USER COM

Information for users of
METTLER TOLEDO thermal analysis systems

December 1996

Dear customer

Since the fall of this year things have yet again been heating up at Mettler Toledo. After many years of waiting, a successor in the form of the TGA/SDTA851^e for the legendary TA1 and TA2 is now on the market. Your local Mettler Toledo dealer will be pleased to provide you with information. The highly motivated TA team is already looking forward to surprising you once again with new features next year.

Optimum utilization of the internal database 4

TA TIP

The STAR^e software stores all data in an internal database. This results in extensive possibilities for data search and data tracing. In order to exploit the available possibilities better, a few points are worthy of consideration before we start. What are the main differences between data storage in a database and data storage in files?

- Different data types (calibration data, method data, sample data, experimental curves, etc.) are stored separately, but are linked with one another. This documents **what, when, with what** and **by whom** measurements were performed.
- A search can be made based on all types of information (not just file name and date).
- All stored data are protected. A method for which experimental data still exist can not be deleted by accident. The traceability is assured.

Each database is based on a model which defines the relationship between the individual data sets. Knowledge of this data structure is useful if the user wishes exploit the possibilities offered by his database to the full. Figure 1 shows the assignment of the different types of information using a simplified scheme. If, for example, an experiment is started, the database sets up a relationship between:

– Customer
– Measurement module (calibration data, settings)
– Current user
– Method (temperature program, crucible, purge gas, etc...)
– Resulting raw curve data

You can manage your data practically using the following setting possibilities:

Sample name

As the sample name allows entry of up to 40 characters, quite a lot of information can be included. A person who, for example, investigates thermoplastics can add a shorthand symbol for the type of plastic before the actual sample name:

Contents

”PE, sample XYZ, film 1”
”PP, sample ABC, part 5”
This notation alone results in several selection possibilities. With „PP*” (see Figure 2), all measurements which have been performed with polypropylene can be immediately selected. In the above example, the filter setting „*part*“ allows all measurements involving finished parts to be selected. Here, even as early as the naming stage, the user can personally determine his subsequent filter possibilities.

Method group
Methods can be assigned to a particular method group when they are developed. Groups such as „Thermoplastics“, „Thermosets“ and „Pharmaceuticals“ are defined as standard. Other groups can be defined using the Install Plus window.

User
Different users can easily separate their measurements via the definition of users in the Install Plus window. However, the user need not necessarily be a name. This field can also be used for the definition of the projects. The advantage: All data of the project in question (methods, curves, evaluations) can be selected at a keystroke and also deleted.

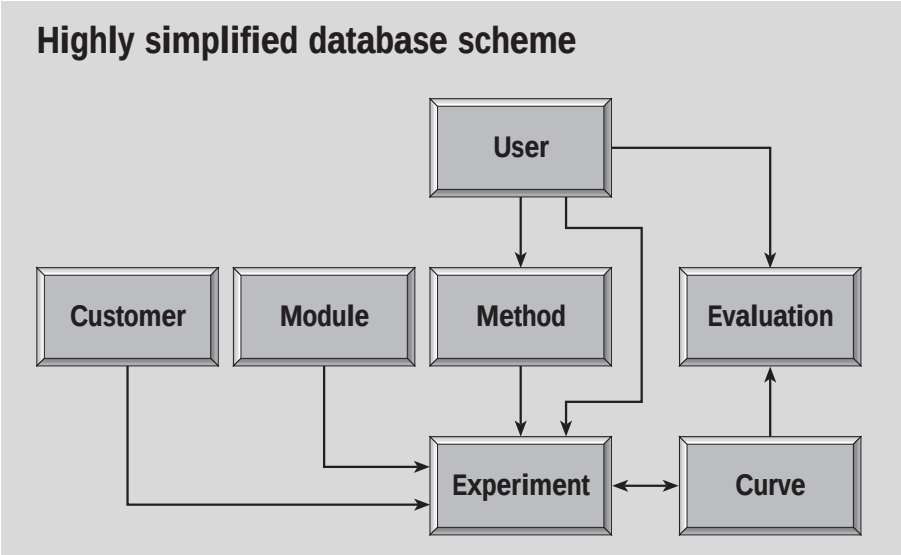


Figure 1: Simplified database scheme

Date
The date is automatically added when the measurement is stored. In the later selection of experimental curves, a particular time period can be chosen or simply a sorting operation by date performed.

Order number (only with STARe software V3.10 and later)
Many labs keep a lab journal which specifies continuous numbering. If an experiment is assigned a number, a powerful selection possibility is available as all measurements with a certain number or within a range of numbers can be selected at a later date.

Measuring cell type
The measuring cell type is automatically set, depending on what type of module you use. In the filter you can use this switch to select, e.g. all measurements with the DSC821e in a very simple manner.

Customer
This offers a further criterion for data management. After entry of the appropriate particulars, each measurement can be assigned a particular customer in the Experiment window. In the above Figure, the curves of, e.g. „Incoming goods“ are selected. This is also information which can be used for projects.

Method name
When a method is stored, it is given a name by the user. In the search for experimental data, there is later the possibility to search for data of a particular method. Figure 2 shows a search for the data of all methods whose name starts with „DSC“. Naturally, different criteria can be linked with one another when data are searched.
Even a large database can thus be managed quickly in an easily surveyed manner.
The TSW870 or the STARe software has very extensive possibilities for data management. However, it has often proved sufficient in practice to use only a few of the possibilities mentioned here. The only important point is that you implement *your concept* methodically from the outset.
In the case of a large number of samples, we recommend systematic use of the following: Name, User and with either Order number or Customer. You lose the advantages of the database only if you delete the relationships between the data.

Special feature „Direct Experiment“ (not conforming to GLP)
For rapid screening measurements, a measurement program with a segment can be directly defined in the Experiment window. When this screening measurement is started, however, no relationship is set up between the measuring module, user and customer. Curves which have been generated with such a „Rapid method“ can thus be selected in the database filter only via name and date.

The deletion of data
As there is a relationship between the individual sets of information in the database, deletion of data has consequences for the traceability.
In principle. there are two deletion strategies for the deletion of an object (e.g. user, methods and the like):

- „Delete“ deletes all data which depend on the corresponding object. The experimental curves are retained as the only exception. (The software shows you what would be deleted in an Info window). As the links of the experimental curves are broken here, these can later be selected in the

filter only via name and date.)
- „Delete all“ deletes actually everything dependent on this object.

For example, in the deletion of a user with „Delete all“, everything ever done by this user will be deleted. If, for example, a person has temporary projects whose data will not be needed later, a single user can be assigned to this project and then simply deleted later.

Data backup

The data are extremely valuable for you as the user. The data backup strategy is thus very important. In principle, there are three possibilities to back up the database.

- Backup on tape, DAT or diskette
- Backup on a network (only with STARe software V3.10 and later)
  → Backup on a network has a considerable advantage with regard to speed.

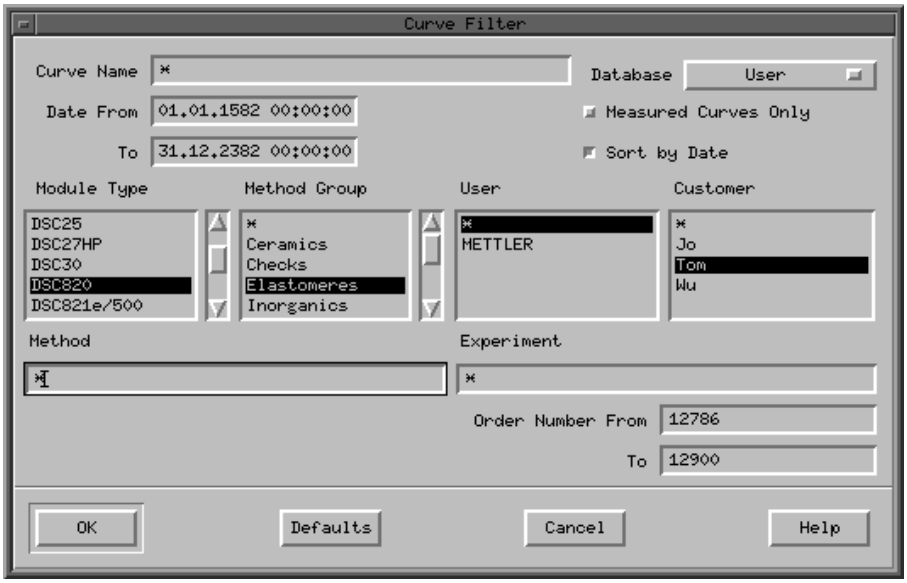


Figure 2: Filter setting possibilities in a search for experimental curves

In addition, in many companies the servers are in any case backed up regularly resulting in additional security.

Tip: Users who wish to keep their database to an easily manageable size can delete, e.g. the oldest experimental curves after first backing them up. (Remove protection.) If such a measurement is required again at a later date, the old database can be reloaded.

The new STAR^{e} SW version V4.0:

SW option MaxRes

With this SW version you have the new software option „MaxRes“ available.

This option allows rapid TGA measurements with simultaneously high resolution.

A prerequisite is a TGA850 or TGA/SDTA851^{e} module (requires module SW V4.0).

Based on the change in the weight or SDTA signal, the heating rate is automatically lowered or raised. This increases the resolution of the measurement as effects which lie close to each other no longer overlap at a low heating rate.

This overlapping can readily be seen on the 1st derivative when this does not return to the baseline between two peaks.

You would naturally obtain identical results if you were to run the entire measurement with a very low heating rate, but then the time needed for measurement would be many times longer.

Parallel reactions as well as consecutive reactions in which the activation energy of the second reaction is much larger that that of the first can not be separated simply by lowering the heating rate at will.

As input possibilities, you have the following parameters available:

- minimum heating rate
- maximum heating rate
- high threshold (derivative of the signal)
- low threshold (derivative of the signal)
- timeout
- factor
- filter

The measurement starts with the maximum heating rate. As soon as the absolute value of the first derivative drops below the upper threshold, the heating rate is lowered by the factor and not raised until the first derivative is lower than the lower threshold.

The resulting temperature program is consequently composed of individual dynamic segments. A second sample can thus be measured with exactly the same temperature program for comparison purposes, which would not be possible with a continuous matching of the heating rate to the 1st derivative. You can thus optimize a MaxRes method and then use it as a routine method.

A further advantage is that you can now combine normal dynamic segments with MaxRes segments.

Let us assume that you are primarily interested in the temperature range between 500 and 700 °C.

Your method could then have the following appearance:

1st segment: RT-500 °C with 50 K/min

2nd segment: 500-700 °C with MaxRes

3rd segment: 700-1000 °C with 50 K/min

Common to all these methods (continuous change in the heating rate or abrupt change in the heating rate) is that usually a screening measurement must first be performed to determine realistic parameters.

Figure 3 shows that with the MaxRes method the required measuring time for a complete step separation is halfed. The small graph represents the MaxRes experiment (= variable heating rate) relative to the temperature. As you can see the heating is automatically very slow when changes in weight occur.

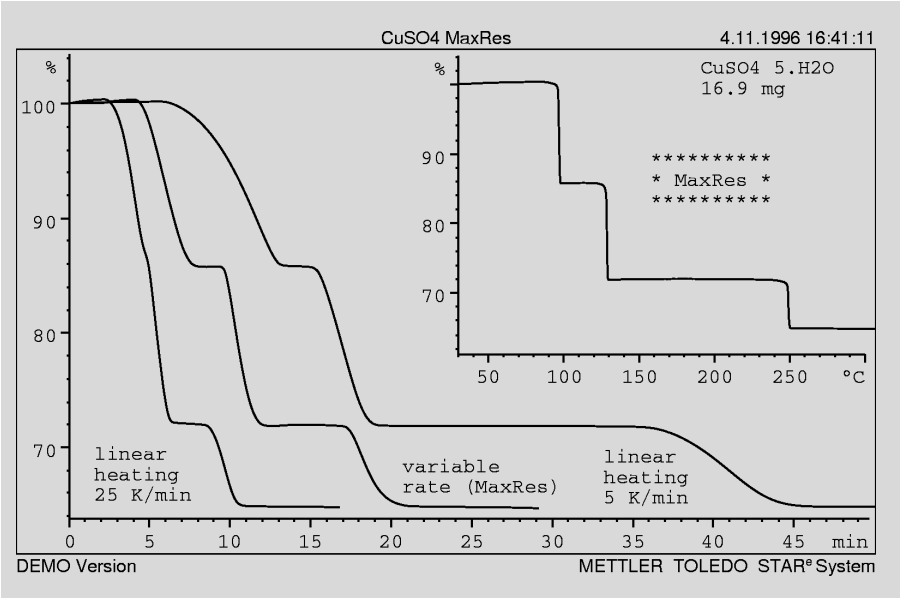


Figure 3: Decomposition of Coppersulfate Pentahydrate with loss of water of crystallization in 3 steps.

The new TGA module TGA/SDTA851^e

At the end of this year we introduce the TGA/SDTA851^e module as the successor to the TGA850 module. It offers a broader temperature range as well as different balance types and selectable furnace capacity. It is also a modular system which can be matched to your requirements.

The module has three basic versions:

- TGA/SDTA851^e small furnace up to 1100 °C (corresponds to the present TGA850)
- TGA/SDTA851^e large furnace up to 1100 °C
- TGA/SDTA851^e large furnace up to 1600 °C.

All 3 types provide the SDTA signal as standard in order to measure simultaneous physical transformations of the sample without mass changes (e.g. melting process).
However, the SDTA signal also allows an extremely accurate temperature calibration with the aid of the melting point of pure metals.
Conversion from one basic version to another is also possible at a later date.

Option Furnace

The small furnace has been optimized so that the temperature distribution is as homogenous as possible. The maximum sample volume is restricted to 100 µl.
On the other hand, the large furnace allows a maximum sample volume of 900 µl, which is particularly desirable with inhomogenous samples.

Option Link

For both types of furnace, a link for MS/FTIR or GC is available.

Option Balance

A new feature is that you can select between 3 balance types:

- MT1: max. 1 g with 1 µg resolution
- MT5: max. 5 g with 1 µg resolution
- UMT5 max. 5 g with 0.1 µg resolution

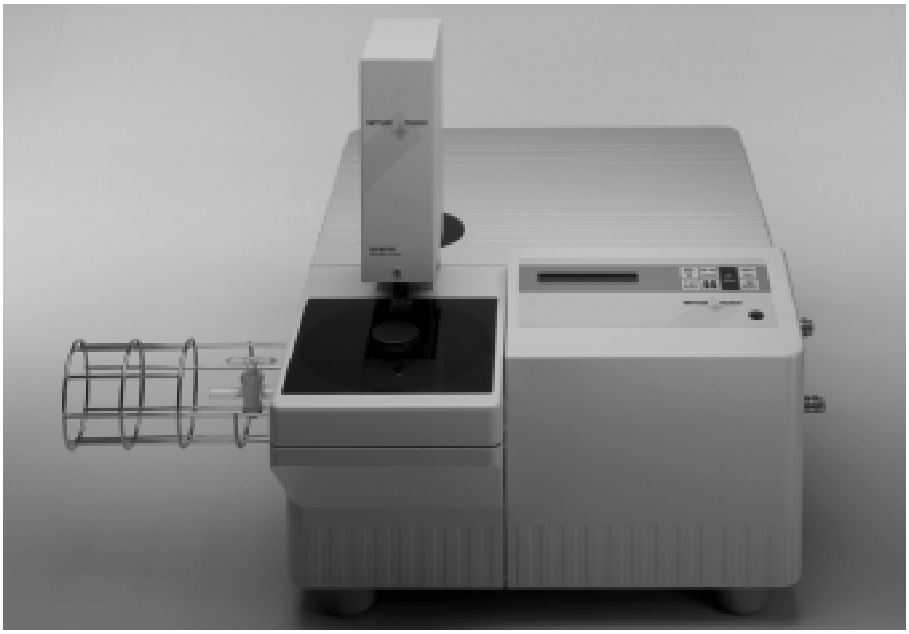


Figure 4: TGA/SDTA851^e

When selecting the balance, please note that the weight of a 900 µl alumina crucible is more than 1 g.
The automatic internal calibration is common to all balances. During pauses in measurements, calibration weights are loaded in a motorized operation and the balance is calibrated to take the latest circumstances into account (eliminates electronic drifts, but also ambient influences such as changes in the pressure, temperature and humidity).
The TGA/SDTA851^e can also be expanded with the sample robot, the TSO801RO.

Universal gripper

When equipped with the new universal gripper, even different crucibles with different diameters can be measured in a series. The accessory for piercing hermetically closed crucibles can of course also be installed.

With the new TGA/SDTA851^e you are thus in the position to measure very small and very large samples automatically in a temperature range from room temperature up to 1600 °C. You always have the full resolution available over the entire weighing range.

Features of the TGA/SDTA851^e module at a glance:

• Large measurement range	1/5/ 5 g (depending on balance type)
• High resolution	0.1/1 µg (depending on balance type)
• Maximum sample volume	100/900 µl (depending on furnace type)
• Definable atmosphere	gas-tight measuring cell
• Large temperature range	RT ... 1100/1600 °C depending on furnace type)
• High temperature accuracy	± 0.25 °C/±0.5 °C (up to 1100 °C)
• SDTA resolution	0.005 °C
• Modular construction	open for the future
• Automatable	sample robot with 34 samples
• Additional options	gas controller, MS/FTIR/GC link, switched line socket
• Cooling	cryostat cooling

Determination of the eutectic composition of the system

Methyl-4-hydroxybenzoate/ p-hydroxybenzoic acid

Prof. Dr. P. C. Schmidt
University Tübingen

Experimental aim
p-hydroxybenzoates are used as preserving agents and contain minor amounts of free 4-hydroxybenzoic acid as an impurity resulting from the synthesis with which they form a eutectic mixture. The example of the system methyl-4-hydroxybenzoate/ p-hydroxybenzoic acid will be used as an example to determine the composition of the eutectic.

Sample
1. Methyl-4-hydroxybenzoate
DAB 10
(methyl ester of p-hydroxybenzoic acid, methyl paraben)

Empirical formula:	$C_8H_8O_3$
CAS No.:	99-76-3
Molar mass:	M: 152.14

Description: white, crystalline, hygroscopic powder, virtually odorless and tasteless

2. p-hydroxybenzoic acid
(4-hydroxybenzoic acid, paraben)

Empirical formula:	$C_7H_6O_3$
CAS No.:	69-72-7
Molar mass:	M: 138.12

Description: colorless crystals

3. Mixtures
Homogeneous mixtures containing 2, 5, 10, 25, 50 and 75 mol% p-hydroxybenzoic acid in methyl-4-hydroxybenzoate were prepared by grinding in an agate mortar. These mixtures as well as the starting substances are the investigation samples.

Experimental conditions
Instrument: DSC820 with TSW870

Sample preparation
The samples were measured in closed standard aluminum crucibles. Initial sample weight: 2 to 4 mg. To assure good contact with the crucible base, the samples were pressed down with a punch.

Measurement method
Temperature program 1: 50 to 250 °C at 10 K/min
Temperature program 2: 115 to 135 °C at 1 K/min
Purge gas: Nitrogen

Interpretation
All diagrams (Figure 5 through 8) show sharp melting peaks of the pure substances and also sharp peaks of the eutectic with the mixtures above 10 mol% p-hydroxybenzoic acid. Asymmetrical peaks which, however, can still be evaluated are found only with 2 and 5 mol% p-hydroxybenzoic acid as impurity.

Evaluation
The evaluation can be performed following Burger (Burger 1982) either via the isobaric phase diagram or via the mass-related heat of fusion of the eutectic peak. In the first case, **the end of melting** of the mixture is plotted against its composition, in the second case **the heat of fusion** per mass unit of the first peak. The second method proved the better one in the present case as not only are straight lines obtained (Figure 9) whose intersection point characterizes the composition of the eutectic, but also the integration of the first peak is easily possible with all mixtures. On the other hand, the end of melting of the mixtures with mixtures whose composition lies near the eutectic can be determined only with difficulty and with no great accuracy.
The following eutectic composition results from Figure 9 (determined by linear regression):
p-hydroxybenzoic acid: 14.16 mol%
Methyl-4-hydroxybenzoate: 85.84 mol%.
The evaluation of the measured curves shows the following onset temperatures:

Methyl-4-hydroxybenzoate	125.4 °C
p-hydroxybenzoic acid	214.4 °C
Eutectic	117.4 °C

Conclusions
The evaluation of the mass-related heat of fusion of the eutectic peak allows an exact determination of the eutectic composition of a pair of substances.

References
Burger, A. ”DTA und DSC: Grundlagen, Methodik und Anwendung” Pharm. unserer Zeit 11**,** 177-189 (1982)
Hasler, C. and Büchi, J. ”Untersuchungen über Bezugssubstanzen zur Bestimmung von Schmelztemperaturen nach Ph.Helv. VI u. Ph.Eur.I” Pharm.Acta Helv. 48, 639 (1973)

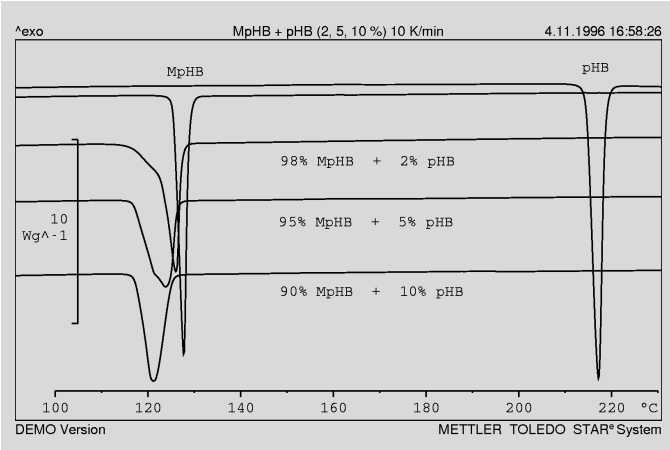


Figure 5: p-hydroxybenzoic acid, methyl-4-hydroxybenzoate and mixtures with 2, 5 and 10 mol% p-hydroxybenzoic acid in methyl-4-hydroxybenzoate at l0 K/min.

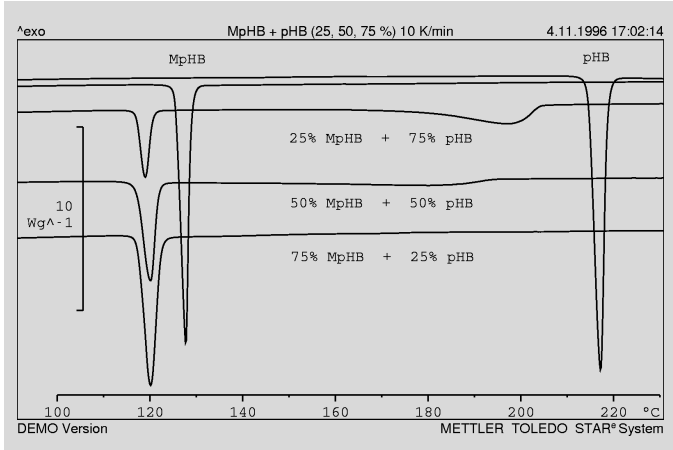


Figure 6: p-hydroxybenzoic acid, methyl-4-hydroxybenzoate and mixtures with 25, 50 and 75mol% p-hydroxybenzoic acid in methyl-4-hydroxybenzoate at l0 K/min.

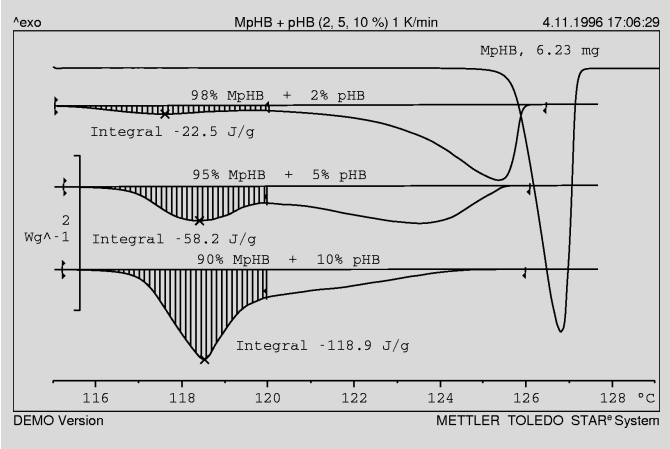


Figure 7: Methyl-4-hydroxybenzoate and mixtures with 2, 5 and 10 mol% p-hydroxybenzoic acid in methyl-4-hydroxy-benzoate at 1 K/min.

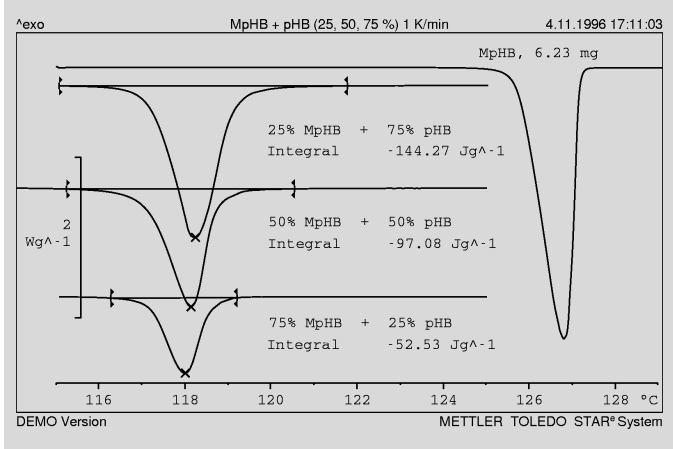


Figure 8: Methyl-4-hydroxybenzoate and mixtures with 25, 50 and 75 mol% p-hydroxybenzoic acid in methyl-4-hydroxy-benzoate at 1 K/min.

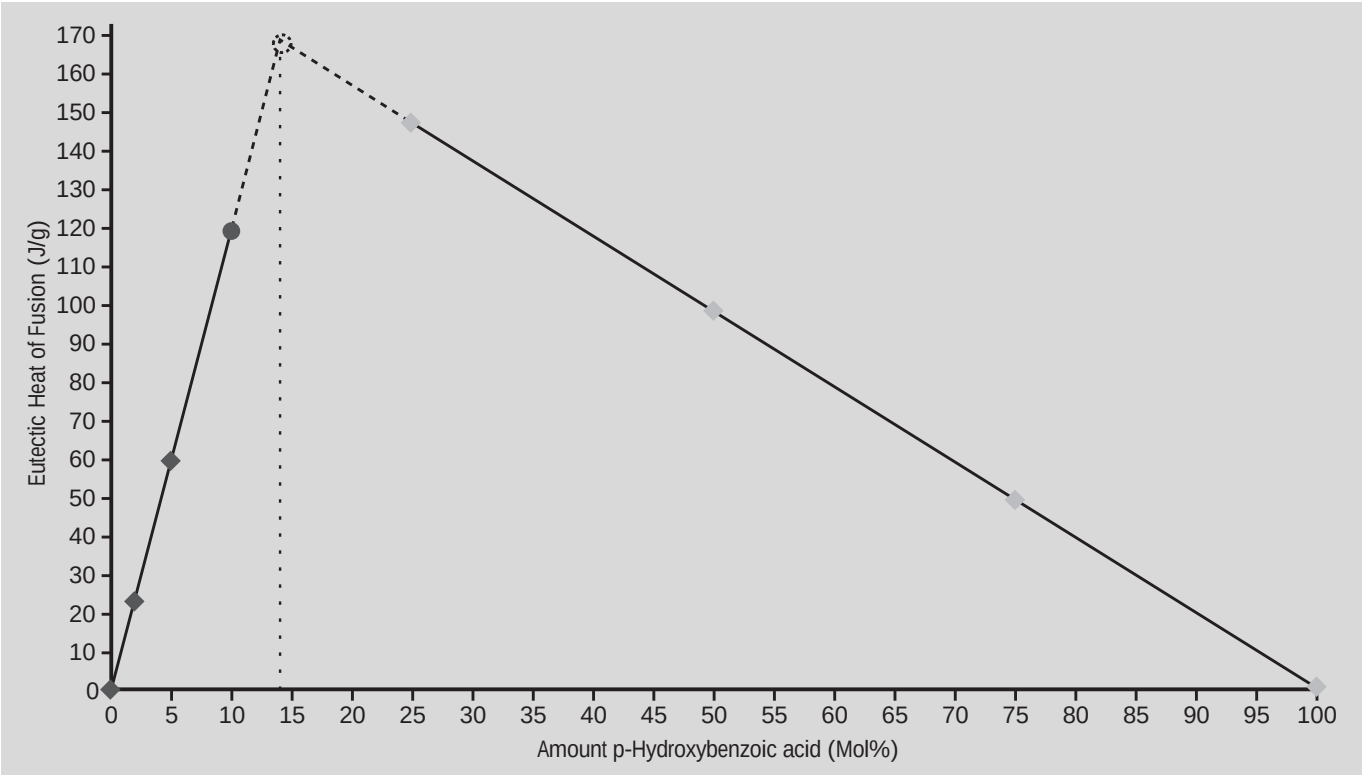


Figure 9: The eutectic heat of fusion of the system methyl-4-hydroxy benzoate with p-hydroxy benzoic acid.

Glass transition temperature of elastomers

Experimental aim

The temperature of the glass transition (T_g) is suitable for the characterization, identification and quality monitoring of elastomers.

Samples

– *Designations:*

ABS	Acrylonitrile-butadiene-styrene copolymers;
Butyl	Butyl rubber, copolymer of 95 to 98% isobutylene and 2 to 5% isoprene, often also called IIR;
EPDM	Copolymer of ethylene (usually 50 mass%), propylene, dienes, often also called EPDM rubber;
NR	Natural rubber: cis-1,4-polyisoprene;
IR	synthetic rubber: synthetic trans-1,4-polyisoprene;
NBR	Nitrile rubber, copolymer of butadiene and acrylonitrile;
SBR	Styrene-butadiene rubber, copolymer of butadiene and styrene (usually 75:25).

– *Constitution:* Compact tests specimens or pellets

– *Properties:* Elastomers are designated as loosely crosslinked macromolecular substances (frequently also called rubber).
The starting materials are rubbers to which are added crosslinking chemicals and, depending on the desired material properties, other additives (mineral fillers etc.). The elastomer is formed by crosslinking (vulcanization).
Elastomers can stretched by at least double their original length by the effect of a weak force at room temperature (or higher temperatures) and return quickly to their original shape (rubber-elastic behavior) on removal of the force. Elastomers are not viscoelastic.

– *Use:* On account of the above-mentioned properties, elastomers have a wide range of uses with their application profile being finally determined by their specific properties.

Examples (with no claim to completeness):

ABS	Automobile components, household apparatus, toys, office machines, telephones, leisure articles:
Butyl	Seals, air and heating tubes, inner liners in tyre construction;
EPDM	Construction and cable industry, vehicle manufacture;
NR	and synthetic rubber (synthetic polyisoprene): Truck tyres, thin-walled articles (surgical gloves, belts, conveyor belts, rain apparel, sponges, balls;
NBR	Oil- and benzene-resistant types, as seals, tubing, roller coatings, swell-resistant molded parts;
SBR	Hardener for floor coverings, shoe soles.

Experimental conditions

Measurement system: DSC30 with TC15 and TA station, cooling option
Sample preparation: Piece cut from strips or a pellet (ABS) was weighed into the standard aluminum crucible (40 µl) and sealed.
Temperature program: After free, i.e. uncontrolled cooling: heating from -110°C to +30°C: Heating rate: 10 K/min.
Purge gas: Nitrogen 50 ml/min

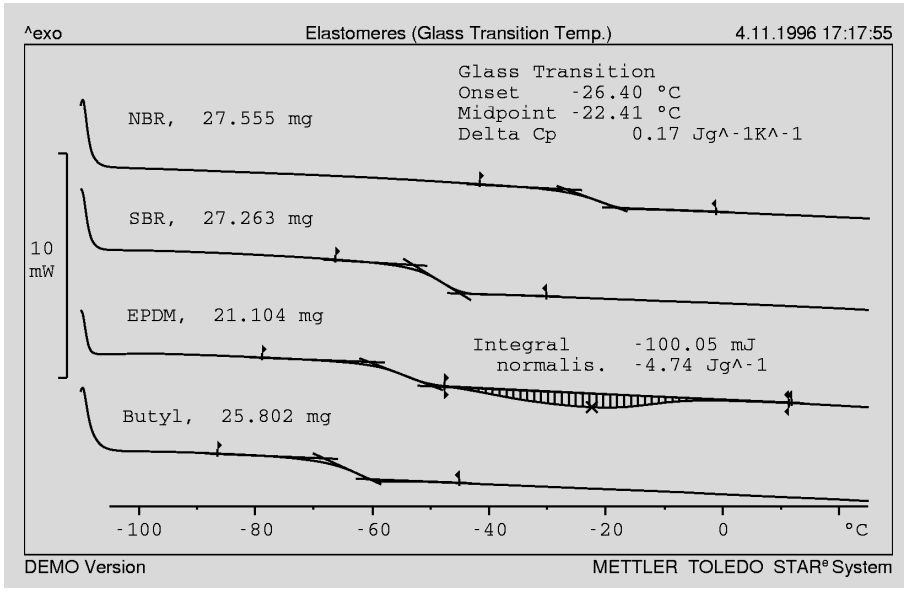


Figure 10: DSC heating curves of NBR, SBR, EPDM and butyl rubber with the evaluation of the recorded glass transitions.

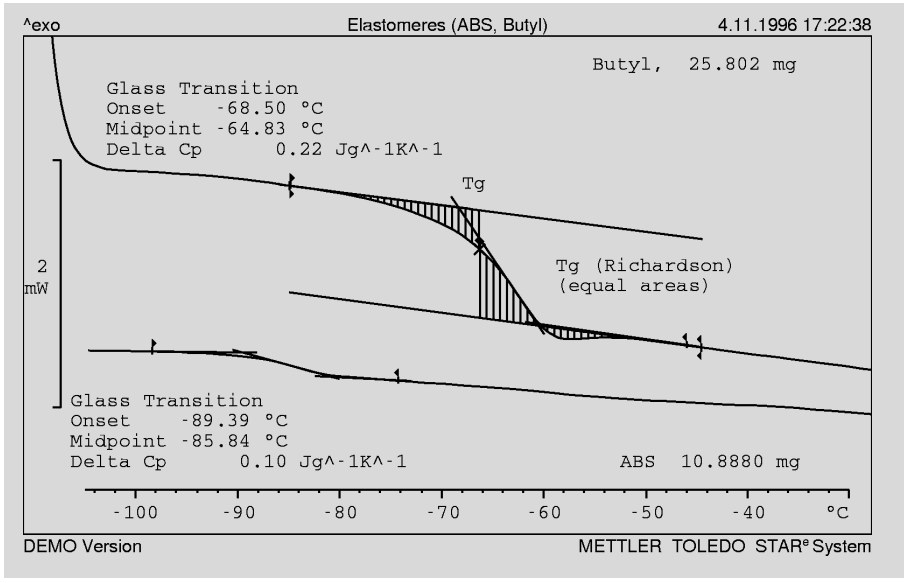


Figure 11: DSC heating curves of butyl rubber (scale of ordinate sensitivity shown enlarged) and ABS with the evaluation of the recorded glass transitions.

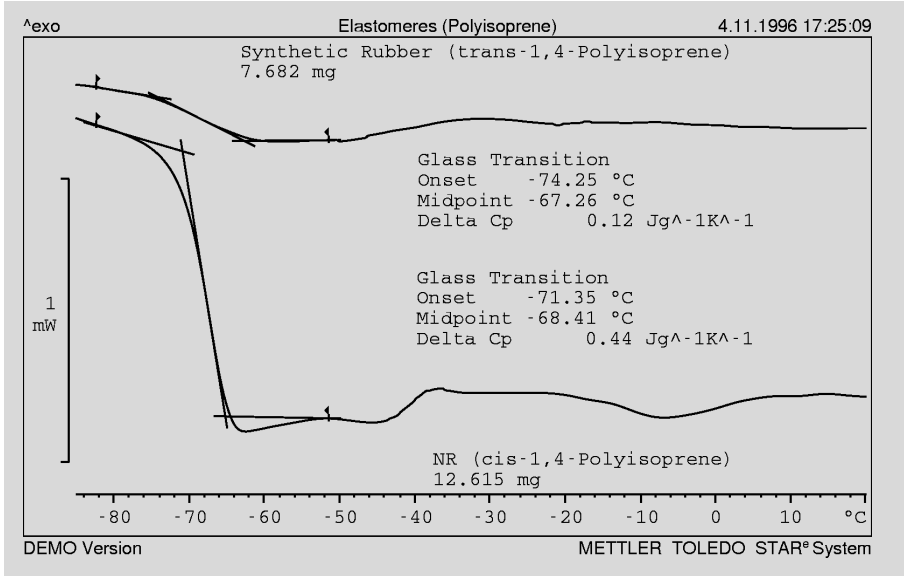


Figure 12: DSC heating curves for NR (cis 1,4-polyisoprene) and synthetic rubber (trans 1,4-polyisoprene) with the evaluation of the recorded glass transitions.

Interpretation:
All investigated elastomers show more or less very pronounced glass transitions. These always include an increase in the specific heat capacity, i.e. an endothermic displacement of the experimental curve.
With one exception (butyl rubber), no enthalpy relaxation can be observed, i.e. the glass transition can be evaluated by the „half-step rule“: the glass transition temperature T_g is at position $c_p/2$. On appearance of a so-called enthalpy relaxation (Figure 11 - butyl rubber), the glass transition is evaluated by *Richardson's* method.
With several samples (EPDM, NR, synthetic polyisoprene - Figure 10 and 12), a minor exothermic effect appears above the glass transition: a cold crystallization. In the case of natural rubber (NR), the crystallites formed already melt again at around -10°C, as can clearly be seen. For EPDM. this effect of the cold crystallization has also been evaluated quantitatively by integration (Figure 10).

***Evaluation*:**
The glass transition temperature is an important application quantity: it shows the upper temperature limit of the material under investigation for its use in the desired rubber-like manner. Below the glass transition temperature, it becomes hard-elastic, i.e. also brittle. The glass transition temperature is thus an application limit at lower temperatures.
Compared with the starting material, crosslining does not change this glass transition temperature or at least by only a little. However, crosslinking does alter the contribution of the change in the specific heat capacity. This expresses the intensity of the intramolecular motion, which decreases as a consequence of the crosslinking. In this respect, both specifications are of great importance for the assessment of elastomers for their intended use.

The following values are determinded from the results of DSC meaurement:

Sample	T_g [°C]	Δc_p [J/g K]
ABS	- 86	0,09
Butylrubber	- 65	0,21
acc.Richardson:	- 66	
EPDM	- 55	0,29
NR	- 68	
IR	- 67	
NBR	- 22	0,17
SBR	- 49	0,27

Conclusion

The glass transition temperature of elastomers is very important for the use since parts made of the respective rubber loose the rubber elasticity when cooled to this temperature. Tg routinely ist determined by DSC easily.

Literature:

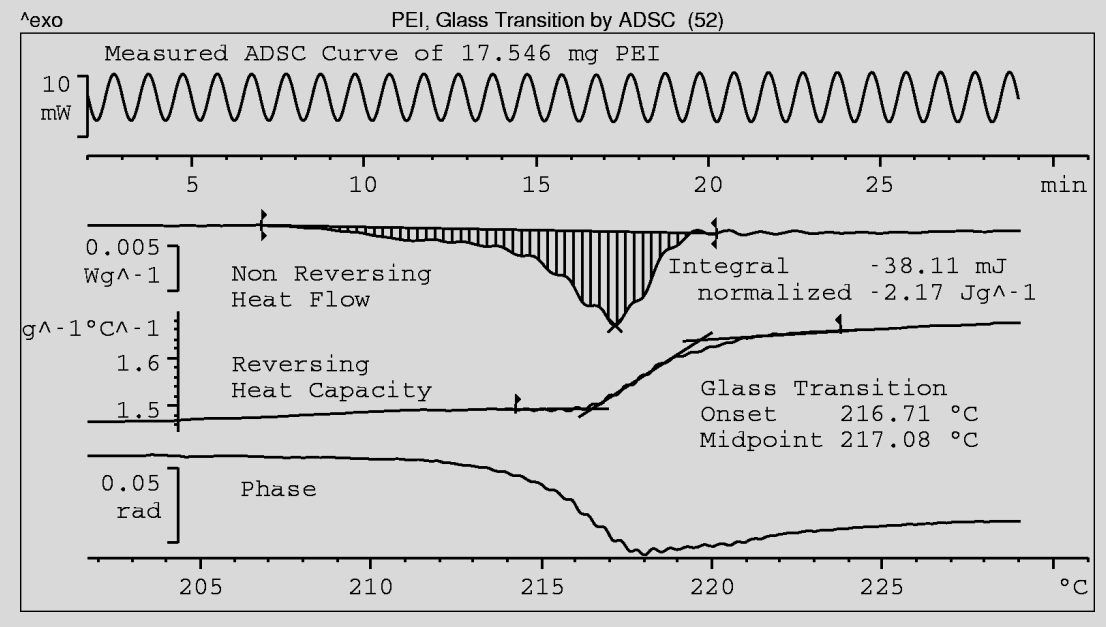
Low Temperature DSC and TMA of Polybutadiene, TA Application Nr. 3107 (METTLER TOLEDO)

M. J. Richardson: Compr. Polymer Science, Vol. 1: Polymer Characterization Pergamon Press, Kidlington, Oxford 1989

PEI, Glass Transition by ADSC

Sample Polyetherimide, PEI, Ultem 1000, injection molded part

Conditions DSC Cell: DSC821 with sample changer and cryostat cooling
Pan: Al standard 40 µl
Sample preparation: 17.546 mg cut with knife in such a way that the bottom is flat
DSC Measurement: Heating from 200 to 229 °C at a mean rate of 1 K/min. Amplitude of sinusoidal oscillation 1 K, period 1 min



Atmosphere: Nitrogen, 50 ml/min.

Interpretation At the top there is the measured sinusoidal ADSC curve. Underneath follow the calculated curves: The „non reversing“ curve shows the peak of the enthalpy relaxation. The next curve is the „reversing“ signal (specific heat capacity). The last is the phase shift.

Evaluation The ADSC curves are evaluated by an algorithm based on the fast Fourier transform. In addition to the shown curves the in phase and the off phase components of the specific heat capacity are available.
Each calculated curve can be evaluated, e.g. the non reversing peak is integrated to get the enthalpy change. On the cp-temperature function the glass transition is evaluated and cp shown in tabular form:

T	210	215	220	225 °C
cp	1.49	1.49	1.62	1.66 $Jg^{-1}K^{-1}$

Conclusion As the example shows, ADSC resolves reversing and non reversing effects that can be very helpful with overlapping reactions. In general cp - changes belong to the reversing effects, e.g. at the glass transition. Non reversing effects are the enthalpy relaxation, the cold crystallization and all kind of chemical reactions.

Exhibitions/conferences

12th Ulm-Freiberger Calorimetry Meeting	March 19 - 21, '97	Feiberg/Sachsen, Germany
TAC97	April 14 - 15, '97	University of Oxford
Thermal Analysis of Advanced Materials II		United Kingdom
ICTAC 2000	August 14 - 18, '97	Copenhagen, Denmark

TA customer courses and seminars (CH)

Customer Seminar in Thermal Analysis	April 28 - 30, '97	Greifensee, Switzerland
Kundenseminar in Thermischer Analyse	May 13 - 15, '97	Greifensee, Switzerland
Cours clients d'analyse thermique	May 20 -22, '97	Greifensee, Switzerland
Kundenseminar in Thermischer Analyse	November 4 - 6, '97	Greifensee, Switzerland
Customer Seminar in Thermal Analysis	November 25 - 27, '97	Greifensee, Switzerland

TA information days and training courses (UK)

Please contact your local instrument specialist or R. Bottom
Phone 0116 235 70 70 or fax 0116 236 55 00

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