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THE UTILITY OF PHASE CORRECTION IN MODULATED DSC

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Abstract

Traditionally, Modulated DSC™ (MDSC®) [1] has been used to simultaneously measure the heat capacity and heat flow of a sample in a single experiment. As first proposed by Reading *et al.* in 1992 [2], this complex heat capacity signal (C_p^*) can be further deconvoluted into components which are in-phase (C_p') or out-of phase (C_p'') with the imposed temperature modulation. The vector sum of these components, respectively termed the reversing C_p and kinetic C_p, is equal to the aforementioned complex C_p (C_p^*).

Recent research has centered around the analysis of these signals and their inclusion into MDSC experiments. For most polymer systems, the contribution of the kinetic C_p is negligible, except at the melt. This signal does contain a small peak at the T_g of PET, but the significance of this peak is to date not clear. Examples of further applications will be presented and discussed, as well as the derivation and interpretation of novel MDSC signals.

Keywords: modulated-temperature DSC, phase-lag

Introduction

MDSC can be used to measure the heat capacity (C_p) of a sample. This is performed by measuring the amplitude of the modulated heat flow signal, and dividing by the amplitude of the modulated heating rate signal. After the predetermined $K(C_p)$ calibration constant is applied, an accurate value of C_p can be obtained.

Recent studies have centered around the calculation of phase-lag and it's contribution to the measured heat capacity signal. Phase-lag calculation involves measuring the heat flow phase angle with respect to the imposed temperature profile. For a sinusoidal heating rate, in the absence of any transition, the heat flow would be expected to be 90° ($\pi/2$ rad.) out-of-phase with the modulated temperature, and 180° (π rad.) out-of-phase with the modulated heating rate (Fig. 1). Signals exhibiting this ideal phase angle are perfectly in-phase, i.e., the magnitude of the phase-lag is equal to 0°. Any deviation from 0° phase-lag results from either sample effects, instrument effects, or a combination of the two.

During some transitions, heat flow can be attributed to two general processes: the heat flow corresponding to C_p i.e. the thermodynamic heat flow, and the heat flow associated with any kinetic processes, such as relaxation, crystallization, or melting. The latter heat flow can have a large time-dependence. If the magnitude of this kinetic heat flow is large enough, it can cause a deviation in the sinusoidal heat-

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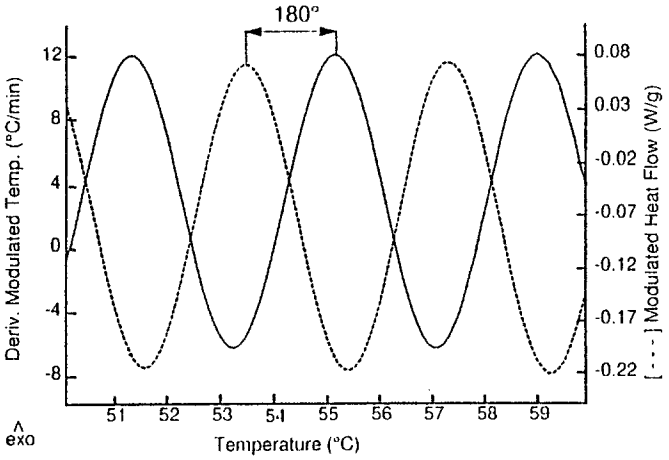

Fig. 1 Phase angle between modulated heat flow and modulated heating rate

flow response, or a phase-lag. This lag may affect the heat capacity measurement, and thus the deconvoluted heat flow signals in MDSC.

The expected effect was first documented by Reading and coworkers in 1992 [2] then later discussed by Schawe [3] and can be explained as follows: Heat capacity can be described as having two components, a real component (C_p') and an imaginary component (C_p''). The real component is the true heat capacity of the material, which is related to fast molecular motion. The heat flow associated with this heat capacity is in-phase (reverses) with respect to the temperature modulation, and is thus referred to as the reversing heat capacity, C_p'. The imaginary component of heat capacity arises from the out-of-phase response of the sample, and has been attributed to kinetic events within the sample, or from dissipation processes relating to entropy production [4]. Thus, it is referred to as the kinetic heat capacity, C_p''. These two components can be used in a vector summation to give complex heat capacity, C_p^*.

$$C_p^{*2} = C_p'^2 + C_p''^2$$

or more simply,

$$C_p^* = (C_p'^2 + C_p''^2)^{0.5}$$

Traditionally, the heat capacity signal in MDSC has been reported as C_p^*.

Examination of the heat-flow phase angle in the MDSC experiment provides the ability to measure any phase-lag occurring within a sample during an MDSC experiment, and use the phase-lag to deconvolute C_p^* into its real (reversing) and imaginary (kinetic) components. This deconvolution is performed by measuring the true heat flow phase during an experiment. The baseline of the heat flow phase signal must then be centered at 0.0 rad, corresponding to zero-phase-lag to eliminate any

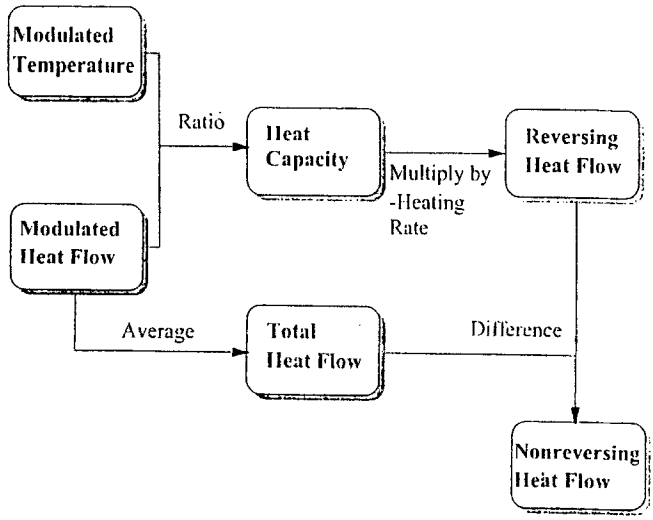

Fig. 2a Derivation of deconvoluted signals in a traditional MDSC experiment

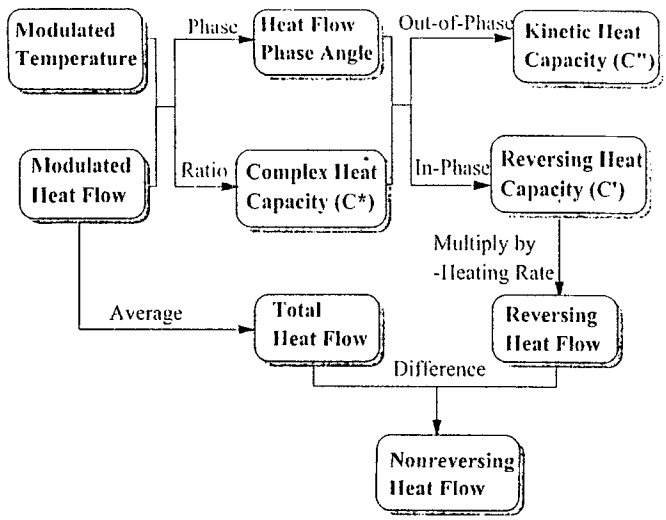

Fig. 2b Derivation of deconvoluted signals in a phase-corrected MDSC experiment

experimental effects such as imperfect sample pan-cell contact. Any deviation from the 0.0 rad baseline can be attributed to true sample phenomena, which give rise to the kinetic component of heat capacity, C_p''.

The reversing C_p (C_p') and kinetic C_p (C_p'') are calculated as follows:

$$C_p^* = \text{Classical } C_p \text{ signal}$$

$$C_p' = C_p^* \cos\theta$$

$$C_p'' = -C_p^* \sin\theta$$

where θ = heat flow phase-lag angle, 0 rad in the absence of any slow process. Thus when no transitions are occurring, $C_p' = C_p^* \cos 0 = C_p^* (1) = C_p^*$, and $C_p'' = -C_p^* \sin 0 = C_p^* (0) = 0$. As the phase-lag angle deviates from 0, the C_p'' contribution gets larger.

New (phase-corrected) deconvoluted heat flow signals can then be easily generated. A phase-corrected reversing heat flow signal is calculated by multiplying C_p' by the underlying ramp rate, and a phase-corrected nonreversing heat flow signal is then calculated by subtraction of the reversing heat flow from the total heat flow. (Total heat flow is not affected by phase). Figure 2 illustrates the derivation of the deconvoluted signals from a traditional and a phase-corrected MDSC experiment.

Phase correction example

A sample of quenched PET was analyzed using MDSC with the following conditions:

Sample mass – 14.157 mg, pan type – standard aluminum, purge gas – helium @ 25 ml min^{-1}, heat rate – 3°C min^{-1}, modulation amplitude – ±1°C, modulation period – 60 s.

Figure 3 shows the total heat flow and the heat flow phase signal from the experiment. The shift of ca. –0.3 rad in the heat flow phase baseline is due to experimental effects, such as purge gas and sample pan contact with the cell. The peaks in this signal indicate regions where deviations from the ideal phase angle of the baseline occur. These are most prevalent at the glass transition, the cold crystallization, and the melt; the regions affected by phase correction.

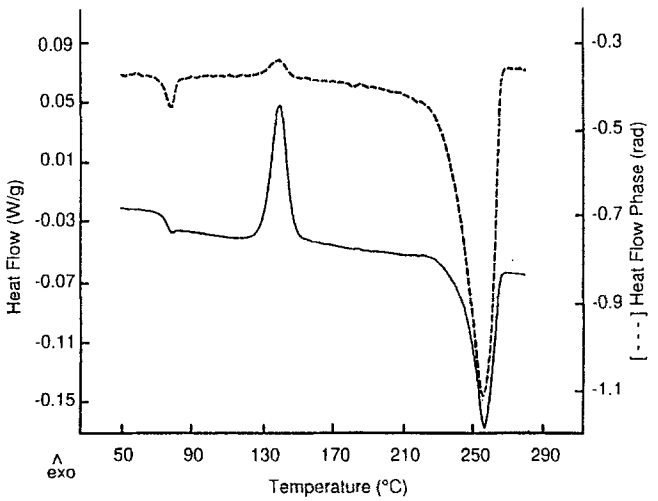

Fig. 3 Heat flow phase (upper curve) and heat flow from quenched PET

Before phase correction is applied, it is necessary to eliminate the experimental effects. This is done by shifting the heat flow phase baseline to 0.00 rad (zero-phase-lag). Figure 4 illustrates this shift.

The phase correction baseline was chosen just before the glass transition, and just after the melt, in regions where the baseline was flat. These points were assigned to define the zero-phase-lag baseline. Once the baseline is assigned to 0.00 rad, any deviation from this baseline is due to sample effects, as opposed to experimental effects. Note that the phase deviation varies in sign for different transitions. Melts and glass transitions are typically endothermic events and cause phase 'lags' (negative deviation), whereas the exothermic cold crystallization induces a phase precedent, or 'lead'.

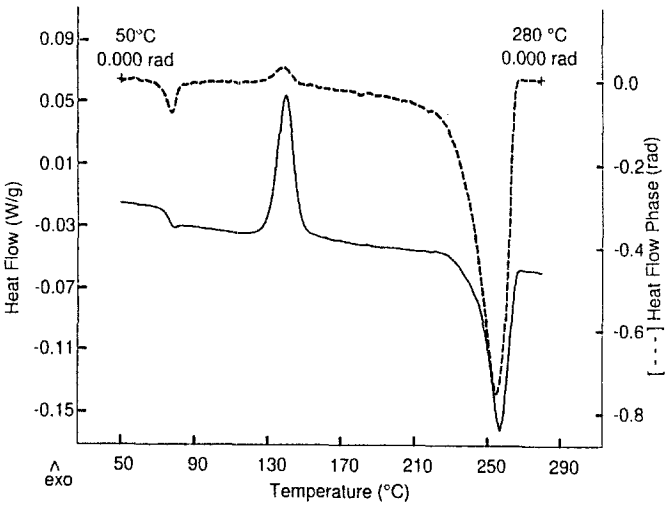

Fig. 4 Heat flow phase shifted to zero-phase-lag baseline

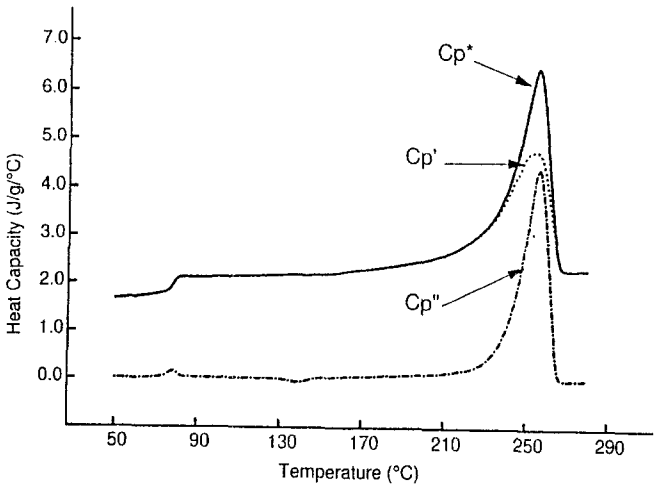

Fig. 5 Phase-deconvoluted heat capacity signals for quenched PET

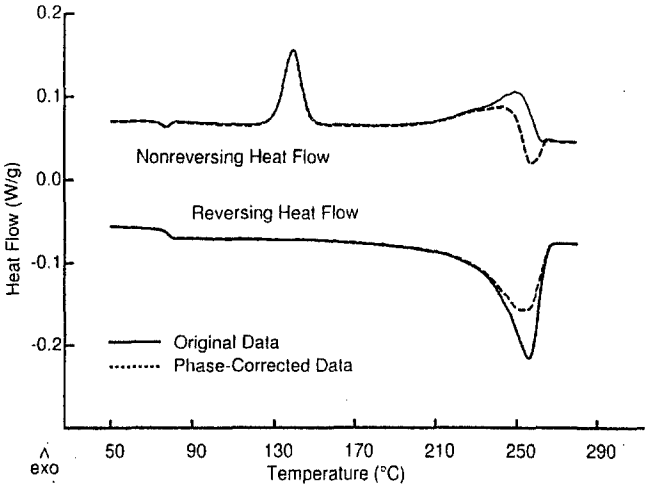

Fig. 6 Effect of phase correction of deconvoluted heat flow signals

Figure 5 shows the deconvoluted heat capacity signals for the quenched PET sample. The kinetic C_p signal is a good indicator of the regions of the curve where phase-lag is occurring. Note, however, the equivalence of the reversing C_p and the complex C_p signals. The phase correction in this experiment affects the results only at the melt, where loss of steady-state conditions occurs, and large kinetic heat flows predominate. Figure 6 compares the reversing heat flow and non-reversing heat flow signals before and after phase correction was applied.

Conclusions

A new capability has been added to Modulated DSC data analysis. This capability provides for the separation of heat capacity into in-phase (real) and out-of-phase (imaginary) components. The vector sum of these components is equal to the complex heat capacity, the signal traditionally measured by MDSC. For most polymer transitions, the out-of-phase component is very small, thus the in-phase component and the complex component will be virtually identical.

Phase correction in MDSC does allow for the measurement of time-dependent heat capacity phenomena, which will be investigated in future work.

References

1 'Modulated DSC' and 'MDSC' are registered trademarks of TA Instruments, Inc., New Castle DE (USA) 1972.
2 M. Reading, D. Elliott and V. Hill, Proc. 21st North American Thermal Analysis Society Conference, 1992, p. 145–150.
3 a) J. E. K. Schawe, Thermochim. Acta, 260 (1995) 1; b) J. E. K. Schawe, Thermochim. Acta, 271 (1996) 127.
4 R. Haase, Thermodynamics of Irreversible Processes, Dover Publications, New York 1990.