PLASTER OF PARIS SPECIFIC HEAT DETERMINATION BY MODULATED DSC
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Abstract
Conventional DSC has been usually used for the determination of specific heats of liquids and solids, from at least three runs: of a blank, standard sapphire and that of the sample. The present paper shows how specific heats can be determined by modulated DSC in a faster way, which was applied to a plaster of Paris sample. After a proper calibration procedure using standard sapphire, the operational parameters were chosen as shown in the text. The method was tested measuring the specific heat of sapphire and deionized water, indicating that good and reliable data can be obtained directly using only one run, instead of the three runs, usually needed when conventional DSC method is used.

Keywords: Modulated temperature DSC, specific heat, plaster of Paris, gypsum.

Introduction
Modulated temperature DSC was introduced in the early 90’s and the discussion of its operating variables and conditions has been extensively presented and discussed in the literature [1, 2]. Adding a sinusoidal modulation term to a constant heating rate control function, a total heat flow curve, equivalent to the conventional DSC curve can be obtained, as well as a reversing and non-reversing heat flow curves [3], which are respectively, the heat capacity and kinetic components of the total heat flow curve. It has been used in many applications, such as poly(ethylene terephthalate) (PET) characterization [3], the direct measurement of heat capacity, [4, 5], analysis of thin films [6], solid state decomposition reactions [7] and PC/PEE blend characterization [8].

In modulated temperature DSC, the programmed temperature (T) can be expressed by [2]:

\[ T(t) = T_o + \beta t + A \sin(\omega t) \]  

(eq. 1)

where \( T_o \) is the starting temperature, \( \beta \) the heating rate, \( t \) the analysis time, \( A \) the amplitude of the temperature modulation and \( \omega \) the frequency, which is equal to \( 2\pi/P \), where \( P \) is the period of the modulation. As detailed in a previous work [9], the resulting modulated heating rate and heat flow curves are cyclic functions that depend on the chosen operating variables. This allows the heat capacity of the sample (\( C_p \)) to be calculated in real time and continuously. Thus, running the experiment in sample constant mass conditions in sealed pans, its specific heat \( c_p \) can be obtained directly by equation 2:

\[ c_p = \frac{C_p}{m} \]  

(eq. 2)

Conventional DSC is usually used for the determination of specific heats, which are calculated from at least three run data: of a blank, of standard sapphire and that of the sample [10]. As will be shown in the present paper, the specific heat expression of any material as a function of temperature can be obtained from a single modulated temperature DSC run.
Objectives

The present paper shows how specific heats can be determined by modulated DSC in a faster way, which was applied to a plaster of Paris sample.

Experimental

The analyses were performed by using a TA Instruments MDSC, model 2920, which was calibrated with standard sapphire. Preliminary test runs indicated that the best conditions, using sealed Al pans, and samples of approximately 5 mg, were: cooling at 2°C/min from ambient temperature to –15°C, then heating at 4°C/min up to 60°C, with +/- 0.5°C temperature modulation amplitude and a modulating period of 100 seconds. These conditions were established to have the plaster of Paris specific heats to be used to normalize non-conventional differential thermal analysis (NCDTA) data of the authors from 20 to 50°C. Figure 1 shows the linear expression obtained from literature standard sapphire $c_p$ data, which were used to calibrate the MDSC equipment [4] and two standard sapphire $c_p$ curve measurements by MDSC after calibration.

![Graph showing the relationship between temperature and specific heat capacity](image1)

Fig. 1 - Literature standard sapphire specific heat ($c_p$) as a function of temperature and Specific heat ($c_p$) curves obtained for 2 runs of standard sapphire at the optimized operating conditions, with respective values at 30°C

As can be seen in Figure 1, the sapphire $c_p$ results are very reproducible and indicated that a cell constant of 1.035 should be used, within the temperature range of 20 to 50°C, when using the chosen operating conditions for the MDSC runs. Figure 2 shows typical curves of total heat flow, modulated heat flow, modulated heating rate and mean heating rate applied during plaster of Paris MDSC analysis. By using Universal Analysis software of the equipment, the reversing $c_p$ values at different temperatures $T$ are
obtained by dividing the respective total heat flow by the mean heating rate at a temperature T, to obtain the heat capacity (Cp) function and then dividing it by the sample mass, to obtain the $c_p$ curve.

Fig. 2 - Typical curves of the operating parameters applied during plaster of Paris analysis.

Fig. 3 - Specific heat curves of deionized water and of a plaster of Paris sample.

It can be noticed that in the used operating conditions, very well established modulated heat flow and modulated temperature curves were obtained from 10°C, a necessary condition to accept any registered data above this temperature.

Figure 3 shows the specific heat curves of deionized water and of a plaster of Paris sample. The obtained values for water are practically equivalent to that of the usually used in literature (4.18 J·g$^{-1}$·°C$^{-1}$). For the plaster of Paris sample, considering data after the operating conditions where in steady state, its
specific heat can be expressed by \( c_p = 0.93 - 0.0003T \), \( c_p \) in J.g\(^{-1}\).\(^{\circ}\)C\(^{-1}\) and \( T \) in \(^{\circ}\)C for the 20 to 50\(^{\circ}\)C temperature range, with a good correlation coefficient.

**Conclusions**

Modulated DSC enables one to obtain in real time the specific heat of materials in a single run, after properly calibrated by using standard sapphire at chosen operating conditions.

This enables one to obtain \( c_p \) curves as a function of temperature in a much faster way than when using conventional DSC methods.

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**References**