

Thermal Analysis



Applications
Handbook

Thermal Analysis of Polymers Selected Applications

METTLER TOLEDO

Thermal Analysis of Polymers

Disclaimer

This application handbook presents selected application examples. The experiments described were conducted with the utmost care using the instruments specified in the conditions at the beginning of each application. The results were evaluated according to the current state of our knowledge.

This does not however absolve you from personally testing the suitability of the examples for your own methods, instruments and purposes. Since the transfer and use of an application is beyond our control, we cannot of course accept any responsibility for the use of these methods.

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Preface

Thermal analysis is one of the oldest analysis techniques. Throughout history, people have used simple heat tests to determine whether materials were genuine or fake. The year 1887 is looked upon as the dawn of present-day thermal analysis. It was then that Henry Le Chatelier, the famous French scientist, carried out his first thermometric measurements on clays.

Just a few years later in 1899, the British scientist William Roberts-Austen performed the first differential temperature measurements and so initiated the development of DTA. Commercial instruments did not however appear until the early 1960s. Since then, thermal analysis has undergone fifty years of intense development.

The driving force behind the development of instruments has been the enormous advances in materials science and in new materials in particular. Nowadays, many different types of polymers are used for a wide diversity of products thanks to their low weight, economical manufacture and excellent physical and chemical properties. Thermal analysis is the ideal technique for determining material properties and transitions and for characterizing polymeric materials.

This handbook focuses on applications of thermal analysis techniques in the field of polymers. The techniques can of course be used in many other industries. The chapters covering the analysis of thermoplastics, thermosets and elastomers were previously published in different issues of UserCom, our bi-annual technical customer magazine (www.mt.com/ta-usercoms).

We hope that the applications described here will be of interest and make you aware of the great potential of thermal analysis methods in the polymer field.

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1. Introduction

1.1 About this Handbook

This handbook shows how thermal analysis techniques can be used to analyze polymers and in particular to study the behavior of thermoplastics, thermosets and elastomers.

The chapters describe many interesting examples that illustrate the power of thermal analysis for measuring physical properties, different types of transitions, aging, the effect of fillers and additives, and the influence of production conditions.

The experiments were performed using different types of plastic materials, namely a thermoplastic (PET), a thermoset (KU600), an ink, an elastomer (W001) and a composite material.

1.2 Important Thermal Analysis Techniques

The following sections give a brief explanation of some of the important thermal analysis techniques. The four main techniques, DSC, TGA, TMA and DMA used in this handbook are often complementary. Sometimes however, only a combination of all four techniques provides a full insight into the sample.

This is illustrated in Figure 1 which shows the measurement of a sample of polyamide 6 using DSC, TGA and TMA.

1.3 DTA

Differential Thermal Analysis

In DTA, the temperature difference between the sample and an inert reference substance is measured as a function of temperature. The DTA signal is °C or K. Previously, the thermocouple voltage in millivolts was displayed.

1.4 SDTA

Single DTA

This technique was patented by METTLER TOLEDO and is a variation of classical DTA that is particularly advantageous when used in combination with thermogravimetric analysis. The measurement signal represents the temperature difference between the sample and a previously measured and stored blank sample.

DTA and SDTA allow you to detect endothermic and exothermic effects, and to determine temperatures that characterize thermal effects.

1.5 DSC

Differential Scanning Calorimetry.

In DSC, the heat flow to and from a sample and a reference material is measured as a function of temperature as the sample is heated, cooled or held at constant temperature. The measurement signal is the energy absorbed by or released by the sample in milliwatts.

DSC allows you to detect endothermic and exothermic effects, measure peak areas (transition and reaction enthalpies), determine temperatures that characterize a peak or other effects, and measure specific heat capacity.

1.6 DSC photocalorimetry

DSC-photocalorimetry allows enthalpy changes in a material to be measured during and after exposure to light of certain wavelengths for different periods of time at different temperatures. This means that the effects of light on the behavior of light-sensitive materials can be investigated.

1.7 TGA

Thermogravimetric Analysis

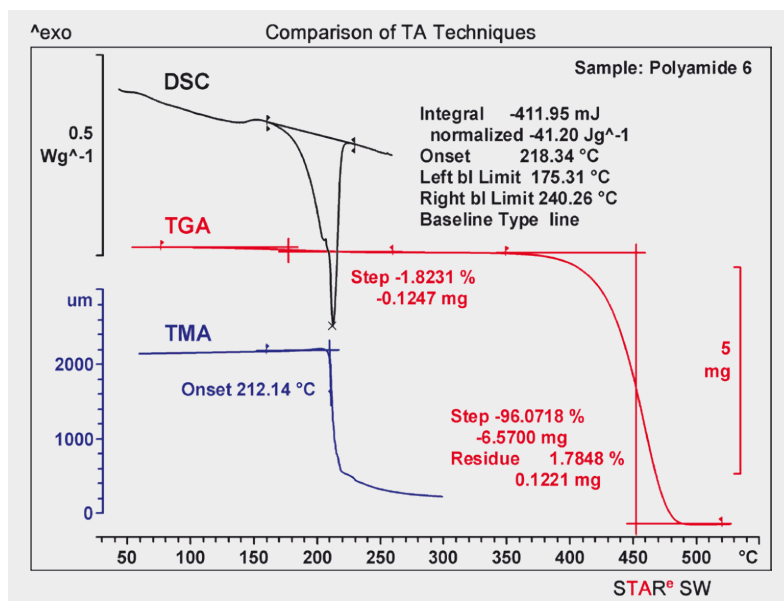
TGA measures the weight and hence the mass of a sample as a function of temperature. Previously, the acronym TG was used for this technique. Nowadays, TGA is preferred in order to avoid confusion with T_g , the glass transition temperature. TGA allows you to detect changes in the mass of a sample (gain or loss), evaluate stepwise changes in mass (usually as a percentage of the initial sample mass), and determine temperatures that characterize a step in the mass loss or mass gain curve.

1.8 EGA

Evolved Gas Analysis

EGA is the name for a family of techniques by means of which the nature and/or amount of gaseous volatile products evolved from a sample is measured as a function of temperature. The most important analysis techniques are mass spectrometry and infrared spectrometry. EGA is often used in com-

Figure 1. The techniques used to measure polyamide 6 show different thermal effects. DSC: melting peak of the crystalline part; TGA: drying and decomposition step; TMA: softening under load.



bination with TGA instruments because TGA effects involve the elimination of volatile compounds (mass loss).

1.9 TMA

Thermomechanical Analysis

TMA measures the deformation and dimensional changes of a sample as a function of temperature. In TMA, the sample is subjected to a constant force, an increasing force, or a modulated force, whereas in dilatometry dimensional changes are measured using the smallest possible load.

Depending on the measurement mode, TMA allows you to detect thermal effects (swelling or shrinkage, softening, change in the expansion coefficient), determine temperatures that characterize a thermal effect, measure deformation step heights, and to determine expansion coefficients.

1.10 DMA

Dynamic Mechanical Analysis

In DMA, the sample is subjected to a sinusoidal mechanical stress. The force amplitude, displacement (deformation) amplitude, and phase shift are determined as a function of temperature or frequency. DMA allows you to detect thermal effects based on changes in the modulus or damping behavior.

The most important results are temperatures that characterize a thermal effect, the loss angle (the phase shift), the mechanical loss factor (the tangent of the phase shift), the elastic modulus or its components the storage and loss moduli, and the shear modulus or its components the storage and loss moduli.

1.11 TOA

Thermo-optical Analysis

By TOA we mean the visual observation

of a sample using transmitted or reflected light, or the measurement of its optical transmission by means of hot-stage microscopy or DSC microscopy. Typical applications are the investigation of crystallization and melting processes and polymorphic transitions.

1.12 TCL

Thermochemiluminescence

TCL is a technique that allows you to observe and measure the weak light emission that accompanies certain chemical reactions.

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1.13 Application overview

Property or application	DSC	DTA	TGA	TMA	DMA	TOA	TCL	EGA
Specific heat capacity	•••	•						
Enthalpy changes, enthalpy of conversion	•••	•						
Enthalpy of melting, crystallinity	•••	•						
Melting point, melting behavior (liquid fraction)	•••	•		•		•••		
Purity of crystalline non-polymeric substances	•••		•••			•		
Crystallization behavior, supercooling	•••	•				•••		
Vaporization, sublimation, desorption	•••	•	•••			•••		•••
Solid–solid transitions, polymorphism	•••	•••		•		•••		
Glass transition, amorphous softening	•••	•		•••	•••	•		
Thermal decomposition, pyrolysis, depolymerization, and degradation	•	•	•••	•		•		•••
Temperature stability	•	•	•••	•		•		•••
Chemical reactions, e.g. polymerization	•••	•	•				•	
Investigation of reaction kinetics and applied kinetics (predictions)	•••	•	•••					•
Oxidative degradation, oxidation stability	•••	•••	•••	•			•••	
Compositional analysis	•••		•••					•••
Comparison of different lots and batches, competitive products	•••	•	•••	•	•	•••	•	•••
Linear expansion coefficient				•••				
Elastic modulus				•	•••			
Shear modulus					•••			
Mechanical damping					•••			
Viscoelastic behavior				•	•••			

••• means “very suitable”, • means “less suitable”

Table 1. Application overview showing the thermal analysis techniques that can be used to study particular properties or perform certain applications.

2. DSC Analysis of Thermoplastics

2.1 Introduction

This chapter describes how DSC is used to analyze a thermoplastic, PET (polyethylene terephthalate), as comprehensively as possible [1]. The results of the various methods are compared with one another. The main topics discussed are:

- Glass transition
- Cold crystallization
- Recrystallization
- Melting
- Thermal history
- Oxidation induction time
- Decomposition.

PET

PET was chosen to represent the group of thermoplastic polymers. It is a polyester produced in a polycondensation reaction between terephthalic acid and ethylene glycol. Its structure is shown in Figure 2.

PET is used for many different applications. One of the most well known is the manufacture of plastic bottles in the

beverage industry. It is also used as a fiber in the sports clothing industry because of its excellent crease-, tear- and weather-resistance properties and low water absorption.

Films of 1 to 500 μm are used for packaging materials, for the manufacture of furniture, sunshades, and so on. The finished films are often coated or laminated with other films and are widely used in the food industry, for example for packaging coffee or other foodstuffs to prevent the loss of aroma. The characterization of the properties of the material is therefore very important in order to guarantee constant quality.

2.2 Experimental details

The DSC measurements described in this chapter were performed using a DSC 1 equipped with an FRS5 sensor and evaluated with the STAR[®] software. PET samples weighing about 3 to 10 mg were prepared and pretreated depending on the application. In general, samples should have a flat surface and make good contact with the crucible. The bottom of the crucible should not be deformed by the sample material when it is sealed.

2.3 Measurements and results

Differential scanning calorimetry

DSC is a technique that measures the heat flow of samples as a function of temperature or time. The method allows physical transitions and chemical reactions to be quantitatively measured [2].

Effects of this type were analyzed with the aid of different DSC measurements. Figure 3 shows the most important events that occur when PET is measured by DSC. These are often characteristic for a substance and serve as a fingerprint, enabling them to be used for quality control.

Figure 3 displays a typical first heating measurement curve of a PET sample. It shows the glass transition, cold crystallization, and melting. The glass transition exhibits enthalpy relaxation, which is shown by the overlapping endothermic peak. The latter occurs when the sample has been stored for a long time at a temperature below the glass transition.

Cold crystallization takes place when the sample is cooled rapidly and has no time to crystallize during the cooling phase. The DSC curve can also be used to determine the specific heat capacity, c_p . Different standard procedures exist for the determination of the glass transition temperature; several of these are evaluated directly by the STAR[®] software and are shown in Figure 3.

Glass transition

The glass transition is a reversible transition that occurs when an amorphous material is heated or cooled in a particular temperature range. It is characterized by the glass transition temperature, T_g . On cooling, the material becomes brittle (less flexible) like a glass, and on heating becomes soft [2, 3, 4, 5]. In the case of thermoplastics, the glass transition correlates with the region above which the material

Figure 2. Structural formula of PET.

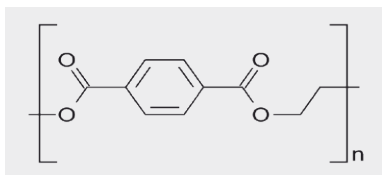
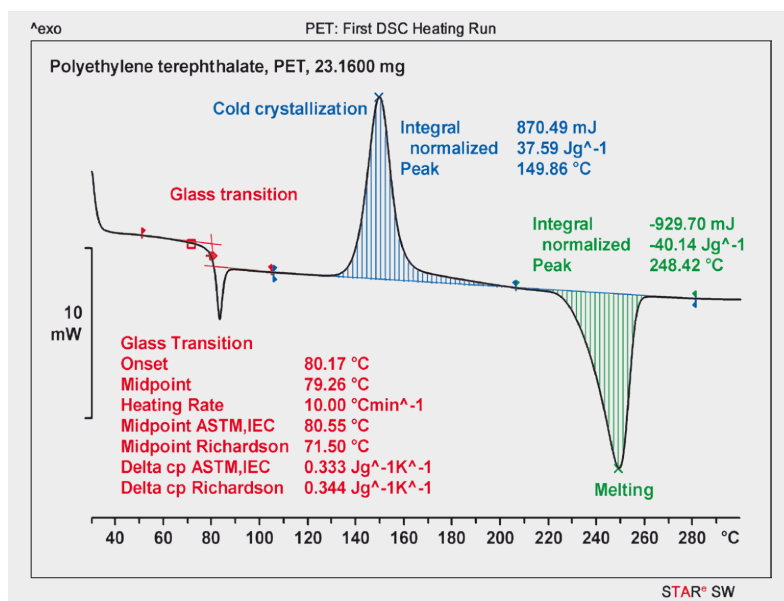


Figure 3. The main effects measured by DSC using PET as a sample. Temperature range 30–300 °C; heating rate 20 K/min; purge gas nitrogen at 50 mL/min.



can be molded. The glass transition is exhibited by semicrystalline or completely amorphous solids as well as by ordinary glasses and plastics (organic polymers).

Above the glass transition, glasses or organic polymers become soft and can be plastically deformed or molded without breaking. This behavior is one of the properties that makes plastics so useful.

The glass transition is a kinetic phenomenon; the measured value of the glass transition depends on the cooling rate, the thermomechanical history of the sample and the evaluation conditions. The lower the cooling rate, the lower the resulting glass transition that is measured in the following heating run. This means that the glass transition temperature depends on the measurement conditions and cannot be precisely defined.

In many cases, an enthalpy relaxation peak is observed that overlaps the glass transition. This depends on the history of the sample. Physical aging below the glass transition leads to enthalpy relaxation.

At the glass transition temperature, T_g , the following physical properties change:

- Specific heat capacity (c_p)
- Coefficient of Thermal Expansion, CTE, (can be measured by TMA)
- Mechanical modulus (can be measured by DMA)
- Dielectric constant

The 2/3 rule can be used as a rule of thumb. This states that the glass transition temperature corresponds to 2/3 of the melting point temperature (in Kelvin):

- For PET: T_{melt} is 256 °C or 529.16 K
- $T_g \sim 352.8$ K or 79.6 °C

The glass transition appears as a step in the DSC curve and shows the change of the specific heat capacity, c_p , from the solid to the liquid phase.

Cold crystallization

Cold crystallization is an exothermic crystallization process. It is observed on heating a sample that has previously been cooled very quickly and has had no time to crystallize. Below the glass transition, molecular mobility is severely restricted and cold crystallization does not occur; above the glass transition, small crystallites are formed at relatively low temperatures. The process is called cold crystallization.

Melting

Melting is the transition from the solid to the liquid state. It is an endothermic process and occurs at a defined temperature for pure substances. The temperature remains constant during the transition: The heat supplied is required to bring about the change of state and is known as the latent heat of melting.

Crystallinity

The degree of crystallinity is the percentage crystalline content of a semicrystalline substance. Thermoplastics normally exhibit a degree of crystallinity of up to 80%. The degree of crystallinity of a material depends on its thermal history. It can be determined by measuring the enthalpy of fusion of the sample and dividing this by the enthalpy of fusion of the 100% crystalline material. 100% crystalline materials can be determined by X-ray diffraction.

Semicrystalline samples such as PET undergo cold crystallization above their glass transition. This makes it difficult to determine their degree of crystallinity before the measurement. This particular topic will therefore not be further discussed in this chapter.

Recrystallization

Recrystallization is a type of reorganization process in which larger crystallites are formed from smaller crystallites. The process is heating-rate dependent: the lower the heating rate, the more time there is for reorganization. Recrystallization is difficult to detect by DSC because exothermic crystallization and endothermic melting occur simultaneously.

Heating-Cooling-Heating

Figure 4 shows a measurement in which a sample was heated, cooled, and then heated again at 20 K/min. This type of experiment is often performed to thermally pretreat the sample in a defined way in the first heating run. In Figure 4, the first heating run corresponds to the curve shown in Figure 3. The figure also shows that the second heating run is very different to the first run – the melting peak is broader and the relaxation at the glass transition and the cold crystallization are no longer present. During cooling the sample had

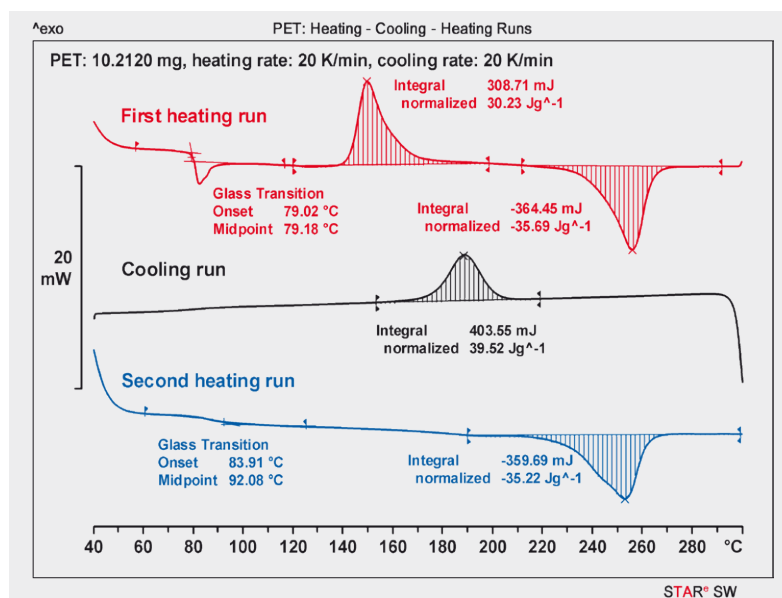


Figure 4. First and second heating runs and the cooling curve demonstrate differences regarding relaxation at the glass transition and the disappearance of cold crystallization.

sufficient time for crystallization to occur. The crystallization peak is clearly visible in the cooling curve. Since the sample was heated immediately afterward, no enthalpy relaxation occurs because it had no time to undergo physical aging.

In practice, heating-cooling-heating experiments are used to eliminate the thermal history of material and to check the production process of a sample. In the second heating run, the glass transition step is smaller. This means that the content of amorphous material is lower and the crystalline content larger than in the first

heating run. Crystallization results in a decrease in the amorphous content and a corresponding increase in the degree of crystallinity.

Different cooling rates

Figure 5 shows the influence of different cooling rates on crystallization and the temperature range in which crystallization occurs. The higher the cooling rate, the more the crystallization peak is shifted to lower temperatures. When the sample is cooled very slowly, cold crystallization is not observed in the heating run performed immediately afterward. In contrast, if the sample is cooled rapidly, it has no time to crystal-

lize and cold crystallization is observed when the sample is heated. For example, if PET is cooled at 50 K/min, the sample cannot crystallize completely. As a result, the amorphous part of the sample exhibits cold crystallization in the following heating run.

Thermal history

Figure 6 illustrates the influence of the thermal history on a PET sample. The sample was cooled under different conditions: first cooled very slowly, second shock cooled, and third shock cooled and annealed at 65 °C for ten hours, that is, stored at a temperature somewhat below that of the glass transition temperature. The heating measurements performed after each cooling run show clear differences. The sample that was slowly cooled shows only a small step at the glass transition and no cold crystallization – sufficient time was available for the sample to crystallize and so the content of amorphous material is low. The shock-cooled sample shows a large glass transition step. This indicates that the amorphous content is high. Furthermore, a cold crystallization peak is observed because the sample did not have sufficient time to crystallize.

The sample annealed at 65 °C for ten hours exhibits enthalpy relaxation as a result of the aging process in addition to the effects seen in the shock-cooled sample. The melting peaks of the three samples are almost identical. The melting peak does not seem to be influenced by the thermal pretreatment.

Figure 7 shows the influence of different annealing times on enthalpy relaxation. The sample was first heated from 30 to 300 °C at a heating rate of 10 K/min and then shock cooled and annealed at 65 °C for different times (0 to 24 h). The measurements were performed from 30 to 300 °C at a heating rate of 10 K/min.

The longer a sample is stored below the glass transition, the greater the enthalpy relaxation and the more pro-

Figure 5. DSC measurements of the same sample performed at different cooling rates. At low cooling rates, cold crystallization cannot be detected on heating because sufficient time was available for crystallization to occur during cooling.

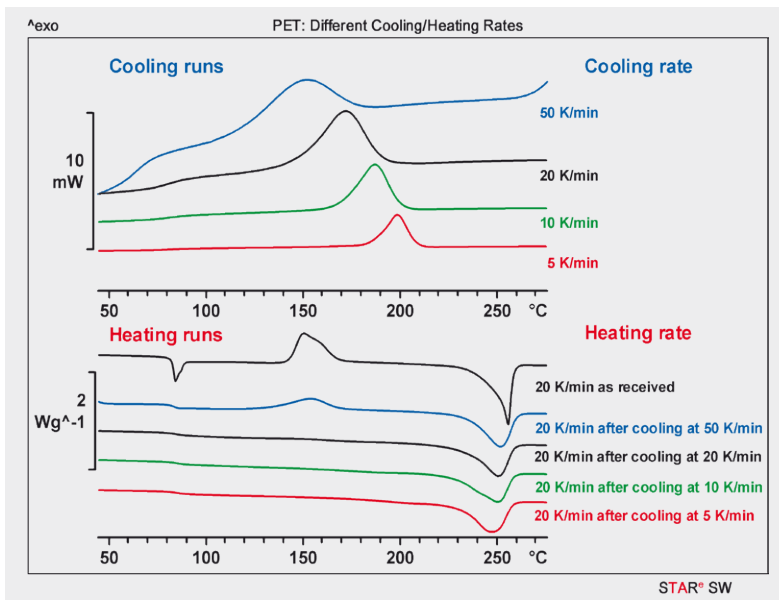
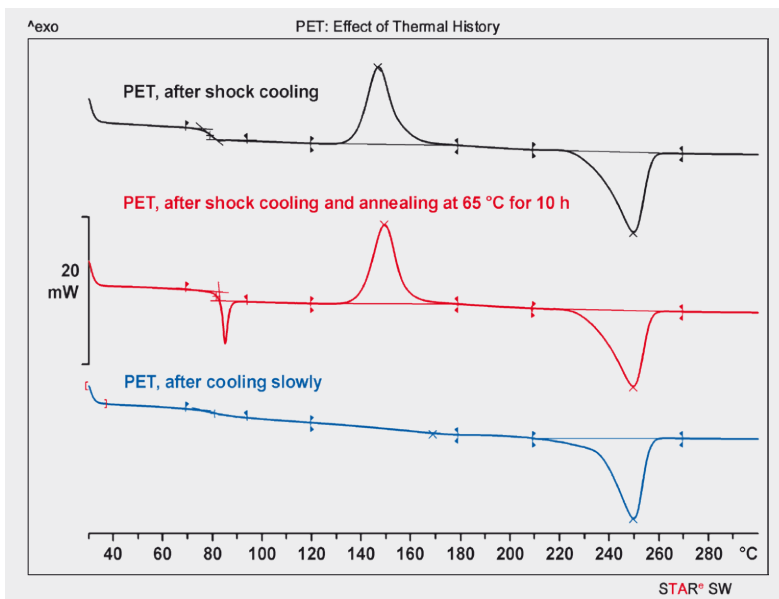


Figure 6. Heating curves of a PET sample after cooling under different conditions.



nounced the effect of physical aging. The enthalpy relaxation peak is often a result of the thermal history of a sample and affects the evaluation of the glass transition. The peak can be eliminated by first heating the sample to a temperature slightly above the glass transition, shock cooling it and then heating it a second time. In fact, enthalpy relaxation contains valuable information about the thermal and mechanical history of a sample (storage temperature, storage time, cooling rate, etc.). In practice, the temperature at which samples or materials are stored is an important factor that should be taken into account in order to prevent undesired physical aging.

Heating rates

Figure 8 illustrates the influence of different heating rates on the DSC measurement of PET samples [6, 7]. The higher the heating rate, the less time there is for crystallization. At 300 K/min, the sample has no time to crystallize and consequently shows no melting peak.

TOPEM™

TOPEM is the newest and most powerful temperature-modulation technique used in DSC alongside IsoStep and ADSC. It allows reversing and non-reversing effects to be separated from each other. Figure 9 shows the results obtained from a **TOPEM** measurement of PET using standard parameters. The sample was preheated to 80 °C and shock cooled by removing the crucible from the furnace and placing it on a cold aluminum plate. The **TOPEM** experiment was performed in a 40- μ L aluminum crucible with a hole in the lid at a heating rate of 0.2 K/min.

The uppermost curve in Figure 9 shows the measurement data before evaluation. The **TOPEM** evaluation yields separate curves for the total heat flow (black), reversing heat flow curve (red) and the non-reversing heat flow curve (blue). In addition, the quasi-static c_{p0} can be calculated from the measurement. In a second step, the

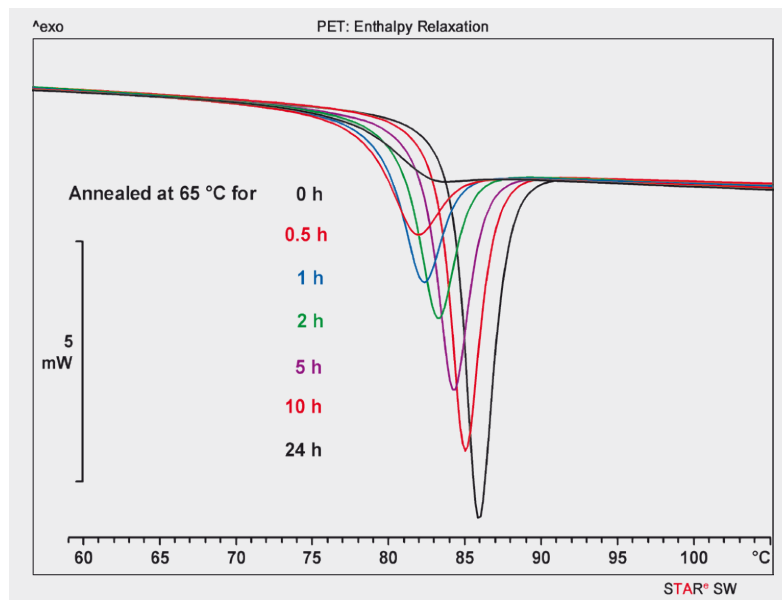


Figure 7. Heating runs showing the influence of different annealing times on the glass transition and the enthalpy relaxation peak of PET.

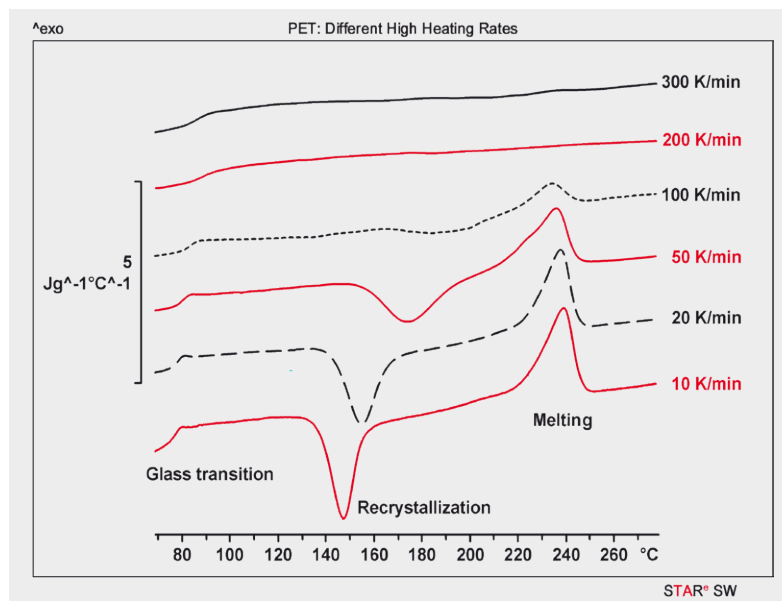


Figure 8. DSC measurements of PET at high heating rates, shown as c_p curves.

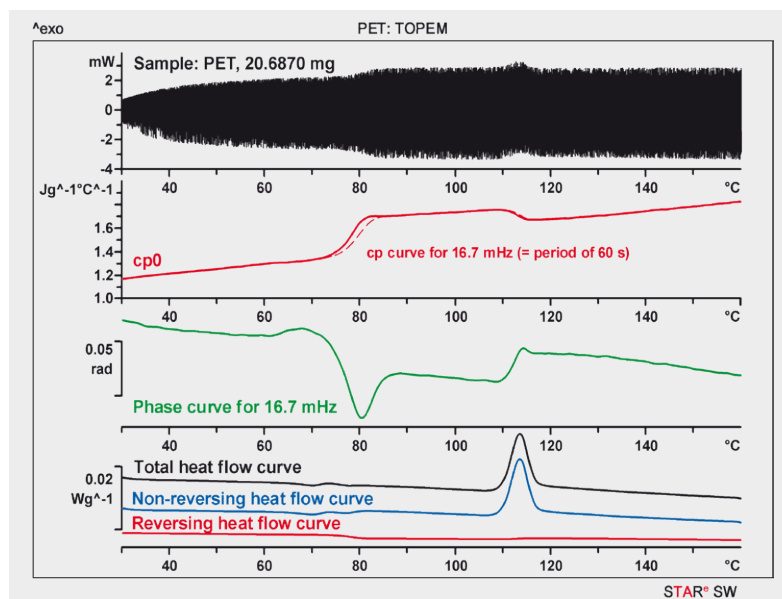


Figure 9. Measurement of a PET sample using **TOPEM** showing the reversing, non-reversing and total heat flow curves.

heat capacity or phase can be determined at user-defined frequencies. In Figure 9, this is done at a frequency of 16.7 Hz. **TOPEM** [8, 9] is also an excellent technique to determine c_p and to separate effects that cannot be separated by DSC. For example, it can separate the enthalpy change associated with a glass transition from the enthalpy produced in a reaction that occurs simultaneously – a glass transition is a reversing effect while a reaction is a non-reversing effect.

The **TOPEM** technique uses a stochastic temperature profile. This allows the sample to be characterized from the results of just one single measurement.

The curves in Figure 10 show the frequency dependence of the glass transition of a sample of PET. In this case, the glass transition shifts to higher temperature at higher frequencies. In contrast, the step in the curve due to cold crystallization occurs at the same temperature and is independent of frequency. The frequency dependence of certain effects shown by unknown substances can thus be studied in order to clarify the interpretation of their origin.

Oxidative stability (OIT/OOT)
Finally, we would like to briefly explain two DSC methods known as OIT and OOT that are used to measure the

oxidative stability [10, 11] of polymers and oils. The methods simulate the accelerated chemical aging of products and allow information to be obtained about their relative stability. For example, different materials can be compared with one another or samples of the same material containing different additives can be analyzed to determine the influence of an additive. In practice, the method is widely used for PE (polyethylene). The application example described below also uses a sample of PE because the decomposition of PET is overlapped by melting and re-esterification and cannot be clearly identified.

Figure 10. Measurement of a PET sample using **TOPEM** showing the frequency dependence of the glass transition.

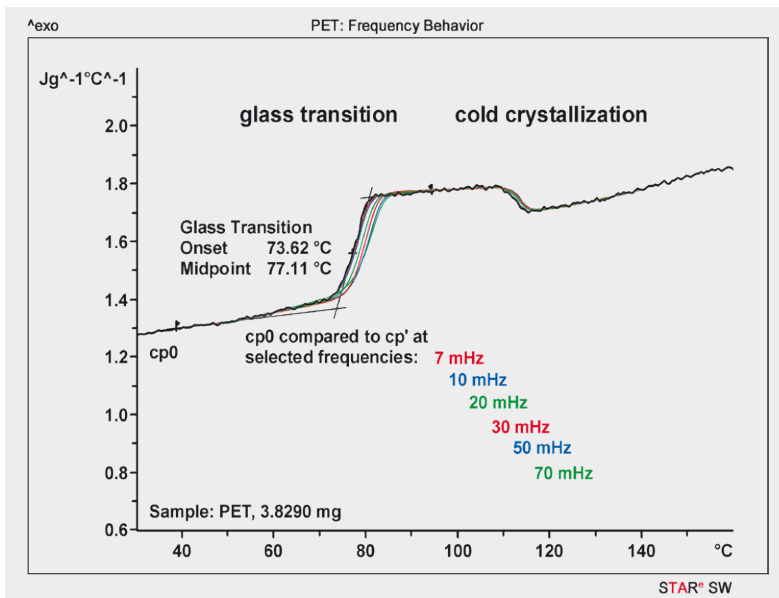
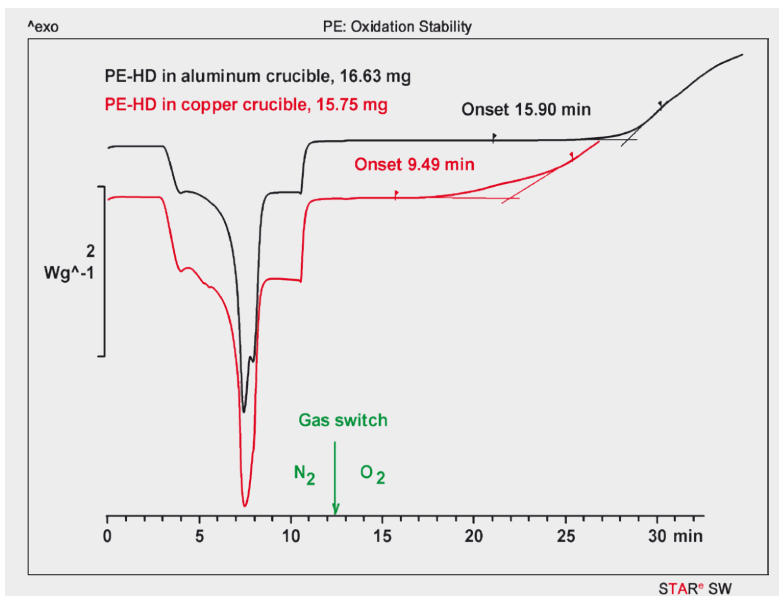


Figure 11. OIT measurements of PE in different crucibles.



The OIT (Oxidation Induction Time) measurement of PE (Figure 11) is often performed in crucibles made of different metals in order to determine the influence of the particular metal on the stability of the PE. In this example, the measurement was started in a nitrogen atmosphere according to the following temperature program: 3 min at 30 °C, heating at 20 K/min from 30 to 180 °C, then isothermal at 180 °C. After 2 min the gas was switched to oxygen. The measurement was stopped as soon as oxidation was observed. The OIT is the time interval from when the purge gas is switched to oxygen to the onset of oxidation. Measurements were performed in open 40- μ L aluminum and copper crucibles for comparison. Oxidation clearly takes place much earlier in the copper crucible than in the aluminum crucible. The copper acts as a catalyst and accelerates the decomposition of PE.

The oxidative stability of samples can also be compared by measuring the Onset Oxidation Temperature (OOT). In this method, the sample is heated in an oxygen atmosphere and the onset temperature at which oxidation begins is evaluated.

Since OIT measurements are easy to perform and do not take much time, they are often used in quality control to compare the stability of products.

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- ▶ www.mt.com/ta-aiwizard



3. TGA, TMA and DMA Analysis of Thermoplastics

3.1 Introduction

This chapter focuses on the use of TGA, TMA and DMA techniques. Effects such as decomposition, expansion, cold crystallization, glass transition, melting, relaxation and recrystallization are discussed in detail. TGA, TMA and DMA yield valuable complementary information to DSC measurements.

3.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a technique that measures the mass of a

sample while it is heated, cooled or held isothermally in a defined atmosphere. It is mainly used for the quantitative analysis of products.

A typical TGA curve shows the mass loss steps relating to the loss of volatile components (moisture, solvents, monomers), polymer decomposition, combustion of carbon black, and final residues (ash, filler, glass fibers). The method allows us to study the decomposition of products and materials and to draw conclusions about their

individual constituents.

The first derivative of the TGA curve with respect to time is known as the DTG curve; it is proportional to the rate of decomposition of the sample. In a TGA/DSC measurement, DSC signals and weight information are recorded simultaneously. This allows endothermic or exothermic effects to be detected and evaluated.

The DSC signal recorded in a TGA/DSC measurement is, however, less sensitive than that obtained from a dedicated DSC instrument and the DSC curves are less well resolved.

Figure 12. Measurement curves of PET recorded from 30 to 1000 °C at a heating rate of 20 K/min using a TGA/DSC 1 equipped with a DSC sensor. The TGA curve shows the change in mass of the sample and the DSC curve the endothermic or exothermic effects.

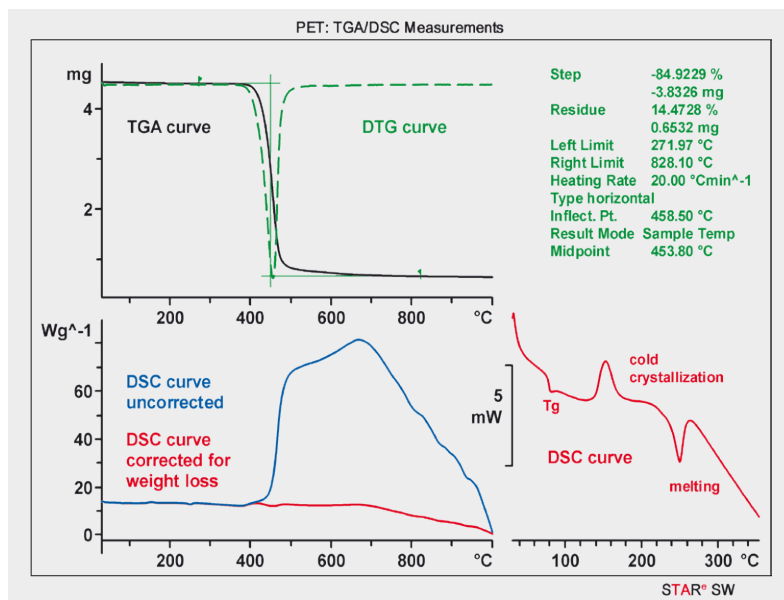
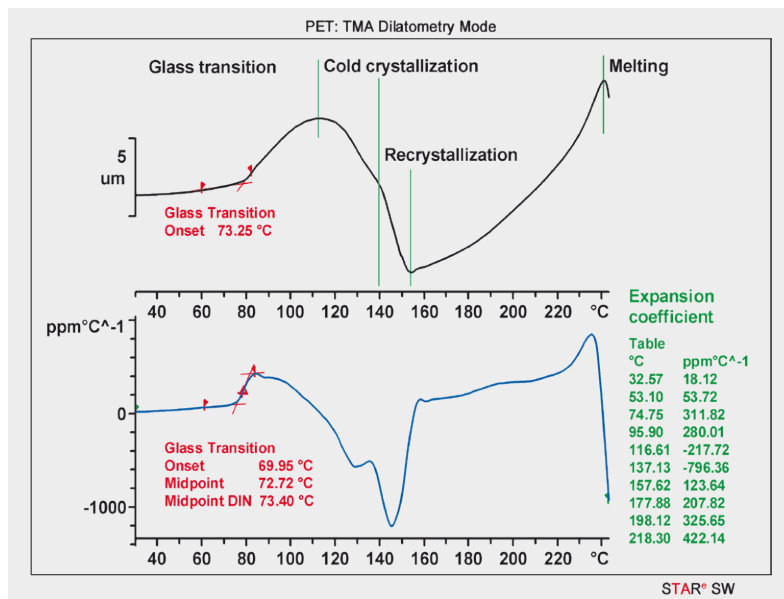


Figure 13. TMA measurement of PET in the dilatometry mode.



The upper diagram of Figure 12 shows TGA and DTG curves of PET. The two lower diagrams are the corresponding DSC curves measured in a nitrogen atmosphere. The DSC curve on the right in the range up to 300 °C shows the glass transition, cold crystallization, and the melting process. The DSC signal can be corrected for the mass lost by the sample during the measurement (left); the blue curve is the uncorrected curve and the red curve is corrected for the loss of mass [1, 2].

Decomposition

In a decomposition process, chemical bonds break and complex organic compounds or polymers decompose to form gaseous products such as water, carbon dioxide or hydrocarbons.

Under non-oxidizing (inert) conditions, organic molecules may also degrade with the formation of carbon black. Volatile decomposition products can be identified by connecting the TGA to a Fourier transform infrared spectrometer (FTIR) or a mass spectrometer (MS).

3.3 Thermomechanical analysis (TMA)

Thermomechanical analysis measures the dimensional changes of a sample as it is heated or cooled in a defined at-

mosphere. A typical TMA curve shows expansion below the glass transition temperature, the glass transition (seen as a change in the slope of the curve), expansion above the glass transition temperature and plastic deformation. Measurements can be performed in the dilatometry mode, the penetration mode, or the DLTMA (Dynamic Load TMA) mode.

Dilatometry

The aim of dilatometry is to measure the expansion or shrinkage of a sample. For this reason, the force used is very low and is just sufficient to ensure that the probe remains in contact with the sample. The result of the measurement is the coefficient of thermal expansion (CTE). The dilatometry measurement shown in Figure 13 was performed using a sample about 0.5 mm thick sandwiched between two silica disks. It was first preheated in the instrument to 90 °C to eliminate its thermal history. After cooling, it was measured in the range 30 to 310 °C at a heating rate of 20 K/min using the ball-point probe and a very low force of 0.005 N.

The curve in the upper diagram of Figure 13 shows that the sample expands only slowly up to the glass transition. The expansion rate then increases significantly on further heating due to the increased mobility of the molecules in the liquid state. Afterward, cold crystallization and recrystallization processes occur and the sample shrinks. The sample expands again after crystallite formation above about 150 °C and finally melts. The melting is accompanied by a drastic decrease in viscosity and sample height.

Penetration

Penetration measurements mainly yield information about temperatures. The thickness of the sample is not usually important because the contact area of the probe with the sample changes during the experiment. The depth of penetration is influenced by the force used for the measurement and the sample geometry.

For the penetration measurement, a sample about 0.5 mm thick was placed on a silica disk; the ball-point probe rested directly on the sample. The measurements were performed in the range 30 to 300 °C at a heating rate of 20 K/min using forces of 0.1 and 0.5 N. In this case, the sample was not preheated.

During the penetration measurement, the probe penetrates more and more into the sample. The ordinate signal decreases significantly at the glass transition, remains more or less constant after cold crystallization, and then decreases again on melting (Figure 14).

DLTMA

DLTMA is a very sensitive method for determining physical properties. In contrast to DSC, it characterizes the mechanical behavior of samples. In DLTMA (Dynamic Load TMA) [3], a high and a low force alternately act on the sample at a given frequency. This allows weak transitions, expansion, and the elasticity (Young's modulus) of samples to be measured. The larger the stiffness of the sample, the smaller the amplitude.

The measurement curve in Figure 15 shows the glass transition at 72 °C followed by the expansion of the

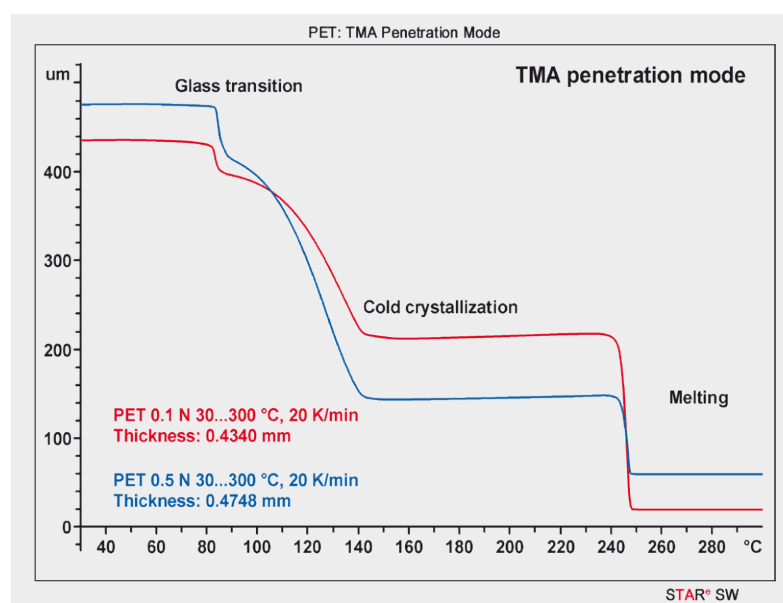


Figure 14. TMA of PET measured in the penetration mode.

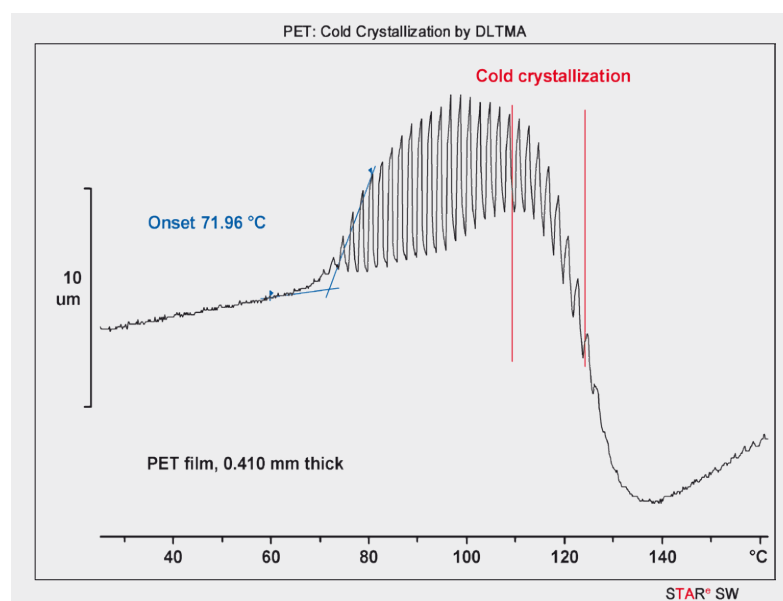


Figure 15. DLTMA measurement of PET from room temperature to 160 °C.

material in the liquid state; the amplitude is large because the material is soft. This is followed by cold crystallization; the PET shrinks and the amplitude becomes smaller. At 140 °C, the sample is once again hard. The sample then expands on further temperature increase to 160 °C.

3.4 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis measures the mechanical properties of a viscoelastic material as a function of time, temperature or frequency while the material is subjected to a periodically oscillating force.

In a typical measurement, an oscillating force is applied to the sample at different frequencies. The elastic modulus is measured as the shear storage modulus, G' , and loss modulus, G'' . This data is used to calculate $\tan \delta$, the loss factor, or the damping coefficient, G''/G' . DMA is much more sensitive than other methods. For example, it can measure glass transitions of filled materials or thin layers on substrate material, that is, transitions which are difficult to detect by DSC.

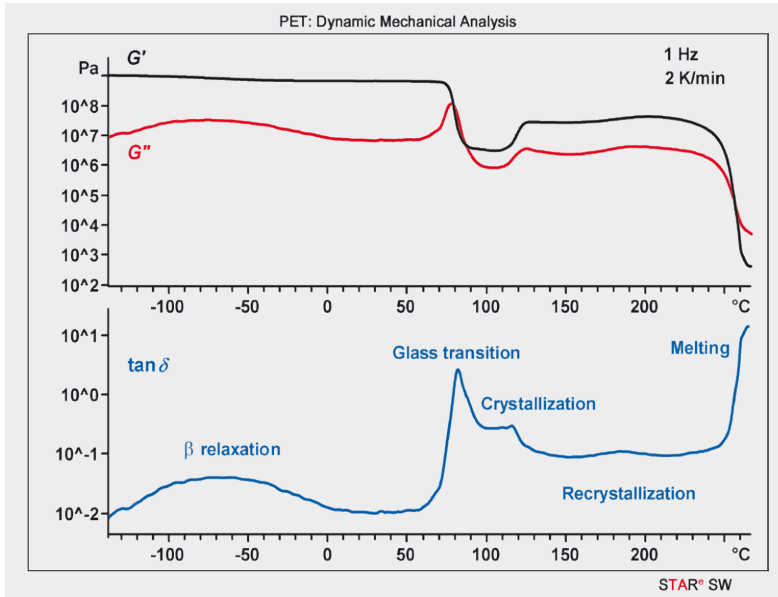
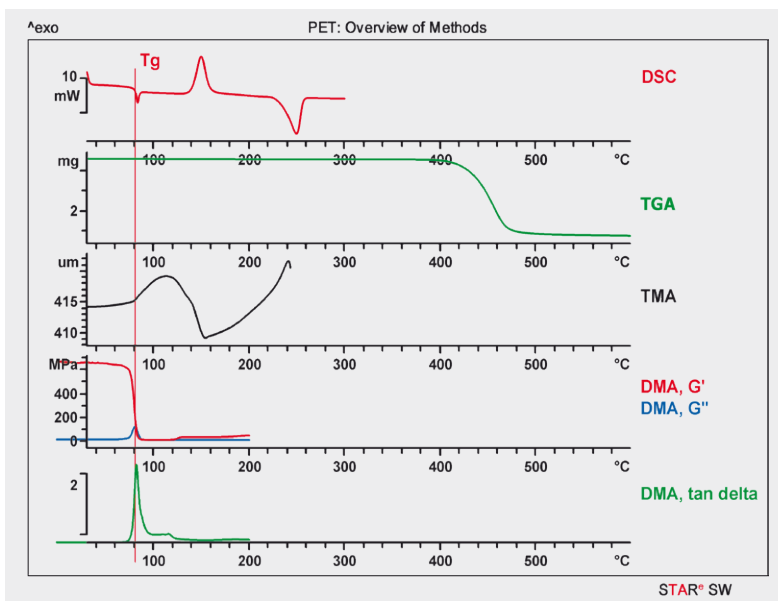


Figure 16. DMA shear measurement of PET in the range -150 °C to +270 °C.

Figure 16 displays the DMA measurement curve of a shock-cooled PET sample 5 mm in diameter and 0.49 mm thick in the shear mode at 1 Hz in the range -150 °C to +270 °C. The heating rate was 2 K/min.

The DMA curve also shows other effects such as β relaxation (local movement of polymer groups) or recrystallization in addition to the effects detected by TMA or TGA/DSC such as the glass transition, crystallization and melting. β relaxation is weak and can only be measured by DMA. Other thermal analysis techniques such as DSC or TGA cannot detect this transition.

Figure 17. Overview of the effects and comparison of the results.



3.5 Overview of the effects and comparison of the results

Figure 17 presents an overview of the different thermal methods used to analyze PET. Table 2 summarizes the effects that can be measured by different thermal methods.

Table 3 compares the results obtained for PET using the various techniques. The temperatures given for TGA/DSC and DSC refer to peak temperatures,

Table 2. Effects measured by different analytical methods.

Effects	DSC	TGA/DSC	TMA	DMA
β relaxation				x
Glass transition	x	x (DSC signal)	x	x
Cold crystallization	x	x (DSC signal)	x	x
Recrystallization	(x)			x
Melting	x	x	x	x
Decomposition	(x)	x	(x)	
OIT	x			

Table 3.
Comparison of the results of PET determined by different techniques.

Effects	DSC (20 K/min)	TGA/DSC (20 K/min, DSC, N ₂)	TMA (20 K/min)	DMA (1 Hz, 2 K/min, tan delta)
β relaxation				-77 °C
Glass transition	80 °C	81 °C	77 °C	81 °C
Cold crystallization	150 °C	154 °C	152 °C	118 °C
Recrystallization				183 °C
Melting	248 °C	251 °C	242 °C	254 °C
Decomposition		433 °C		

the TMA temperatures to the beginning of the change in expansion, and the DMA temperatures to the peaks in the tan delta curve.

It is evident that the different methods yield consistent results, complement one another and provide important information for the characterization of material properties. This is particularly useful for the quality control of substances, for the examination of unknown materials or for damage and failure analysis, for example to detect possible impurities in a material. In practice, a comprehensive analysis using several techniques is very informative.

Conclusions

The first two chapters illustrated the different possibilities that are available for characterizing a thermoplastic by

thermal analysis. The techniques used were DSC, TGA, TMA, and DMA.

The thermoplastic chosen for the measurements was PET. The results agree well with one another. The main effects investigated were the glass transition, cold crystallization, recrystallization, melting and decomposition. Topics such as OIT and the thermal history of samples were also covered. Similar effects to those described for PET occur with other polymers.

A particular effect can often be measured by different thermal analysis techniques. The results obtained from one technique are used to confirm those from another technique. For comprehensive materials characterization, samples are usually first investigated by TGA, then by DSC and TMA, and finally by DMA.

3.6 References

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- [3] PET, Physical curing by dynamic load TMA, UserCom 5, 15.

For more information:

- ▶ www.mt.com/ta-libraries
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4. DSC Analysis of Thermosets

4.1 Introduction

This chapter presents a number of DSC applications. The main effects described are the glass transition and specific heat capacity, curing reactions and kinetics, thermal history, temperature-modulated DSC (ADSC).

Thermal analysis encompasses a number of techniques that are used to measure the physical properties of a substance as a function of time while the substance is subjected to a controlled temperature program. The tech-

niques include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA).

Thermal analysis is employed in research and development, process optimization, quality control, material failure and damage analysis as well as to investigate competitive products. Typical applications include making predictions about the curing behavior of products, testing the compatibility

of composite materials or investigating the frequency dependence of the glass transition.

KU600

The well-known product KU600 is based on an epoxy resin and a catalyst. It is a good example of a powder coating material for electrical and electronic components. It is used to insulate metal components or as a protective coating for ceramic condensers.

It provides good adhesion to substrates, an excellent combination of mechanical, electrical and thermal properties, and very good resistance to chemicals.

4.2 Experimental details

The analytical techniques used to measure KU600 in Chapters 4 and 5 were DSC, TGA, TMA and DMA.

The following instruments were employed: DSC 1 with FRS5 sensor, TGA/DSC 1 with DSC sensor, TMA/SDTA840^o, and DMA/SDTA861^o. The results were evaluated using the STAR^o software. KU600 as a single component powder was used for all measurements without any special sample preparation.

4.3 Differential Scanning Calorimetry (DSC)

Main effects

DSC is used to measure the heat flow to or from a sample as a function of temperature or time. The technique can quantitatively analyze both physical transitions and chemical reactions [1]. Figure 18 shows the basic effects that are observed when an initially uncured thermoset is measured by DSC. The figure displays three heating runs. The first heating run (blue) was stopped at 100 °C and shows the glass transition accompanied by enthalpy relaxation. The latter occurs when the sample is stored for a longer period below the glass transition temperature. It has to do with physical aging of the material.

Figure 18. KU600: DSC experiment of a heating rate of 10 K/min showing the first, second and third heating runs.

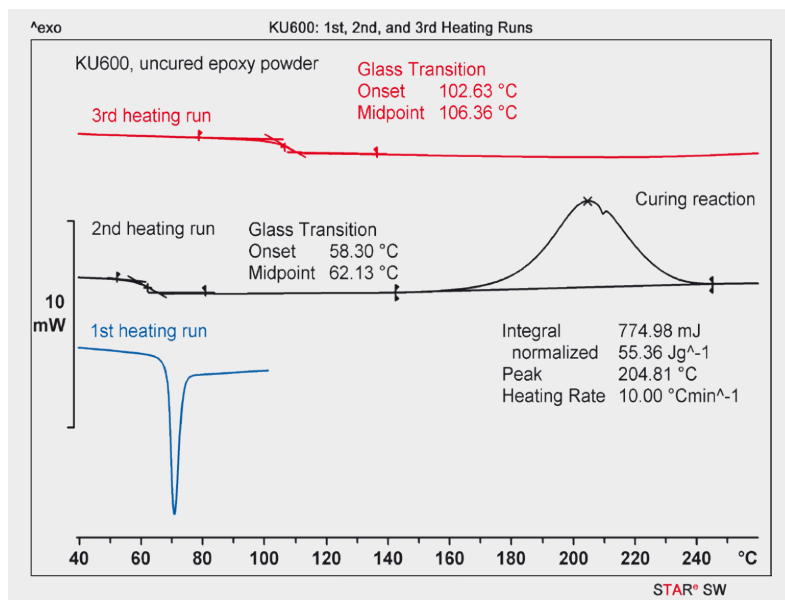
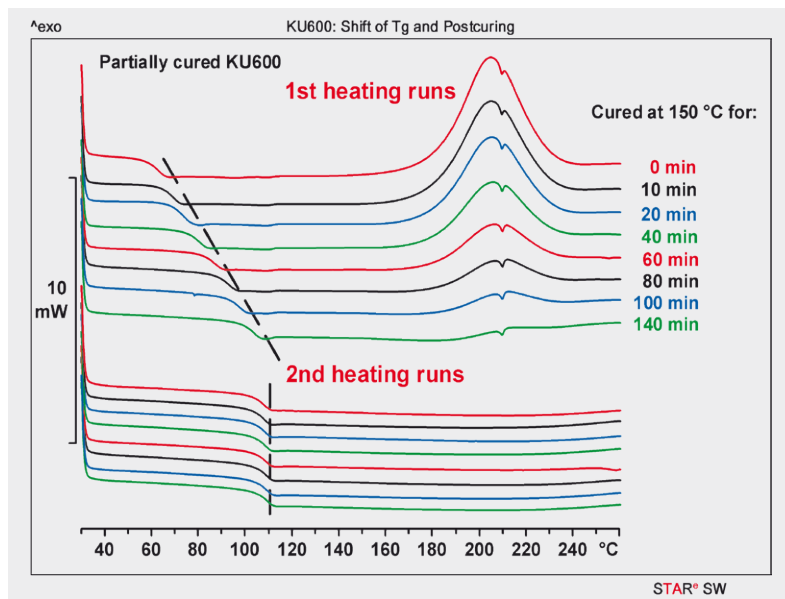


Figure 19. KU600: The first and second DSC heating runs measured at a heating rate of 10 K/min after curing isothermally at 150 °C for different times.



The first heating run eliminates the thermal history of the sample. The second heating run shows the glass transition followed by a large exothermic reaction peak that characterizes the curing of the epoxy resin. A small endothermic peak can be seen at about 210 °C in the middle of the exothermic curing peak. This is caused by the melting of an additive (dicyandiamide) in the KU600.

The third heating run looks completely different. The material has obviously undergone a drastic change. Initially, the sample was present as a powder.

This coalesced and cured during the second heating run to form a solid crosslinked material that exhibits different properties. In particular, the third heating run shows that the glass transition has shifted to higher temperature and that no further exothermic reaction occurs.

Figure 19 summarizes the results obtained when KU600 was stored isothermally for different times at 150 °C and then measured in dynamic DSC experiments. In each case, first and second heating runs were performed. The results show that the glass transition temperature clearly depends on the degree of cure. The higher the degree of cure, the more the glass transition shifts to higher temperature. The first heating run also shows that the area of the postcuring reaction peak decreases with increasing degree of cure. Completely cured material shows no post-curing at all [2].

Thermal history

Figure 20 shows the effect of different cooling rates on the glass transition. Cured KU600 was first cooled at different rates and the effect on the glass transition measured in subsequent heating runs at 10 K/min. Low cooling rates have the same effect as long annealing times below the glass transition temperature. The lower the cooling rate, the larger the enthalpy relaxation effect. The enthalpy relaxation can

therefore be used to check whether the process or storage conditions remain the same.

Isothermal and dynamic curing

Figure 21 shows the isothermal DSC curves and calculated conversion curves for the curing of KU600. The higher the curing temperature, the shorter the curing time. In this example, samples of KU600 at room temperature were inserted into a pre-heated instrument at 180 and 190 °C. The upper diagram shows the two isothermal curing curves and the lower diagram the corresponding conversion curves. The latter indicate the

time taken to reach a particular conversion.

For example, a degree of cure of 80% takes about 10.8 min at 180 °C and about 6 min at 190 °C. To achieve complete curing or 100% cured material, the isothermal curing temperature must be greater than the glass transition temperature of the fully cured material.

Dynamic curing is another possible approach. In Figure 22 (1, above left) the KU600 was measured dynamically at different heating rates. The results show that the glass transition with the

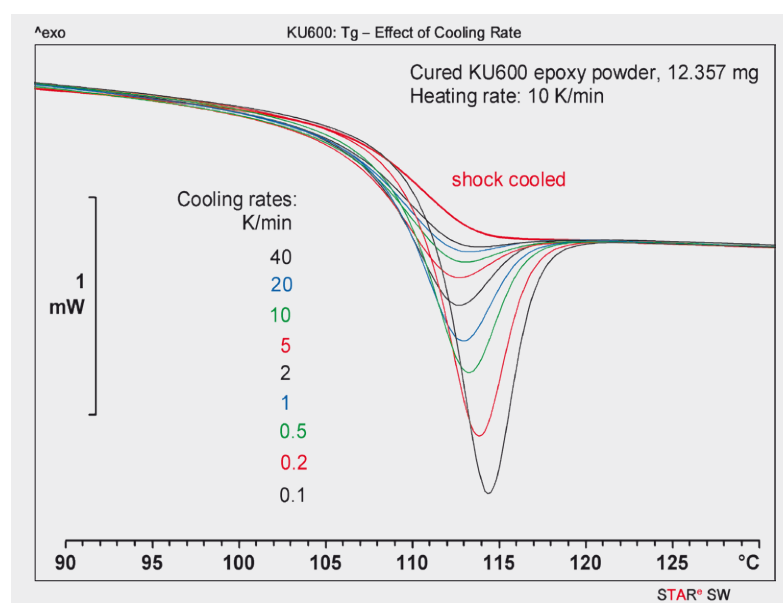


Figure 20. KU600: DSC experiment showing the effect of different cooling rates on the glass transition.

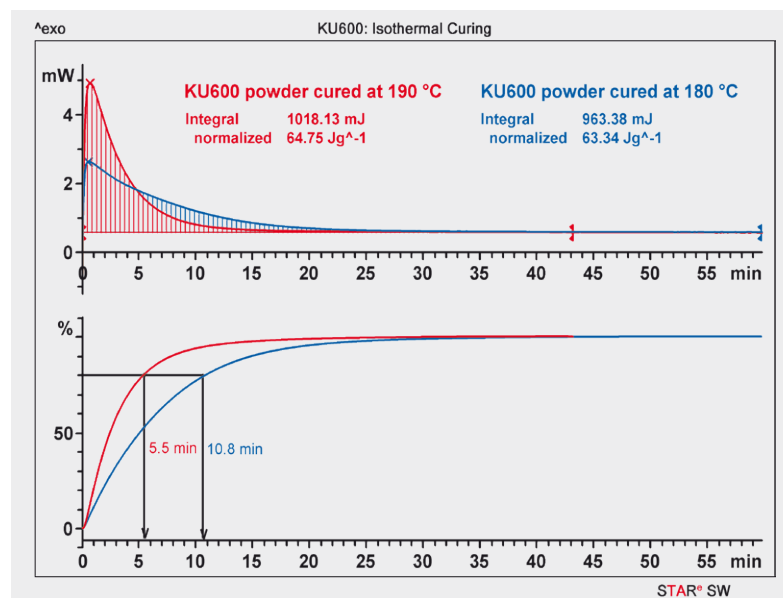


Figure 21. KU600: Isothermally cured at 180 and 190 °C. Above: the DSC curves. Below: the calculated conversion curves.

enthalpy relaxation peak and the curing reaction shift to higher temperature at higher heating rates, while the small melting peak always appears at the same temperature.

Kinetics

Chemical kinetics, also called reaction kinetics, is a method used to study the rate at which a chemical process proceeds. The most important application of kinetics in thermal analysis is to predict reaction behavior under conditions in which it is practically impossible to make measurements, for example for very short or very long reaction times.

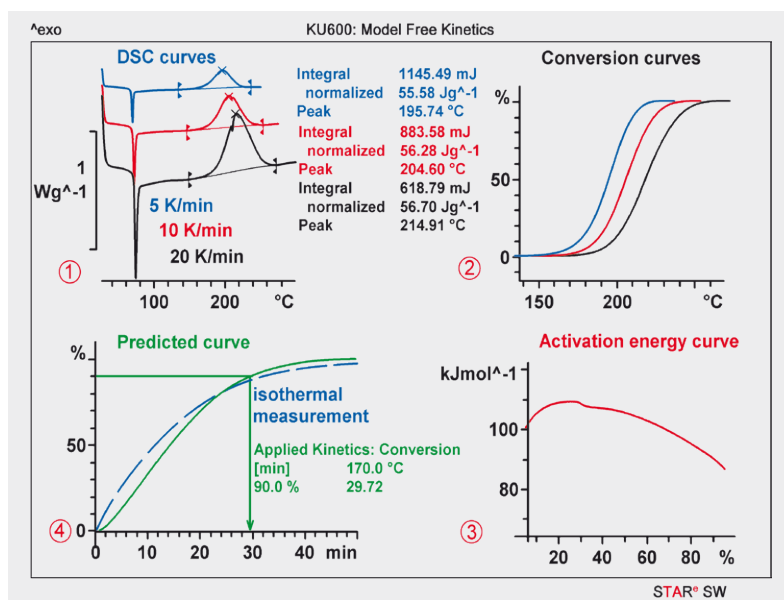
The method should be able to predict how long a reaction takes to reach a desired conversion at a particular process temperature. This will be explained using KU600 as an example. The determination and evaluation are performed using a special kinetics software program known as model free kinetics (MFK) [3, 4].

The evaluation makes no assumptions concerning possible reaction models. The chemical changes are summarized in a global reaction and the activation energy can vary with the degree of conversion.

The model free kinetics method requires at least three dynamic heating experiments performed at three different heating rates (Figure 22, 1). The DSC curves are then used to determine conversion curves (Figure 22, 2) from which the activation energy is finally calculated (Figure 22, 3).

The activation energy changes with the conversion. This information allows predictions to be made (Figure 22, 4) that can be checked by performing practical experiments. For example, MFK predicts that it takes almost 30 minutes to achieve a degree of cure of 90% at 170 °C. The figure shows that the predicted curve agrees well with the measured curve.

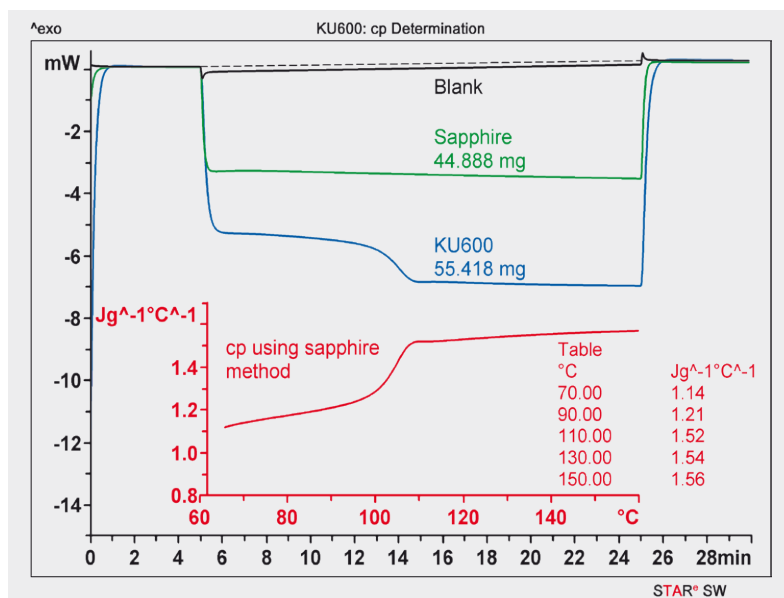
Figure 22. Model free kinetics using the curing of KU600 as an example.



Determination of c_p

This section describes a method known as the sapphire method that is used to determine the specific heat capacity [2]. The sample chosen was fully cured KU600. The c_p determination involves separate measurements of the sample (about 55 mg), the sapphire standard (two sapphire disks) and empty crucibles. It is important to note the weight of the crucible and store it in the software. The weights of the crucibles should also be as close as possible (±0.4 mg). The measurements were performed from 60 to 160 °C at a heating rate of 5 K/min with isothermal segments of 5 minutes before and after the start and end temperatures.

Figure 23. Determination of the specific heat capacity, c_p, of KU600.



The sapphire method (DIN 51007) is a standard method for c_p determination and provides the most exact results with a reproducibility of about 5%. Three measurements are needed: the sample, the sapphire standard, and the empty crucible (blank).

The sample and sapphire curves are blank corrected and the c_p value determined from the two blank-corrected curves using a specific software option.

Figure 23 shows the DSC curves plotted as a function of time. The sample mass was large in order to generate a large

signal. The heating rate of 5 K/min was relatively low to minimize possible temperature gradients in the sample. The heat capacity, c_p , (drawn red in Figure 23) was plotted as a function of the sample temperature. The increase of c_p of about 0.3 J/gK between 90 and 110 °C shows the glass transition very clearly.

Other possibilities of determining c_p include measurements using the **TOPEM™** or **ADSC** techniques. ADSC will be described in the following section.

ADSC: Separation of overlapping effects

ADSC [5], like IsoStep™ and **TOPEM**, is a temperature-modulated DSC technique that allows overlapping effects such as the glass transition (change in the heat capacity) and enthalpy relaxation to be separated from each other. This is illustrated in the following example. In addition, c_p can be determined.

The uncured KU600 sample was measured from 30 to 130 °C at a mean heating rate of 1 K/min using a temperature amplitude of 0.5 K and a period of 48 s. Three ADSC experiments were performed under the same conditions: First a blank measurement with empty sample and reference crucibles without lids; then a calibration measurement with an empty sample crucible with a lid and the same empty reference crucible without a lid as before.

The reference material (crucible lid) was aluminum. Finally, the sample was measured using a crucible filled with sample and a lid and the same empty reference crucible without lid as before. The right part of Figure 24 shows the blank measurement (bottom, black), the calibration measurement (middle, blue) and the sample measurement curves (top, red). The left part of the figure displays the individual heat flow

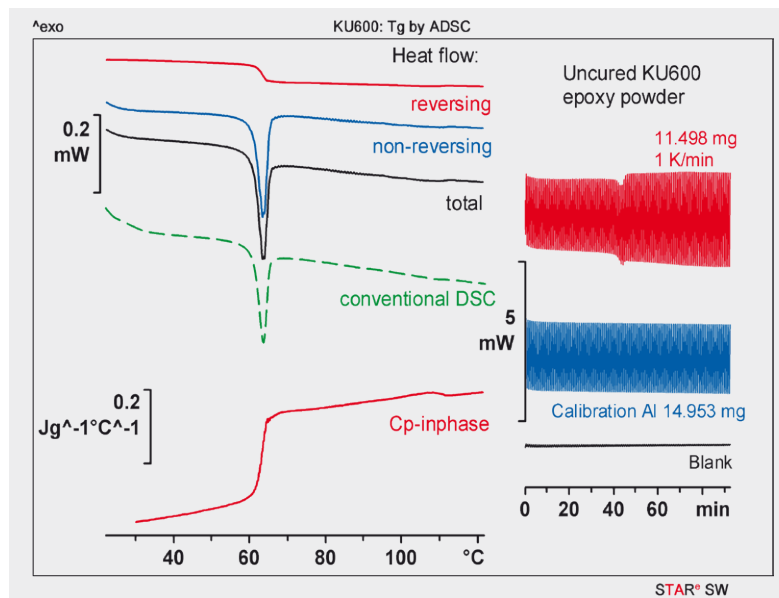


Figure 24. ADSC measurement of KU600.

curves resulting from the evaluation: the reversing curve (red), the non-reversing curve (blue), and the total heat flow curve (black). The green curve obtained from a conventional DSC measurement is shown for comparison. This corresponds to the total heat flow measured under the same conditions.

Comparison of the reversing and non-reversing curves shows quite clearly that the endothermic peak of the enthalpy relaxation is on the non-reversing curve and the glass transition on the reversing curve. Besides this, we can calculate the specific heat capacity curve from the reversing curve. This however depends on the measurement frequency chosen.

The ADSC measurement thus makes it very easy to separate the effects that overlap on the normal DSC curve by splitting the total heat flow into reversing and non-reversing components. A typical reversing effect is for example the glass transition whereas non-reversing effects may be due to enthalpy relaxation, vaporization, a chemical reaction or crystallization.

4.4 References

- [1] Interpreting DSC curves. Part 1: Dynamic measurements, UserCom 11, 1–6.
- [2] METTLER TOLEDO Collected Applications Handbook: Thermosets, Volume 1.
- [3] Model free kinetics, UserCom 2, 7.
- [4] Ni Jing, Model free kinetics, UserCom 21, 6–8.
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For more information:

- ▶ www.mt.com/ta-thermosets-hb
- ▶ www.mt.com/ta-dsc

5. DSC Photocalorimetry of Thermosets

5.1 Introduction

This chapter focuses on the use of DSC with a photocalorimetry option. In DSC photocalorimetry, a sample is exposed to light of a particular wavelength range and intensity for a defined time while recording the heat flow from the sample. This technique is mainly used to study light-induced curing reactions. Light curing, also known as photoinduced polymerization or photopolymerization, is only technically possible for thin material layers.

Photopolymerization is nowadays a widely used process. Systems are used for medical applications, for example in dentistry, for adhesive ap-

plications, in coating technology, and quite recently for 3D printing [1]. This chapter describes how the curing behavior of an ink sample at 30 °C can be investigated.

5.2 Setup

The DSC measurements were performed using a DSC equipped with the METTLER TOLEDO UV accessory [2]. The standard DSC cover was replaced by a special cover with quartz windows (Figure 25). The measurements were performed in open standard aluminum crucibles at 30 °C.

The light source was a Hamamatsu "Lightning Cure LC8" with mercury-xenon lamp. The UV light emitted by this lamp is mainly in the UV-A wavelength range (300 to 450 nm). The measurement setup for this type of measurement is shown in Figure 26. Other light sources can be used for other applications, e.g. halogen light or LED light sources emitting at 365 nm, 385 nm, 400 nm or 465 nm.

5.3 Experiment

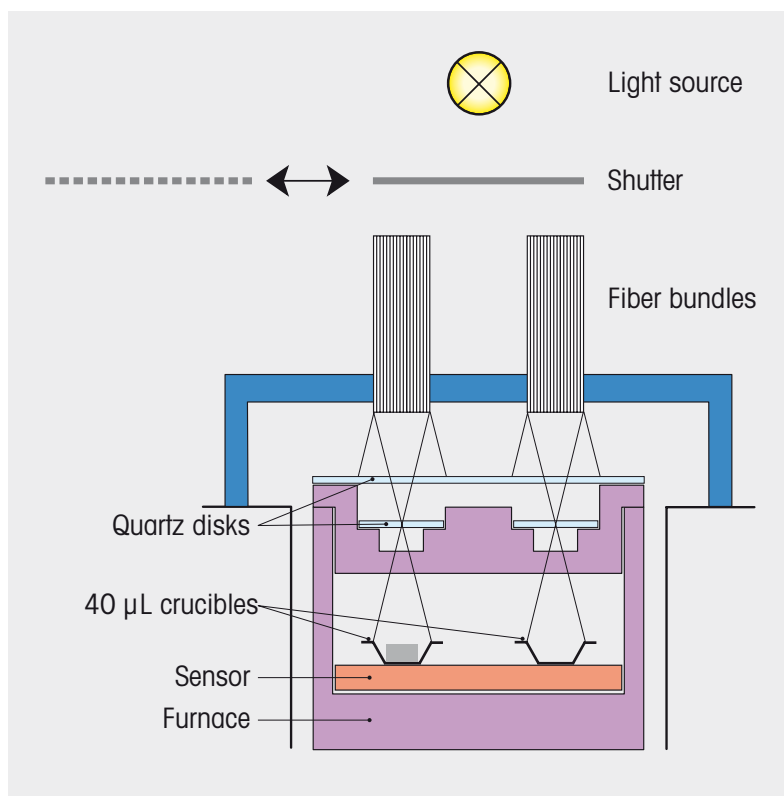
To set the UV intensity the carbon black method was used. For this purpose a crucible is filled with carbon black. Then an isothermal measurement is started and the light intensity is varied until the required light intensity is obtained. For the experiments described here the intensity was set to 246 mW/cm² (Figure 27).

Figure 28 shows the UV curing of the ink sample at 246 mW/cm². The ink was analyzed at 30 °C and after 5 minutes the UV lamp was switched on and after 12 minutes switched off again. The measured curves for the 1st exposure of the sample (red curve) and the 2nd exposure (blue curve) are displayed, together with the subtracted curve (1st exposure subtracted from the 2nd exposure, black curve). The 2nd exposure is subtracted in order to eliminate the deflection caused by switching the lamp on and off. In addition, the curve of a second sample is shown in green (also 1st exposure subtracted from the 2nd exposure). The curves show that curing begins as soon as the UV lamp is turned on. The reaction is extremely fast and produces a large, very sharp exothermic peak that finishes after less than 1 minute. As can be seen, the results are highly reproducible.

Figure 25. Special cover lid with quartz windows.



Figure 26. Optical setup for projecting UV light into the DSC.



5.4 Summary

In this chapter, DSC photocalorimetry was discussed and the special setup was demonstrated. An ink sample was cured using UV light at 30 °C, the reaction is fast and shows a huge curing enthalpy, the results are highly reproducible.

5.5 References

- [1] Wikipedia
- [2] M. Schubnell, Curing of powder coatings using UV light, UserCom 19, 13–15.

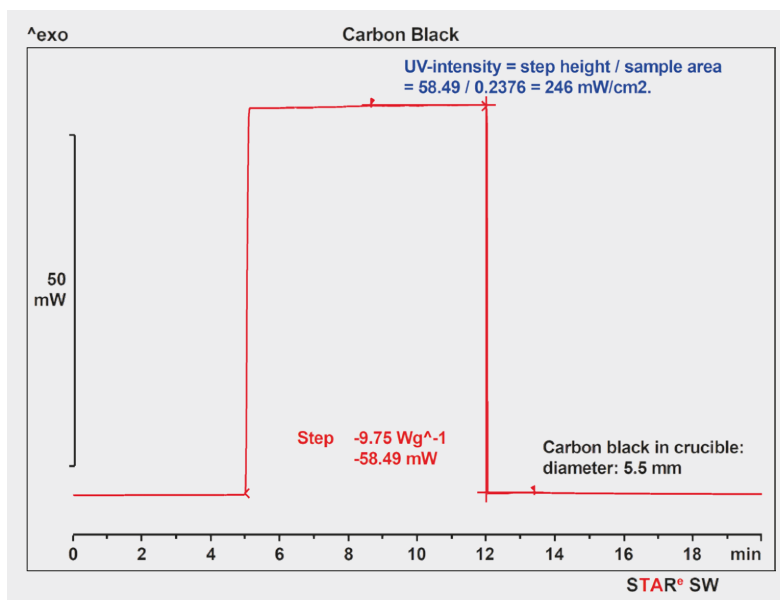


Figure 27. Carbon black experiment to set the light intensity.

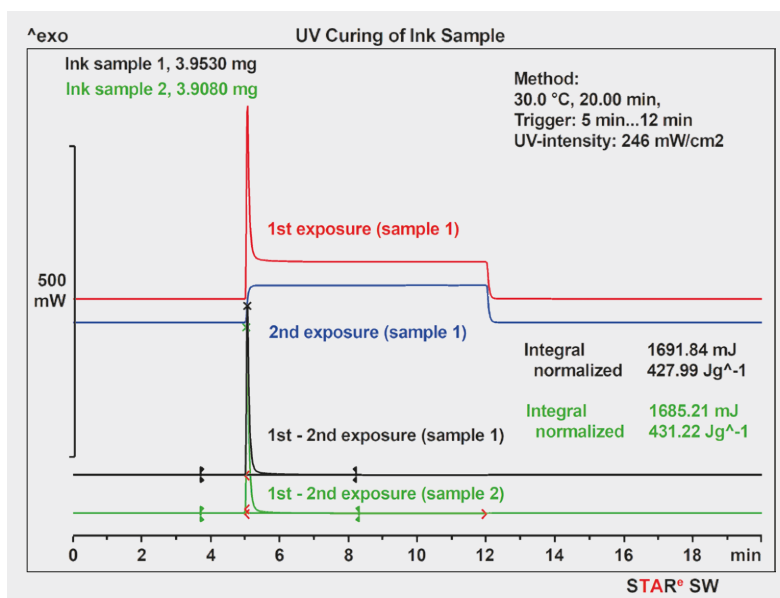


Figure 28. UV curing of ink: 1st exposure (red curve), 2nd exposure (blue curve), subtracted curve (black curve) and repeat determination (green curve).

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- ▶ www.mt.com/ta-calibration

6. TGA, TMA and DMA Analysis of Thermosets

6.1 Introduction

This chapter focuses on the application of TGA, TMA and DMA and shows how additional information can be obtained using these techniques. In particular, it discusses decomposition, expansion, the glass transition and its frequency dependence.

6.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a technique that measures the mass of a sample while it is heated, cooled or held at constant temperature in a de-

finied atmosphere. It is mainly used for the quantitative and compositional analysis of products [1].

Figure 29 (middle curve, red) shows the decomposition curve of KU600 epoxy resin measured by TGA. The finely powdered sample was heated from 30 to 700 °C at a heating rate of 20 K/min in a 30- μ L alumina crucible without a lid using a purge gas flow rate of 50 mL/min. The purge gas was switched from nitrogen to air at 600 °C.

The polymer content of the material is

determined from the loss of mass due to pyrolysis up to about 500 °C. The purpose of the switching the purge gas to air at 600 °C was to oxidize the carbon black formed during the pyrolysis reaction.

The final residue consisted of inorganic fillers such as silicates or oxides. The first derivative of the TGA curve is known as the DTG curve and is a measure of the decomposition rate. Both the DTG curve (blue) and the DSC curve (black) are usually plotted together with the TGA curve. The DSC curve is recorded simultaneously with the TGA measurement and often provides valuable additional information about the sample.

In this example, we can identify the glass transition at about 60 °C and the curing reaction between 120 and 240 °C. The DSC curve also yields information about the decomposition reaction and the combustion process.

Figure 29. TGA/DSC 1 curves of KU600 epoxy powder measured from 30 to 700 °C at a heating rate of 20 K/min. The TGA curve (red) measures the loss of mass and the DSC curve (black) provides information about endothermic and exothermic effects.

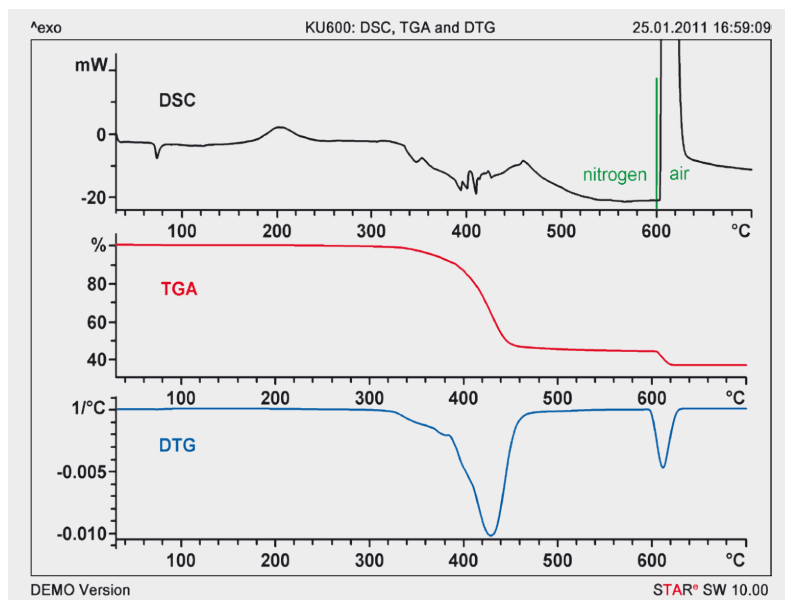
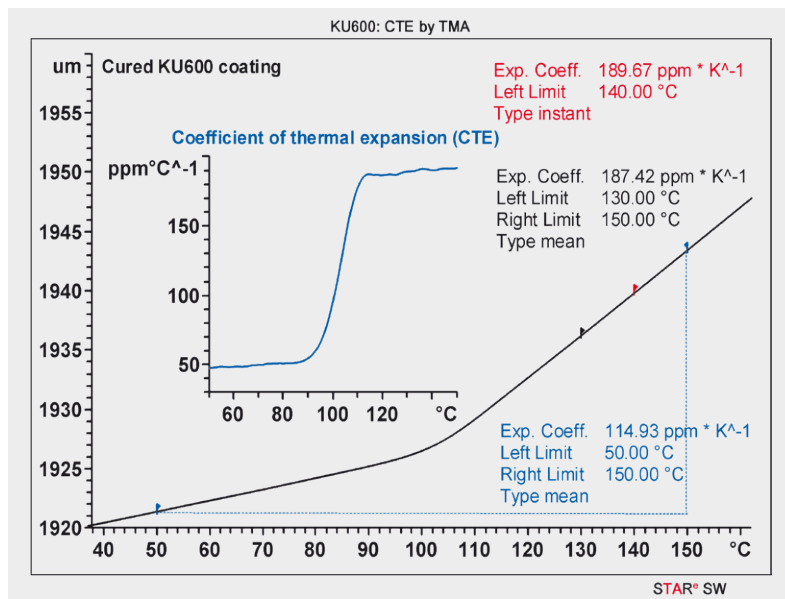


Figure 30. Determination of the coefficient of thermal expansion (CTE) of cured KU600 using the second heating run.



6.3 Thermomechanical analysis (TMA)

Thermomechanical analysis (TMA) is used to measure the dimensional changes of a sample while it is heated or cooled in a defined atmosphere. The most important analyses are the determination of the coefficient of thermal expansion (CTE, expansion coefficient), the glass transition, and the softening of materials. The modulus of elasticity (Young's modulus) and the swelling behavior of samples in solvents can also be determined. Another important application is the determination of the gel point.

Determination of the expansion coefficient

The determination of the expansion coefficient will first be described using cured KU600 powder as an example.

Information about the expansion behavior of materials resulting from a

temperature change is very important in connection with the use of composite materials. If materials with different expansion coefficients are bonded together, there is always the risk that the composite might fracture on temperature change. Measurements of cured KU600 powder show how the expansion coefficient is determined.

A 1.9-mm thick sample was placed between two thin quartz disks and positioned on the TMA sample holder. The 3-mm ball-point probe used for the measurement rested on the upper disk. This ensured that the force exerted by the probe was uniformly distributed over the entire surface of the sample.

A low force of 0.02 N was used. This was sufficient to maintain good contact between the probe and the sample without deforming the sample. The sample was first measured from 40 to 160 °C. This also eliminated any relaxation effects. After cooling, a second heating run was performed and used for the evaluation.

Figure 30 shows the results obtained from the second heating run. The black curve is the measurement curve; the blue inserted diagram shows the temperature-dependent expansion coefficient. Expansion of the sample is noticeably greater after the glass transition at about 100 °C.

A mean expansion coefficient was evaluated from the TMA curve in the range 50 to 150 °C using the "Type mean" function. The expansion coefficient at 140 °C was also determined from the slope of the TMA curve using the "Type instant" function.

DLTMA for the determination of T_g and Young's modulus

DLTMA (Dynamic Load TMA), [2] can be used to measure the glass transition of a thin coating of a cured sample and at the same time determine the change in Young's modulus. The sample was a coating on a metal sheet.

The measurement was performed in static air from 50 to 240 °C at a heating rate of 5 K/min in the 3-point bending mode using a 3-mm ball-point probe. The force alternated between 0.1 and 1 N. The period was 12 s, that is, the force changed every 6 s. The results are presented in Figure 31.

The top curve shows the initial measurement curve. Below the glass transition, the amplitude is small, only about 40 µm; above the glass transition, the amplitude however increases to 200 µm.

The onset evaluated for the mean curve (top curve, red) is a character-

istic temperature. The amplitude of the DLTMA curve is a measure of the elasticity or the Young's modulus of the sample. The modulus curve can also be used to determine the glass transition as shown in the middle curve. The bottom curve displays tan delta; the peak temperature is also used as a value for the glass transition.

Determination of the softening temperature of a thin coating

The measurement shows the determination of the softening temperature of a thin coating of cured KU600 with a thickness of 27 µm. The measurement was performed in static air from 40 to 190 °C at a heating rate of 5 K/min

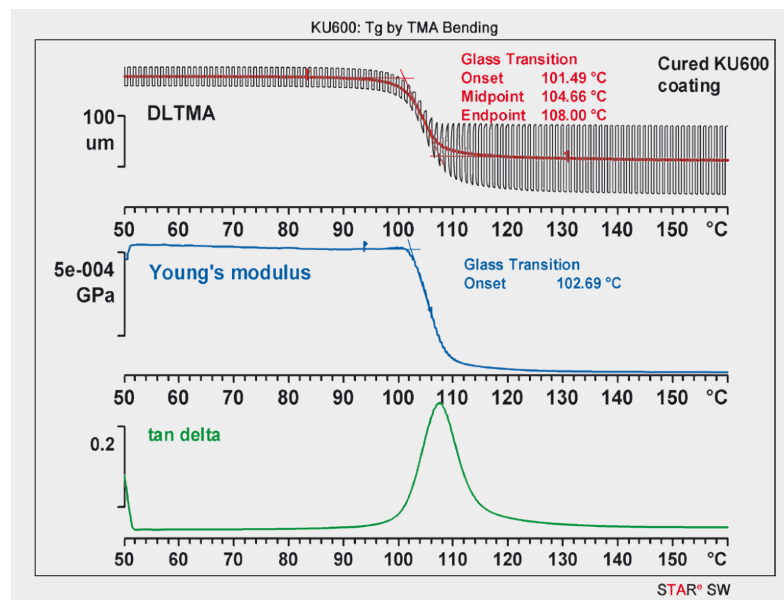


Figure 31. DLTMA measurement of a cured KU600 coating.

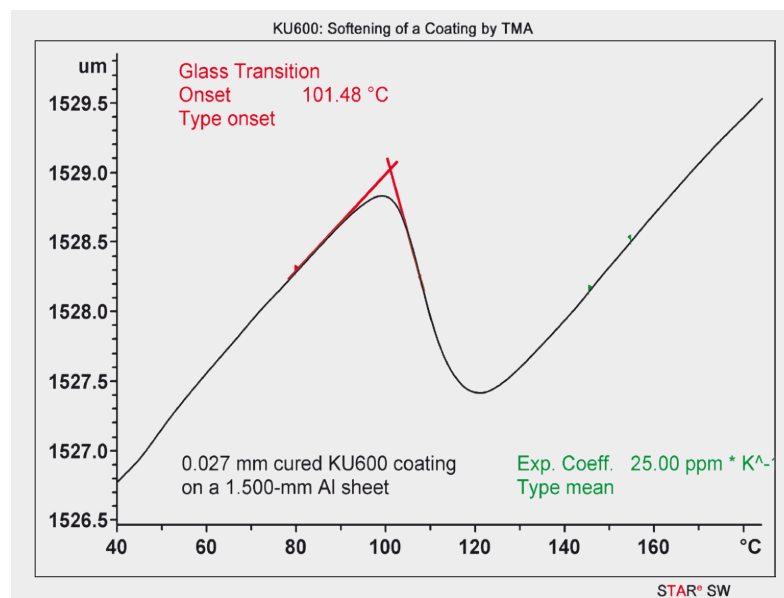


Figure 32. TMA measurement of a thin coating of cured KU600 to determine the softening temperature.

using a 3-mm ball-point probe and a force of 1 N. The probe was in direct contact with the sample.

Figure 32 shows the resulting TMA curve with the softening temperature (T_g). The expansion before and after penetration of the probe into the coating (i.e. at the glass transition) corresponds to the expansion of the aluminum substrate; the coating itself makes almost no contribution.

The inflection, endpoint and midpoint are important characteristic temperatures in addition to the onset. The example shows that a very thin coating is ideal for determining the softening

temperature. Special sample preparation is not necessary. The glass transition is measured directly in the first heating run.

6.4 Dynamic mechanical analysis (DMA)

As described in reference [3], dynamic mechanical analysis (DMA) is used to determine the mechanical properties of viscoelastic materials as a function of time, temperature or frequency. The measurement is performed by applying a periodic oscillating force to the material.

The following section describes the evaluation of the glass transition and its frequency dependence [4, 5].

Determination of the glass transition

Figure 33 shows a DMA measurement of cured KU600 in the shear mode. Two disks with a diameter of 5 mm and thickness of 0.56 mm were prepared by pressing KU600 powder in a suitable die.

The disks were loaded in the shear sample holder, heated to 250 °C at a heating rate of 2 K/min and then cooled at the same rate. They were then measured at 2 K/min in the range 40 to 160 °C at a frequency of 1 Hz using a maximum force amplitude of 5 N and a maximum displacement amplitude of 20 μ m.

Figure 33. DMA measurement of KU600 from 90 to 160 °C, in linear and logarithmic ordinate presentation.

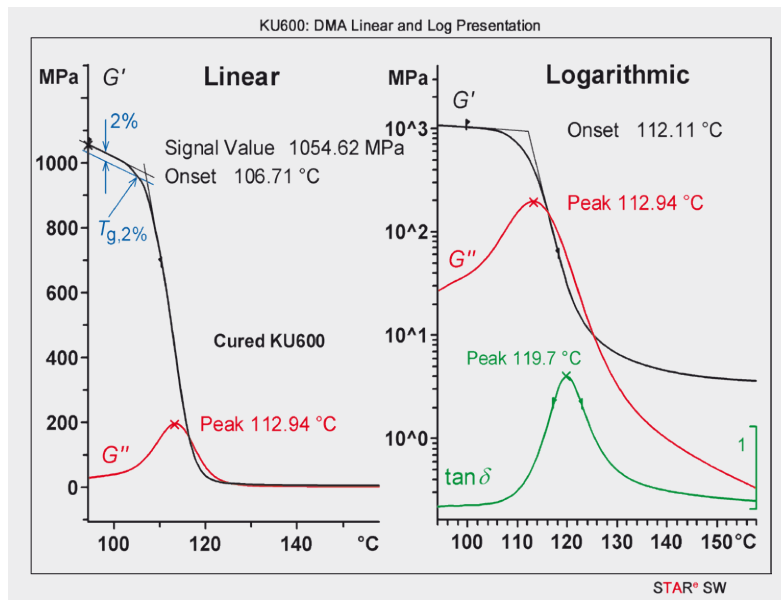


Figure 33 shows measurement curves from the second heating run and in particular the storage modulus (G'), the loss modulus (G'') and tan delta of the cured material. Here, the focus is on the presentation of the ordinate and the evaluation of the glass transition.

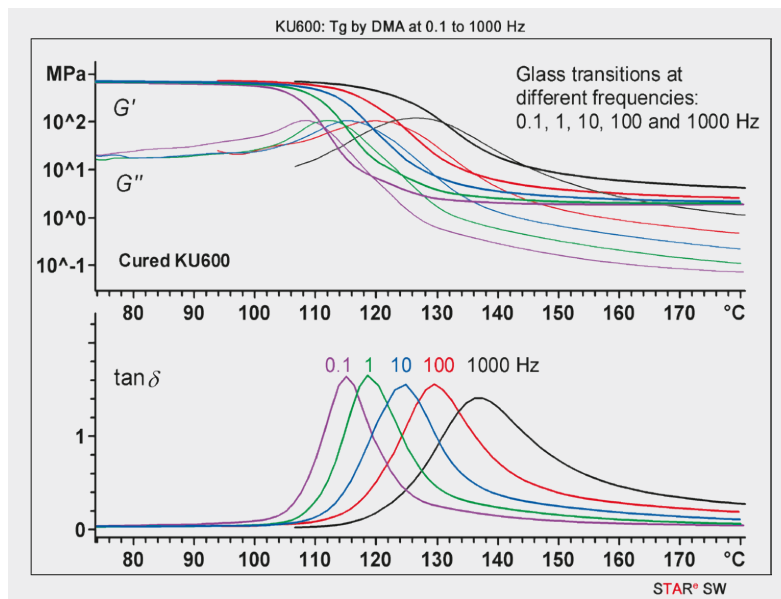
In the diagram on the left, the ordinate scale is linear and on the right, logarithmic. In both cases, the glass transition is at about 110 °C. The storage modulus decreases with increasing temperature and the loss modulus and tan delta exhibit a peak. Two methods are used to determine the onset.

The linear presentation shows the evaluation according to DIN 65583, the so-called 2% method, and the diagram on the right with the logarithmic ordinate, the ASTM E6140 evaluation.

Each method yields different results for T_g . For this reason, it is important to quote the measurement conditions and evaluation procedures when evaluating and comparing glass transition temperatures.

Comparison of the two diagrams shows that the differences between the storage and loss moduli are clearer in the logarithmic presentation. The logarithmic curve presentation is therefore usually recommended to make it easier to detect the different effects.

Figure 34. DMA measurement of KU600 at different frequencies to demonstrate the frequency dependence of the glass transition.



Frequency dependence of the glass transition

Figure 34 shows a DMA experiment in which different frequencies were simultaneously applied. The sample preparation was the same as for the measurements in Figure 33. The cured sample was measured from 70 to 180 °C using a maximum force amplitude of 5 N and a maximum displacement amplitude of 30 μm. The frequency range was between 0.1 and 1000 Hz.

The upper diagram displays the storage and loss moduli and the lower diagram tan delta as a function of time in a logarithmic ordinate presentation. The storage moduli show a step in the glass transition whereas the loss moduli and tan delta display a peak. The tan delta peaks are always at a somewhat higher temperature compared with the corresponding peaks of the loss modulus.

The results clearly show that the glass transition depends on the frequency and that it is shifted to higher frequencies at higher temperatures. The reason for this is that the glass transition is a relaxation effect. This phenomena is discussed in more detail in reference [6].

6.5 Overview of effects and comparison of results

Figure 35 presents an overview of the thermal analysis methods used to investigate KU600. It shows quite clearly that the different techniques yield similar values for the glass transition (see red line in Figure 31).

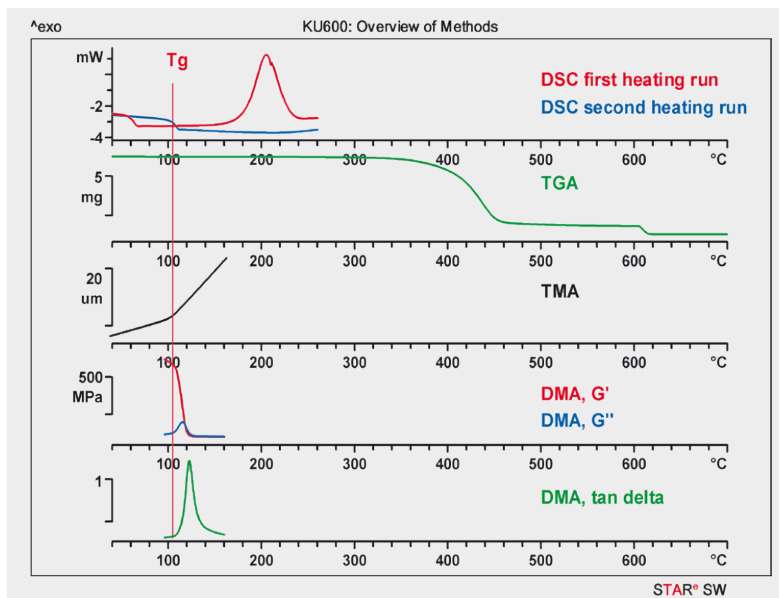


Figure 35. Overview of the effects and comparison of results.

6.6 Conclusions

This chapter and the previous chapter discussed the different possibilities available for characterizing a thermoset (KU600) using DSC, TGA, TMA, and DMA techniques. The various methods yield consistent results.

The main effects investigated were the glass transition, the curing reaction, expansion, decomposition. Furthermore, the application of model free kinetics was discussed and the frequency dependence of the glass transition shown using DMA measurements. Other thermosets show similar effects.

A particular effect can often be measured by different thermal analysis techniques. The results obtained from one technique often provide comple-

mentary information and confirm the results from another technique. Ideally, a material is first analyzed by TGA, then by DSC and TMA, and finally by DMA.

6.7 References

- [1] Elastomer Analysis in the TGA 850, UserCom 3, 7–8.
- [2] PET, Physical curing by dynamic load TMA, UserCom 5, 15.
- [3] Georg Widmann, Interpreting DMA curves, Part 1, UserCom 15, 1–5.
- [4] Jürgen Schawe, Interpreting DMA curves, Part 2, UserCom 16, 1–5.
- [5] Klaus Wrana, Determination of the glass temperature by DMA, UserCom 16, 10–12.
- [6] METTLER TOLEDO Collected Applications Handbook: Thermosets, Volume 1.

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7. DSC and TGA Analysis of Elastomers

7.1 Introduction

This chapter deals with the thermal analysis of elastomers [1, 2] and covers the properties of elastomers that can be characterized by DSC and TGA.

Elastomers is the name given to a group of lightly-crosslinked polymers that exhibit elastic or viscoelastic deformation. Thermal analysis plays an important role in the analysis of elastomers. It is widely used to characterize raw materials, intermediate products and vulcanization products. The information obtained is valuable for quality control, process optimization, research and development of advanced materials, and failure analysis.

This chapter discusses physical properties and chemical reactions that are typical and important for elastomers. The properties include the glass transition temperature, melting, vulcanization, compositional analysis, fillers and additives, creep and recovery, master curve and compatibility of polymer blends.

The elastomers used in experiments to illustrate these properties were EPDM (ethylene-propylene-diene rubber), SBR (styrene-butadiene rubber), NBR

(natural butadiene rubber) and EVA (ethylene-vinyl acetate copolymer).

7.2 Experimental details

The measurements described in Chapters 6 and 7 were performed using the following instruments: DSC 1 with FRS5 sensor; TGA/DSC 1; TMA/SDTA840° and 841°; and DMA/SDTA861°. Details of the samples and experimental conditions are described in the individual applications.

7.3 Measurements and results

Differential scanning calorimetry (DSC)

DSC is the most frequently used thermal analysis technique. It is used to measure enthalpy changes or heat capacity changes in a sample as a function of temperature or time. This allows physical transitions involving a change in enthalpy or a change in specific heat capacity (c_p) to be investigated. Elastomers are often analyzed with respect to their glass transition temperature, compatibility behavior, melting and vulcanization.

Glass transition temperature

Figure 36 shows the determination of the glass transition temperature of two

samples of unvulcanized EPDM with different ethylene contents. EPG 3440 is completely amorphous. The glass transition temperature is observed as a step in the heat flow with a midpoint temperature at about $-53\text{ }^\circ\text{C}$.

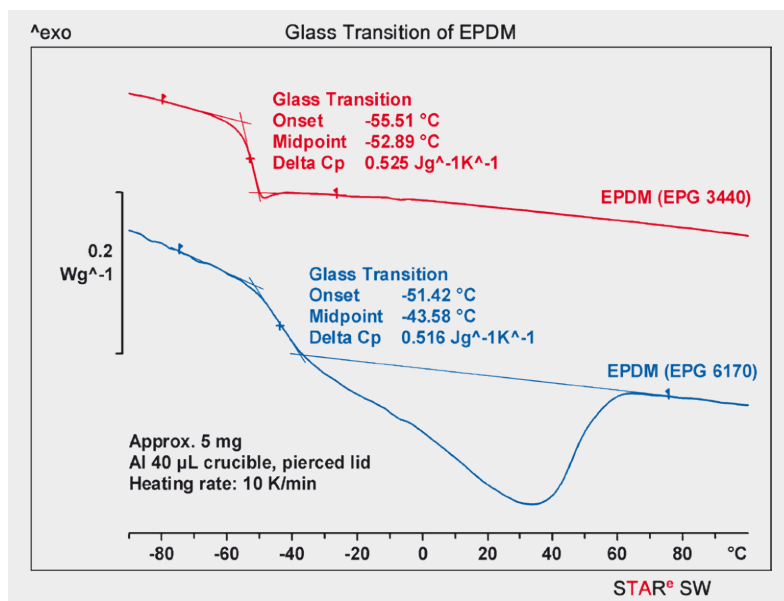
In contrast, EPG 6170 exhibits a glass transition that is immediately followed by a broad melting process that depends on the structure of the macromolecules. For reliable determination of the glass transition temperature, it is very important that the melting process does not overlap the glass transition.

The evaluation was therefore performed by drawing the second tangent to a point on the curve at about $75\text{ }^\circ\text{C}$. Linear extrapolation of the heat flow curve from the melt above $70\text{ }^\circ\text{C}$ makes a good baseline for the melting peak and for the tangent for the evaluation of the glass transition. The characterization of the glass transition temperature yields valuable information about the compatibility of elastomer blends. Figure 37 shows the glass transition temperature of two vulcanized blends of SBR.

The SBR/BR (butadiene rubber) blend exhibits a broad glass transition that extends over a temperature range of 60 K between $-110\text{ }^\circ\text{C}$ and $-50\text{ }^\circ\text{C}$. The occurrence of just one glass transition in the polymer blend indicates that the two polymer components are compatible and exhibit only a single phase. A distinct broadening of the glass transition step is noticeable between $-80\text{ }^\circ\text{C}$ and $-50\text{ }^\circ\text{C}$. This type of curve shape is typical for a polymer blend that is not ideally homogeneous.

The SBR/NR (natural rubber) blend exhibits two individual glass transitions, one for NR at $-58.8\text{ }^\circ\text{C}$ and the other for SBR at $-44.1\text{ }^\circ\text{C}$. This behavior indicates the presence of two separate polymer phases and that the two poly-

Figure 36. Determination of the glass transition temperature of two samples of unvulcanized EPDM with different ethylene contents.



mer components are incompatible. The ratio of NR to SBR can be estimated from the step height of the individual glass transitions and in this case was about 4:1.

Melting

Figure 38 shows the melting behavior of an unvulcanized sample of EPDM (EPG 6170). Three heating runs were performed to demonstrate the influence of sample pretreatment on melting.

All three curves show a step at $-45\text{ }^{\circ}\text{C}$ due to the glass transition. Melting begins immediately afterward and is completed by about $70\text{ }^{\circ}\text{C}$. The relatively broad melting range has to do with the wide size distribution of crystallites in the polymer. The smallest crystallites melt at the lowest temperatures, while the larger crystallites melt at higher temperatures.

In the first run, the melting range consists of three peaks. The first peak is broad and has a maximum at $14\text{ }^{\circ}\text{C}$. There then follows a narrower peak with a maximum at $43\text{ }^{\circ}\text{C}$ and a smaller peak at $52\text{ }^{\circ}\text{C}$. This complex melting behavior is the result of the storage and processing conditions.

The second run no longer shows signs of storage-induced crystallization. All the crystallites present were formed during cooling. The result is a broad melting peak without structure due to the different types of crystallites. The width of the melting peak of about 100 K indicates a wide size distribution of the crystallites.

The third run was performed after storing the sample at room temperature for 20 days. During this time, larger crystallites formed through slow recrystallization. The third component no longer crystallized.

Separation of overlapping effects by temperature-modulated DSC

DSC analyses of elastomers often give rise to a number of weak effects that

partially overlap one another. This makes it more difficult to interpret and evaluate a measurement. In such cases, temperature-modulated DSC techniques like ADSC, **TOPEM**[™] and IsoStep[™] can be used to reliably interpret the measured effects.

In ADSC (Alternating DSC), the temperature program is overlaid with a small periodic sinusoidal temperature oscillation. As a result, the measured heat flow changes periodically. Signal averaging yields the total heat flow curve, which corresponds to the conventional DSC curve at the underlying heating rate.

The heat capacity can be determined from the amplitudes of the heat flow and heating rate and the phase shift between them. The reversing heat flow is calculated from the heat capacity curve and corresponds to the heat flow component that is able to directly follow the heating rate.

The reversing heat flow curve shows effects such as the glass transition and other changes of heat capacity. The non-reversing heat flow curve is the difference between the total heat flow and the reversing heat flow and shows effects such as enthalpy relaxation, crystallization, vaporization or chemical reactions.

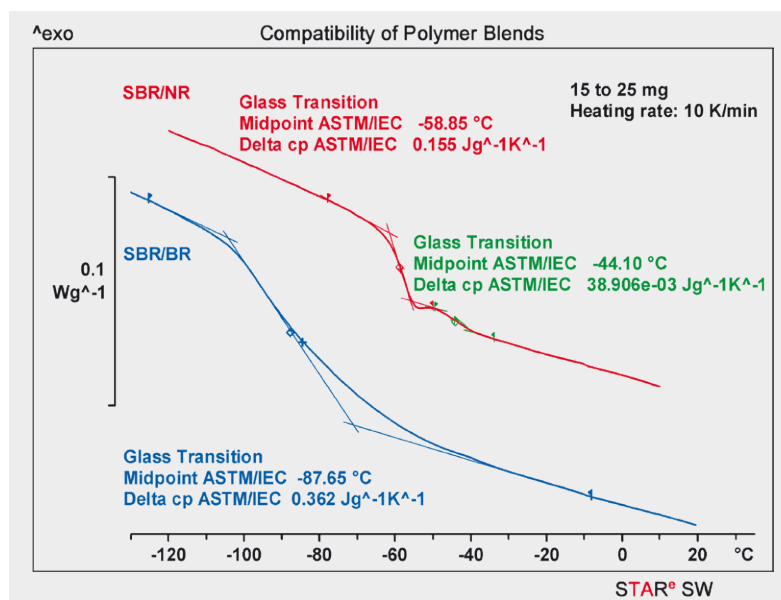


Figure 37. DSC analysis of the compatibility of two SBR polymer blends.

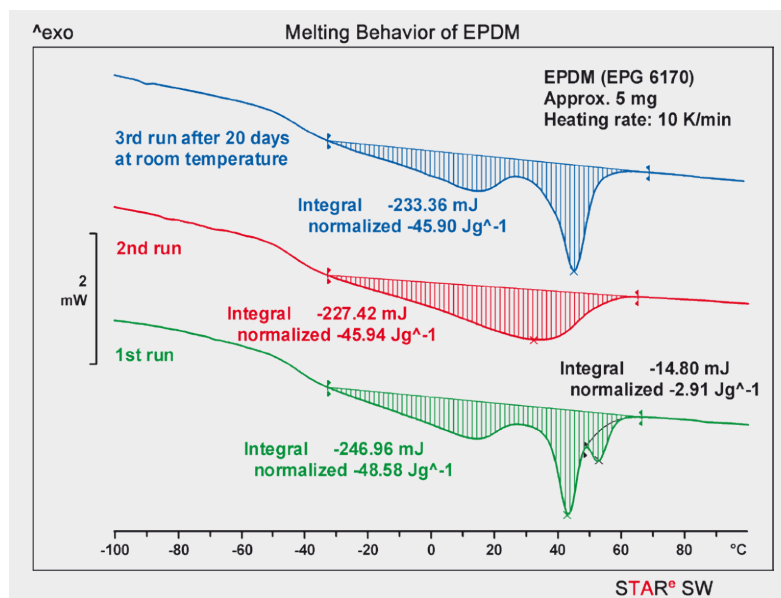


Figure 38. Influence of pretreatment on the melting of a sample of unvulcanized EPDM.

An important practical advantage of this technique is that it allows processes that occur simultaneously to be separated. Figure 39 shows an example of the use of ADSC.

The diagram shows the curves from an ADSC experiment performed on a sample of unvulcanized SBR. The different thermal effects observed in the total heat flow curve can be interpreted in different ways. The curve corresponds to a conventional DSC curve.

The reversing heat flow curve yields more selective information:

1. Glass transitions are measured as a step in the heat capacity.

2. Crystallization phenomena and chemical reactions only show an effect if the process is accompanied by a change in heat capacity.
3. Melting processes are measured as peaks whose area depends on the period.
4. Taking these points into consideration, one can extrapolate the reversing heat flow curve above the glass transition temperature to lower temperatures (the dashed curve).

A comparison of the total and reversing heat flow curves allows the following interpretation of the curve to be made:

A is a glass transition.

B is an exothermic process. No change is observed in the reversing heat flow. The process must therefore involve crystallization that is overlaid by the glass transition. Crystallization only begins above the glass transition.

C1 and C2 are endothermic processes that are better separated at this low heating rate of 2 K/min than in a conventional DSC measurement at a heating rate of 10 K/min. A smaller peak can be seen on the reversing heat flow curve that has to do with the melting process.

Figure 39. Separation of overlapping effects of unvulcanized SBR using ADSC.

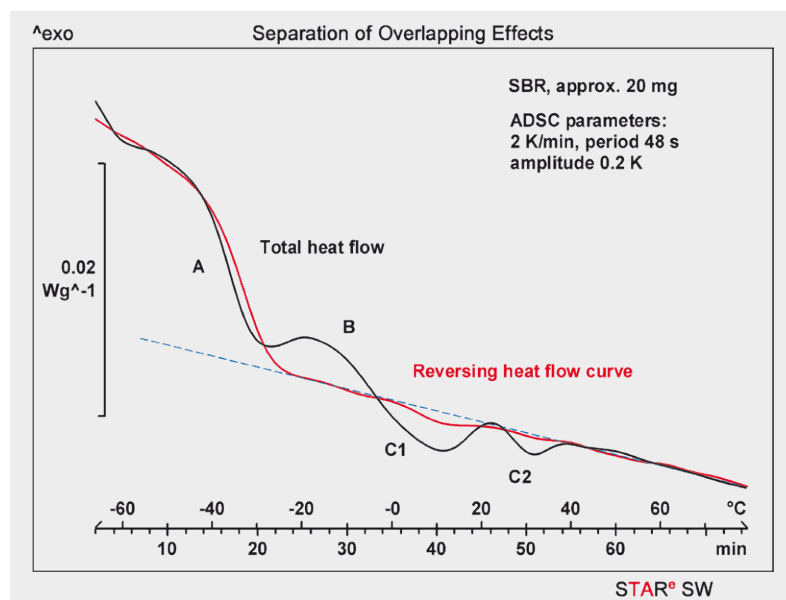
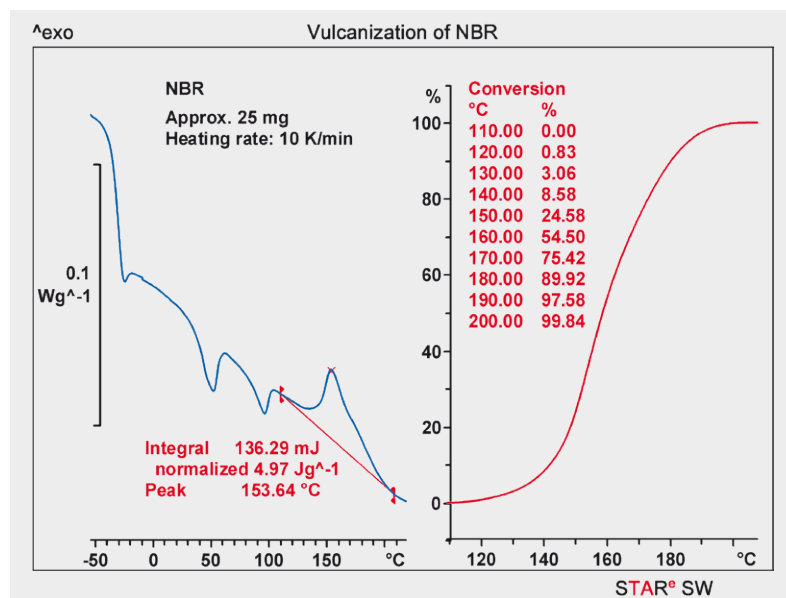


Figure 40. DSC measurement curve of an unvulcanized sample of NBR.



Vulcanization

Vulcanization is the crosslinking reaction of an uncrosslinked polymer using a vulcanizing agent to produce an elastomer. Vulcanization is normally performed at temperatures between 100 °C and 180 °C. Classical vulcanizing agents are sulfur or peroxides. Sulfur, for example, is used to crosslink unsaturated polymers. The sulfur content is normally relatively low. The network density determines whether a soft or hard elastomer is produced.

DSC measurements of unvulcanized elastomers provide useful information about the vulcanization reaction such as the temperature range, reaction enthalpy and kinetics. This information can be used to optimize processing conditions and the vulcanization system.

Figure 40 shows the DSC curve of the vulcanization reaction of an unvulcanized sample of NBR (acrylonitrile-butadiene rubber). The glass transition is at about -30 °C followed by melting processes at about 50 °C and 95 °C. The exothermic vulcanization reaction takes place with a peak maximum at 153.6 °C.

The specific reaction enthalpies of vulcanization reactions depend on the filler content, the crosslinking system

and the crosslinker content and are relatively low compared with other thermal effects. The course of the reaction can be estimated from the conversion curve. The reaction begins relatively slowly and reaches a maximum reaction rate between 150 and 160 °C.

The reaction rate in the individual stages of the reaction can be selectively influenced by varying the content of vulcanization agents, accelerators, retarders and activators in the vulcanization system.

The crosslinking system can be optimized with the aid of conversion curves. These curves can also be used for kinetic analyses (e.g. Model Free Kinetics).

Kinetics

Kinetics describes how fast a chemical reaction proceeds. It provides us with valuable information about the influence of temperature, time, concentration, catalysts, and inhibitors.

Different kinetics programs are available for kinetics evaluation. These include n^{th} order kinetics, Model Free Kinetics (MFK) and Advanced Model Free Kinetics (AMFK).

The activation energy can be calculated from the conversion curves. This can then be used to predict isothermal reaction behavior under conditions where measurements are difficult to perform or where the reaction times are very short or very long.

Figure 41 shows the evaluation of the vulcanization reaction of an unvulcanized NBR system using Model Free Kinetics. MFK requires at least three measurements to be performed at three different heating rates. In this case, the measurements were made at 1, 2 and 5 K/min. The conversion curves were then determined and are displayed on the left of the figure.

The apparent activation energy is cal-

culated from the three curves as a function of conversion. The shape of the activation energy curve reveals changes in the reaction mechanism of the reaction. The curve for the vulcanization of NBR shows two reaction steps. The first step has an apparent activation energy of about 90 kJ/mol. At 60% conversion, the activation energy of the second step increases to about 110 kJ/mol.

The activation energy curve can be used to predict reaction conversion as a function of time for isothermal reactions at different temperatures. The accuracy of such predictions should

however be verified by performing suitable isothermal measurements.

Thermogravimetric analysis (TGA)

Compositional analysis

TGA measures sample mass as a function of temperature or time. The technique is often used in quality control or product development to determine the composition of elastomers. Different components such as moisture or solvents, plasticizers, polymers, carbon black or inorganic fillers can be determined. Figure 42 shows a typical TGA analysis of an SBR elastomer.

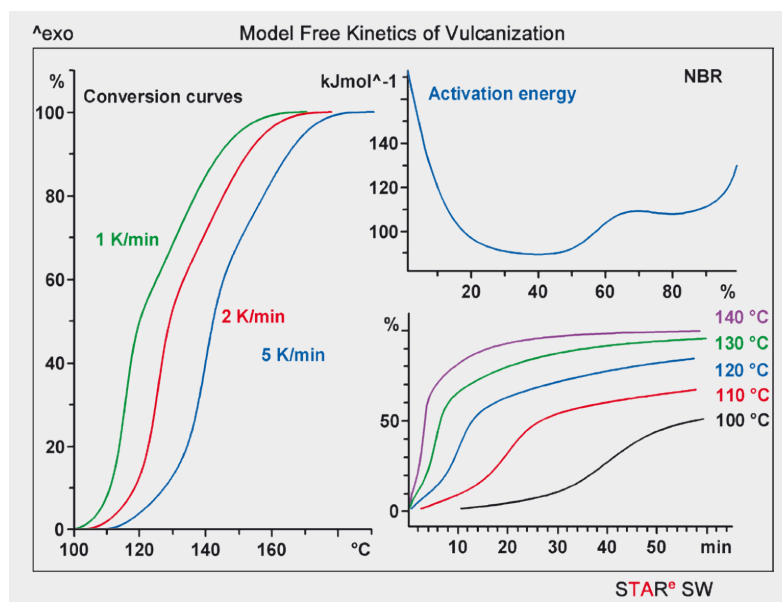


Figure 41. Model Free Kinetics of the vulcanization of NBR.

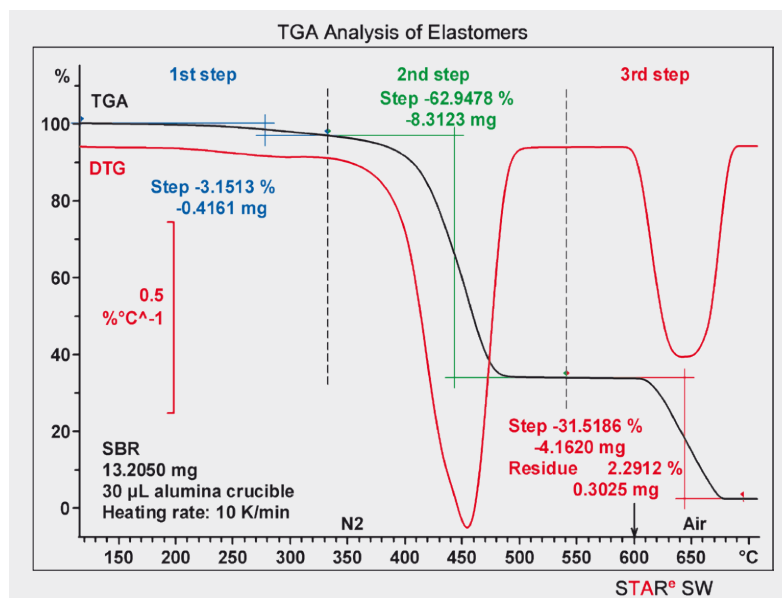


Figure 42. TGA analysis of an SBR elastomer.

The TGA curve exhibits three steps. The DTG curve (the first derivative of the TGA curve) is used to set the correct temperature limits for the evaluation of the steps. The first step below about 300 °C amounts to 3.1% and corresponds to the loss of small quantities of relatively volatile components. Pyrolysis of the elastomer takes place between 300 and 550 °C. The step corresponds to a polymer content of about 62.9%.

The atmosphere is then switched from nitrogen to air (oxidative) at 600 °C. The carbon black filler in the elastomer burns. With many elastomers,

the amount of carbon black formed during pyrolysis can be neglected. The carbon black filler content can therefore be determined from the third step between 600 and 700 °C and yields a value of 31.5%. The residue of 2.3% corresponds to the ash content, which in this case contains inorganic fillers.

TGA at reduced pressure

Elastomers often contain an appreciable amount of oil as a plasticizer. In many cases, accurate determination of the oil and the polymer content is difficult because the oil vaporizes in the same temperature range in which pyrolysis of the polymer begins.

The separation of the vaporization of the oil and the pyrolysis of the polymer can be improved by using lower heating rates for the measurement or by performing the measurement at reduced pressure (under vacuum).

Figure 43 demonstrates the influence of pressure on the determination of the oil content of an SBR/NR blend. Measurements were performed under nitrogen at 1 kPa (10 mbar) and 100 kPa (1 bar) using a heating rate of 10 K/min. The figure displays the resulting TGA and DTG curves.

The DTG curve shows that at a pressure of 1 kPa (10 mbar) the oil vaporizes at a lower temperature while the pyrolysis of the polymer takes place at the same temperature as before without vacuum. This means that the separation of the two effects is better at a pressure of 1 kPa (10 mbar). This in turn allows the oil and polymer contents to be more accurately determined. The results obtained for the oil and polymer contents of the sample were approximately 9.9% oil and 35.7% polymer.

Flame retardants

Flame or fire retardants are often added to elastomers for fire prevention depending on the field of application. The effect of flame retardants on the decomposition behavior of materials and the energy involved in the process can be investigated by thermal analysis.

Figure 44 shows the TGA analysis of three ethylene-vinyl acetate copolymers (EVA) containing different flame retardants: $\text{Al}(\text{OH})_3$ (ATH: aluminum trihydrate); and $\text{Mg}(\text{OH})_2$ (MDH: magnesium dihydrate). The diagram displays the TGA and DTG curves of the samples as a function of temperature. Water is first eliminated from the hydroxides of the flame retardants between 300 and 400 °C.

This is followed by the pyrolysis of the EVA at about 460 °C. Quantitative analysis is however difficult because

Figure 43. Determination of the oil content of an SBR/NR elastomer using TGA at ambient pressure and reduced pressure.

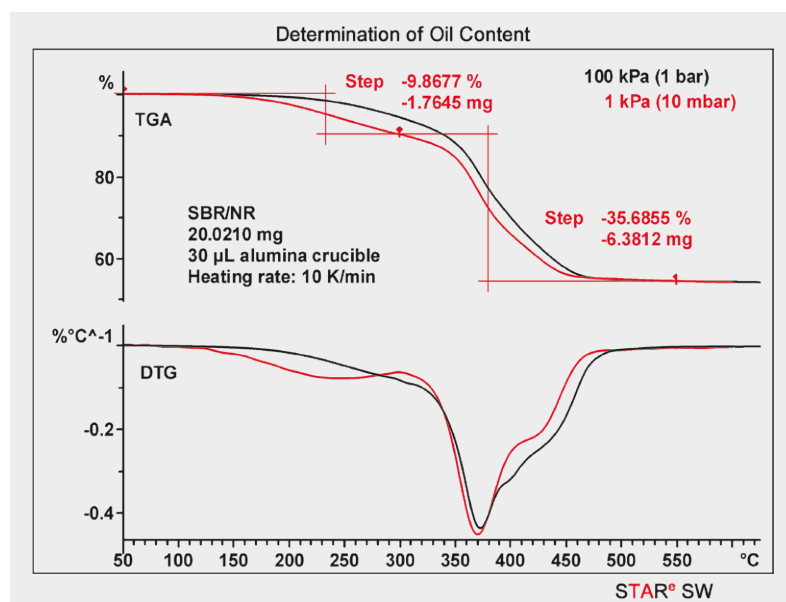
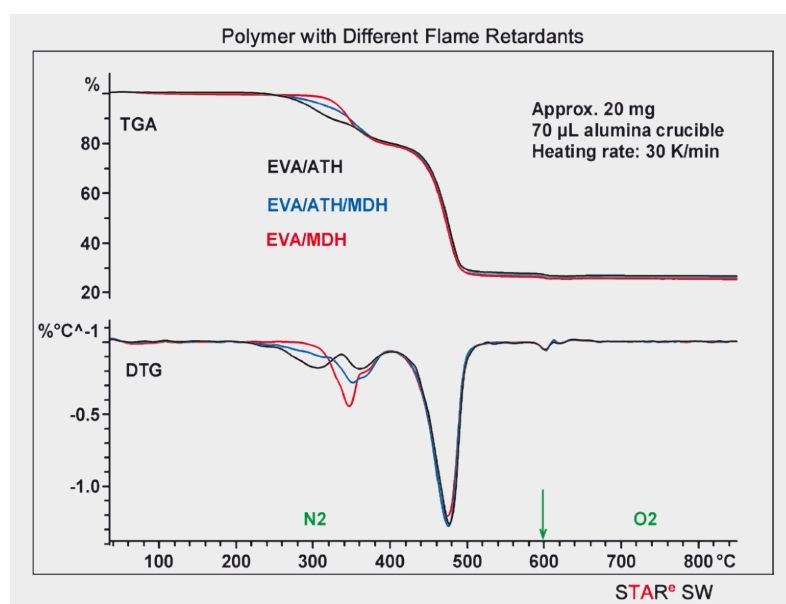


Figure 44. TGA analysis of EVA containing different flame retardants.



EVA eliminates acetic acid between 360 and 400 °C.

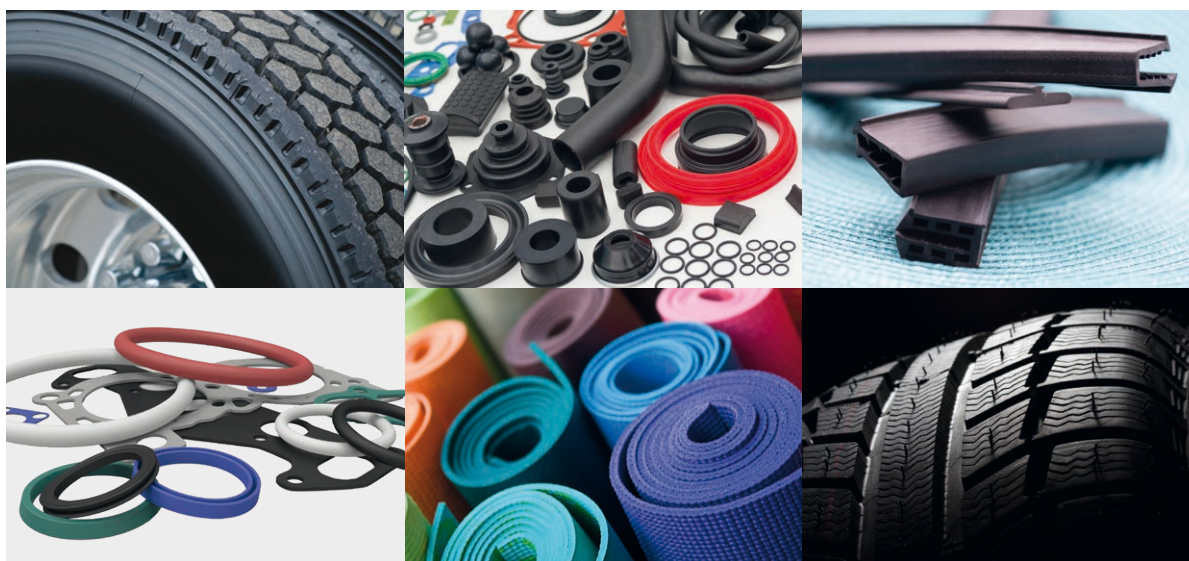
The presence of flame retardants in polymers can therefore be investigated using simple TGA measurements. Information about the energy involved in the dehydration process of the flame retardant can be obtained by DSC. This is important because it corresponds to the energy extracted from the fire.

7.4 References

- [1] METTLER TOLEDO Collected Applications Handbook: Elastomers, Volume 1.
- [2] METTLER TOLEDO Collected Applications Handbook: Elastomers, Volume 2.

For more information:

- ▶ www.mt.com/ta-elastomers-hb
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8. TMA and DMA Analysis of Elastomers

8.1 Introduction

The previous chapter described the most important effects that can be investigated by DSC and TGA in the field of elastomers. This chapter focuses on effects and properties of elastomers that can be measured by TMA and DMA.

These include expansion, the glass transition, the modulus (frequency dependence and master curves), creep behavior and creep recovery, and swelling behavior [1, 2].

8.2 Measurements and results

Thermomechanical analysis (TMA)

Isothermal creep and recovery

The term "creep" refers to the time- and temperature-dependent deformation of a material when it is subjected to a load or stress [3]. Creep deformation in polymers consists essentially of two components: reversible viscoelastic relaxation and irreversible viscous flow.

The deformation due to viscoelastic relaxation recovers over time when the

stress is reduced or removed. Viscous flow however causes permanent deformation and geometry change.

In an isothermal creep and recovery experiment (Figure 45), a constant mechanical stress (in this case, the force exerted by the TMA probe) is suddenly applied to the sample, held constant for a certain time, and then quickly removed. The deformation (in this case the relative change in sample thickness) is recorded as a function of time and comprises three components: the initial almost instantaneous reversible elastic response, the slower viscoelastic relaxation, and the more or less constant viscous flow.

When the force is removed, the elastic response is immediately completely recovered whereas viscoelastic recovery takes longer. The measurement curve does not return to the initial baseline. The difference is a measure of the irrecoverable viscous flow component. The elastic response is not considered as being part of creep deformation.

The curve in Figure 45 shows the elastic deformation, creep and recovery behavior of an EPDM elastomer measured at 30 °C. In the initial phase, the thickness of the sample was measured using a negligibly low force of 0.01 N. This was sufficient to ensure good contact between the TMA probe and the sample but low enough to exclude any sample deformation. The force was then suddenly increased to 1 N. The resulting deformation consists of three components: the immediate elastic deformation and the time-dependent viscoelastic and viscous flow components.

The force was reset to 0.01 N after 60 minutes and the recovery phase measured for a further 30 minutes. The almost immediate elastic response is followed by slow viscoelastic relaxation. The remaining deformation

Figure 45. TMA curves showing the creep and creep recovery behavior of a rectangular EPDM sample (width 3.5 mm, length 3.5 mm, thickness 1.5 mm) measured at 30 °C.

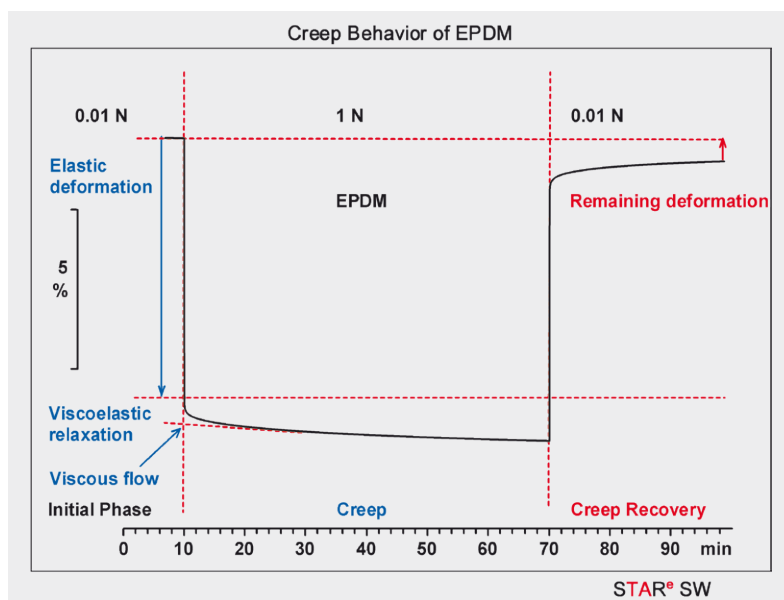
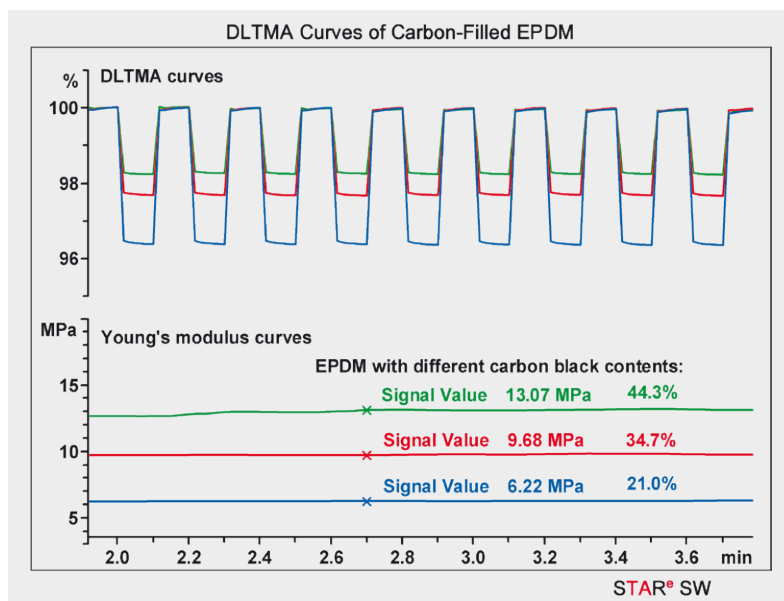


Figure 46. Determination of the Young's modulus of three rectangular EPDM samples (width 2 mm, length 2 mm, thickness 1.5 mm) with carbon black contents of 21.0, 34.7 and 44.3% by DLTMA.



shows the extent to which the sample was permanently deformed through viscous flow.

Determination of Young's modulus by DLTMA

DLTMA (Dynamic Load TMA) is a special TMA measurement mode in which the force applied to the sample alternates between a high and a low value at a given frequency. DLTMA measurements can be used to determine the Young's modulus of elastomers. The technique is very sensitive to changes in the modulus of materials and is therefore an excellent method for studying weak physical transitions or chemical reactions.

Figure 46 shows the influence of carbon black as filler on the Young's modulus of an elastomer. Three samples of EPDM containing different amounts of carbon black (N550) were measured in the compression mode at 25 °C using forces that alternated between 0.05 and 1 N.

The resulting DLTMA curves are shown in the upper diagram and display the relative sample thickness as a function of measurement time. Evaluation of the DLTMA curves yields values of the Young's modulus of 6.22, 9.68, and 13.07 MPa for carbon black contents of 21.0, 34.7, and 44.3%. These values are typical for elastomers. The results show that with higher carbon black contents the deformation amplitude becomes smaller and the Young's modulus larger.

Swelling in solvents

The swelling behavior of elastomers in different solvents is important for special applications. In a TMA swelling measurement, the sample specimen is equilibrated at the temperature of interest and the thickness measured. The TMA furnace is then opened briefly and the glass vial containing the sample is filled with solvent preconditioned at the same temperature using a syringe. The TMA probe measures the change in thickness of the specimen as it swells.

The curves in Figure 47 compare the swelling behavior of an EPDM elastomer (ethylene-propylene-diene terpolymer) and a fluoroelastomer (FPM) in toluene. The diagram shows the normalized TMA curves as a function of time. FPM swells only about 2% in toluene. This material is clearly resistant toward toluene. It can therefore be used as a sealing ring for applications in which exposure to toluene or similar solvents is required. The situation is very different for the EPDM elastomer. This material swells by more than 25% in toluene and is therefore clearly unsuitable for use as a seal in contact with toluene.

Dynamic mechanical analysis (DMA)

The mechanical properties of elastomers depend on temperature and frequency. DMA is therefore an important method for characterizing elastomers. Typical application areas are:

- Determination of the glass transition and other thermal effects such as crystallization, melting, vulcanization, relaxation and flow behavior;
- Frequency dependence of the glass transition;
- Influence of fillers, degree of vulcanization, frequency and deformation on mechanical properties, and linearity behavior;

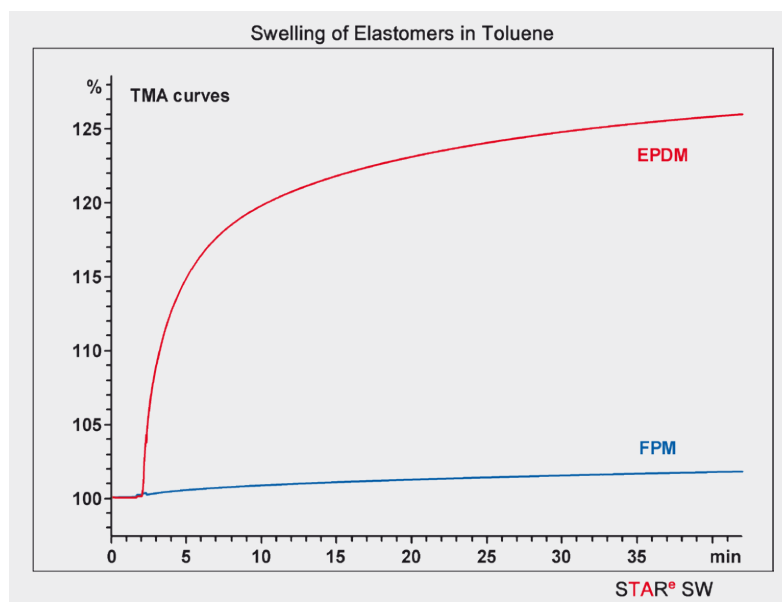


Figure 47. Swelling measurements of cylindrical EPDM and FPM elastomer samples (diameter 2 mm, thickness 2.5 mm) in toluene at 30 °C.

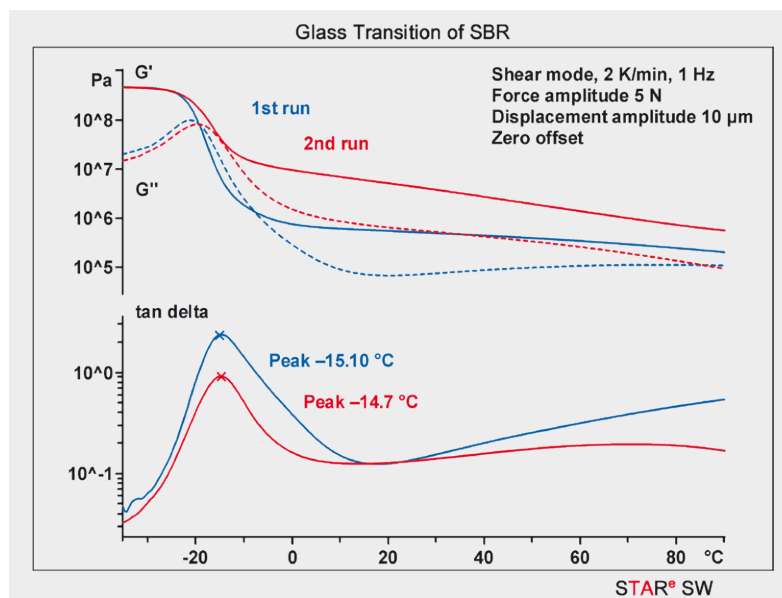


Figure 48. The curves show the first and second heating runs of a cylindrical sample of unvulcanized SBR (diameter 6.5 mm, thickness 0.7 mm) without filler, measured by DMA in the shear mode.

- d. Damping behavior;
e. Master curves.

Determination of the glass transition

The modulus of an elastomer changes by several orders of magnitude at the glass transition. DMA is in fact the most sensitive thermal analysis technique for determining the glass transition. The relatively weak glass transitions of highly filled materials are often difficult to detect by DSC or TMA but can readily be measured by DMA due to the greater sensitivity of the technique.

Figure 48 displays DMA curves from the first and second heating runs of a sample of unvulcanized SBR without

filler. The diagram shows the storage modulus (G'), loss modulus (G''), and loss factor ($\tan \delta$).

DMA curves are usually presented on a logarithmic ordinate scale so that changes in the lower modulus range can be more clearly seen. The glass transition is typically observed as step decrease in the storage modulus and corresponding peaks in the loss modulus and $\tan \delta$. The glass transition temperature can be defined as the onset of the log G'' step, or as the temperature of the peak maxima of G'' or of $\tan \delta$.

In the first heating run, G' changes by about 3 decades from 10^9 to 10^6 Pa at the glass transition and then remains

almost constant at about 10^6 Pa. This is the region of the rubbery plateau. After this, the modulus gradually decreases. The decrease is coupled with a slight increase in the loss modulus. From about 40°C onward, the material begins to melt.

In the second heating run, the step height of G' at the glass transition is only about 1.5 decades. G' then decreases in a broad step between -10°C and $+80^\circ\text{C}$.

The loss modulus increases in this range. The material does not exhibit flow behavior because the polymer undergoes crosslinking or vulcanization during the first heating run.

Figure 49. Temperature scan of a cylindrical sample of unvulcanized SBR (diameter 4 mm, thickness 1.0 mm) without filler at 1, 10, 100 and 1000 Hz.

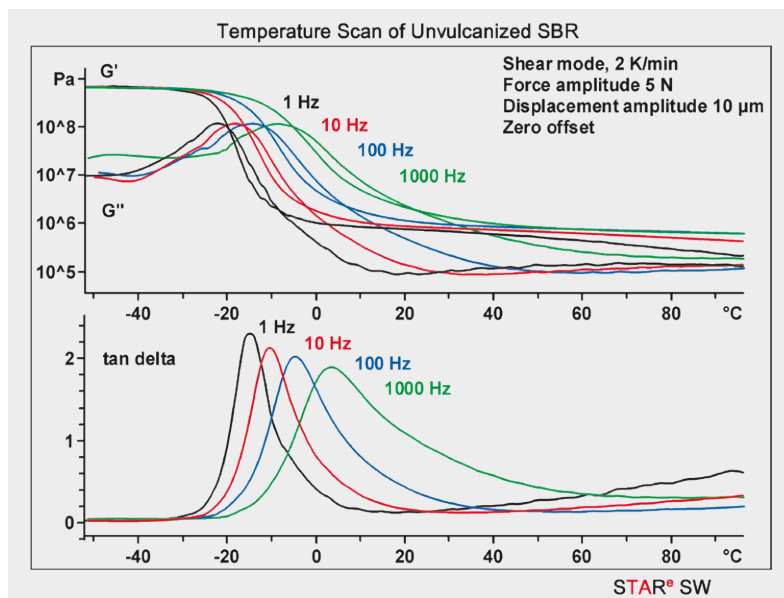
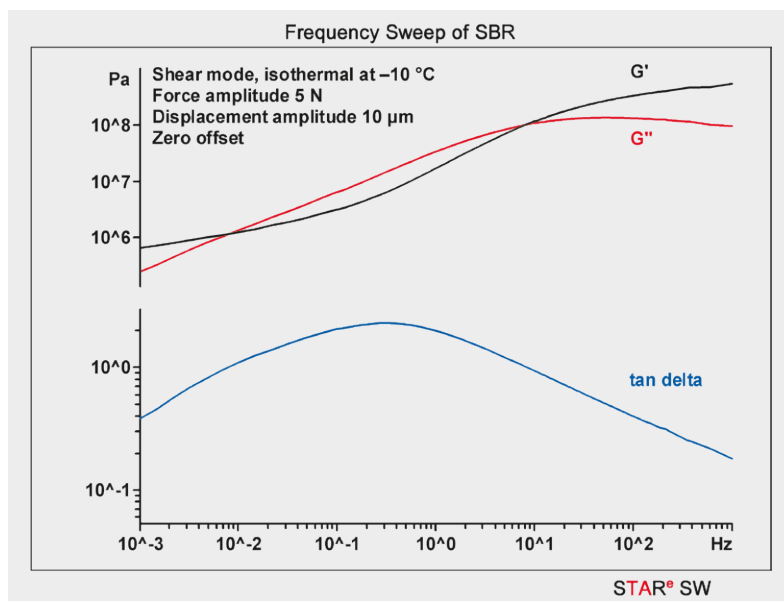


Figure 50. Frequency measurements of a cylindrical sample of unfilled SBR (diameter 5.0 mm, thickness 1.2 mm) vulcanized with 2 phr sulfur.



Frequency dependence of the glass transition

The glass transition can be described as the cooperative movement of molecular units in a polymer and exhibits frequency dependence. This phenomenon can be investigated by means of a DMA temperature scan measured at different frequencies. There are two ways to perform measurements at different frequencies in an experiment.

The first possibility is the "Multi Frequency" mode at four frequencies with a fixed ratio of 1:2:5:10. For example, if a frequency of 1 Hz is selected, then the measurement is performed simultaneously at 1, 2, 5 and 10 Hz. The second possibility known as "Frequency Series" is a sequential series of up to ten frequencies that ideally begins with the highest frequency.

Figure 49 shows the DMA curves of a sample of unvulcanized SBR without filler measured in the shear mode at 2 K/min in a frequency series of 1, 10, 100 and 1000 Hz. The curves clearly exhibit frequency dependence. The glass transition shifts to higher temperatures at higher frequencies.

Typically the glass transition shifts by about 5 K for a frequency change of one decade. When reporting glass

transition temperatures that have been determined by DMA, it is therefore essential to specify the frequency used besides other experimental or evaluation conditions. Further evaluation of the frequency dependence of the glass transition at different temperatures can be made using the Vogel-Fulcher or WLF (Williams, Landel and Ferry) equations.

Since the glass transition is frequency dependent, information about relaxation behavior can be obtained by performing isothermal measurements in which the frequency is varied. Figure 50 shows a so-called isothermal frequency sweep in the frequency range 1 mHz to 1000 Hz of an unfilled sample of SBR vulcanized with 2 phr sulfur (parts per hundred of rubber).

The modulus of the SBR changes with frequency. In the relaxation range, there is a step change in the storage modulus, G' . At high frequencies, the storage modulus is higher than at low frequencies and the sample appears harder. At low frequencies, molecular rearrangements are able to react to external stress. The sample is soft and has a low storage modulus.

In the relaxation range, a peak appears in the loss modulus curve with a maximum at a frequency of 54 Hz. The shape of the peak in the loss modulus corresponds to the distribution of relaxation times and is due to the complex intermolecular or intramolecular structures.

Master curves

The mechanical behavior of viscoelastic materials depends on frequency and temperature. In general, there is equivalence between the frequency and temperature behavior during relaxation processes.

This phenomenon is known as the Time-Temperature Superposition principle (TTS). This principle can be used to construct master curves at a reference temperature from a series of

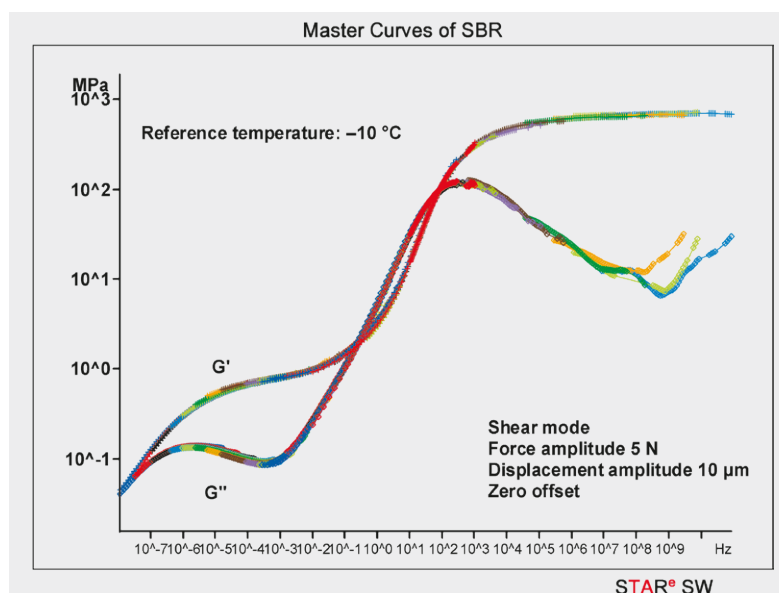


Figure 51. Master curves of the storage and loss moduli of a cylindrical sample of unvulcanized SBR without filler (diameter 4.00 mm, thickness 1.0 mm) at a reference temperature of $-10\text{ }^{\circ}\text{C}$ measured in the shear mode.

isothermal frequency sweeps. A master curve describes the mechanical relaxation behavior of a sample over a wide frequency range.

To construct master curves, frequency sweeps are performed in a frequency range directly accessible to the DMA instrument (Figure 50). Curves measured at temperatures below the reference temperature are shifted horizontally to higher frequencies so that the end sections of the curves overlap to the greatest possible extent. In the same way, curves measured at higher temperatures are shifted to lower frequencies. This results in a diagram like that shown in Figure 51.

Master curves cover frequency ranges that are much wider than those accessible by direct measurement. They allow an insight to be gained into the mechanical properties of materials over a wide frequency range.

Figure 51 shows the master curves of the storage and loss moduli of a sample of unvulcanized SBR without filler at a reference temperature of $-10\text{ }^{\circ}\text{C}$.

At low frequencies, both the storage and the loss modulus have the same value of about 30 kPa. The material is in the flow range. The peak at 10^2 Hz in the loss modulus curve is due to flow relaxation. The storage modulus

Effect / Technique	DSC	TGA	TMA	DMA
Glass transition	X		X	X
Vulcanization and Kinetics	X			
Composition	X	X		
Thermal stability, decomposition		X		
Fillers and additives	X	X		
Elastic modulus			X (DLTMA)	X
Creep and creep recovery			X	
Swelling in solvents			X	
Master curves				X
Melting and crystallization	X			X
Compatibility	X			X

Table 4. Effects that can be measured by different thermal analysis techniques

curve exhibits a rubbery plateau with a modulus value slightly below 1 MPa in the frequency range 10^{-5} to 10^{-2} Hz. The curve then increases in a step of about 3 decades which coincides with a peak in the loss modulus curve.

This is the main relaxation effect or the glass transition with a characteristic frequency of about 300 Hz (frequency at the maximum of the G'' peak). At higher frequencies the storage modulus is almost constant at about 800 MPa.

8.3 Overview of effects and applications

Figure 52 summarizes the typical effects of elastomers that can be measured by different thermal techniques.

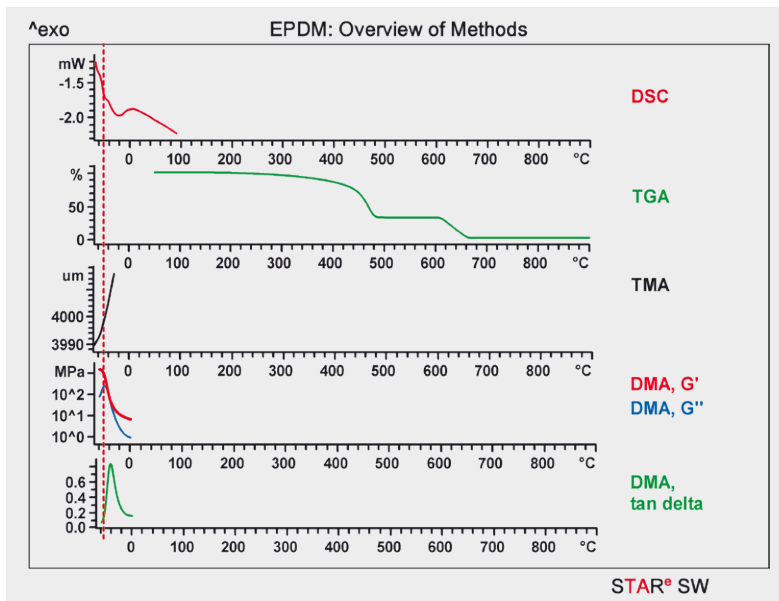
8.4 Summary

Chapters 6 and 7 describe the different possibilities available for characterizing elastomers by DSC, TGA, TMA, and DMA. EPDM and SBR are used as examples to illustrate some of the typical effects and applications that are

important for elastomers. The main topics covered are the glass transition and its frequency dependence, vulcanization, compositional analysis, fillers/filler content and the influence of fillers, creep behavior and creep recovery, swelling in solvents, master curves and compatibility.

Different techniques provide different perspectives and can be used to characterize the same processes such as the glass transition, melting, and crystallization depending on the information required.

Figure 52. Overview of effects and comparison of results. The glass transition temperature is shown by a vertical dashed line.



8.5 References

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- [2] METTLER TOLEDO Collected Applications Handbook: Elastomers, Volume 2.
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For more information:

- www.mt.com/ta-applications
- www.mt.com/ta-standards

9. Thermal Analysis of Composites

A composite is made by combining two or more different materials together. The resulting combination has better properties than the individual materials used to make it. This allows the strength or durability of a product to be enhanced depending on the particular properties required. The article describes how a composite material, in this case a printed circuit board (PCB), can be characterized by thermal analysis.

9.1 Introduction

Thermal analysis comprises several different techniques that are used to measure the physical properties of a material as a function of time while the material is subjected to a controlled temperature program. The techniques include DSC, TGA, TMA and DMA. Thermal analysis is used in research and development, process optimization, quality control, damage and failure analysis as well as for investigating competitive products. The techniques allow the curing behavior of products, the compatibility of composite materials and the frequency dependence of the glass transition to be investigated [1].

9.2 Composites

A composite consists of two or more different materials. The properties of the new material are different to those of the individual materials. The individual materials used to make the composite remain distinct and do not mix with one other.

The purpose of making a composite can, for example, be:

- to improve mechanical properties (tensile strength, strain at failure, impact resistance)
- to change the color (through pigments)
- to improve flame resistance (of flammable binders)
- to stabilize (improve weather resistance)
- to aid processing (to make the polymer lighter and easier to process).

Composite materials can be classified according to their geometrical form. Besides the commonly used particle composites or fiber composites in which particles or fibers are embedded in a matrix (e.g. printed circuit boards, PCBs), there are laminate or multilayer composites and infiltration composites (foamed ceramics: a porous substrate filled with a binder).

Composites can also be classified according to the types of material used. This distinguishes between ceramic, organic or mineral particles or fibers as the reinforcement, and polymers, glass, metal or ceramics as the matrix. Good examples of fiber-reinforced composites are carbon-fiber-reinforced polymers or plastics (CFRP). In recent years, these have become more and more important for products that need to be stiff but at the same time should have low weight, such as walking sticks, bicycle frames or boats.

The fillers often used for composites are chalk (calcium carbonate), talc (magnesium silicate) or carbon black.

The most well-known composites include colored materials, polypropylene filled with chalk or glass fibers, or ABS (acrylonitrile-butadiene-styrene), PC (polycarbonate) and PP with flame retardants [2].

This article describes how a printed circuit board can be characterized.

9.3 PCB

A printed circuit board, PCB (Figure 53), provides a mechanical support for electronic components. It fixes components in defined locations and connects them electrically. PCBs are used in almost all types of electronic equipment. They are composite materials and are manufactured by molding together a support material (glass fiber cloth) and a matrix (a binder: curable plastic, epoxy resin) under pressure. The outer layer consists of a thin copper foil laminated onto the non-conductive substrate. The foil provides separate conductive tracks that remain behind after the excess copper areas have been etched away. Industrial electronics employ high-quality printed circuit boards designated FR-4 (FR: flame retardant). These PCBs use glass fiber cloth, a special epoxy resin as the matrix resin, and a bromide compound (tetrabromobisphenol A) as a flame retardant [3].

9.4 Requirements for a printed circuit board

The main requirements for a printed circuit board are:

- Structural rigidity and stability
- Low thermal expansion:
 - since printed circuit boards are anisotropic; the coefficients of

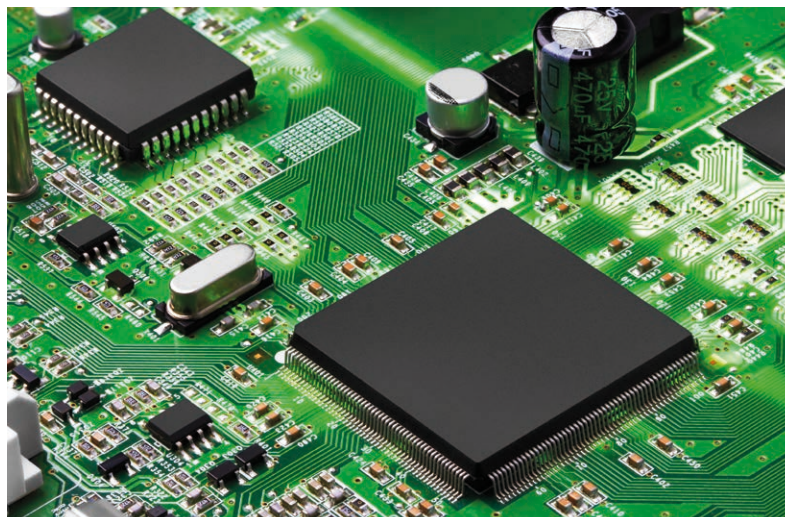


Figure 53. Example of a printed circuit board.

- thermal expansion in the length (x), width (y) and thickness (z) directions are different.
- High softening temperature:
 - mechanical and dielectric properties deteriorate when the matrix resin softens (glass transition).
 - Thermal stability of the matrix resin:
 - in order to withstand the temperature of the soldering bath and



Figure 54.
The printed circuit board investigated.

Figure 55.
DSC curves of the PCB sample: 1st and 2nd heating runs and the cooling curve.

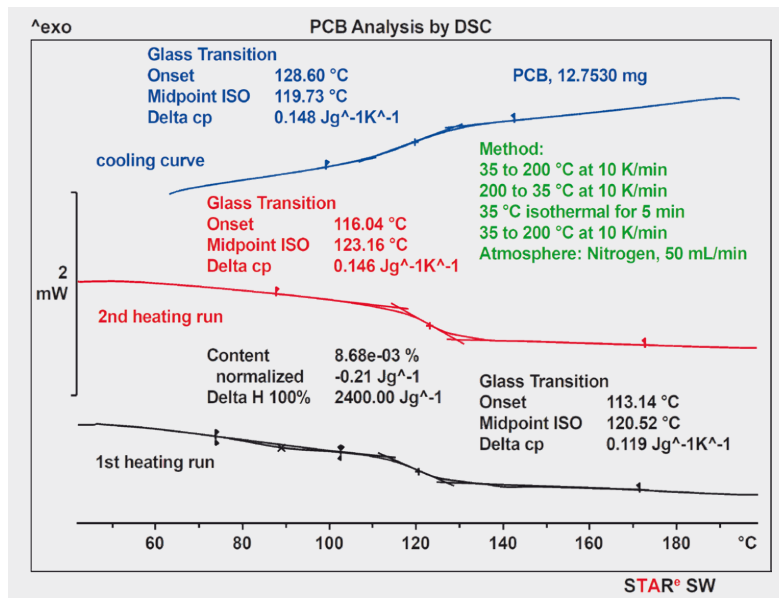
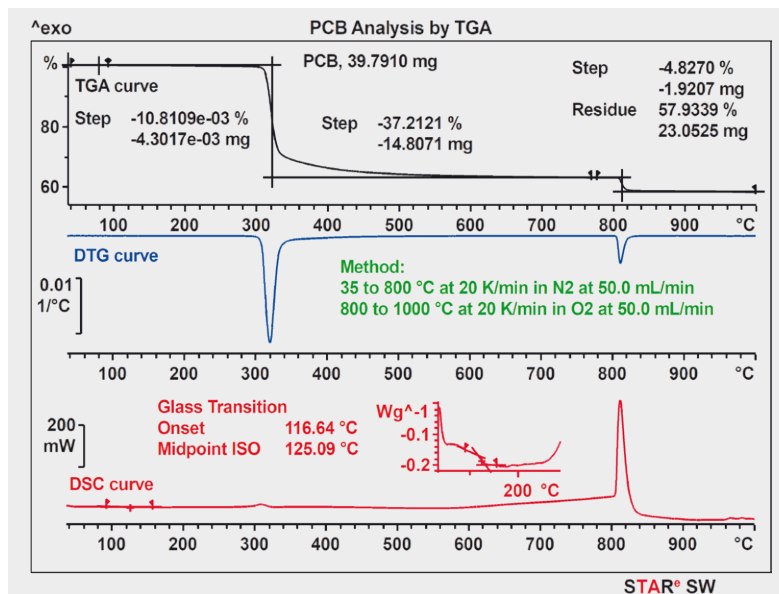


Figure 56.
TGA, DTG and DSC curves of the PCB sample.



possible heat accumulation in later operation. Any initial decomposition of the matrix resin is accompanied by the formation of gases, which can cause the layers to burst open (delaminate) and destroy the laminate.

- Flame resistance [3].

9.5 Experimental details

A PCB sample (Figure 54) was analyzed by DSC, TGA/DSC, TMA and DMA using a DSC 3+ equipped with an FRS 6+ sensor, a TGA/DSC 3+ with a DSC sensor, a TMA/SDTA 2+, and a DMA/SDTA 1+. The measurements were evaluated using the STAR[®] software. No special sample preparation was performed.

DSC

Differential scanning calorimetry is used to measure the heat flow of a sample as a function of temperature or time. A DSC instrument can quantitatively analyze physical transitions and chemical reactions [4].

DSC measurements of PCBs mainly involve the determination of the glass transition. The sample (about 12 mg) was subjected to a heating-cooling-heating cycle in a 40- μ L standard aluminum crucible with a pierced lid in a nitrogen atmosphere. A marked increase in the glass transition temperature in the second heating run would indicate that the curing process was incomplete. The first heating run in Figure 55 shows a small endothermic peak between 75 and 100 °C in addition to the glass transition at 118 °C. This could possibly be caused by the vaporization of water. If we assume that the enthalpy of vaporization of water is about 2400 J/g, we obtain a value of 0.009% for the water content in the sample. Such small amounts are more difficult to detect by TGA. In the second heating run, the glass transition is slightly higher. This could be due to postcuring or to the vaporization of water.

TGA

Thermogravimetric analysis is a technique that records the weight of a sample when the sample is heated cooled or held isothermally in a defined atmosphere. It is mainly used to analyze the quantitative composition of products [4].

Figure 56 shows the decomposition curve of the PCB sample (black), the corresponding DTG curve (blue), and the DSC curve (red). The sample was measured from 35 to 1000 °C at a heating rate of 10 K/min in a 150- μ L aluminum oxide crucible without a lid. There was a gas change from nitrogen to oxygen at 800 °C. The flow rate was 50 mL/min. The polymer content of the material can be determined from the pyrolysis reaction, which occurs up to about 500 °C. The atmosphere was

switched from nitrogen to an oxidative atmosphere at 800 °C in order to burn pyrolytic carbon that had formed in the pyrolysis reaction. Inorganic fillers such as silicates or oxides are left behind as residues. Besides the weight loss curve, the DTG curve (1st derivative, blue curve, decomposition rate) and the DSC curve (red curve) were also recorded. The DSC curve is measured simultaneously with the TGA measurement curve and provides valuable additional information. In this case, for example, we can also detect the glass transition at about 120 °C and obtain information about the decomposition reaction (exothermic peak at 300 °C) and the combustion process (large exothermic peak at 800 °C) [3, 5]. In the TGA curve, step evaluation from room temperature to about 100 °C shows a small step of about 0.01% that might possibly be due to the vaporization of water. This value agrees well with the water content determined by DSC (0.009%).

TMA

Thermomechanical analysis (TMA) measures the dimensional changes of a sample when it is heated or cooled in a defined atmosphere. The most important measurements involve the determination of the expansion coefficient, the glass transition, and softening. It is also possible to determine the modulus of elasticity or to investigate the swelling behavior of samples in solvents. Another important application is the detection of the gel point. Measurements can be performed in the dilatometric and penetration modes or as a DLTMA measurement (Dynamic Load TMA) [4, 5].

Expansion coefficient

Knowledge of the expansion behavior of materials with temperature is very important for applications involving the use of composite materials. When materials with different expansion properties are combined, there is a risk of breakage and hence structural damage to the composite when the temperature changes. With anisotropic materials,

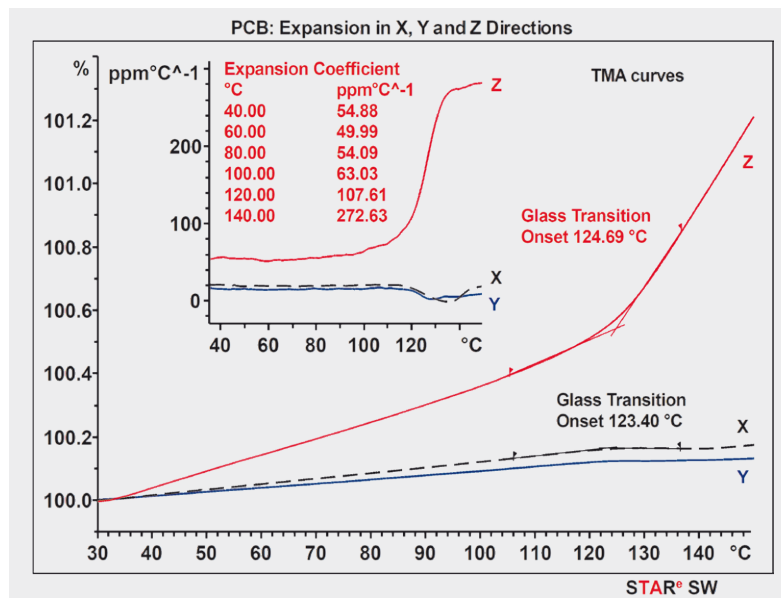


Figure 57. TMA curves of PCB (in the x, y and z directions) and the CTE evaluation (linear expansion coefficient).

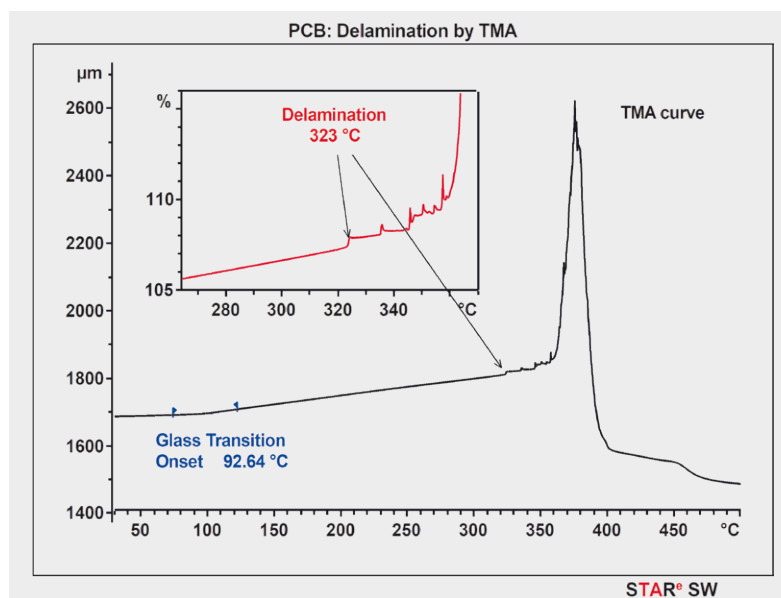


Figure 58. TMA curve of a PCB up to 460 °C showing the first signs of delamination at about 323 °C.

expansion can vary depending on the orientation of a material. The coefficient of thermal expansion of the PCB sample was measured in the dilatometric mode using a low force that was just sufficient to keep the probe in constant contact with the sample.

The PCB samples (plane-parallel test specimens, height about 2 to 5 mm) were measured in all three orientations (x, y and z directions) from 30 to 160 °C at a heating rate of 5 K/min using the 3-mm ball-point probe and a force of 0.05 N. The measuring force of 0.05 N was distributed uniformly over the samples by covering them with a quartz glass disk. The TMA curves shown in

Figure 57 are the second heating runs. These are usually evaluated in order to eliminate effects due to the thermal history of samples.

The curves show that that the samples behave similarly in the x and y directions (the expansion of the matrix resin is hindered parallel to the glass fibers) whereas in the z direction the behavior is different. In this direction, the expansion is significantly greater both below and above the glass transition, which is observed at about 124 °C due to a change in the slope of the curve. Expansion coefficients are given in ppm (parts per million) per degree Celsius (10⁻⁶ °C⁻¹).

The coefficient of thermal expansion, CTE, can be evaluated and characterized in two different ways. First, by calculating the instantaneous coefficient of thermal expansion, α , from the derivative of the relative length with respect to temperature as shown in Figure 57 [5]:

$$\alpha = \frac{dL}{dT} \frac{1}{L_0} \quad (\text{see Figure 57})$$

and second, as the mean CTE, a value for the mean expansion over a given temperature interval.

Delamination

By delamination we mean the (undesired) separation of layers in composite materials such as PCBs at higher temperatures. The TMA curve shown in Figure 58 was measured up to 460 °C using the same conditions as in Figure 57. The curve exhibits sudden spikes from about 323 °C onward. The spikes indicate the composite is beginning to delaminate. This means that the up-



Figure 59. PCB sample installed in the 3-point bending accessory in the DMA/SDTA 1+.

Figure 60. DMA measurement of the PCB from 70 to 200 °C showing the storage and loss moduli and tan delta curves.

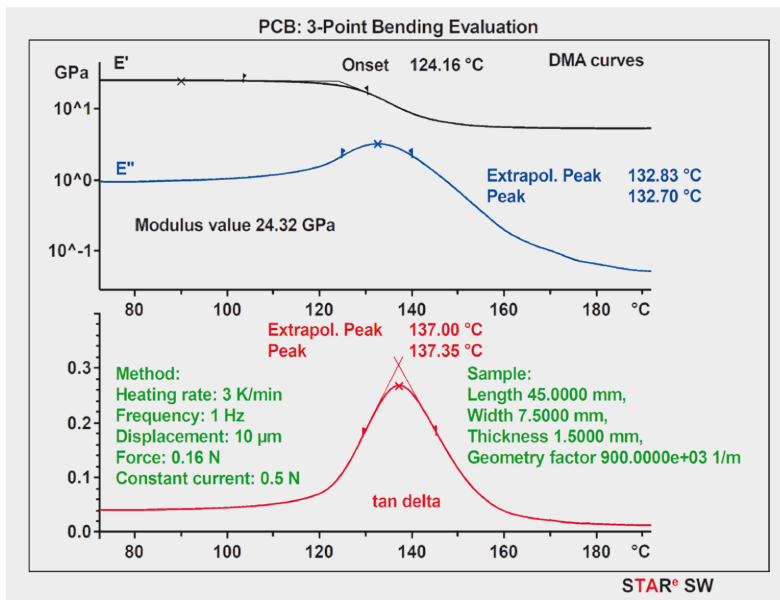
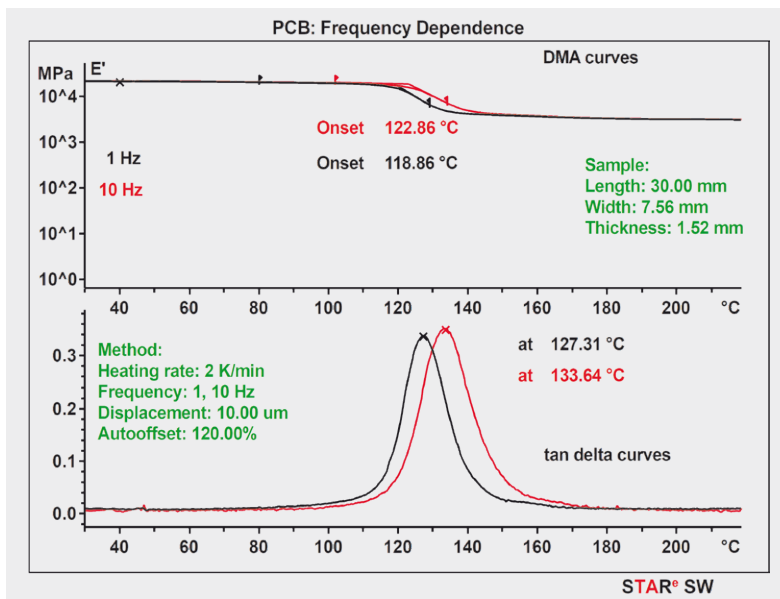


Figure 61. DMA measurement of a PCB at two different frequencies to demonstrate the frequency dependence of the glass transition.



per temperature limit for this material is about 310 °C.

DMA

Dynamic mechanical analysis (DMA) measures the mechanical properties of a viscoelastic material as a function of time, temperature or frequency when the material is deformed by a periodic oscillating force. The following section explains the evaluation of the glass transition in more detail [5].

Glass transition

The PCB sample was a sheet measuring 10 cm by 7.5 cm by 1.5 mm. The sample specimen was installed in the 3-point bending accessory of the DMA/SDTA 1+ (Figure 59) and measured up to 200 °C at a heating rate of 3 K/min using a maximum force amplitude of 0.16 N and a maximum displacement amplitude of 10 µm. The measurement frequency was 1 Hz.

Figure 60 presents the DMA results for the second heating run of the PCB measured in the 3-point bending mode. The upper and lower diagrams show the storage (E') and loss (E'') moduli and the tan delta curves of the material. The ordinate axis of the upper two curves is presented logarithmically because it shows the difference between the storage and loss modulus more clearly. The storage modulus has a value of 24 GPa before the glass transition. This then decreases after the glass transition (at about 124 °C). The glass transition can be characterized as the onset (logarithmic onset) in the storage modulus curve. The loss modulus curve (peak at 133 °C) and the tan delta curve (peak at 137 °C) both exhibit peaks during the glass transition. This demonstrates why it is important to state the measurement conditions and evaluation procedure when comparing the evaluation of glass transitions [5].

Frequency dependence of the glass transition

Figure 61 shows a DMA experiment in which two different frequencies were simultaneously applied (1 and 10 Hz).

Sample preparation was similar to that used for the measurement in Figure 60. The measurement was performed between 30 and 220 °C at frequencies of 1 and 10 Hz using a maximum force amplitude of 2 N, an autooffset of 120% and a maximum displacement amplitude of 10 µm. The heating rate was 2 K/min. The upper diagram shows the storage modulus curves (with logarithmic ordinate) as a function of time and the lower diagram the tan delta curves. The glass transition is observed as a step in the storage modulus curves and as a peak in the tan delta curves. The transition is clearly dependent on the frequency and shifts to higher temperatures at higher frequencies. The reason for this is that the glass transition is a relaxation effect. More details on this can be found in reference [6].

9.6 Overview of effects and comparison of results

Figure 62 presents an overview of the thermal analysis methods used to investigate the PCB sample. It shows quite clearly that the glass transition temperatures obtained using the different techniques are similar (shown by the blue line in Figure 62).

9.7 Conclusions

The article describes the possibilities available for characterizing a PCB sam-

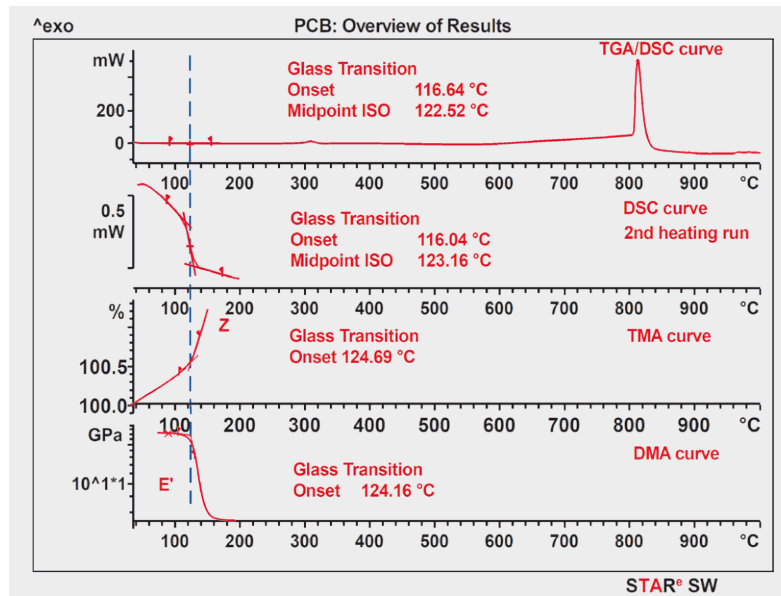


Figure 62. Overview of the effects and comparison of results.

ple using the standard thermal analysis techniques DSC, TGA, TMA and DMA. The results are clearly consistent. The main effects investigated were the glass transition, expansion and decomposition.

The results show that different effects can be investigated by various thermal analysis techniques and that the techniques can often be used to obtain complementary information. For comprehensive material characterization, samples are usually first investigated by TGA, then DSC and TMA and finally by DMA [5].

9.8 References

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10. Evolved Gas Analysis of Polymers

10.1 Introduction

In thermogravimetric analysis, the mass of a sample is continuously measured as a function of temperature. Changes in mass of just a few micrograms can be detected with high accuracy. Modern thermobalances such as the METTLER TOLEDO TGA/DSC can also simultaneously measure the heat flow to and from the sample. This provides information about thermal changes that occur during the mass change and also about effects that are not associated with a change in mass such as melting, crystallization, or solid-solid transitions.

Questions regarding the identity of the gaseous products evolved during the mass change however remain unanswered. This information can be obtained by coupling the TGA to a suitable system for gas analysis. In these five chapters of this handbook, we will discuss the various techniques that METTLER TOLEDO offers for such analyses. The first chapter presents an overview of the different techniques and discusses their application possibilities.

In the four chapters that follow, we show how TGA-MS (thermogravimetric analysis coupled with mass spec-

trometry), TGA-FTIR (thermogravimetric analysis coupled with Fourier transform infrared spectroscopy), TGA-GC/MS (thermogravimetric analysis coupled with gas chromatography and mass spectrometry), and TGA-Micro GC/MS (thermogravimetric analysis coupled with micro gas chromatography and (optionally) mass spectrometry can be applied in practice.

10.2 The various techniques

The gas analysis techniques discussed here all have something in common, namely that the gases and volatile products evolved during the heating process in the TGA have to be transferred to the gas analysis system. This is accomplished using a transfer line. This is typically maintained at a temperature of 200 °C to prevent gaseous products from condensing.

In TGA-GC/MS, the decomposition gases are however normally not measured online, in contrast to TGA-MS, TGA-FTIR and TGA-Micro GC/MS). Instead, gas samples are taken at particular furnace temperatures during the TGA measurement and stored in a special interface.

The gas samples are analyzed afterward by GC/MS after the TGA measurement has finished.

10.3 TGA-MS

The operating principle of a mass spectrometer is shown schematically in Figure 63. Gas molecules entering the ionization chamber from the TGA are bombarded with electrons. The molecules are ionized and form both positively charged molecular ions and numerous fragment ions. The ions produced and their relative intensities depend on the energy of the electrons used for ionization. This can be set on the mass spectrometer and is typically 70 eV. This voltage produces mainly singly charged ions.

The ions then enter an alternating electromagnetic field, a so-called mass filter, that separates the ions so that at any one instant only ions of a particular mass-to-charge ratio, (m/z) reach the detector.

In mass spectrometry, the ions are characterized by the ratio of their mass, m , and their electrical charge, z . After passage through the filter, ions of a particular m/z ratio arrive at the detector where their intensity is measured.

The mass spectrometer can be operated in several different ways. A so-called mass spectrum can be obtained by scanning the whole or part of the mass range, for example from m/z 18 to m/z 80. This is done by periodically varying the alternating electromagnetic field. The intensities of the different ions are presented as a function of m/z . The mass spectrum provides information about the nature and structure of the molecule being measured.

In combination with TGA, the user often sets the MS to detect and monitor the intensity of one or more individual masses (e.g. m/z 18, m/z 28, and m/z 44). This mode is extremely sensitive and is known as selected ion monitoring (SIM) or multiple ion detection (MID). The resulting m/z curve shows

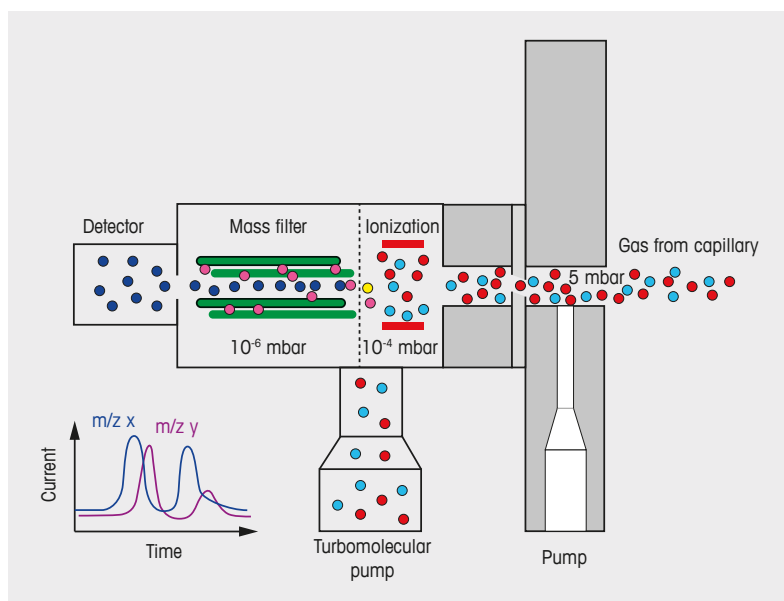


Figure 63. Schematic diagram showing the operating principle of a mass spectrometer.

the intensity of the selected ion as a function of time. Peaks in the ion current signal for a particular m/z mean that molecules are present in the gas flow that after ionization fragment to ions of this mass-to-charge ratio.

As an example, Figure 64 displays the mass spectrum of methane (CH_4). The singly charged CH_4 molecule is detected by the m/z 16 and m/z 17 ions (the molecular peaks correspond to $^{12}\text{CH}_4^+$ and $^{13}\text{CH}_4^+$). Besides this, electron bombardment produces numerous fragment ions that are formed by the removal of different numbers of hydrogen atoms from the methane molecule (e.g. m/z 12, 13, 14, and 15 fragment peaks, corresponding to C^+ , CH^+ , CH_2^+ , CH_3^+).

In certain cases, doubly charged ions can also be formed through the removal of two electrons from the molecule. For example, the mass spectrum of argon consists mainly of singly charged $^{40}\text{Ar}^+$ (m/z 40) and doubly charged $^{40}\text{Ar}^{2+}$ (m/z 20).

The mass spectrum of a substance allows a substance to be unambiguously identified and can be recorded in a few seconds. This means that TGA and MS measurements are effectively performed simultaneously. In TGA experiments, a number of different compounds are often evolved at the same time. In such cases, the identification of the substances is not always easy because different compounds often exhibit fragment ions with the same mass-to-charge ratio in their mass spectra (for example, ammonia yields the fragment ions m/z 14 (N^+), m/z 15 (NH^+), m/z 16 (NH_2^+) and m/z 17 (NH_3^+) just like for methane. For more information about the interpretation of mass spectra, see reference [1] or go to the link found in "For more information", both at the end of this chapter.

In summary, the interpretation of the mass spectra of gas mixtures containing many "large" molecules (for example a mixture of long chain organic molecules) is difficult because of

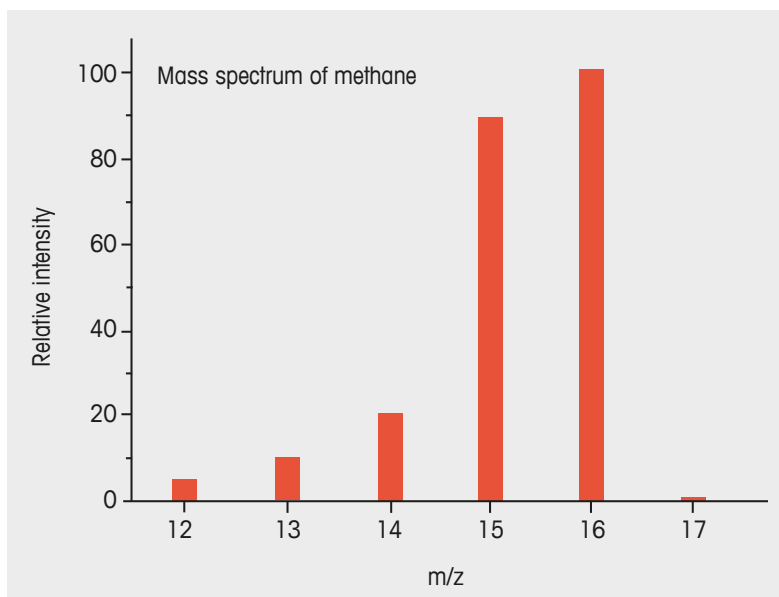


Figure 64. Mass spectrum of methane (CH_4). The m/z 17 ion corresponds to the singly charged CH_4 molecule containing a ^{13}C atom. On the Earth, the two stable carbon isotopes ^{12}C and ^{13}C are present in a ratio of about 99 to 1.

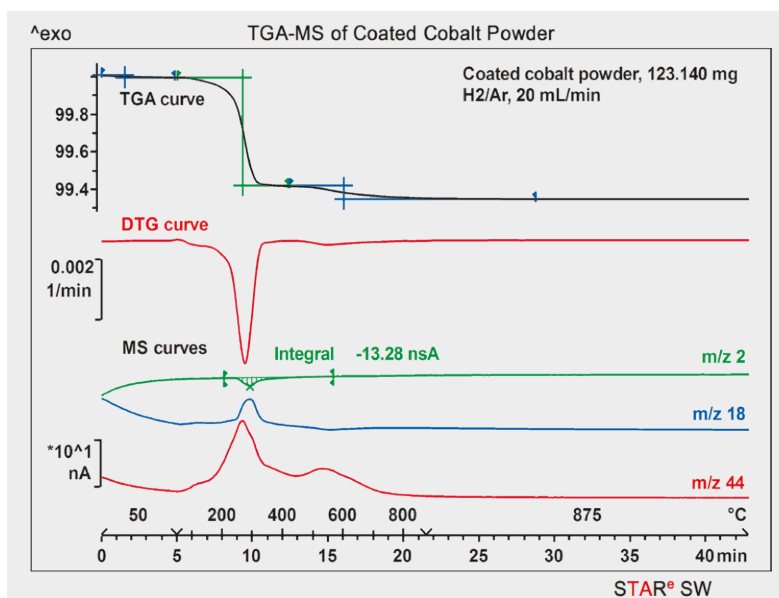


Figure 65. TGA-MS curves of coated cobalt powder measured in inert hydrogen.

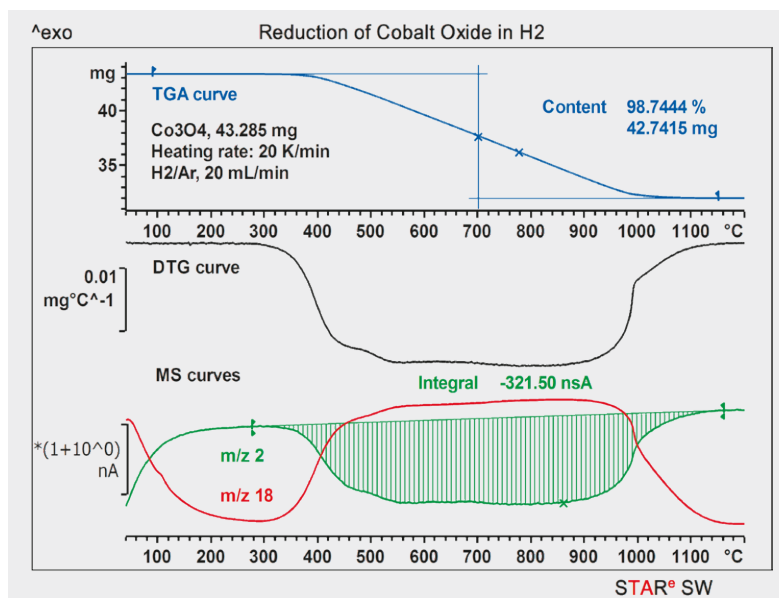


Figure 66. TGA-MS curves of cobalt oxide (Co_3O_4) measured in inert hydrogen.

their fragmentation. On the other hand, TGA-MS is extremely useful for the detection of small molecules (for example water, CO_2 , HCl , SO_x , NO_x , NH_x , etc.). For further details, see the METTLER TOLEDO Evolved Gas Analysis Handbook [1].

TGA-MS: Example

Cobalt powder is used in the manufacture of pigments in the glass, enamel and ceramic industries. Cobalt oxidizes very rapidly to cobalt oxide (Co_3O_4) in air. To prevent oxidation, finely powdered cobalt is coated with a very thin protective film of paraffin, polyethylene glycol or polyethylene.

Despite the protective coating, cobalt oxide is still formed. The content can be determined by performing TGA-MS measurements. The cobalt powder is heated in an inert hydrogen atmosphere (4% H_2 , 96% Ar) in a TGA coupled to a mass spectrometer.

Figure 65 displays some typical measurement curves. The figure shows the TGA and DTG (first derivative) curves together with the MS curves for hydrogen (m/z 2), water (m/z 18) and CO_2 (m/z 44). Three mass loss steps can be seen. The first step corresponds to the loss of moisture. The second step is mainly due to the reduction of the cobalt oxide in the sample.

This process consumes hydrogen and produces water as a reaction product ("negative" peak with a decrease in the m/z 2 signal, and a "positive" peak with an increase of the m/z 18 signal). At the same time, part of the coating degrades (signal on the m/z 44 curve). The rest of the coating decomposes from about 400 °C onward, mainly with the production of CO_2 . However, the content of cobalt oxide in the sample cannot be reliably determined from the TGA measurement because the decomposition of the coating and the reduction of the cobalt oxide overlap.

The content could however be determined if we knew how much hydrogen is needed to reduce a known amount of cobalt oxide. This information was obtained from a TGA-MS measurement of cobalt oxide performed in a similar way as before in inert hydrogen (see Figure 66). In this experiment, the cobalt oxide is reduced to metallic cobalt by the hydrogen with the release of water. This can be seen from the opposing MS curves of m/z 2 and m/z 18.

Figure 66 shows that a hydrogen equivalent of 321.5 nCb is needed (integration of the broad peak in the m/z 2 curve) for the reduction of 42.75 mg Co_3O_4 . The MS curve in Figure 65 showed that a hydrogen equivalent

of 13.28 nCb was needed to reduce the Co_3O_4 present in the coated cobalt powder. This evaluation gives a mass of 1.77 mg Co_3O_4 in the coated cobalt powder sample and corresponds to a Co_3O_4 content of 1.44%.

10.4 TGA-FTIR

FTIR spectroscopy is based on the interaction of molecules with electromagnetic radiation in the mid-infrared spectral region 4000 to 400 cm^{-1} . In contrast to MS, the energy involved is so low that ionization, fragmentation or dissociation cannot occur.

If a molecule is irradiated with broadband infrared light, it absorbs energy at certain frequencies corresponding to the vibrations or rotations it excites in that molecule. The infrared spectrometer measures the transmittance of the incident radiation as a function of wavelength. The resulting infrared spectrum is characteristic for the particular molecule and allows the functional groups of a molecule to be identified. The technique is therefore ideal for the identification of small molecules produced during TGA analysis.

This is illustrated in Figure 67 which displays the infrared spectrum of gaseous HCl . In this example, the absorbance (ordinate) is plotted as a function of the wavenumber (abscissa). This is the usual presentation for FTIR spectra. The transmittance (T) is the ratio of the light intensity transmitted by the sample (I) to that incident on it (I_0), that is I/I_0 at a particular wavelength and is usually expressed as a percentage value. The absorbance (A) is the negative logarithm of the transmittance and is given by $A = -\log T$. Compared with transmittance, the absorbance has the advantage that it is a linear function of concentration.

The wavenumber is expressed in cm^{-1} . It is the reciprocal of the wavelength (λ) of the absorbed light and is calculated by dividing 10,000 by the wavelength (λ) in microns. The unit is a linear function of energy.

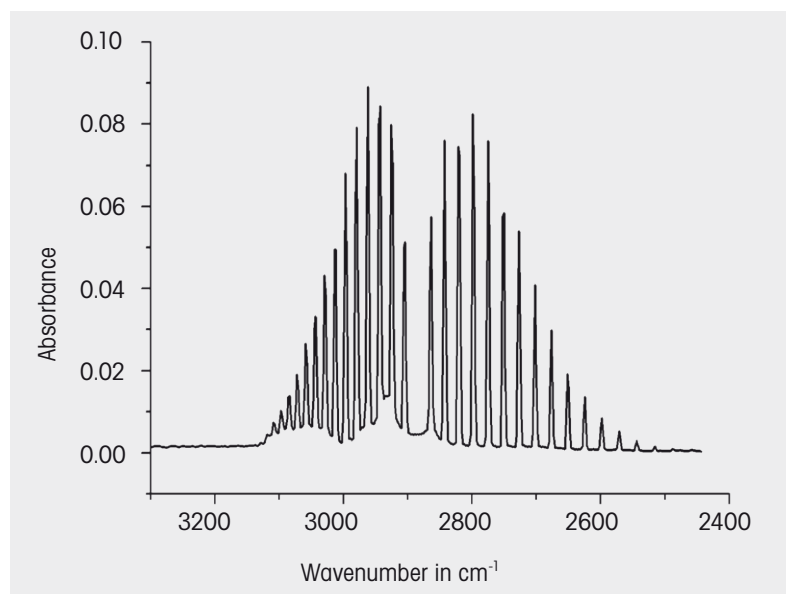


Figure 67. FTIR spectrum showing the rotational-vibrational fine structure of hydrogen chloride at room temperature.

Fourier transform infrared spectroscopy (FTIR) is nowadays the usual method for recording infrared spectra. In contrast to the previously used dispersive IR spectrometers, an FTIR spectrometer can record a spectrum in just a few seconds or even less. This means that TGA and FTIR measurements are effectively performed simultaneously.

In TGA experiments, several gaseous substances are often evolved at the same time. Each of these compounds exhibits a characteristic IR spectrum. The measured IR spectrum is therefore usually the sum of numerous individual spectra. Even with the aid of reference spectra, the complete interpretation of the measured spectra is a difficult task. Quite often, however, the identification of specific functional groups (e.g. of alcohols or of aromatic compounds, etc.) in the reaction products is also important. For further details, see the METTLER TOLEDO Evolved Gas Analysis Handbook [1].

TGA-FTIR: Example

Figures 68 and 69 show a typical application example of TGA-FTIR. The sample analyzed was an active pharmaceutical ingredient (API) that had been recrystallized in a solvent. The purpose of the TGA-FTIR analysis was to identify the solvent that had been used and to determine how much of it was still present in the product.

Figure 68 shows the TGA of the API and the calculated DTG curve. The TGA and DTG curves show three main processes: The small mass loss from room temperature up to about 50 °C is presumably due to the loss of moisture. We interpret the first clear mass loss step between 50 and about 125 °C as being due to the loss of the residual solvent. The substance finally decomposes from about 125 °C onward.

To identify the solvent, the IR spectrum of the gases evolved at a TGA temperature of 88 °C was examined more closely. Comparison of the spectrum with database spectra gave

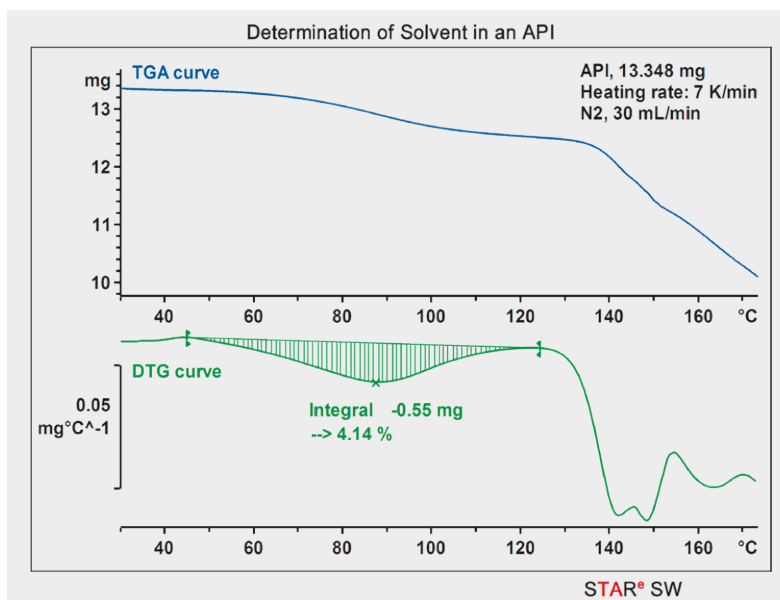


Figure 68. TGA-FTIR measurement of an active pharmaceutical ingredient (API) that had been recrystallized in an unknown solvent.

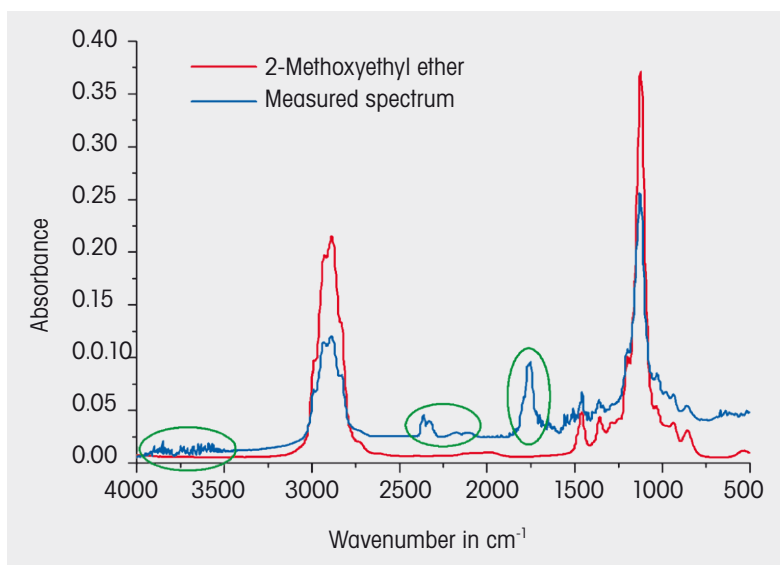


Figure 69. Measured IR spectrum (blue curve) at a TGA temperature of 88 °C and the database IR spectrum of 2-methoxyethyl ether (best fit, red curve).

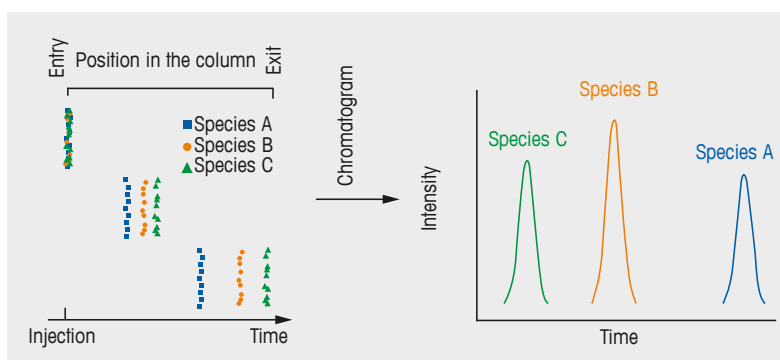


Figure 70. Separation of gases by gas chromatography: Different species of molecules take different times to pass through the column. The graph showing the intensity of the species arriving at the end of the column as a function of time is the gas chromatogram.

good agreement with 2-methoxyethyl ether, MEE, (Figure 69). This was therefore the solvent used to recrystallize the API.

Close comparison of the spectrum measured at 88 °C with the reference spectrum of MEE (Figure 69) shows

that weak absorption bands occur in the measured spectrum that are not present in the reference spectrum von MEE. For example, there are indications for the presence of water (bands around 3700 cm⁻¹), CO₂ (bands around 2300 cm⁻¹), and carbonyl compounds (bands around 1750 cm⁻¹).

interface can store up to 16 gas samples. The gas samples are analyzed one after the other in the GC/MS after the TGA experiment. Each peak in the chromatogram corresponds to a substance that can be identified by the MS.

Example

As an example, Figures 72 and 73 show the results of a TGA-GC/MS measurement of an unknown elastomer in nitrogen. The purpose of the measurement was to identify the elastomer. Figure 72 shows the resulting TGA and DTG curves.

The curves indicate two pyrolysis steps. This suggests that the elastomer sample consists of two different elastomers. The DTG curve was used to select the temperatures at which the gas samples were taken in a second experiment. Three such temperatures are marked in the figure by vertical red lines. The gas samples were analyzed by GC/MS after the TGA experiment. An example of such an analysis is shown in Figure 73. The upper diagram shows the chromatogram of the gas sample at a TGA temperature of 425 °C. Mass spectra were recorded for every peak in the chromatogram. The mass spectrum corresponding to the peak marked by the black arrow in the chromatogram is displayed in the lower part of Figure 73. Comparison of this

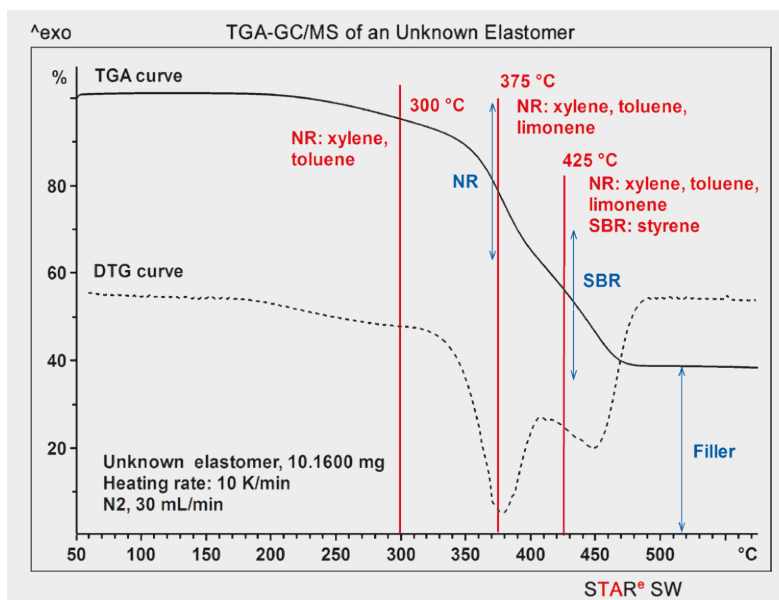


Figure 72. The TGA and DTG curves and results of gas analysis using GC/MS of an unknown elastomer. The measurement was performed at a heating rate of 10 K/min and a flow rate of 30 mL/min nitrogen.

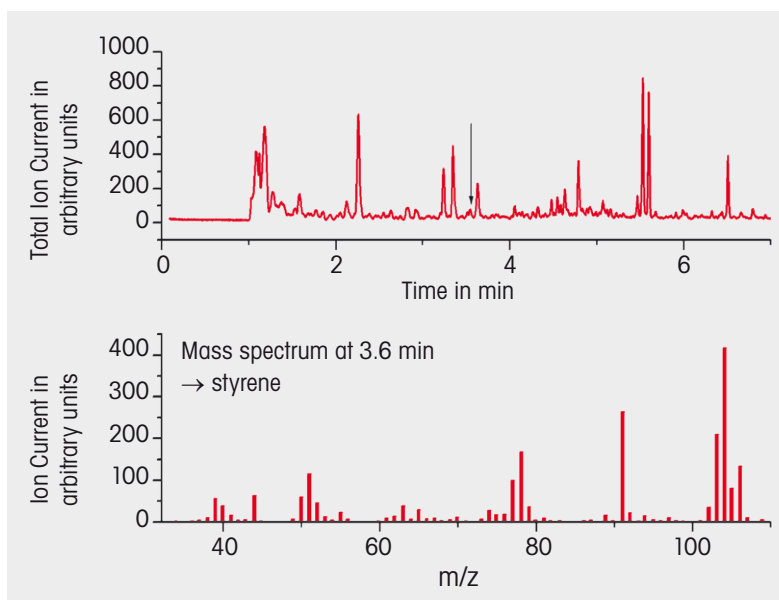


Figure 73. Above: Chromatogram of the decomposition products of an unknown elastomer collected at a TGA furnace temperature of 425 °C. Below: The mass spectrum of the substance (styrene) corresponding to the peak marked by the black arrow in the chromatogram.

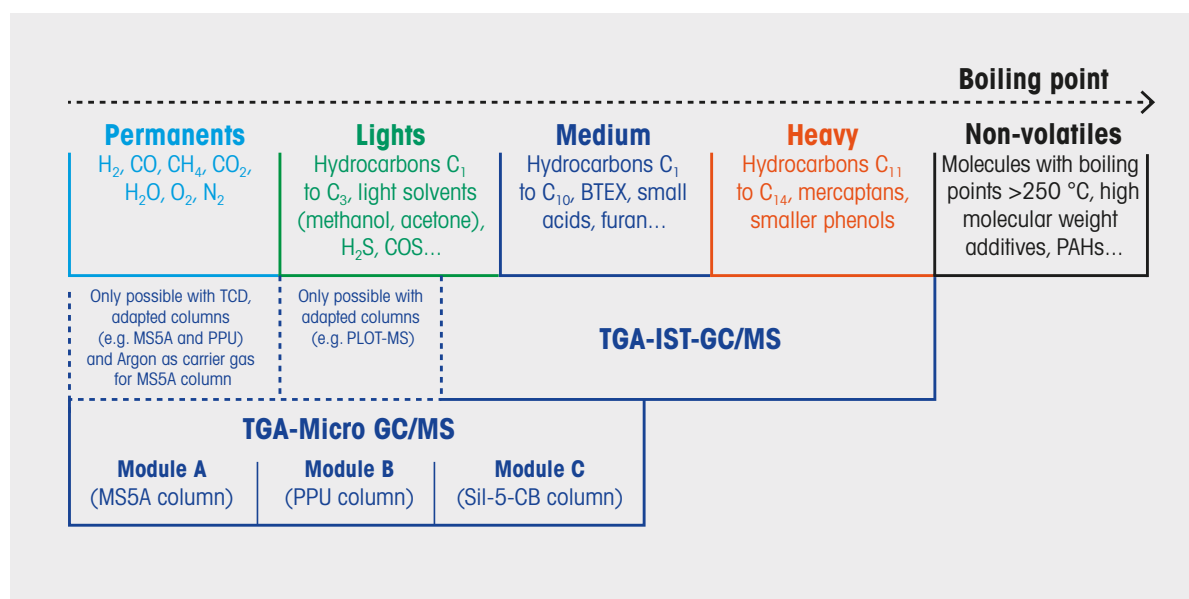


Figure 74. Application range of TGA-Micro GC/MS and TGA-IST-GC/MS.

spectrum with reference spectra in a database indicated that the measured MS spectrum was that of styrene. This allows us to conclude that SBR is present in the unknown elastomer. In a similar way, decomposition products were detected that are typical for natural rubber, NR, (limonene, toluene,

xylene, see Figure 72). The unknown elastomer therefore appears to be a mixture of NR and SBR.

The composition of elastomers can be estimated from the TGA curve, namely about 30% NR, 30% SBR and 40% carbon black (filler). It would not have

been possible to identify the two elastomer components by MS alone, and only with considerable difficulty by FTIR.

10.6 TGA-Micro GC/MS

In contrast to conventional GC, a gas sample can be analyzed in a Micro GC within a few minutes. Micro GC is therefore an online method, like MS or FTIR, except that the temperature resolution is not so good as with MS and FTIR: an analysis time of 3 minutes and a heating rate of 10 K/min results in a temperature resolution of 30 K.

The METTLER TOLEDO Micro GC is modular and can be equipped with up to 3 modules. Each of these modules is a Micro GC that has its own column. This enables different "groups" of gases be identified depending on the number of columns used. A Micro GC is of course ideal for the detection of small molecules (e.g. CO, CO₂, H₂O, NO_x, hydrocarbons up to C₁₀) which cannot be detected or only detected with difficulty using a conventional GC (e.g. H₂O, H₂).

Figure 75. TGA curve and its first derivative (DTG curve) of lignite (brown coal). The measurement was performed at 10 K/min in nitrogen.

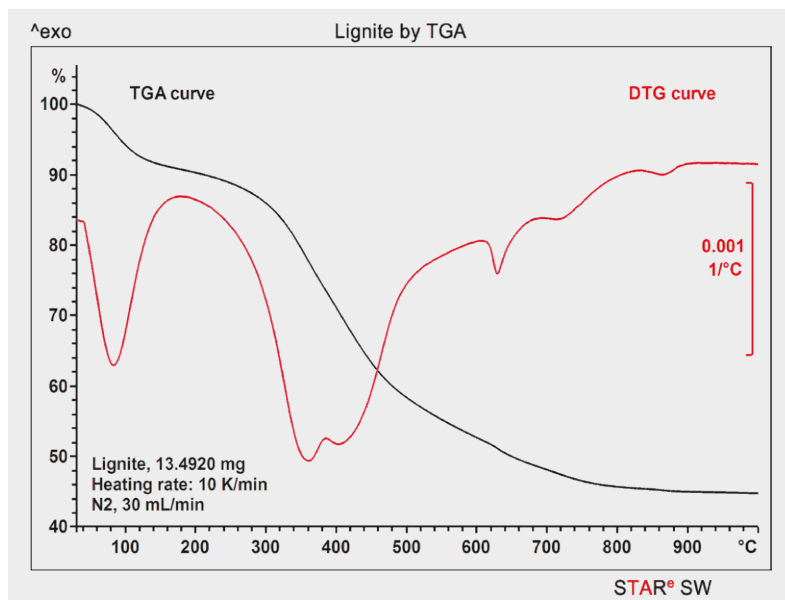


Figure 76. TGA curve and temperature profiles of different decomposition gases measured using a Micro GC equipped with a TCD detector. The profiles are normalized and do not represent the actual composition of the pyrolysis gases.

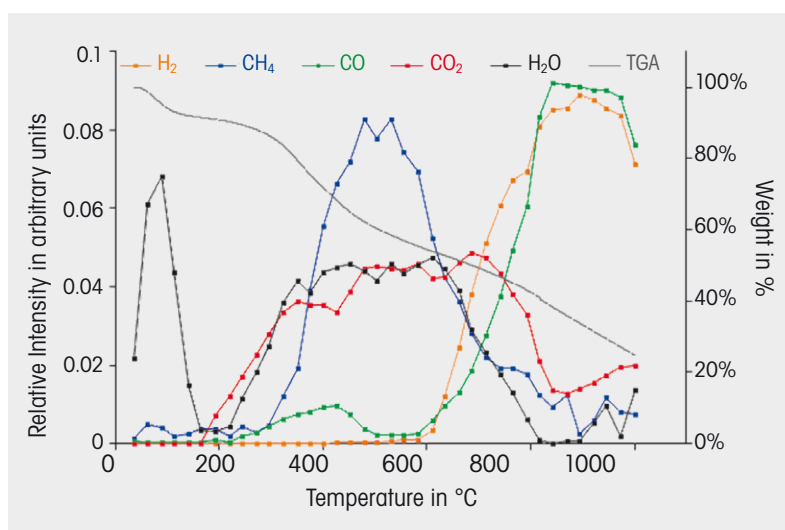
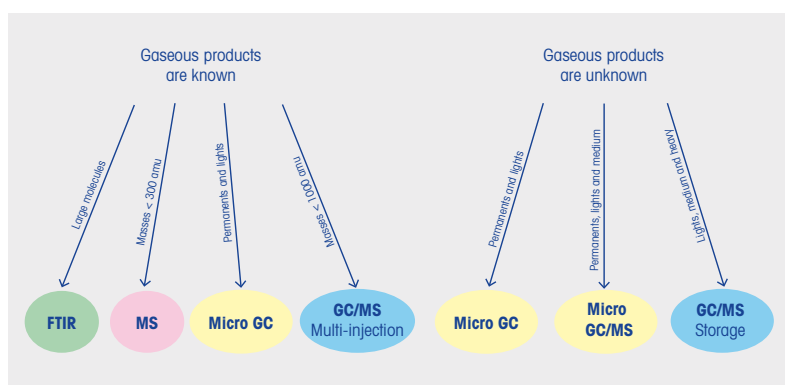


Figure 74 illustrates the application range of TGA-Micro GC/MS and TGA-GC/MS. If a column for C₄ to C₁₀ hydrocarbons is used in the Micro GC, the identification of the particular compound based on its retention time is difficult. MS detection is recommended for such columns instead of the TCD (thermal conductivity detector) normally used in the Micro GC. For more information on micro GC, see reference [1] or go to the link found in "For more information", both at the end of this chapter.

Figure 77. Recommendations for choosing an EGA technique.



Example

As an example, Figure 75 shows the TGA and DTG curves of a sample of brown coal (lignite). The measurement was performed at a heating rate of 10 K/min in nitrogen. Mainly CO₂, H₂O, H₂, CH₄ and CO are expected as pyrolysis gases. The Micro GC is ideal for the detection of these gases.

Figure 76 shows the emission profiles of the main decomposition gases

Table 5.
Comparison of MS,
FTIR, GC/MS and
Micro GC(/MS).

Technique	Advantages	Limitations	Typical applications
MS Pfeiffer Vacuum Thermostar GSD 320 T	<ul style="list-style-type: none"> - Online technique, typical resolution¹ 2 °C - High dynamic sensitivity (>5 decades) - Quantitative evaluation is possible 	<ul style="list-style-type: none"> - Maximum mass 300 amu - Interpretation of the data requires previous information about the sample - Gas inlet can become blocked by large molecules (condensation) - Data format is not compatible with other data bases 	<ul style="list-style-type: none"> - Detection of small molecules (CO_x, NO_x, SO_x, H₂O, HCl, etc.) - Residual solvents in active pharmaceutical ingredients
FTIR Thermo Scientific Thermo Nicolet iS10/50	<ul style="list-style-type: none"> - Online Technique, typical temperature resolution² 2 °C - Can also be used for the analysis of solids but needs an ATR accessory, (only iS50) - It also provides information about the structure of the detected gases 	<ul style="list-style-type: none"> - Dynamic sensitivity is about 3 decades (DTGS detector) - Quantitative evaluation is difficult - Interpretation of the IR data requires experience and previous information about the sample - Less sensitive than MS and GC/MS 	<ul style="list-style-type: none"> - Detection of simple and complex compounds - Residual solvents in active pharmaceutical ingredients
GC/MS SRA IST16 Agilent 7590 GC Agilent 5975 MS	<ul style="list-style-type: none"> - Gas mixtures can be easily analyzed (separation by GC, identification by MS) - Quantitative evaluations are possible (chromatogram) - GC/MS can also be used as a "stand alone" system for the analysis of liquids 	<ul style="list-style-type: none"> - Storage mode: up to a maximum of 16 gas samples can be stored during a TGA experiment; GC/MS measurements need much time - Online operation: poor separation power of the GC column - Maximum mass 1050 amu 	<ul style="list-style-type: none"> - Volatile molecules up to about 250 amu
GC and Micro GC/MS	<ul style="list-style-type: none"> - Quasi online-technique, typical temperature resolution 30 °C³; - Up to 2 different columns can be used simultaneously for different groups of gases - Quantitative analyses are possible (concentrations) - Can be used in combination with MS 	<ul style="list-style-type: none"> - Columns are only sensitive for a limited number of gases - Acidic gases cannot be detected (e.g. HCl, SO_x, HF). 	<ul style="list-style-type: none"> - Detection of small molecules ("permanents") possible without MS - Detection of light and medium weight compounds by Micro GC/MS

¹ Single ion (MID) scan with 20 masses, integration time 0.5 s, heating rate 10 K/min.

² Resolution 4 cm⁻¹, averaging over 8 spectra, heating rate 10 K/min.

³ Heating rate 10 K/min, analysis time of Micro GC 3 min.

expected as a function of temperature. For better visualization, the profiles were normalized to their total intensity (area under the emission profile). This representation does not therefore indicate the actual concentrations of the different decomposition gases.

Up until about 180 °C, mainly moisture is evolved. Between 200 °C and 600 °C, methane and CO are also released besides water and CO₂. From about 600 °C onward, the actual gasification of carbon occurs whereby mainly CO and hydrogen (synthesis gas) are produced.

10.7 Conclusions and recommendations

TGA-MS, TGA-FTIR, TGA-GC/MS and TGA-Micro GC(/MS) are powerful techniques that yield both quantitative (mass loss) and qualitative (identification) information about the gaseous products released during a TGA measurement. Table 5 presents a comparison of the four methods.

Not all techniques are equally suitable for dealing with specific questions. The overview in Figure 77 shows which technique is best for solving a particular application problem.

The GC/MS multi-injection mode is a special operating mode of the GC in which the separation power of the GC is greatly reduced. The advantage of this operating mode is that GC/MS can be performed online like MS or FTIR.

10.8 References

- [1] N. Fedelich, METTLER TOLEDO Collected Applications Handbook: Evolved Gas Analysis, Second Edition.

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