

Information for users of METTLER
TOLEDO thermal analysis systems

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We are pleased to report that 2001 has been another very successful year for METTLER TOLEDO and that we have enjoyed above average growth in Thermal Analysis. We are delighted to see that more and more customers want to share their knowledge and publish their applications work in UserCom.

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Interpreting TMA curves

Georg Widmann

Artifacts

Artifacts can sometimes be observed in thermomechanical analysis:

- When the force exerted by the probe on the sample or the fused silica disk covering the sample is very weak. The probe can then begin to jump around or “dance” on the sample. This leads to an extremely large noise level or spikes ($\geq 0.5 \mu\text{m}$). If vibrations in the building are the cause of the problem, install the TMA on a stone bench with oscillation dampers. Otherwise increase the load to at least 0.01 N.
- When the surfaces of a sample are not parallel, i.e. with wedge-shaped samples. This often gives rise to artifacts that re-

semble a series of steps. This is caused by the sample slipping stepwise down the sloping surface of the sample.

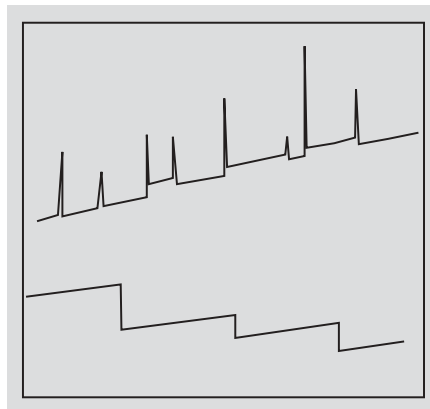


Fig. 1. TMA artifacts due to a “dancing” probe (above) and wedge-shaped sample (below).

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Measurement modes

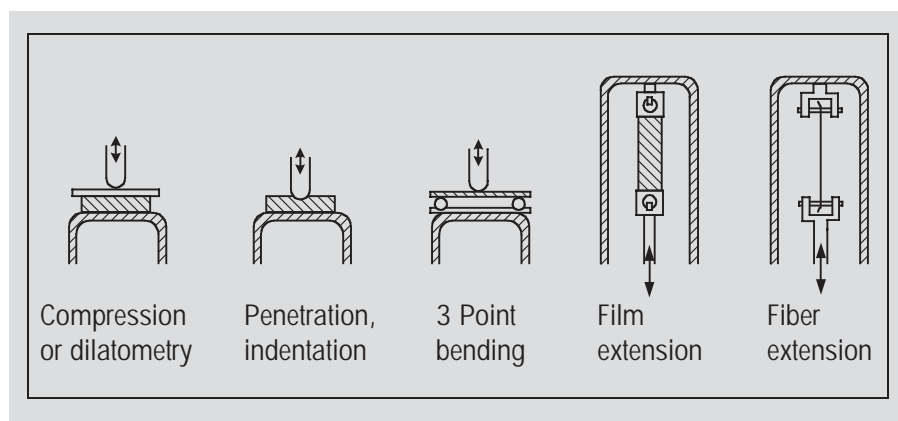


Fig. 2. The standard TMA measurement modes: compression or dilatometry, penetration, bending, film extension and fiber extension. In the first three configurations, the probe (usually a ball-point tip of 3 mm diameter) exerts a force on the sample from above. In the two other configurations, the probe pulls the sample downward. The force can be set from 0.001 N to 1 N.

Dilatometric measurements are used to determine the coefficient of thermal expansion. They are performed under conditions of low compressive or tensile stress in order to prevent deformation of the sample. The compressive stress, i.e. the force per area, is kept low by applying a very weak force (e.g. 0.01 N) over a large sample area (quartz glass disk between the sample and the ball-point probe). Since most materials have positive coefficients of expansion, a dilatometric curve exhibits an upward tendency with increasing temperature, unless the sample contracts in certain regions due to changes in internal stress or orientation.

TMA measurements are performed using a significant force e.g. 0.5 N. The standard measurement modes are penetration and bending. The aim is to measure the deformation of the sample under load. The ball-point probe is often used for penetration experiments. Initially only a small area of the probe is in contact with the sample. As soon as the sample softens, the probe penetrates more and more into the sample, resulting in a rapid increase in the area of the probe that is in contact with the sample.

Whether the measurement has a more dilatometric character or is in fact a TMA measurement depends on the applied force and the stiffness of the sample. For exam-

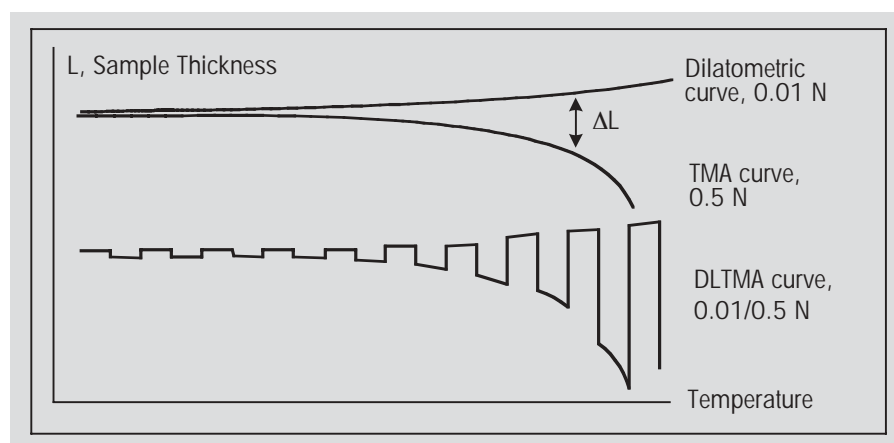


Fig. 3. The dilatometric curve (measured with negligible compressive stress) usually exhibits an upward tendency due to the thermal expansion of the sample. The TMA curve measured with an appreciably larger compressive stress shows that the ball-point probe sinks into the sample on softening. DLTMA is therefore able to alternately measure sections of both curves in one experiment.

ple, the dilatometric curve of a quartz crystal can be measured with a force of 0.5 N without any sign of the sample deforming. In contrast, if an organic substance, e.g. an edible fat between quartz glass disks, is measured through the melting region with 0.01 N, then the expansion is only visible when the fat is in the solid state. On melting, the stiffness sinks to such an extent that the slightest force squeezes out or deforms the liquid. With metals, a larger force is needed to squeeze out the melt, e.g. 0.5 N, because the oxide film on the surface also has to be deformed.

DLTMA measurements are TMA measurements performed with a periodically changing load. If the two forces are prop-

erly chosen, it is in fact possible to alternatively measure sections of the dilatometric curve at low load and sections of the penetrometric TMA curve at high load. With polymers, however, the transition is delayed, especially in the glass transition region, due to the effects of relaxation processes.

TMA measurements are usually performed with a dynamic temperature program at a rate of 2 K/min to 10 K/min, very often at 5 K/min.

The measurement is normally terminated before the sample decomposes (to avoid contamination of the sample holder due to molten or foaming decomposition products).

Interpretation

TMA effects of physical transitions

To investigate melting behavior, the sample is usually placed between two quartz disks and then measured with a force of 0.5 N at a heating rate of 5 K/min. The smaller the amount of sample between the quartz glass disks, the shorter the melting time. The liquid phase is consequently squeezed out earlier and more rapidly. For small samples, the onset corresponds to the melting point (Fig. 4a).

Flat samples, such as plastic films or surface coatings, can be measured directly with the ball-point probe. When the sample melts, the probe penetrates completely through the melt.

Semicrystalline polymers are squeezed out rather slowly from between the quartz glass disks on melting because the melt is very viscous. With three-dimensional cross-linking (e.g. cross-linked PE, PE-X), an elastomer remains that is compressed but not squeezed out (Fig. 4b).

No TMA effect is observed on cooling molten samples because the melt has already been squeezed out. An exception is cross-linked PE, which crystallizes with volume contraction.

Amorphous polymers with a tendency to crystallize exhibit so-called cold crystallization on warming (Fig. 4c).

Solid-solid transitions (polymorphism) can be detected because they are accompanied by dimensional changes (strongly anisotropic). This is best measured by placing a single crystal under the 1 mm² probe (Fig. 4d).

TMA at the glass transition

One of the TMA measurements most frequently

performed is the determination of the glass transition temperature. The expansion coefficient shows a marked increase at the glass transition. This is the reason why the slope of the dilatometric curve becomes steeper at the transition (Fig. 5a).

The first heating curve of a new sample usually exhibits typical anomalies at the glass transition. These are caused by effects such as volume and stress relaxation, drying effects, or a foreign body (dust particle) penetrating the sample as it softens (Fig. 5b, c).

In penetration measurements, the ball-point probe rests directly on the sample and penetrates more and more into the sample at the glass transition (Fig. 5d).

With highly filled polymers e.g. carbon fiber reinforced composites, the probe can hardly penetrate at all. These materials should be measured with the bending accessory using a load of 0.5N for example (Fig. 5e).

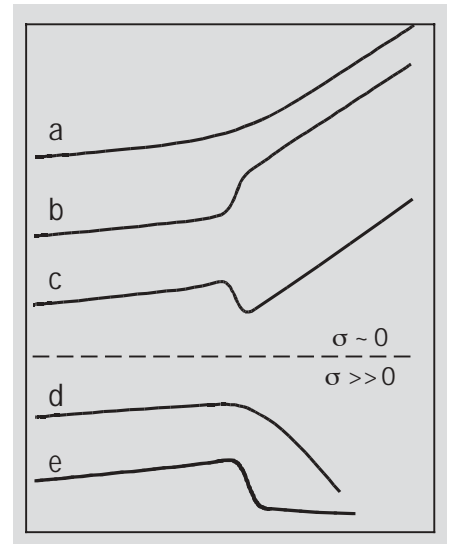


Fig. 5. TMA glass transition (a...c dilatometric with very low compressive stress σ):

- a: ideal glass transition due to the increasing expansion coefficient,
- b: swelling of the sample at the glass transition,
- c: contraction of the sample at the glass transition,
- d: glass transition measured in penetration mode,
- e: the bending accessory allows T_g to be determined even with samples of highly filled polymers that show hardly any effects with other measurement modes.

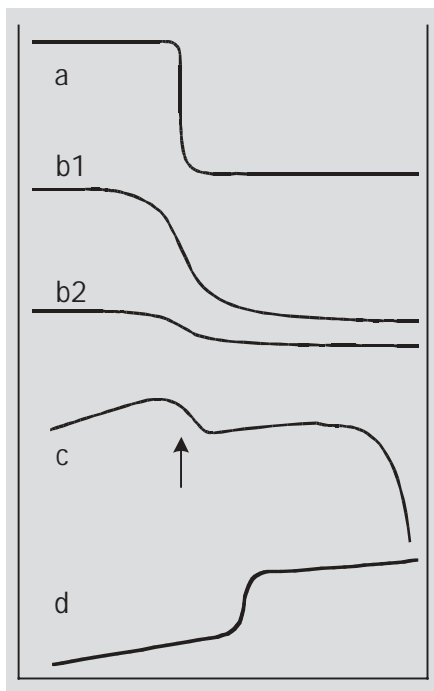


Fig. 4. Typical TMA curves of transitions:
a: melting with or without decomposition
b1: melting of semicrystalline polymers with a wide melting range
b2: the cross-linked PE-X does not melt
c: cold crystallization (arrow) can be measured because of the volume change. Afterward, the sample melts.
d: polymorphism: solid-solid transition

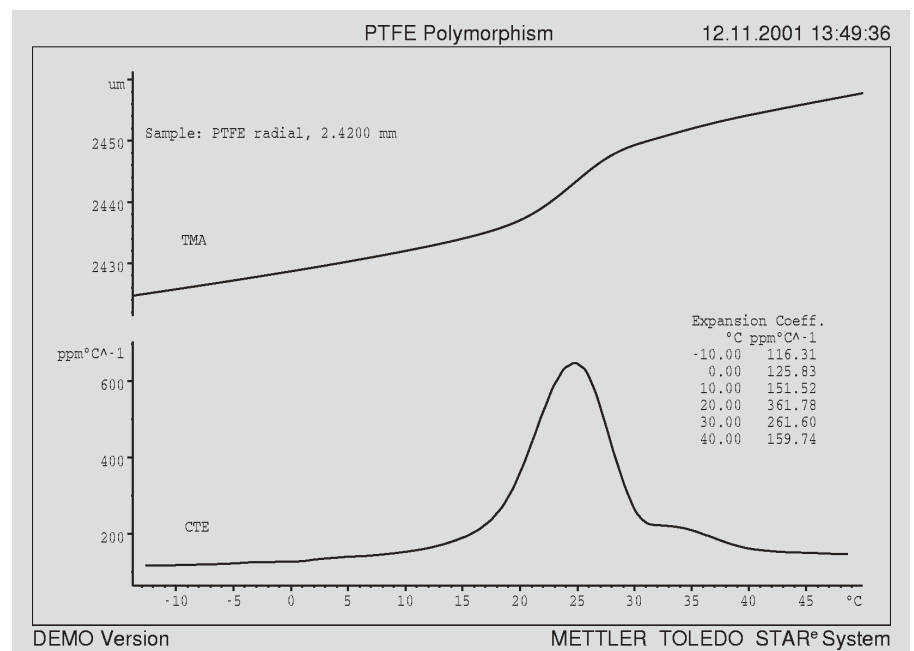


Fig. 6. The thermal expansion of PTFE. The solid-solid transition around 25 °C causes the additional expansion. Measurement conditions: heating rate 5 K/min, force 0.05 N; a quartz glass disk between the sample and the ball-point probe distributes the force uniformly. The coefficient of thermal expansion α is shown below (CTE).

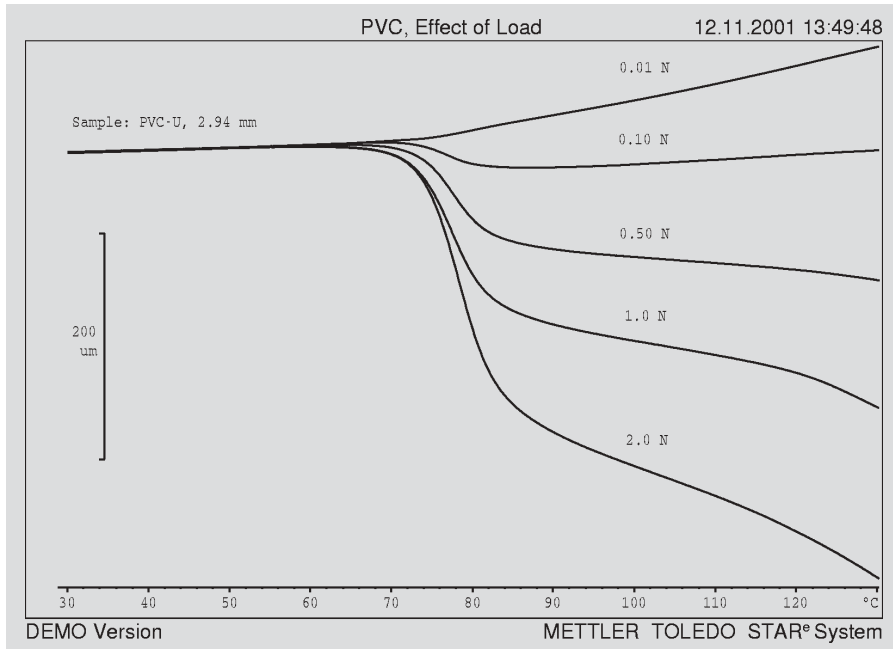


Fig. 7. The transition from purely dilatometric to purely penetrometric TMA measurement using PVC-U as an example. Heating rate 5 K/min, ball-point probe 3 mm diameter. The onsets are practically independent of the applied force.

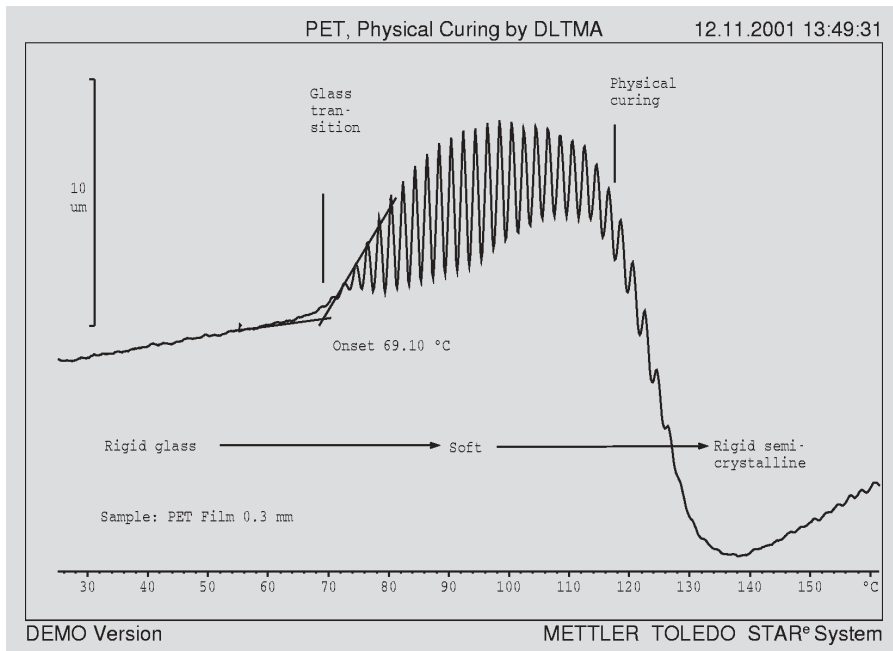


Fig. 8. The DLTA curve of polyethylene terephthalate shows the glass transition at 70 °C (amplitude increasing, i.e. modulus decreasing) and the cold crystallization at about 120 °C (modulus increasing, thickness decreasing due to increasing density).

Chemical reactions

TMA is mainly used to measure surface reactions, e.g. the thermal or oxidative decomposition of surface coatings. If complete decomposition occurs, the step height

corresponds to the thickness of the coating (Fig. 9a). In some cases, ash, inorganic fillers and fiber additives remain behind. The decomposition of organic samples is sometimes accompanied by foaming. Cer-

tain additives are used to expand the polymer to a foam as it softens. In such cases, the increase in volume is then often of interest. These samples are best measured in a crucible with a lid resting on top of the sample. After reaching maximum expansion the foam usually collapses. With molded laminates, decomposition of the matrix resin results in the formation of gaseous decomposition products that cause the layers to swell and delaminate.

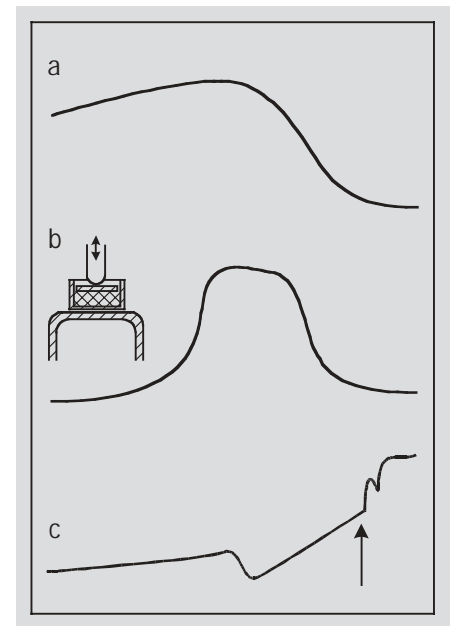


Fig. 9. a: decomposition of organic samples, e.g. surface coatings, b: on heating, the sample forms a voluminous foam that afterward collapses, c: delamination of molded laminates (arrow).

Final remarks

The information presented above on the origin and physical and chemical background of typical TMA effects should help you interpret your own measurement curves. If the interpretation of the results is still unclear, you might well consider using other techniques such as:

- DSC and TGA measurements,
- the analysis of any gaseous compounds evolved (EGA),
- the observation of the sample under the hot stage microscope.

Determination of the specific heat of the dry substance of moist samples using modulated DSC (ADSC)

Dr. Markus Schubnell, Dr. Jürgen E. K. Schawe

Introduction

Samples analyzed by Differential Scanning Calorimetry (DSC) often contain residual moisture (or, in general, solvent residues). In a conventional DSC experiment, the measurement curve then exhibits a broad endothermic evaporation peak. Such peaks often overlap other thermal processes, making the evaluation more difficult. In addition, solvent residues can influence other thermal effects. For example, residual moisture can act as a plasticizer and shift the glass transition of a sample to lower temperature. One way to separate the evaporation of residual moisture from other overlapping thermal effects is to use temperature modulated DSC. In ADSC, the linear temperature program is overlaid with a sinusoidal temperature modulation. This results in a sinusoidal heat flow. The analysis of such modulated heat flow curves allows overlapping effects to be separated. In this article, a possible procedure for the analysis of a pharmaceutical substance containing residual moisture is described as an example.

Experimental details

The experiments were performed using a DSC822^e equipped with an IntraCooler. The temperature program used was as follows: underlying heating rate of 1 K/min, temperature amplitude of 0.5 K, period of 48 seconds. The sample was a spray-dried mixture of two incompatible amorphous pharmaceutical substances with a residual moisture content of about 8%. The samples were measured in hermetically sealed cru-

cibles, in a self-generated atmosphere, and in open crucibles.

The self-generated atmosphere was obtained by piercing a 50 μm hole in the aluminum lid of a sealed crucible.

showed a weight loss of 8.4% between room temperature and 150 °C (see Fig. 2). If the sample weight for the DSC experiment in the open crucible (5.652 mg) is taken into account, then a value of 2557 J/g is ob-

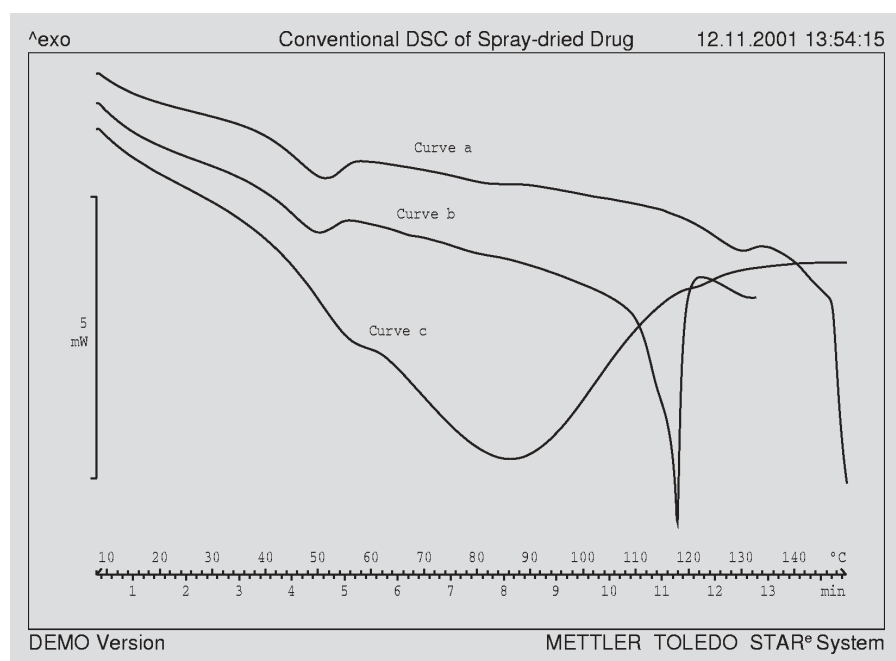


Fig. 1. Conventional DSC measurements of a spray-dried pharmaceutical substance under different measurement conditions: curve a: hermetically sealed crucible; curve b: crucible with a 50 μm hole in the crucible lid; curve c: open crucible. Sample weight about 5 mg; heating rate 10 K/min.

Figure 1 shows the three DSC curves measured in the usual way at 10 K/min. In the open crucible (curve c), a broad evaporation peak can be observed in the range 10 °C to 120 °C whose total enthalpy is about 1214 mJ (the measurement in the sealed crucible (curve a) was used as the baseline). Measurements with a TGA/SDTA851^e

tained for the weight-normalized heat of vaporization, which agrees well with the heat of vaporization of water (2400 J/g). From this we conclude that the water liberated was only weakly bound to the substrate. The weight loss can therefore be interpreted as being due to the evaporation of adsorbed water.

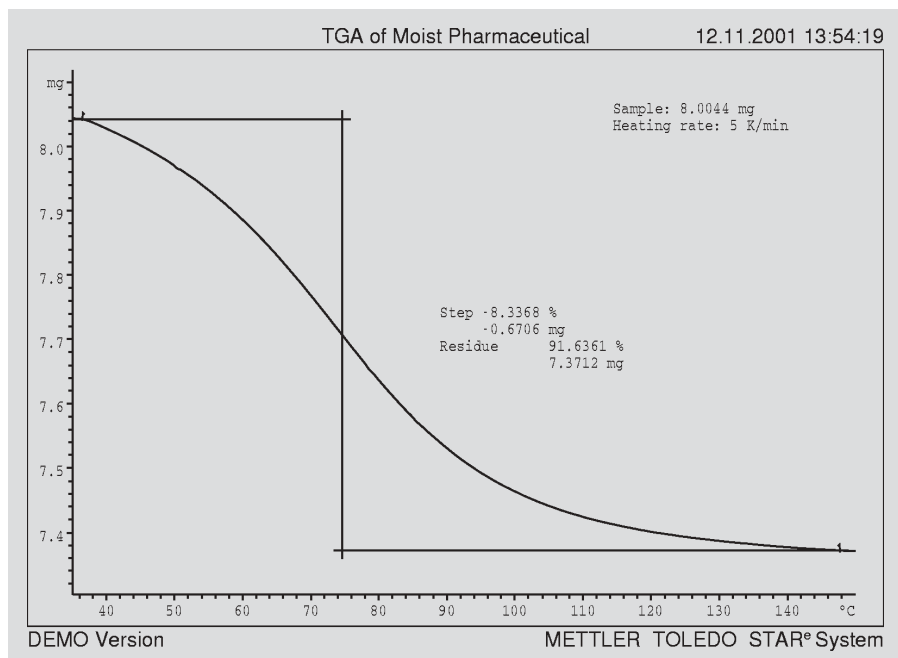


Fig. 2. TGA curve of the moist sample: sample weight 8.004 mg; heating rate 5 K/min.

If the sample is measured in a hermetically sealed crucible, curve a is obtained. The marked deflection in the curve above 140 °C is caused by the rapid release of water vapor, which occurs when the crucible lid ruptures as a result of pressure build-up inside the crucible. The interpretation of the two endothermic peaks at about 50 °C and 130 °C is not so obvious. In a self-generated atmosphere (curve b), the evaporation process shifts toward the boiling point. Here again, a small endothermic peak can be seen at 50 °C just like in the curve obtained from the hermetically sealed crucible. In the open crucible, this peak shifts to a somewhat higher temperature. Since the moisture content is somewhat lower in an open crucible than in the sealed crucible or in a self-generated atmosphere (due to the evaporation process), we conclude that the moisture content directly influences the position of the effect.

Figure 3 summarizes the results of the temperature-modulated experiments. The “total heat flow” curves correspond to the conventional DSC curves. Once again, measurements were performed in open crucibles (curves a and d) and in a self-generated atmosphere (curves b and c). The curves are however shifted to lower temperatures

because the underlying heating rate is a factor 10 slower. In an open crucible, apart from the evaporation peak no other peak can be detected. In the self-generated atmosphere, an endothermic effect at about 55 °C is visible that is, however, overlapped by a broad evaporation peak. In temperature-modulated DSC, one obtains the heat capacity curves shown in the

lower part of Figure 3 from the periodic component of the heat flow. In a self-generated atmosphere, the glass transitions can be clearly seen at 54 °C and 132 °C. In an open crucible, however, a slight decrease in the heat capacity is at first observed as a result of the evaporation process. Afterward, glass transitions are observed at 107 °C and 137 °C. This indicates that the residual moisture acts as a plasticizer: in a self-generated atmosphere, i.e. in the moist sample, the glass transition is at 54 °C. The dry sample however shows a glass transition at 107 °C for the same component. The glass transitions at 137 °C (in the open crucible) and at 132 °C (in a self-generated atmosphere) are due to a second amorphous component in the original sample. The temperature difference between the two glass transitions can again be explained as being due to different moisture contents. The difference is however appreciably smaller because the moisture content in this temperature range is much lower (0.65%, see Fig. 6). In summary we conclude that the small thermal effects that are also visible in the conventional DSC curves (see Fig. 1) therefore correspond to enthalpy relaxation peaks at the glass transition.

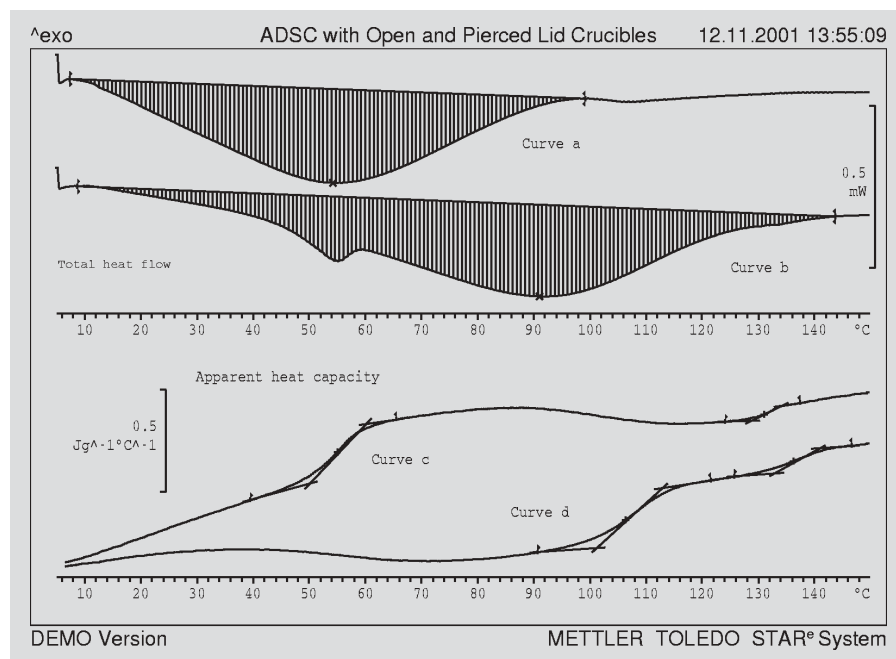


Fig. 3. Total heat flow and apparent heat capacity from a temperature modulated experiment in an open crucible (curves a and d) and in a self generated atmosphere (curves b and c). Underlying heating rate 1 K/min, period 48 s, amplitude 0.5 °C.

Quantitative determination of the heat capacity

The heat flow, Φ , in a moist sample can be described by the following equation:

$$\Phi = c_v m_v \beta + c_s m_s \beta + \frac{dm_v}{dt} \cdot \Delta h_e + \xi \quad (1)$$

Here c_v and c_s are the specific heat capacities of the volatile components and the dry sample, m_v the mass of the volatile components, m_s the mass of the dry sample, β the heating rate, Δh_e the specific heat of vaporization and ξ describes other possible thermal effects. If one assumes that the contribution of ξ to the heat flow can be neglected in comparison with vaporization peak, equation 1 can be simplified and written as:

$$\Phi \approx \frac{dm_v}{dt} \cdot \Delta h_e + \Phi_b(t) = \Phi_v + \Phi_b \quad (2)$$

Here Φ_v is the heat flow necessary to vaporize the residual moisture and Φ_b is the baseline for the vaporization peak.

The quantity of vaporized liquid, $m_v(t)$, can be calculated from the baseline corrected DSC curve at any time or as a function of temperature according to the equation:

$$m_v(t) = \frac{1}{\Delta h_e} \int_{t_0}^t \Phi_v dt, \quad (3)$$

where t_0 is the time at the beginning of the vaporization process.

The procedure is illustrated in Figure 4. The total heat flow, measured in the open crucible, corresponds to curve a. Curve b was used as the baseline. The difference between these two curves yields Φ_{peak} (curve c). The residual moisture in the sample (curve d) is obtained by integration according to equation (3).

The temperature modulated DSC experiment first of all yields an apparent heat capacity normalized to the original sample amount, $m_i = m_s + m_v(t=0)$, (Fig. 5, curve a). This apparent heat capacity must now be corrected for the continual loss in mass arising from the vaporization process.

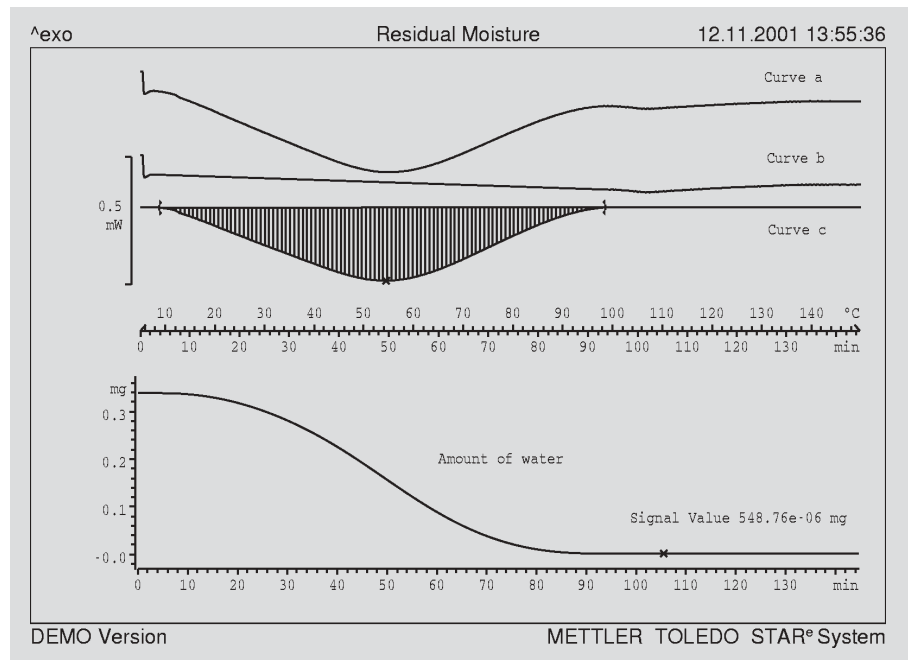


Fig. 4. Determination of the residual moisture: curve a: total heat flow; curve b: baseline; curve c: baseline corrected total heat flow; curve d: residual moisture in the sample

This correction is performed using the results from Figure 4. For the heat capacity of the dry sample, c_s , we therefore obtain

$$c_s = \frac{m_i}{m_s} \cdot c_a - \frac{m_v(t)}{m_s} \cdot c_v \quad (4)$$

The result is also shown in Figure 5. If the

apparent heat capacity (curve a) is corrected for the heat capacity contribution resulting from vaporization (curve b), then the continuously increasing heat capacity function for the dry sample is obtained. This allows even weak effects such as glass transitions to be unambiguously identified in the heat capacity curve.

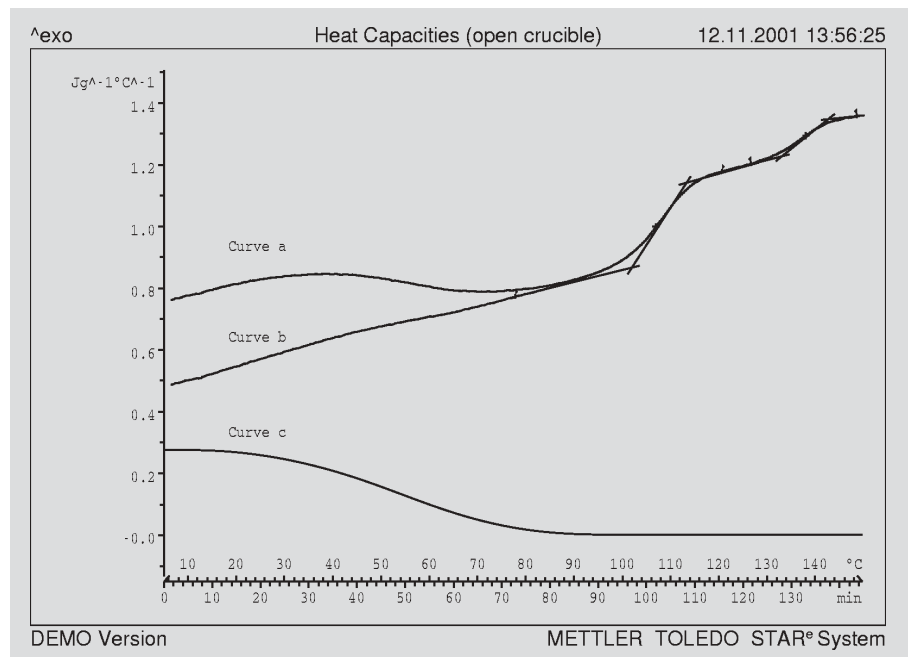


Fig. 5. Correction of the apparent heat capacity for the heat capacity contribution of the residual moisture (curve a: apparent heat capacity (c_a), curve b: heat capacity of the dry sample; curve c: heat capacity contribution of the residual moisture).

The same procedure can be applied to measurements in a self-generated atmosphere. The results are shown in Figure 6. As already mentioned, an endothermic enthalpy relaxation peak can be seen in the total heat flow (curve a) at about 54 °C. To determine the residual moisture it is necessary to correct the total heat flow for this peak and the baseline. From the corrected heat flow curve (curve b), the residual moisture content can be determined as a function of temperature (curve c) and the apparent heat capacity (curve d) can be corrected by the corresponding heat capacity contribution of the vaporized moisture (curve e). It is important to notice that the glass transition of the second amorphous component at around 132 °C is about 5 °C lower than the corresponding glass transition in the dry sample (see Fig. 5). The reason for this is that at this temperature the sample still has a residual moisture content of 0.65%. A comparison with Figure 5 shows in addition that the initial and final values of the apparent heat capacity function and of the heat capacity function corrected for the residual moisture in open crucibles and in a self-generated atmosphere agree.

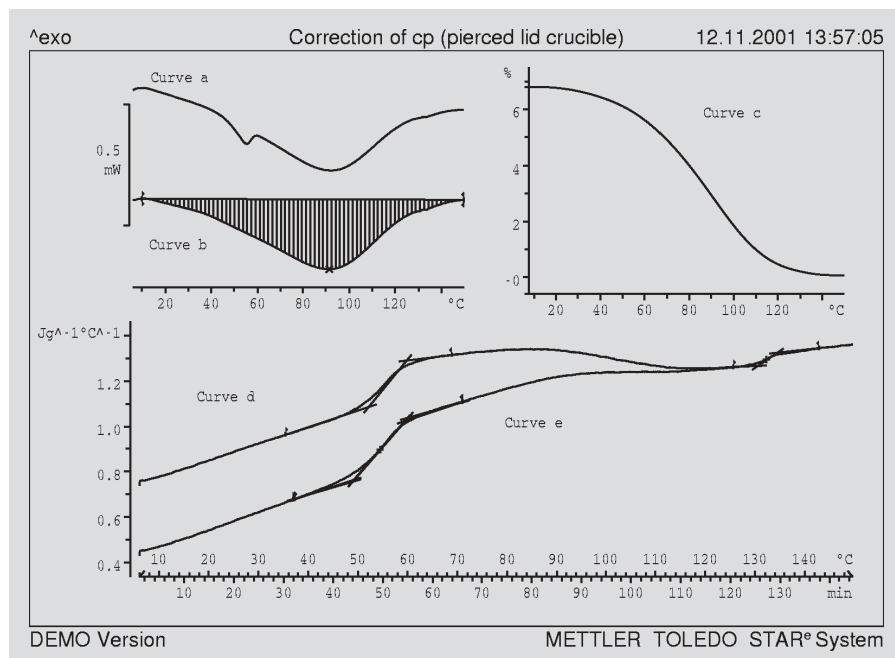


Fig. 6. Determination of the specific heat in a self-generated atmosphere (for details, see text).

Conclusions

Temperature-modulated DSC can be used to quantitatively determine the specific heat capacity of moist samples. First of all the contribution of the vaporized moisture is determined from the total heat flow. The apparent heat capacity can then be corrected, which enables the temperature

function of the heat capacity of the dry sample to be obtained. Furthermore, in the example described, the use of crucibles sealed in different ways allows the effect of residual moisture on the glass transition to be investigated. The results showed that a moisture content of 6.2% shifted the glass transition from 107 °C to about 54 °C.

Investigation of the thermal stability of CN_x with TGA/MS

Dr. Markus Schubnell

Introduction

Carbon nitride (CN_x) is a new type of material that is remarkable in having a degree of hardness similar to that of diamond [1]. Thin layers of this compound are routinely made at the Institute of Ceramics of the Chinese Academy of Sciences in Shanghai. The Chinese researchers wanted to learn more about the thermal stability of such layers and asked METTLER TOLEDO if they could help. Samples of the material were investigated in the METTLER TOLEDO applications laboratory in Schwerzenbach using a TGA/SDTA851^e coupled to a Balzers Thermostar mass spectrometer (MS).

Results

CN_x was available in the “pure” form (as thin flakes with a typical diameter of 2 mm) and also as thin layers on a silicon substrate. The samples were prepared by reactive sputtering onto NaCl or silicon. The CN_x layer was afterward separated from the NaCl substrate, resulting in the CN_x flakes mentioned above.

TGA measurements of a CN_x layer on a silicon substrate are shown in Figure 1. The sample was measured in a stationary air atmosphere at a heating rate of 10 K/min. After weight loss steps at 300 °C and 700 °C, a weight increase is observed at about 1300 °C. This increase is due to

the oxidation of the surface of Si substrate. The oxidation is also visible as a small exothermic peak on the SDTA signal. This is then followed by much larger peak due to the melting of the silicon.

at a heating rate of 10 K/min. A number of decomposition steps can be identified in the DTG curve that correlate well with certain peaks in the mass spectrometric fragment ion curves. For example, the first

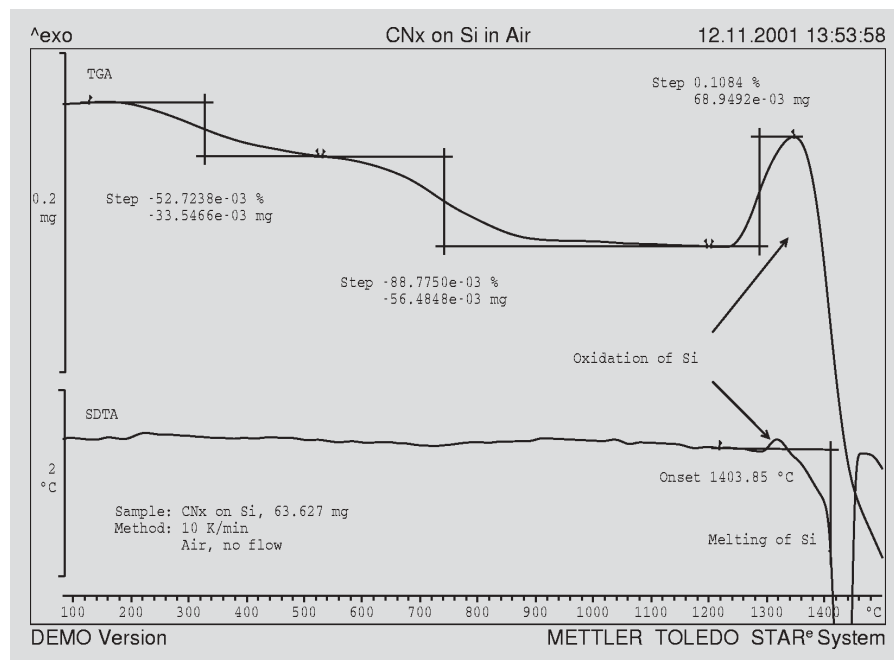


Fig. 1. Thermogravimetric measurements of CN_x on a Si substrate: heating rate 10 K/min, stationary air atmosphere, 70 μ alumina crucible (open), sample weight 63.627 mg CN_x on a Si substrate.

In order to obtain a better understanding of the decomposition of the CN_x layer, a sample of the CN_x flakes was analyzed using a TGA coupled to an MS. The results are shown in Figure 2. The measurements were performed under argon (30 ml/min)

weight loss step beginning at about 100 °C correlates well with the peak in the m/z 30 (NO) ion curve. This step can be attributed to the desorption of NO that had been absorbed on the layer during the production process. The m/z 26 (CN) ion curve exhib-

its a single peak at about 400 °C while the m/z 52 (C₂N₂) ion curve shows two peaks at about 400 °C and 700 °C. The total weight loss resulting from the loss of CN and C₂N₂ is about 6%. The weight loss beginning at about 600 °C is presumably due to the reaction of carbon with residual oxygen in the system; this assumption is supported by the increase of CO₂ as shown by the m/z 44 ion curve.

Conclusions

The thermal stability of thin layers of CN_x sputtered on silicon substrates and of pure CN_x flakes was investigated under different atmospheric conditions using a TGA combined with a mass spectrometer. The results showed that CN_x decomposes in several steps. These could be assigned to different processes with the aid of the MS data.

Literature

- [1] Cohen, M. L., *Phys. Rev. B* 23, p. 7988, 1985
- [2] Lu, C. W., *Proc. 1st Int. Conf. on thermo-physical properties of materials*

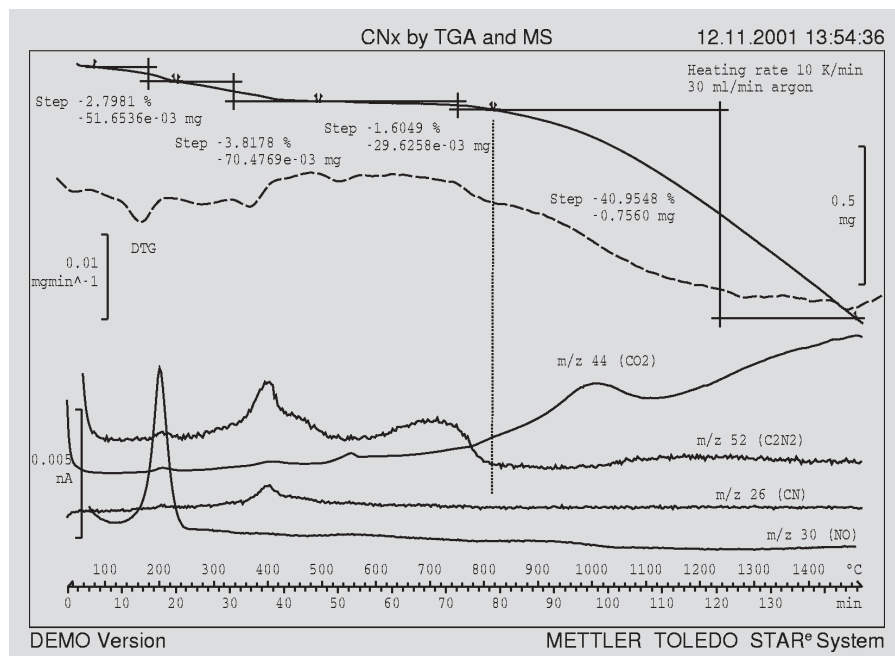


Fig. 2. TGA-MS measurements of CN_x flakes: heating rate 10 K/min, purge gas 30 ml/min argon, 70 μl alumina crucible, sample weight 1.846 mg CN_x (pure flakes, no substrate).

Optimization of DSC measurement conditions

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Introduction

Semicrystalline polymers are normally characterized using DSC heating curves. The numerical values obtained with the technique are:

- Peak temperature (“crystallite melting point”)
- Peak area (heat of fusion)

The results depend to some extent on the actual measurement parameters used. But even under apparently identical conditions, certain variations in the results can be observed.

The aim of this work was to establish the optimum measurement parameters using an elegant set of measurements.

Experimental details

The measurements were performed according to ISO 11357-1 1997.

Measuring cell: DSC30

Crucible: Al standard 40 μ l, pierced lid

Samples: Two closed-cell polyolefin foams:
 - PE-LD (90.7 kg/m³),
 - PE-LD-EVA (87.6 kg/m³)
 Polyamide film (1272 kg/m³).

Sample preparation: Disk-shaped samples taken from points close to each other.

DSC measurement: Heating from -40 °C to 200 °C (foam), or from -40 °C to 320 °C (polyamide). For other measurement parameters, see Table 2.

Preliminary experiments

The PE-LD-EVA foam was measured three times under the same conditions (2.5 mg sample, 10 K/min, 100 ml/min nitrogen). The PE-LD peak temperature and the heat of fusion were evaluated; the following

95% confidence intervals were obtained:

- 0.15 °C for the peak temperature,
- 4.8% for the heat of fusion.

The reproducibility of the heat of fusion is not good enough to characterize the samples. For this reason, we began an improvement project to identify the measurement parameters that affect reproducibility and which should therefore be optimized.

The Taguchi procedure

The Taguchi procedure [1, 2] was used to identify the optimum measurement parameters for the heat of fusion and the peak temperature with relatively few measurements.

Particularly advantageous is the fact that measurements are very robust after Taguchi optimization, i.e. the results are relatively insensitive to external factors such as changes in the ambient conditions.

The Taguchi procedure is, by the way, also used to improve the quality of products such as automobiles. In principle, any process can be optimized with this method.

The Taguchi procedure calculates the influence of all the factors on a process. In the case at point here, these factors consist of all the possible parameters that could influence the measurement. They are divided into

- “Control” factors, i.e. ones that can be kept under perfect control such as the heating rate, and
- “Noise” factors, i.e. ones that have undesirable effects such as non-reproducible heat transfer between the crucible and the sample or changes in the ambient temperature.

The various factors involved were worked out in thermal analysis team meetings (Table 1).

Process step	Control factors	Noise factors
Sample registration		Thermomechanical sample history
Switching on the DSC	Warm-up time	
Calibration	Temperature range, temperature calibration, heat flow calibration	
Cutting the sample	Geometry of the sample	Change in the sample due to pressure or contamination
Weighing	Type of balance (micro-, semimicro- or analytical).	Error due to fluctuating temperature, reading error
Crucible	Type of crucible	Cleanness, type of reference crucible
Performing the measurement	Temperature range, heating rate, type of purge gas and flow rate, type of furnace lid (DSC30!), Saving of measurement data	Insertion of the crucible and the furnace lid manually, drafts, mechanical disturbances.
Evaluation	Temperature range, type of baseline	none

Table 1. The process steps and the factors that influence them

After all the factors had been identified, reasonable values had to be assigned to at least two such sets of parameters:

Control factors	Level 1	Level 2
Temperature calibration; (range)	3 points (In, Zn, Pb); 100...500 °C	4 points (n-octane, H ₂ O, In, Zn); -100...+500 °C
Heat flow calibration	1 point (In)	3 points (n-octane, In, Zn)
DSC warm-up time	none	1 hour
Geometry of the sample	flat surface	arbitrary surface
Furnace lid	medium height	flat
Heating rate	10 K/min	5 K/min
Sample weight	2 mg	10 mg
Purge gas	nitrogen	air
Purge gas rate	120 ml/min	60 ml/min
Integration limits	near the peak, according to (ISO 11357)	10 °C further away (on both sides)

Table 2. The parameters selected with two sets of factors

DSC measurements were then performed in order to calculate the Taguchi optimization on the basis of the results.

In actual fact, a total of 24 measurements had to be performed for the optimization, which is of course a small number compared with the thousands of possible combinations. The measurements were limited to PE-LD foam and PA 66 because their thermal properties are sufficiently different to guarantee that the conclusions also apply for very different types of samples. Using the Taguchi procedure, the following parameters were identified as those having the greatest influence on the results:

- sample weight
- type of purge gas
- heating rate

The following parameters were found to be optimal:

- 2 mg sample weight
- nitrogen as purge gas
- 50 ml/min purge gas flow rate
- 10 K/min heating rate

- 4-point temperature calibration
- 3-point heat flow calibration

The influence of all the other factors was, in comparison, negligibly small.

Confirmatory test

As a confirmatory test, PE-LD-EVA foam was measured three times under the optimum conditions. The reproducibility of the DSC curves was in actual fact better than with the parameters originally chosen and the confidence interval for the heat of fusion improved to 2.5%.

Summary

The Taguchi procedure identifies and weights the parameters that influence a measurement. Better understanding of these factors allows the measurement conditions to be optimized.

The accuracy of the heat of fusion was significantly improved. Besides this, the measurement was significantly more robust.

Literature

- [1] R. Roy, *A Primer on The Taguchi Method*, Society of Manufacturing Engineers, Michigan, 1990.
- [2] P. J. Ross., *Taguchi Techniques for Quality Engineering. Loss Function, Orthogonal Experiment, Parameters and Tolerance Design*, Mc Graw-Hill, 1988.

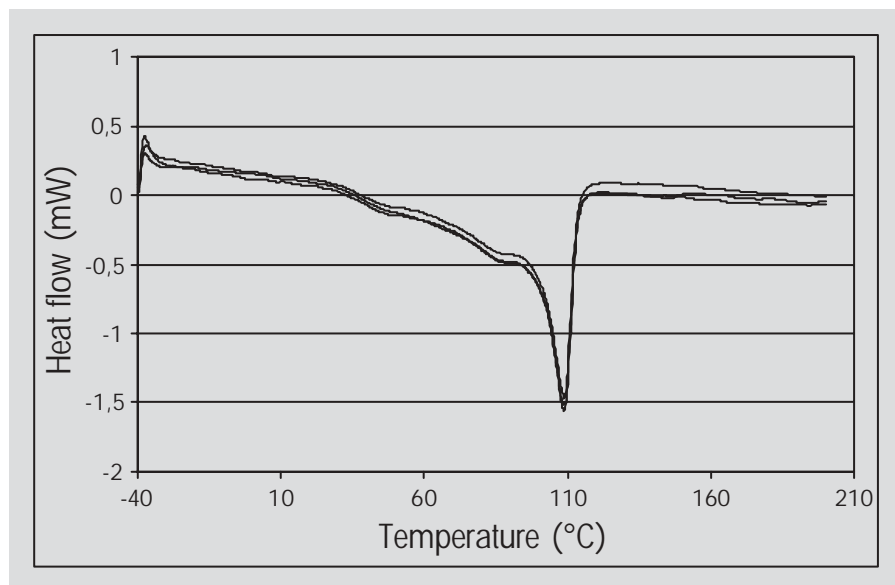


Fig. 1. Three DSC curves of PE-LD-EVA foam measured under optimum conditions.

Investigating the curing of amino resins with TGA-MS and TGA-FTIR

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Introduction

The monomers used for preparing amino resins (aminoplasts) are urea (for UF resins) or melamine (for MF resins) and formaldehyde. The latter undergoes an addition reaction with amino groups with the formation of N-methylol groups. In principle, with a primary amine, two methylol groups can be formed. With melamine (Fig. 1), the addition reaction of formaldehyde to the primary amine group (Fig. 2) is faster than to the secondary amine group; there is nevertheless the possibility of six-fold methylation. Urea however only undergoes two-fold methylation. Amino resins are available commercially in precondensed form, usually in aqueous solution, with molar masses of 500 to 1500 g/mol.

During curing, the amino resin undergoes cross-linking as a result of condensation reactions (Fig. 3). The curing reaction is acid-catalyzed; p-toluenesulfonic acid (PTS) is normally used. The methylol groups react with amino or other methylol groups and form either methylene bridges

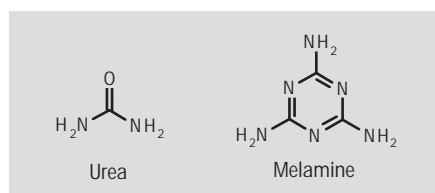


Fig. 1. Structural formulas of urea and melamine

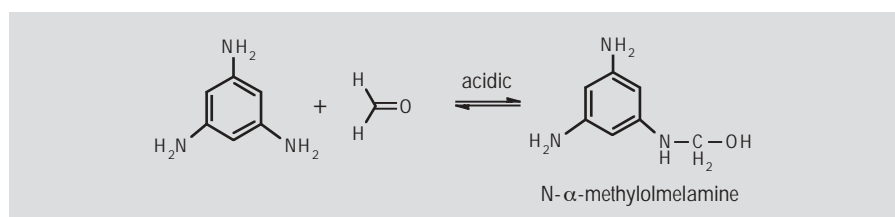


Fig. 2. Acid-catalyzed addition of formaldehyde to an amine group with the formation of a methylol group

according to reaction (1), or ether bridges according to reaction (2). The methylol groups of the MF resin are present in partially methylated form. Correspondingly, the cross-linking reaction results in the liberation of not only water but also methanol. The conversion of ether bridges to methylene bridges with the elimination of formaldehyde according to reaction (3) does not occur until higher temperatures. The cross-linking density of the cured

aminoplast is determined by the number of methylol groups on an amine.

The aim of the TGA-MS and TGA-FTIR measurements was to gain an insight into the reactions taking place by analyzing the volatile substances evolved. The detection

of methanol, for example, should enable one to decide whether the MF prepolymer is involved in the cross-linking reaction or whether it serves only as an external plasticizer.

It should also be possible to obtain information on the reaction kinetics. The evolved gases were to be identified by coupling the thermobalance (TGA) with mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR).

(1) Condensation of a methylol group and an amine group to form a methylene bridge:



(2) Condensation of two methylol groups to form an ether bridge:



(3) Degradation of the ether bridge to a methylene bridge with the elimination of formaldehyde:



R = Melamine or urea residue

R' = H or CH₃

R'' = Proton or methylol group

Fig. 3. The most important reactions in the curing of amino resins

Experimental details

An open aluminum crucible of 100 μl volume was used for the measurements. The TGA temperature program ran dynamically from 25 $^{\circ}\text{C}$ to 250 $^{\circ}\text{C}$ at a heating rate of 10 K/min; nitrogen was used as inert gas with a flow rate of 70 ml/min. The gaseous components evolved were detected by coupling the METTLER TOLEDO TGA/SDTA851^e thermobalance either to a mass spectrometer (Balzers Thermostar[®]) or a Fourier transform infrared spectrometer (Nicolet Nexus). The mass spectrometer was set to record masses with m/z values of 17, 18, 30 and 31 (see Table 1) and the FTIR measured and averaged 16 scans at a resolution of 4 cm^{-1} for each spectrum. UF and MF resins were mixed well in a ratio of 90:10 by weight with 0.4% PTS catalyst and then weighed out. Pre-curing was done at 60 $^{\circ}\text{C}$ for 90 minutes in the DSC. The assignment of the IR absorption bands is shown in Table 2.

m/z	Gas
17	water (OH), ammonia (NH ₃)
18	water (H ₂ O)
30	formaldehyde (CH ₂ O)
31	methanol (CH ₃ O)

Table 1. Peak assignment in MS analysis

Results

The TGA curve (Fig. 4) shows that the sample loses weight during the curing reaction from room temperature to 220 $^{\circ}\text{C}$; the total weight loss is 12.2%. The products eliminated during the reaction vaporized continuously. Above 200 $^{\circ}\text{C}$ the weight loss increased markedly. This can be clearly

Wavenumber, cm^{-1}	Gas
3325	ammonia (NH ₂ stretching vibration)
3200-2700	methanol (O-H stretching vibration)
2340, 2360	carbon dioxide
1770	formaldehyde (carbonyl stretching vibration)
1620	ammonia (NH ₂ scissoring vibration)
1340	methanol (O-H deformation vibration)
1035	methanol (C-O stretching vibration)
965, 930	ammonia (fingerprint)
670	carbon dioxide

Table 2. Absorption band assignment in the IR analysis

seen in the TGA curve and its 1st derivative. From this we assumed that the residual curing had been completed by 220 $^{\circ}\text{C}$. Afterward, degradation began causing the sample to lose weight rapidly. The sample

foamed and turned brown.

The mass spectrometer was set so that fragment ions of particular mass/charge ratios were detected throughout the measurement time (multiple ion detection, see Table 1).

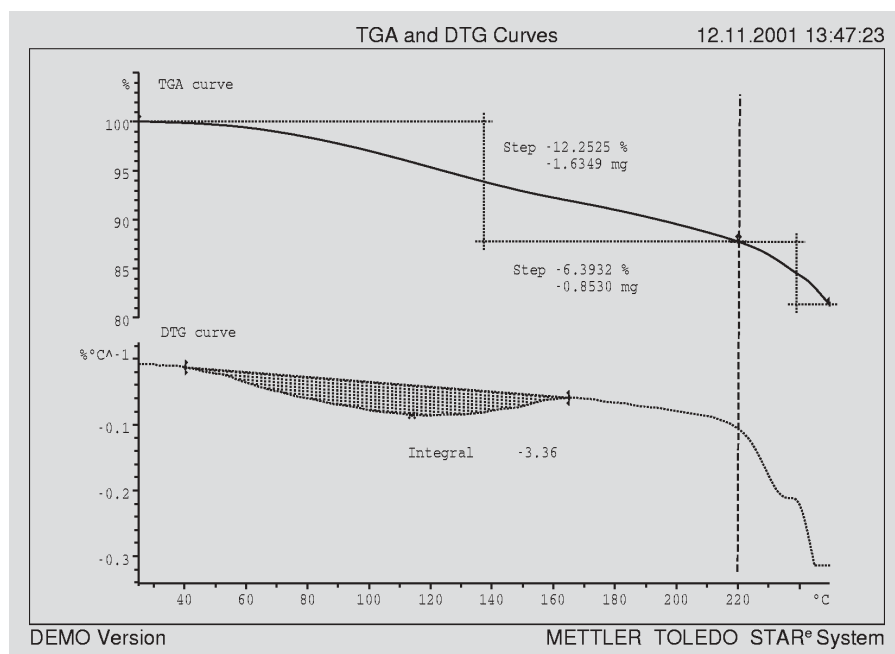


Fig. 4. TGA curve (continuous curve), 1st derivative of the TGA curve (dotted line)

As expected, in the initial heating phase, the MS ion curves (Fig. 5) showed a strong signal for water. In contrast neither methanol nor formaldehyde were detected during this curing reaction. In the second temperature segment (from 220 °C to 250 °C) the MS curves of formaldehyde (m/z 30) and methanol (m/z 31) showed a sharp increase. The signal from water (m/z 18) became weaker. At temperatures above 240 °C, the m/z 17 signal increased rapidly while the m/z 18 signal decreased. This indicates the beginning of the elimination of ammonia (m/z 17) (compare with Fig. 6). The degradation products of the aminoplast are therefore formaldehyde, ammonia and methanol.

The results from the FTIR spectra (Fig. 6) agreed with those obtained from the MS curves. Here again only water was detected in the initial heating phase. When sample degradation occurred, formaldehyde and methanol, as well as ammonia and carbon dioxide were found. The sensitivity of FTIR spectroscopy for the substances was less than that of mass spectrometry.

Conclusions

The objectives defined were to a large degree achieved through the use of TGA coupled with MS and FTIR spectrometers:

- The analysis of volatile gases up to 220 °C showed that during the curing reaction only water was eliminated in agreement with equations (1) and (2) in Figure 3. During the degradation of the aminoplast (220 °C to 250 °C) methanol, ammonia, formaldehyde and carbon dioxide were liberated.
- The quantity of water eliminated was determined quantitatively and was found to be 12.2 weight%.
- Methanol was not detected until above 220 °C. This indicates that the ether methylol groups do not take part in the

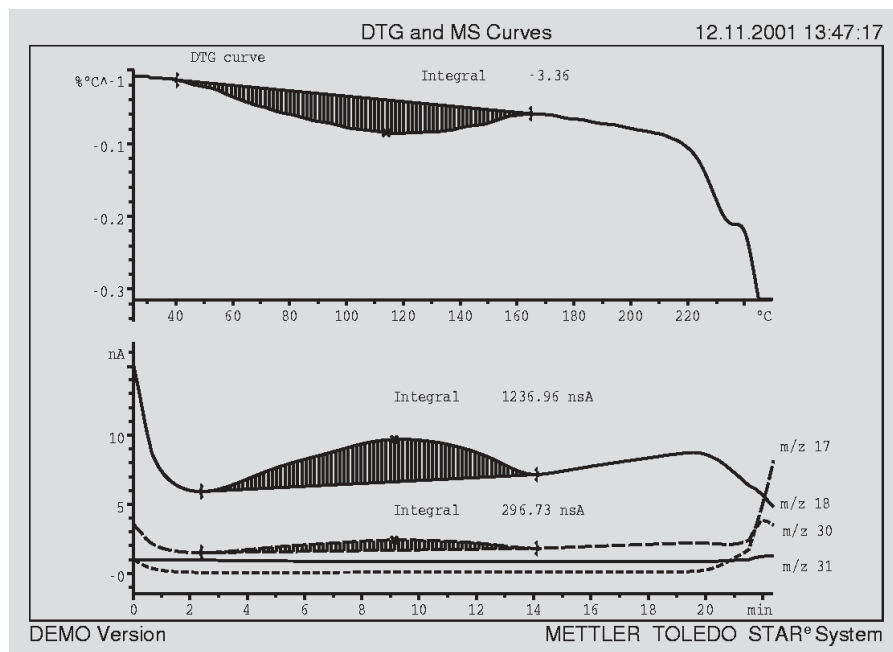


Fig. 5. MS fragment ion curves (assignment according to Table 1)

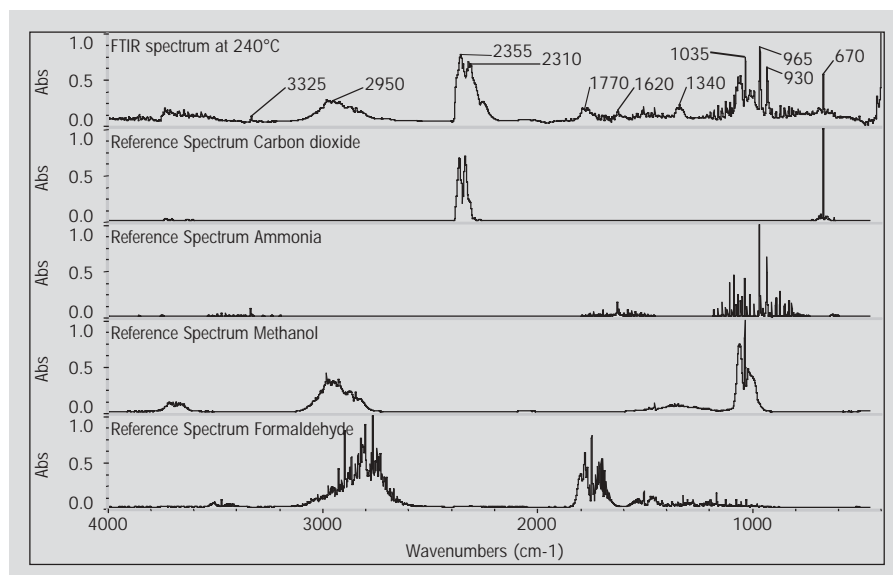


Fig. 6: FTIR spectrum at 240 °C and reference spectra of methanol, ammonia, formaldehyde and carbon dioxide

curing reaction. It does not exclude the participation of melamine in the reaction because this was only partially but not completely etherified.

- The FTIR measurements confirmed that methanol, carbon dioxide and ammonia as well as smaller amounts of formaldehyde were liberated.

Reproducible evaluation of DSC measurements: glass transition followed by chemical reaction

Dr. Jürgen Schawe

Introduction

The reproducible quantitative determination of heats of reaction plays an important role both in quality assurance and in research and development. This necessitates both a careful measurement and a reliable evaluation procedure. In practice, it is often difficult to choose an optimum baseline when determining peak areas. This is particularly the case when different relatively small or broad thermal effects follow one another. This study presents a method for the reproducible evaluation of such DSC curves using the postcuring of an epoxy resin as an example.

Postcuring

At temperatures below the glass transition temperature the epoxy resin is in glassy state and behaves like a solid. Diffusion of the reactants is restricted. Almost no curing reaction can therefore take place. At the glass transition the diffusion improves suddenly by several degrees of magnitude. The sample becomes liquid and the chemical reaction begins.

An example of this is shown in Figure 1. In this case, it is the postcuring reaction of an epoxy-amine system (DGEBA: diglycidyl-ether of bisphenol A; DDM: diamino diphenylmethane). Samples of the mixture were cured at 100 °C for different periods of time, shock-cooled, and then heated at 10 K/min. In the DSC curves, the glass transition and the postcuring reaction are immediately apparent. The reaction begins as soon as the glass transition occurs and shows a relatively broad exothermic peak. With longer reaction times the glass transi-

tion shifts to higher temperatures and the exothermic postcuring reaction becomes smaller. In particular, with reaction times of more than 50 minutes, an endothermic peak due to enthalpy relaxation is superimposed on the glass transition. In such cases, it is then difficult to perform a reproducible evaluation of the glass transition and reaction peak.

erations, a practicable evaluation algorithm for the evaluation of the peak area and the glass transition is presented below. The evaluation is shown in Figure 2 using the curve originating from the sample that was cured for 80 min at 100 °C. Curve (1) in Figure 2 is the corresponding measurement curve. At temperatures below the glass transition the measurement curve is

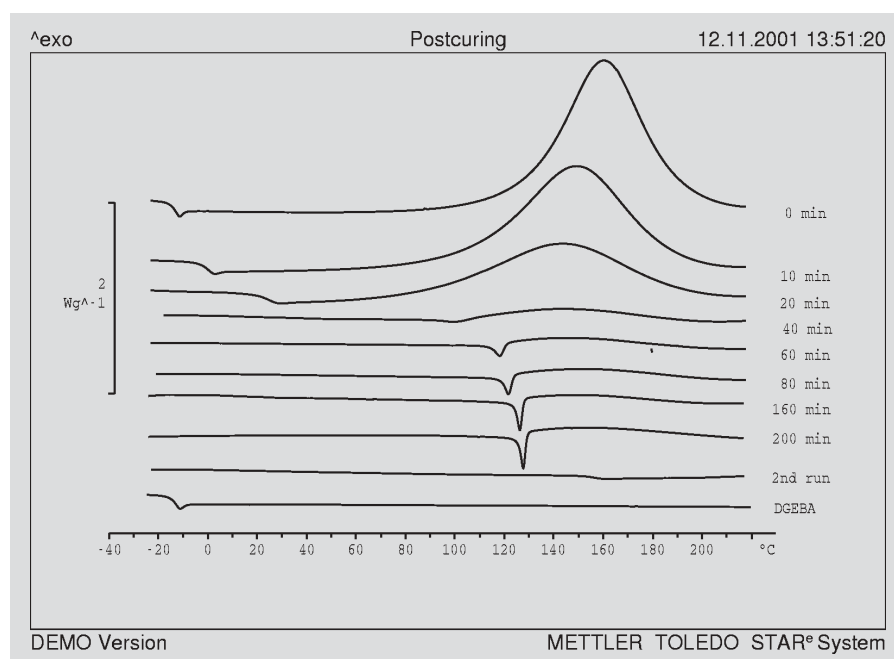


Fig. 1. Specific heat capacity curves of DGEBA-DDM after curing for different periods of time at 100 °C. The heating rate is 10 K/min. For comparison, the curves of the pure epoxy resin (without cross-linker) and the fully cured material (second run) are shown.

Evaluation procedure

Richardson has described how the baseline of the reaction peak can be determined with the help of the curve of the fully cured material [1]. On the basis of these consid-

determined by the heat capacity of the glassy state. The glass transition is associated with an enthalpy relaxation effect that has to do with the time the sample spent below the glass transition temperature.

The peak maximum is around 120 °C. Immediately after the glass transition, the exothermic reaction begins. If a reaction did not take place, the heat capacity would, after the endothermic peak of the enthalpy relaxation, reach a value that is given by the heat capacity of the liquid. This fictive curve corresponds to the “true” baseline for the peak evaluation. It cannot be measured directly.

The measurement of a fully cured sample is used to determine the baseline. This curve can for example be obtained by measuring the same sample a second time and is shown in Figure 2 as curve (2). This curve shows very clearly the glass transition that has shifted to higher temperature (about 160 °C) and afterward the linear increase of the heat flow in the liquid. The expected heat flow curve of the non-reacting liquid is obtained by adapting a line to the range above the glass transitions of curve (2). This line (curve 3) is obtained by simply fitting a line visually to the measurement curve (2).

Subtraction of curve (1) and line (3) gives curve (4), which can then be easily evaluated. With the subtracted curve, the baseline of the reaction peak is a horizontal line (choose “horizontal right” in the baseline settings). The left integration limit is given by the point of intersection of the baseline with the curve. This horizontal line can also be used as a tangent for a reproducible evaluation of the glass transition. This is done by calculating the curve (5) with the software command “TA/Baseline” using the same integration limits as for the peak calculation.

If several measurements with similar material (as in Fig. 1) are compared, it is sufficient to use just one measurement of the

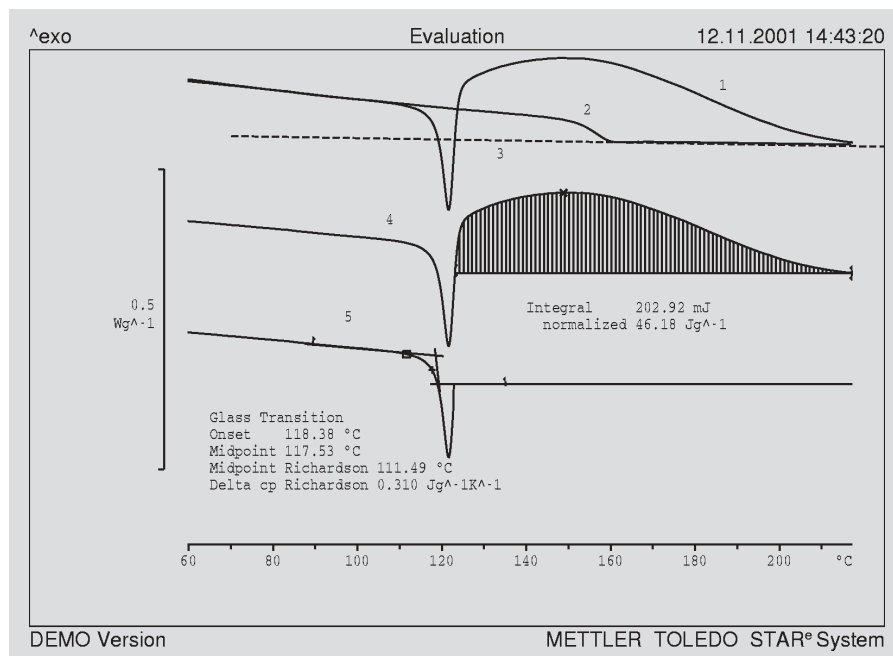


Fig. 2. Diagram showing the evaluation using the epoxy-amine system precured for 80 min at 100 °C. 1: Normalized DSC curve during postcuring. 2: Normalized DSC curve of fully cured material (e.g. second measurement after cooling). 3: Line obtained by fitting to curve 2 above the glass transition. 4: Curve to be evaluated calculated by subtraction of curve 1 with curve 3. 5: Curve for the determination of the glass transition, calculated with the software command “TA/Baseline”.

fully cured material to determine the extrapolated line (3). The line can then be used to evaluate the whole series.

Summary

A reproducible evaluation routine is proposed for evaluating a glass transition and a subsequent reaction when the two events lie close to each other. For this evaluation, the curve of the fully reacted material (second measurement) is necessary. The evaluation is performed on the normalized heat flow curve in three steps:

- Construction of a line fitted to the heat flow of the fully cured material above the glass transition.

- Subtraction of the line from the measurement curve.
- Integration of the subtracted curve using a horizontal baseline.

To evaluate the glass transition, a tangent is drawn above the glass transition that coincides with the baseline of the peak integration.

Literature

- [1] M. J. Richardson, in C. Booth and C. Price (Eds.): *Comprehensive Polymer Science*, Vol. 1, Pergamon, Oxford, (1989) p. 867 ff.

Rapid thermogravimetric analysis of coal

Dr. Rudolf Riesen

Introduction

The quantitative determination of moisture, volatile compounds, chemically bound carbon, and ash content has long been used to determine the quality and economic value of different types of coal. High ash content is undesirable for the operation of thermal power stations because inert material increases transport and waste disposal costs, and also means that the heat exchangers have to be cleaned more frequently. To make sure that assays can be properly compared, the analysis procedures have been standardized and described in many standard methods [1-10].

Quite early on, measurement routines were developed for thermogravimetric instruments that enabled faster and more automated analyses to be performed. These techniques have been compared with the standard manual methods [11-14].

TGA (thermogravimetric analysis) is, however, also very useful for coal research, e.g. to compare combustion profiles or to determine the nature of volatile components with TGA-MS. Even the lime deposits (fur) formed in hot water systems have been investigated with TGA [15].

The determination of moisture, volatile content, soot, ash or fillers is also required for other applications. Analogous to the analysis of coal, a standardized thermogravimetric procedure is nowadays used to determine the content of elastomers, thermoplastics and thermosets, as well as lubricants [16, 17].

Conversely, procedures developed for the determination of carbon black in rubber [17] are used for the analysis of brown coal, lignite and or other renewable fossil fuels [e.g. 18].

Speeding up the TGA procedure

As already indicated, the standard methods for coal analysis are laborious and often time-consuming.

To determine the moisture content exactly, the measurement is usually started at room temperature, or slightly above. This leads to long cooling times before the next sample can be measured, which in turn limits the throughput of samples.

The METTLER TOLEDO STAR^e system allows the analysis time to be reduced by half compared to the ASTM E1131 standard method. In this case, the measurement is started directly at 110 °C (or even higher), which means the otherwise long cooling time down to 30 °C is avoided. The moisture is, however, still accurately measured - the weight loss up to the start is automatically measured by determining the starting weight on reaching 110 °C. This is done by measuring the weight of the sample and the crucible during the sample preparation, which is in fact normal in the manual procedure [1 -10]. Buoyancy effects are compensated in the TGA measurement by subtraction of a blank curve.

Besides this, oxygen is used instead of air, resulting in much shorter combustion times. One must of course make sure that coal particles are not blown out of the crucible by the rapid generation of gas. This can manifest itself for example in widely differing measurement values for the ash content. As with all analytical methods, it is essential that the coal samples are homogeneous and representative if one, for example, wants to characterize one hundred tons of coal. Vaporization, degassing and combustion proceed more rapidly when shallow, open crucibles are used and small sample weights are analyzed.

Experimental details

A METTLER TOLEDO TGA/SDTA851^e with the small furnace (up to 1100 °C) was used for the measurements. The system was automated with a TSO800RO sample robot and a TSO800GC1 gas controller for gas switching.

The balance was purged with 40 ml/min of nitrogen as protective gas. During the measurement, first 80 ml/min of nitrogen, and afterward 80 ml/min of oxygen were used as reactive gas.

The following samples were used as examples for coal analysis:

1. Coal A with a particle size of 65 µm to 90 µm,
2. Coal B with a particle size up to 1 mm,
3. Coke, finely powered, manufactured from petroleum oil.

Unless otherwise specified, alumina crucibles (30 µl) were filled with about 20 mg of coal powder. During weighing-in, the crucible weight and the sample weight were noted and entered in the software program.

Immediately after weighing-in, the special aluminum lid was placed on the crucible to prevent contamination of the sample and any large change in moisture content during the waiting time. The lid is removed by the sample robot during measurement.

At the end of the measurement, the measuring cell automatically cools down to the starting temperature.

The blank curve is automatically subtracted and the evaluation macro-program calculates the weight loss immediately after the measurement is finished.

Results

Fast method

Figure 1 shows the TGA curves of the coal analyses performed with the fast method described above. The measurement conditions were chosen as follows:

Under nitrogen: 110 °C for 0.5 min, then heating at 100 K/min to 900 °C and held at this temperature for 2.5 minutes. The system was then purged with oxygen for the following 4 minutes (furnace atmosphere is made up of 80 ml/min O₂ and 40 ml/min N₂).

The blank curve was measured in the same way before the measurement series with an empty crucible.

and the equilibration of the temperature at 110 °C (automatic “settling”), the total weight is determined at this instant with the first measurement point. The difference between this and the sample weight before the measurement yields the dry content (or the amount of moisture evolved). The starting weight is given by the Signal Value (Fig. 1) at the beginning of the normalized TGA curve. This means that drying or moisture uptake during the waiting time up to the actual measurement has no influence on the original moisture content. However, especially with very moist coal samples, the use of an aluminum lid is recommended as described in the experimental section.

thermal phase at 900 °C because degassing and combustion have finished.

The measured values are summarized in Table 1. The reproducibility is shown by the standard deviation and how well the measurement curves coincide. The slight differences in combustion rates are caused by small differences in the sample weights, e.g. with Coal B 19.801 mg as opposed to 21.547 mg (see Fig. 1).

In routine operation, the analysis including evaluation takes approximately 36 minutes; of this, about 15 minutes is for the actual measurement. The assay according to ASTM E1131 takes about 60 minutes because somewhat longer isothermal times are necessary and because an additional cooling time of 10 minutes is needed to reach 30 °C.

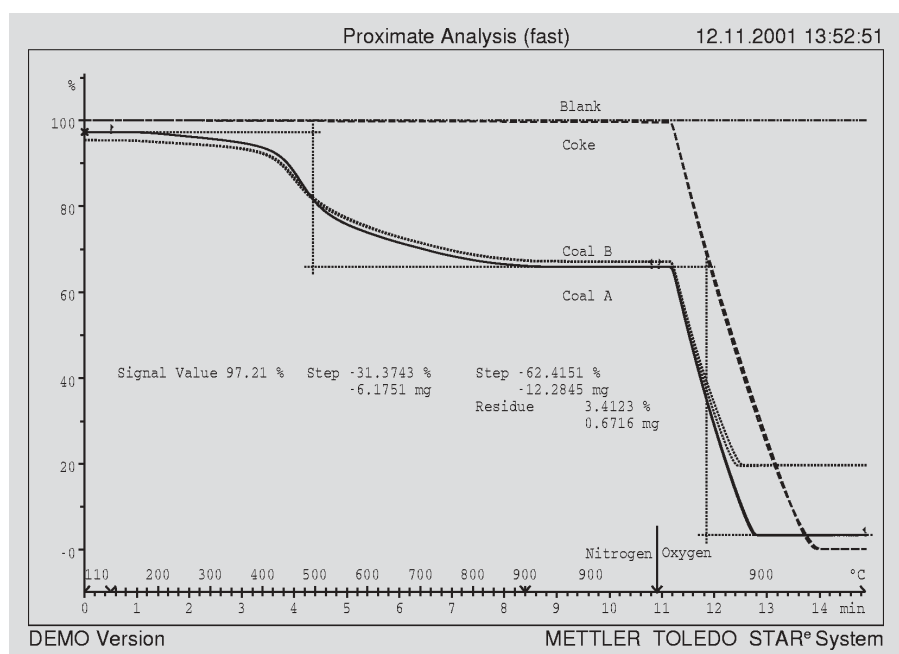


Fig. 1. TG curves showing two measurements of each of the three types of coal. At 10.9 min the purge gas was switched from nitrogen to oxygen. One of the measurements of Coal A (continuous curves) was used to evaluate the weight loss steps. The uppermost horizontal curve is a measurement without a sample (i.e. a blank curve).

For all measurements (including the blank curve), the weight of the crucible is also entered in the software in addition to the sample weight, i.e. the total weight is determined directly after weighing-in. After insertion of the sample by the sample robot

In the first 30 seconds, the TG curves are practically horizontal with a loss of less than 3 µg (this corresponds to 0.01%), proving that drying is complete at the beginning of the measurement. The curves are also horizontal at the end of the iso-

As Table 1 shows, the corresponding mean values for both methods are very close. The differences are less than the reproducibility of >0.3% given in the manual methods [5 - 7]. It is noticeable that there is a tendency for the fast method to yield higher moisture values and lower volatile contents. This can be explained by a loss due to drying of about 0.4% with the ASTM method [16] before the actual measurement. This can only be prevented if the weighed-in sample is immediately measured.

The comparatively high standard deviations with Coal B are also worth noting. This is also apparent in the manually weighed residues. Measurements in crucibles with alumina lids (with a hole) and in taller crucibles (70 µl) showed that the differences cannot however be explained through too rapid combustion with “fire-work-like” ejection of material (“sparkling coal”). Better grinding and homogenization of the sample however reduced the standard deviations by a factor three. The reason is the inhomogeneity of this coal

Coal type	Method	Moisture	Volatile content	Coal	Ash	Residue
Coal A	Fast (M)	2.80	31.36	62.45	3.38	3.48
	(SD)	0.01	0.05	0.03	0.06	0.02
	ASTM	2.53	31.59	62.46	3.21	
Coal B	Fast (M)	4.69	28.45	47.80	19.02	19.11
	(SD)	0.05	0.33	0.66	1.00	1.02
	ASTM	4.27	28.66	47.62	18.89	
Coke	Fast (M)	0.00	0.48	99.38	0.13	0.10
	(SD)	0.00	0.01	0.02	0.02	0.00
	ASTM	0.01	0.48	99.38	0.17	

Table 1. Comparison of the contents measured using the fast method with the values according to the ASTM E1131 standard. In each case, the mean values (M) and the corresponding standard deviations (SD) are calculated from three measurements. The residue is determined by manually reweighing when the measurement is completed as specified in the standards [2 and 6]. All the values refer to the initial sample weight.

sample. This underlines the necessity of good sample preparation. The comparison of the two coal types A and B show this very clearly.

Conclusions

The assay of moisture, volatile content, carbon and ash in coal and coke using TGA is a standardized routine method. The time required for the method can be shortened by up to 50% without affecting the accuracy by using the METTLER TOLEDO STAR[®] system and adapting the temperature program. In automated operation, this allows at least 35 analyses to be performed per day.

The TGA curves show whether degassing and combustion are complete. This is necessary in order to optimize the method and for the control of routine measurements. Thermogravimetry, in addition, allows drying and combustion behavior to be investigated and different coal types to be characterized.

Inhomogeneous samples must be well ground to achieve a high degree of reproducibility. If necessary, larger amounts of sample can be measured thermogravimetrically in 900 µl crucibles.

Literature

1. DIN 51718 Analysis of solid fuels - determination of water content and analysis moisture (in German).
2. DIN 51719 Analysis of solid fuels - determination of ash content. (in German)
3. DIN 51720 Analysis of solid fuels - determination of the content of volatile components. (in German)
4. ASTM D3172 Standard Practice for Proximate Analysis of Coal and Coke.
5. ASTM D3173 Standard Test Method for Moisture in the Analysis Sample of Coal and Coke.
6. ASTM D3174 Standard Test Method for Ash in the Analysis Sample of Coal and Coke.
7. ASTM D3175 Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke.

8. ISO 11722 as well as BS 1016-104.1 Methods for analysis and testing of coal and coke. Proximate analysis. Determination of moisture content of the general analysis test sample.
9. ISO 562 as well as BS 1016-104.3 Methods for analysis and testing of coal and coke. Proximate analysis. Determination of volatile matter content.
10. ISO 1171 as well as BS 1016-104.4 Methods for analysis and testing of coal and coke. Proximate analysis. Determination of ash content.
11. Richard L. Fyans, "Rapid Characterization of Coal by Thermogravimetric and Scanning Calorimetric Analysis", Presentation at the 28th Pittsburgh Conference in Cleveland, Ohio, March (1977).
12. John W. Cumming, Joseph McLaughlin, "The thermogravimetric behavior of coal", *Thermochimica Acta*, 57 (1982) 253-272.
13. F. S. Sadek, A. Y. Herrell, "Proximate analysis of solid fossil fuels by thermogravimetry", *American Laboratory*, March (1984) 75-78.
14. Danny E. Larkin, "The development of a standard method", ASTM STP 997 "Compositional analysis by thermogravimetry", C.M. Earnest, Ed., *American Society for Testing and Materials*, Philadelphia (1988) 28-37.
15. Paul Baur, "Thermogravimetry speeds up proximate analysis of coal", *Power*, March (1983) 91-93.
16. ASTM E1131 Standard Test Method for Compositional Analysis by Thermogravimetry.
17. ISO 9924 Rubber and rubber products. Determination of the composition of vulcanizates and uncured compounds by thermogravimetry.
18. M.C. Mayoral, et. al., "Different approaches to proximate analysis by thermogravimetry analysis", *Thermochimica Acta*, 370 (2001) 91-97.

TGA-FTIR and TGA-MS measurements

Cyril Darribère

Introduction

In thermogravimetry (TGA), the weight of the sample is measured continuously as a function of temperature and time. During the measurement, volatile products are evolved resulting in weight loss steps in the TGA curve. Information on the chemical structure and functional groups of the evolved gases can be obtained by coupling the TGA to an evolved gas analyzer (EGA). This is normally either an FTIR spectrometer, which measures the IR absorption of molecules, or a mass spectrometer in which the gas molecules are ionized and the positively charged fragment ions separated according to their mass-to-charge ratio.

The purpose of this article is to make the user aware of some important practical points and to suggest several tests that should be performed before and after the measurement.

Temperature of the transfer line

The transfer line is maintained at about 200 °C for all measurements so that evolved vapors do not condense during their passage to the analyzer. It prevents carry-over of fractions and possible blockage of the transfer line.

Blockage test

If the transfer line is blocked, the EGA no longer reacts to thermal effects taking place in the thermobalance. Blockage of

the transfer line can occur when substances such as rubber decompose. In the MS, an unusually high vacuum (less than 10^{-6} mbar) can also indicate that the transfer line is blocked. The transfer line can be checked using a volatile solvent. About 5 mg acetone are sealed hermetically in a 40 μ l aluminum crucible. The crucible is inserted in the TGA and heated to 200 °C at 10 K/min. The pressure in the crucible increases until it finally bursts. Acetone vapor is suddenly developed and should be detected in the EGA: wavenumber range 1725-1640 cm^{-1} (FTIR) or m/z 15, 43, 58 (MS).

Choice of carrier gas

FTIR: the carrier gas should not exhibit any absorption bands. Nitrogen, oxygen, synthetic air and argon are therefore suitable.

MS: the choice of the carrier gas depends on the mass of the ion you want to detect. The following pairs interfere: m/z 28 (N_2 and CO), m/z 36 (Ar and HCl), m/z 44 (CO_2 and NO_2).

Leak-tightness of FTIR

The volatile substances evolved from the sample in the TGA can only reach the gas cell in the FTIR if the TGA-FTIR system is leak-tight. For this reason, the entire system should be tested to make sure that it is gas-tight. This can be done by connecting a piece of flexible rubber tubing to the

FTIR outlet and dipping the other end into a beaker of water. The height of the water column that still produces gas bubbles should be at least 10 cm. If no bubbles appear, press the furnace to the right against the O-ring. If necessary, replace the O-ring. Check the flange on the FTIR interface.

FTIR sensitivity

For the best possible FTIR sensitivity use a relatively low carrier gas flow rate, e.g. 20 ml/min. Another parameter is the heating rate: the higher the heating rate the better the sensitivity. Normally heating rates of 5 K/min to 20 K/min are used. Be careful, however, because high heating rates lead to effects overlapping each other! A weight loss of at least 0.5 mg in the TGA curve is sufficient to ensure good IR absorption. This should be taken into account in the sample weight used. A weight loss that is too large could lead to undesirable aerosol formation, the droplets of which could then be deposited as a film in the gas cell.

FTIR background spectrum

The background spectrum recorded prior to the actual measurement is automatically subtracted in the following measurements. Even so, the residual carbon dioxide and the moisture in the FTIR spectrometer should be reduced as much as possible by purging with dry air or nitrogen free of CO_2 .

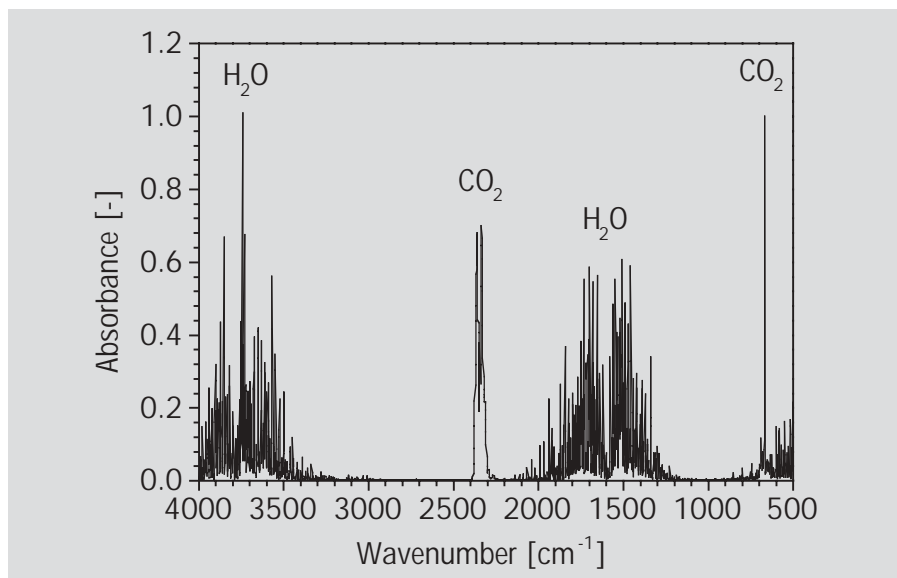


Fig. 1. Background spectrum of air

MS measurement modes

Before the analysis, you usually do not know which fragment ions will occur. It is therefore best initially to measure in Scan Analog or Scan Bargraph mode (from m/z 10 up to m/z 300). The relevant fragment ions (m/z values) can then be detected in a second measurement in MID (multiple ion detection) mode.

Conclusions

Decisive for a successful EGA measurement is the optimum choice of carrier gas, heating rate and sample size. The problem of blockage of the transfer line can be solved by routine checks and cleaning. Even under optimum measurement conditions, the curves still have to be properly interpreted!

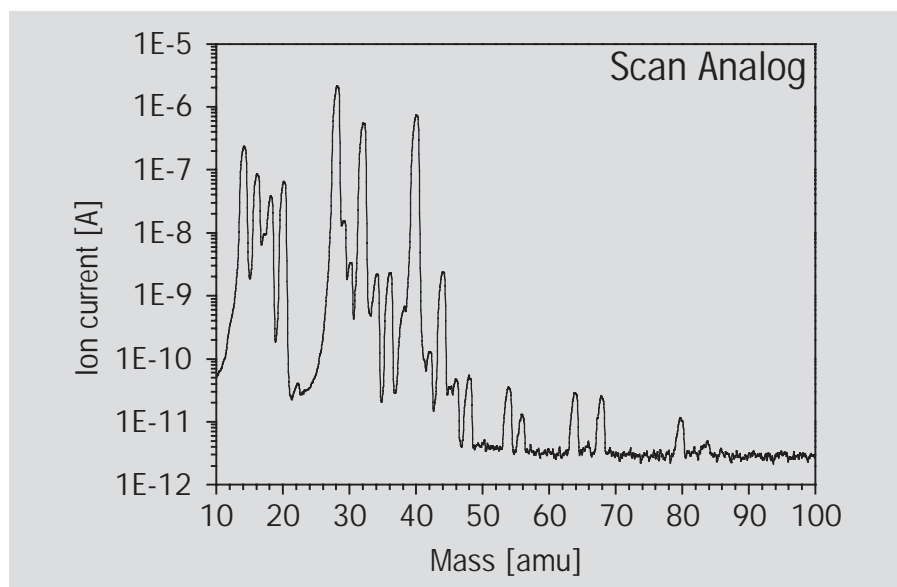


Fig. 2. Scan Analog of the orientation measurement

Dates

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Pittsburgh Conference	March 17-22, 2002	New Orleans LA (USA)
Forum LABO	March 26-29, 2002	Paris (F)
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TMA-DMA/SW Basic (Deutsch)	16. September 2002	TMA-DMA/SW Basic (English)	September 23, 2002
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DSC Basic (Deutsch)	18. September 2002	DSC Basic (English)	September 25, 2002
DSC Advanced (Deutsch)	19. September 2002	DSC Advanced (English)	September 26, 2002
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