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COMPENSATION OF THE INFLUENCES ON DYNAMICAL THERMAL MEASUREMENTS CAUSED BY HEAT FLUX EFFECTS - A PRACTICABLE MODEL FOR THE DSC

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ABSTRACT

A simple mathematical model for the DSC is proposed. It allows to calculate the original heat flux and temperature of the sample and, thus, the real heat capacity, uneffected by the measuring system. Two examples of the calculation are discussed.

INTRODUCTION

The shape of DSC-curves is determined not only by heat capacity and heat of reaction of the sample, but also by several instrumental effects. Since a heat flux is necessary between sample holder and sample, a temperature difference results. It is easy to show, that a differential scanning calorimeter works not strongly linear in that sense, that an increase of the heat capacity C_S or heat of reaction would influence not only the height, but also the shape of the output-signal. For that reason the common advised deconvolution of apparent DSC-signals with an apparatous function - the response to an elementar event - is not adequate to the real experimental conditions /1, 2/. Here a new solution of this problem is offered.

MODEL

Since the DSC-signal is mainly determined by the thermal conduction between sample holder and sample, this system can be described by a simple chain of heat capacities and thermal resistances in analogy to the electrical case of capacities and resistances /3/. Figure 1 shows the principal experimental arrangement of the DSC and the scheme of capacities and resistances; the parameters are described in the figure.

The simplified picture considers only the sample, sample container and sample holder (heater). It can be described with a system of differential equations, connecting the temperatures T_H, T_C and T_S with the difference of heat fluxes; ' refers to the reference heater:

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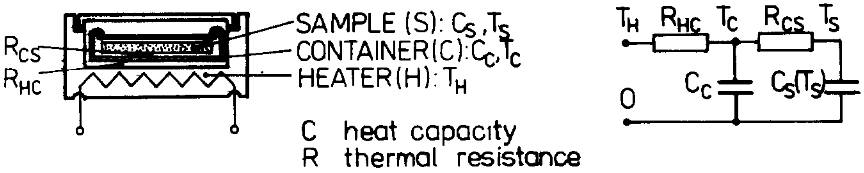

Fig. 1: Illustration of experimental arrangement of the DSC and simplified scheme with heat capacities and thermal resistances

$$\Delta \dot{Q} = \dot{Q} - \dot{Q}' = \frac{T_C' - T_C}{R_{HC}} = \frac{T_H - T_C - \dot{T}_H \cdot R_{HC} C_C}{R_{HC}} ,$$

$$T_C = T_S + R_{CS} \cdot C_S(T_S) \cdot dT_S/dt ,$$

$$dT_C/dt = \frac{T_H - T_C}{R_{HC} C_C} - \frac{T_C - T_S}{R_{CS} C_C} . \qquad (1)$$

It is surprising, that this system of differential equations (1) can be solved analytically. Assuming, that the DSC is in the scanning mode and the sample container and heater are symmetrical to the reference side, we get for the temperature of the sample

$$T_S = T_H - \dot{T}_H \cdot R_{HC} \cdot C_C - (R_{HC} + R_{CS}) \cdot \Delta\dot{Q} - R_{HC} \cdot R_{CS} \cdot C_C \cdot d(\Delta\dot{Q})/dt \qquad (2)$$

and for the heat capacity of the sample

$$C_S(T_S) = \frac{\Delta\dot{Q} + R_{HC} \cdot C_C \cdot d(\Delta\dot{Q})/dt}{\dot{T}_H - (R_{HC} + R_{CS}) \cdot d(\Delta\dot{Q})/dt - R_{HC} \cdot R_{CS} \cdot C_C \cdot d^2(\Delta\dot{Q})/dt^2} \qquad (3)$$

with $C_S(T_S) = (dH_S/dT_S)$.

The heat capacity C_S includes besides the normal thermodynamical specific heat C_p also other possible sources of heat production.

This model describes usual curves of melting and crystallization of pure substances excellently. The comparision of measured and calculated curves allows the determination of the model parameters. By particularly samples (sandwich-arrangement) the model parameters can be determined also for unknown substances.

PRACTICAL REALISATION

For the practical realisation we need the first and second derivation of the DSC-signal $\Delta\dot{Q}$. To get representative values a smoothing procedure is necessary, for instance by cubic splines /4/. Figure 2 shows DSC-signals $\Delta\dot{Q}$ and the calculated original heat flux $C_S(T_S) \cdot \dot{T}_H$ over the temperature. Mean features of the results are:

- + In the case of small values of $d(\Delta\dot{Q})/dt$ the curve doesn't change.
- + The greater the slope $d(\Delta\dot{Q})/dt$, the greater is the difference between the measured and the calculated curve.
- + Creases in the DSC-signal were drastically amplified, they produce peaks.
- + The area under measured and calculated curve is certainly the same.

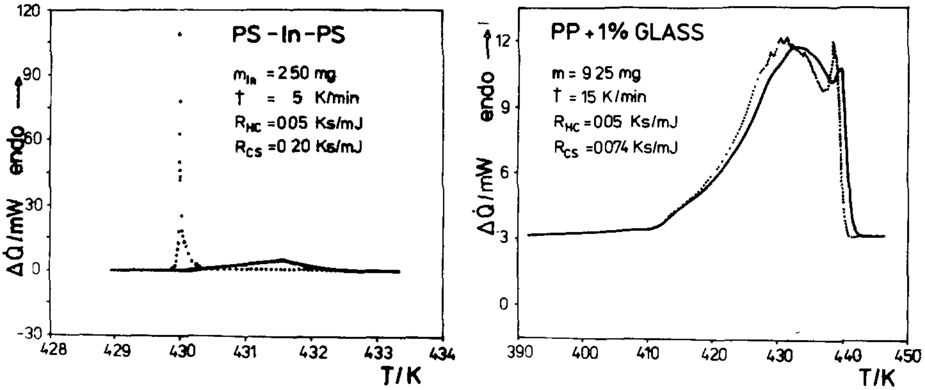

Fig. 2: Measured (solid) and calculated (dotted) curves for two DSC scans.

Left: Sandwich arrangement with indium embedded in polystyrene to simulate the thermal resistance of polystyrene; right-hand side: Melting of glass reinforced polypropylene

CONCLUSIONS

If DSC-curves contain rapid changes in $\Delta \dot{Q}$ it is inevitable for detailed kinetic interpretation to calculate first of all the original heat flux of the sample. For on-line calculation with the data station of the DSC parallel to the measurement an other smoothing procedure will be necessary.

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