Dynamic behaviour of power-compensated differential scanning calorimeters.
Part 4. The influence of changes in material properties [☆]

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Abstract

The influence of sample material properties on the smearing of measured curves has been proved experimentally. As shown by model calculations, changes in material properties at the glass transition result in a change in Green's function for the liquid state compared to that for the glassy state. From experimental investigations, moreover, it follows that these effects are overlapped by influences of the change in the thermal contact between sample and pan. It was found that change in the thermal contact influences the determined Green's function more than changes in material properties do.

The error in the desmeared curves, determined using a Green's function obtained via other materials properties, is within the limits of accuracy of the measurements. Therefore the Green's function estimated from the switch-on as well as from the switch-off behaviour can be used to desmear the whole measured curve, if the material properties do not change markedly, as is the case during the glass transition of polymer materials.

Keywords: Desmearing; DSC; Glass transition

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1. Introduction

In every differential scanning calorimeter (DSC), heat transfer causes a tempera-ture gradient in the furnace–pan–sample system. This results in a falsification ("smearing") of the DSC curves, especially in the case of measurements on substances with low thermal conductivity [1].

Under certain conditions, it is possible to describe the DSC as a linear apparatus [1–4], and we can correct the smearing of the measured curve with the aid of the theory of linear response [1]. The measured heat flow rate signal Φ_{out} is, in this case, the convolution product of the true (unsmeared) heat flow rate Φ_{in} and the Green's function G of the system

$$\Phi_{out}(t) = \int_0^t G(t - \tau)\Phi_{in}(\tau)\, d\tau \qquad (1a)$$

or in short terms

$$\Phi_{out}(t) = G(t) * \Phi_{in}(t) \qquad (1b)$$

$\Phi_{in}(t)$ can be interpreted as the heat flow rate into an infinitely thin, thermally ideal, coupled sample.

The smearing of the measured curve is caused both by the thermal resistance between the sample and DSC furnace, and by that from the sample which causes a temperature profile inside the sample during the measuring run. These phenomena are to be described by the Green's function $G(t)$ which may be determined ex-perimentally from the relaxation behaviour of the DSC curve at the beginning or at the end of the heating or cooling run [3].

The validity of the algorithm in question (Eq. (1)) presupposes a stable tempera-ture profile inside the sample and the DSC during the run. In the case of a thermal event in the sample, the profile must be nearly unchanged [3]. This implies that the material properties of the sample (specific heat capacity c_p, density ρ, and thermal conductivity λ) are also unchanged [1,5].

In the case of a glass transition this assumption is usually fulfilled. However, there is a small change in the temperature profile inside the sample due to the small changes in the material properties at the glass transition. However, Green's function $G(t)$ contains the behaviour of the sample in either the glassy state or the liquid state but not the behaviour of the changes at the glass transition. As a result, the desmeared curve must be faulty in the glass transition region. In a previous paper [2], the maximum error of this erroneous desmearing was determined with the aid of model calculations. We found that the maximum temperature error of the glass transition temperature determined from the desmeared curve is 0.25 K for a 20 mg polystyrene (PS) sample at a heating rate of 20 K min^{-1}. The calculated tempera-ture profiles in the glassy and liquid state of that sample differed by 0.25 K as well. In the time frame, after switching from isothermal to scanning mode, the heat flow reaches the half-step height of 0.75 s earlier in the glassy state of the sample than in the liquid state [2]. In addition, a change in the thermal contact between DSC pan and sample at the glass transition also influences the Green's function. Because

of the decreased viscosity of the liquid material compared with the glass, the thermal contact should be better during glass transition. This effect should cause a decrease of the relaxation time in the liquid state.

This paper presents an experimental examination of the model calculations.

2. Experimental conditions and evaluation

The measurement conditions were chosen to correspond closely to the model assumptions of the calculations in question [2]. This allows a direct comparison of the experiments with the results of the model calculations.

The measuring instrument was a DSC-2 (Perkin-Elmer Corp.), upgraded by a modern computer control [6].

In a first step, the DSC behaviour when switching on and switching off the scan rate was analysed. The conditions of these experiments are described in section 3.1, below. Then the glass transition region of a polystyrene (PS) sample (mass; 24.5 mg) was investigated in a temperature range from 310 to 450 K at a heating rate of 20 K min^{-1}.

To obtain defined conditions from the thermodynamic point of view, the sample was always kept at 450 K for 2 min and then cooled at 20 K min^{-1} before every measurement. In order to decrease the influence of the reference furnace on the experimentally determined Green's function [4,7], the zero line was determined in a separate empty pan run and subtracted from the curve of the sample run.

In a third series of measurements, the glass transition of PS samples, measured in the normal way (see above) and with a film of silicon oil between sample and pan bottom, were compared. The silicon film (4.06 mg of oil) should guarantee an unchanged good thermal contact between both the glassy and the liquid PS and the pan. In this experiment the mass of the sample was 19.40 mg.

The measured curves were desmeared by numerical methods using the following procedure:

(1) (a) Determination of Green's function for the switch-off step response behaviour of the measured curve by means of numerical differentiation and subsequent smoothing.

   (b) Fourier transformation of both the measured curve and Green's function with the aid of the Fast-Fourier-Transformation (FFT) algorithm.

   (c) Division of the measured curve by the Green's function in Fourier space.

   (d) Smoothing of the result by Wiener filtering.

   (e) Retransformation of the result from Fourier space into time space [8–10].

(2) (a) Determination of Green's function from the switch-on step response behaviour of the measured curve ($\Phi_{out}(t)$) by solution of the convolution integral (Eq. (1)) in time space, where the function $\Phi_{in}(t)$ is the sum of a step function and a linear increasing function. The slope of the latter was determined from the temperature dependence of c_p [3]. The integral equation (Eq. (1)) was solved in this case by the numerical regularization method of Tickonov [11,12].

    (b) The measured curve and Green's function were deconvoluted by means of the same regularization method.

(3) As in 2, but with determination of Green's function from the switch-off step response behaviour of the measured curve. In this case the function $\Phi_{in}(t)$ is a pure step-function.

3. Analysis of step response behaviour

3.1. Comparison of the switch-on and switch-off behaviour of a DSC run

As mentioned, the experimental Green's function can be determined either from the behaviour of the measured curves on switching-on or switching-off the scan rate. Before discussing the influence of the sample properties on $G(t)$ (see sections 3.2 and 3.3), we will begin with the analysis of the differences in switch-on and switch-off behaviour. A PS sample (18.41 mg) was heated from isothermal equilibrium at 300 K with a scan rate of 20 K min^{-1} to 330 K and then held isothermally for 10 min. During this time the measuring system relaxes to equilibrium state. Then the sample was heated with the same scan rate to 360 K and held isothermally again. The zero line (with empty pans) was measured in the same manner.

The zero-line-corrected measured curves are shown in Fig. 1.

As can be seen, curve 2 relaxes more slowly to equilibrium on switching of the scan rate than does curve 1. This refers to the influence of the glass transition region (enthalpy retardation).
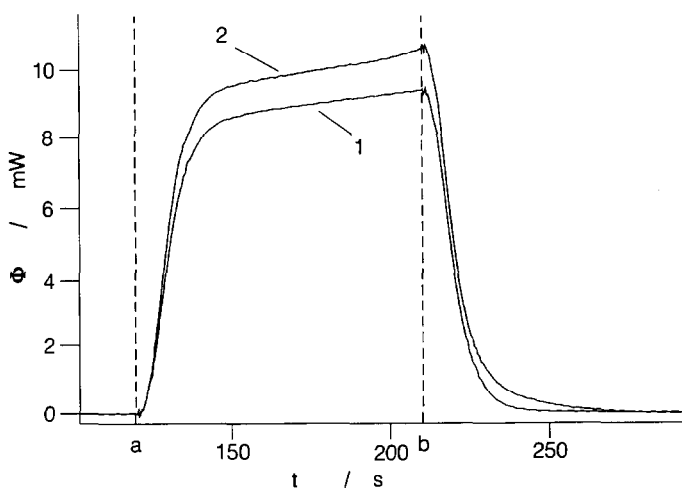

Fig. 1. Measured curves of PS (mass, 18.41 mg; heating rate, 20 K min^{-1}). Curve 1 measured from 300 to 330 K; curve 2 measured from 330 to 360 K; a, moment of switching on the scan rate; b, moment of switching off the scan rate.
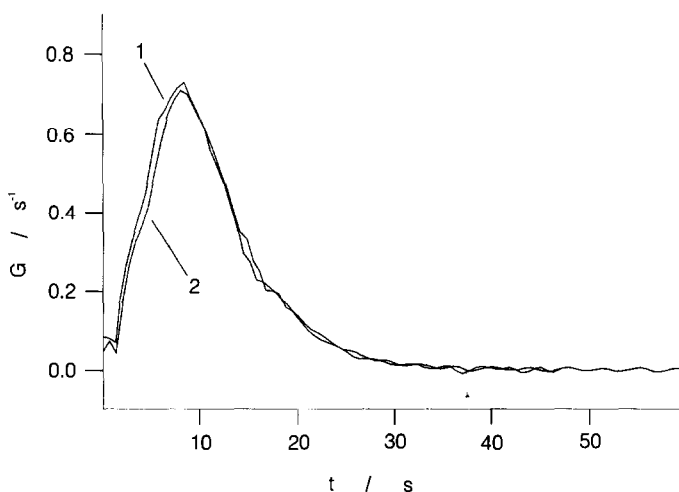
Fig. 2. Green's functions determined from switching behaviour at 330 K. Curve 1, from switching on behaviour, curve 2, from switching off behaviour.

We have to compare the switch-on step behaviour of curve 2 with the switch-off step behaviour of curve 1, which both took place at 330 K. A characteristic quantity of the switch behaviour is the time $t_{1/2}$ from the moment of switching the heating rate until the step height of the measured curve. In the switch-on case, this time is 9.45 s, which at a heating rate of 20 K min^{-1} is equivalent to a temperature shift of 3.15 K. In the switch-off case, these values are 9.47 s and 3.16 K respectively. Both results are equal within the limits of measurement accuracy.

The Green's functions were estimated from the measured curves at 330 K by means of procedures 2 and 3 (see section 2). The results are shown in Fig. 2.

There is no significant difference between the two Green's functions and we have to conclude that there is no difference in physical behaviour of DSC on switching-on and switching-off the scanning rate.

3.2. Influence of the sample properties on the switching behaviour

To analyse the influence of material properties on the switching behaviour, a sample of 24.5 mg PS was used. The waiting times before and after the heating run (at 20 K min^{-1}) were 120 and 540 s respectively. The temperature range was 310–450 K. The zero-line-corrected curves were desmeared using procedure 1.

Model calculations (presented in Part 3 [2] of this series) predict a decrease in the "half-step-time" of about 0.75 s (respectively, 0.25 K) in the case of desmearing the switching-on behaviour of the measured curve in the glassy state with the aid of the Green's function from the liquid state (at switching off the scan).

The results from the measurements are shown in Figs. 3 and 4 and in Table 1.

The time Δt from the moment of switching the heating rate until the half-step height of the curve is reached depends significantly on the Green's function in
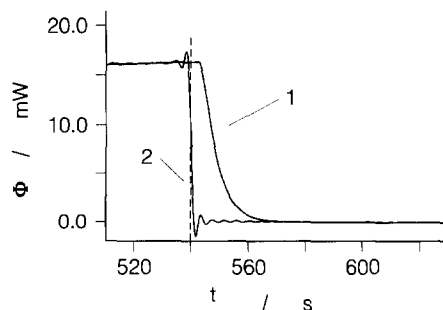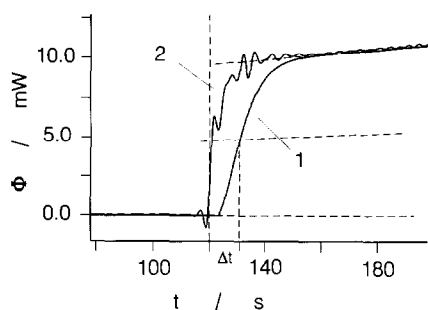
Fig. 3. Behaviour of a PS sample (mass, 24.5 mg) in DSC on switching on the heating rate (20 K min^{-1}) after isothermal mode. Curve 1; measured curve; curve 2, with switch-off Green's function desmeared curve.

Fig. 4. Behaviour of a PS sample (mass, 24.5 mg) in DSC on switching off the heating rate (20 K min^{-1}) after isothermal mode. Curve 1, measured curve; curve 2, with switch-off Green's function desmeared curve.

Table 1
Characteristic times and temperature differences of relaxation behaviour (step response) after switching the scan rate (20 K min^{-1})

	Switch-on behaviour		Switch-off behaviour	
	Δt in s	ΔT in K	Δt in s	ΔT in K
For measured curve	9.80	3.27	7.89	2.63
For desmeared curve	0.73	0.24	0.00	0.00

question. But the dependence is opposite to that predicted by model calculations. This must be interpreted as resulting from a large influence of the thermal contact between sample and pan, which was not taken into consideration by the model calculations. In reality this contact must have been considerably better during the experiment, as the solid PS (before glass transition) has only three point contacts to the aluminum pan, whereas the liquid PS (above the glass transition) has contact all over the (total) surfaces. This results in significantly shorter times until half-step height, which accounts for the predicted effect.

3.3. Influence of different thermal contact

To confirm the hypothesis postulated above, a sample was measured which was coupled to the pan bottom in a different manner. First it was measured as usual (with only the second run being analysed). Then the sample was coupled to the pan with the aid of about 4 mg of silicon oil. In this case the thin silicon oil film between the bottom of the pan and the sample defines the thermal contact and it should be independent of viscosity changes in the sample.
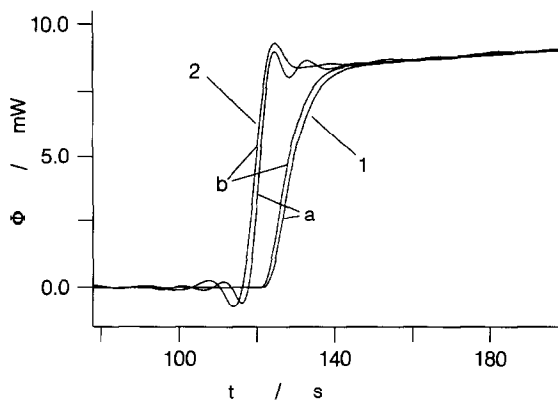
Fig. 5. Curves as in Fig. 3 (sample mass, 19.40 mg) but: curve a, without oil film; curve b, with oil film between sample and pan.
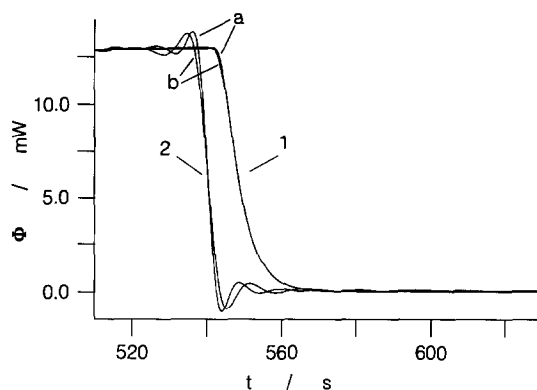

Fig. 6. Curves as in Fig. 4 (sample mass, 19.40 mg) but: curve a, without oil film; curve b, with oil film between sample and pan.

For both cases the switch behaviour is shown in Figs. 5 and 6, and the characteristic quantities are listed in Table 2.

The result is as expected. The oil film decreases the thermal resistance between sample and pan and thus the time until half-step height of the signal decreases (and with it temperature difference in question). Furthermore, the rise time of the well-coupled sample is smaller in the glassy state (switch-on behaviour) than in the liquid state (switch-off behaviour), as predicted from the model calculations. The magnitude of the difference (-0.48 s, respectively -0.16 K) is in reality about 30% smaller than the worst case approximation from the model (-0.75 s, respectively -0.25 K [2]).

As another result, it has been shown that the change in the thermal contact between sample and pan during glass transition influences the Green's functions more than change in material properties does.

Table 2
Characteristic times and temperature differences of relaxation behaviour (step response) after switching
the scan rate (20 K min^{-1}) showing the influences of an oil film between sample and pan

	Switch-on behaviour		Switch-off behaviour	
	Δt in s	ΔT in K	Δt in s	ΔT in K
For measured curve without oil	8.48	2.83	7.57	2.52
For measured curve with oil	7.27	2.42	7.57	2.52
For desmeared curve without oil	0.61	0.20	0.00	0.00
For desmeared curve with oil	−0.48	−0.16	0.00	0.00

4. Influence on glass transition measurements

To evaluate the influence of the described effects on the Green's function used for exact determination of the glass transition temperature, we first consider conventional measurements of PS.

In Fig. 7, the measured heat capacity c_p is shown as a function of temperature, together with desmeared curves obtained by different procedures (see section 2).

As can be seen the desmeared curves show a higher, sharper peak of enthalpy retardation and a more narrow glass transition region than the measured curves do. The glass transition temperatures T_g were not determined at half-step height but as "fictive temperatures" [13]. For that purpose, tangents were fitted to the DSC curves in the glass and liquid region and the areas included were compared to give the correct T_g. The reproducibility of the T_g determination was about ± 0.1 K.
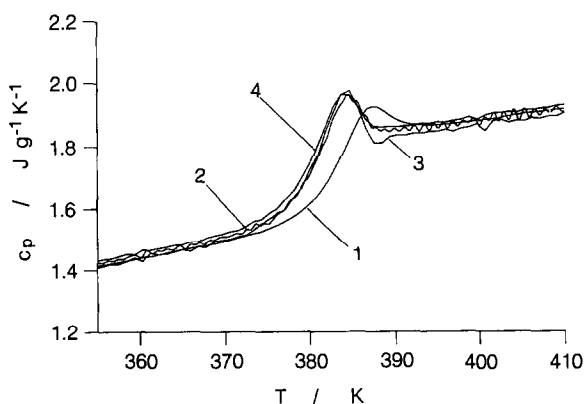

Fig. 7. Heat capacity of PS ($m = 24.5$ mg) as a function of temperature determined from measured and different desmeared curves: 1, measured at a heating rate of 20 K min^{-1}; 2, desmeared with procedure 1; 3, desmeared with procedure 2; 4, desmeared with procedure 3.

Table 3
Results of determination of glass transition temperatures and change in the heat capacity from measured curves and from curves desmeared with different procedures (Fig. 7)

Desmeared by	T_g in K	Δc_p in J g^{-1} K^{-1}
As measured	380.10	0.279
Procedure 1	377.49	0.282
Procedure 2	377.48	0.277
Procedure 3	377.47	0.283

Both these glass temperatures T_g and the changes in heat capacity on glass transition Δc_p are listed in Table 3 for the measured and desmeared curves as well. All values are averages of ten independent determinations of T_g from each measurement.

The glass transition temperatures determined from the different desmeared curves coincide rather well. The differences in the Green's functions seem in this case not to have any influence on T_g.

If we look at the different procedures for desmearing we find that, for the first procedure, slow oscillations appear on the resulting curve due to the numerical Fourier transformation (maximum amplitude, 0.01 J g^{-1} K^{-1}; decreasing with increasing sampling rate).

The curves desmeared by means of procedures 1 and 2 (curves 2 and 3 in Fig. 7) correspond within the limits of accuracy, whereas small differences appear between the desmeared curve and the measured curve in the glassy state (method 1) or those in the liquid state (method 2).

The temperature difference between measured and desmeared curves is about 3.7 K. The difference between the $c_p(T)$ values of the different desmeared curves is about ± 0.01 J g^{-1} K^{-1} (i.e. 1%). This is about the experimental uncertainty. The values of Δc_p and T_g coincide within experimental error, independent of the desmearing method. Figure 8 shows the measured and desmeared curves of c_p, which were obtained by evaluating the influence of the heat contact on the Green's function (see section 3.3). Only the first desmearing procedure is used here. It can be seen that both desmeared and measured curves are similar to those discussed above. Additional information cannot be obtained in this case.

5. Conclusions

It is possible to desmear glass transition DSC curves with the aid of step-response Green's functions. The Green's function can be obtained from the switch-on or switch-off behaviour of the DSC in question. As the material properties change during the glass transition and the material properties influence the Green's function and, thus, the smearing of the measured curve, the Green's functions obtained from the sample in both the glassy state and in the liquid state are
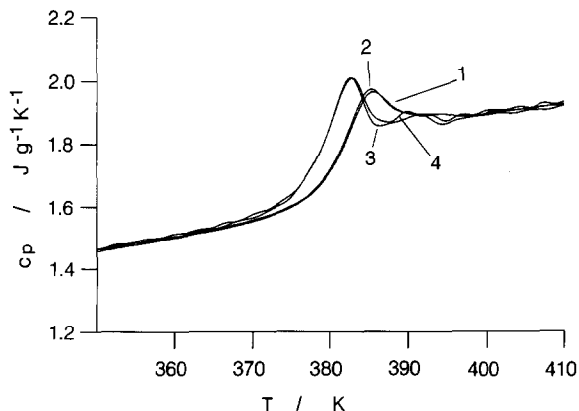
Fig. 8. Influence of an oil film between sample and pan on the heat capacity of PS ($m = 19.40$ mg) determined from measured and desmeared curves. 1, measured at a heating rate of 20 K min^{-1}; 2, as 1 but with oil film; 3, desmeared from curve 1; 4, desmeared from curve 2.

not correct for desmearing the glass transition curve. But the errors in determination of the glass transition temperature are rather small and mostly within the limits of accuracy of the measurement. This has been proved both by model calculations and experimentally.

In every case, desmearing the measured curves with the aid of the (somewhat erroneous) Green's function from the glassy or liquid state gives much better values of the glass temperature than if we determine them from uncorrected DSC curves. This is especially true if rather thick (>0.3 mm) samples are used for T_g determinations at heating rates of 10 K min^{-1} or higher.

The desmearing procedure described in this series of papers is capable of providing improved results from DSC measurements on materials with low thermal conductivity, e.g. polymers. It can be used successfully if the material properties do not change markedly during the measurement.

Acknowledgements

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