UserCom

2/2004

Information for users of
METTLER TOLEDO thermal analysis systems

20

Dear Customer,

Thanks to the rapid development of digital photography, CCD cameras are nowadays relatively inexpensive and extremely sensitive. Digital images can easily be stored and mathematically evaluated. This opens up many interesting new application possibilities in thermal analysis.
We are delighted to announce the introduction of a worldwide brand-new product - the High Pressure DSC chemiluminescence/microscopy instrument. You can now perform a DSC measurement and at the same time capture images of the sample or measure its light emission (luminescence).

Contents

TA Tip

New in our sales program

Applications

Dates

The advantages of DSC cooling measurements for characterizing materials

Ni Jing

Introduction

Very often, only heating measurements are performed when DSC is used to analyze materials. In many cases, however, heating measurements alone are not sufficient to understand and characterize the properties and behavior of a sample. Cooling measurements are then a simple way to gain valuable additional information.

The data from cooling experiments is extremely useful if you want to

1. differentiate between materials with different thermal history, for example to distinguish between new and recycled materials;
2. examine differences in molecular structure or composition;
3. rapidly analyze the phase behavior of materials with mesomorphic structures, for example liquid crystals;
4. separate several overlapping thermal effects.

This article describes a number of experiments that illustrate the importance of cooling measurements. The experiments were performed using a $DSC822^e$ equipped with an IntraCooler and an automatic sample robot.

Differentiation of new and recycled polypropylene

The differentiation of new and recycled material is an important aspect of product development and quality assurance. Very often, recycled material and new material differ noticeably in their crystallization behavior.

Figure 1 shows the heating and cooling curves of new and recycled polypropylene (PP) measured at 10 K/min. It can be seen that the heating curves of both samples are practically identical. The cooling curves of the new and recycled PP, however, show significant differences with respect to crystallization behavior. The recycled PP begins to crystallize at a slightly higher temperature. Furthermore, the crystallization peak of the recycled material is broader and not so high as that of new PP. The enthalpies of crystallization (peak areas) are, however, practically the same and are independent of the type of PP.

These results show that the main difference between the two PP samples is to be found in the crystallization behavior. The reason for this is that the content of athermal crystallization nuclei is greater in recycled material.

The cooling curves of several samples of similar weight and prepared in the same way were very reproducible. This means that crystallization behavior can be used as a criterion to distinguish between samples of new and recycled PP.

Characterization of different polypropylene samples

Polymers are often modified structurally or additives are blended with the polymer in order to optimize important properties for a particular application. The following DSC measurements (Fig. 2) show the (second) heating curves and cooling curves of three different polypropylene (PP) samples: a standard PP film, a nucleated PP and a resin-modified PP.

The heating curves do not show any significant differences apart from the small melting peak at 123 °C in the curve of the resin-modified PP. Clearly, it is not possible to distinguish between the three materials in this way.

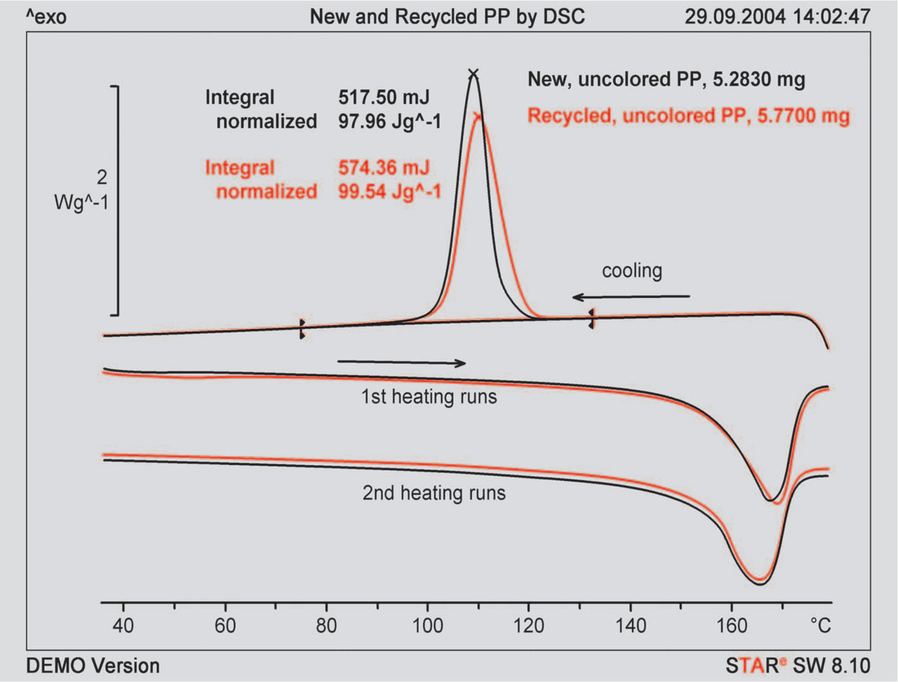


Fig. 1. DSC heating and cooling curves of new and recycled PP samples measured at 10 K/min.

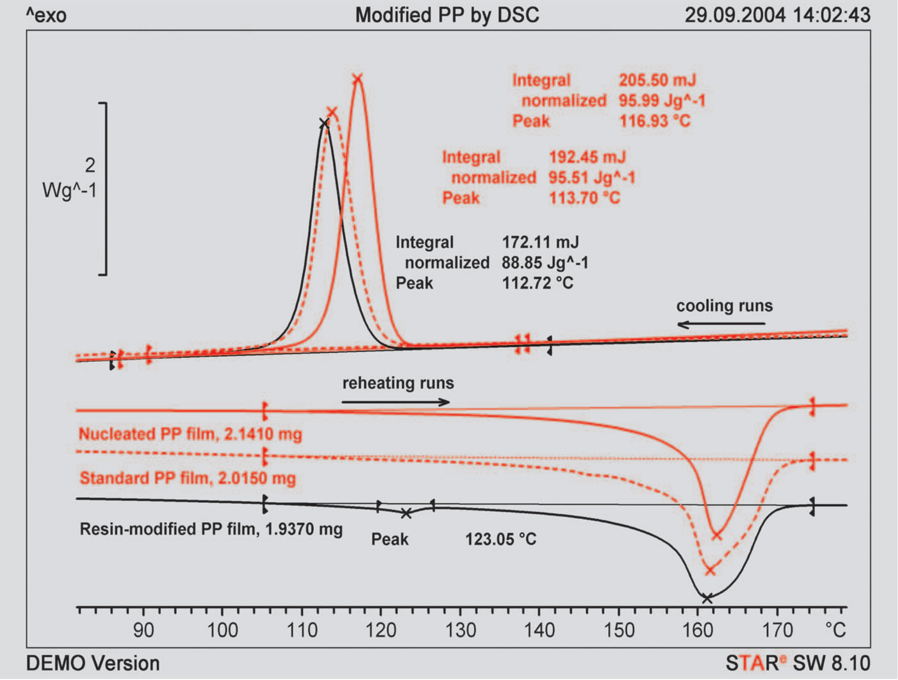


Fig. 2. DSC heating and cooling curves of standard and modified PP samples measured at 10 K/min.

In contrast, the cooling curves show greater differences. As expected, the nucleated PP undergoes crystallization at a higher temperature and also more rapidly than the standard PP. The peak temperature is 116.9 °C, which is about 3 K higher than that of the standard PP. Nucleation does not, however, influence the enthalpy of crystallization of PP.

The cooling curve of the resin-modified PP sample shows that the material crystallizes at an even lower temperature and indicates that the resin interferes with and hinders the crystallization process. In addition, the enthalpy of the crystallization (88.9 J/g) is about 7% less than that of the other two samples.

Characterization of liquid crystals

DSC is an excellent method to study the phase transitions of liquid crystalline materials. To rapidly characterize unknown samples (for screening purposes), heating rates of at least 10 K/min are used in order to save time. Under these conditions, the main melting peak (solid-liquid) may overlap some of the liquid-liquid phase transitions, which therefore go unnoticed. In such cases, controlled cooling measurements are a very effective and convenient way to ensure that all the transitions are in fact identified.

Figure 3 displays the heating and cooling curves of cholesteryl myristate measured at 10 K/min. The heating curve shows the main melting peak at 73 °C (A) and a small peak at 83 °C (C). This is due to the transition from the nonisotropic to the isotropic liquid. The shoulder (B) that can be made out in the main melting peak at about 77 °C cannot with certainty be interpreted as a phase transition.

In the cooling experiment, besides the crystallization peak at about 20 °C (A'), two small well-separated peaks occur at about 80 °C (C') and 72 °C (B'). These small peaks correspond to the peak C and the shoulder B. They are transition peaks that relate to changes between liquid crystal mesophases. In general, transitions of this type supercool less than the actual crystallization. In addition the enthalpies associated with these transitions are much smaller.

The heating curve can be interpreted as follows. After melting (A), the cholesteryl myristate is present in the smectic (liquid crystalline) state. The shoulder (B) marks the subsequent transition to the cholesteric phase, and at C the liquid loses its liquid crystalline properties and melts to form an isotropic liquid. The example shows that transitions that overlap on heating can be separated in a cooling experiment because the supercooling behavior is different. Experiments like this can be optimized by heating and cooling more slowly and using smaller sample weights.

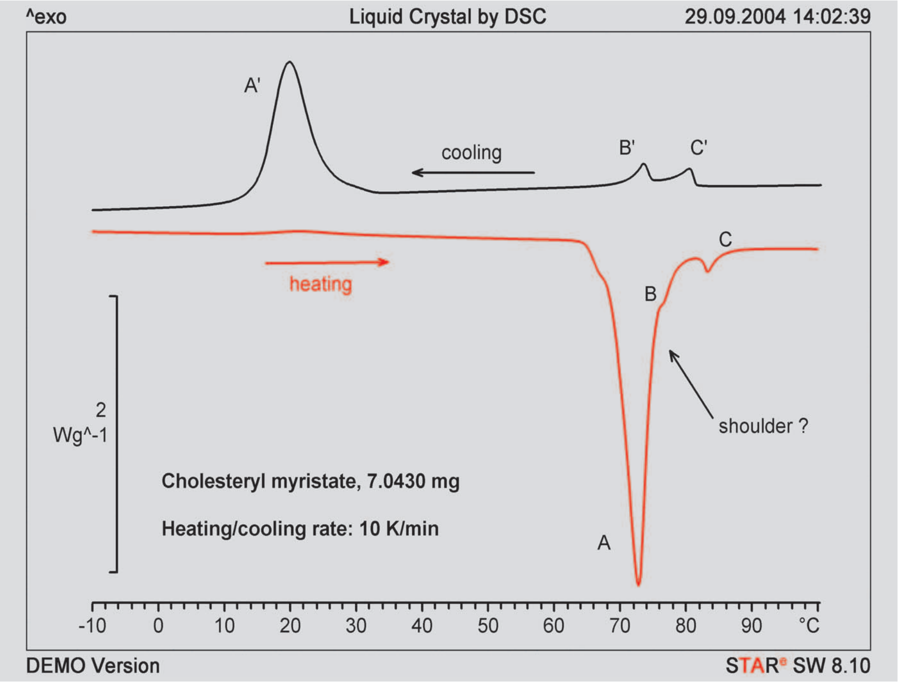


Fig. 3. Heating and cooling measurements of cholesteryl myristate measured at 10 K/min.

Overlap of glass transition and melting

DSC cooling experiments can also be used to separate other types of overlapping effects. This is illustrated in Figure 4 using a sample of PET blended with a wax.

As shown in the figure, the sample was first heated at 10 K/min, then cooled at 10 K/min and finally heated again at 10 K/min. The first heating run shows two endothermic overlapping peaks (A and B). These might at first sight be interpreted as two overlapping melting peaks. The second heating run, however, shows only one endothermic peak D followed by a small apparently exothermic effect instead of the peak B.

The explanation of this behavior becomes apparent using the additional information obtained from the cooling curve. This shows an exothermic peak C that is shifted to lower temperature compared with the peaks observed in the first and second heating curves (A and D). The reason for this again has to do with supercooling. Furthermore, the well-defined step in the cooling curve between 60 °C and 80 °C clearly indicates the presence of a glass transition.

The two heating curves can now be interpreted as follows. In the first heating run, the wax melts (peak A); at the same time, the glass transition of the PET occurs accompanied by an endothermic relaxation peak (peak B). In the second heating, run this relaxation peak no longer occurs, and

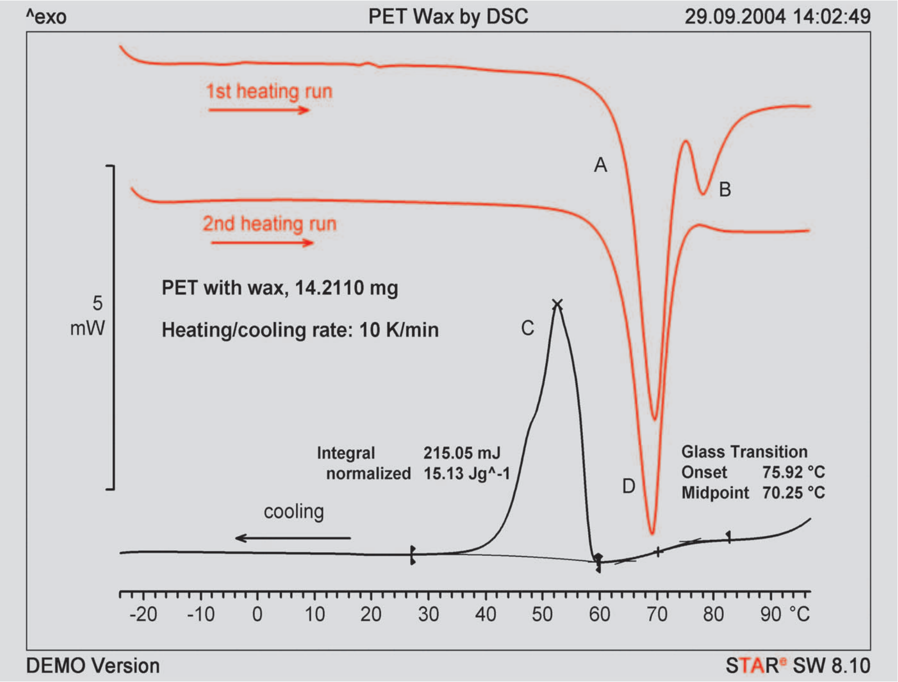


Fig. 4. DSC heating and cooling curves of a PET/wax blend measured at 10 K/min.

the apparently "exothermic" peak immediately after the melting peak of the wax in fact corresponds to final part of the glass transition of the PET. The displacement of the baseline before and after the various peaks (A and B, and D) also indicates that the melting peak is overlapped by a glass transition.

Conclusions

The DSC822^e can be used to perform controlled cooling experiments to study effects such as the glass transition, crystallization and polymorphism and so gain valuable additional information about the sample.

The crystallization of a material is observed as an exothermic peak in the DSC curve. In general, the crystallization peak occurs at a lower temperature than the corresponding melting peak on heating because the melt supercools. Modification of the material usually influences the crystallization behavior more than the melting behavior. Cooling curves are therefore superior to heating curves for characterizing and differentiating between similar materials.

Polymorphic transitions can occur both on heating and on cooling. Here again, the different supercooling behavior exhibited by the various transitions allows effects that overlap in a heating measurement to be separated in a cooling experiment.

Glass transitions can be identified as a step change in the DSC curve. If a glass transition and a melting peak overlap in a heating measurement, the two effects can usually be separated in a cooling experiment because the crystallization is shifted due to supercooling of the melt.

In general, heating-cooling-heating experiments provide appreciably more information about a sample than a single heating measurement. It is therefore advisable, particularly with unknown samples, to perform such experiments. The maximum cooling rate at which a sample can be cooled under control depends on the temperature range and on the cooling possibilities with which the instrument is equipped (air cooling, IntraCooler, liquid nitrogen cooling). Further details about this can be found in UserCom 11.

New in our sales program

Microscopy

Microscopy experiments can be performed with a camera costing less than the highly sensitive CCD camera. A new accessory allows you to upgrade your HP DSC827^e to a pressure DSC-reflected light microscope system. With this system you can perform DSC measurements at high sensitivity under pressure and at the same time observe the sample.

Microscopy also allows you to detect processes that generate little or no change in enthalpy (e.g. a color change) or to interpret effects that are visible on the DSC signal only as peaks (e.g. polymorphic transitions). Color changes or structural changes of the sample can easily be detected by microscopy.
You can also equip your microscope with a camera and a hot stage to perform transmission microscopy (e.g. the FP82). With the METTLER TOLEDO FP84 you can even simultaneously perform transmission microscopy and measure a DSC signal. The advantage of transmission microscopy is that polarized light can be used and birefringent crystals can therefore be clearly detected.

For more detailed information on chemiluminescence and microscopy, please ask you sales representative for the corresponding data sheets.

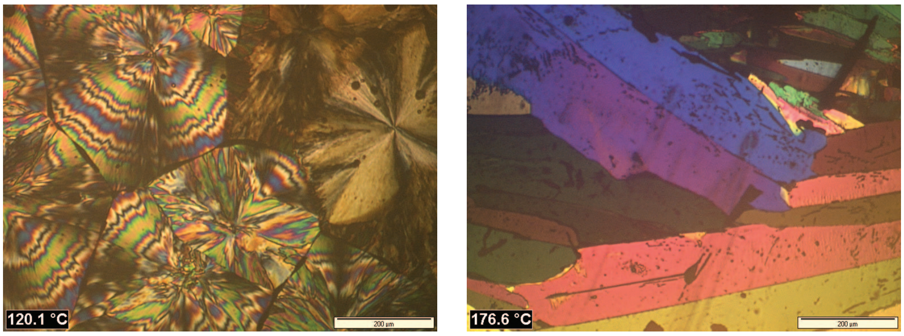


Fig. 1. Two different crystalline forms of sulfapyridine at about 120 °C and 176 °C.

Chemiluminescence

Chemiluminescence (CL) is the term used to describe the emission of light (usually in the visible range) during a chemical reaction.
For many years, this type of light emission was measured by photomultiplier techniques. The new, high sensitivity CCD cameras now provide similar sensitivity, but are much easier to use. CCD cameras also have the great advantage that they record digital image data. Suitable software enables the data to be analyzed and evaluated. The light-emission intensity curve is one of several possibilities to evaluate images.

Classical CL instruments can easily measure oxidation induction times. The more modern instruments based on CCD cameras, however, have the image information available and can measure how the oxidation spreads. When CL and pressure DSC are used in combination, temperature and pressure act as additional acceleration factors. The measurements quickly provide valuable information on the long-term stability of materials. This technique is an interesting alternative to time-consuming aging tests in climatically controlled ovens.

With the aid of a special accessory, you can also use an HP DSC827^e as a pressure DSC-CL instrument.

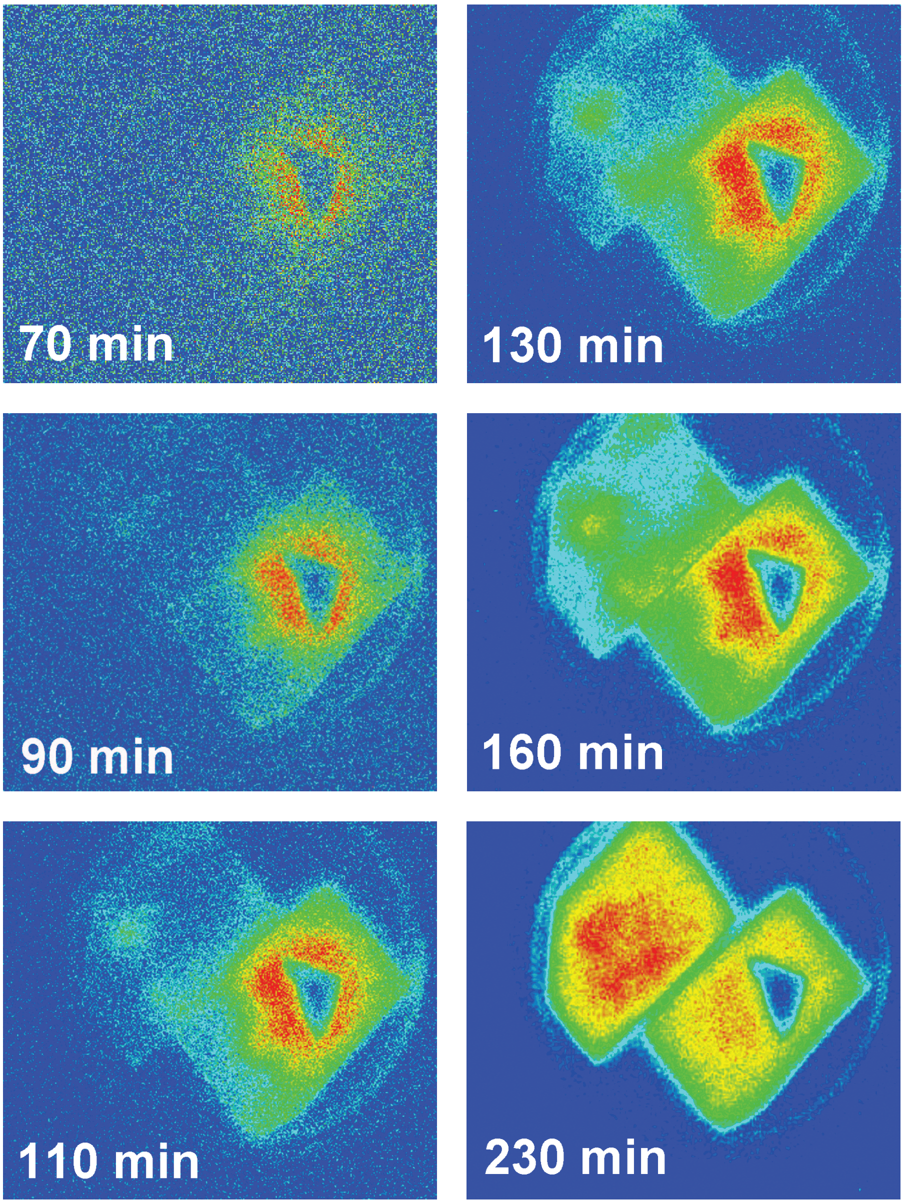


Fig. 1. Images due to chemiluminescence resulting from the oxidation of two identical polypropylene films. A triangular piece of copper was placed on the film on the right. This accelerates the decomposition reaction. You can find further information on this application in the article entitled "Chemiluminescence of polypropylene", page 12).

Fig. 2. HP DSC827^e with the chemiluminescence accessory.

From liquid to solid – measurement of mechanical quantities over more than 10 decades

Dr. Jürgen Schawe, Dr. V. Zschuppe (Thermo Electron GmbH, Karlsruhe, Germany)

The change in mechanical behavior of more than 10 orders of magnitude is discussed using an isothermal curing reaction as an example. The material passes through several different states (the low viscosity Newtonian liquid, non-Newtonian liquid, gel and glassy states). Such changes can now be measured over the complete range using a DMA/SDTA861^e and a Haake RheoStress 600.

Introduction

The mechanical properties of materials can change by many decades as a function of temperature or chemical structure. For example, when ice melts it changes from an elastic solid to a liquid with a viscosity of about 2 mPa·s. This represents a change of more than 12 decades in the mechanical properties. Similar changes of mechanical behavior occur with polymers. The two extremes in this case are the glassy state and the melt at high temperature. But reactive materials such as adhesives and polymeric coating materials can also exhibit changes in mechanical behavior of the same order during the reaction.

Knowledge of the mechanical properties provides information about structure and molecular interactions. In practical applications, for example adhesives or the production of composites, it is very important to have information about flow behavior, gelation and vitrification. To obtain this data, the mechanical quantities have to be determined over a range that is as wide as possible. From the point of view of measurement, this presents a problem because the change in material properties occurs on a logarithmic scale, but the sensors used in measuring instruments have a linear resolution. The classical solution to this problem is to use several different instruments and different sample geometries, whereby one instrument typically covers 3 to 5 decades with one sample geometry. If measurements are required that cover a large range, several measurement curves have to be recorded that correspond to one another reasonably well in the range of overlap. This problem was addressed in the development of the METTLER TOLEDO DMA/SDTA861^e and particular attention was paid to expanding the measurement range. In the shear mode, the DMA can determine modulus changes of up to 8 decades in one measurement using the same sample geometry. This makes it possible to determine the mechanical behavior of a material from the glassy state to below the gel point in a single measurement. To obtain measurement data in the range from the gel point through to the low viscosity liquid state, the DMA measurements can be combined with rheometric data (measured with the Haake RheoStress 600). In this case, the large overlap range of the two instruments is very advantageous.

This study shows how the results from a METTLER TOLEDO DMA/SDTA861^e and the Thermo Electron Haake RheoStress 600 can be combined to determine the modulus change over 10 decades using the isothermal curing of an epoxy resin as an example.

As model substance, a two-component stoichiometric epoxy resin mixture consisting of the diglycidylether of bisphenol A (DGEBA) and diaminodiphenylmethane (DDM) as hardener or curing agent was used.

Mechanical quantities during a polymerization: from the low molecular weight liquid to the polymeric glass

The relationship between viscosity, η, and shear modulus, G, is given by the equations

$$G' = \omega \eta' \qquad (1)$$

and

$$G'' = \omega \eta'' \qquad (2)$$

where G´ is the storage modulus and G˝ the loss modulus, $\omega = 2\pi f$ the angular frequency, and f the frequency.

The curing of an epoxy resin system is a polymerization reaction. The change in mechanical behavior of such a system during the reaction is shown in Figure 1 using a stoichiometric reaction mixture of DGEBA-DDM as an example. The conversion is displayed on the abscissa and was measured during the isothermal reaction using a DSC822^e [1].

Before the reaction begins, the sample consists of a low molecular weight mixture of resin and hardener. This is raised as quickly as possible to the reaction temperature. Initially relatively small molecules are formed in the reaction and the material behaves like a Newtonian liquid. This means that only the real part of the viscosity exists. For the shear modulus, it follows then from eqs (1) and (2) that the storage modulus is practically non-existent. The loss modulus is less than 100 Pa. As the molecules become larger, the viscosity increases.

At a conversion of 50%, the molecules are so large that the liquid loses its Newtonian behavior due to the stronger hydrodynamic interaction. The storage component of the shear modulus is now significant, but still much smaller than loss modulus. The material therefore still retains the characteristic behavior of a liquid (G˝ > G´).

At about 70% conversion the molecules begin to assume macroscopic dimensions. Storage and loss moduli are of the same order of magnitude and finally G´ becomes larger than G˝. The material is dimensionally more stable and has the properties of a solid. A gel is formed. The gel point can be defined as the time at which the ratio of the storage and loss modulus (i.e. the loss factor, tan δ) is independent of frequency. In a stoichiometric system this is the intersection of the two curves G´ and G˝. With a storage modulus of about 1 Mpa, the material has the modulus of an elastomer, but because of the lower degree of polymerization, a larger loss modulus.

At a conversion of about 80% there is a stepwise increase in G´ that coincides with a peak in the G˝ curve. The storage modulus reaches a value of about 1 GPa. This behavior describes a chemically induced glass transition because molecular mobility is severely restricted through the formation of the polymer network. Finally the material vitrifies at a conversion of about 85%, and because diffusion is hindered the reaction practically stops.

It is clear that the positions of the individual regions in Figure 1 depend very much on the reaction temperature. For example, with a reaction temperature above the glass transition of the fully cured sample (here above 160 °C), vitrification cannot occur. This is discussed in detail in reference [1].

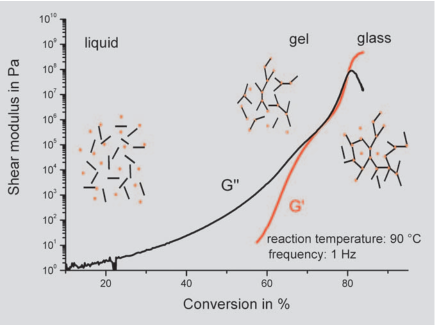


Fig. 1. Change of the complex shear modulus (G´ storage modulus, G˝ loss modulus) as a function of conversion in the curing reaction of an epoxy resin system.

Measurement of viscous liquids, gels and glasses by DMA

For liquids, a special sample holder is available that allows a defined sample thickness to be set. Samples for the DMA/SDTA861^e can be prepared externally. The sample holder with sample can then be very quickly installed in the preheated furnace chamber (in less than 1 min). This results in excellent reproducibility.

When choosing the measurement parameters, several points need to be considered. First of all the large modulus range must be taken into account. At the end of the measurement the sample has a modulus of about 1 GPa. The force should therefore be as large as possible to ensure that sufficiently large displacement values are measured. With liquids, however, the force to be measured will be very small. In other words the maximum displacement must be chosen so that the force can in fact still be measured. The linear range of the sample must also be taken into account. This puts limits on the maximum amplitude. For the measurements presented here, a maximum force of 10 N and a maximum displacement of 100 μm were used.

Figure 2 displays the measurement curves for an isothermal reaction at 90 °C for frequencies of 1 Hz and 0.1 Hz. Since the viscosity, η, in the liquid at short reaction times is almost independent of frequency, the modulus values of the 1-Hz measurement in this range should, according to eq (2), be a decade greater than those of the 0.1-Hz measurement in this range. The data in Figure 2 show that this is in fact the case.

The time at the intersection of the storage and loss modulus is the gel point. As the measurement shows, this point is independent of frequency.

At the glass transition that follows, one sees that at 1 Hz the maximum value of G˝ is reached earlier than in the measurement at 0.1 Hz. The reason for this has to do with the frequency dependence of the glass transition. When chemically stable materials are measured in the DMA in a heating experiment, with higher frequencies, the glass transition is observed at higher temperatures [2]. This means that with higher frequencies, the glass transition is observed at greater molecular mobility. In the case studied here, the cross-linking reaction lowers the molecular mobility with increasing reaction time. In other words, with higher frequencies the glass transition is measured after shorter reaction times.

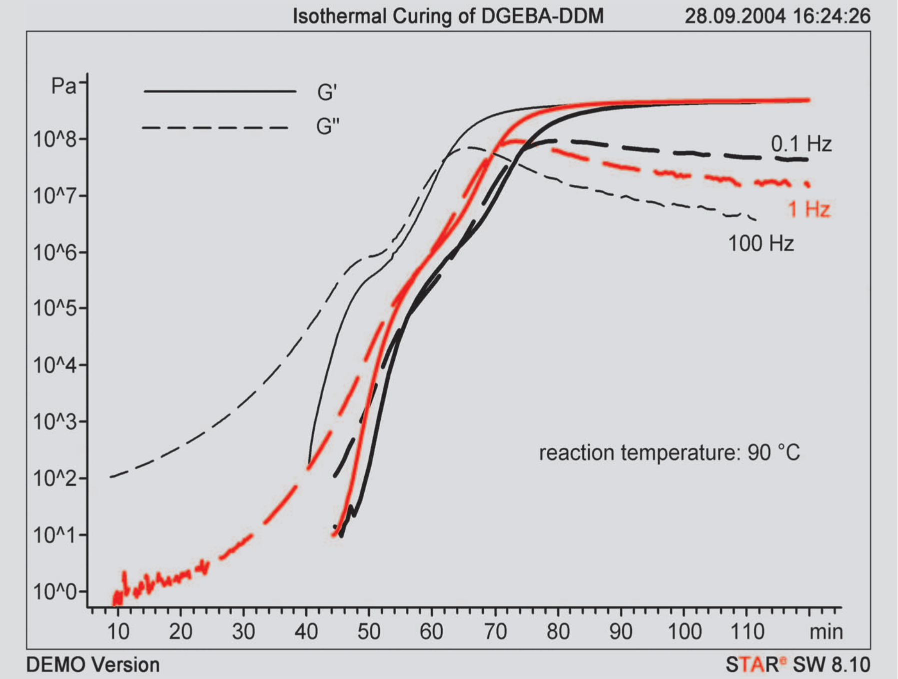


Fig. 2. Storage and loss components of the shear modulus as function of measurement time in an isothermal cross-linking reaction at 90 °C. The measurement frequencies are 1 Hz and 0.1 Hz. The frequency-independent intersection of G´ and G˝ is the gel point.

Following the glass transition the material vitrifies. The reaction practically stops. For this reason the G˝ curves remain almost unchanged.

To perform a measurement with the best possible accuracy, the volume change of the sample due to shrinkage can be calibrated using DSC and TMA and the small temperature delay at the beginning of the measurement taken into account. These corrections are however small and were not applied.

Extension of the measurement range using a rheometer

The DMA/SDTA861^e was designed for samples with a shear modulus above 100 kPa. For this reason, with smaller molecules the accuracy decreases. Rheometric techniques are excellent for measuring liquids. Although the DMA/SDTA861^e can measure liquids with viscosities down to about 10 Pa·s with good accuracy (see Fig. 3), in some analyses it is important to be able to characterize the material at lower viscosities. In such cases, the combination of measurements from a DMA and a Thermo Electron Haake RheoStress 600 is ideal.

And in this example of a cross-linking reaction, we also successfully measured the full range of mechanical behavior using a combination of the two techniques. To achieve the best possible agreement between the two methods, periodic experiments were performed with the Haake RheoStress 600 at a frequency of 1 Hz. An arrangement with parallel plates with a diameter of 6 cm was chosen for this. The deformation was 5%. Disposable sample holders had to be used because the sample is a system that undergoes curing.

With the Haake RheoStress 600 the sample can be transferred directly to the preheated sample holder. Figure 3 shows a typical viscosity measurement curve. It can be seen from the figure that the DMA and rheometer measurements are in good agreement. The large range of overlap that can be achieved with the two instruments is very advantageous.

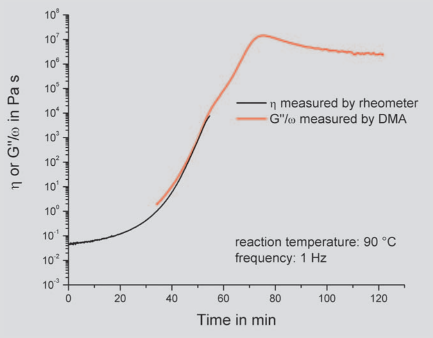


Fig. 3. Viscosity as a function of time during a curing reaction at 90 °C. The curves were measured using a rheometer and DMA at 1 Hz.

Figure 4 displays the shear modulus as a function of time. It shows that at the beginning of the measurement the reaction mixture has a loss modulus of about 0.1 Pa, which continuously increases to 300 kPa as the reaction proceeds up until the gel point. Viscoelastic behavior of the material begins with the appearance of a measurable storage modulus of 0.1 Pa after about 45 min. A DSC determination showed that this reaction time corresponds to a conversion of about 50%.

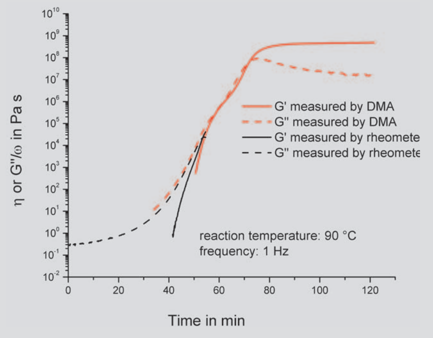


Fig. 4. The complex shear modulus during the isothermal cross-linking reaction at 90 °C.

Conclusions

To measure the mechanical behavior of materials from the solid state to the low viscosity liquid state means that changes in the mechanical parameters of more than 10 orders of magnitude have to be measured. Although the DMA/SDTA861^e covers a modulus range of about 8 decades, a Haake RheoStress 600 is a useful addition to the DMA, especially for liquids with viscosities below 100 Pa·s.

Particularly advantageous for the comparison of DMA and rheometer curves measured in isothermal cross-linking studies is the fact that both instruments allow the sample to be inserted into a preheated sample chamber.

A combination of DMA/SDTA861^e and the Haake RheoStress 600 is ideal for the analysis of systems with very large changes in modulus or viscosity because of the large overlap of their measurement ranges.

Literature

[1] J. Schawe, UserCom 18 (2003), 13.
[2] G. Widmann, J. Schawe, R. Riesen, UserCom 15 (2002), 1.

The author would like to thank Dr. V. Zschuppe (Thermo Electron GmbH) for help with the measurements on the Haake RheoStress 600.

Quality assurance of plastic molded parts by DSC. Part 2: Process control

Dr. Achim Frick, Claudia Stern, Fachhochschule Aalen, Kunststofftechnik, Aalen, Germany

This article describes several applications that illustrate the use of DSC for the quality assurance of plastic molded parts in process control. It shows how process parameters such as the temperature of the polymer mass (melt temperature), the mold temperature, and the time the polymer spends in the melt (dwell time in the melt) can be optimized and controlled by DSC. Furthermore it describes how the use of recycled material and the quality of molded parts can be evaluated using DSC measurements. Part 1 was published in UserCom 19.

Introduction

Although the quality of technical plastic products is primarily influenced by their morphology (microstructure of the materials used), in practice, quality assessment very often only consists of determining the dimensional accuracy of the parts. In other words, a plastic part meets the quality requirements if its dimensions are within the specified tolerances. However, to satisfy the quality profile for plastic parts more closely, it is often necessary in quality assurance to include parameters that characterize the morphology of the parts. A relatively simple and rapid way to determine these parameters is to use differential scanning calorimetry (DSC).
In the first part of this article series, we discussed applications of DSC for the incoming goods control of polymers. This second part covers practical examples of the use of DSC in process control.

Temperature of the polymer mass

In the processing of semicrystalline plastics, the choice of the melt temperature is a decisive factor for the quality of molded parts. Temperatures that are too high lead to thermal degradation of the polymer and thereby impair the mechanical properties of the product. With increasing thermal disruption, progressive chain degradation leads to an increase in crystallization rate.

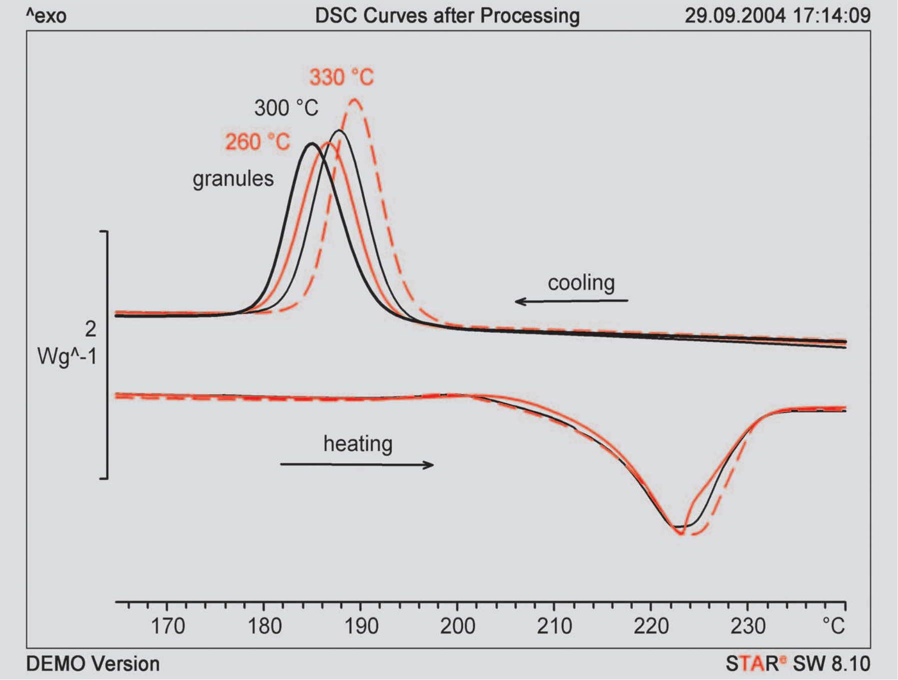


Fig. 1. DSC curves (heating and cooling) of PBT-GF30 natur after processing at different melt temperatures (T_{ma}) between 260 °C and 330 °C. (Temperature program: heating and cooling between 30 °C and 280 °C at 20 K/min; sample weight: 3.5 ± 0.1 mg; sample: test bar 4 x 2 mm^2; material: Ultradur B4300 G6 natur, purge gas: N_2).

This is illustrated in the DSC curves displayed in Figure 1 using polybutylene terephthalate (PBT) as an example. The heating curves show only small effects originating from the melt temperature. The cooling curves, however, reveal marked changes in the position and shape of the crystallization peaks. Due to the greater crystallization rate, with higher melt temperatures the peak temperatures increase and the peaks become narrower and higher.

Influence of longer dwell times

When residues of production material (recyclable material) are used, the dwell time of the material in the molten state in the plastifying unit increases. The increased thermal stress that the material is subjected to can significantly reduce the quality of the molded part and limits the possibilities for recycling. These aspects are particularly important with the new innovative injection molding processes such as thin-wall technology and micro-injection molding. Here, because the weight of each shot is small, the dwell time of the molten polymer in the plastifying unit of the injection-molding machine increases to 2 to 9 minutes.

The influence of the dwell time on the crystallization behavior on cooling from the melt is illustrated in the cooling curves of unreinforced PBT natur shown in Figure 2. Here the polymer mass spent between 3.7 and 18.1 min in the injection molding process at a temperature of 290 °C. As has already been discussed in the previous paragraph, progressive degradation due to increased thermal stress of the polymer melt causes a change in the shape of the crystallization peak and a shift to higher temperatures. In a similar way to that described in the Section "Evaluating the quality of molded parts" (page 11), this information can be used to evaluate the quality of the recyclable material. The degradation of the polymer during its dwell time in the plastifying unit was also confirmed by measurement of the viscosity number.

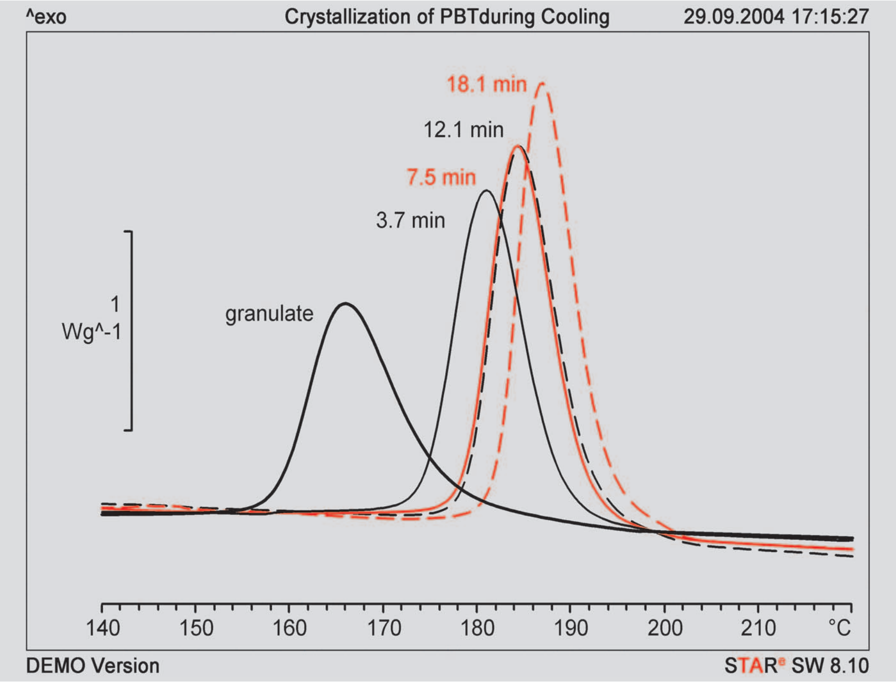


Fig. 2. DSC cooling curves of PBT after different dwell times at 290 °C. (Material: Ultradur B4520 natur; cooling rate: 20 K/min; purge gas: N_2; sample weight: 3.5 ± 0.1 mg).

Influence of mold temperature

In the processing of plastics, factors such as the melt temperature and mold temperature determine the processibility and the cooling rate of the polymer melt. Since the morphology of the plastic parts depends on the cooling conditions, their properties are of course also influenced. Maintaining an optimum temperature in the mold is therefore a very important factor in the injection molding of thermoplastics.
With semicrystalline polymers, there is a relationship between the degree of crystallinity and the cooling rate and hence also the mold temperature. To a large extent this therefore determines the shrinkage behavior of the plastic parts (see Fig. 3).

The influence of the surface temperature of the mold on the morphology of polymers can be seen in the crystallization effect observed as an exothermic peak between the glass transition and the melting peak in a DSC heating measurement. This is illustrated in Figure 4 using polyamide (PA-GF20) as an example. The crystallization occurs at significantly lower temperatures if the mold temperature is below the glass transition temperature (here 80 °C). For optimum injection molding of plastics the rule is that the mold temperature should be higher than the glass transition temperature. Otherwise tight tolerance limits cannot be maintained and possible distortion may occur that cannot be corrected.

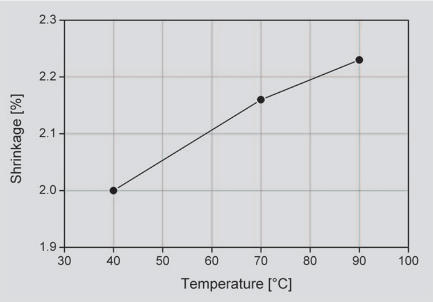


Fig. 3. Shrinkage after 30 days as a function of the temperature of the mold surface. (Material: Ultradur B4520 black 0110).

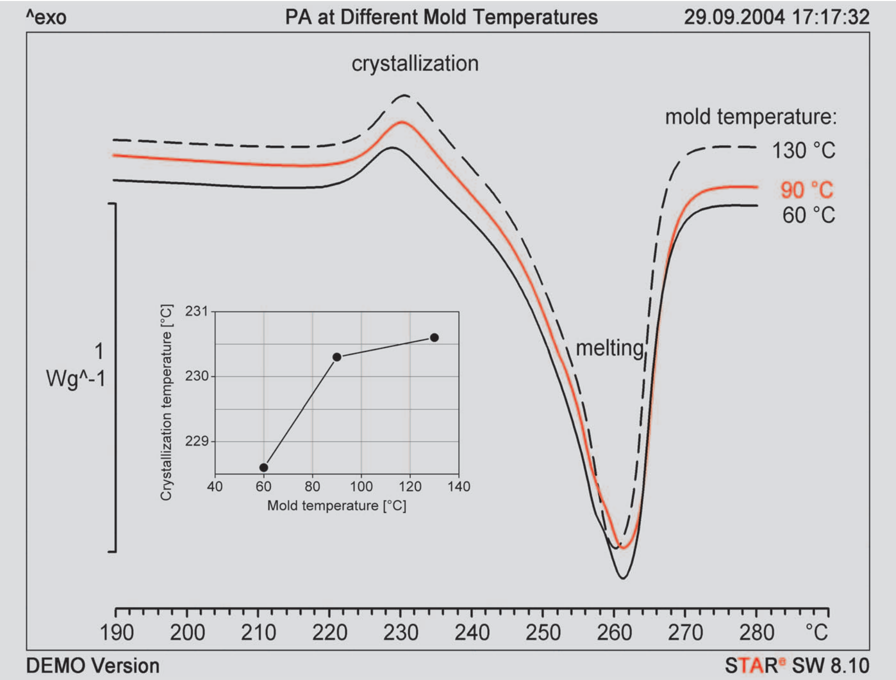


Fig. 4. Influence of the mold temperature on the crystallization behavior of partially aromatic PA-GF 20 black. (Material: Grivory GV2H black 9815; sample: test bar 4 x 1 mm^2; heating rate: 20 K/min; purge gas: N_2; sample weight: 7.9 ± 0.1 mg).

Detection of the annealing conditions

Molded parts are often subjected to an annealing process after production to ensure that their properties remain constant during their usable lifetime. The annealing process changes the morphological structure of the parts through crystallization. These structural changes can be detected by analyzing the melting behavior of the parts using DSC. Examples to illustrate this are shown in Figures 5 and 6 for a glass-fiber reinforced polyamide.

Figure 5 shows the DSC curves of samples that have been annealed for different times in a circulating air oven at 100 °C. The annealing process influences the exothermic crystallization peak at about 225 °C. With increasing annealing time, the peak becomes narrower and higher. The area of the melting peak that follows (melting enthalpy) increases somewhat with increasing annealing time. This indicates an increase in the degree of crystallization. The change in the shape of the melting peak between 240 and 270 °C shows the influence of annealing on the morphology. With short annealing times a double peak is observed, but with annealing times of

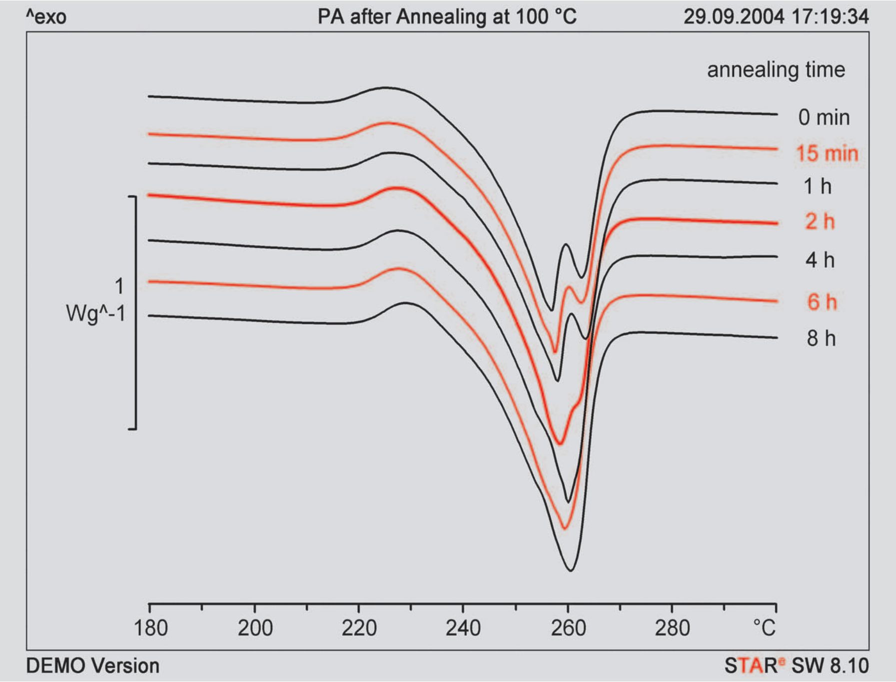


Fig. 5. Influence of annealing time on the DSC curve of PA-GF20 black. (Material: Grivory GV2H black 9815, partially aromatic; annealing temperature: 100 °C; heating rate: 20 K/min; purge gas: N_2; sample weight: 7.9 ± 0.1 mg).

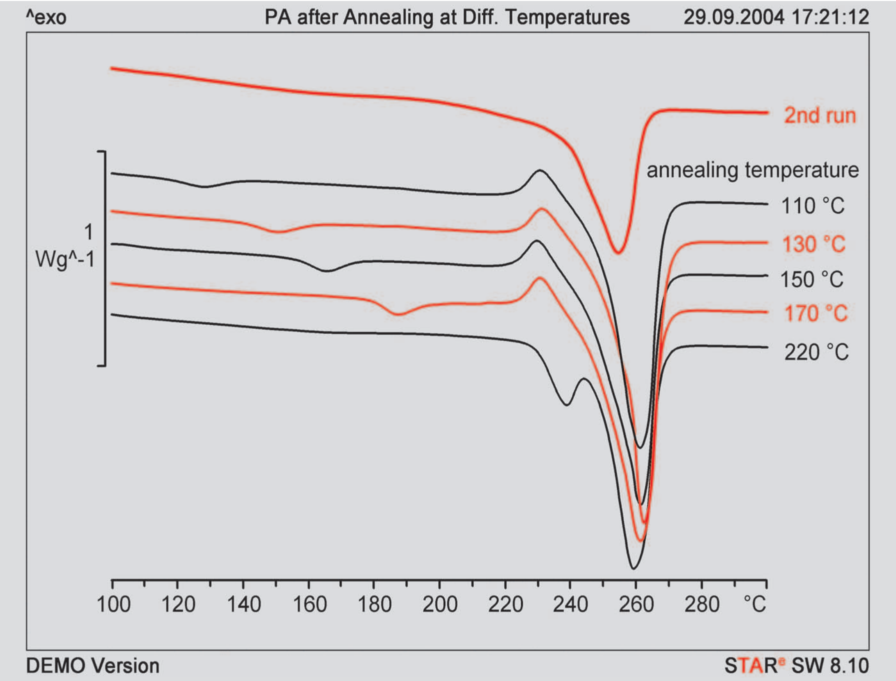


Fig. 6. DSC curves after annealing PA-GF20 black for one hour at different temperatures. For comparison purposes, a second heating curve is shown. (Material: Grivory GV2H black 9815, partially aromatic; heating rate: 20 K/min; purge gas: N_2; sample weight: 7.9 ± 0.1 mg).

more than 2 hours this changes to a single peak whose maximum shifts to higher temperatures with increasing annealing time. With longer annealing times, recrystallization causes the original unstable microstructure in the molded part to take on a more stable morphology with a higher melting temperature.
To produce molded parts of constant quality and thus avoid quality problems, the injection molding process must be optimized for the material used. In this example, after optimization, the DSC curves of the molded parts should ideally yield melting peaks that correspond to those of samples that have been annealed for at least 2 hours.

In a further series of measurements, the PA samples were annealed for one hour at temperatures between 120 and 220 °C in a circulating air oven. The DSC curves are displayed in Figure 6. Besides the crystallization and melting peaks already discussed, a small annealing peak is noticeable in all the curves about 10 to 20 K above the annealing temperature. This peak is due to the melting of small unstable crystallites that were formed during annealing but that melt at somewhat higher temperatures.
The possible occurrence of an annealing peak means that DSC measurements can also be used to afterward assess the thermal conditions under which the plastic parts were used. In the first heating curve an annealing peak cannot be distinguished from an effect of another material component in the molded part. The second heating curve makes matters clear: the annealing peak disappears because the thermal history has been eliminated (see Fig. 6), whereas other material components continue to show thermal effects.

Evaluating the quality of molded parts

In practice, the quality of molded parts is often assessed by determining the viscosity number (VN) using solution viscometry. This is usually done by rule of thumb. According to this, a plastic part does not meet the requirements and is rejected if the viscosity number after processing has decreased by more than 10% with respect to the value before processing.
This procedure has the disadvantage that it is relatively time-consuming and results in considerable amounts of waste solvents that have to be specially disposed of.

DSC measurements provide a rapid alternative for the characterization of the quality of the molded part. This method involves the use of the relationship between the crystallization temperature on cooling and the viscosity number. It only requires a calibration curve and a selection criterion.

The calibration curve is obtained according to Figure 7 by measuring the viscosity number and the crystallization temperature of materials that have been differently thermally stressed. From this calibration curve, the maximum permissible crystallization temperature, $T_{c,max}$, at which VN is 10% less than the original value is taken as the selection criterion.

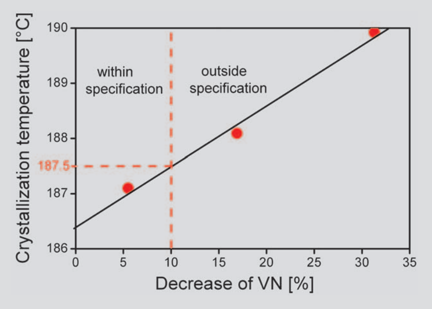


Fig. 7. Relationship between the crystallization temperature and the decrease of viscosity number and the determination of the limiting temperature, $T_{c,max}$. (Material: Ultradur B4300 G6 natur, sample: test bar 4 x 2 mm^2; cooling rate: 20 K/min; purge gas: N_2; sample weight: 3.5 ± 0.1 mg).

Figure 8 shows how a simple direct assessment of the quality of molded parts can be made with the aid of DSC measurements. If the crystallization temperature of the molded part is less than the limiting temperature, $T_{c,max}$, the molded part has the required quality. Otherwise it is rejected as a bad part. This type of rapid quality assessment can be automated through the use of the AutoEval software option.

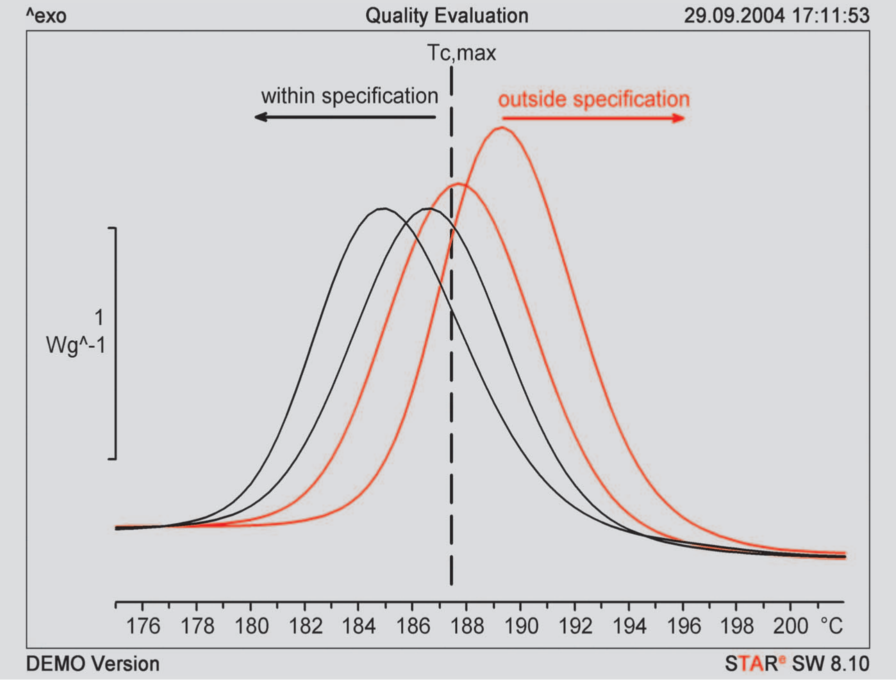


Fig. 8. Quality evaluation of molded parts by DSC according to Figure 7. (Material: Ultradur B4300 G6 natur; sample: test bar 4 x 2 mm^2; cooling from 280 to 30 °C; cooling rate: 20 K/min; purge gas: N_2; sample weight: 3.5 ± 0.1 mg).

Conclusions

The examples presented in this series on quality assurance in plastics technology show very clearly how useful the DSC technique is in this field. It enables plastic molding material and the molded parts produced from it to be reliably characterized, and yields a vast amount of meaningful and relevant information. It can be used to identify polymers and determine their melting and crystallization behavior.

DSC furthermore allows possible production-induced polymer degradation to be qualitatively and quantitatively measured, which in turn permits the quality of molded parts to be assessed. DSC is also a good method to study the production-induced morphology of semicrystalline thermoplastics.

Comprehensive information on sample preparation and the application possibilities of DSC in plastics technology is given in the DSC technical manual. This book can be obtained from Prof. Dr.-Ing. Achim Frick at the Fachhochschule Aalen, Germany.

Chemiluminescence of polypropylene

Dr. M. Schubnell

Introduction

Chemiluminescence (CL) is the term used to describe the emission of (usually) visible light as a result of a chemical reaction. In the 1960s, different polymers were also studied with respect to this phenomenon. Under natural conditions, most polymers degrade or decompose as a result of oxidation due to atmospheric oxygen. In a first step, unstable alkyl radicals are formed through the action of heat, mechanical stress or the effect of light. The radicals

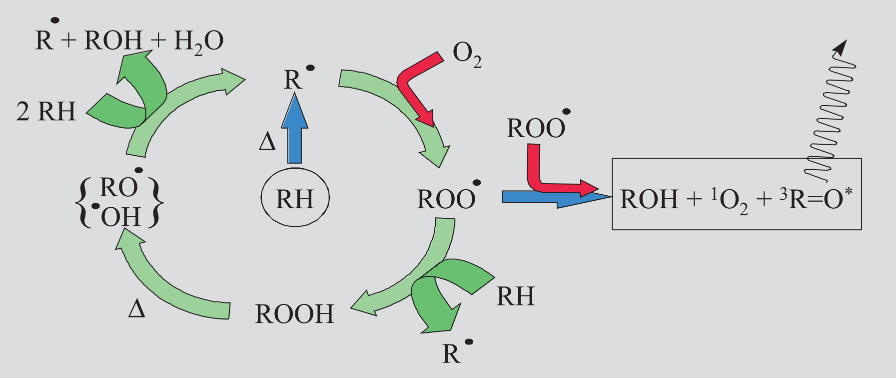


Fig. 1. Possible reaction mechanism for the oxidative decomposition of polyolefines [1].

then react with oxygen to form peroxide radicals. Peroxide radicals can also be produced during the production of plastics and be present in the plastic as an undesirable secondary product. In the presence of oxygen, the peroxide radicals accelerate the decomposition of the polymer through a chain reaction mechanism.

The step of the reaction in which chemiluminescence occurs has not been fully clarified. A mechanism often described in the scientific literature assumes that it takes place when two peroxide radicals recombine, whereby, besides oxygen, an excited carbonyl radical is formed (Russell mechanism [2]). Chemiluminescence measurements allow specific studies to be made on the oxidation of polymers and hence on the influence of stabilizers. This article shows how this can be done using an HP DSC827^{e}.

Experimental details

Chemiluminescence measurements can be made with (non-imaging) photomultipliers or with highly sensitive CCD cameras. The latter technique produces images and has the advantage that you can "see" the individual centers where chemiliminescence occurs. This is of particular interest, for example, if you want to investigate the influence of impurities or inhomogeneity in the sample on its decomposition behavior. In this study, we used a CCD camera (SensiCam from PCO.imaging) together with an objective of high light-gathering power (Navitar, f-number 0.95, focal length 50 mm) to investigate the chemiluminescence of a sample in the HP DSC827^{e}. The instrumental set-up used for these measurements is shown schematically in Figure 2.

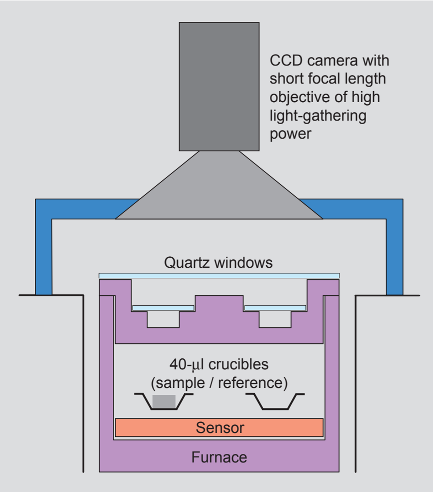


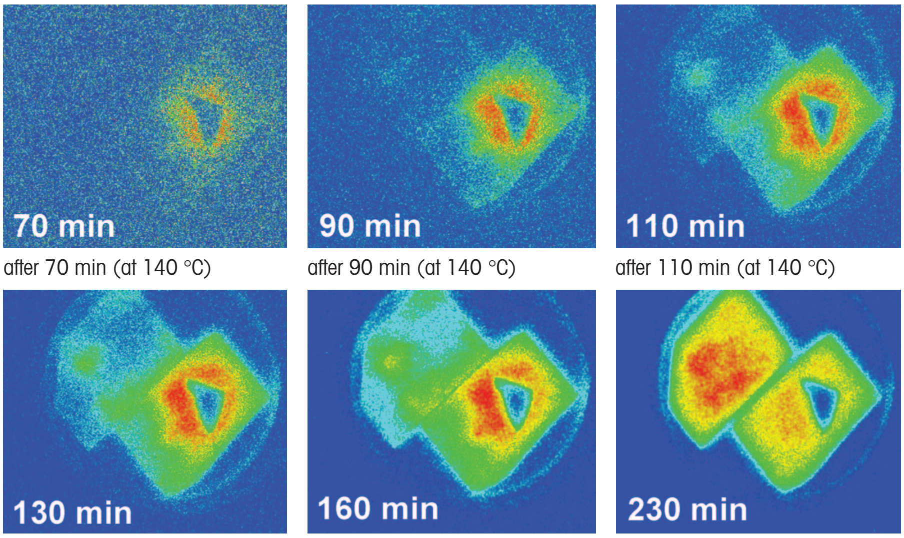
Fig. 2. Schematic diagram of the setup for measuring chemiluminescence. The focal length of the objective was 50 mm; in addition a 30-fold converter was used. The f-number of the objective was 0.95. Camera type: PCO Sensicam.

The experiments were performed with small samples cut from a polypropylene (PP) film. Each sample weighed about 0.4 mg and had an area of 4 mm^2. Two such samples were arranged side-by-side in a crucible and a small piece of copper placed on the upper surface of one of the samples. The measurements were performed in the HP DSC at different temperatures in an oxygen atmosphere (50 ml/min). The chemiluminescence was measured by integrating the light intensity for different periods of time depending on the measurement temperature used, that is 5 minutes at 150 °C, 10 minutes at 140 °C and 130 °C, and 15 minutes at 120 °C. In each experiment, the first image measured was used as a "background image" and subtracted from the images that followed (blank correction). The chemiluminescence curves were constructed by plotting the mean gray values of the two samples individually as a function of time.

Results

Figure 3 shows images taken at different times of samples measured at 140 °C. The first signs of chemiluminescence become apparent after 60 to 70 minutes. The dark triangle on the images is due to the small piece of copper that was placed on one of the two samples. The images show that the oxidation clearly develops from this piece of copper - as if the copper acts as a kind of nucleus for decomposition. The second piece of film (without copper) only begins to exhibit chemiluminescence after about 110 minutes. It is noticeable that the chemiluminescence intensity over the surface of the film is not uniform. "Centers of decomposition" apparently form from which oxidation of the sample develops.

Figure 4 shows the chemiluminescence (CL) intensity curves for the samples at 140 °C together with the measured DSC signal. Induction times (OIT) can then be determined from the CL intensity curves of the two samples. For the sample with copper, the OIT is about 60 minutes, and for the sample without copper about 100 minutes. The determination of the OIT from the DSC curve is however not so straightforward because the baseline is not horizontal at any point. The reason for this is that polypropylene undergoes significant recrystallization at higher temperatures, which affects the shape of the DSC curve. In contrast, this has no influence on the chemiluminescence so that the OIT can be determined with good reproducibility. An OIT of about 80 minutes can be estimated from the DSC curve. However, the value has however no real significance because here the DSC records the sum of the decomposition processes of two "different" samples. The CL intensity of the sample without the copper triangle is significantly higher after about 150 minutes. The slope of the CL intensity curve of the sample without copper



after 70 min (at 140 °C) after 90 min (at 140 °C) after 110 min (at 140 °C)

after 130 min (at 140 °C) after 190 min (at 140 °C) after 230 min (at 140 °C)

Fig. 3. Chemiluminescence of two samples of polypropylene at 140 °C. The dark triangle is due to a small piece of copper. This accelerates the decomposition of the polypropylene film.

is also steeper, indicating that the value for the activation energy is larger.
If the chemiluminescence observed occurs as a result of the recombination of two radicals, the square root of the CL intensity (sum of both samples) should be proportional to the DSC signal. This relationship is plotted in Figure 5. The figure shows that the square root of the CL intensity is in fact, to a good approximation, proportional to the DSC signal. After the maximum CL intensity has been reached, the relationship is again linear but with a different slope. This indicates that from this time onward other decomposition mechanisms operate.

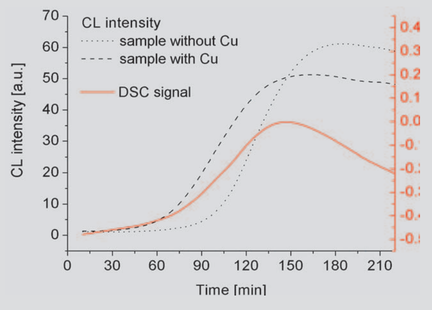


Fig. 4. Chemiluminescence curves for the two samples and the corresponding DSC curve. At 140 °C, the presence of copper reduces the OIT by about 40 minutes.

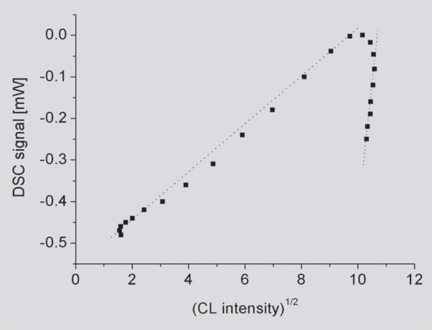


Fig. 5. Relationship between the DSC signal and the square root of the CL intensity. The CL intensity is proportional to the square of the radical concentration; and the DSC signal proportional to the radical concentration. (Assumption: chemiluminescence occurs during the termination reaction).

Figures 6 and 7 show the CL intensity as a function of time for samples with and without copper at different temperatures. The curves show that at 120 °C apparently two increases of the CL intensity occur. In addition, the slope of the CL intensity seems to increase with decreasing temperature. The images measured at 120 °C and 130 °C (not shown) indicate that at these temperatures the chemiluminescence no longer develops exclusively from the copper. Rather the first “centers of chemiluminescence” develop far away from the copper.

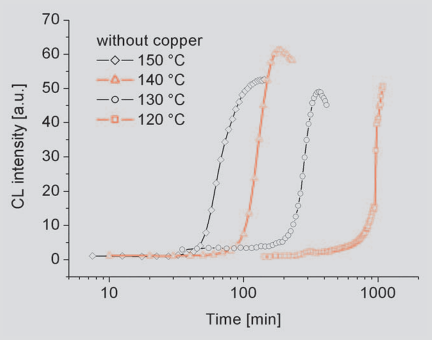


Fig. 6. CL intensity curves for PP without copper at different temperatures.

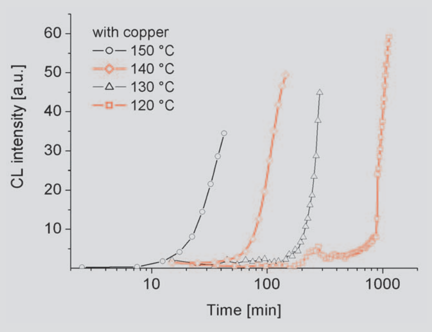


Fig. 7. CL intensity curves for PP with copper at different temperatures.

This result can be interpreted as follows. The decomposition of the stabilizer and the actual polymer take place at different kinetic rates. At higher temperatures these two processes overlap, which leads to an increase in the CL curve (and also in the DSC curve). At lower temperatures the stabilizer decomposes first (increase in the CL curve at 120 °C after about 250 minutes). The actual decomposition of the polymer does not however begin until after about 700 minutes, with a marked acceleration from about 1000 minutes onward. Comparison of the OIT of the samples with and without copper shows that, at higher temperatures, the copper has a significant effect (see Fig. 8). It seems that, in the presence of copper, the activation energy of decomposition changes, in particular at the higher temperatures. In contrast, at lower temperatures, the presence of copper seems to have no effect.

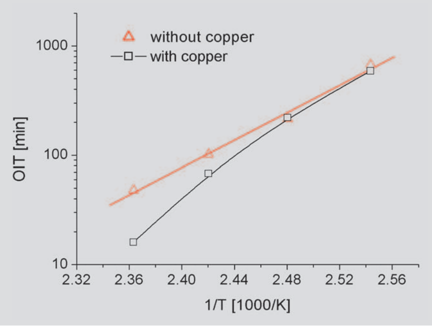


Fig. 8. Arrhenius diagram for the samples with and without copper. With decreasing temperature, the influence of the copper becomes negligible.

Conclusions

The decomposition of polymers can be observed by means of chemiluminescence measurements. This method allows the influence of stabilizers or other additives on the stability of polymers to be studied.

Compared with pure DSC measurements, chemiluminescence experiments with a CCD camera offer a number of interesting advantages.

1. Chemiluminescence occurs specifically only during the decomposition of the polymer. It is therefore appreciably more selective and specific than DSC, which measures the sum of different processes that proceed at the same time (e.g. in the above example, recrystallization and decomposition).
2. Chemiluminescence can be measured very efficiently with the detectors available today. This allows decomposition processes to be studied at lower temperatures, which is of course more relevant in practice.
3. The distribution of the observed chemiluminescence allows propagation and nucleation phenomena relating to the decomposition to be studied.
4. Chemiluminescence can be measured even with very small samples.

Measurements performed on a polypropylene film as an example showed that the decomposition spreads out from “decomposition nuclei”. Using polymer samples on which a small piece of copper had been placed, it was clearly demonstrated that at higher temperatures the copper functioned as a “decomposition nucleus”. At lower temperatures, the nucleating effect of the copper was insignificant.

Literature

[1] *D. J. Lacey, V. Dudler, Polymer degradation and Stability 51, 101, 1996*

[2] *G. A. Russell, J. Am. Chem. Soc. 79, 3871, 1956*

Elucidation of thermal transitions by hot-stage microscopy

Dr. Matthias Wagner, Dr. Rod Bottom

Introduction

DSC is an excellent tool for the analysis of phase transitions in materials. It can quickly and easily measure the temperatures at which melting and crystallization processes, and solid-solid and liquid crystal transitions occur. The results are displayed as exothermic or endothermic peaks in so-called DSC curves or thermograms. On the basis of the DSC curves alone, one does not of course know how the thermal events relate to the structure of the material. To obtain this information requires the use of an optical display system.

Hot-stage microscopy is a technique that is widely used for the characterization of thermal transitions. The possibility of directly observing the morphological change of the sample as it is heated makes it much easier to interpret the DSC curve in question. Changes in the shape and structure of crystals are seen as well as their size and number. Hot-stage microscopy also has the advantage that the sensitivity of the system is not influenced by different heating rates.

Current measurement techniques

In the past, the recording of photographic information was not exactly easy. It has long been possible to mount cameras and video cameras on microscopes but the archiving of pictures was restricted to photographic paper and video recorders. Today it is absolutely essential that the information is available in digital form. This means that the still and video images must be saved on a PC system. It is also essential to document other parameters such as the sample temperature, the magnification or scale, the sample name, and the time and date besides the actual images themselves.

For this reason, two new software packages are now available for the METTLER TOLEDO FP82 hot-stage system:
Studio Capture as an economical solution for standard applications and
analySIS® for the high-end user.

Both programs make use of the latest PC video recording technology and allow the user to observe images of the sample on the hot-stage on the PC screen and to save moving and still images directly to the hard disk of the computer. If the FP90 control instrument, used to control the FP82, is connected to the computer, both programs can read the sample temperature and overlay it onto each image and video frame.

A computer-aided system has the following advantages compared with conventional video recordings:

- Time-lapse video capture: In this mode, video images are captured at user-selectable video frame capture rates that are slower than with the simultaneous online display. This has the advantage that an hour's measurement time is compressed into a few minutes' playback time so that the transition process is clearer.
- Offline image capture: Individual images can be extracted afterward from videos downloaded directly to the PC. This avoids time-consuming observation of the online recording at slow heating rates.
- Excellent data availability: still images and even videos can be made available electronically, sent via e-mail, placed on Internet pages or copied to storage media. Modern data compression algorithms guarantee that the file size is still manageable even with long periods of measurement.
- 21 CFR 11 compliance: Pharmaceutical companies must comply with FDA regulations. With regard to electronically stored data and electronic signatures, this has to be done according to the FDA rules described under 21 CFR Part 11. For *Studio Capture*, a pharmaceutical package is available in which each image or each video is stored with user name, date and time. Videos and images are stored in a special folder in which files cannot be changed or deleted once they have been saved. In addition, an audit trail documents the saving of files and logging in and out with date, time and user identification.

AnalySIS as *analySIS* FDA in addition provides the complete set of tools necessary for compliance with the FDA 21 CFR Part 11 regulations.

Application examples

Two examples of applications performed with both systems will now be described:

Sulfapyridine

Sulfapyridine belongs to a class of drugs with a powerful antibacterial action known as sulfonamides. The most well known preparation in which it is used today is sulfasalazine, a substance with a structure consisting of sulfapyridine and salicylic acid. It is used to treat rheumatic arthritis. Studies of the polymorphism of sulfapyridine can be found in the pharmacological literature [e.g. 1].

Sulfapyridine exhibits crystallization and several solid-solid transitions as soon as it is heated from the glassy state. These transitions can be easily recognized in the DSC curve (Fig. 1), but it is not possible to know which transition is actually occurring at any moment. If one uses an FP82 with image display system, it is possible to identify the individual processes that correspond to each the DSC peak. Figure 2 shows the sample at 120.1 °C. Spherulite crystals have grown out of the glassy phase. At 176.6 °C (Fig. 3) the spherulites have changed through melting and recrystallization to the new rhombic modification.

This application was performed with the *analySIS* software.

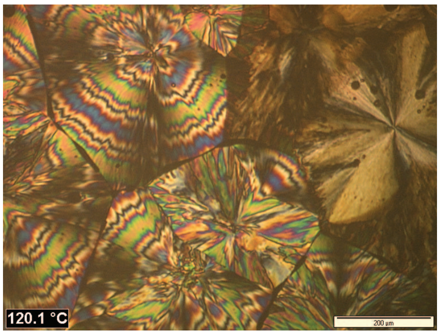


Fig. 2. Sulfapyridine crystals at 120.1 °C.

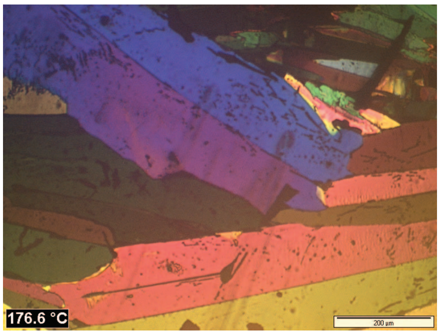


Fig. 3. Sulfapyridine crystals at 176.6 °C.

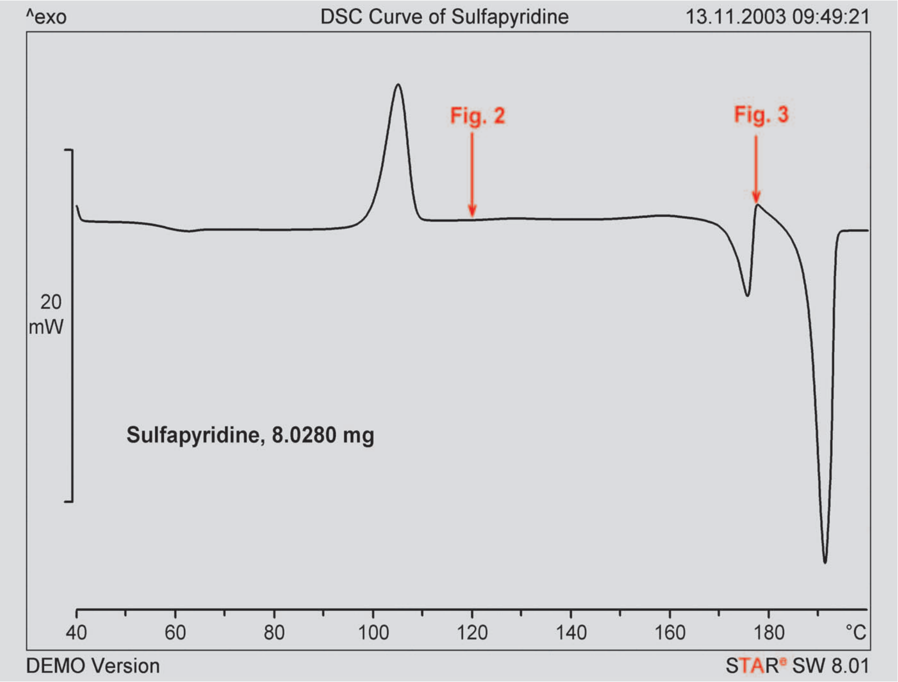


Fig. 1. DSC curve of sulfapyridine.

Chlorpropamide

Chlorpropamide is a drug that is used to treat diabetes mellitus. It is an antidiabetic agent that belongs to a class of substances known as sulfonylureas. This group of drugs acts by augmenting insulin secretion, which lowers the blood sugar level in the body.

From the scientific literature [2, 3] it is well known that chlorpropamide can exist in up to five different modifications, each of which exhibits different solubility behavior. This significantly influences the release velocity of the drug. For example, at body temperature (37 °C), modification II (melting point 125 °C) dissolves 55% more easily than modification III (melting point 123 °C).

This is the reason why the analysis of the polymorphism of active pharmaceutical substances is important. The individual polymorphic forms and their properties can be optimally observed using hot-stage microscopy.

The DSC curve in Figure 4 shows the polymorphic transitions of at least two forms of

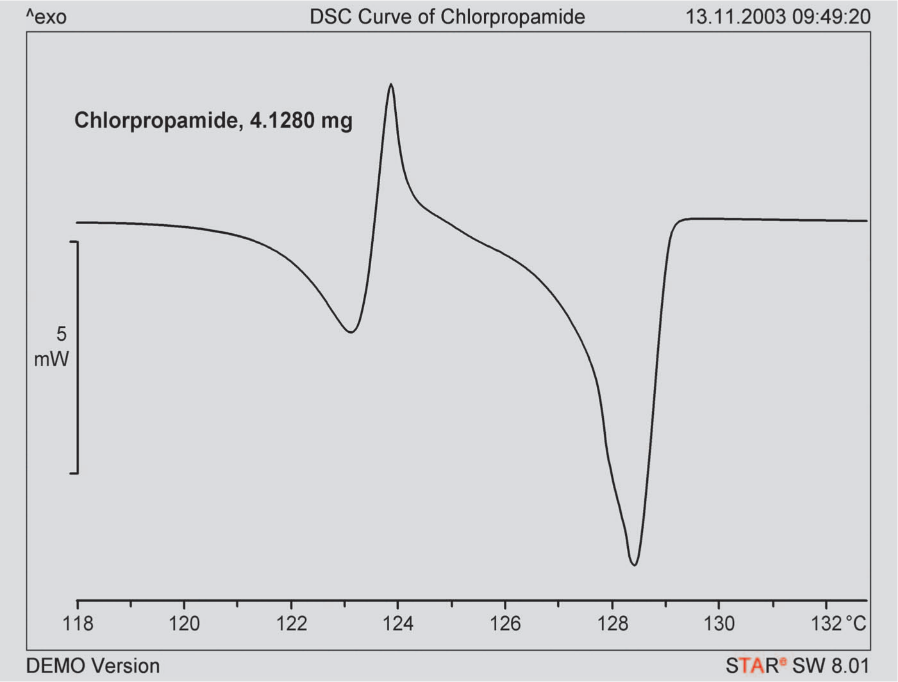


Fig. 4. DSC curve of chlorpropamide.

chlorpropamide recorded during the first heating run.
Another important point is to investigate the crystallization behavior as a function of cooling rate.
Chlorpropamide crystallizes readily from the melt. The sample can be cooled at constant rate or held isothermally. Crystals of different morphology form depending on the cooling profile.

Figures 5 to 7 show different crystalline forms of chlorpropamide that were obtained through isothermal crystallization at 100, 90 and 80 °C. Both the size and the number of crystals are influenced by temperature. At high temperatures, nucleation rate is low and crystal growth rate high so that a small number of large crystals are formed (Fig. 5). The lower the temperature, the higher the nucleation rate and the lower the crystal growth rate. This can be seen from the increasing number of small crystals at lower temperature (Figs. 6 and 7).

This application was performed with the *Studio Capture* software.

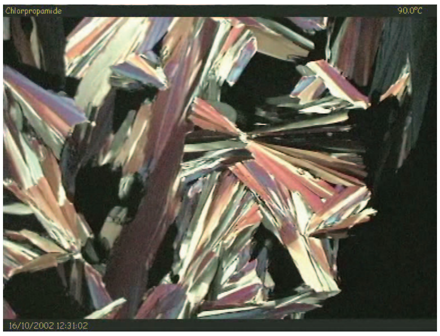


Fig. 6. Chlorpropamide crystals cooled from 135 °C at 10 K/min and then held isothermally at 90 °C.

Fig. 5. Chlorpropamide crystals cooled from 135 °C at 10 K/min and then held isothermally at 100 °C.

Fig. 7. Chlorpropamide crystals cooled from 135 °C at 10 K/min and then held isothermally at 80 °C.

Summary

Hot-stage microscopy is an extremely valuable tool for the characterization of polymorphic forms and the study of melting and crystallization processes. The advantages of this technique are greatly improved in combination with modern image and video recording technologies. The exchange of image data in electronic form then becomes a very simple matter.

Literature

[1] *Burger, K. Schulte u. R. Ramberger: Study of themodynamic relationships between five polymorphic modifications of sulfapyridine by DSC. J. Therm. Anal. 19, 475 - 484 (1980)*
[2] *Burger: Influence of polymorphism of the active ingredient on the properties of tablets: chlorpropamide, Part I. Pharm. Ind. 38, 306 - 312 (1976)*
[3] *Burger: Influence of polymorphism of the active ingredient on the properties of tablets: chlorpropamide, Part II. Pharm. Ind. 38, 639 - 643 (1976)*

TA Tip on the sample robot: change in moisture content before analysis

Dr. R. Riesen

Sample changers are often used in thermal analysis when large series of samples have to be measured. The advantage is that the samples can be prepared all together at the same time and the analyses performed overnight or even over the weekend. Especially in lengthy thermogravimetric experiments, the samples ready for measurement on the turntable are however exposed to atmospheric conditions for longer periods. During this time the samples may lose volatile components such as moisture, or conversely, if hygroscopic, absorb moisture. Both processes have a direct influence on the accuracy of the analytical results.
There are two ways to prevent such effects from occurring with samples stored on the turntable of the sample robot:

1. The samples are hermetically sealed in aluminum crucibles and the lid is not pierced until just before the measurement. To do this, the sample robot must be equipped with the crucible lid piercing kit (see Fig. 1). This method is particularly suitable for the determination of moisture, for example in pharmaceutical substances.

Fig. 1. The sample robot is equipped with a needle that pierces the special aluminum lid immediately before the measurement.

2. The samples are stored in ceramic crucibles with special aluminum lids. The sample robot removes the lid during the measurement.

The following experiments performed with polyamide 6 illustrate the effect of sample storage in an open crucible and demonstrate the importance of the crucible lid piercing kit.

Determination of the moisture content of polyamide 6

Depending on the environmental conditions, polyamide 6 can absorb up to 10% moisture, which of course results in large changes in its physical properties. With material used for clothing, this storage effect may even be desirable. The moisture content of the sample was analyzed thermogravimetrically by performing multiple determinations with the sample robot. Small granules of PA 6 weighing 8 to 10 mg that had been stored at 100% relative humidity were placed in 40-µl aluminum crucibles. The crucibles of 8 samples (Samples A) were hermetically sealed with the special lids (for automatically piercing prior to measurement); 8 other crucibles (Samples B) were sealed with standard lids that had 0.35-mm holes. The A and B samples were analyzed alternately in order to demonstrate the effect of storage time on the sample robot turntable. Each sample was heated from 30 to 230 °C at 5 K/min and the weight loss curve recorded. Figure 2 summarizes and compares the measured curves all together in one diagram.

The B samples lose moisture and dry during storage because the lid is effectively open. Only 4.6% moisture was for example measured in the B sample stored for 20 hours. In contrast the hermetically sealed A samples show a constant moisture content of 9.23% (standard deviation 0.11%). The slight differences in the TGA curves of the A samples are due to minor differences in the sample material.

Figure 3 summarizes the results; the measured moisture content of each sample is plotted against storage time on the sample turntable. The drying rate can be estimated from an exponential regression curve over the B samples. For example, about 6% of the moisture originally present in the sample has already been lost after storage for one hour in an open crucible.

Conclusions

By definition, thermogravimetric measurements have to be performed with open crucibles. Samples that undergo weight changes under ambient conditions (e.g. due to changes in moisture content, vaporization of volatile components) must therefore be measured immediately. When series of samples are measured with the sample robot, the special lid piercing kit is very advantageous. It ensures that the samples remain hermetically sealed during storage on the turntable until the measurement is performed. Otherwise weight changes are measured that do not properly represent the original sample.

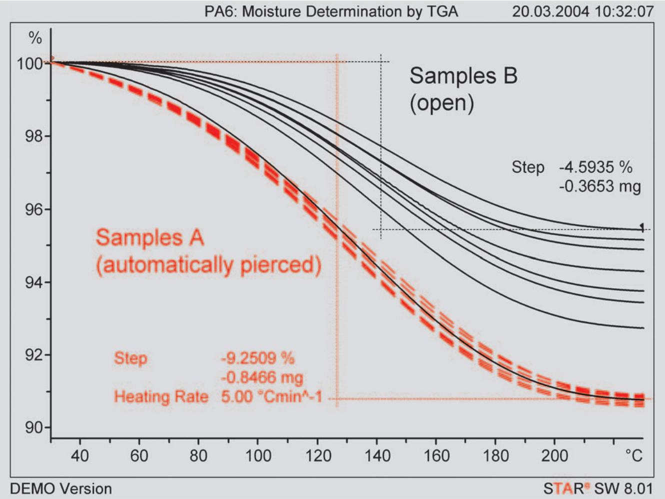


Fig. 2. The TGA weight loss curves of PA 6 (see text). The continuous black lines show the curves of the samples sealed with lids with 0.35-mm holes (Samples B), and the dashed red lines the curves of hermetically sealed samples (Samples A) that were pierced automatically with a 0.1-mm needle immediately before measurement.

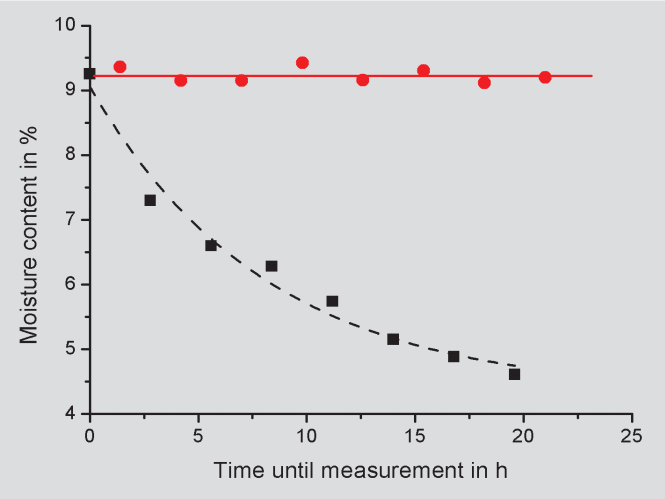


Fig. 3. Moisture content of PA 6 samples measured by TGA. The red circles show the results of samples that were stored in hermetically sealed crucibles (Samples A). The black squares are the results of the samples stored in open crucibles (Samples B). The black dashed curve is the exponential regression curve: $m = 4.32 + 4.74 * \exp(-t/8.146)$ with m in % and t in hours.

Dates

Exhibitions, Conferences and Seminars – Veranstaltungen, Konferenzen und Seminare

PITTCON 2005	February 27-March 4, 2005	Orlando (Florida, USA)
8th European Symposium on Polymer Blends and Eurofillers	May 9-12, 2005	Bruges (Belgium)
ILMAC 2005	May 24-27, 2005	Basel (Switzerland)
Workshop AIM «Tecniche Innovative di Caratterizzazione di Materiali Polimerici»	May 23-27, 2005	Gargnano (Italy)
IRC 2005	June 7-9, 2005	MECC Maastricht (Netherlands)
VI Congreso Nacional de Materiales Compuestos	June 27-29, 2005	Valencia (Spain)
MEDICTA 2005	July 2-6, 2005	Thessaloniki (Greece)
Khimia 2005	September 5-9, 2005	Moscow (Russia)
XVII Convegno Nazionale AIM	September 11-15, 2005	Naples (Italy)
NATAS 2005	September 17-21, 2005	Universal City (California, USA)
RICH-MAC 2005	October 4-7, 2005	Milan (Italy)
Expoquimia 2005	November 14-18, 2005	Barcelona (Spain)

TA Customer Courses and Seminars in Switzerland – Information and Course Registration: TA-Kundenkurse und Seminare in der Schweiz – Auskunft und Anmeldung bei:

Frau Esther Andreato, Mettler-Toledo, Analytical, Schwerzenbach, Tel: ++41 1 806 73 57, Fax: ++41 1 806 72 40, e-mail: esther.andreato@mt.com

Courses / Kurse

SW Basic/TMA/DMA Basic (Deutsch)	7. März 2005	SW Basic/TMA/DMA Basic (English)	March 14, 2005
DMA Advanced/TGA (Deutsch)	8. März 2005	DMA Advanced/TGA (English)	March 15, 2005
TGA-MS/DSC Basic (Deutsch)	9. März 2005	TGA-MS/DSC Basic (English)	March 16, 2005
DSC Advanced/TGA-FTIR (Deutsch)	10. März 2005	DSC Advanced/TGA-FTIR (English)	March 17, 2005
SW Advanced (Deutsch)	11. März 2005	SW Advanced (English)	March 18, 2005
SW Basic/TMA/DMA Basic (Deutsch)	19. September, 2005	SW Basic/TMA/DMA Basic (English)	September 26, 2005
DMA Advanced/TGA (Deutsch)	20. September, 2005	DMA Advanced/TGA (English)	September 27, 2005
TGA-MS/DSC Basic (Deutsch)	21. September, 2005	TGA-MS/DSC Basic (English)	September 28, 2005
DSC Advanced/TGA-FTIR (Deutsch)	22. September, 2005	DSC Advanced/TGA-FTIR (English)	September 29, 2005
SW Advanced (Deutsch)	23. September, 2005	SW Advanced (English)	September 30, 2005

TA-Kundenkurse und Seminare in Deutschland

Für nähere Informationen wenden Sie sich bitte an: Frau Petra Fehl, Mettler-Toledo GmbH, Giessen, Tel: ++49 641 507 404, e-mail: petra.fehl@mt.com

Anwenderworkshop DSC	26./27.04.2005 Giessen	11./12.10.2005 Giessen
Anwenderworkshop TGA	28./29.04.2005 Giessen	
Fachseminar «Thermoanalytische und rheologische Messmethoden für die Materialcharakterisierung in Qualitätssicherung, Produktentwicklung sowie F&E»		September 2005

Weitere Informationen zu diesen Veranstaltungen finden Sie unter: www.labtalk.de

Cours et séminaires d'Analyse Thermique en France

Renseignements et inscriptions par

Christine Fauvarque, Mettler-Toledo S.A., 18-20 Av. de la pépinière, 78222 Viroflay Cedex, Tél: ++33 1 3097 1439, Fax: ++33 1 3097 1660

Cours clients

DMA/TMA et le logiciel STAR^e	3 octobre 2005 Viroflay (France)	TGA et logiciel STAR^e	6 octobre 2005 Viroflay (France)
DSC les bases et logiciel STAR^e	4 octobre 2005 Viroflay (France)	Logiciel STAR^e	7 octobre 2005 Viroflay (France)
DSC avancé et logiciel STAR^e	5 octobre 2005 Viroflay (France)		

Cursos y Seminarios de TA en España

Para detalles acerca de los cursos y seminarios, por favor, contacte con:
Francesc Catala, Mettler-Toledo S.A.E., Tel: ++34 93 223 76 00, e-mail: francesc.catala@mt.com

Seminario de aplicaciones TA:	Febrero 22, 2005 Sevilla	Seminario de aplicaciones TA:	Octubre 18, 2005 Barcelona
Seminario de aplicaciones TA:	Febrero 23, 2005 Granada	Seminario para usuarios STAR^e:	Octubre 19, 2005 Barcelona
Seminario de aplicaciones TA:	Marzo 1, 2005 Santiago de Compostela	Seminario de aplicaciones TA:	Octubre 25, 2005 Madrid
Seminario de aplicaciones TA:	Marzo 1, 2005 Bilbao	Seminario para usuarios STAR^e:	Octubre 26, 2005 Madrid

Corsi e Seminari di Analisi Termica in Italia

Per ulteriori informazioni Vi preghiamo di contattare:
Marina Varallo, Mettler-Toledo S.p.A., Novate Milanese, Tel: ++39 02 333 321, Fax: ++39 02 356 2973, e-mail: marina.varallo@mt.com

Corsi per Clienti:

DSC base	1 Marzo 2005	7 Giugno 2005	27 Settembre 2005	Novate Milanese
DSC avanzato	2 Marzo 2005	8 Giugno 2005	28 Settembre 2005	Novate Milanese
TGA	3 Marzo 2005	9 Giugno 2005	29 Settembre 2005	Novate Milanese
TMA	4 Marzo 2005	10 Giugno 2005	30 Settembre 2005	Novate Milanese

Seminari di Analisi Termica

«L'Analisi Termica nell'Industria Farmaceutica - Applicazioni e novità strumentali»	Roma,	8 Febbraio 2005	Milano,	22 Febbraio 2005
«Tecniche termoanalitiche per la caratterizzazione dei materiali polimerici - Applicazioni e novità strumentali»	Roma,	9 Febbraio 2005	Milano,	23 Febbraio 2005

TA Customer Courses and Seminars in the UK

For details of training courses and seminars, please contact:
Rod Bottom, Mettler-Toledo Ltd, Leicester, Tel: ++44 116 234 5025, Fax: ++44 116 236 5500, e-mail: rod.bottom@mt.com

DSC training courses

DSC Basic	1 March, 2005	Leicester	DSC BASIC	25 October, 2005	Leicester
DSC Basic	2 March, 2005	Leicester	DSC BASIC	26 October, 2005	Leicester

TA Customer Courses and Seminars in Japan

For details of training courses and seminars please contact:
Yoshiaki Suzuki at Mettler-Toledo Japan, Tel: ++81 3 5762 0746, Fax: ++81 3 5762 0758, or by e-mail to yoshiaki.suzuki@mt.com

TA/FP Workshop	February 22, 2005	Tokyo Service Center	STAR^e Infoday Seminar	June15, 2005	Tokyo Technical Center
TA/FP Workshop	February 25, 2005	Osaka Service Center	STAR^e Infoday Seminar	June17, 2005	Osaka Branch

TA Customer Courses and Seminars

Thermal Analysis Training based on the STAR^e System is being offered at various locations. For information, please contact:

Belgium: Annick Van Hemelrijck, Tél: ++32 2 334 02 01 or e-mail: annick.vanhemelrijck@mt.com

Ceské Republice: Helena Beránková, Tel: +420 272 123 152 or e-mail: helena.berankova@mt.com

China: Lu LiMing, Tel: ++86 21 64850435 or e-mail: liming.lu@mt.com

Latin America: Francesc Català, Tel: ++34-932 237 615 (Spain) or e-mail: francesc.catala@mt.com

Malaysia: Ms Candace Leong, Tel. (603)-78455773 or e-mail: candace.leong@mt.com

Netherlands: Hay Berden of Ko Schaap, Tel: ++31 344 63 83 63 or e-mail: hay.berden@mt.com

Österreich: Frau Geraldine Braun, Tel. +43-1-604 19 80 - 33 or e-mail: geraldine.braun@mt.com

Singapore: Edwin Ho, Tel. ++ 65 8900011 or e-mail: edwin.ho@mt.com

Sweden: Fredrik Einarsson, Tel: ++46 455 30 0080 or e-mail: fredrik.einarsson@mt.com

Taiwan: Kimmy Wu, Tel: ++886 2 6578898 or e-mail: kimmy.wu@mt.com

Thailand: W. Techakasembundit, Tel. ++ 662 7230336 or e-mail: wutti.techakasembundit@mt.com

USA and Canada: Tom Basalik, Tel. +1 614 438 4687 or e-mail to: tom.basalik@mt.com

Editorial team


Dr. J. Schawe,
Physicist


Dr. R. Riesen,
Chem. Engineer


J. Widmann,
Chem. Engineer


Dr. M. Schubnell,
Physicist


Dr. M. Wagner,
Chemist


Dr. D. P. May,
Chemist


Ni Jing,
Chemist


Marco Zappa,
Material Scientist


Urs Jörimann,
Electr. Engineer

METTLER-TOLEDO GmbH, Analytical, Sonnenbergstrasse 74, CH-8603 Schwerzenbach, Switzerland
Kontakt: urs.joerimann@mt.com, Tel: ++41 1 806 73 87, Fax: ++41 1 806 72 60
Internet: http:/www.mt.com/ta