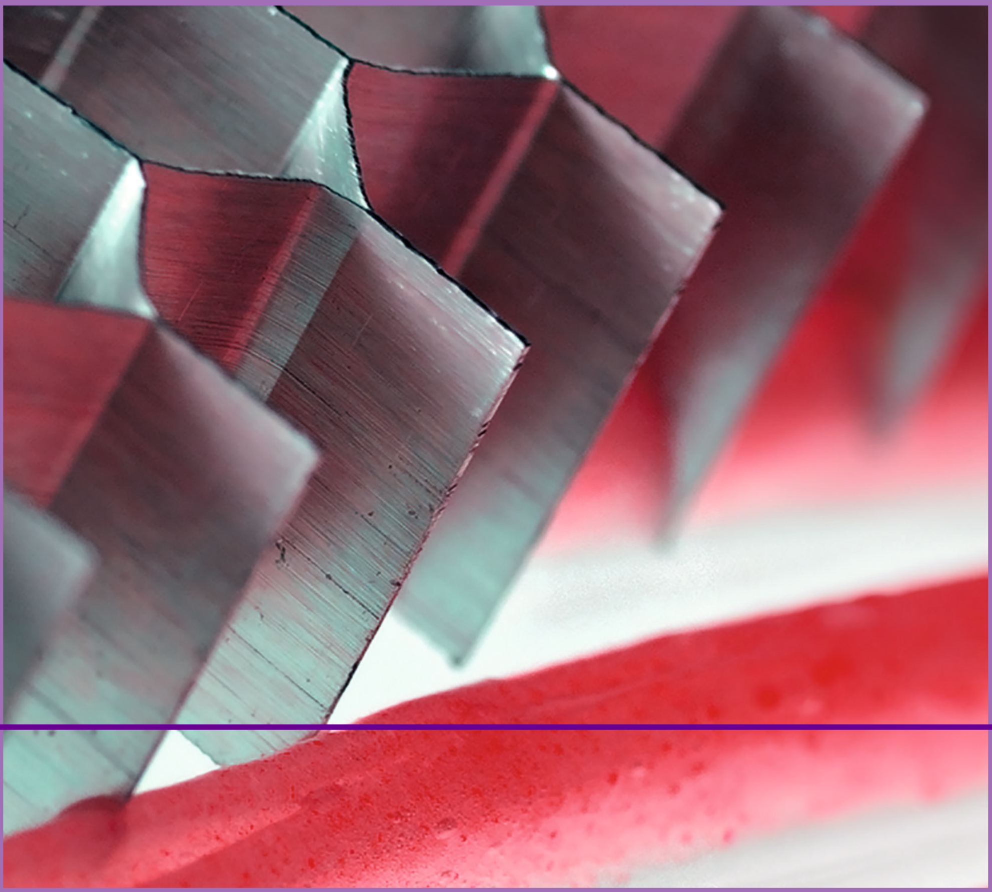
Andreas Bach

Thermal Analysis of Thermosets



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Preface to the First Mettler Toledo Edition, 2006

This applications booklet provides an insight into the thermal analysis of thermosets and presents a large number of practical examples. The main techniques used for sample measurement are differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA). In special cases, combined on-line techniques such as SDTA, visual monitoring, and evolved gas analysis have also been employed.

Thermosets are thermosetting polymers that have undergone a permanent chemical reaction known as curing or crosslinking to form a giant crosslinked network structure. They are rigid, typically insoluble materials of high mechanical strength and high temperature stability. In contrast to thermoplastics, thermosets cannot be remelted or remolded into another shape after curing. Thermosetting materials include a wide range of chemically different compounds. Nowadays, more and more different types of polymers are being combined in order to develop new material properties. This makes it sometimes difficult to distinguish between thermosets, thermoplastics, and elastomers. For this reason, the focus in this booklet is on relatively simple systems that can be clearly identified as thermosets.

The Thermosets Collected Applications booklet is published in two separate volumes.

Volume 1 first presents an overview and brief description of the analytical techniques commonly used to characterize thermosets. The second part deals with the chemistry of individual thermosets and discusses the use of these materials. This section is intended for readers who are new to the field of thermosetting polymers and who wish to learn more about the properties and applications of thermosets. Finally, the third and larger part discusses the properties and effects that can be investigated using different thermoanalytical techniques. In general, the same resin systems were used for the measurements in order to facilitate comparison.

Volume 2 concentrates on practical examples. These have been subdivided according to the type of resin system. The applications describe the different properties that can be investigated, measured, or simply checked during the lifecycle of a thermoset.

I hope that the applications described in these two volumes will find wide interest and stimulate new ideas both for experts and for newcomers to this rather complex but immensely interesting field.

I am very grateful for the many contributions in this volume supplied by my colleagues at METTLER TOLEDO. Some of these experiments have already been described in past issues of the METTLER TOLEDO thermal analysis UserCom journal or elsewhere. My thanks therefore go to Mrs. Ni Jing, Dr. Jürgen Schawe, Dr. Markus Schubnell, Dr. Matthias Wagner, Georg Widmann and Marco Zappa. Mrs. Myrta Pfister deserves special mention for the large number of sample measurements she performed for this publication.

Finally, I thank all my colleagues, especially Dr. Jürgen Schawe and Georg Widmann for valuable discussions and proofreading, and Dr. Dudley May for translating the original German manuscript into English.

Schwerzenbach, November 2006

Dr. Rudolf Riesen

Preface to This Hanser Edition, 2025

Since the first edition published in 2006, METTLER TOLEDO's line of thermal analysis instrumentation has expanded and now also includes chip calorimetry by Flash DSC. METTLER TOLEDO has also introduced several new techniques in addition to mass spectroscopy (MS) and Fourier transform infrared (FTIR) that can be connected to a TGA for advanced evolved gas analysis (EGA), including gas chromatography/mass spectrometry (GC/MS) and Micro GC. A modular humidity generator can now also be coupled to the TMA for investigations at defined relative humidity levels using a TMA Sorption Analyzer System.

This edition of the handbook is now published as a single, unified volume, and includes a number of experiments recently obtained using the new techniques mentioned above. In addition, the handbook now includes an expanded section with a brief description of these analytical techniques, which are commonly used to characterize thermosets. The section dealing with the chemistry of individual thermosets was also updated. I would like to thank several colleagues for their valuable support in producing this handbook:

- The Materials Characterization Support Group, especially Nicolas Fedelich
- Naomi Towers and Dr. Markus Schubnell for reviewing the text

Nänikon, January 2025 Dr. Andreas Bach

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PART 1

1 Introduction to Thermal Analysis

Thermal analysis is the name given to a group of techniques used to measure the physical and chemical properties of materials as a function of temperature. In all these methods, the sample is subjected to a heating, cooling or isothermal temperature program. According to ICTAC (International Confederation for Thermal Analysis and Calorimetry): "Thermal analysis is the study of the relationship between a sample property and its temperature as the sample is heated or cooled in a controlled manner."

The measurements can be performed in different atmospheres. Usually either an inert atmosphere (nitrogen, argon, helium) or an oxidative atmosphere (air, oxygen) is used. In some cases, the gases are switched from one atmosphere to another during the measurement. Another parameter sometimes selectively varied is the gas pressure.

DSC can also be used in combination with instruments that allow the sample to be simultaneously observed (DSC microscopy) or exposed to light of different wavelengths (photocalorimetry).

1.1 Differential thermal analysis (DTA, SDTA)

In differential thermal analysis (DTA), a sample and a reference material are heated in a furnace. According to ICTAC, DTA is defined as "a technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed". The temperature difference between the sample and the reference material is measured using thermocouples. If a thermal event occurs in the sample (such as a phase transition or chemical reaction), the additional uptake or release of energy changes the heating rate of the sample. This results in a temperature difference between the sample and reference sides. For example, during an exothermic reaction, the temperature difference between the sample and reference is larger than before or after the reaction. Thermal effects are indicated by the presence of steps and peaks, in the same way as observed in a DSC measurement curve.

In SDTA (single DTA), no reference material is used. The reference temperature corresponds with the program temperature and the sample temperature only is measured. The SDTA technique enables the DTA signal to be simultaneously measured in TGA, TMA and DMA experiments. This often aids interpretation because it detects thermal events that are not accompanied by a change in mass or dimensions. For example, in TMA measurements, simultaneous SDTA can distinguish between exothermic and endothermic transitions, and also detect chemical reactions.

1.2 Differential scanning calorimetry (DSC)

In DSC, the heat flow to and from the sample is measured. DSC can be used to investigate thermal events such as physical transitions (the glass transition, crystallization, melting, and the vaporization of volatile compounds) and chemical reactions. The information obtained characterizes the sample with regard to its thermal behavior and composition. In addition, properties such as the heat capacity, glass transition temperature, melting temperature, heat and extent of reaction can also be determined.

1.2.1 Conventional DSC

Conventional DSC employs a linear temperature program. The sample and reference material (or just an empty crucible) are heated or cooled at a linear rate, or in some cases, held at a constant temperature (i.e. isothermally). Often several partial programs or so-called segments are joined together to form a complete temperature program. A typical DSC curve is shown schematically in Figure 1.1. The change in the curve at the beginning of the measurement is due to the initial "startup deflection" (1). In this transient region, the conditions suddenly change from an isothermal mode to a linear heating mode. The magnitude of the startup deflection depends on the heat capacity of the sample and the heating rate. If volatile substances such as solvents are present in the sample, an endothermic peak (2) is observed due to the vaporization; the sample loses mass. Further information on such peaks can be obtained by weighing the sample before and after the measurement and by using different types of crucibles. In contrast to open crucibles, hermetically sealed crucibles prevent vaporization of the sample. At a glass transition (3), the heat capacity of the sample increases and therefore an endothermic step is observed. This is often accompanied by an enthalpy relaxation peak. Chemical reactions produce exothermic or endothermic effects (4) depending on the type of reaction involved. Finally, at higher temperatures, decomposition begins (5). The type of purge gas used in the experiment often has an influence on the reactions that occur, especially at high temperatures.

Transitions and reactions can be differentiated by cooling the sample and measuring it again – chemical reactions are irreversible whereas crystalline materials melt then crystallize again on cooling or on heating a second time. Glass transitions are also reversible but not the enthalpy relaxation often observed in the first heating measurement of a glass transition.

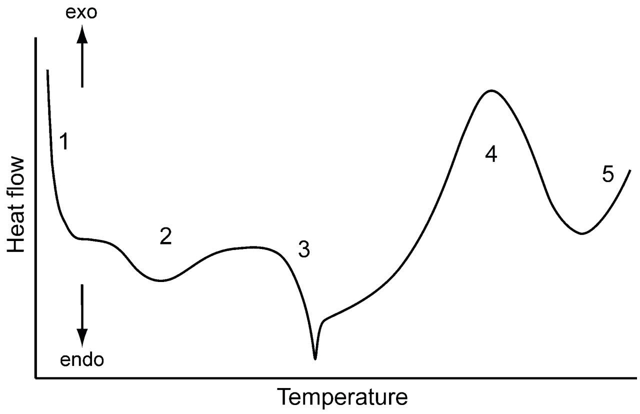

Figure 1.1: Schematic DSC curve: 1 initial startup deflection; 2 evaporation of moisture; 3 glass transition with relaxation peak; 4 reaction (e.g. curing); 5 beginning of decomposition.

1.2.2 Chip calorimetry

In recent decades, tremendous efforts have been made to increase the scan rate of conventional DSC for gaining additional insights into materials and their application possibilities. This gave rise to chip calorimetry, also known as fast-scanning DSC, which is capable of achieving extremely fast heating and cooling rates of up to 10,000 K/s (Figure 1.2). Chip calorimeters are conceptually similar to conventional DSCs and are principally used to investigate fast crystallization behaviors, the exploration of metastable states, and the analysis of extremely small sample quantities.

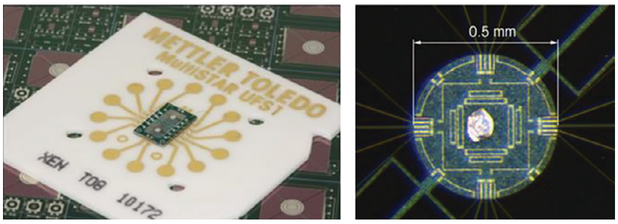

Figure 1.2: The revolutionary Flash DSC UFS 1 Sensor based on MEMS technology (left). The sample is positioned directly on the sample side of the UFS 1 sensor (right).

1.2.3 Temperature-modulated DSC

In temperature-modulated DSC (TMDSC), a periodic temperature modulation is superimposed on the constant heating or cooling rate of a conventional DSC measurement. METTLER TOLEDO offers three different techniques for performing temperature-modulated DSC measurements. They are known as ADSC, IsoStep and TOPEM. The following sections summarize their most important features.

1.2.3.1 ADSC

Alternating DSC (ADSC) is a particular type of temperature-modulated DSC. In contrast to conventional DSC, the linear temperature program is overlaid with a small periodic temperature change. The temperature program is characterized by the underlying heating rate, the temperature amplitude and the duration of the periodically changing temperature (Fig. 1.3). With quasi-isothermal measurements, the underlying heating rate β_u can also be zero.

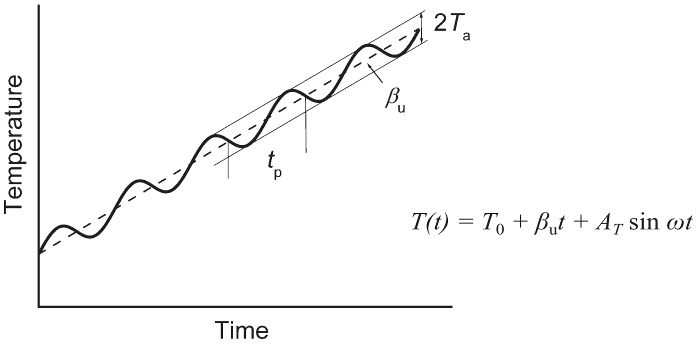

Figure 1.3: Typical ADSC temperature program: β_u is the underlying heating rate, A_T the temperature amplitude, t_p period. The angular frequency ω is defined as $2\pi/P$ where P denotes the period of the sine wave.

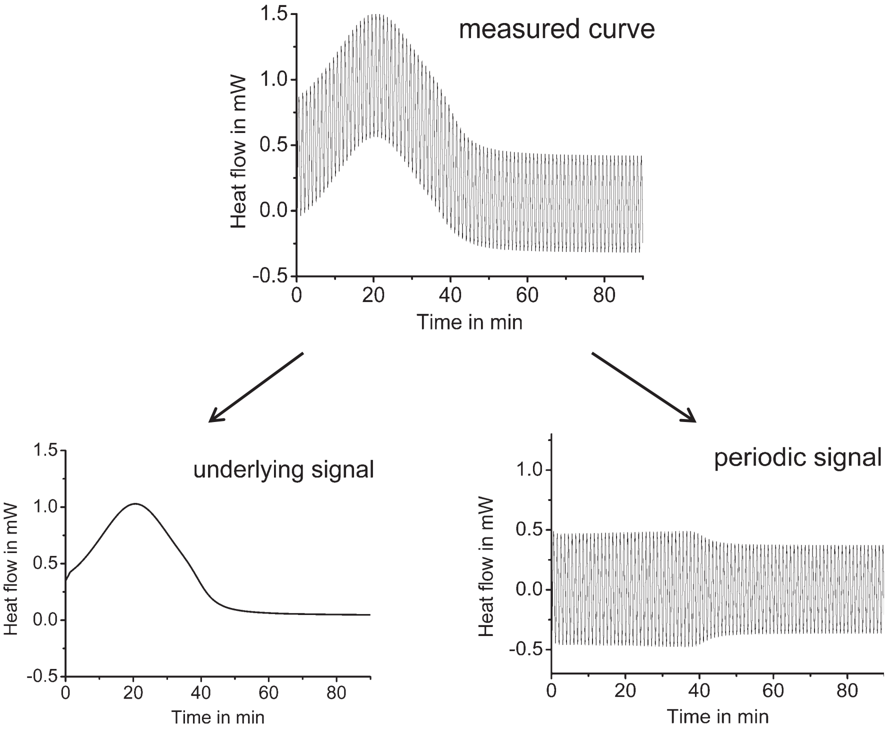

Figure 1.4: Separation of the measured ADSC curve into the underlying and the periodic signal components.

As a result of temperature modulation, the measured heat flow changes periodically. This can be separated into two parts as shown in Figure 1.4. Signal averaging yields the underlying signal (total heat flow), which corresponds to the conventional DSC curve. As additional information, one also obtains the periodic signal component. The reversing heat flow corresponds to the heat flow component that is able to follow the heating rate change directly and is computed from the in-phase heat capacity. The difference between the total heat flow and the reversing heat flow yields the non-reversing heat flow. One advantage of this technique is that it allows processes that occur simultaneously to be separated. For example, the change in heat capacity during a chemical reaction can be measured directly.

The evaluation of the ADSC curves is based on Fourier analysis. The modulus of the complex heat capacity c_p^* is calculated using the equation

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

where A_Φ and A_β denote the amplitudes of the modulated heat flow and heating rate, and m the sample mass. The phase angle between the ADSC heat flow signal and the heating rate is used to calculate the in-phase c_p.

1.2.3.2 IsoStep

IsoStep is a special type of temperature-modulated DSC. In this method, the temperature program consists of a number of dynamic segments that begin and end with an isothermal segment (Fig. 1.5).

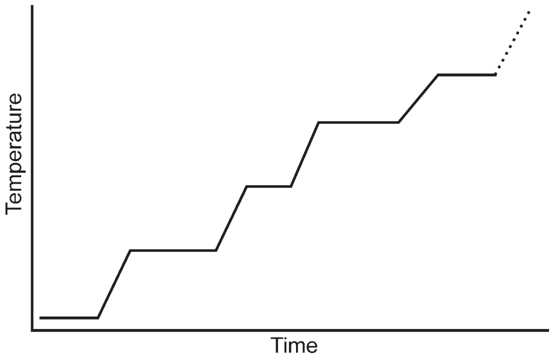

Figure 1.5: IsoStep temperature program consisting of different isothermal and dynamic segments.

The isothermal segments allow the isothermal drift of the dynamic segments to be corrected. This results in better heat capacity accuracy. The isothermal step may also contain kinetic information, for example of a chemical reaction. Heat capacity determinations can be made using a sapphire reference sample, and kinetic effects can be separated from changes in heat capacity.

1.2.3.3 TOPEM

TOPEM is an advanced temperature-modulated DSC technique that is based on the full mathematical analysis of the response of a DSC (both the apparatus and the sample) to a stochastically modulated underlying temperature program (Fig. 1.6). Due to the randomly distributed temperature pulses, the system is subjected to temperature oscillations over a wide frequency range and not just at one single frequency (ADSC). An analysis of the correlation of the oscillating input signal (heating rate) and the response signal (heat flow) provides much more information than can be obtained using conventional temperature-modulated DSC. Not only can reversing and non-reversing effects be separated, but the quasi-static heat capacity of the sample is also measured and frequency-dependent heat capacity values are determined. This can be