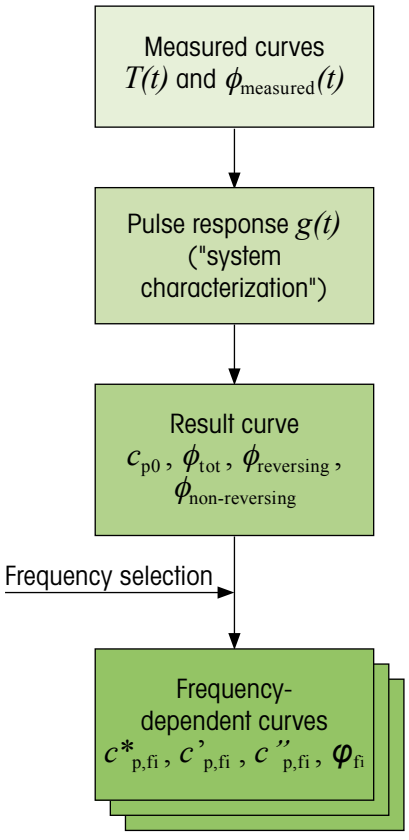
TOPEM® – the new advanced multi-frequency TMDSC technique

TMDSC methods allow both temperature-dependent and time-dependent processes to be separated.
The basic idea of TOPEM® is to overlay the isothermal or ramped temperature with a time series of stochastic (random) temperature pulses of different durations.
Methods used up until now have overlaid the isothermal temperature or heating ramp with a (usually) sinusoidal temperature modulation of just one frequency. In contrast TOPEM®, the new advanced multi-frequency temperature modulation technique, uses a large number of different frequencies (broadband).

As a result, the underlying heating rate is modulated with a broad band of frequencies. The modulation is a relatively rapidly changing signal. Sample properties can be determined as a function of time and temperature over a wide frequency range using PEM, a state-of-the-art mathematical method.
Thanks to the frequency information, effects that shift with frequency can easily be distinguished from frequency-independent effects. This greatly simplifies the interpretation of samples that exhibit overlapping effects.

At the same time, TOPEM® allows the quasi-static frequency-independent heat capacity to be measured.



Flow diagram of the TOPEM® evaluation

Features and benefits

- **One measurement** – simultaneous measurement of sample properties as a function of time and temperature over a large frequency range
- **c_p determination from the pulse response** – very accurate determination of the quasi-static heat capacity
- **Simultaneous high sensitivity and high resolution** – allows the measurement of low energy transitions and/or close-lying temperature-dependent effects
- **Separation of reversing and non-reversing processes** – heat capacities can be determined with unrivaled quality even if the effects overlap
- **Simplifies interpretation** – frequency-dependent effects (e.g. glass transitions) can be very easily distinguished from frequency-independent effects (e.g. loss of moisture)
- **Extended PEM technique** – eliminates instrumental influences and extends the measurable frequency range
- **Automatic c_p adjustment** – provides accurate frequency-dependent heat capacity values based on one single measurement

METTLER TOLEDO

Application fields

A number of interesting applications are foreseen for this new technique:

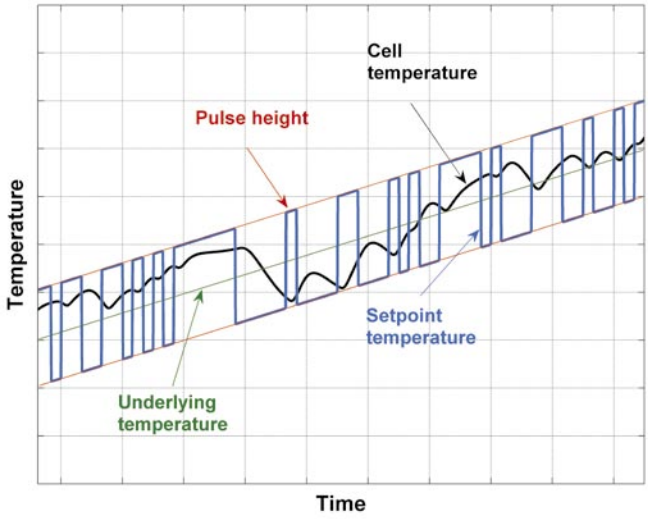
Industry	Effects that can be analyzed with TOPEM®
Automobile and aerospace	Curing reactions, influence of moisture, glass transition, vitrification
Chemical	Exothermic reactions (safety investigations), glass transition, kinetics, crystallization behavior, polymorphism, drying, heat capacity
Electronics	Curing reactions, glass transition, vitrification
Paints	Curing reactions, influence of moisture, glass transition, drying, vitrification
Rubber (elastomers)	Glass transition, phase separation, melting, vulcanization
Plastics (thermoplastics, thermosets, fibers, films, textiles, adhesives, packaging and cables)	Curing reactions, influence of moisture, enthalpy relaxation, glass transition, cold crystallization, phase separation, melting, melting and crystallization, vitrification, heat capacity
Foodstuffs	Influence of moisture, gelation, glass transition, stickiness, polymorphism, drying
Pharmaceuticals	Influence of moisture, glass transition, melting (isothermal step melting point), crystallization behavior, polymorphism, drying, heat capacity, decomposition behavior, stability
Research and development	Everything given above plus the physical nature of transitions

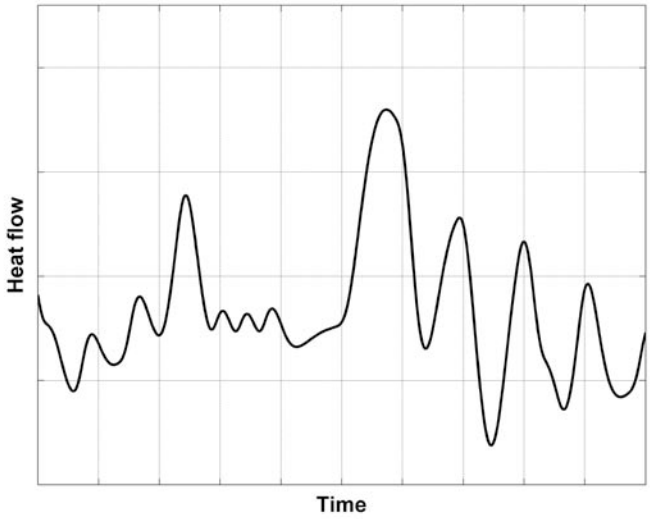
Theory

Linear system

If the temperature modulation is sufficiently small, one can assume that the current state of the sample is almost unaffected and that it is in equilibrium.
One can therefore describe the sample in a limited temperature range as a linear system.

$u(t)$ →	Linear system $g(t)$	→ $y(t)$
$u(t) = T(t)$	$g(t)$	$y(t) = \phi_{\text{measured}}(t)$
Temperature as a function of time	The system is defined by the sample and instrument	Heat flow as function of time





Theory

From the measured heat flow $\phi_{measured}(t,T)$ both the reversing heat flow $\phi_{reversing}(t,T)$ and the non-reversing heat flow $\phi_{non\text{-}reversing}(t,T)$ can be calculated. The total heat flow is the sum of $\phi_{reversing}(t,T)$ and $\phi_{non\text{-}reversing}(t,T)$ according to the equation

$$\phi_{total}(t,T) = \phi_{reversing}(t,T) + \phi_{non\text{-}reversing}(t,T)$$

where

Heat flow:	$\phi(t,T)$
Reversing component:	$\phi_{reversing}(t,T) = mc_{p0}(t,T)\,\beta$
Non-reversing component:	$\phi_{non\text{-}reversing}(t,T)$
Mass:	m
Specific heat capacity:	$c_p(t,T)$
Heating rate:	β

Pulse response (time domain)

For a linear time-invariant system with an input signal $u(t)$ and output signal $y(t)$, the output signal is given as an integral of the input signal with the pulse response $g(t)$ of the system:

$$y(t) = g(t) * u(t) = \int_0^\infty g(\tau)u(t-\tau)\,d\tau$$

The pulse responses characterize the system over the measured temperature range and can be described using the PEM method with parameter sets a_i and b_i.

Frequency response function

The information concerning frequency will be extremely useful and advantageous to users of **TOP**EM®. This is most easily visualized in the frequency diagram (Figure 1). In reality there would be such a diagram for each temperature point.

The directly accessible measurement range in this example is from 10^{-2} to 10^{-1} Hz. The range can be extended using the PEM method.

The point entered at 1/60 Hz is the value measured at one frequency with a conventional TMDSC method like ADSC. A similar measurement range could be determined by performing a large number of individual measurements at different frequencies, but this would of course take an enormous amount of time.

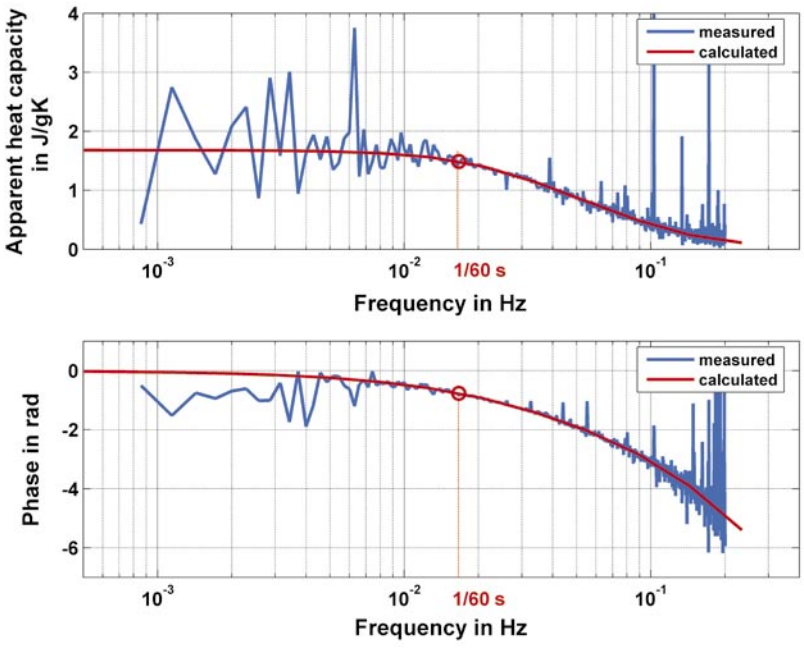


Figure 1. Display of the frequency response factor (corresponds to the step response in the frequency display) with amplitude response (above) and phase response (below) as a function of the frequency, *f*, for polystyrene at 100 °C.

Theory

Basic principles of the TOPEM® technique

For digitally sampled signals it is usual to describe the system by means of a discrete Laplace transformation (called a z-transformation) in the z-plane.
With digital sampling systems the signals are no longer continuous but are data points f_k of a certain sampling period P.

z-transformation:

$$f(z) = \sum_{k=0}^{\infty} f_k \cdot z^{-k}$$

with

$$f_k = f(kP)$$

The equation

$$y(t) = g(t) * u(t) = \int_0^{\infty} g(\tau) u(t-\tau)\, d\tau$$

can be written in the z-plane as follows:

$$y(z) = H(z) u(z)$$

Equations of the time domain can be described and solved more easily in the z-plane.

Often one can exactly describe H(z) using a rational function:

$$H(z) = \frac{B(z)}{A(z)}$$

where B(z) and A(z) are polynomials of degree q or p in the variable z. In the z-plane one then obtains the equation

$$y(z) = \frac{B(z)}{A(z)} u(z)$$

or

$$A(z) y(z) = B(z) u(z)$$

This last equation in the time domain presents itself as follows:

$$y(t) = g(q) u(t)$$

or respectively

$$A(q) y(t) = B(q) u(t)$$

where q is the so-called shift operator:

$$q^k f(t) = f(t-k)$$

Explicitly this equation means:

$$a_0 y(t) + a_1 y(t-1) + a_2 y(t-2) + \ldots + a_p y(t-p) = b_0 u(t) + b_1 u(t-1) + \ldots + b_q u(t-q)$$

The unknown parameters a_i and b_i can be determined using the measured input and output quantities and the least squares fit method.
If these parameters are known, the values of the pulse response $g(t)$ for a certain frequency can easily be calculated.

Theory

Calculation of c_{p0}

The quasi-static heat capacity c_{p0} is calculated with high accuracy even during thermal events from the pulse response $g(t)$.

$$m \cdot c_{p0} = \int_0^\infty g(t)\ dt$$

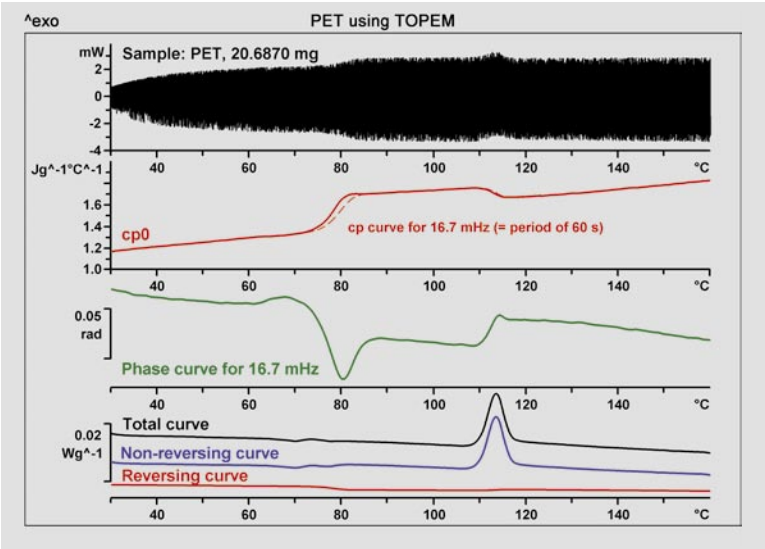
This heat capacity is frequency independent and corresponds to the well-known heat capacity that could be determined using conventional methods if no additional thermal effects occurred.

Calculation of $c_{p,fi}$

By inserting $j\omega_i$ ($\omega_i = 2\pi f_i$) and the parameters a_i and b_i into the function H(z), one obtains a complex quantity of the pulse response from which the phase φ_{fi} and $c_{p,fi}$ can be determined. Thanks to the known quasi-static heat capacity c_{p0} the frequency dependent heat capacities $c_{p,fi}$ can be correctly adjusted.

Tutorial example

PET using TOPEM®

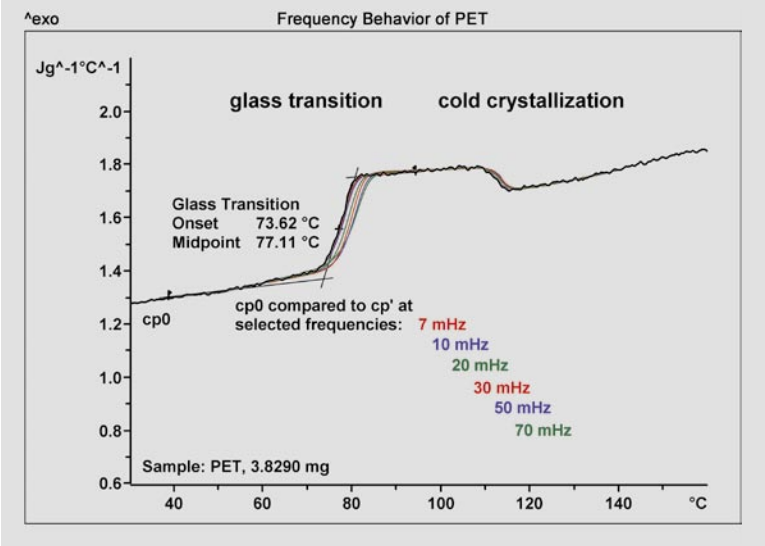


In a **TOP**EM® evaluation, the software first determines the following four curves:

- Total heat flow
- Reversing heat flow
- Non-reversing heat flow
- Quasi-static heat capacity, c_{p0}

In a second step, the additional curves listed below can then be calculated at user-selectable frequencies:

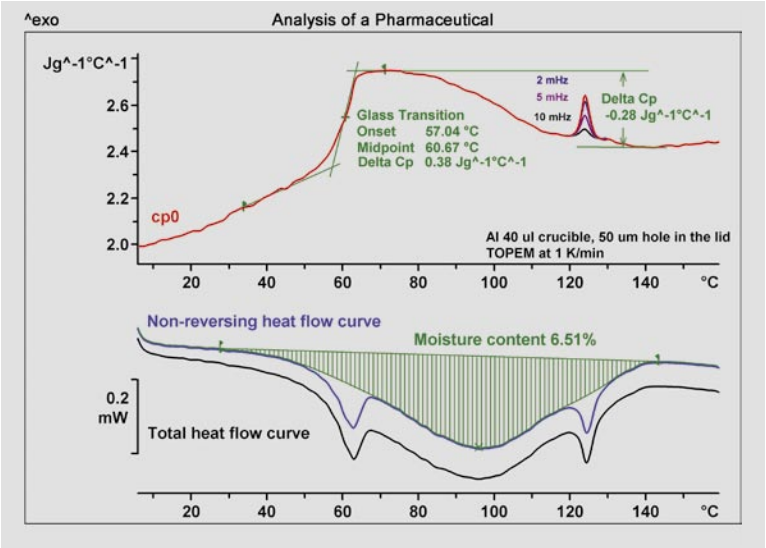
- In-phase heat capacity, $c'_{p,fi}$
- Out-of-phase heat capacity, $c''_{p,fi}$
- Complex heat capacity, $c^*_{p,fi}$
- Phase



Information about the frequency dependence facilitates the interpretation of unknown events. For example, a glass transition shifts to higher temperatures at higher frequencies. This can be seen in the measurement of PET shown in the figure on the left. In contrast, with cold crystallization, the jump in the heat capacity is clearly independent of frequency.

Application examples

Separation of overlapping events in pharmaceutical formulations

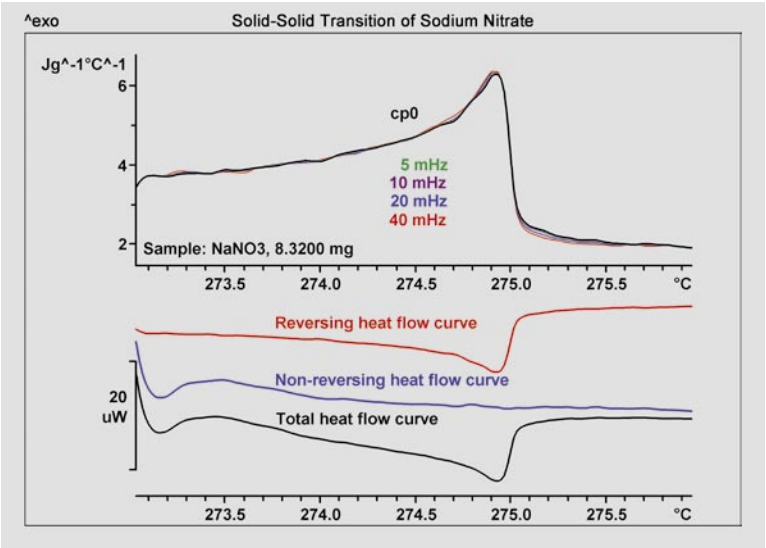


The DSC curves of pharmaceutical formulations often exhibit several overlapping thermal effects. In this example, the total heat flow curve (analogous to the conventional DSC curve) shows a broad vaporization peak that overlaps two sharp peaks at 60 °C and 125 °C. The quasi-static heat capacity curve shows that the first peak at 61 °C is due to a glass transition. The peak is therefore the result of enthalpy relaxation.

The second event is a phase transition that also appears as a peak in the c_{p0} curve. The frequency evaluation shows that the peak temperature is independent of frequency.

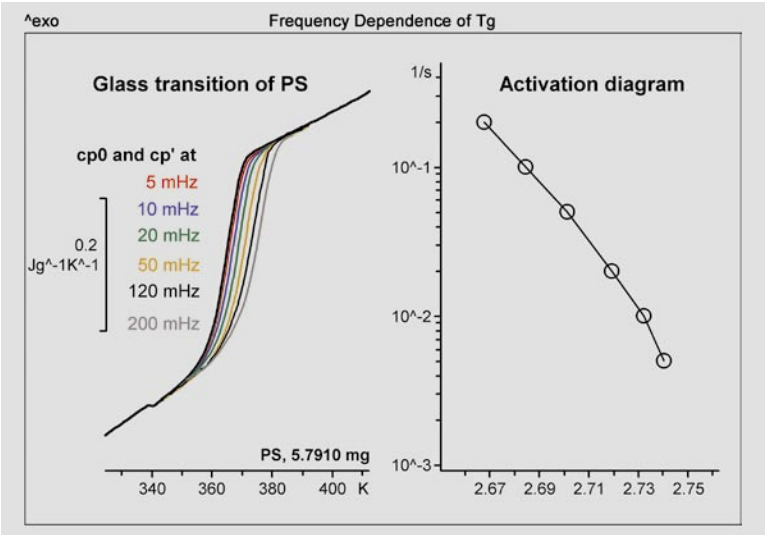
Evaluation of the non-reversing heat flow curve yields a moisture loss of about 6.5%, which is the reason for the slight reduction of 0.28 J/gK in the heat capacity.

Solid-solid transition of sodium nitrate



During the course of the phase transition of sodium nitrate, the heat capacity first increases with increasing temperature and then suddenly decreases within 100 mK at the critical temperature of about 275 °C. To gain information about the physical nature of such transitions, measurements have to be performed at very low heating rates (20 mK/min) and very small pulse heights (5 mK). In the non-reversing heat flow curve, it can be seen that the transition occurs without the release of latent heat. This behavior is expected for a pure second-order phase transition.

Frequency dependence of the glass transition



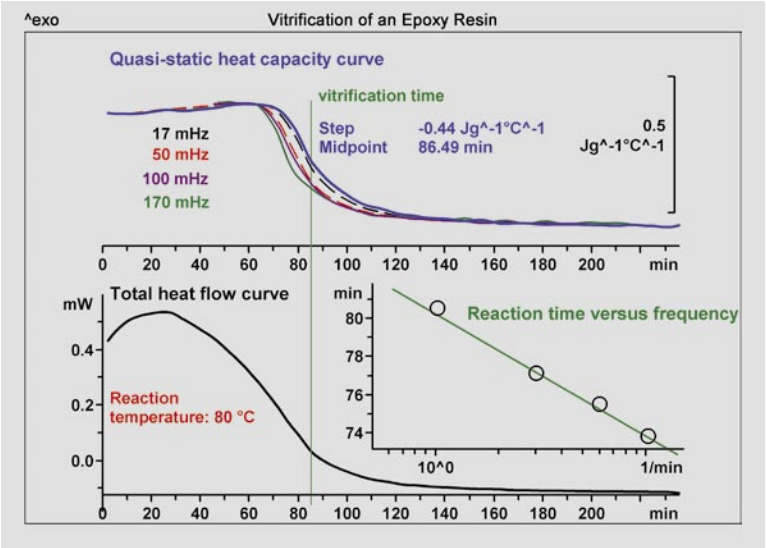
The glass transition is a relaxation process. Knowledge of its frequency dependence allows information to be obtained about molecular dynamics and permits predictions to be made regarding the stability of the material's structure.

A sample of technical polystyrene was measured at a cooling rate of 0.2 K/min. The frequency-dependent heat capacity at six frequencies between 200 mHz and 5 mHz was then calculated from this single measurement.

One important result is the dependence of the relaxation frequency on temperature as shown in the activation diagram (log f versus 1/T). The frequency range can be extended to low frequencies by increasing the maximum switching time in the **TOP**EM® temperature program.

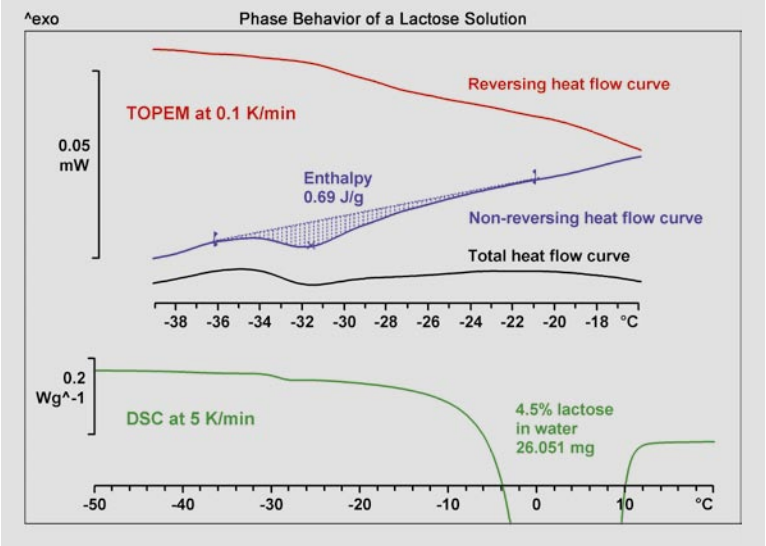
Application examples

Vitrification of isothermally cross-linked epoxy resins



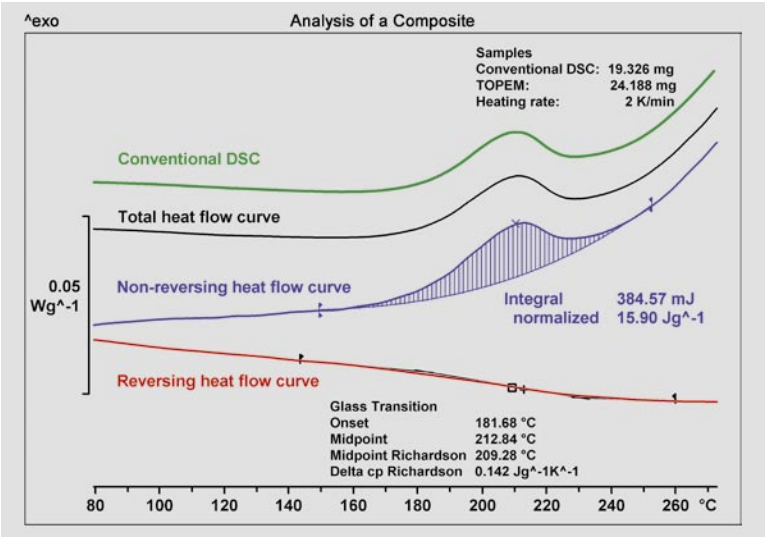
An epoxy resin (DGEBA) was cured isothermally using a cross-linking agent (DDM) at 80 °C. The total heat flow curve shows the exothermic reaction peak. The quasi-static heat capacity (c_{p0}) curve can be simultaneously determined. As the reaction proceeds, c_{p0} first increases and then decreases in a distinct step due to vitrification. In vitrified material diffusion is greatly hindered and the reaction rate slows down until the reaction almost stops. The vitrification time (86.5 min) characterizes the curing reaction.
Since vitrification is in fact a chemically induced glass transition, the step is also frequency dependent. The multi-frequency evaluation shows that the step shifts to shorter times at higher frequencies. An important advantage of this type of evaluation is that all the curves originate from a single measurement of the same sample.

Investigation of the phase behavior of a lactose solution



Knowledge of the thermal behavior of lactose-water solutions is important in the development freeze-drying processes. Depending on the conditions, phase transitions can occur that are difficult to interpret. The example shows the very large melting peak of water in a 4.5% lactose solution and an effect at –30 °C (DSC curve). This could be interpreted as a melting process or as a glass transition.
The **TOP**EM® measurement under quasi-equilibrium conditions (heating rate of 0.1 K/min with temperature pulse heights of 0.005 K) yields a non-reversing heat flow curve with an endothermic peak. This information indicates that the effect at –30 °C is a melting process that is accompanied by a small c_p change, as seen in the reversing heat flow curve.

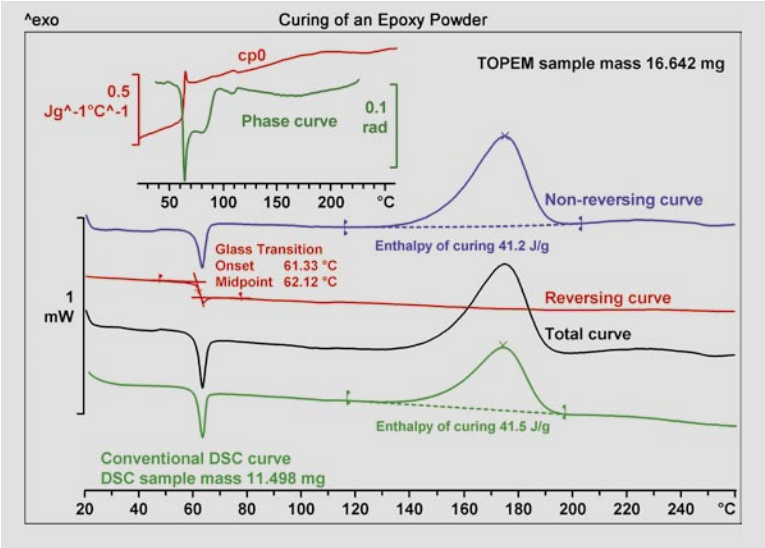
Composite of carbon fibers and epoxy resin



The glass transition and degree of cure of the polymer matrix are important quality criteria for composite materials. Due to the high fiber content, the glass transition is usually broad and is accompanied by only a small change in c_p. In addition, it may be overlapped by a post-curing reaction.
In the example, the post-curing reaction and onset of decomposition mask the expected glass transition. Conventional DSC therefore shows only an exothermic post-curing reaction followed by decomposition. Using **TOP**EM® the glass transition of the material can be clearly seen in the reversing heat flow curve at 216 °C. The non-reversing heat flow shows the post-curing reaction and the onset of decomposition. **TOP**EM® thus enables the glass transition to be clearly separated from the two other processes. The total heat flow corresponds to the result of a conventional DSC experiment.

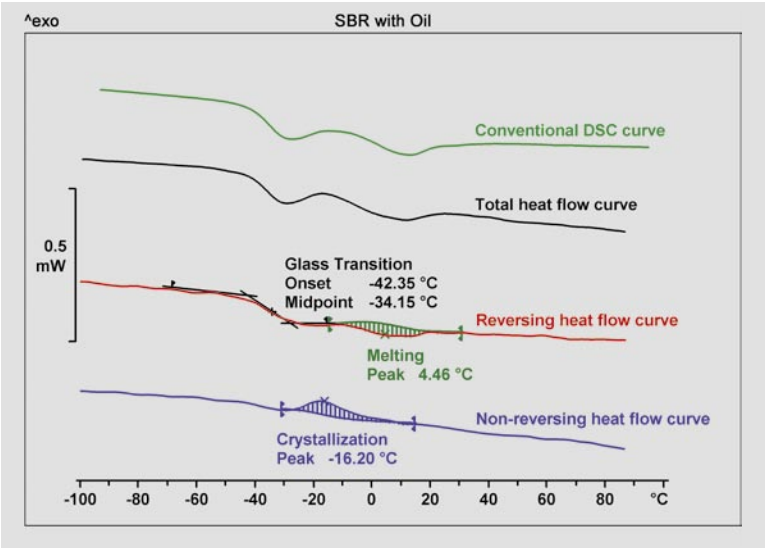
Application examples

Curing of powder coatings



When powder coatings are applied to sheet metal and other surfaces, the particles first soften, then coalesce and finally cure.
The glass transition at 62 °C is accompanied by a large relaxation peak. In a DSC measurement, the effect could be interpreted as "melting" and is difficult to evaluate as a glass transition. The reversing and non-reversing heat flow curves in the **TOP**EM® analysis, however, very clearly show that two effects overlap. The phase curve at 110 °C indicates the coalescence of the powder particles. This can be simultaneously observed using DSC microscopy. This effect causes a change in the heat transfer in the sample. The total heat flow curve is practically the same as the DSC curve. The enthalpy of curing obtained from the conventional DSC curve is also the same as that from the **TOP**EM® measurement.

SBR elastomer containing a low molecular weight oil



The conventional DSC curve of SBR containing a low molecular weight oil shows overlapping thermal effects that are difficult to identify and properly assign. In contrast, a **TOP**EM® measurement performed at 2 K/min allowed the transitions to be quickly and unambiguously identified.

In the reversing heat flow curve, the glass transition of the elastomer is observed as a characteristic step at –34 °C. In addition, the reversing heat flow curve exhibits an endothermic effect at 4 °C. This can be assigned to the melting of the oil.
The non-reversing heat flow shows an exothermic effect at about –16 °C. This is due to the cold crystallization of the low molecular weight constituents.

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