Temperature Modulated DSC / ADSC

Introduction

Differential scanning calorimetry (DSC) is widely used for the characterization of materials with respect to phase transitions such as melting and crystallization. Recently, a novel technique known as Temperature Modulated DSC (TMDSC) has been introduced [1,2,3]. In TMDSC a periodic temperature modulation is superimposed on the constant heating or cooling rate of a conventional DSC measurement. METTLER TOLEDO has commercialized TMDSC as Alternating Differential Scanning Calorimetry (ADSC). It allows modulation with either simple waveforms such as steps or sawtooths ("Steady-State ADSC"), or with sinusoidal waveforms characterized by a temperature amplitude A_T and an angular frequency ω, defined as $2\pi/P$, where P denotes the period of the sine wave. In this latter case, the general temperature program, $T(t)$, is given by

$$T(t) = T_0 + \beta_0 t + A_T \sin\omega t$$

where T_0 denotes the initial temperature, t the time and β_0 the underlying (average) heating rate. As shown in Figure1, setting different values for the parameters allows a wide variety of different temperature programs to be used.

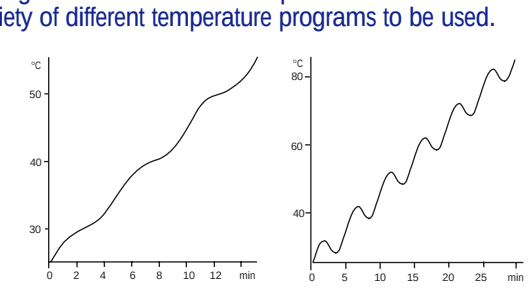

Fig. 1. Temperature programs with various parameter settings: left, β_0 = 2 K/min, A_T = 1 K, P = 5 min, right, β_0 = 2 K/min, A_T = 3 K, P = 5 min

The measured heat flow in response to this temperature program is also periodic. Certain effects such as changes in the specific heat capacity due to a glass transition can follow the applied heating rate ("reversing" phenomena), whereas other effects such as crystallization cannot ("non-reversing" phenomena). The periodic heat flow signal is therefore the superposition of an in-phase heat flow component and a component that is out of phase with the heating rate.

The analysis of an ADSC signal is shown schematically in Figure 2. Using the dynamic definition of the heat capacity,

$$c_p = \frac{dQ}{dt} \cdot \frac{1}{m \cdot \beta_0}$$

where dQ/dt denotes the heat flow and m the sample mass, the complex heat capacity is calculated according to the equation

$$\left| c_p^* \right| = \frac{A_q}{A_\beta} \cdot \frac{1}{m}$$

where A_q and A_β denote the amplitudes of the modulated heat flow and heating rate. Furthermore, a phase angle between the ADSC signal and the heating rate is established. Averaging the ADSC-signal yields the "total heat flow", which corresponds to the result of a conventional DSC experiment run at the underlying heating rate. By means of the phase angle, the in-phase and out-of-phase components of the complex heat capacity can be calculated. The reversing heat flow is computed from the in-phase heat capacity, and the difference between the average or total heat flow and the reversing heat flow yields the non-reversing heat flow. Figure 3 shows the typical output of an ADSC experiment for a sample of PET.

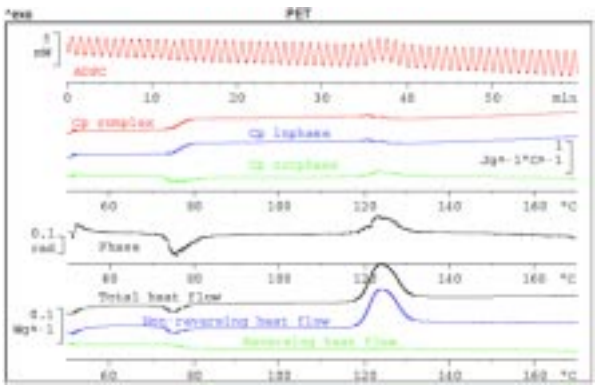

Fig. 3. ADSC evaluation of PET. The glass transition can be seen in the reversing heat flow curve, and the enthalpy relaxation and the cold crystallization in the non-reversing heat flow curve. The total is equivalent to a non-modulated DSC curve. A typical indication of the glass transition is the negative peak shown by the phase curve at about 75 °C.

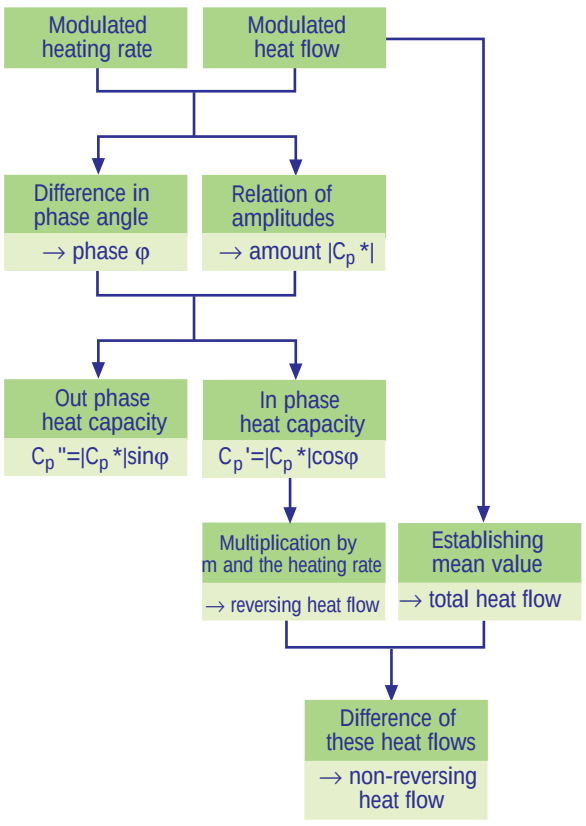

Fig. 2. Evaluation and results of a modulated DSC curve

Experimental

First of all, from a practical point of view, it is important to have a good idea about the effects that might appear in an ADSC experiment. To do this, a preliminary conventional DSC experiment is recommended. This allows suitable temperature regions to be identified and further investigated with ADSC.

Secondly, in order to set the ADSC parameters properly (underlying heating rate, amplitude and period of the modulation function), one should ensure that about 5 to 10 cycles cover the transition range under investigation. Furthermore, the maximum cooling and heating rates of the instrument have to match the corresponding values of the ADSC temperature program.

Finally the mass of the sample should usually be kept to just a few milligrams in order to ensure quasi-equilibrium conditions, and samples with poor heat transfer properties should be submitted to longer time periods and to smaller temperature amplitudes than samples of good thermal conductivity.

Applications

ADSC has been used very successfully to separate superimposed effects such as glass transitions and enthalpy relaxations [3, 4]. Typical examples are shown in Figures 4 and 5.

Apart from that, ADSC allows the accurate measurement of the specific heat capacity under quasi-isothermal conditions even during chemical or physical transitions [5, 6, 7]. Figure 6 shows the results of an ADSC analysis of a spray-dried pharmaceutical formulation with residual moisture content. An example of a quasi-isothermal c_p measurement during a chemical reaction is shown in Figure 7.

Conclusions

ADSC is a very promising technique that yields very meaningful information in cases where conventional DSC is unsuccessful. Its main features and possibilities are:

- high temperature resolution and sensitivity
- separation of overlapping effects in a wide variety of different applications (e.g. polymers, food, pharmaceuticals)
- accurate measurement of specific heat capacities under quasi-isothermal conditions even during chemical or physical transitions.

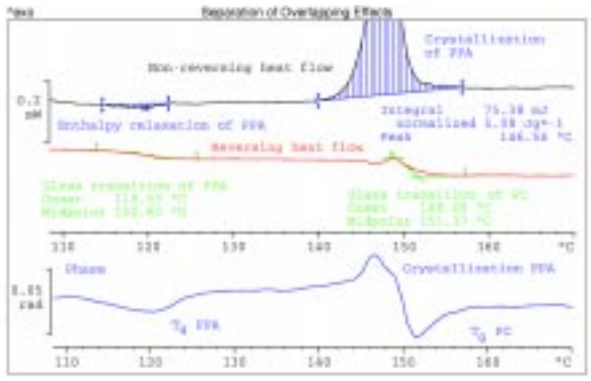

Fig. 4. ADSC of a mixture of Polyphthalamide (PPA) and Polycarbonate (PC). The non-reversing heat flow first shows a slight enthalpy relaxation during the glass transition and the crystallization of PPA. The glass transitions of PPA and PC are seen in the reversing curve and also, but less clearly, in the phase curve. In a conventional DSC measurement, the glass transition of the PC would be hidden by the crystallization peak of the PPA.

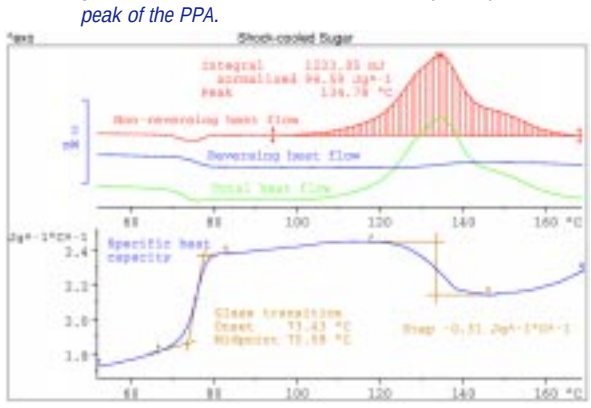

Fig. 5. ADSC of shock-cooled amorphous sugar. The glass transition can be seen in the reversing heat flow curve at about 75 °C. The non-reversing curve shows the crystalli-zation. Both the glass transition and the crystallization can be clearly seen in the specific heat capacity curve.

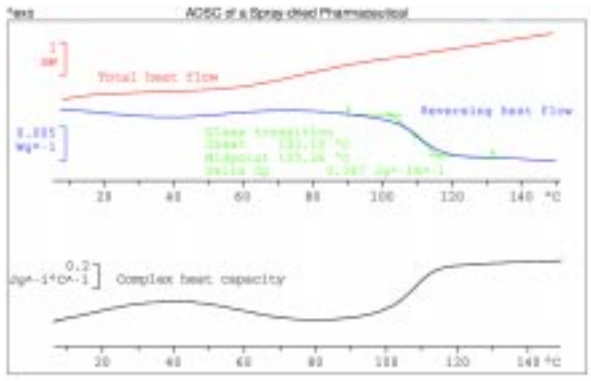

Fig. 6. ADSC of a spay-dried pharmaceutical formulation with a residual moisture content of 10.8%. Both the reversing heat flow and the complex heat capacity curves clearly show the glass transition at about 110 °C. This cannot be seen in the total heat flow curve because of the evaporation of the water.

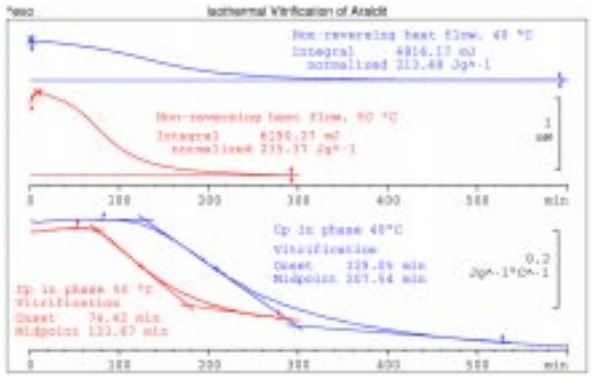

Fig. 7. Isothermal vitrification of Araldit. The non-reversing heat flow curve shows the course of the vitrification. The Cp in-phase curve shows how the specific heat decreases during the reaction.

References

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