B. Wunderlich, Thermochim. Acta, 300 (1997) 43.
7 M. Pyda and B. Wunderlich, Proceedings of the NATAS Annual Conference on Thermal Analysis and Applications (1998), 26th, p. 287.
8 B. Wunderlich, Y. Jin and A. Boller, Thermochim. Acta, 238 (1994) 277.
9 K. Ishikiriyama, I. Okazaki, B. Wunderlich and A. Boller, Thermochim. Acta, 324 (1998) 77.
10 J. Cao, Y. Long and R. A. Shanks, J. Therm. Anal. Cal., 50 (1997) 365.
11 J. Cao, Thermochim. Acta, 325 (1999) 101.
12 J. Cao, Thermochim. Acta, 329 (1999) 89.
13 S. R. Aubuchon and L. C. Thomas, Proceedings of the NATAS Annual Conference on Thermal Analysis and Applications (1999), 27th, p. 724.
14 L. C. Thomas, American Laboratory (Shelton, Connecticut), 33 (2001) 26.
15 S. R. Aubuchon and L. C. Thomas, Proceedings of the NATAS Annual Conference on Thermal Analysis and Applications (1999), 27th, p. 718.
16 A. Toda, T. Arita, C. Tomita and M. Hikosaka, Polymer J. (Tokyo), 31 (1999) 790.
17 K. Ishikiriyama and B. Wunderlich, Macromolecules, 30, 14 (1997) 4126.
[18 P. Whittingstall and L. C. Thomas, Proceedings of the NATAS Annual Conference on Thermal Analysis and Applications (1999), 27th, p. 743.
19 M. Mayo-Pedrosa, C. Alvarez-Lorenzo and A. Concheiro, J. Therm. Anal. Cal., 77 (2004) 681.
20 S. Clarke, P. Folland and J. Matisons, Thermochim. Acta, 351 (2000) 29.
21 S. X. Xu, Y. Li and Y. P. Feng, Thermochim. Acta, 360 (2000) 131.
22 S. X. Xu, Y. Li and Y. P. Feng, Thermochim. Acta, 359 (2000) 43.
23 K. Ishikiriyama, A. Boller and B. Wunderlich, J. Therm. Anal. Cal., 50 (1997) 547.
24 F. Cser, F. Rasoul and E. Kosior, J. Therm. Anal. Cal., 50 (1997) 727.