UserCom

1/2002

Information for users of METTLER TOLEDO thermal analysis systems

Dear Customer

This year is a very special year for all of us in thermal analysis. For the first time ever in our company's history, we will be introducing a completely new Dynamic Mechanical Analyzer (DMA). Despite enormous pressure, we have taken the time necessary to develop a DMA that is clearly superior to the present generation of commercially available instruments and that opens up exciting new application possibilities.
Besides this, two interesting new developments, IsoStep™ and an enhanced version of Model Free Kinetics, are now available for DSC and TGA.

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Contents

Interpreting DMA curves, Part 1

Georg Widmann, Dr. Jürgen Schawe, Dr. Rudolf Riesen

The first part of this work introduces the technique of dynamic mechanical analysis (DMA) and deals with non-isothermal DMA measurements. The second part (UserCom16) will cover various aspects of isothermal measurements, concentrating primarily on frequency-dependent elasticity.

Introduction

By the term **elasticity** we mean the way in which materials change their shape through the action of external forces. The **modulus of elasticity** of a material is the ratio of the mechanical stress to the relative deformation.
In **Dynamic Mechanical Analysis**, DMA, a sample is subjected to a sinusoidal mechanical deformation of frequency, f, and the corresponding forces measured. Conversely, the sample can be subjected to a defined force amplitude and the resulting deformation measured.

Measurement modes

A number of different measurement modes are used:

- Shear for samples with a shear modulus in a very large range from about 1 kPa to 2 GPa. This allows viscous liquids and even solid samples, e.g. polymers in the glassy state, to be measured.
- Three-point bending for stiff samples with a modulus of elasticity of up to 1000 GPa.
- Single and dual cantilever bending for samples that deform too strongly with three-point bending.
- Tension for thin bars, films and fibers.
- Compression for samples with a modulus of elasticity of up to about 1 GPa.

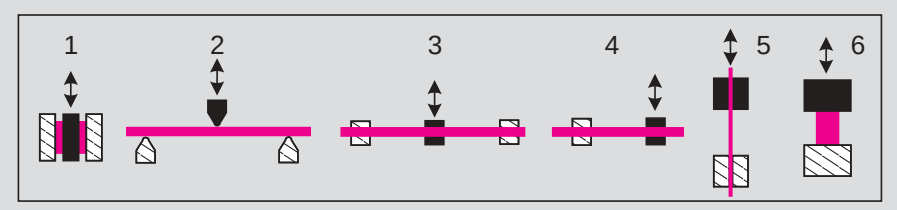

Fig. 1. DMA/SDTA861^e measurement modes: 1 shear; 2 three-point bending; 3 dual cantilever (similar to bending but the sample is fixed); 4 single cantilever; 5 tension for thin bars, films and fibers; 6 compression. The clamping assembly is colored black and the sample red. The hatched areas show the parts of the clamping assemblies that remain fixed in position.

The quantities measured

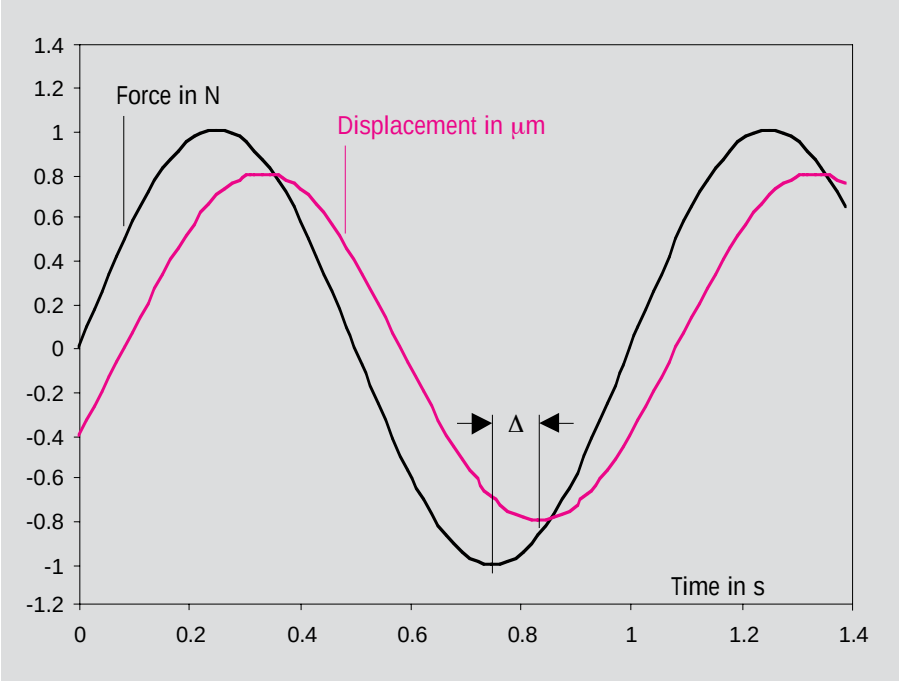

Fig. 2. Force and displacement at a frequency (f) of 1 Hz. The phase shift, δ, can be calculated from the time delay, Δ, using the equation $\delta = 2\pi f\Delta$.

The raw data, i.e. the measured force and displacement amplitudes, F_a and L_a, and their phase shifts, δ, are used to calculate the desired material properties:

- Complex modulus (M*): modulus of elasticity, Young's modulus (E*) or shear modulus (G*)
- Storage modulus, M′, proportional to the energy stored elastically and reversibly
- Loss modulus, M", proportional to the energy transformed into heat and irreversibly lost
- Loss factor, tan δ. With completely elastic materials no phase shift, δ, occurs; completely viscous materials show a 90° phase shift. The loss factor of viscoelastic materials is between 0 and infinity ($\delta = 90°$).

The term tan δ corresponds to the ratio of M" to M'.

The moduli are calculated according to the following formulas:

$$|M^*| = \frac{F_a}{L_a}\, g \qquad M' = |M^*| \cos\delta$$

$$M'' = |M^*| \sin\delta \qquad \tan\delta = \frac{M''}{M'}$$

where g is known as the geometry factor calculated from the sample dimensions.

E and G are related by Poisson's ratio, µ:

$$E = 2\,(1 + \mu)\,G$$

For most isotropic materials, µ lies between 0.2 and 0.5, and E is 2.4 to maximum 3 times greater than G. In the rubbery-elastic region of unfilled materials, $E \approx 3\,G$ and in the glassy state $E = 2.7\,G$.
With anisotropic materials, e.g. unidirectional fiber reinforced plastics, E can be more than one hundred times larger than G.

If a material is heated, the storage modulus decreases step-wise by several orders of magnitude. The step corresponds to a peak in the loss modulus. If the transitions are frequency-dependent, they are in fact relaxation transitions, which with increasing frequency shift to higher temperatures.

Measurement details

- Usually with DMA measurements, the measurement is performed at constant **displacement amplitude**, and a **maximum force** is set that should not be exceeded even with stiff samples.
  An unsuitable choice of the displacement or force amplitude can affect the measurement accuracy. Amplitudes greater than 1 µm and 10 mN are optimal, as long as the displacement amplitude does not exceed 1% of the corresponding sample dimension. With larger amplitudes, the modulus can change (non-linearity of the sample).

- **Heating rates of** ≤ 3 K/min are usually used because of the low thermal conductivity of plastics and the relatively large samples – except for trial measurements. The same applies to cooling measurements.
- To determine the **frequency dependence**, measurements are performed with several frequencies. The frequencies can be either mixed (simultaneous multi-frequency mode) or applied individually one after the other (sequential frequency series).

Besides measurements with a dynamic temperature program, the DMA/SDTA861^e can also perform isothermal measurements with increments of increasing or decreasing

- frequency,
- displacement amplitude and
- force amplitude.

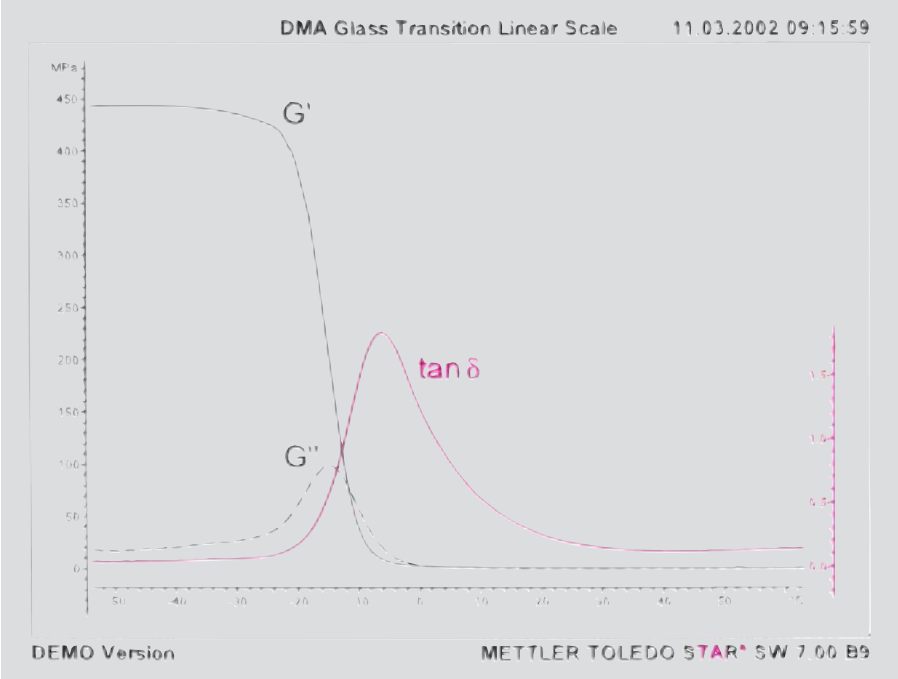

Fig. 3. The linear presentation of the modulus overemphasizes the region with high values. The point of inflection of the storage modulus corresponds approximately to the maximum of the loss modulus. The latter is often referred to as the glass transition temperature, T_g, at the frequency concerned. Because tan δ = G" / G', the maximum of tan δ is at higher temperature. At the point of intersection of G' and G", tan δ = 1. Sample: SBR, 1 Hz, 2 K/min.

The presentation of DMA curves

Since moduli can change by several orders of magnitude, a linear presentation cannot adequately display the measurement data (Fig. 3). For example, a step of 1 GPa to 10 MPa cannot be distinguished from a step of 1 GPa to 1 MPa. In the logarithmic display, however, such differences can be easily seen (Fig. 4).

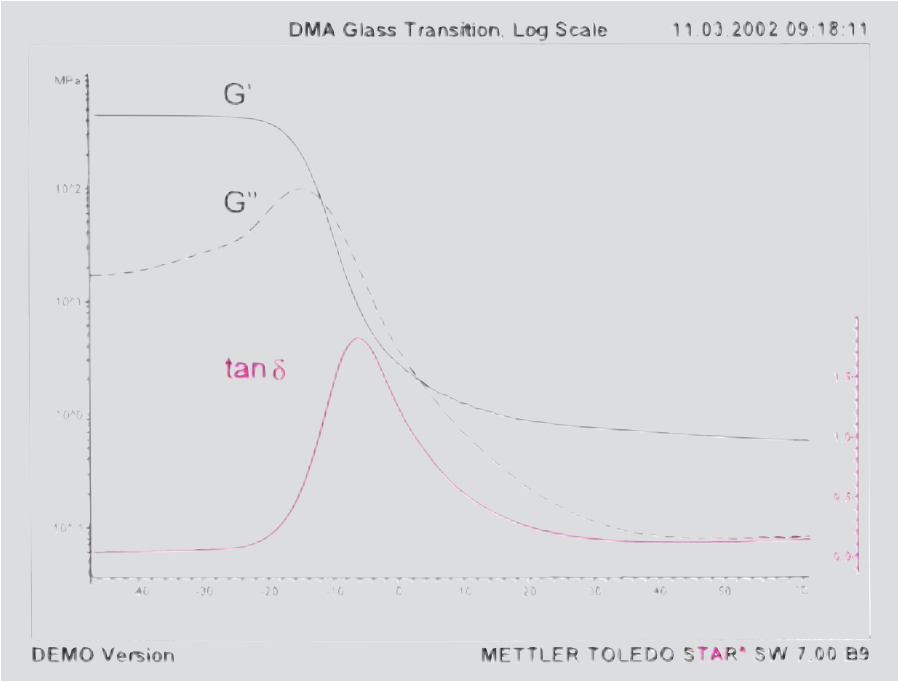

Fig. 4. Same measurement as in Figure 3, but displayed in the usual logarithmic presentation. Compared with the linear presentation, the low-value region of the modulus now appears scale-expanded. In this presentation, T_g corresponds to the onset of the decrease of G'. The loss factor in the rubbery-elastic state is clearly larger than in the glassy state. The ordinate of the loss factor is displayed on the right of the diagram.

Interpretation of DMA curves with a dynamic temperature program

The storage modulus of commonly used materials decreases with increasing temperature. The storage modulus of metals used for constructional purposes such as steel or aluminum alloys hardly changes up to temperatures of 400 °C (Fig. 5). Stepwise changes are caused by relaxation transitions (e.g. glass transition) or phase transitions (e.g. melting and crystallization). Peaks in the loss modulus and the loss factor, tan δ, correspond to the steps in the storage modulus.

Amorphous materials go through a glass transition on heating or cooling. The modulus changes by one to four decades. The same occurs when the crystallites of semicrystalline polymers melt. Such phase transitions do not of course exhibit the large frequency dependence of relaxation transitions.

Commonly used **thermoplastics** such as polyvinylchloride and polystyrene have a modulus of elasticity of about 3 GPa. Their glass transition temperatures lie

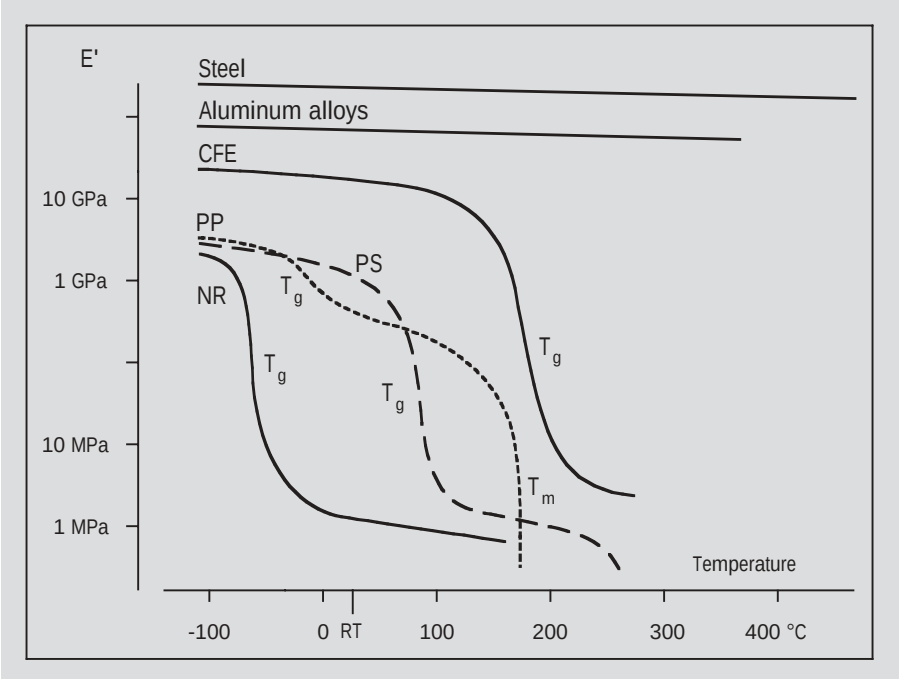

Fig. 5. The storage part of the modulus of elasticity, E', of various materials as a function of temperature. The E' of steel decreases only slightly (210 GPa at room temperature, 177 GPa at 400 °C). In contrast, the storage modulus (proportional to stiffness) of organic materials decreases rapidly in one or more steps. T_g is the glass transition temperature and T_m the melting temperature. CFE is a carbon fiber-reinforced epoxy resin, PP polypropylene, PS polystyrene, and NR natural rubber.

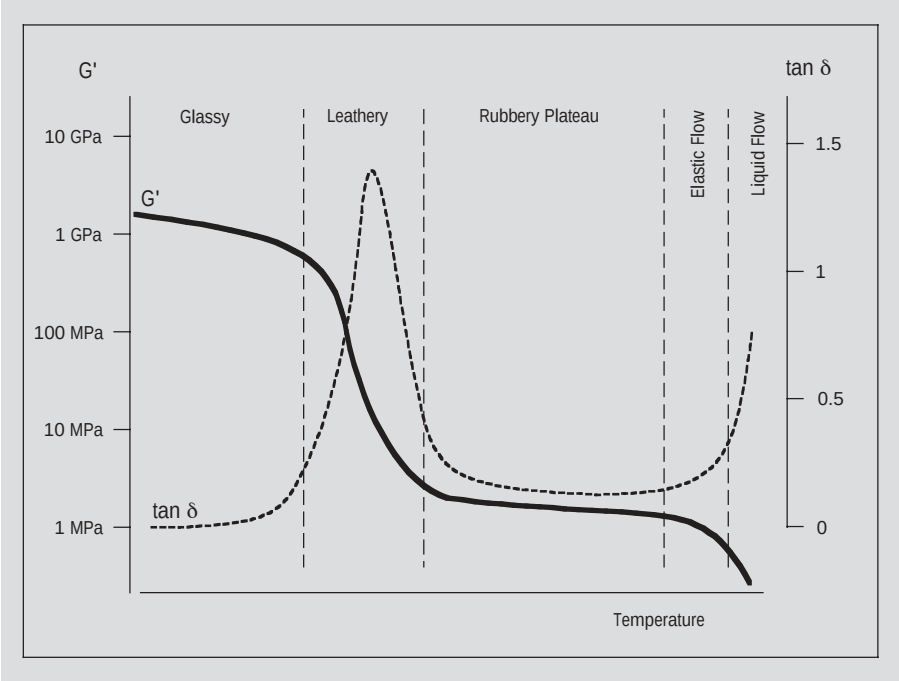

Fig. 6. Theoretical behavior of an amorphous thermoplastic. In the glassy state it exhibits almost ideal elasticity. At the glass transition it becomes leathery and afterward behaves like soft elastic rubber. The width of the rubbery-elastic region increases with increasing average molar mass. If the degradation temperature of the thermoplastic is sufficiently high, elastic flow begins. The viscoelastic region extends from the leathery to the rubbery-elastic state through to the region of elastic flow.

between room temperature and approx. 200 °C. At about 100 K above the glass transition, the polymers flow and can be plastically deformed (Fig. 6).

Elastomers such as natural rubber, NR, exhibit a glass transition below room temperature and, because of chemical cross-linking, do not flow (Fig. 5). This low degree of cross-linking occurs during vulcanization of the originally thermoplastic rubber.

Thermosets such as epoxy resins are three-dimensionally cross-linked macromolecules. Their glass transition region is significantly above room temperature. Due to their three-dimensional cross-linking, they do not flow when the temperature is increased. The starting materials of thermosets consist of several different components, which are usually referred to as the "resin" and the "hardener" or "curing agent". When the thermoplastic starting materials harden or cure, a three-dimensional network is produced and the glass transition temperature increases by 50 K to 300 K (Fig. 10).

If the macromolecules are mainly aligned as a result of processing, they are referred to as orientated polymers. They are then **anisotropic**, i.e. their properties are orientation-dependent. This also applies to fiber-reinforced polymers.

With amorphous and semicrystalline materials, several relaxation transitions are observed; the transition at the highest temperature is known as **α-relaxation** or the **glass transition**. It is assigned to cooperative molecular movement over a range of several nanometers, while the weaker **secondary relaxation** or **β-relaxation** is due to the movement of short segments.
Relaxation processes are **frequency-dependent**, in contrast to melting processes, crystallization and chemical reactions, and can therefore be easily identified. The glass transition shifts by 5 K to 10 K per frequency decade. β-relaxation (Fig. 7) is even more frequency-dependent with values of at least 10 K/decade.

Incompatible **mixtures** of amorphous polymers and block copolymers show the glass transitions of the individual components. Compatible mixtures and random copolymers exhibit only one glass transition between the glass transitions of the individual components (Fig.8).

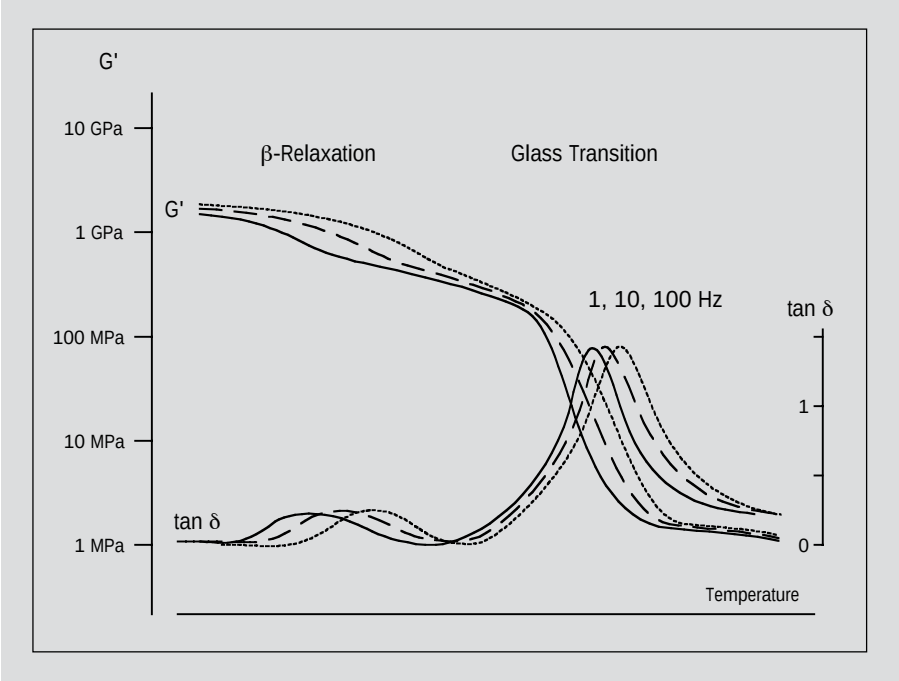

Fig. 7. Shear modulus and loss factor measured at three frequencies differing by a decade. The β-relaxation shifts more strongly than the glass transition. Usually the loss factor only exceeds a value of 1 at the glass transition.

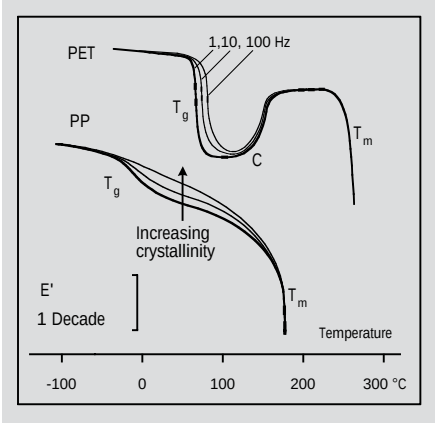

Fig. 9.
Above: Amorphous polyethylene terephthalate softens at the glass transition and crystallizes at the point C. Afterward, the modulus increases somewhat because crystallites with a greater degree of perfection are formed. Finally the crystallites melt. Only the glass transition shifts with increasing frequency.
Below: The modulus of a semicrystalline thermoplastic such as polypropylene increases with increasing crystallinity. With highly crystalline materials, the change at the glass transition becomes smaller.

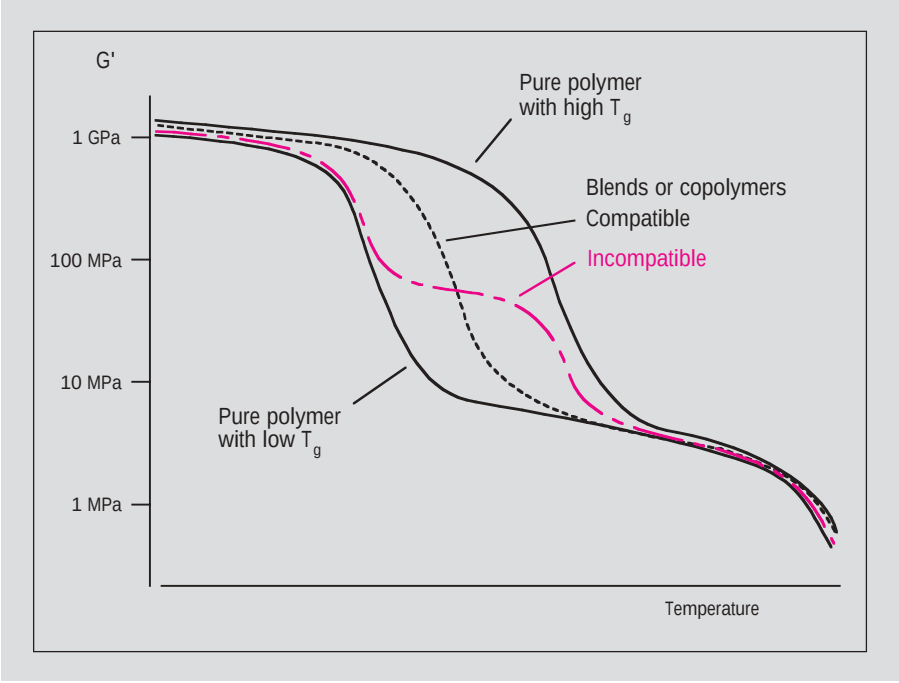

Fig. 8. Compatible and incompatible polymer mixtures or copolymers compared with the basic pure polymers.

The relative content of such samples can be estimated from the curves of pure polymers.

Semicrystalline thermoplastics have properties that depend on the **crystallinity**. Some plastics, e.g. polyethylene terephthalate, remain amorphous after shock cooling from the melt, and then crystallize when heated to above their T_g (Fig. 9).

With **thermosets**, the main interest is in the behavior of the thermoplastic starting materials, the increase of the modulus on gelation, and the glass transition of the fully cured thermoset (Fig.10). Such measurements, which can cover a modulus range of more than 4 decades, can only be performed in the shear mode.

Final comments

DMA measurements provide an insight into temperature- and frequency-dependent molecular movement, and also supply the engineer with information on material properties regarding stiffness, damping behavior and the range of temperature in which materials can be used. DMA measurements show especially well how the glass transition depends on factors such as moisture or the degree of curing (see UserCom11, pages 8 to13).

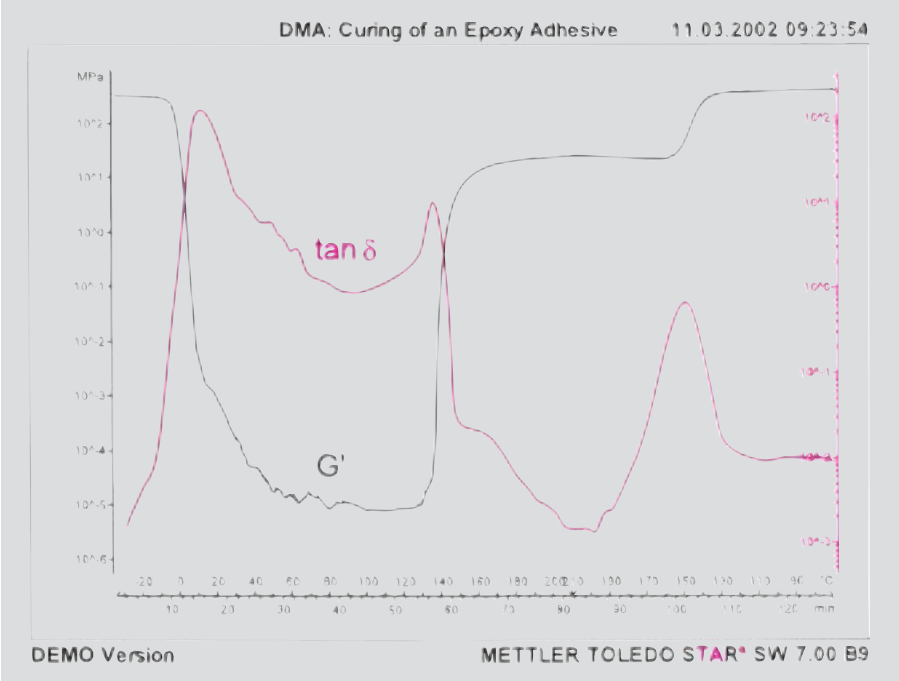

Fig. 10. Shear modulus and loss factor of the liquid (at room temperature) epoxy resin system DGEBA, (diglycidylether of bisphenol A) and DDM, (diaminodiphenylmethane). Heating and cooling rates of 3 K/min, frequency 10 Hz, sample geometry: 11 mm diameter, 0.2 mm thick. At the starting temperature of -50 °C, the 2-component mixture is frozen in the glassy state, and becomes liquid above 0 °C. At the same time, the storage modulus decreases by 7 decades and the loss factor increases by 5 decades. During curing, the resin gels at 140 °C. After reaching the end temperature of 210 °C, the thermoset is cooled to below its glass transition temperature of 145 °C, whereby the modulus shows a further increase.

When unknown samples are measured with DMA, it is always a good idea to perform a DSC measurement at 20 K/min over a relative large temperature range. From the DSC curve one can often choose a reasonable temperature range for the DMA measurements to prevent the sample from melting completely or decomposing in the DMA. This also gives one the opportunity to perform a second measurement on the same sample, if need be, even with new sample geometry.

In general, DSC measurements aid the interpretation of DMA curves (and vice versa). DSC and DMA measurements provide different information and complement one another ideally; one technique cannot however replace the other.

New in our sales program

STARe V7.00

The new Windows2000 and WindowsNT compatible STARe SW Version V7.00 replaces all previous STARe Versions ≤ V6.20 (Unix or WindowsNT).
Data compatibility with all previous software versions is guaranteed. You can therefore easily transfer your existing data to the new software and if necessary reprocess it.

The new software version provides you with the following possibilities:

- Control of the METTLER TOLEDO DMA/SDTA861e
- DMA curve display and evaluation
- New and enhanced version of Model Free Kinetics (the Advanced Model Free Kinetics software option)
- New IsoStep™ evaluation, which separates kinetic effects from changes in the heat capacity (the IsoStep™ software option).

Besides these four important new features, many minor details have also been improved such as:

- Formatting possibilities (choice of color, font type, character size and line type)
- Different types of coordinate systems with new and improved scaling possibilities (linear-linear, logarithmic-linear, logarithmic-logarithmic, linear-logarithmic)
- New evaluation routines, even in non-linear coordinate systems
- Polynomial fit function with enhanced possibilities
- Improved c_p by sapphire method if the temperature program consists of several dynamic segments. We recommend this for c_p measurements over a large temperature range.

Advanced Model Free Kinetics

The current version of Model Free Kinetics (MFK software option) allows only dynamic curves to be evaluated. The enhanced version of Model Free Kinetics (Advanced MFK software option) uses a new evaluation algorithm that was originally developed by Prof. Dr. S. Vyazovkin [1] and most re-

cently improved by Prof. Dr. S. Vyazovkin and Prof. Dr. Ch. A. Wight [2]. The new algorithm can evaluate curves measured with any desired temperature programs.

The new software allows you to analyze
- dynamic curves,
- isothermal curves and
- curves measured with any desired temperature programs.

This means that Model Free Kinetics can now be used for isothermal measurements. It is well known that isothermal measurements offer a number of advantages:
1. The reaction of interest can be measured practically free of any disturbing influences. Side reactions and decomposition usually only occur at higher temperatures.
2. Changes in the heat capacity of the sample do not influence the DSC curve.
3. Interpretation of isothermal DSC curves is easy because at the end of the reaction, the heat flow asymptotically reaches a value of 0 mW.

It was established a long time ago that isothermal DSC measures the entire reaction and that the heat of reaction obtained is therefore correct [3]. Now that fast DSC sensors with time constants of less than 3 s have become available, no data is "lost" at the beginning of the reaction.
With TGA, however, there has always been the disadvantage that it takes a relatively long time to reach the desired isothermal temperature (because of slow heat exchange across the furnace atmosphere). This means that the beginning of the reaction cannot be properly detected.
For problems such as this, it would be a big advantage to be able to perform kinetic evaluations of mixed dynamic-isothermal measurements. For example, a sample is heated at 5 K/min to 150 °C and afterward left to react. With this temperature program, part of the reaction occurs in the dynamic segment.

Both the MFK and advanced MFK kinetic software options have the following in common:
- Kinetic evaluations can be made without previous selection of a reaction model
- Both programs can be applied to simple and complex reactions
- Simulation possibilities (prediction of the reaction kinetics under other conditions)

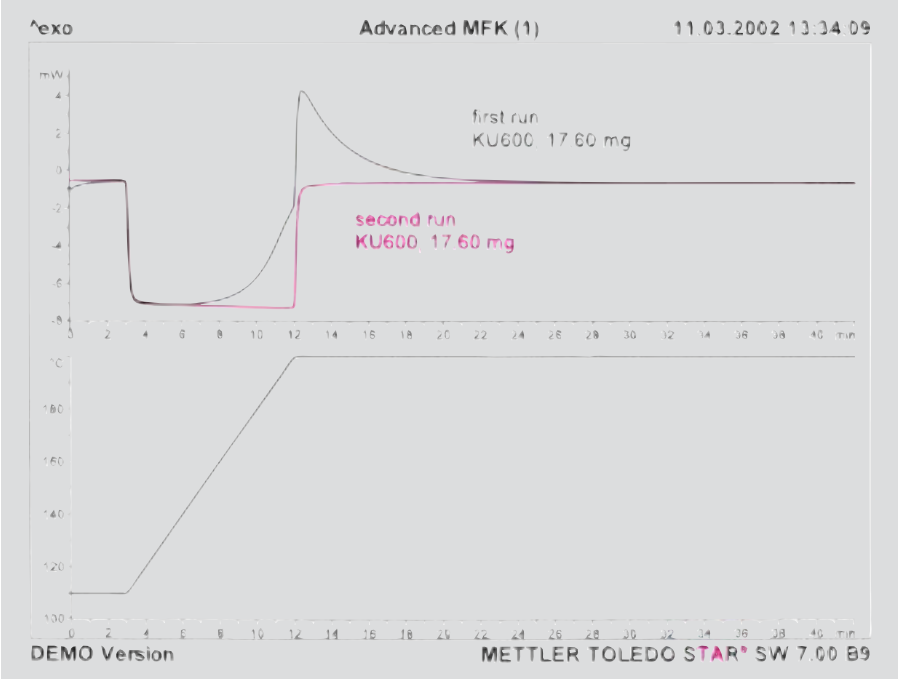

Fig. 1. In the upper coordinate system, the dynamic-isothermal DSC curve of the curing of KU600 epoxy powder is displayed. The second measurement serves as a "baseline". After this has been subtracted from the first curve, only the chemical reaction remains (see Fig. 2 below). The lower coordinate system shows the temperature program of both measurements.

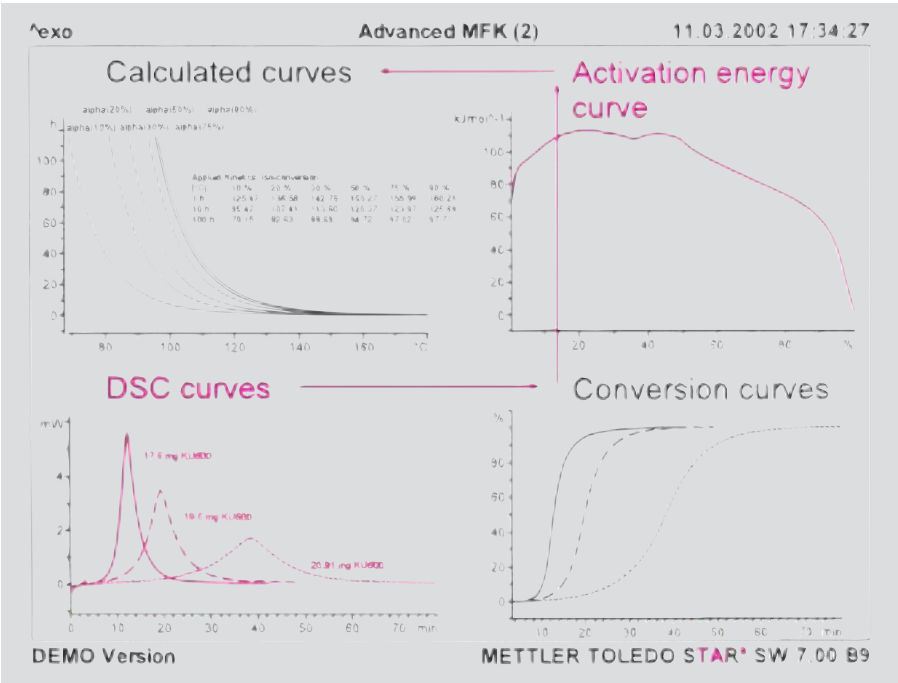

Fig. 2. Below left: This shows the three dynamic-isothermal DSC curves obtained after the second run has been subtracted. The heating rates were 2, 5 and 10 K/min, and the isothermal temperatures 180 °C, 190 °C and 200 °C. Below right: The conversion curves are obtained by integration. From this data, the new enhanced MFK program calculates the activation energy as a function of the conversion (above right). Finally, predictions for conversions between 10% and 90% are calculated (above left). From the table, one can for example see that, at 160.2 °C, the sample would cure to 90% in one hour (1 h).

These kinetic evaluation possibilities are therefore ideally suited for use in safety investigations and process optimization.

Literature

[1] *S. Vyazovkin, Evaluation of the activation energy of thermally stimulated solid-state reactions under an arbitrary variation of the temperature, J. Comput.Chem., 1997, v. 18, N3, 393-402.*

[2] *S. Vyazovkin, C.A. Wight, Estimating realistic confidence intervals for the activation energy determined from thermoanalytical measurements, Anal. Chem., 2000, v. 72, N14, 3171-3175 and to S. Vyazovkin, Modification of the integral isoconversional method to account for variation in the activation energy, J. Comput. Chem., 2001, v. 22, N2, 178-183*

[3] *G. Widmann, Thermochimica Acta, 11 (1975) 331-333*

IsoStep™

In this method, the temperature program consists of a number of dynamic segments that begin and end with an isothermal segment.

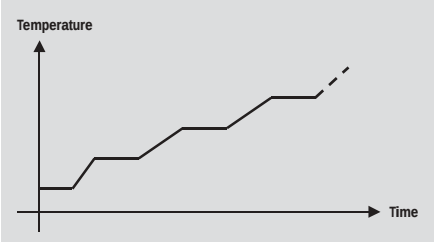

Fig. 3. IsoStep™ temperature program consisting of different isothermal and dynamic segments.

The evaluation is based on an idea of Dr. S. C. Mraw and Dr. H. Dörr. The isothermal segments allow the isothermal drift of the dynamic segments to be corrected. This results in better c_p-accuracy. The isothermal step may also contain kinetic information, for example of a chemical reaction.

This new technique therefore allows

- accurate c_p determinations to be made using a sapphire reference sample and
- kinetic effects to be separated from changes in heat capacity.

We foresee a number of interesting applications for this technique:

Industry	Effects that can be analyzed with IsoStep™
Automobile and aerospace	Curing reactions, influence of moisture, glass transition, vitrification
Chemical	Exothermic reactions (safety investigations), glass transition, kinetics, crystallization behavior, polymorphism, drying, heat capacity
Electronics	Curing reactions, glass transition, vitrification
Paints	Curing reactions, influence of moisture, glass transition, drying, vitrification
Rubbers (elastomers)	Glass transition, phase separation, melting, vulcanization
Plastics (thermoplastics, thermosets, fibers, films, textiles, adhesives, packaging and cables)	Curing reactions, influence of moisture, enthalpy relaxation, glass transition, cold crystallization, phase separation, melting, melting and crystallization, vitrification, heat capacity
Foodstuffs	Influence of moisture, gelation, glass transition, stickiness, polymorphism, drying
Pharmaceuticals	Influence of moisture, glass transition, melting (isothermal step melting point), crystallization behavior, polymorphism, drying, heat capacity, decomposition behavior

As a tutorial example, IsoStep™ is used to evaluate a measurement of PET.

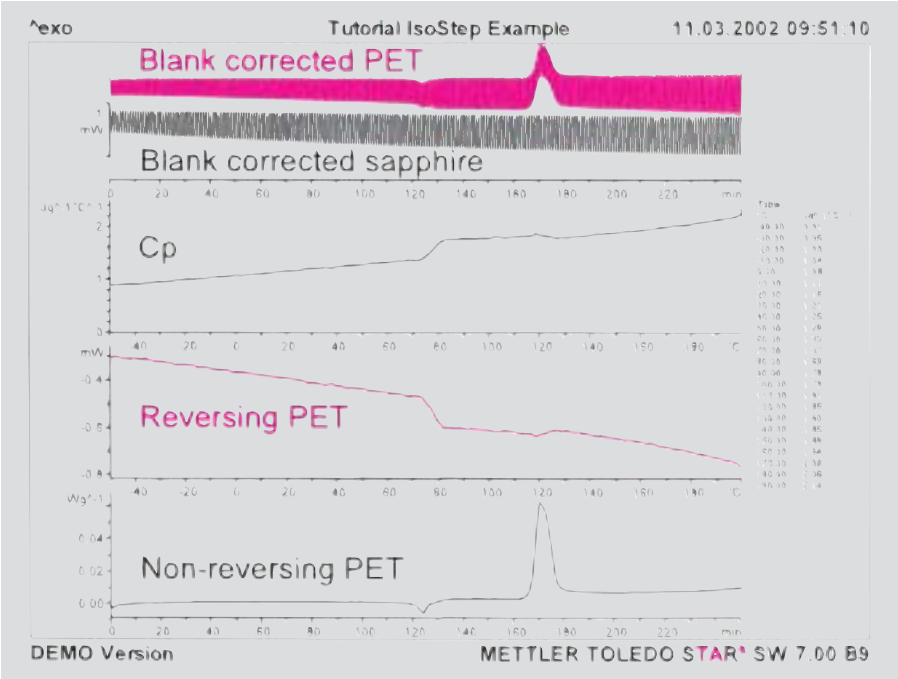

Fig. 4. The uppermost coordinate system shows the blank curve corrected PET and sapphire measurements. From this data, the following three curves can be calculated:
1. c_p curve, which shows an increase in c_p at about 75 °C (glass transition) and a decrease in c_p (cold crystallization) at 170 °C
2. Reversing curve (heat capacity curve recalculated to a heat flow curve)
3. Non-reversing curve, which shows an enthalpy relaxation at about 75 °C (125 min) and the cold crystallization process at about 120 °C (170 min)

An application of IsoStep™ can be found on page 18.

Applications booklets

We are pleased to announce the availability of two new application booklets in the Collected Applications series. They should be of great assistance for your daily work.

The new "Elastomers" and "Evolved Gas Analysis" (TGA-FTIR and TGA-MS) booklets further enhance our already wide range of applications literature still further.

Applications booklet	**Language / Order No.**	**Contents**
Tutorial Kit	Booklet German: 51 709 919 English: 51 709 920 French: 51 709 921 Booklet with test substances: German: 51 140 877 English: 51 140 878 French: 51 140 879	This applications booklet together with the corresponding test substances is excellent for self-study in thermal analysis. The power of thermal analysis is clearly demonstrated with 22 well-chosen examples.
Thermoplastics	German: 51 725 001 English: 51 725 002	The thermal behavior of more than 20 thermoplastics is discussed with the aid of more than 100 DSC curves. 16 TMA and 9 TGA measurements complete the picture. The effects investigated are: melting, crystallization, glass transition, softening, drying, thermal decomposition, oxidative stability, and expansion and contraction behavior. Practical questions such as thermogravimetric compositional analysis or how to avoid mistakes in the identification of materials are also dealt with.
Elastomers (NEW)	English: 51 725 058	The booklet begins with an introduction to thermal analysis and the structure and properties of elastomers, and then presents some 50 examples of elastomer analysis. Besides DSC, TGA and TMA, the use of combined techniques for gas analysis (TGA-MS and TGA-FTIR) and dynamic mechanical analysis (DMA) are also included. The practical section of the booklet is divided into two chapters. The first chapter deals with the basic principles of thermal effects and their evaluation. Besides compositional analysis using TGA, the measurement of vulcanization and crystallization processes and the glass transition are also covered. Information on how to optimize measurement and evaluation techniques is also included. There then follows an extensive chapter dealing with practical examples of elastomer analysis starting with relatively simple examples through to analyses of complex systems.
Pharmaceuticals	German: 51 725 005 English: 51 725 006 A	The application possibilities of thermal analysis in the pharmaceutical industry are described with the aid of 47 carefully selected examples. Melting behavior, polymorphism, purity, moisture as well as the stability of active and inactive ingredients are analyzed using DSC, TGA, EGA and TOA. The influence of measurement conditions and instrument calibration is also discussed.
Food	German: 51 725 003 English: 51 725 004	The application of thermal analysis to proteins, carbohydrates, fats and oils is demonstrated with the aid of 53 DSC, 2 TGA and one TMA curve. The most important effects investigated are the: denaturation of proteins, swelling of starch in water, melting of sugar, thermal decomposition of sugar and starch, and the melting and crystallization of fats, oils and chocolate.
Evolved Gas Analysis (NEW)	English: 51 725 056	The booklet describes the combination of thermogravimetry (TGA) with gas analysis. The first part covers the basic principles of mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) as well as the interpretation of results and spectra. The practical part discusses 17 application examples of the TGA-MS and TGA-FTIR techniques. Organic and inorganic samples as well as polymer systems are investigated. An example of an application performed with a TMA-MS combination is also described.

Thermal analysis of toners

Dr. Markus Schubnell

Introduction

Toners, as used in modern laser printers and photocopiers are, in fact, complicated mixtures that consist of a thermoplastic base material to which different ingredients such as flowing agents, pigments, UV-stabilizers and other additives have been mixed.

The glass transition temperature of the base material and the melting temperatures and melting enthalpies of the additives are characteristic for the toner. These properties can be easily and reliably determined by thermal analysis, in particular with differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

This article describes how the two techniques were used to measure a toner sample, and compares the results and information obtained. The work was done with a DSC821^e and a DMA/SDTA861^e.

DSC measurements

The sample was first heated at 10 K/min. Afterward it was cooled at 10 K/min and then heated a second time at 10 K/min. The first heating run shows two endothermic peaks that are not completely separated from each other. In addition, a slight shift of the baseline is noticeable. In the cooling curve, several exothermic peaks can be observed that appear shifted to lower temperature in comparison with the heating curve. Furthermore, a step-shaped displacement of the baseline occurs between 70 °C and 45 °C, i.e. in the same temperature range as the heating run. This indicates that a melting process and a glass transition overlap in the first heating run. In the second heating run of the same sample, only one clear peak is observed. This suggests that the second endothermic peak in the first heating run can be interpreted as an enthalpy relaxation peak that occurs due to enthalpy relaxation in the glassy state on heating (see also UserCom 10, page 13).

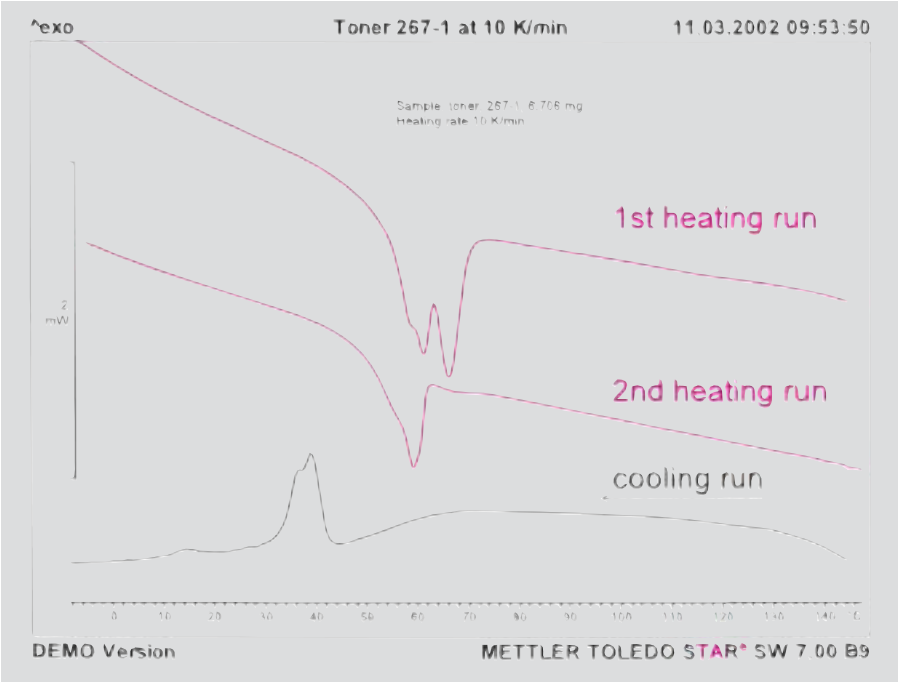

Fig. 1. DSC curves of the first heating run, the cooling run and the second heating run of a toner sample.

This interpretation can be confirmed by measuring new samples at different heating rates. Under these conditions, the melting peak should be more or less independent of the heating rate, but the enthalpy relaxation should shift to higher temperature with increasing heating rates. The experimental results are given in Figure 2. This displays the DSC curves obtained for the first heating runs at heating rates of 0.5, 10 and 150 K/min. The curves show that with increasing heating rates the enthalpy relaxation peak does in fact shift to higher temperatures, but that the melting point is observed practically unchanged at about 60 °C.

DMA measurements

In dynamic mechanical analysis, a sample is subjected to a periodically changing sinusoidal force. In the linear (Hooke's) region, this leads to a sinusoidal deformation of the sample. The deformation is, however, shifted with respect to time in comparison with the force exerted. The relationship of the force to the deformation amplitude, and the phase shift between the force and the deformation, allow one to obtain information on the molecular dynamics of the sample. Quantitatively, a dynamic mechanical analyzer yields the storage and loss moduli and the mechanical loss factor (damping).

An important parameter in DMA measurements is the period, i.e. the oscillation frequency of the sample. The frequency dependence of measurement curves often

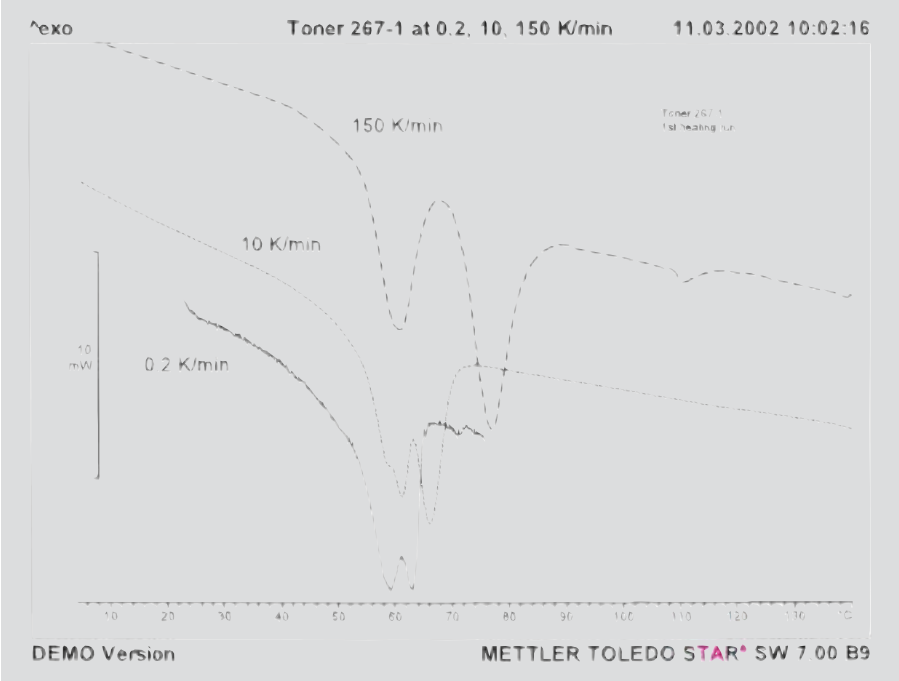

Fig. 2. First heating run of a toner sample at different heating rates.

allows certain effects to be positively identified. For example, crystallization and melting are generally frequency-independent processes. In contrast, relaxation phenomena such as the glass transition are always frequency-dependent. If, in the case of the toner sample, we assume that the measured curve is due to the overlap of a melting process and a glass transition, then it should be possible to distinguish between the two processes from their behavior at different frequencies.

The sample was a fine powder. One way to measure materials in powder form in a DMA is to press the powder to a cylindrical disk. The disks are then mounted in the shear clamp of the DMA. Using this technique, we prepared a number of samples from the material with a diameter of 12 mm and a height of 1.5 mm. A pressure of 100 N/cm^2 was used.

Figure 3 shows the storage component of the shear modulus of the sample as a function of temperature for frequencies of 1, 10, 100 and 800 Hz. A heating rate of 2 K/min was used. The experiment was performed under displacement control with a displacement amplitude of 1 µm. The maximum value for the force amplitude was set to 3 N. The curve for 1 Hz shows a broad step in the modulus. With increasing frequency, a second step becomes increasingly apparent. The first step always shows approximately the same starting temperature independent of the frequency. It follows that this step is due to the frequency-independent melting process. The second step, which is clearly visible at high frequencies, corresponds to the glass transition of the thermoplastic constituents in the sample.

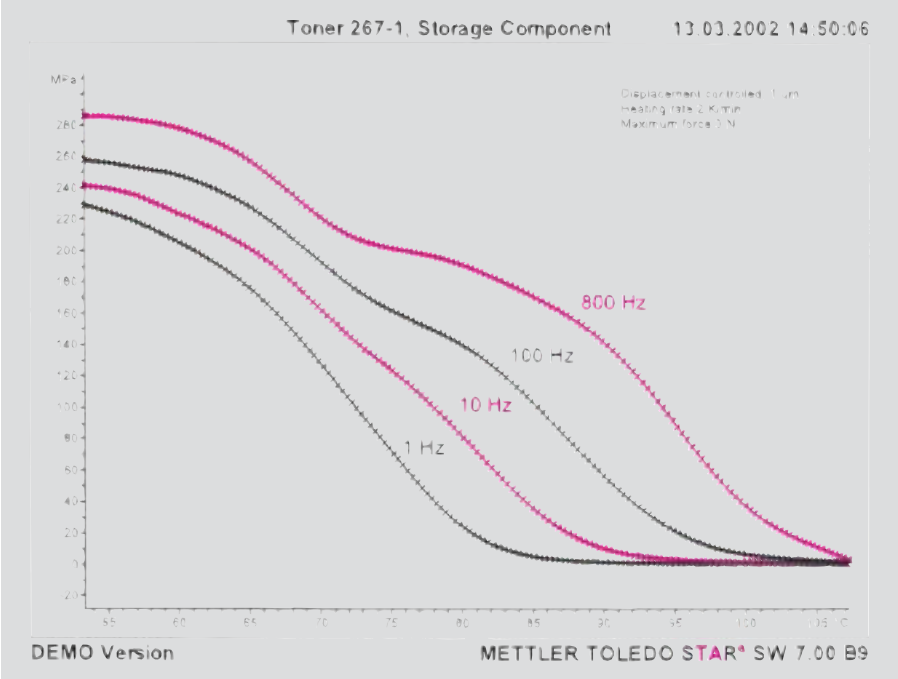

Fig. 3. Storage components of the shear modulus of a toner sample at different frequencies. All four curves were measured at 2 K/min.

Conclusions

Overlapping melting and glass transition processes can be easily separated with DSC and DMA. In DSC, the fact that the glass transition is dependent on the heating rate is used to separate the two effects. With DMA, separation is achieved because the frequency dependence of the two effects is different. In principle, both methods yield equivalent results. The sensitivity of the DSC with regard to glass transitions is of course appreciably lower than its sensitivity toward melting processes. The DMA, however, is much more sensitive toward changes in molecular mobility, which occur in melting processes and glass transitions to the same extent. The wide frequency range of the DMA/SDTA861^e opens up exciting new possibilities for dynamic mechanical analysis.

The characterization of resins in lithographic processes

Dr. M. Ribeiro, Dr. J-P. E. Grolier ; Laboratoire de Thermodynamique des Solutions et des Polymères, AUBIERE, France;
L. Pain; LETI-CEA, GRENOBLE, France; C. Gourgon ; LTM-CNRS, GRENOBLE, France.

Introduction

The Laboratoire d'Electronique de Technologie et d'Instrumentation (LETI) specializes in the application of photosensitive resins for lithographic processes in the semiconductors industry (transistors for integrated circuits). The ever-increasing miniaturization of transistors is the driving force behind numerous technological advances. Currently, the best possible resolution that can be achieved for isolated lines is 40 nm, and 60 nm for lines in dense patterns.

These limits are most probably due to the different resin components presently used. The current challenge is therefore to develop new resin formulations (chemically amplified resists or so-called CARs) that will allow a resolution of 20 nm to be obtained.

CARs are multi-component mixtures consisting of a polymer matrix (the combination of two polymers), a photo acid generator, PAG, and other additives, depending on the properties desired.

In order to improve the properties of CARs, the production process has to be optimized. This in turn requires an understanding of the physicochemical behavior of each component of the CAR and its effect on the process. The LETI-LTM (Laboratoire de Technologie Microélectronique) and the "Laboratoire de Thermodynamique des Solutions et des Polymères" cooperate in this area of research. Temperature-modulated DSC (ADSC), FTIR and thickness measurement techniques are used to investigate the influence of the different resin components on resolution in the lithographic process.

The main advantage of ADSC is that the glass transition temperature and the thermal effects associated with the lithographic process (vaporization and cross-linking) can be determined in one single measurement [1].

Experimental details

Various resins manufactured by Sumitomo Incorporated (Japan) differing in at least one component were investigated in order to understand the physicochemical behavior of the mixtures. To do this, the influence of several parameters such as the polymer matrix, the molecular weight of the individual polymers, the PAG and the solvent was measured.

First of all, ADSC curves of all the resins were measured to determine the glass transition region and cross-linking temperature. This is illustrated in Figure 1 with the NEB22 resin.

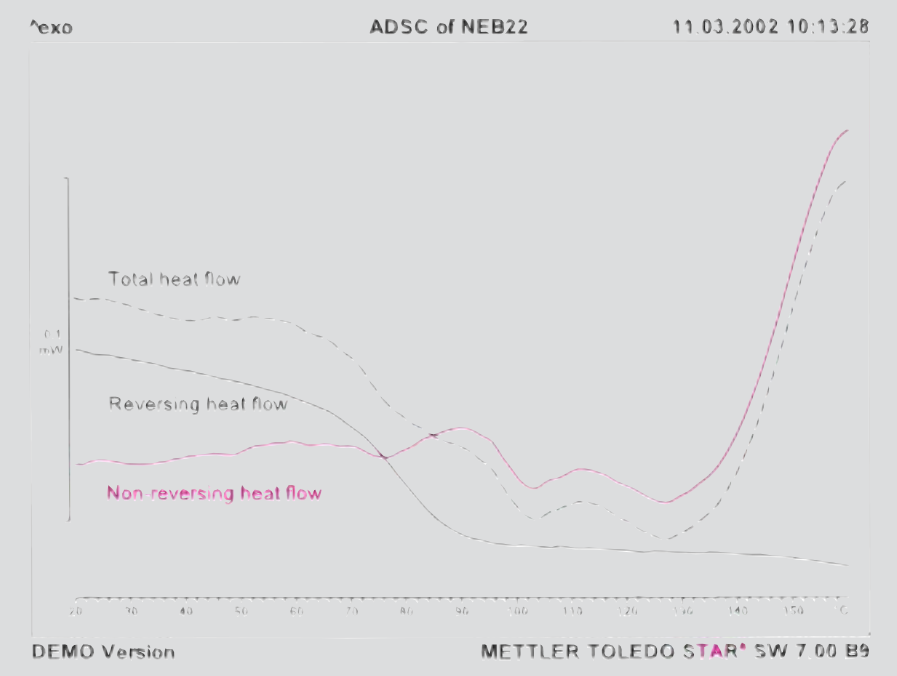

Fig. 1. ADSC curves of NEB22 resin, measured after baking at 80 °C for 10 min and cooling at 5 K/min. Φ_{tot}: total heat flow, $\Phi_{rev.}$: reversing heat flow component, $\Phi_{non\text{-}rev.}$: non-reversing heat flow component. The step in $\Phi_{rev.}$ shows the glass transition range (60 °C to 100 °C); the increase of $\Phi_{non\text{-}rev.}$ shows the curing reaction (from about 130 °C).

These investigations are necessary to optimize the processing conditions, to control diffusion processes and to minimize the sensitivity to contamination.

The type of CAR and the processing temperatures influence the film thickness. If the bake temperature is increased, the films become thinner whereby so-called stable temperature domains can also occur. This is illustrated in Figure 2 with the NEB22 resin. The right processing temperature helps to optimize the compactness of the resin layer.

The lithographic process is initiated at about 100 °C. It is therefore important to investigate what happens in this temperature range. The decrease in thickness of the resin with increasing processing temperature (see Fig. 2) indicates that the film is not completely stable. This is due to internal processes such as the vaporization of different components. Free volume is thereby generated, which is then eliminated during further baking. In order to identify the components responsible for

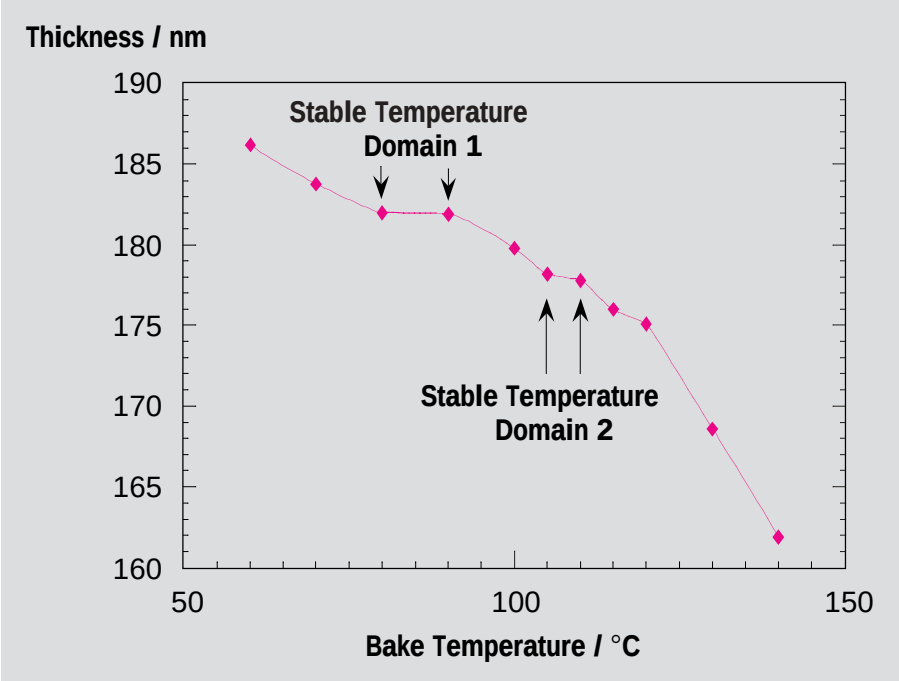

Fig. 2. Film thickness of the NEB22 resin after the coating process as a function of the processing temperature.

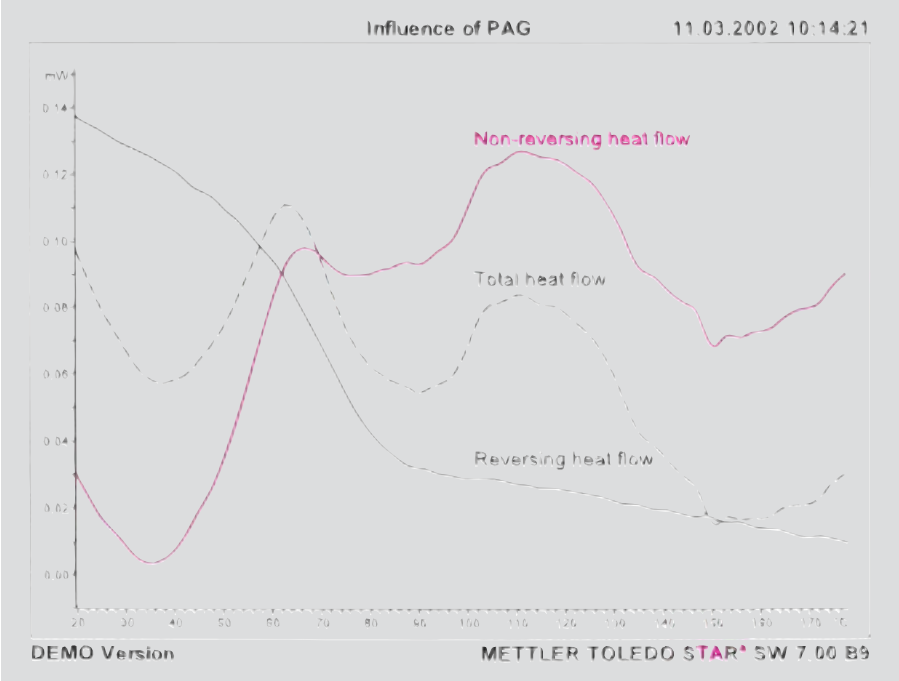

Fig. 3. ADSC curves of the polymer matrix with PAG (for curve notation see Figure 1). The influence of PAG and the vaporization of solvent residues (peak at 35 °C) results in a $\Phi_{non\text{-}rev.}$ curve that is clearly different to that shown in Figure 1.

this instability, partial CAR formulations were prepared in which one of the components was missing each time. The thermal behavior of each formulation was measured. This led to the following results [2]:

- The maximum permissible processing temperature for the polymer matrix alone was 115 °C.
- The addition of cross-linkers does not significantly change the ADSC curves. In addition, another CAR (NEB33) was measured that differed from NEB22 in the type of cross-linker used. Both CARs exhibited the same thermal behavior.
- If a photo acid generator (PAG) is added, the thermal behavior changes. It can be seen in Figure 3 that the effect observed at about 100 °C is due to partial vaporization of the PAG. This was confirmed by FTIR measurements.
- The solvent content of the polymer matrix cannot be neglected because it influences the film thickness during processing. A large proportion of the solvent should be eliminated at the beginning of processing at about 80 °C. DSC measurements, however, showed that solvent residues also evaporated at higher temperatures. These residues were probably retained through the formation of a surface skin (see Fig. 4). For the pure solvent, DSC measurements yielded a vaporization temperature of 140 °C. The apparently endothermic peak at about 130 °C in the curve in Figure 4 shows that in all probability a coating speed that is too slow results in more solvent residues, and is therefore the cause of less "stable" resins. The presence of solvents was confirmed by FTIR measurements. The spectra show a peak at about 1740 cm^{-1} that can be assigned to the C=O group of the solvent. The intensity of this peak decreases significantly if the resin samples are heated to different temperatures before the measurement to 150 °C is performed [3].

The influence of different parameters in the polymer matrix such as the polydispersity of the polymer mixture and molar mass was investigated using the same techniques. It was shown that improved optical resolution could be obtained by reducing the molar mass. This enabled a resolution of 30 nm to be obtained for isolated lines.
The investigation of materials with thermal analysis and other techniques with a view to process optimization is still in progress. At the moment we are investigating different resins with respect to the effect of the different processing parameters.

Conclusions

DSC, ADSC and FTIR measurement techniques enable valuable information for the

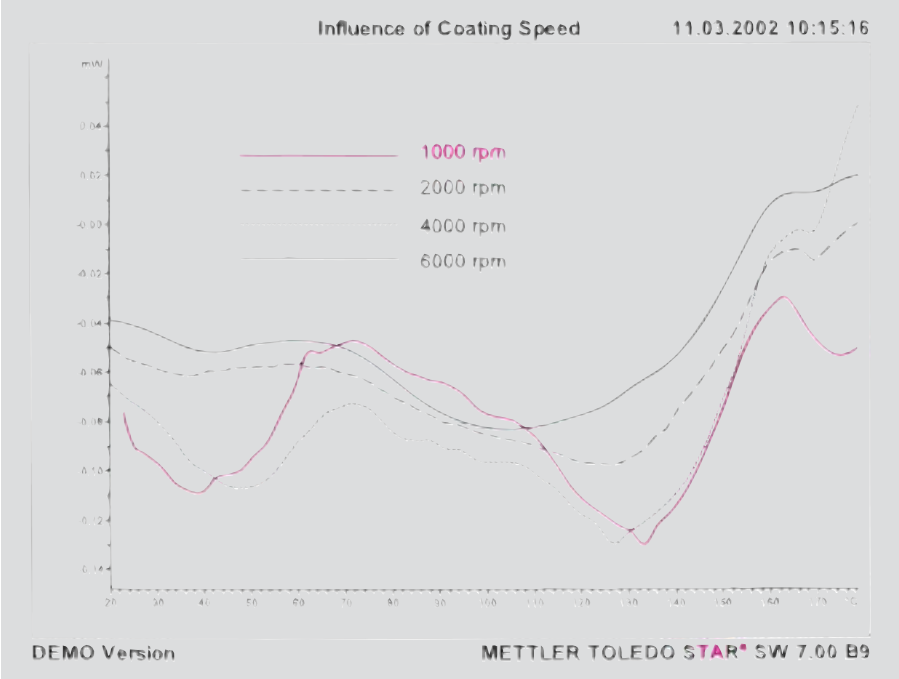

Fig. 4. The non-reversing heat flow component ($\Phi_{non\text{-}rev.}$) of unbaked NEB22, coated at different speeds (1000, 2000, 4000 and 6000 rpm). If the coating process is performed at higher speeds, more solvent evaporates. The intensity of the endothermic peak at 130 °C thereby decreases, indicating that smaller amounts of solvent residue are present in the CAR layer.

improvement of CAR formulations to be obtained. The study shows that thermal analysis can help one to understand the behavior of CAR components and to optimize the lithographic process. ADSC is a useful technique to measure the glass transition and vaporization/curing effects that take place almost simultaneously.

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Quantitative analysis of polyolefine blends

D. Seifert, Institut für Nichtmetallische Werkstoffe, Fachgebiet Polymertechnik, Technische Universität Berlin, Fasanenstr. 90, 10623 Berlin

Introduction

Plastic blends represent the largest fraction of plastic materials that occurs in the recycling of plastics from waste packaging. These mixed plastics consist mainly of polyolefines, i.e. polyethylene and polypropylene. For material recycling purposes, the fraction can be processed via dissolution. Recycling via dissolution is in fact a process that results in recycled material with properties superior to those obtained with the usual melting procedure [1].

To produce material of high quality with reproducible material properties, it will however be necessary to develop new methods that can separate the polyolefinic material into its individual components, i.e. into low-density (LDPE) and high-density polyethylene (HDPE), and polypropylene (PP) [2].

The composition of the recycled plastic is of course a measure of the efficiency of the separation. We have therefore developed a method to determine the composition of polyolefinic samples. The method uses DSC measurements and is particularly interesting in that it not only distinguishes between polyethylene and polypropylene, but also between high- and low-density polyethylene.

The basic principle of the method is to describe the melting enthalpies (measured in the melting curve) of a polyolefinic sample by the mass fractions (which follow from the sample composition) and the standard melting enthalpies of the components involved.

The melting curve of a mixture cannot however be described exactly by the sum of the pure melting curves. Correction factors have to be introduced. Theses are determined iteratively from the measurement results of a series of polyolefinic samples of known composition.

Experimental details

First of all, a series of samples of known composition, i.e. calibration samples, were prepared. The compositions of these calibration samples were chosen so that the three distribution ratios (in weight percent) of 5:5:90, 10:10:80 and 20:20:60 corresponded to compositions in which each of the three plastics was the main component. These nine mixtures are shown graphically in Figure 3. The samples were mixed in solution, precipitated and dried. To obtain statistically meaningful results, three sample crucibles of each mixture were prepared.

The samples were measured with a METTLER TOLEDO DSC822^e with the following temperature program.

1. Heating the sample from 20 °C to 200 °C at 10 K/min (to eliminate or equalize the thermal history of all the samples)
2. Cooling from 200 °C to 20 °C at 10 K/min
3. Isothermal for 10 minutes
4. Heating from 20 °C to 200 °C at 10 K/min (the actual measurement)
5. Cooling from 200 °C to 20 °C at 10 K/min.

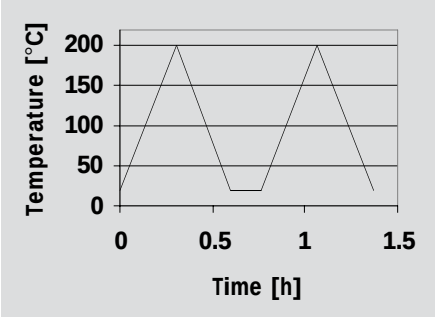

Fig. 1. Temperature profile of the DSC program.

Evaluation of the melting curves

Since the initial melting curves of thermoplastics always show effects that relate to the different thermal history of the samples, only the second heating runs were used for evaluation purposes.

The evaluation must be performed in a reproducible way. To do this, a straight baseline is extrapolated from the melt. To determine the melting enthalpies, the area under the entire curve is first integrated. In the next step, the melting enthalpies of polyethylene and polypropylene are separated. This turns out to be relatively easy because PE and PP are, in the thermodynamic sense, practically immiscible, and the two signals overlap to only a small extent in the melting curve. A vertical line can therefore be drawn at the minimum between the PE and PP melting regions. The melting enthalpies of LDPE and HDPE, however, still have to be separated. This is more difficult because these two polyolefines are partially miscible and their melting temperatures are so close to each other that the signals overlap in the melting curve. At this stage, one must therefore distinguish between three different situations (1, 2, 3) given below (see Fig. 2):

1. LDPE and HDPE show their own clearly defined maxima and there is a clearly defined minimum is between the two maxima. This situation occurs when the mass ratio of LDPE to HDPE is sufficiently large, i.e. when there is more LDPE than HDPE in the sample.
2. LDPE only shows a shoulder in the HDPE peak. This situation occurs when LDPE and HDPE are present to about the same extent in the mixture.
3. LDPE can no longer be detected in the HDPE peak. This situation occurs when the LDPE to HDPE mass ratio is low, i.e. when there is less LDPE than HDPE in the sample.

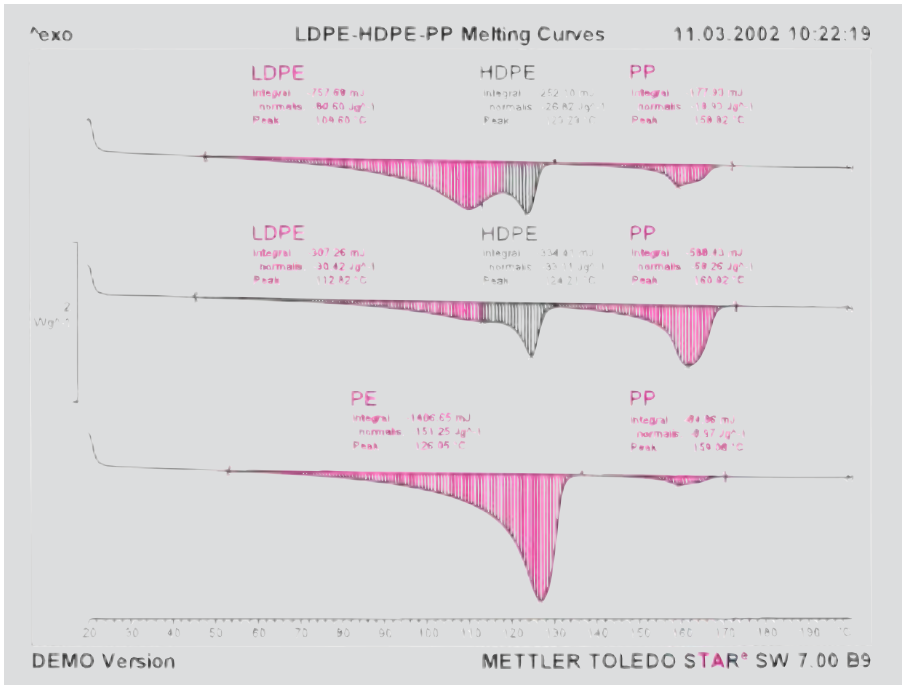

Fig. 2. Three-component melting curves with different features in the LDPE-HDPE melting range. From top to bottom: situations 1, 2 and 3.

In the first situation, it is relatively easy to separate the two melting regions. The vertical separating line is drawn at the minimum between the LDPE and HDPE melting regions.
In the second situation, the first derivative of the melting curve is used. The vertical separating line is drawn between the LDPE and the HDPE at the shoulder in the in the PE melting curve, i.e. at the point where the where the slope is least.
In the third situation, the partial areas of LDPE and HDPE cannot be resolved. The melting enthalpy evaluated for LDPE is zero.

Calibration of the three-component system

First the standard melting enthalpies (ΔH^0) of the three polyolefines were determined in the pure state, i.e. not mixed.
The three polyolefines are indexed in the following formulas with their first letter, i.e. L for LDPE, H for HDPE and P for PP.

ΔH^0_L = 91 J/g
ΔH^0_H = 129 J/g
ΔH^0_P = 84 J/g

If the three plastics had no influence on each other on crystallization and melting, one would expect the melting enthalpies, ΔH, found in the evaluation of the melting curve to be equal to the product of the mass fraction, x, of the component and the standard melting enthalpy, ΔH^0, of the component. Using PP as an example, the melting enthalpy would therefore be

$$\Delta H_P = x_P \ \Delta H^0_P. \qquad (1)$$

This simple formula cannot be used for mixtures of polyolefines for the following reasons:

1. The baseline drawn as a linear extrapolation from the melt does not take the actual thermal reality in this temperature range fully into account . It should show a convex curve to lower temperatures [3]. But for the sake of reproducibility this type of baseline will still be used.
2. Polyethylene and polypropylene are, in the thermodynamic sense, practically immiscible; the two polyethylenes, LDPE and HDPE, are however partially miscible. This means that the peak areas of the individual components are influenced by the mixing enthalpy.
3. Although the vertical line divides the integrals reproducibly, it does however cut off – in a physical sense, randomly – the beginning and end of the melting curves.

A correction factor must therefore be introduced for the calculation of the expected melting enthalpy. This correction factor has to be determined for each component. The factor (for PP this is called c_P) must also be determined for each DSC system, and again after every instrument adjustment. Formula (1) must therefore be expanded to:

$$\Delta H_P = c_P \, x_P \, \Delta H^0_P \qquad (2)$$

Since one cannot measure the absolute melting enthalpy with sufficient reliability in recycled plastics, partial areas are used for the following calculations. The partial area of a component is the melting enthalpy of the component evaluated in the melting curve divided by the sum of the melting enthalpies, e.g. for PP

$$F_P = \frac{\Delta H_P}{\Delta H_L + \Delta H_H + \Delta H_P} \qquad (3)$$

If equation (2) is introduced into equation (3), one obtains:

$$F_P = \frac{c_P \Delta H^0_P x_P}{c_L \Delta H^0_L x_L + c_H \Delta H^0_H x_H + c_P \Delta H^0_P x_P} \qquad (4)$$

Applied to both polyethylenes this gives:

$$F_L = \frac{c_L \Delta H^0_L x_L}{c_L \Delta H^0_L x_L + c_H \Delta H^0_H x_H + c_P \Delta H^0_P x_P} \qquad (5)$$

$$F_H = \frac{c_H \Delta H^0_H x_H}{c_L \Delta H^0_L x_L + c_H \Delta H^0_H x_H + c_P \Delta H^0_P x_P} \qquad (6)$$

If the three equations are resolved according to the mass fractions, x_L, x_H and x_P, this gives:

$$x_L = \frac{F_L / c_L \Delta H^0_L}{F_L / c_L \Delta H^0_L + F_H / c_H \Delta H^0_H + F_P / c_P \Delta H^0_P} \qquad (7)$$

$$x_H = \frac{F_H / c_H \Delta H^0_H}{F_L / c_L \Delta H^0_L + F_H / c_H \Delta H^0_H + F_P / c_P \Delta H^0_P} \qquad (8)$$

$$x_P = \frac{F_P / c_P \Delta H^0_P}{F_L / c_L \Delta H^0_L + F_H / c_H \Delta H^0_H + F_P / c_P \Delta H^0_P} \qquad (9)$$

To determine the correction factors, c_L, c_H and c_P, the mixtures of known composition were measured and evaluated. The mass fractions, x_L, x_H and x_P, were calculated with starting values of $c_L=c_H=c_P= 1.0$. These experimentally determined mass fractions were compared with the mass fractions of the sample weights, i.e. the difference, Δx_P, calculated for each calibration mixture. The three correction factors were then changed (iteratively) until the sum of the differences, Δx_{PP}, was a minimum. At this point, only the measurement results for the PP component were included because this component is the only one that can be evaluated over the whole range.

An example of the result of such an iterative process is shown in Figure 3. This iteration yielded the following correction factors: $c_L = 1.76$, $c_H = 1.46$ and $c_P = 1.31$. All three correction factors are greater than 1 because the choice of the baseline results in the areas determined in the mixture being larger than those of the individual components.

Figure 3 shows that the experimental data for samples with higher contents of LDPE agrees well with the area contents determined from the sample weights, but that the method fails if the mass ratio of HDPE to LDPE is too large. For the other compositions the maximum error is 3% w/w (for PP) and 6% w/w (for LDPE and HDPE).

Determination of the composition of all three components

Three crucibles are prepared for each sample of unknown composition. This is done to improve statistical reliability and to check sample homogeneity. The crucibles are measured with the temperature program described above. The evaluation must be performed according to the same criteria for reproducibility that were used for the evaluation of the calibration samples. The composition can now be determined from the evaluated partial areas using equations (7), (8) and (9) and the standard melting enthalpies and correction factors.

If LDPE cannot be detected in the melting curve, the concentration of this component cannot be determined. Instead, only a result such as "x_L is less than 20%" can be given. Where exactly this limit is, depends on the measuring system used and the measurement conditions.

If mixtures of other types polyolefines are to be analyzed, then a new calibration must be performed for these polyolefines, i.e. determination of the standard melting enthalpies and the correction factors. Since recycled material is often a mixture of many different types of plastics, a specific calibration cannot be performed in this case. Instead, plastic materials should be used that are as close as possible to the recycled material.

Finally, the method can be used for comparative purposes, even if it is not calibrated with similar types of polyolefines.

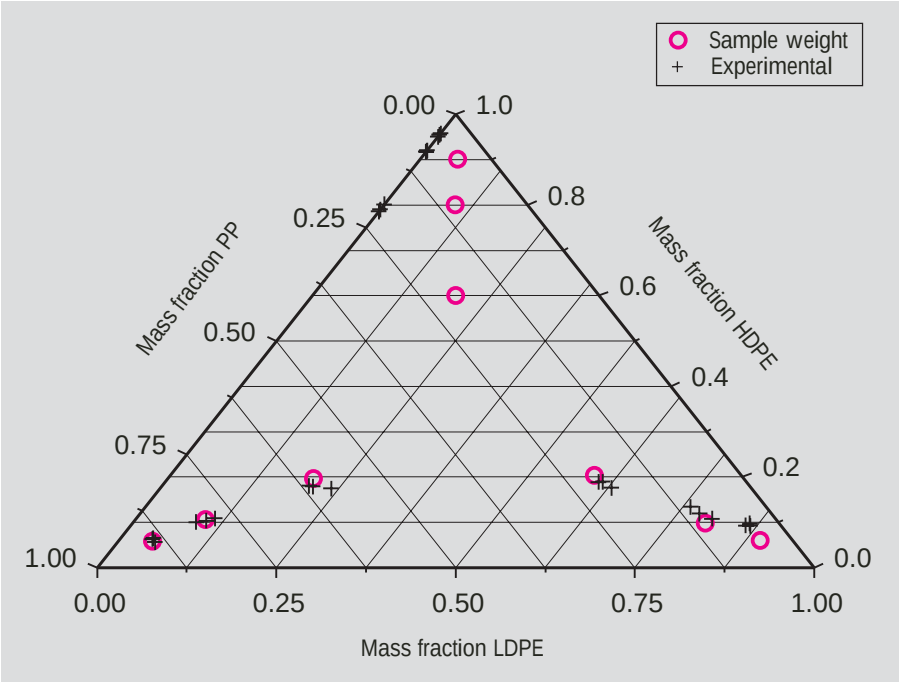

Fig. 3. Ternary diagram for the three components LDPE, HDPE and PP.

Summary

This article describes a method that allows the composition of polyolefine samples to be determined using DSC. The method is based on the principle that the enthalpies of the three components LDPE, HDPE and PP can be derived from their standard melting enthalpies and their concentration in the mixture. Since the components of the mixture do not behave ideally, the relationships described above have to be corrected with correction factors. These are determined using sample mixtures of known composition. The evaluation of the calibration mixtures and the samples under analysis must be performed reproducibly.

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The investigation of curing reactions with IsoStep™

Dr. Uwe Hess

Introduction

Curing reactions play an important role in the manufacture of polymeric materials. Besides so-called prepregs and coatings, composites are worth mentioning here in particular. Composites are an important class of materials because of their mechanical properties and low weight. They usually consist of glass fiber or carbon fiber material that is held together by a cured resin. The resin and the fiber give the material its characteristic properties. Composite materials are often used in areas where safety is of major importance, e.g. in the construction of aircraft and automobiles. This means that the curing behavior of the resin must be precisely monitored and characterized.

Fully cured material is relatively hard and might even be unsuitable for some applications because of its brittleness. In this case, material that is not completely cured would be preferable. Incompletely cured material can, however, undergo changes over a long period of time, which in turn results in the material properties changing. An important criterion for the determination of the degree of cure of a material is the glass transition temperature. Material with a higher degree of cure has a higher glass transition temperature than material with a lower degree of cure. An accurate DSC measurement of the glass transition temperature is however difficult, or even impossible, if the curing reaction takes place at the same time because the exothermic reaction peak then overlaps the glass transition. Vitrification can also occur, particularly with resins that cure at higher temperatures. Here the resin changes from the liquid to the glassy state and the reaction rate decreases significantly.

Usually, one wants to characterize the material, and to determine the limiting conditions for the curing process and for the material's practical use afterward. Typical questions are for example:

- What is the relationship between the glass transition temperature and the material properties?
- Under what conditions does vitrification of the material occur?
- Under what conditions does incompletely cured material continue to cure during storage or use?

Especially for applications where safety is involved, the manufacturing process must ensure that uniformly cured material is produced, and that the long-term stability of the material under defined conditions is guaranteed.

In the following example, the curing behavior of a two-component epoxy resin consisting of the diglycidylether of bisphenol A (DGEBA) and diaminodiphenylmethane (DDM) as hardener or curing agent were investigated.

If the reaction takes place slowly, the material has sufficient time to form more cross-links and the glass transition temperature shifts to higher and higher temperatures. If the glass transition temperature is higher than the actual reaction temperature, vitrification can suddenly occur. The curing reaction in the now solid material slows down significantly [1]. This can, for example, lead to problems in thermally forming or molding equipment. If certain regions heat up too slowly, the temperature is not uniform throughout, and the curing process is incomplete.

To determine whether a material vitrifies with DSC, the heat capacity curve has to be separated from the reaction peak. The measurements presented here were performed with the new IsoStep™ method and the results compared with those obtained from conventional DSC.

Measurement and results

The samples were measured twice, once relatively slowly and once somewhat more rapidly. The segments had isothermal periods and heating times of 60 s and 30 s and incremental temperature changes of 0.5 K and 1 K respectively. The conventional DSC curve was measured at the same average heating rate. The results for the sample heated relatively rapidly are shown in Figure 1: the DSC curve has a glass transition at about -20 °C and a curing peak with a maximum at about 115 °C. The heat capacity curve increases gradually during the reaction with the greatest increase at the highest reaction rate (DSC peak). This is due to increased molecular movement at the cross-linking points [2]. Vitrification would become apparent through a sharp decrease in the heat capacity. It appears that vitrification does not occur under these experimental conditions and the reaction remains chemically controlled throughout the entire curing process. The non-reversing curve shows the rate of the reaction.

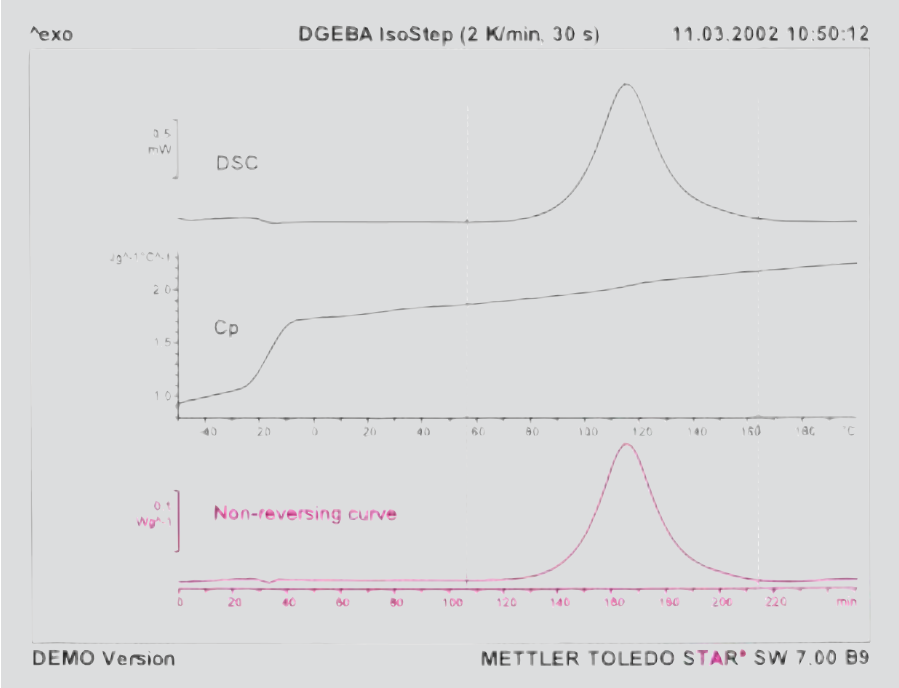

Fig. 1. The conventional DSC curve was measured at a constant heating rate of 1 K/min. The C_p and the non-reversing curves were measured with typical isothermal periods and heating times of 30 s and temperature changes of 1 K.

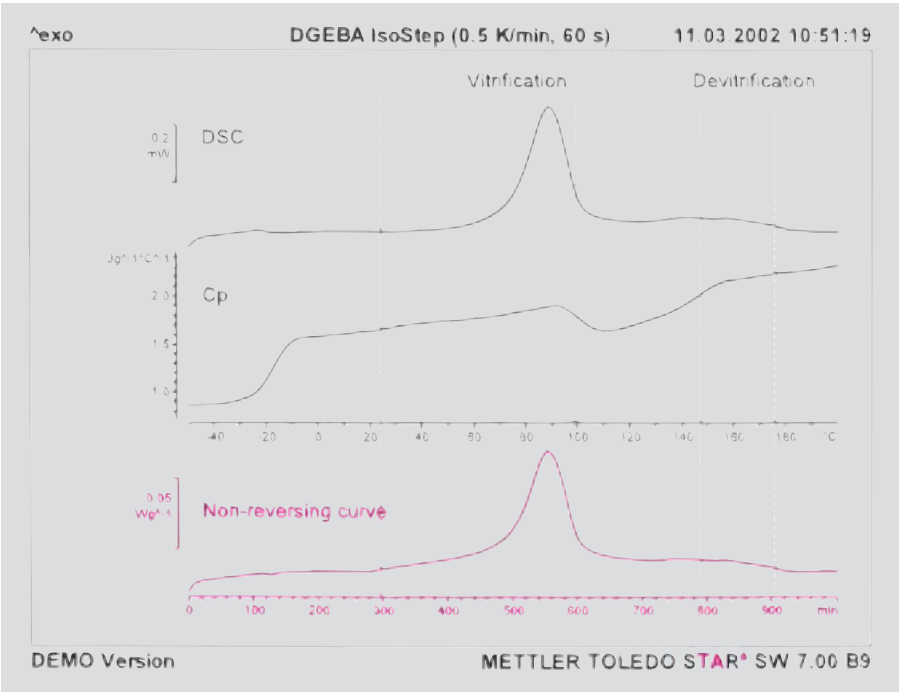

Fig. 2. The DSC curve was measured at a heating rate of 0.5 K/min. The C_p and non-reversing curves of the IsoStep™ method were measured with typical isothermal periods and heating times of 60 s and temperature changes of 0.5 K. The relatively slow curing reaction leads to a vitrification of the sample followed by a glass transition.

The DSC curve and the heat capacity curves of a sample that was heated more slowly are shown in Figure 2. Under these conditions, a rapid decrease in the heat capacity can be seen at about 100 °C in the heat capacity curve during the curing process. This decrease is due to vitrification. The very slow heating process allows the sample sufficient time to form a relatively dense polymeric network whose glass transition temperature is above the reaction temperature. The sample changes to the glassy state and the curing reaction then becomes diffusion controlled and slows down. On further heating, the glass transition of the partially cured material is finally reached at about 150 °C. From this temperature onward, the material is again liquid and the rate of the reaction (now chemically controlled) increases. To perform a kinetic evaluation of the curing peak, it would be better to use the non-reversing curve because this is free from heat capacity changes.

Conclusions

The IsoStep™ method is an excellent technique for separating glass transitions and overlapping kinetic processes such as curing reactions, crystallization and vaporization processes. The investigation of the curing reactions of resin systems is particularly important. It enables the materials used to be characterized, the production conditions to be determined, and yields information on long-term behavior and aging. Polymer resins are nowadays used in so many important materials such as composites, coatings and prepregs.

Literature

[1] *S. Montserrat, Y. Calventus and P. Colomer, UserCom 11, 2000*

[2] *J. E. K. Schawe, Therochim. Acta, 2002, submitted*

Thermal decomposition of copper sulfate pentahydrate

Dr. Jean-Nicolas Aebischer, Dozent für Physikalische Chemie, Hochschule für Technik und Architektur Freiburg, Bd. Pérolles 80, CH-1705 Fribourg, e-mail: jnicolas.aebischer@eif.ch

Introduction

When learning a new method, it is always a good idea to measure a system whose behavior is well known and documented under particular conditions. The thermal decomposition of $CuSO_4 \cdot 5\ H_2O$ is a good example of this, and the interpretation of the TGA curve poses no problems for the beginner.

Experimental details

The measurements were performed with a TGA/SDTA851^e (range: 5 g; resolution 1 µg), coupled to an Inficon Themostar QMS mass spectrometer (mass range 1-300).

Evaluation

The first three steps show a total relative weight loss of 35.58% (Figure 1). This corresponds to the loss of all five water molecules. In the last step, a further loss of 32.87% occurs so that finally only CuO remains.

Table 1 summarizes the relative weight losses and the reactions involved in each step.

Confirmation of the proposed reaction steps by measuring the relevant MS ion currents

If the ion currents of the corresponding m/z values for water and SO_3 are continuously measured, it should be possible to check whether the proposed reaction scheme is in fact correct.

As can be seen in Figure 2, water is indeed eliminated in the first three steps. However, rather unexpectedly, no SO_3 is formed in the last step. The derivative curve shows that this last step is in fact a two-step process.

Interpretation of the experimental results

The fact that SO_3 was not detected can have two possible reasons. It could be that O_2 and SO_2 are eliminated from the crystal lattice of the $CuSO_4$ and not SO_3. Alternatively, it is also possible that SO_3 is initially formed, but is unstable under the conditions of temperature and pressure in the instrument.

The question of the stability of SO_3 can be answered with the help of thermochemical calculations.

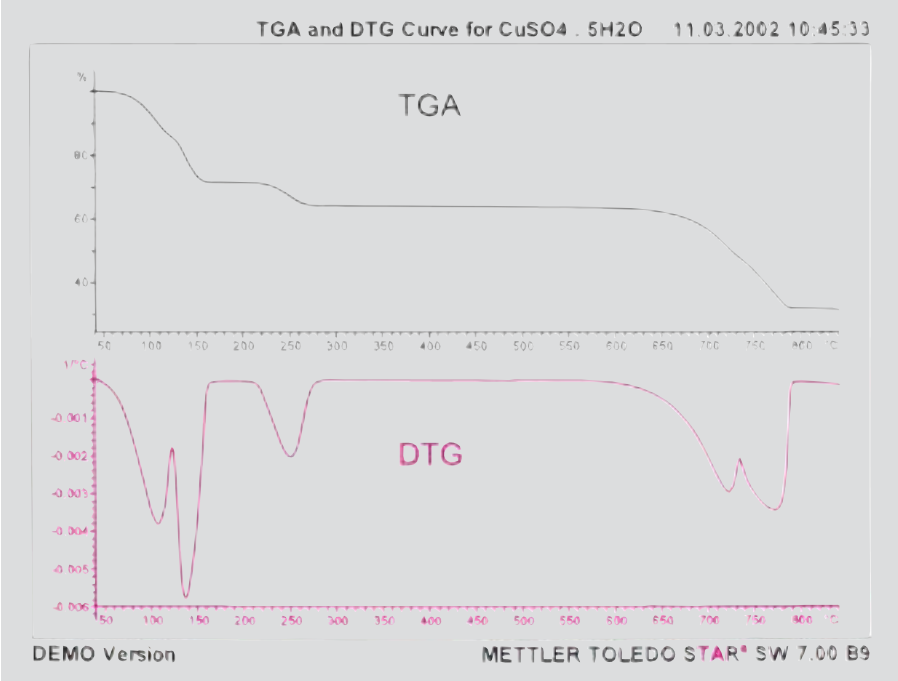

Fig. 1. TGA curve of the thermal decomposition of $CuSO_4 \cdot 5\ H_2O$ in the temperature range 40 °C to 840 °C.

Step	Reaction	Relative loss of mass in %
1-3	$CuSO_4 \cdot 5\ H_2O(s) \rightarrow CuSO_4(s) + 5\ H_2O(g)$	35.89 (calc) 35.58 (exp)
4	$CuSO_4(s) \rightarrow CuO(s) + SO_3(g)$	32.07 (calc) 32.87 (exp)

Table 1. The reactions and corresponding relative loss of mass for the thermal decomposition of $CuSO_4 \cdot 5\ H_2O$ in the temperature range 40 °C to 840 °C; (calc) refers to the theoretically calculated loss of mass, and (exp) refers to the experimentally determined loss of mass; all values refer to the original starting mass of the sample.

For the decomposition reaction, the following thermochemical data is available for 25 °C:

$$SO_3(g) \rightarrow SO_2(g) + 0.5\ O_2(g)$$

At room temperature, the equilibrium is completely on the SO_3 side.

	SO_3 (g)	SO_2 (g)	O_2 (g)
$\Delta_f H°$ / kJmol^{-1}	-395.77	-296.81	0
S° / JK^{-1}mol^{-1}	256.77	248.223	205.07
cp / JK^{-1}mol^{-1}	50.644	39.874	28.915

Table 2. Thermochemical data for oxygen, sulfur dioxide and sulfur trioxide

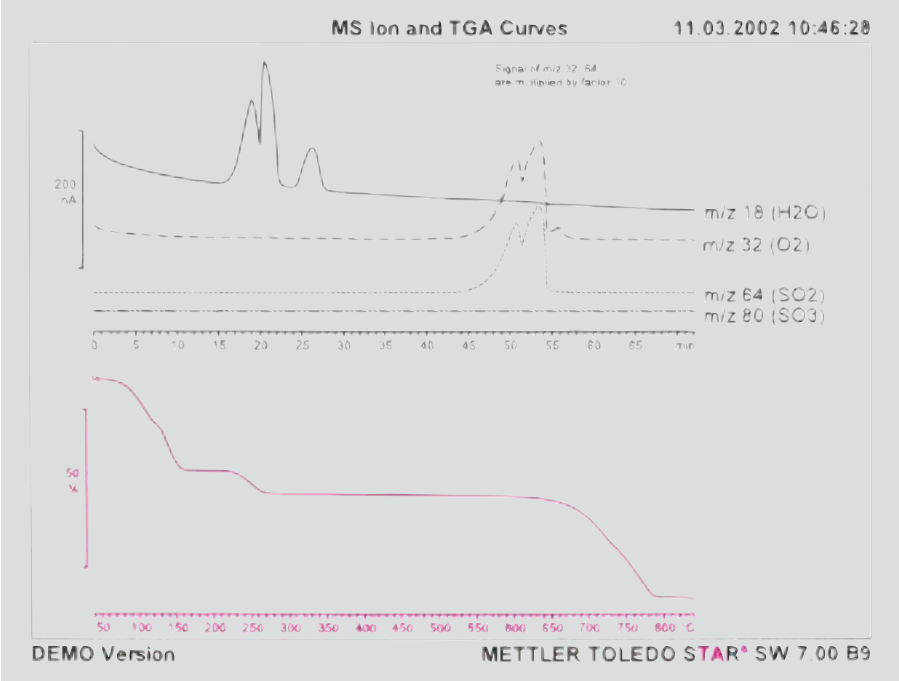

Fig. 2. TGA-MS curves for the thermal decomposition of $CuSO_4 \cdot 5\ H_2O$ in the temperature range 40 °C to 840 °C. For better presentation, some of the curves were zoomed and offset.

The following four equations can be used to determine the temperature at which the equilibrium is on the SO_2 and O_2 side.

$$\Delta_r G°(T) = \Delta_r H°(T) - T \cdot \Delta S°(T)$$

$$\Delta_r G°(T) = -R \cdot T \cdot \ln(K)$$

$$\Delta_r H°(T) = \Delta_r H°(298\ K) + \int_{298}^{T} \Delta c_p(T)\,dT$$

$$\Delta S°(T) = \Delta_r S°(298\ K) + \int_{298}^{T} \frac{\Delta c_p(T)}{T}\,dT$$

At temperatures below 780 °C, the Gibbs' free reaction enthalpy for the decomposition of SO_3 is positive, then the sign changes and the equilibrium is on the side of SO_2 and O_2.
This explains the observation that the ion current for SO_3 as a function of time remains constant. The question of the initially formed decomposition products cannot therefore be answered. The fact that O_2 and SO_2 are observed in the last two steps is evidence against a step-wise elimination of O_2 and SO_2.

What practical educational value does this experiment have?

The decomposition reaction of $CuSO_4 \cdot 5\ H_2O$ is an ideal example for demonstrating the principles of TGA-MS to students. The initially unexpected observation that SO_3 is not formed under the conditions used makes students realize the advantages that such an online coupling of the two instruments offers.
The experiment is also useful because students can apply the basic principles of chemical thermodynamics that they covered in the theoretical course to explain the experimental observations.

Investigation of delamination and foaming by TMA-MS

Cyril Darribère

Einführung

Thermomechanical analysis (TMA) measures the dimensional changes of a sample as a function of temperature. The online coupling of TMA with mass spectrometry (MS) allows the simultaneous measurement of decomposition gases and blowing or foaming agents and their effect on sample dimensions. For example, it is possible to investigate the delamination of printed circuit boards to determine the temperatures at which particular decomposition products are formed, or to follow the behavior of plastics on blowing or foaming. TMA combined with a gas analyzer (MS or FTIR) allows the dimensional changes caused by decomposition processes to be rapidly investigated or foaming processes to be optimized.
A METTLER TOLEDO STAR^e system TMA/SDTA840 was coupled to an Inficon Thermostar QMS300 mass spectrometer (mass range 1-300) by means of a heated capillary in much the same way as for the TGA-MS coupling [1].

Delamination and decomposition of a printed circuit board

Printed circuit boards (PCBs) are manufactured from woven fiberglass embedded in an epoxy resin matrix and are used as supports for electronic components.
Disks (4 mm diameter and 1.683 mm thick) were prepared from the material and the expansion behavior of the samples measured using a ballpoint probe with a load of 0.05 N. The samples were first heated up to 100 °C to remove any "memory" effects, then cooled and heated from von 30 °C to 650 °C at 20 K/min under a protective atmosphere of nitrogen (10 ml/min).
The PCB sample measured exhibits a glass transition at 92 °C. This can be seen as a change in slope in the curve in Figure 1. The sudden dimensional change the z-direction at temperatures above 320 °C indicates that the sample begins to delaminate. This process was followed simultaneously

with MS by measuring the intensities of the m/z 79 and 94 fragment ions. Theses m/z values are characteristic of bromine and methyl bromide, i.e. decomposition products of tetrabromobisphenol A (TBBA, flame-retardant). Reaction products containing bromine can even be detected immediately after the glass transition. The rapid increase in the formation of bromine-containing decomposition products above 330 °C also indicates the reason for the delamination process.

Expansion behavior of a polymer powder

Plastic granules containing a dissolved gas or a chemical blowing agent exhibit unique properties when exposed to heat. The increase in the vapor pressure of the blowing agent and the softening of the polymer result in a large increase in volume in the temperature range 80 °C to 190 °C. The increase in volume can be easily measured with TMA.

About 3 mg to 4 mg of the powder were filled in a 150-µl alumina crucible and covered with a 6-mm diameter quartz disk. A force of 0.01 N was applied to a 3-mm ballpoint probe placed on the disk. The samples were then heated from 50 °C to 400 °C at 15 K/min .

The TMA curve is displayed in Figure 2. Foaming is detected as a sudden increase in the signal, which reaches a maximum at 142 °C. Under the conditions used, the maximum volume increase is about 6000%. At temperatures above 150 °C, the foam softens still further and collapses. The two upper MS curves show that decomposition of the polymer begins above about 230 °C.

The type of blowing agent used was investigated by recording the intensity of the m/z 43 fragment ion, which was detected as soon as the expansion in the TMA began. This fragment ion is characteristic of hydrocarbons and confirms that the blowing agent is isopentane.

Information on the polymer was obtained by evaluating the fragmentation pattern of the decomposition products formed at higher TMA measurement temperatures. The results indicated that a thermoplastic copolymer based on vinylidene chloride (HCl m/z 36) and styrene (benzene m/z 78) was used.

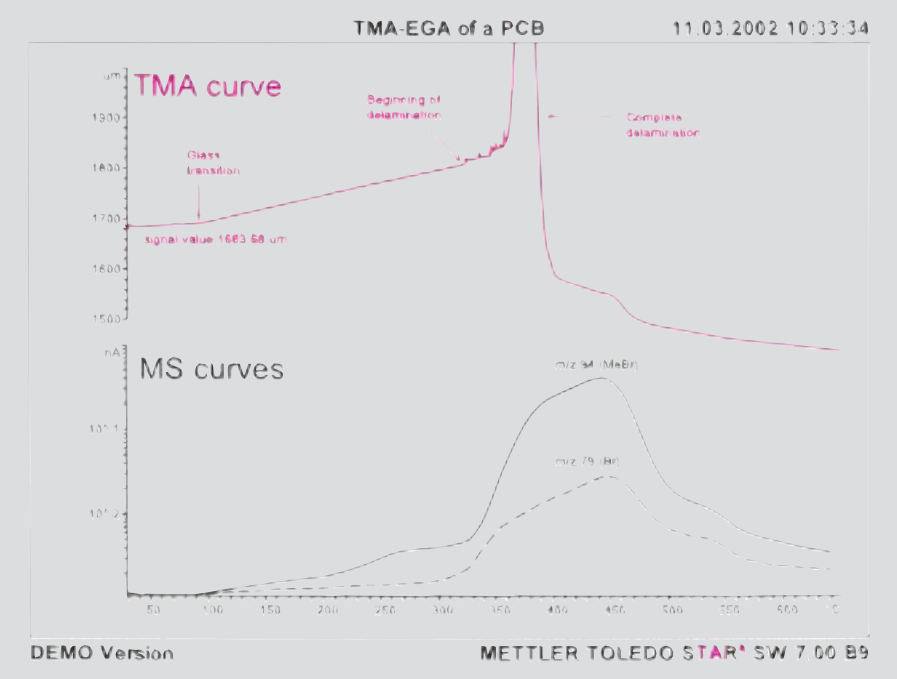

Fig. 1. TMA and MS curves of a PCB up to 650 °C. The m/z 79 and 94 fragment ion curves are displayed. These are characteristic for bromine and methyl bromide.

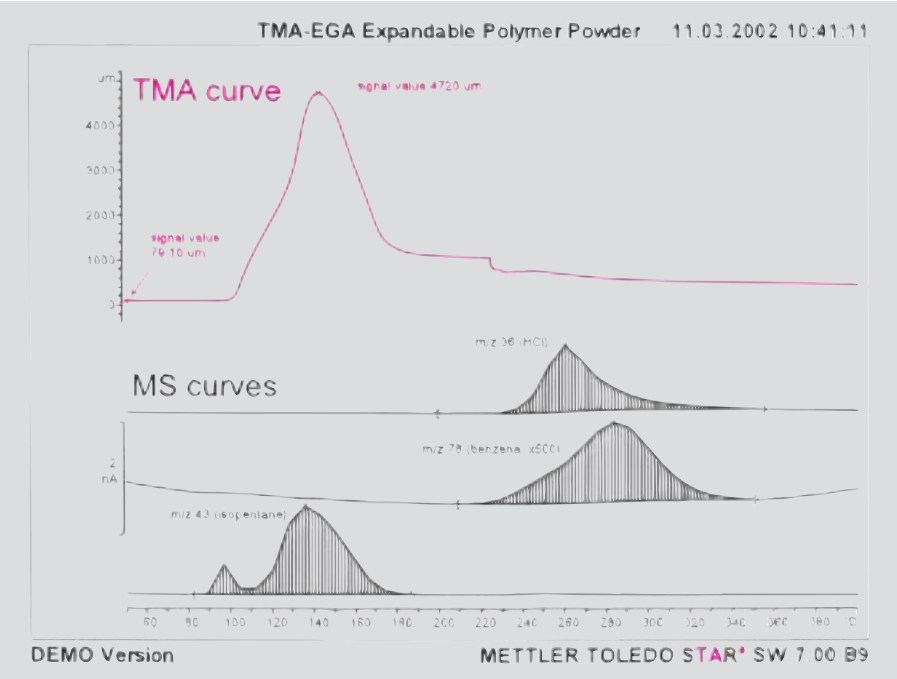

Fig. 2. TMA and MS curves of an expandable polymer powder. The m/z 36, 43 and 78 fragment ions correspond to HCl, isopentane and benzene. The m/z 78 ion curve was scale-expanded 500 times.

Summary

The application possibilities of an online combination of a thermomechanical analyzer and a mass spectrometer (TMA-MS) were demonstrated by using the system to measure a printed circuit board and an expandable copolymer. Changes in the dimensions of the sample were correlated with the release of gaseous substances. Qualitative information on the composition of the samples was obtained by mass spectrometry. TMA-MS is an excellent technique to investigate the influence of temperature on sudden changes in volume and the reasons for such changes.

Literature

[1] *Evolved Gas Analysis, Collected Applications for Thermal Analysis, Mettler-Toledo GmbH (2001), page 5 and following pages.*

Dates

Exhibitions, Conferences and Seminars - Veranstaltungen, Konferenzen und Seminare

6 th International Conference on Pharmacy and Applied Physical Chemistry	May 26-30, 2002	Ascona, Switzerland
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Urs Jörimann Electr. Engineer

e-mail: urs.joerimann@mt.com, Tel.: ++41 1 806 73 87, Fax: ++41 1 806 72 60

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