MODULATED DIFFERENTIAL SCANNING CALORIMETRY
The effect of experimental variables

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Abstract

The reproducibility and reliability of the TA Instruments Modulated Differential Scanning Calorimeter (MDSC) was tested over a range of conditions. The equipment baseline was found to be fairly constant with a very small fluctuation (10 μW), which means a 0.1% fluctuation on the scale of a normal polymer MDSC curve. The excellent stability of the baseline and the reasonable reproducibility of the curves (5%) suggest that frequent calibration is not required.

The heat capacities calculated from the modulated response to the variable temperature depend on the frequency for a given cell constant. The heat capacity cell constant is a unique function of the modulation frequency:

\[ K_c = \frac{K_c^o}{p/p-6.3} \]

where \( p \) is the time of the periodicity expressed in seconds and \( K_c^o \) is the heat capacity cell constant measured on a standard material and reduced to zero frequency. The cell constants depend on the flow rate of the helium according to:

\[ K(He) = K^o(1.298-0.004424He+1.438\times10^{-5}He^2) \]

where \( He \) is the flow rate of helium in ml min\(^{-1}\) and \( K^o \) represents a constant at 100 cm\(^3\) min\(^{-1}\). There is a strong dependence of cell constant on the flow rate ranges from 10 to 80 cm\(^3\) min\(^{-1}\), while above this rate (up to 135 ml min\(^{-1}\)) the cell constant approaches a plateau.

Keywords: frequency dependence, heat capacity, MDSC, thermal analyses

Introduction

Basics of MDSC

Modulated DSC (MDSC) was developed by Reading et al. [1, 2] and was produced commercially by TA Instrument. It combines a linear change of tempera-
ture with a sinusoidal modulation in a heat flow type of DSC cell. This enables the instrument to record the heat capacity of the sample parallel with the heat flow, because of the modulated change of the temperature. The response function (instantaneous heat flow) of the tested material to the temperature function is compared for normal and modulated measurements in Table 1 [3–5]:

The total heat flow can be divided into two parts, i.e. the reversible and kinetic heat flows according to Eq. (1):

$$\frac{dQ}{dt}_{\text{total}} = \frac{dQ}{dt}_{\text{reversible}} + \frac{dQ}{dt}_{\text{kinetic}}$$  \hspace{1cm} (1)

where the reversible heat flow is defined by Eq. (2):

$$\frac{dQ}{dt}_{\text{reversible}} = -C_p(T)\beta$$  \hspace{1cm} (2)

i.e. the heat capacity multiplied by the negative of the overall rate of temperature change ($\beta$ see Table 1).

The equipment records the actual (modulated) temperature, the instantaneous (modulated) heat flow in response to temperature function and phase angle of these two harmonic functions. If the change in the temperature is within the harmonic range (which depends on the parameters of the modulation, the actual temperature, the overall heating rate and the power of the heating/cooling devices) a Fourier analysis of the response of the temperature function will result in two functions: the heat capacity ($C_p$) which is determined mainly by the amplitude of the responses, and the total heat flow which is the average of the heat flow, $\Delta H_t$. The Fourier analysis uses one and a half periods of the modulation and it will produce an artificial peak if there are less than 4 modulation periods through a transition [3–5].

The problem

Several publications have appeared in the literature in the recent years dealing with the theoretical background of the MDSC, particularly with the steady state conditions of the modulated or oscillating DSC cell [6–8]. In this paper we present our experiences with the TA MDSC Instrument and to show its reproducibility. The influence of various equipment parameters on the measured calorific data are also presented. These parameters are cell constants, rate of heating/cooling, modulation frequency, and rate and quality of the purging gas.

The cell constant is determined by the geometry and the construction of the cell, and is given by the producer upon delivery of the equipment (primary calibration). In this study it has been recalibrated by new sets of calibrating parameters, using indium as the standard material, with different heating rates.

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