ELSEVIER

Thermochimica Acta 351 (2000) 29–31

thermochimica acta

www.elsevier.com/locate/tca

Clarification about obtaining heat capacities using TMDSC

Stephen Clarke*, Peter Folland, Janis Matisons

Polymer Science Group, Ian Wark Research Institute, Levels Campus, University of South Australia, Mawson Lakes, SA 5095, Australia

Received 30 August 1999; accepted 16 January 2000

Abstract

We have evaluated the theoretical investigation, by [J. Cao, Y. Long, J. Shanks, J. Therm. Anal. 50 (1997) 365–373.], into the new temperature modulated differential scanning calorimetry (TMDSC) technique which was developed by [M. Reading, B. Hahn, B. Crowe, US Pat. 5,224,775, 1993.] and commercialized by TA Instruments. In a recent series of papers, Cao et al. (1997) came to the conclusion that TMDSC was not capable of determining heat capacity. This was in contradiction to previous work by [B. Wunderlich Y. Jin, A. Boller, Thermochimca Acta, 238 (1994) 277–293.] who suggested that the technique was capable of directly determining heat capacity. The primary aim of our evaluation was to clarify this conflict of opinion, and we have come to the judgment that when Cao's mathematical treatment is taken to its logical conclusion, there is no difference between either theory, and that both Wunderlich's and Cao's mathematical treatments confirm that TMDSC can be used to determine heat capacity.

Keywords: Temperature Modulated Differential Scanning Calorimetry (TMDSC); Modulated Differential Scanning Calorimetry (MDSC); Heat capacity; Modulated heat flow; Modulated temperature

1. Introduction

Thermal analysis has become one of the most important tools for the characterization of polymers and other materials [1,2]. Temperature modulated differential scanning calorimetry (TMDSC) [1,3–7] was developed and patented jointly by Reading and TA Instruments [8], and a detailed mathematical treatment of heat capacity measurement by TMDSC has subsequently been provided by Wunderlich [9–11]. Therefore, it was hardly surprising that three recent publications by Cao [12–14] criticizing the ability of TMDSC to directly determine heat capacity, the cornerstone of TMDSC, have caused a considerable degree of concern. We consequently set out to analyze, in detail, Cao's mathematical treatment [12], published earlier in this journal.

2. Discussion

Cao has shown that total TMDSC heat flow can be described by Eq. (1) [12].

$$H_{f(t)} = \lambda\left[\mathrm{K_r}e^{-\lambda t/C_{\mathrm{pr}}} - \mathrm{K_s}e^{-\lambda t/C_{\mathrm{ps}}}\right] + \beta\left(C_{\mathrm{ps}} - C_{\mathrm{pr}}\right) + H^{m}_{f(t)} \quad (1)$$

Where λ is the heat transfer coefficient from Newton's law of cooling; C_{ps} and C_{pr} are the heat capacities for the sample (including the pan) and the reference pan;

* Corresponding author. Tel.: +61-8-8302-5146; fax: +61-8-8302-3683.
E-mail address: stephen.r.clarke@unisa.edu.au (S. Clarke)

0040-6031/00/$ – see front matter
PII: S0040-6031(00)00405-6

β is the underlying heating rate; t is time and K_s and K_r are integration constants.

The last part of Eq. (1) $(H^m_{f(t)})$ is the modulated component of total heat flow and is given by Eq. (2) [12].

$$H^m_{f(t)} = \left[A(C_{ps} - C_{pr})\lambda^2\omega \times \frac{\sqrt{\lambda^2\omega^2(C_{ps} + C_{pr})^2 + (C_{ps}C_{pr}\omega^2 - \lambda^2)^2}}{(C^2_{ps}\omega^2 + \lambda^2)(C^2_{pr}\omega^2 + \lambda^2)}\right] \times \sin(\omega t - \delta) \quad (2)$$

Where A is the amplitude of the modulated temperature for the heating block; ω is the frequency of the heating block temperature modulation; and δ is the phase lag between the sample and reference thermocouples.

The amplitude of the modulated component of the total heat flow is given by Eq. (3) [12,13].

$$A_{HF} = A(C_{ps} - C_{pr})\lambda^2\omega \times \sqrt{\frac{\lambda^2\omega^2(C_{ps} + C_{pr})^2 + (C_{ps}C_{pr}\omega^2 - \lambda^2)^2}{(C^2_{ps}\omega^2 + \lambda^2)(C^2_{pr}\omega^2 + \lambda^2)}} \quad (3)$$

Cao and Shanks [13] have referred to the papers by Wunderlich et al. [9,10] in which the latter define that heat capacity is proportional to the amplitude of the modulated component of total heat flow divided by the amplitude of the modulated sample temperature. The analysis by Cao of Wunderlich's work lead him to the conclusion that if Wunderlich was correct then heat capacity must be directly proportional to the amplitude of the modulated component of heat flow. However, he incorrectly substituted the amplitude of the modulated sample temperature with the amplitude of the modulated block temperature [13]. Knowing that the amplitude of the modulated block temperature is constant Cao concluded that there should be a linear relationship between amplitude of the modulated component of heat flow Eq. (3) versus heat capacity [12]. He plotted this, obtained a non-linear relationship [12] and, therefore, concluded that TMDSC cannot be used to determine heat capacity [12,13].

Unfortunately Cao used the amplitude of modulated block temperature to obtain sample heat capacity. This is not the procedure used by TMDSC to obtain sample heat capacity. Rather than divide the amplitude of the modulated component of total heat flow Eq. (3) by the amplitude of modulated block temperature, the authors should have divided by the amplitude of the modulated sample temperature [9–11,15]. The sample temperature is given by Eq. (4). This same equation was derived by both Wunderlich [9–11] and Cao [12] (albeit by slightly different procedures) in their mathematical treatments.

$$T_s = K_s e^{-\lambda t/C_{ps}} + T_o + \beta\left(t - \frac{C_{ps}}{\lambda}\right) + \frac{A\lambda}{C_{ps}} \times \left[\frac{\lambda \sin\omega t/C_{ps} - \omega\cos\omega t}{\omega^2 + \left(\lambda/C_{ps}\right)^2}\right] \quad (4)$$

Eq. (4) can be rewritten as Eq. (5) where ε is the phase lag between the heating block and the sample thermocouple.

$$T_s = K_s e^{-\lambda t/C_{ps}} + T_o + \beta\left(t - \frac{C_{ps}}{\lambda}\right) + \frac{A\lambda}{\sqrt{C^2_{ps}\beta\omega^2 + \lambda^2}}\sin(\omega t - \varepsilon) \quad (5)$$

The amplitude of the modulated component for the sample temperature (A_{T_s}), from Eq. (5), is shown in Eq. (6).

$$A_{T_s} = \frac{A\lambda}{\sqrt{C^2_{ps}\omega^2 + \lambda^2}} \quad (6)$$

The amplitude of the modulated heat flow Eq. (3) can be expanded under the square root term, and simplified, to result in an expression given by Eq. (7).

$$A_{HF} = \frac{A(C_{ps} - C_{pr})\lambda^2\omega}{\sqrt{\left(C^2_{ps}\omega^2 + \lambda^2\right)\left(C^2_{pr}\omega^2 + \lambda^2\right)}} \quad (7)$$

Eq. (7) can now be divided by the amplitude of the modulated sample temperature to give Eq. (8), which is proportional to the heat capacity difference between the sample (including the pan) and the reference.

$$\frac{A_{HF}}{A_{T_s}} = \frac{\lambda\omega(C_{ps} - C_{pr})}{\sqrt{C^2_{pr}\omega^2 + \lambda^2}} \quad (8)$$

Since $\sqrt{C_{\rm pr}^2\omega^2+\lambda^2}=\omega\sqrt{\left(\frac{\lambda}{\omega}\right)^2+C_{\rm pr}^2}$ Eq. (8) can be rewritten as Eq. (9).

$$\frac{A_{\rm HF}}{A_{T_{\rm S}}}=(C_{\rm ps}-C_{\rm pr})\frac{\lambda}{\sqrt{(\lambda/\omega)^2+C_{\rm pr}^2}} \tag{9}$$

Eq. (9) can then be rearranged to give the heat capacity difference between the sample (including the pan) and the reference (Eq. (10)).

$$(C_{\rm ps}-C_{\rm pr})=\frac{A_{\rm HF}}{A_{T_{\rm S}}\lambda}\sqrt{\left(\frac{\lambda}{\omega}\right)^2+C_{\rm pr}^2} \tag{10}$$

When matched DSC pans are used, $(C_{\rm ps}-C_{\rm pr})=(mc_{\rm s})$ where m is the mass of sample and $c_{\rm s}$ is the specific heat capacity of the sample. The heat capacity of the sample is, therefore, given by Eq. (11) where $(C_{\rm pr}^{\#})$ is the heat capacity of matched DSC pans.

$$mc_{\rm s}=\frac{A_{\rm HF}}{A_{T_{\rm S}}\lambda}\sqrt{\left(\frac{\lambda}{\omega}\right)^2+\left(C_{\rm pr}^{\#}\right)^2} \tag{11}$$

Eq. (11) is the result of an extension to Cao's mathematical procedure, but taken to its logical conclusion. Eq. (11) is identical, in every respect, to Wunderlich's result [9–11] which showed that sample heat capacity was directly proportional to the ratio of the amplitude of the modulated component of total heat flow and the amplitude of the modulated sample temperature.

3. Conclusions

In this article we have shown that Cao and Shanks have incorrectly assumed that the heat capacity from TMDSC is found by dividing the amplitude of the modulated component of total heat flow with the amplitude of the modulated block temperature. Rather than using the amplitude of the modulated block temperature, Cao should have used the amplitude of the modulated sample temperature. When these corrections are incorporated into Cao's mathematical treatment and then taken to a logical conclusion the same ultimate result for sample heat capacity is found as was obtained by Wunderlich in 1994. [9–11]

Whilst this section of Cao's mathematical treatment was flawed, the rest of his work should not be discounted out of hand. Although we have not had an opportunity to scrutinize, in detail, the rest of the work it would appear that the information related to total heat flow, modulated heat flow and heat flow phase lag [12–14] may be of considerable significance. However any work related to heat capacity must be discounted for the reasons discussed above.

References

[1] E. Turi (Ed.), Thermal Characterization of Polymeric Materials, Vol. 1 and 2, 2nd Edition, Academic Press, San Diego, 1997.

[2] B. Wunderlich, Thermal Analysis, Academic Press, Boston, MA, 1990.

[3] S.R. Clarke, T.P. Matisons, J.G. Wilks, Chem. Austr. 65 (10) (1998) 16.

[4] S.R. Clarke, Thermal Analysis, Getting the most from MDSC: science 2000 professional seminar series, The Scientific Suppliers Association of Australia, The Melbourne Exhibition Centre, Melbourne, Vic., Australia, September 1998.

[5] M. Reading, Trends in Polym. Sci. 8 (1993) 248.

[6] M. Reading. Modulated temperature DSC: Where are we now? In: Proc. 25th NATAS Conference, 622, 1997.

[7] Technical Applications Note — TA210, Modulated DSC Compendium: Basic Theory and Experimental Considerations, (1997), and Thermal Applications Note — TA2llB, Thermal Analysis Review: Modulated DSC Theory (1997); TA Instruments, Thermal Analysis and Rheology (A Subsidiary of Waters Corp.) New Castle, DE, USA.

[8] M. Reading, B. Hahn, B. Crowe, US Pat. 5224, 775, 1993.

[9] B. Wunderlich, Y. Jin, A. Boller, Thermochim. Acta 238 (1994) 277–293.

[10] A. Boller, Y. Jin, B. Wunderlich, J. Therm. Anal. 40 (1994) 307.

[11] B. Wunderlich, Thermal analysis in research and production: lecture and workshop notes, in: RACI 10th National Convention, Adelaide Convention Centre, South Australia, RACI Polymer Division, September 1995.

[12] J. Cao, Thermochim. Acta 325 (1999) 101–109.

[13] J. Cao, Y. Long, R.A. Shanks, J. Therm. Anal. 50 (1997) 365–373.

[14] J. Cao, Thermochim. Acta 329 (1999) 89–95.

[15] R. Blame, G. Dallas, Personal communication, T.A. Instruments, Delaware USA, 6th of August 1999.