APPLICATION**NOTE**

Fast Temperature Modulation by Means of the DSC 214 *Polyma* for More Information without Time Loss

Claire Strasser, Andrea Kesselboth and Dr. Stefan Schmölzer

Introduction

Temperature modulation is a method in which the linear temperature ramp is superimposed with a sinusoidal temperature signal, as depicted in figure 1:

$$T(t) = T_0 + \beta t + A \cdot \sin(\omega t)$$

T_0 initial temperature
β underlying heating rate
A amplitude of temperature oscillations
ω radial frequency

As a result, the DSC signal is also sinusoidal:

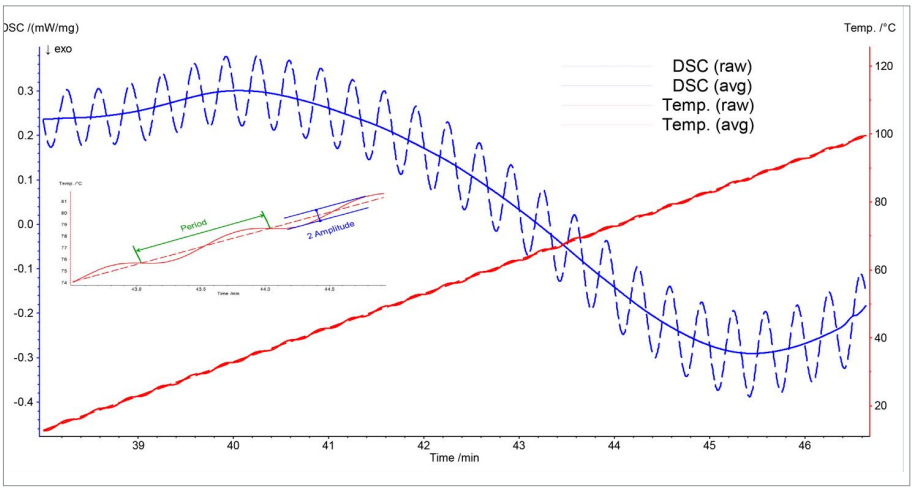
$$DSC(t) = DSC_0 + A_{DSC} \cdot \sin(\omega t + \phi)$$

DSC_0 underlying DSC signal
A_{DSC} amplitude of DSC oscillations
ϕ phase shift between temperature and DSC

Such a measurement allows for the separation of effects that oscillate with the temperature (reversing signal), such as a glass transition, from time-dependent processes (non-reversing signal), such as curing or evaporation.

The three parameters of heating rate, amplitude and frequency (or period) are set by the user. For mathematical separation of the reversing and non-reversing signals, the heating rate and frequency have to be chosen such that the effects to be separated contain at least 5 oscillations. This means, the period has to go down if the heating rate is increased.

But there are some limitations from the physical point of view, e.g., thermal inertia of the instrument furnace or the thermal conductivity of the samples which is quite small for polymers. As heat-flux DSCs always had difficulties following fast oscillations, heating rates for temperature-modulated measurements were limited to a few K/min ... that is, until the launch of the DSC 214 *Polyma*.



1 Underlying (red dashed curve) and oscillating part (red continuous curve) of the temperature signal during a TM-DSC measurement and the resulting DSC signals (blue).

One of the instrument's distinguishing features is *Arena*, a furnace with a low thermal mass allowing for temperature-modulated measurements at a heating rate of 10 K/min – i.e., as fast as a conventional DSC measurement.

Test Conditions

The curing of a two-component epoxy resin was measured with the DSC 214 *Polyma*. The polymer was heated four times at 10 K/min: first to 100°C, the second time to 120°C, then to 140°C, and finally to 160°C. Oscillations with a period of 20 s and an amplitude of 0.5 K were used as the modulation parameters. Between the heating runs, the sample was cooled to 0°C as quickly as possible.

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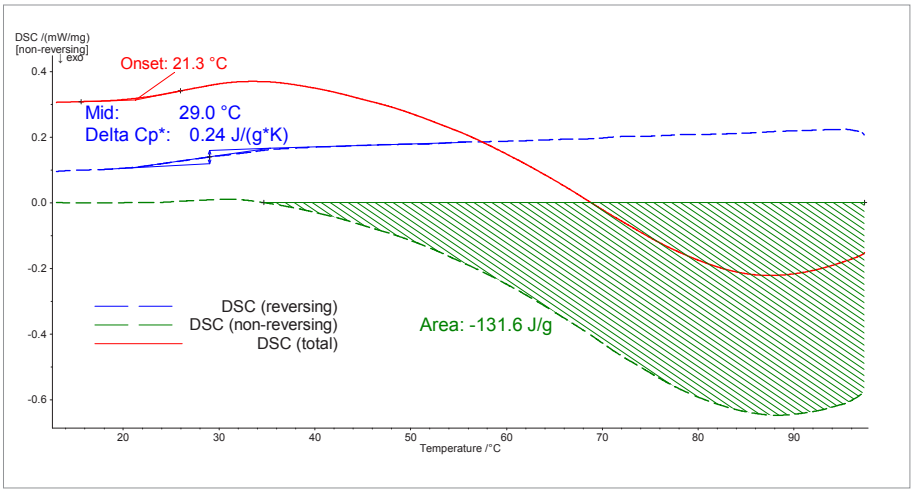
NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com



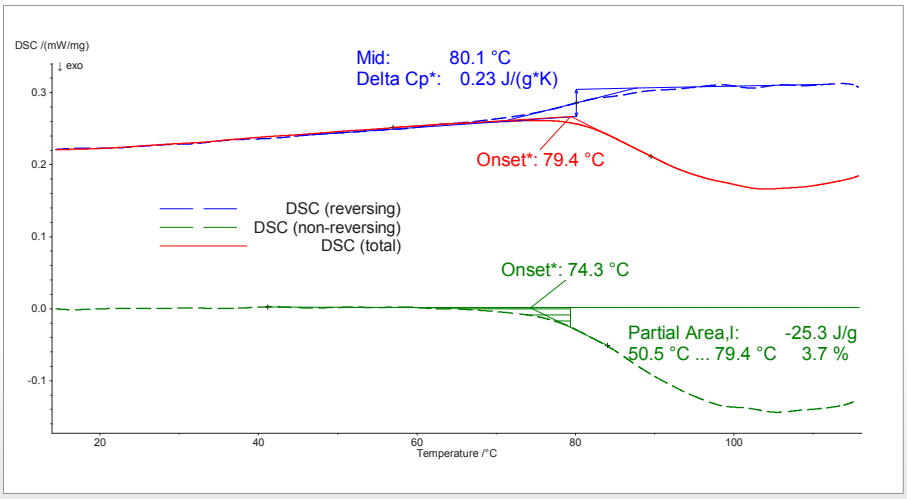
2 Total heat-flow DSC signal during the 1st heating up to 100°C

Test Results

The results of the 1st heating are given in figure 2. The red line represents the total heat flow; i.e., the signal that would be detected during a conventional (not modulated) DSC measurement. An endothermic effect beginning at 21°C (onset temperature) cannot be correctly assessed because it is partly superimposed upon by the exothermic curing peak.

Correct evaluation of both effects is only possible by separating the signal into the reversing and non-reversing parts. As expected, the glass transition occurs in the reversing heat flow (at 29°C) whereas the curing peak is detected in the non-reversing curve. At the end of this 1st heating, curing had not finished, as the non-reversing heat flow had not gotten back to the baseline.

The results of the 2nd heating to 120°C after rapid cooling are displayed in figure 3. Here, the importance of a modulated measurement is even greater than for the 1st heating: an exothermic peak beginning at 79°C (onset temperature) was all that could be found in the total heat-flow signal. However, analysis of the reversing and non-reversing heat-flows clearly shows that this effect is actually the sum of a glass transition at 80°C and a curing reaction beginning clearly at 74°C, 5°C sooner than in the evaluation of the total heat flow signal. The partial area integration between



3 Reversing (dashed lines) and non-reversing (dotted) heat-flow signals during the 2nd heating to 120°C. The glass transition temperature increases with the proceeding curing reaction.

NETZSCH-Gerätebau GmbH
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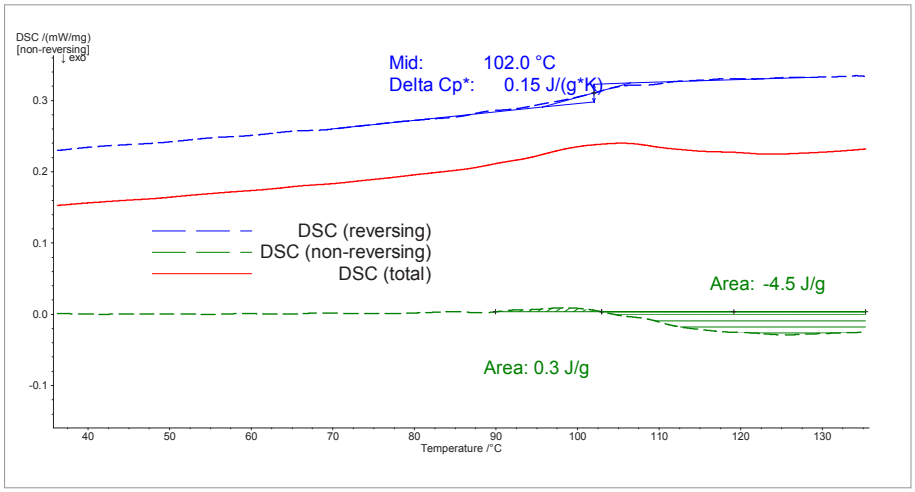
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com



4 Reversing (dashed line) and non-reversing (dotted) heat-flow signals during the 3rd heating to 140°C

the beginning of the peak and 79°C delivers a value of 4%, which would have been missing with an non-modulated measurement.

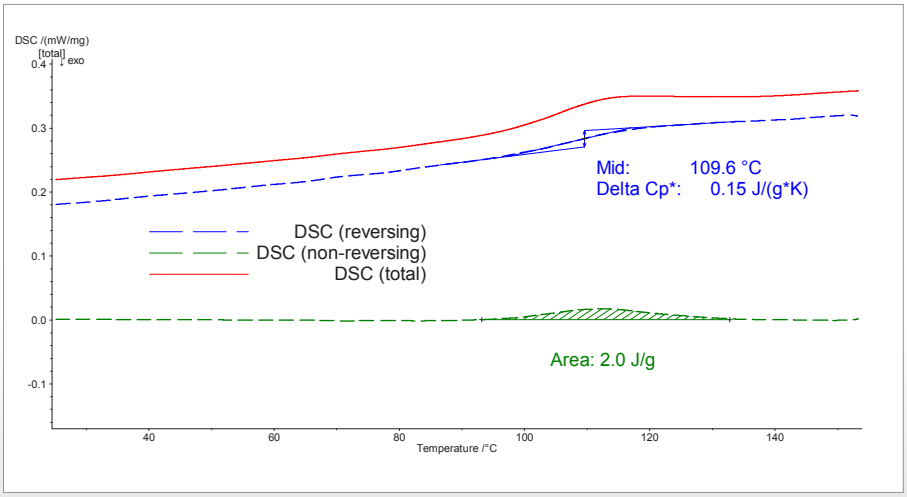
During the 3rd heating to 140°C (figure 4), the epoxy resin cured further, as can be seen in the exothermic peak detected in the non-reversing heat flow. The endothermic peak found is due to relaxation of mechanical stress in the sample as a result of the fast cooling. The glass transition was determined at 102°C.

The 4th heating (figure 5) to 160°C shows the properties of the completely cured resin: a curing peak is no longer detected. The glass transition found at 110°C is overlapped with a relaxation peak.

Conclusion

The curing behavior in a DSC is sometimes difficult to determine because of overlapping effects such as relaxation, glass transition, curing, etc.

In order to gain a detailed insight into the curing behavior, it becomes necessary to separate the superimposed effects. This can be done by means of temperature-modulated DSC. Up until now, the TM-DSC method was very time-consuming, but with the DSC 214 *Polyma*, TM-DSC measurements as fast as standard DSC tests can be achieved.



5 Reversing (dashed lines) and non-reversing (dotted) heat-flow signal during the 4th heating to 160°C

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