Thermal Analysis

Application
Handbook

Thermal Analysis of Polymers

Selected Applications

METTLER TOLEDO

Thermal Analysis of Polymers

This application handbook presents selected application examples. The experiments were conducted with the utmost care using the instruments specified in the description 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.
When chemicals, solvents and gases are used, general safety rules and the instructions given by the manufacturer or supplier must be observed.

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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 three different types of plastic materials, namely a thermoplastic (PET), a thermoset (KU600), and an elastomer (W001).

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.

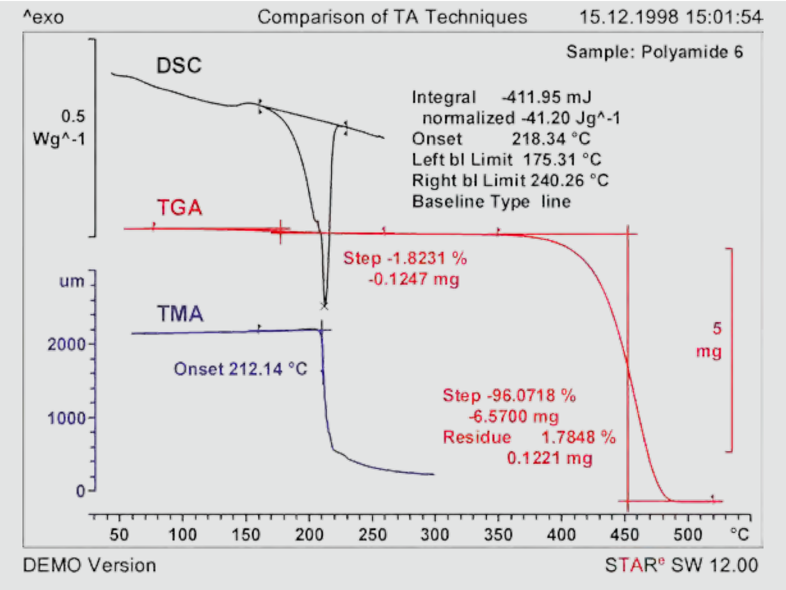


Figure 1.
The techniques used to measure polyamide 6 show different thermal effects. DSC: melting peak of the crystalline part; TGA: drying and decomposition step; TMA: softening under load.

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 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 Tg, 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.

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

1.8 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.

1.9 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 funtion 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.

1.10 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.

1.11 TCL

Thermochemiluminescence

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

1.12 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**^{e} 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].

Figure 2.
Structural formula of PET.

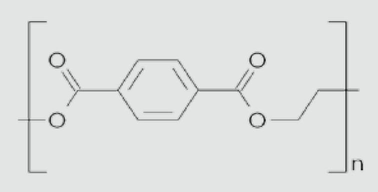
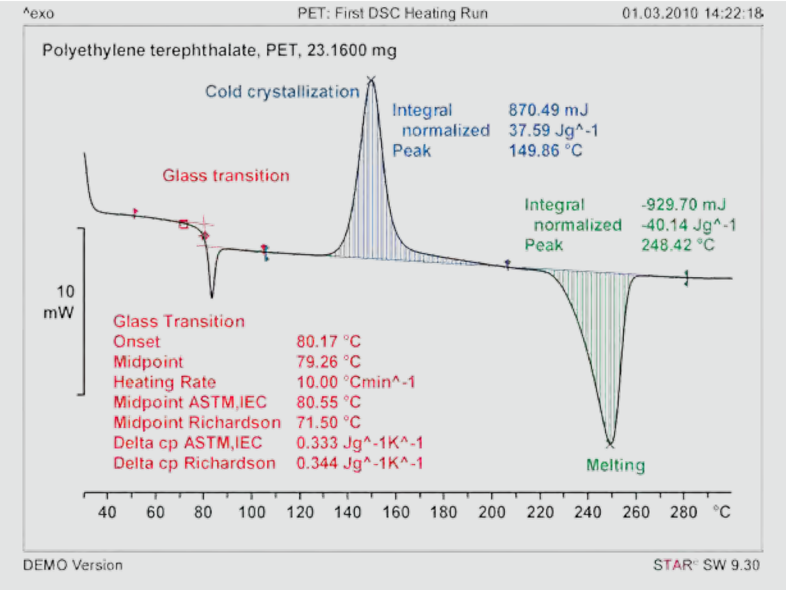


Figure 3.
The main effects measured by DSC using PET as a sample. Temperature range 30–300 °C; heating rate 20 K/min; purge gas nitrogen at 50 mL/min.



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 theses are evaluated directly by the **STAR**^{e} 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 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 ~ 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 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 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

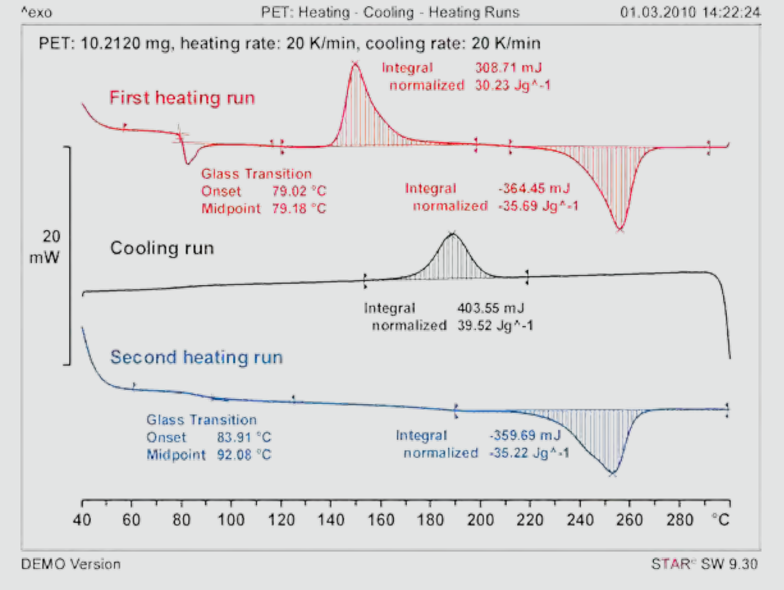


Figure 4.
First and second heating runs and the cooling curve demonstrate differences regarding relaxation at the glass transition and the disappearance of cold crystallization.

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 crystallize 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.

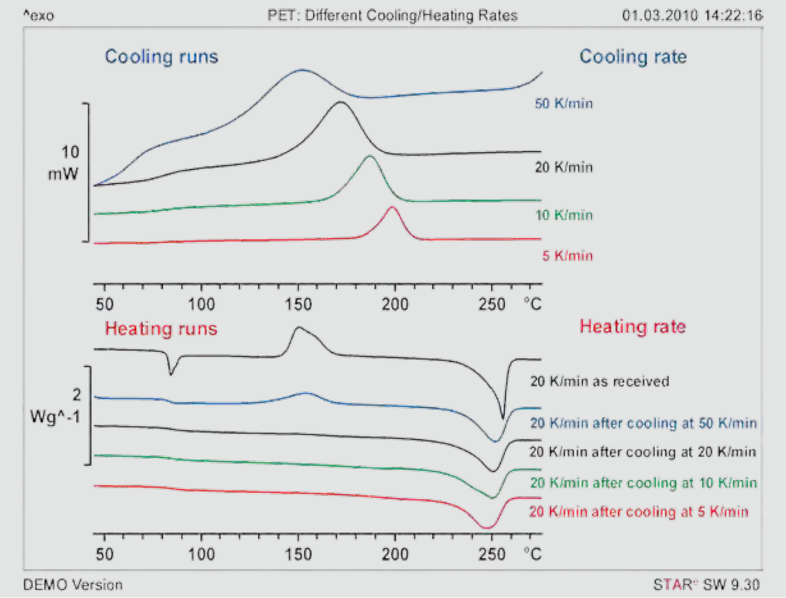


Figure 5.
DSC measurements of the same sample performed at different cooling rates. At low cooling rates, cold crystallization cannot be detected on heating because sufficient time was available for crystallization to occur during cooling.

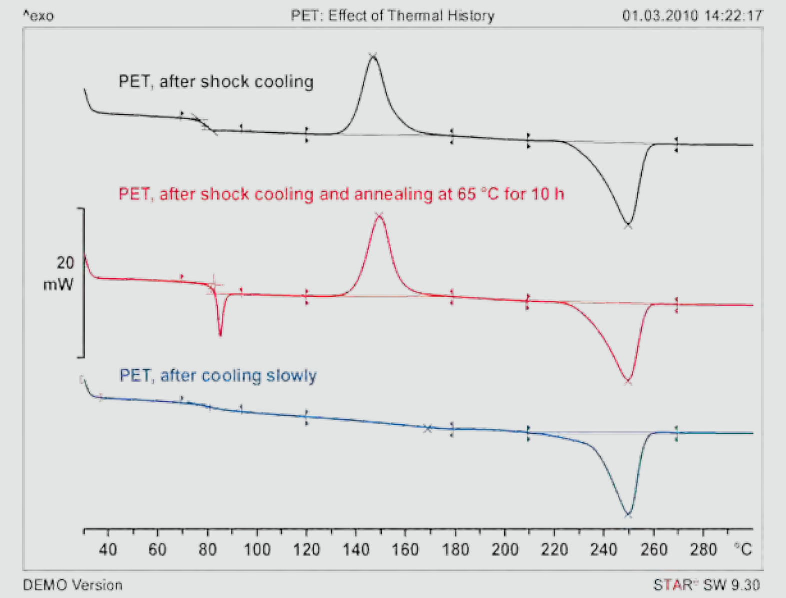


Figure 6.
Heating curves of a PET sample after cooling under different conditions.

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 pronounced 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 **TOP**EM® 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 **TOP**EM® experiment was performed in a 40-µL 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 **TOP**EM® 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 heat capacity or phase can be determined at user-defined frequencies. In Figure 9, this is done at a frequency of 16.7 Hz. **TOP**EM® [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 **TOP**EM® 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

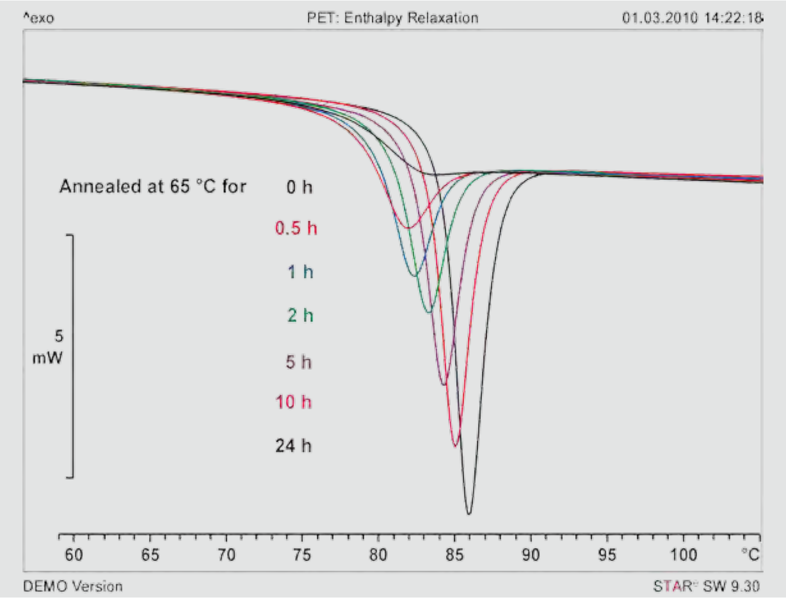


Figure 7.
Heating runs showing the influence of different annealing times on the glass transition and the enthalpy relaxation peak of PET.

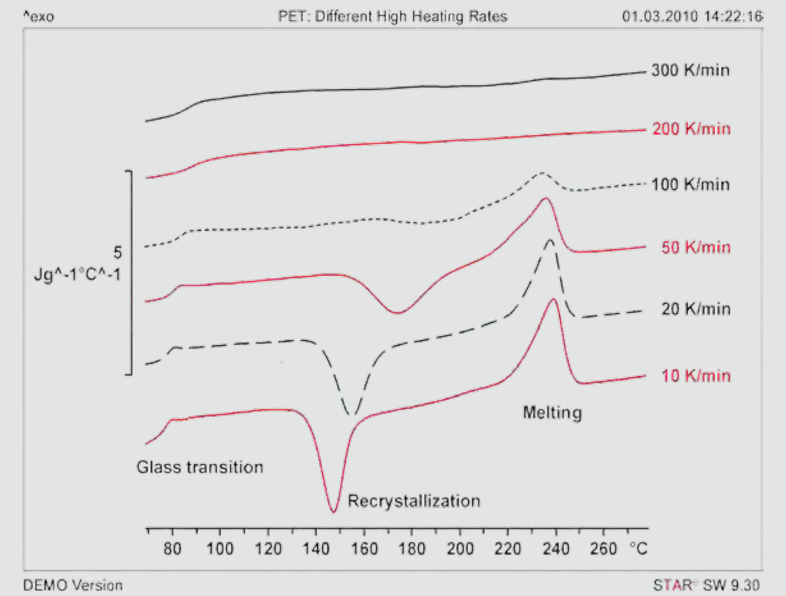


Figure 8.
DSC measurements of PET at high heating rates, shown as c_p curves.

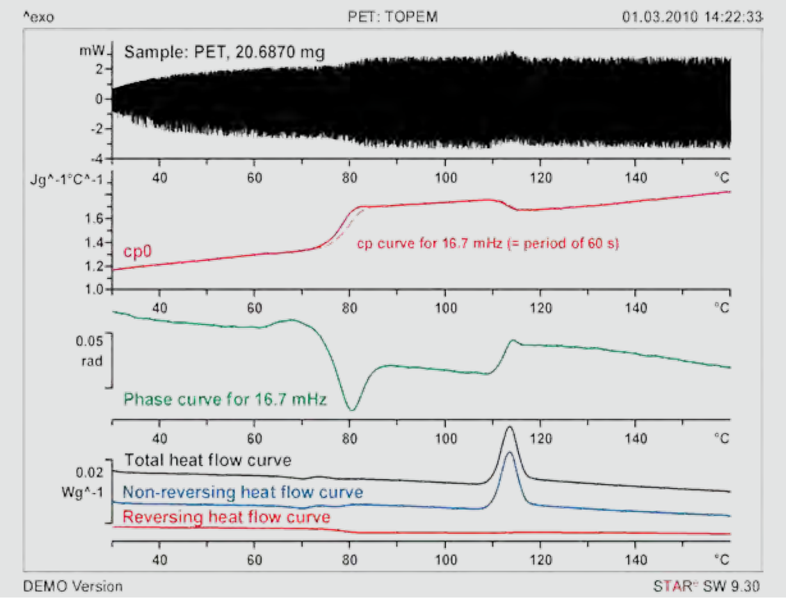


Figure 9.
Measurement of a PET sample using **TOP**EM® showing the reversing, non-reversing and total heat flow curves.

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.

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-µL 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.

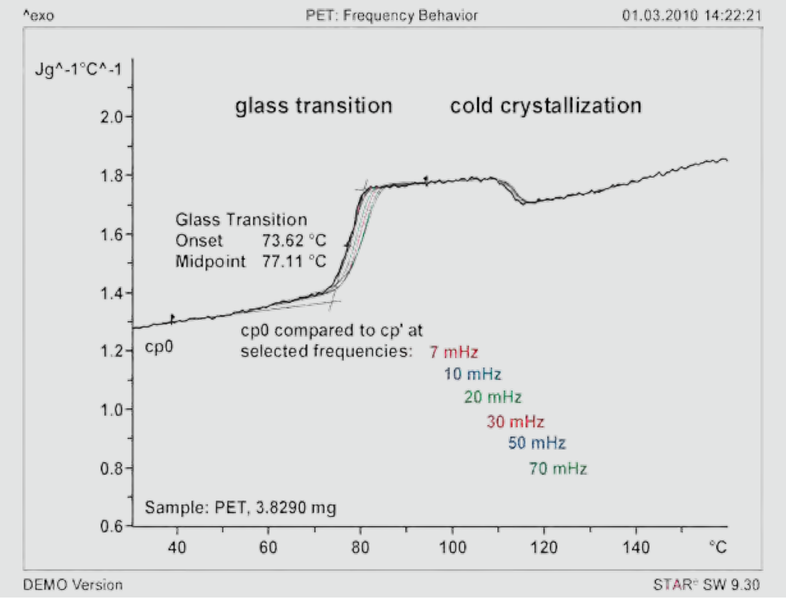


Figure 10.
Measurement of a PET sample using **TOP**EM® showing the frequency dependence of the glass transition.

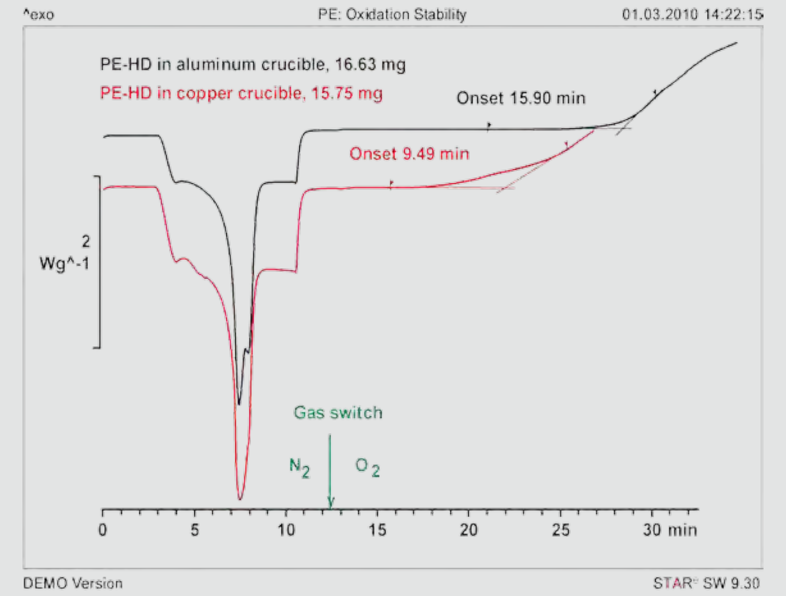


Figure 11.
OIT measurements of PE in different crucibles.

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

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 [2, 3].

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 atmosphere. A typical TMA curve shows expansion below the glass transition temperature, the glass transition (seen as a change in the slope of the curve),

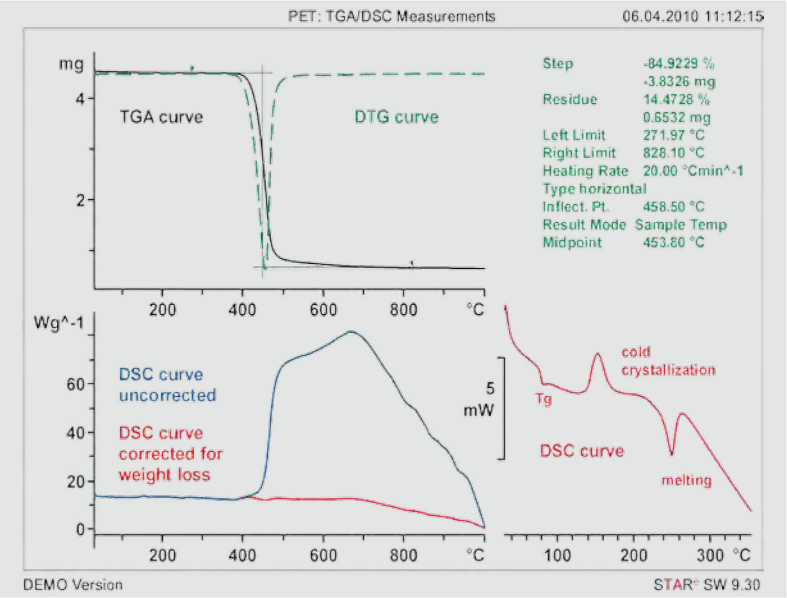


Figure 12. Measurement curves of PET recorded from 30 to 1000 °C at a heating rate of 20 K/min using a TGA/DSC 1 equipped with a DSC sensor. The TGA curve shows the change in mass of the sample and the DSC curve the endothermic or exothermic effects.

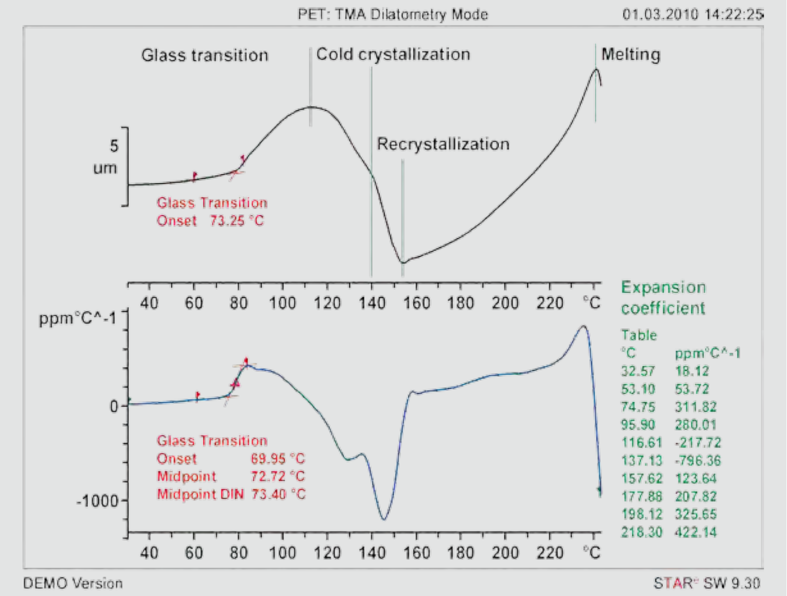


Figure 13. TMA measurement of PET in the dilatometry mode.

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.

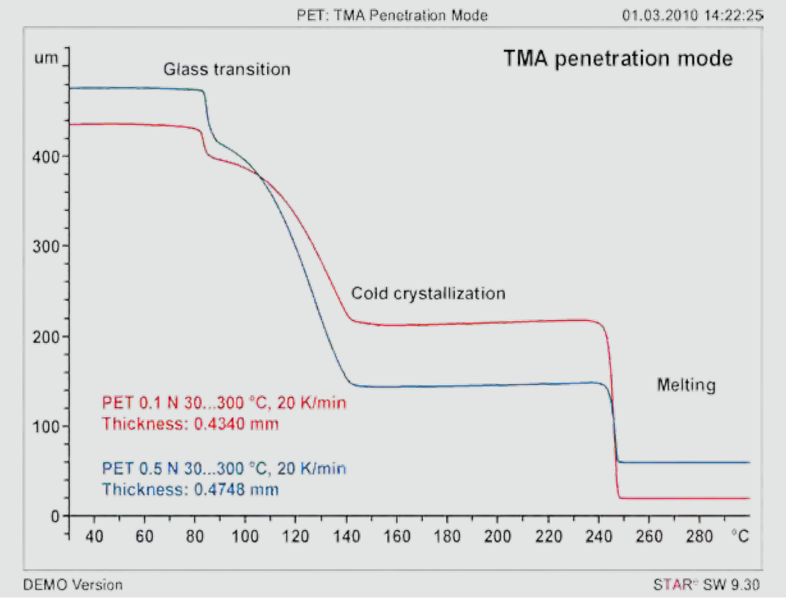


Figure 14.
TMA of PET measured in the penetration mode.

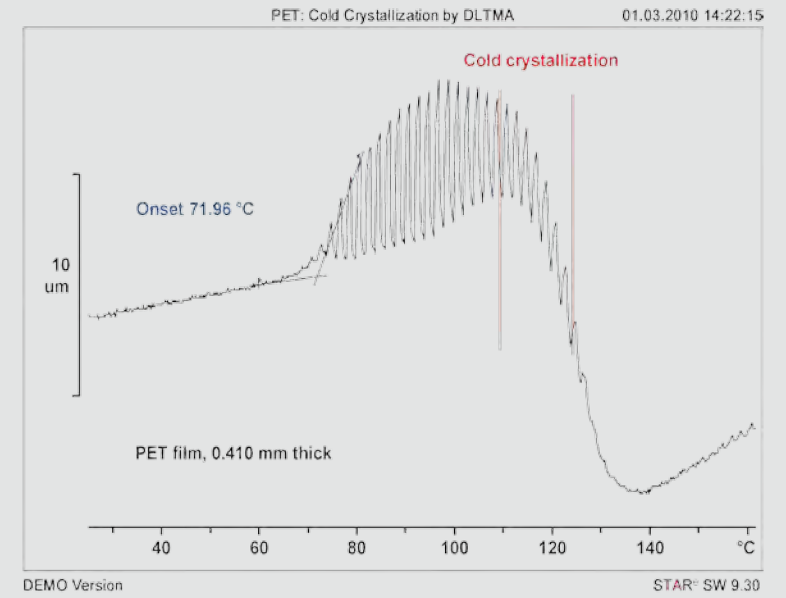


Figure 15.
DLTMA measurement of PET from room temperature to 160 °C.

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) [4], 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 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 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.

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.

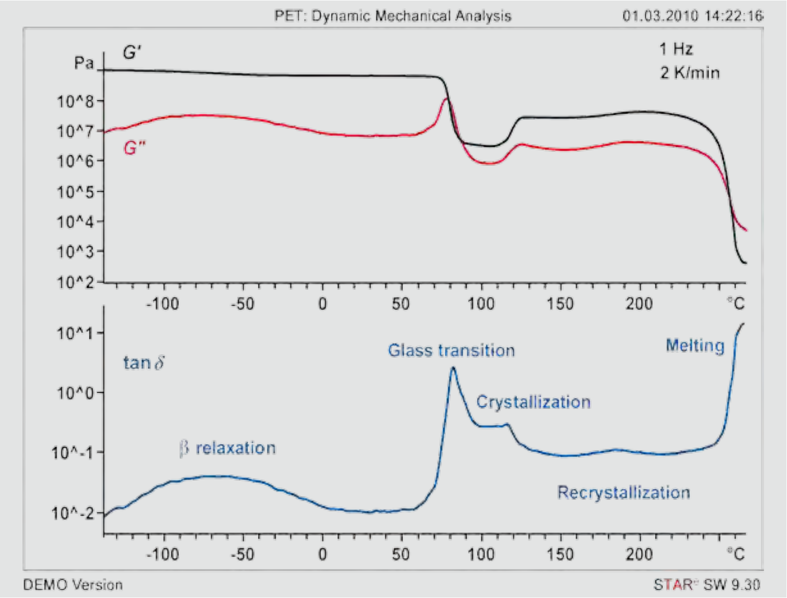


Figure 16.
DMA shear measurement of PET in the range –150 °C to +270 °C.

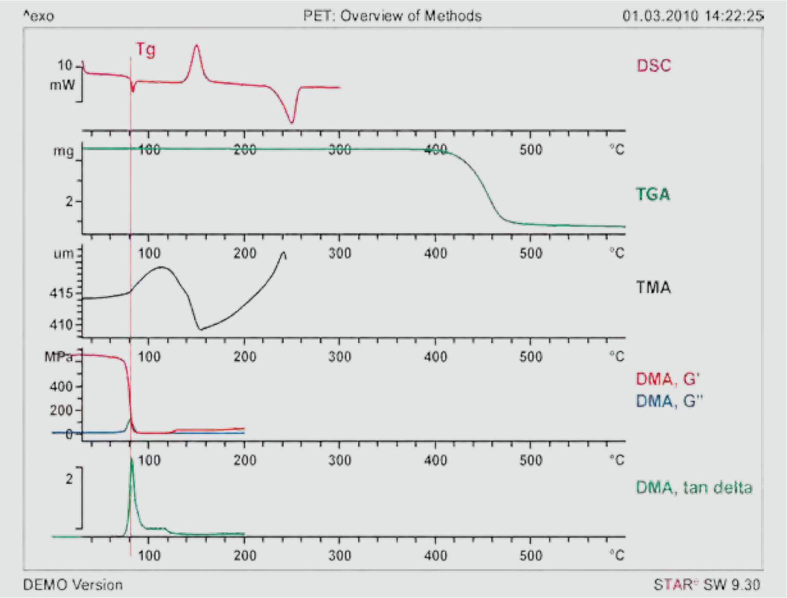


Figure 17.
Overview of the effects and comparison of the results.

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

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 2.
Effects measured by different analytical methods.

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

[1] A. Hammer, Thermal analysis of polymers. Part 1: DSC of thermoplastics, UserCom 31, 1–6.

[2] R. Riesen, Heat capacity determination at high temperatures by TGA/DSC. Part 1: DSC standard procedures, UserCom 27, 1–4.

[3] R. Riesen, Heat capacity determination at high temperatures by TGA/DSC. Part 2: Applications, UserCom 28, 1–4.

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

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		

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 techniques 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^e, and DMA/SDTA861^e. The results were evaluated using the **STAR**^{e} 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 [3].

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.

The first heating run eliminates the thermal history of the sample. The second heating run shows the glass transition

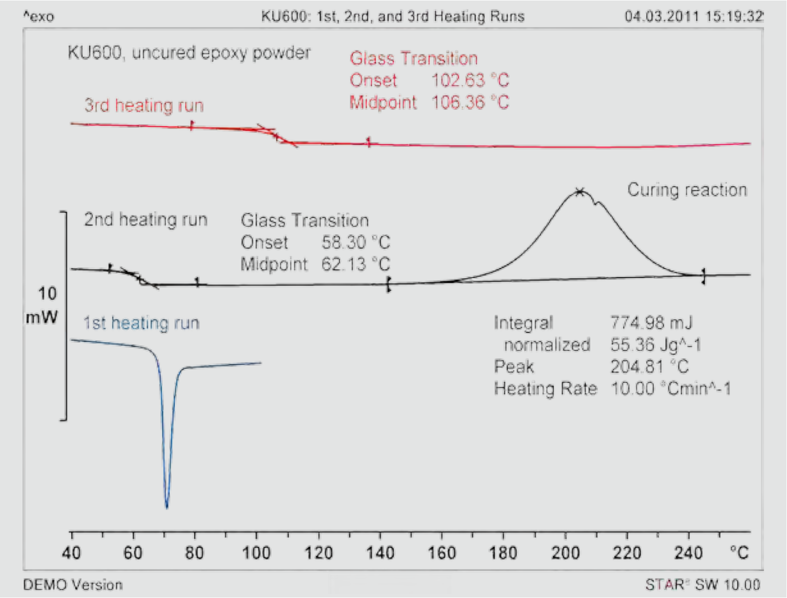


Figure 18.
KU600: DSC experiment at a heating rate of 10 K/min showing the first, second and third heating runs.

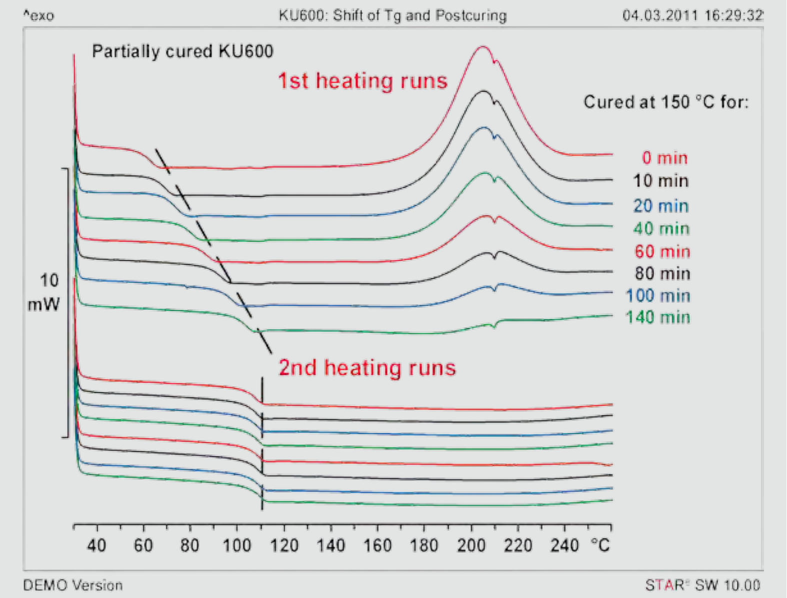


Figure 19.
KU600: The first and second DSC heating runs measured at a heating rate of 10 K/min after curing isothermally at 150 °C for different times.

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 cross-linked 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 postcuring at all [4].

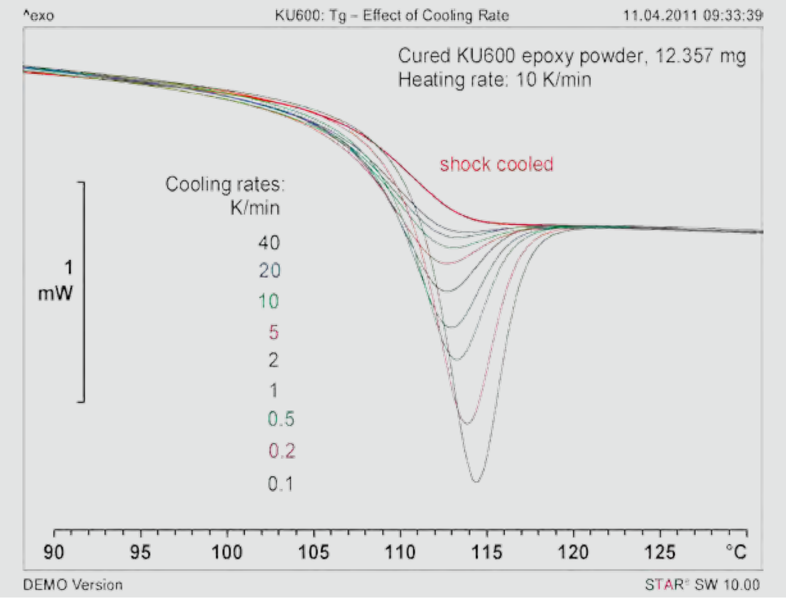


Figure 20.
KU600: DSC experiment showing the effect of different cooling rates on the glass transition.

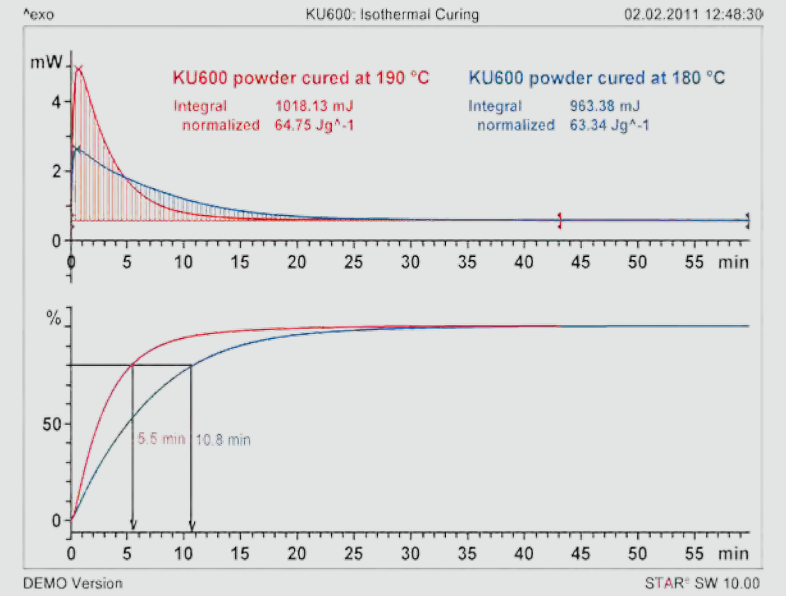


Figure 21.
KU600: Isothermally cured at 180 and 190 °C.
Above: the DSC curves. Below: the calculated conversion curves.

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 preheated 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 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) [5, 6].

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.

Determination of c_p

This section describes a method known as the sapphire method that is used to determine the specific heat capacity [4]. 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. 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 **TOP**EM®or ADSC techniques. ADSC will be described in the following section.

ADSC: Separation of overlapping effects

ADSC [7], like IsoStep® and **TOP**EM®, is a temperature-modulated DSC technique that allows overlapping effects such as

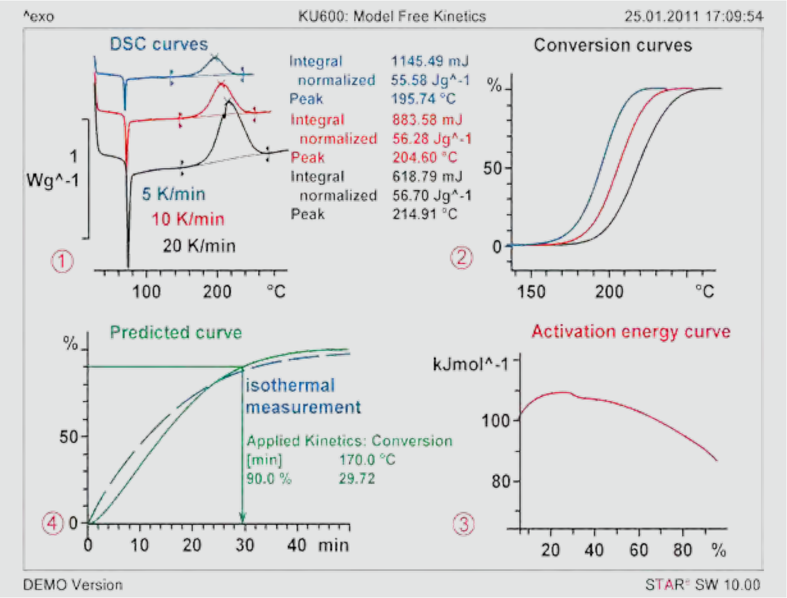


Figure 22. Model free kinetics using the curing of KU600 as an example.

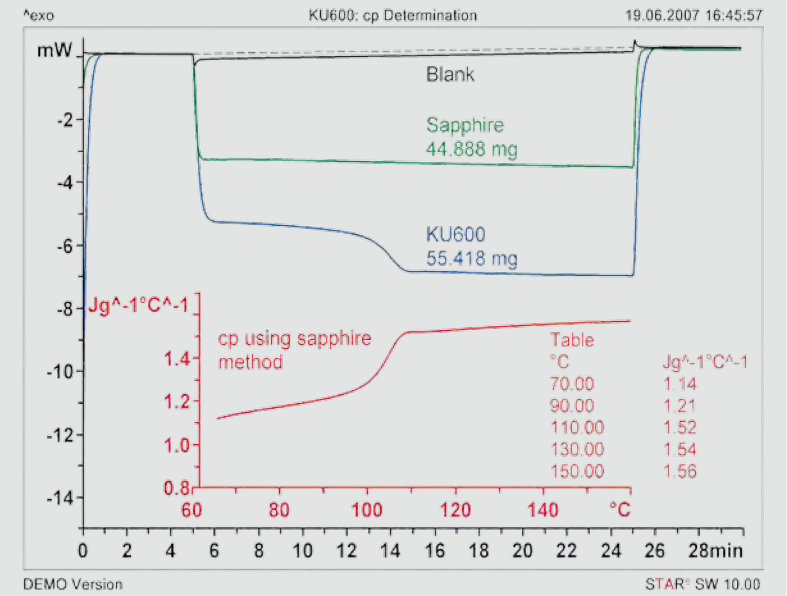


Figure 23. Determination of the specific heat capacity, c_p, of KU600.

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 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.

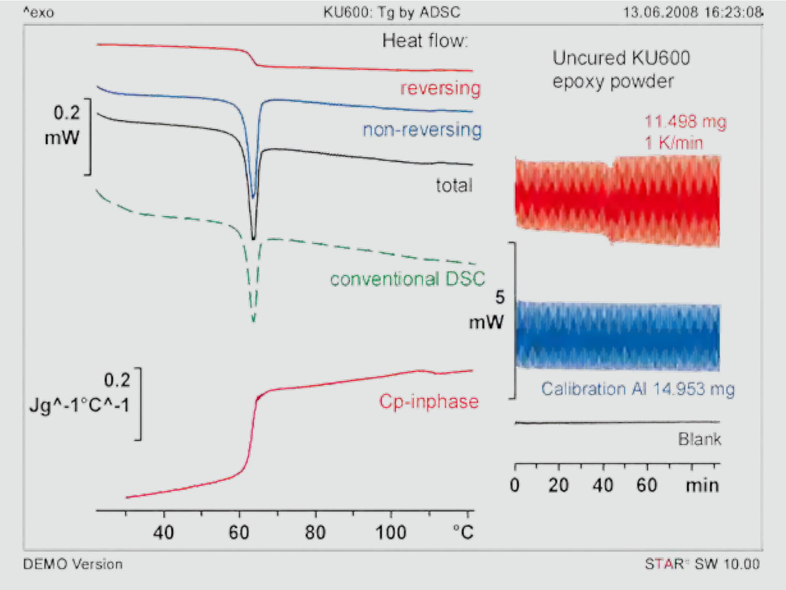


Figure 24.
ADSC measurement of KU600.

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] A. Hammer, Thermal analysis of polymers. Part 1: DSC of thermoplastics, UserCom 31, 1–6.
[2] A. Hammer, Thermal analysis of polymers. Part 2: TGA, TMA and DMA of thermoplastics, UserCom 31, 1–5.
[3] Interpreting DSC curves. Part 1: Dynamic measurements, UserCom 11, 1–6.
[4] METTLER TOLEDO Collected Applications Handbook: Thermosets, Volume 1.
[5] Model free kinetics, UserCom 2, 7.
[6] Ni Jing, Model free kinetics, UserCom 21, 6–8.
[7] ADSC in the glass transition region, UserCom 6, 22–23.

5. TGA, TMA and DMA Analysis of Thermosets

5.1 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.

5.2 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 defined atmosphere. It is mainly used for the quantitative and compositional analysis of products [2].

Figure 25 (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-µL 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.

5.3 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

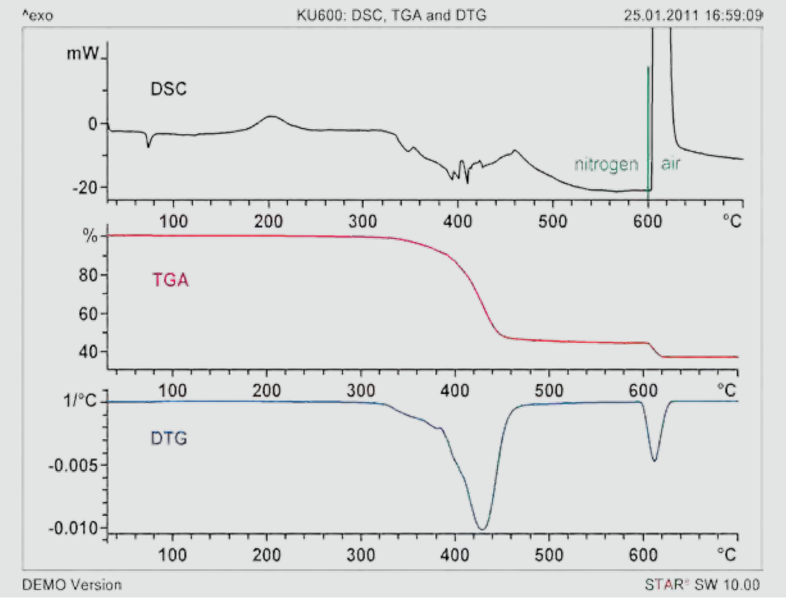


Figure 25. TGA/DSC 1 curves of KU600 epoxy powder measured from 30 to 700 °C at a heating rate of 20 K/min. The TGA curve (red) measures the loss of mass and the DSC curve (black) provides information about endothermic and exothermic effects.

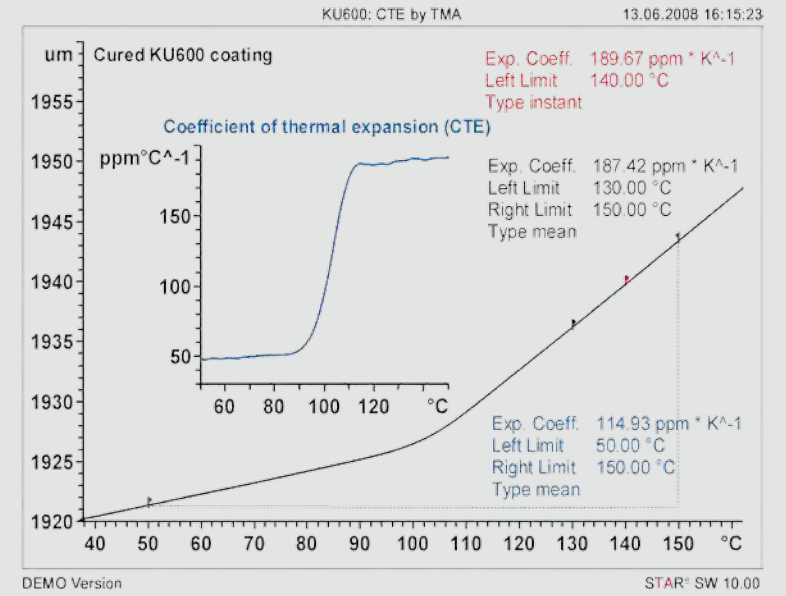


Figure 26. Determination of the coefficient of thermal expansion (CTE) of cured KU600 using the second heating run.

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 26 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.

Figure 27.
DLTMA measurement of a cured KU600 coating.

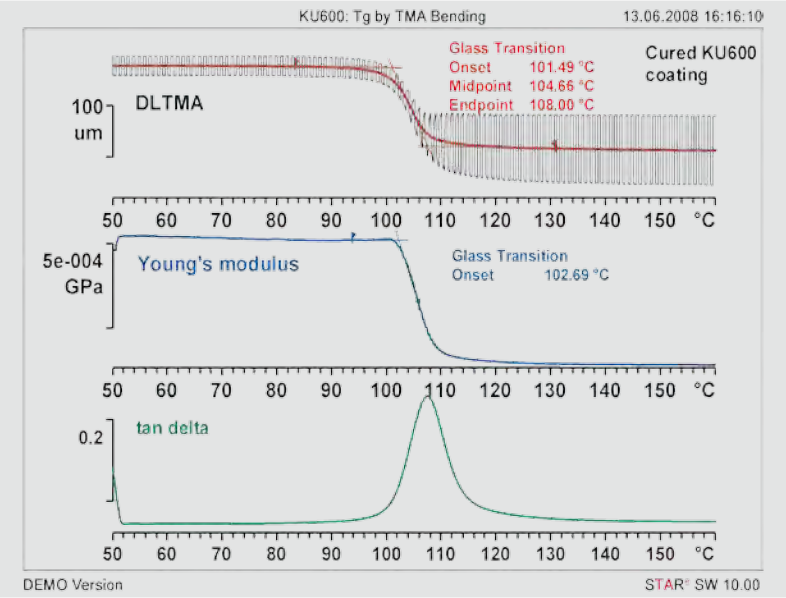
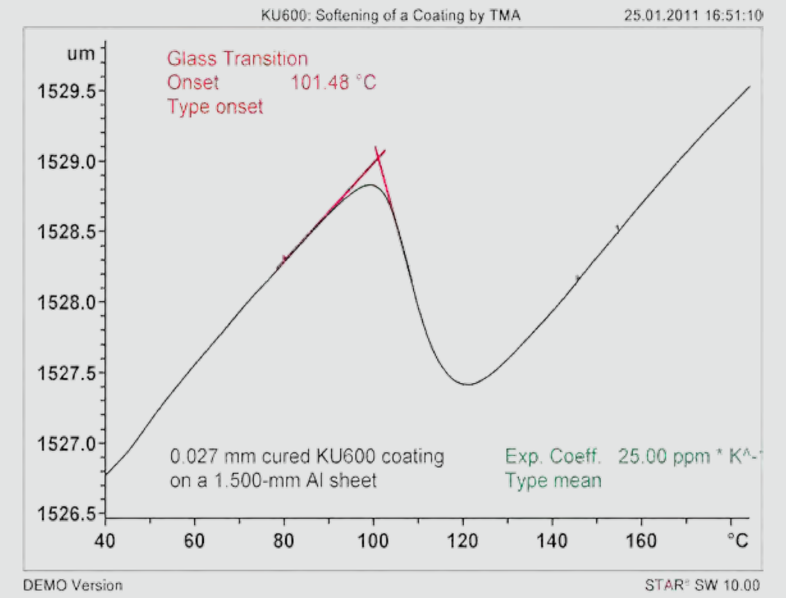


Figure 28.
TMA measurement of a thin coating of cured KU600 to determine the softening temperature.



DLTMA for the determination of T_g and Young's modulus

DLTMA (Dynamic Load TMA), [3] 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 27.

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

Figure 28 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.

5.4 Dynamic mechanical analysis (DMA)

As described in reference [4], 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 [5, 6].

Determination of the glass transition

Figure 29 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 µm.

Figure 29 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.

Frequency dependence of the glass transition

Figure 30 shows a DMA experiment in which different frequencies were simultaneously applied. The sample preparation was the same as for the measurements in Figure 29. The cured sample was measured from 70 to 180 °C using a maximum force amplitude of 5 N and a maximum displacement amplitude of

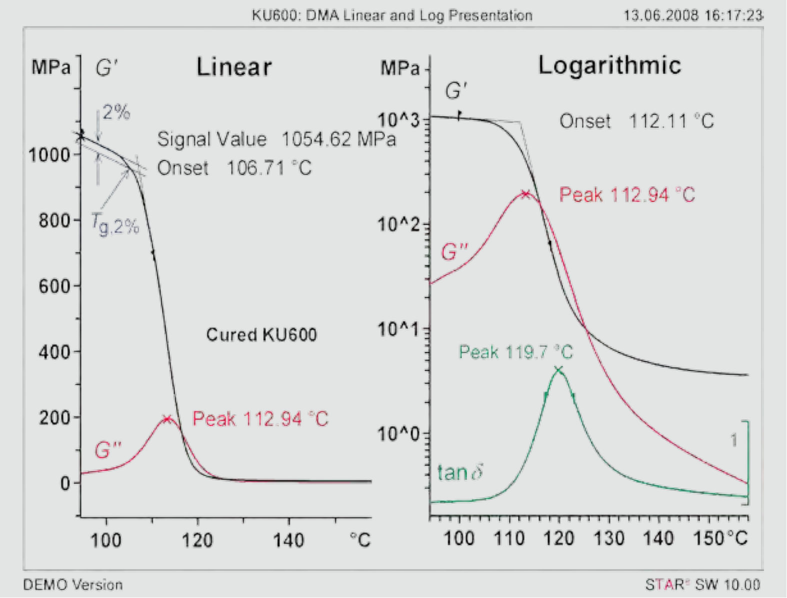


Figure 29.
DMA measurement of KU600 from 90 to 160 °C, in linear and logarithmic ordinate presentation.

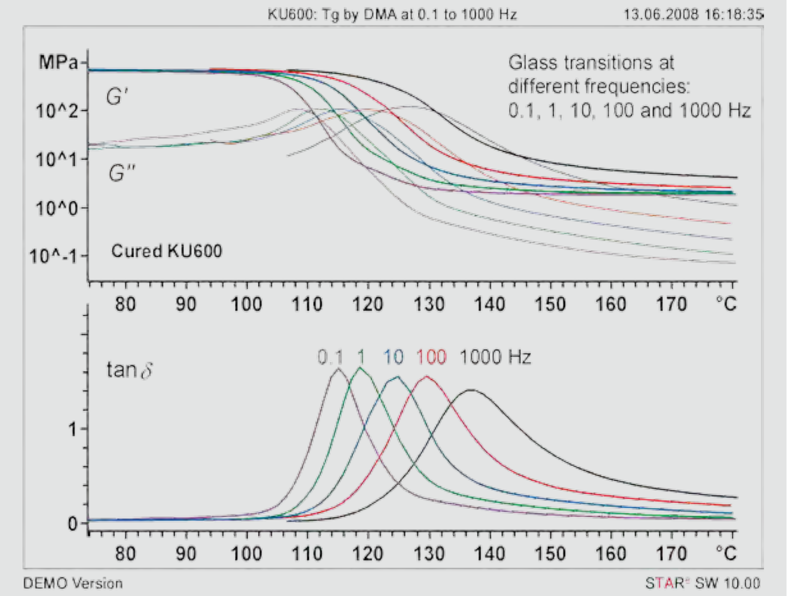


Figure 30.
DMA measurement of KU600 at different frequencies to demonstrate the frequency dependence of the glass transition.

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 [7].

5.5 Overview of effects and comparison of results

Figure 31 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).

5.6 Conclusions

This chapter and the previous chapter [1] discussed the different possibilities available for characterizing a thermoset (KU600) using DSC, TGA, TMA, and DMA techniques. The various methods yield consistent results.

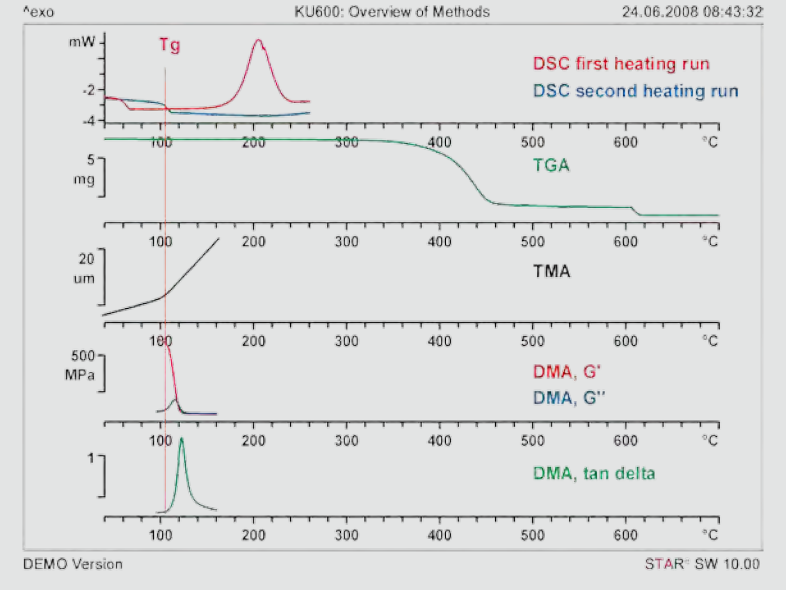


Figure 31. Overview of the effects and comparison of results.

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 complementary 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.

5.7 References

[1] A. Hammer, Thermal analysis of polymers, Part 3: DSC of thermosets, UserCom 33, 1–5.
[2] Elastomer Analysis in the TGA 850, UserCom 3, 7–8.
[3] PET, Physical curing by dynamic load TMA, UserCom 5, 15.
[4] Georg Widmann, Interpreting DMA curves, Part 1, UserCom 15, 1–5.
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[6] Klaus Wrana, Determination of the glass temperature by DMA, UserCom 16, 10–12.
[7] METTLER TOLEDO Collected Applications Handbook: Thermosets, Volume 1.

6. DSC and TGA Analysis of Elastomers

6.1 Introduction

This chapter deals with the thermal analysis of elastomers [5, 6] 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).

6.2 Experimental details

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

6.3 Measurements and results

6.3.1 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 32 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 °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 °C. Linear extrapolation of the heat flow curve from the melt above 70 °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 33 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 °C and –50 °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 °C and –50 °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 °C and the other for SBR at –44.1 °C. This behavior indicates the presence of two separate polymer phases and that the two polymer 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 34 shows the melting behavior of an unvulcanized sample of EPDM

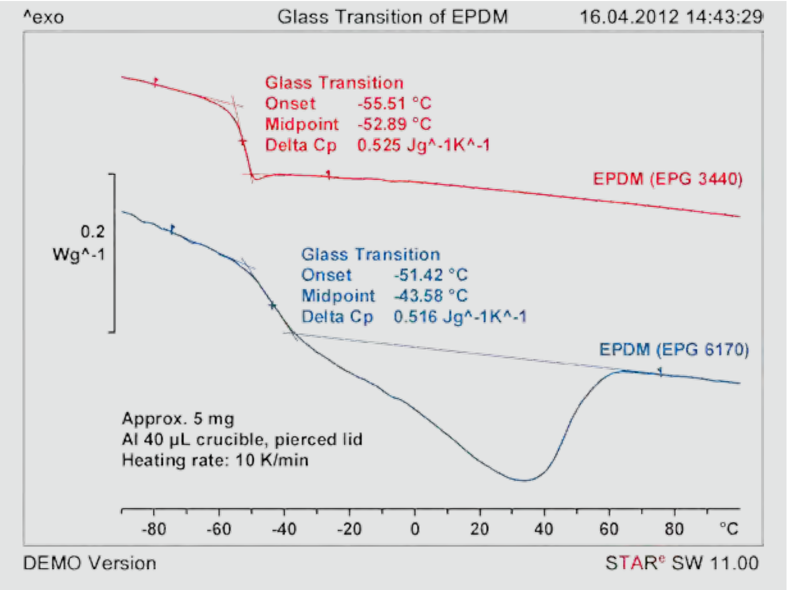

Figure 32. Determination of the glass transition temperature of two samples of unvulcanized EPDM with different ethylene contents.

(EPG 6170). Three heating runs were performed to demonstrate the influence of sample pretreatment on melting.

All three curves show a step at –45 °C due to the glass transition. Melting begins immediately afterward and is completed by about 70 °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 °C. There then follows a narrower peak with a maximum at 43 °C and a smaller peak at 52 °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.

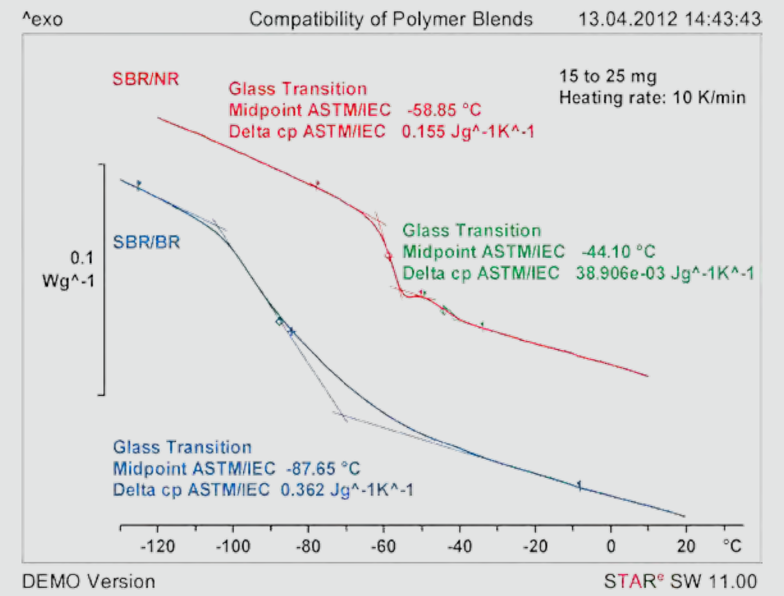

Figure 33.
DSC analysis of the compatibility of two SBR polymer blends.

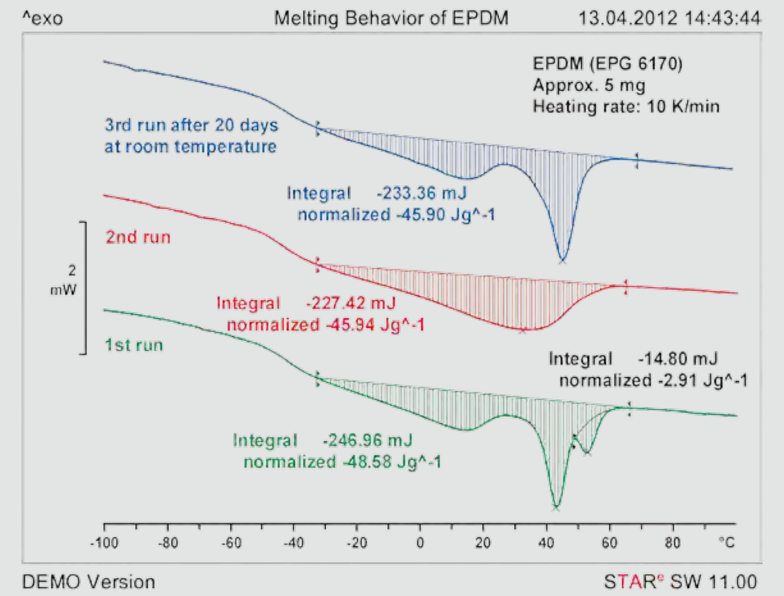

Figure 34.
Influence of pretreatment on the melting of a sample of unvulcanized EPDM.

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, **TOP**EM® 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.

An important practical advantage of this technique is that it allows processes that occur simultaneously to be separated. Figure 35 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.

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.

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 36 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).

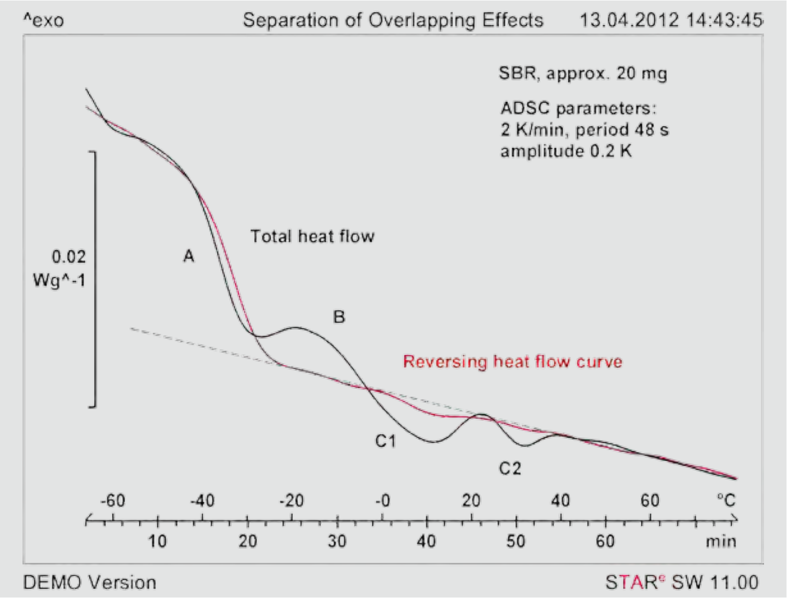

Figure 35.
Separation of overlapping effects of unvulcanized SBR using ADSC.

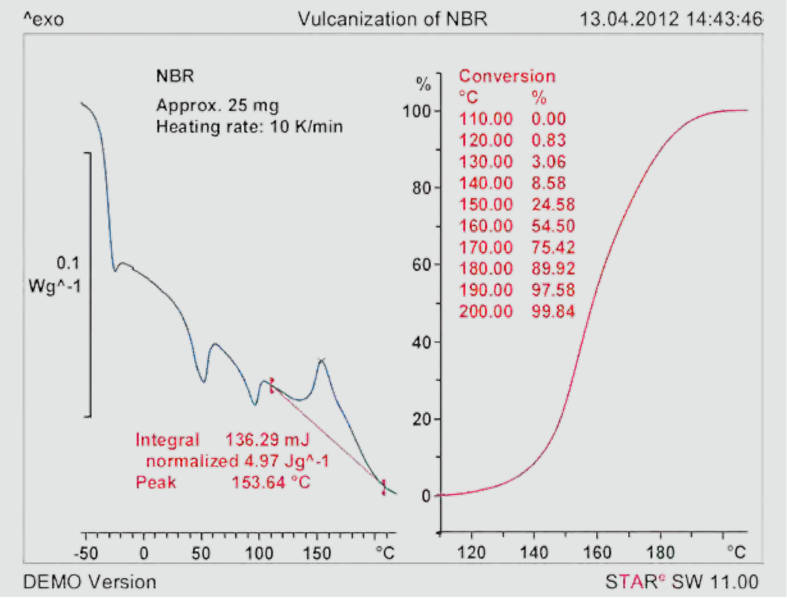

Figure 36.
DSC measurement curve of an unvulcanized sample of NBR.

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 nth 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 37 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 calculated 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.

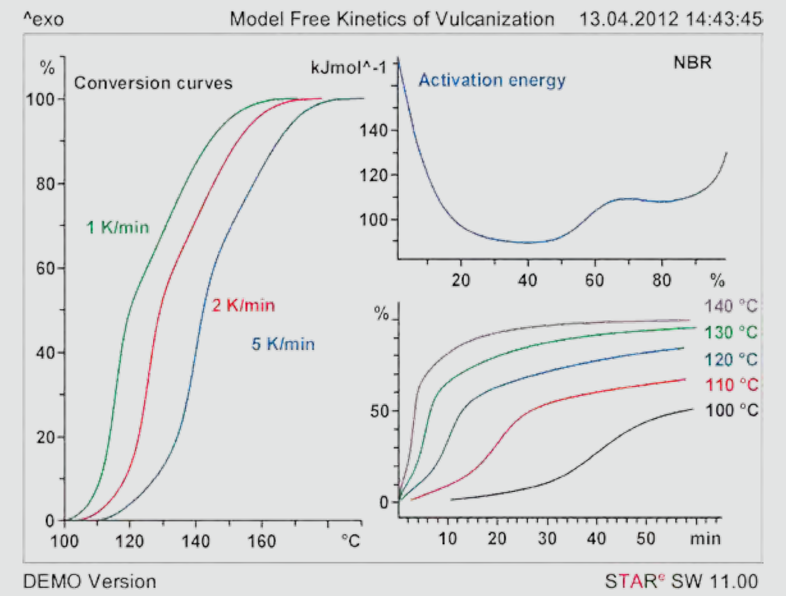

Figure 37.
Model Free Kinetics of the vulcanization of NBR.

6.3.2 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 38 shows a typical 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.

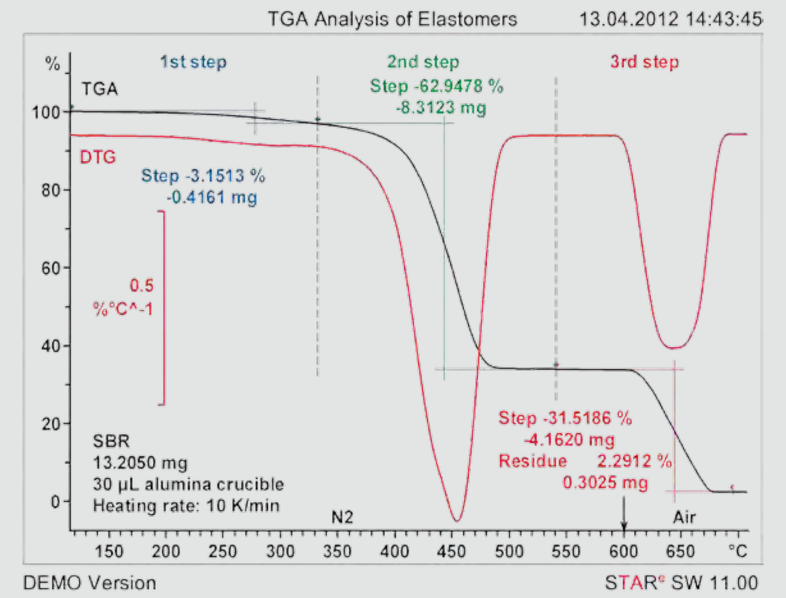

Figure 38.
TGA analysis of an SBR elastomer.

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 39 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.

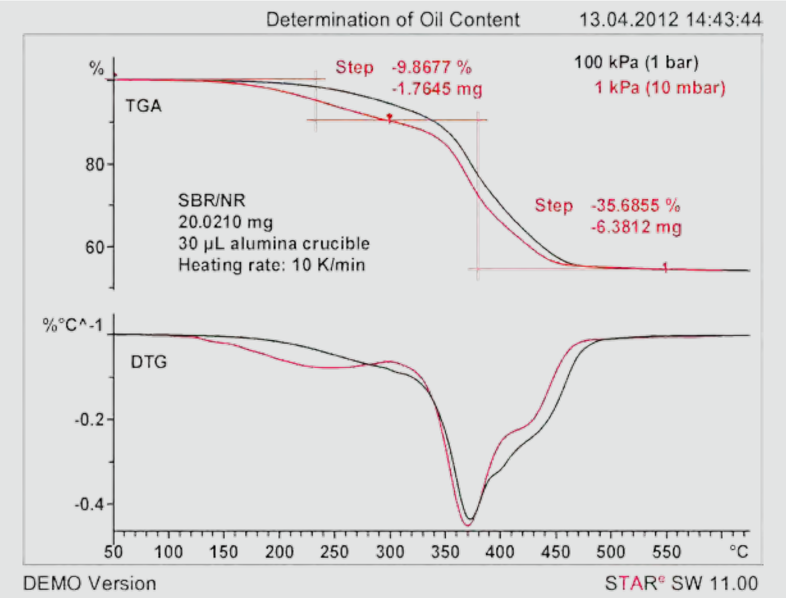

Figure 39. Determination of the oil content of an SBR/NR elastomer using TGA at ambient pressure and reduced pressure.

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 40 shows the TGA analysis of three ethylene-vinyl acetate copolymers (EVA) containing different flame retardants: $Al(OH)_3$; (ATH: aluminum trihydrate); and $Mg(OH)_2$ (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.

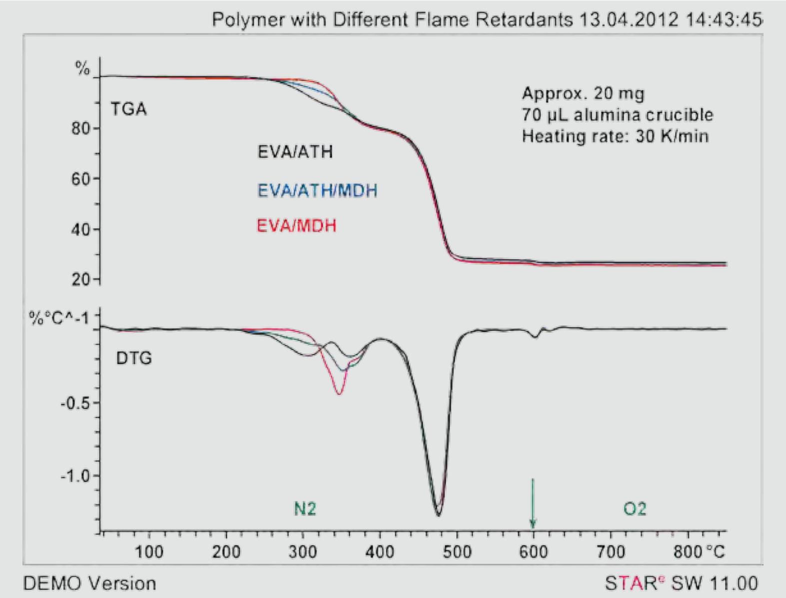

Figure 40. TGA analysis of EVA containing different flame retardants.

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

6.4 References

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[2] A. Hammer, Thermal analysis of polymers. Part 2: TGA, TMA and DMA of thermoplastics, UserCom 32, 1–5.
[3] A. Hammer, Thermal analysis of polymers. Part 3: DSC of thermosets, UserCom 33, 1–5.
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7. TMA and DMA Analysis of Elastomers

7.1 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 [2, 3].

7.2 Measurements and results

7.2.1 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 [4]. 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.

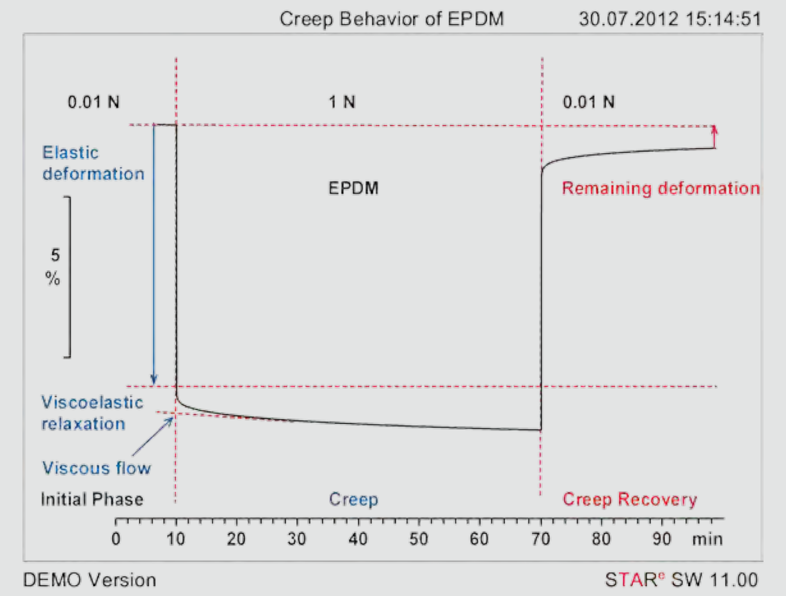

Figure 41.
TMA curves showing the creep and creep recovery behavior of a rectangular EPDM sample (width 3.5 mm, length 3.5 mm, thickness 1.5 mm) measured at 30 °C.

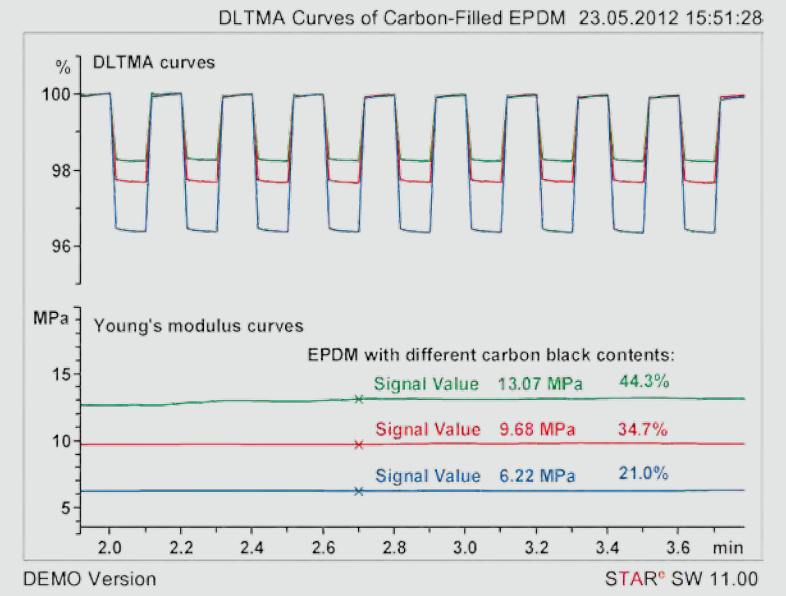

Figure 42.
Determination of the Young's modulus of three rectangular EPDM samples (width 2 mm, length 2 mm, thickness 1.5 mm) with carbon black contents of 21.0, 34.7 and 44.3% by DLTMA.

In an isothermal creep and recovery experiment (Figure 41), 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 41 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 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 42 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 43 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.

7.2.2 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:

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

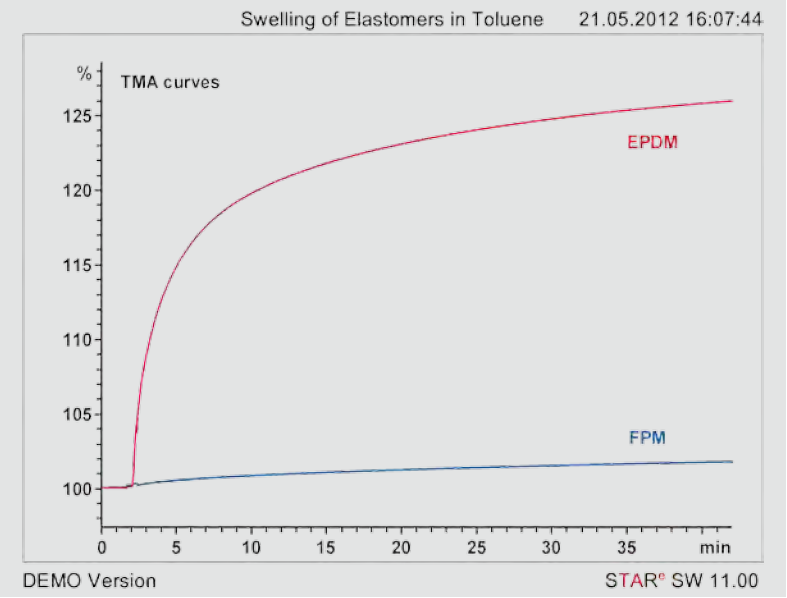

Figure 43.
Swelling measurements of cylindrical EPDM and FPM elastomer samples (diameter 2 mm, thickness 2.5 mm) in toluene at 30 °C.

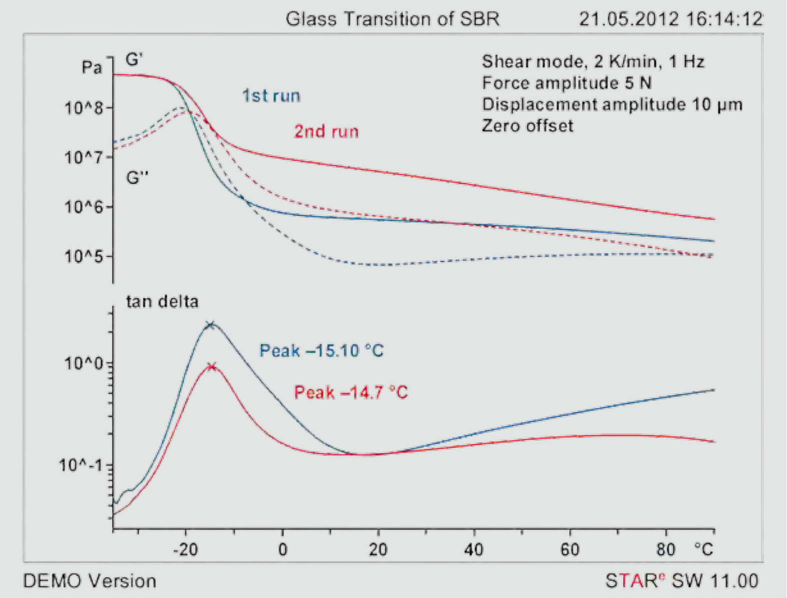

Figure 44.
The curves show the first and second heating runs of a cylindrical sample of unvulcanized SBR (diameter 6.5 mm, thickness 0.7 mm) without filler, measured by DMA in the shear mode.

sitive 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 44 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.

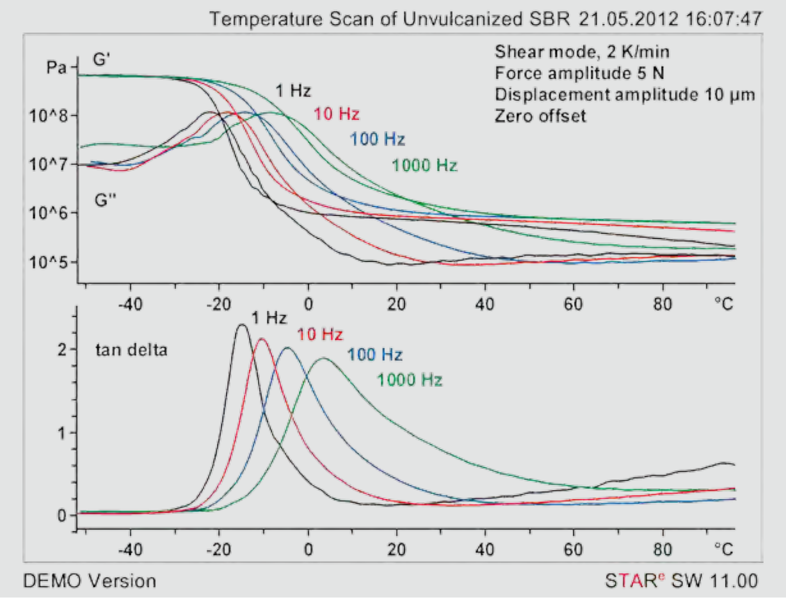

Figure 45.
Temperature scan of a cylindrical sample of unvulcanized SBR (diameter 4 mm, thickness 1.0 mm) without filler at 1, 10, 100 and 1000 Hz.

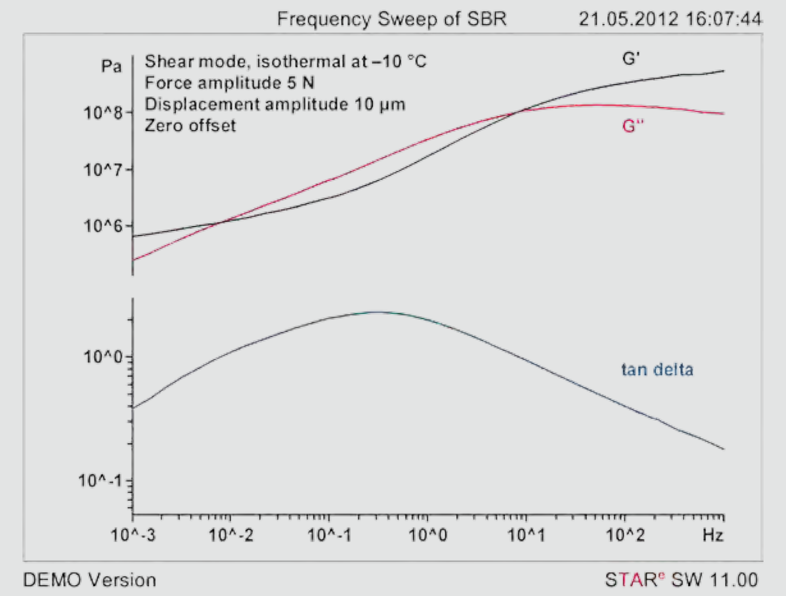

Figure 46.
Frequency measurements of a cylindrical sample of unfilled SBR (diameter 5.0 mm, thickness 1.2 mm) vulcanized with 2 phr sulfur.

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 °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.

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 45 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 46 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 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 (as in Figure 46). 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 47.

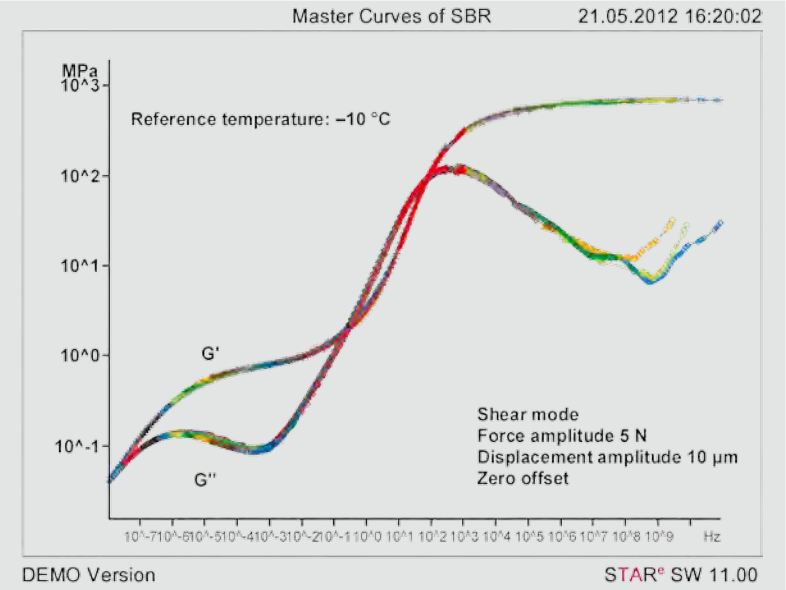

Figure 47.
Master curves of the storage and loss moduli of a cylindrical sample of unvulcanized SBR without filler (diameter 4.00 mm, thickness 1.0 mm) at a reference temperature of –10 °C measured in the shear mode.

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 47 shows the master curves of the storage and loss moduli of a sample of unvulcanized SBR without filler at a reference temperature of –10 °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^{-6} Hz in the loss modulus curve is due to flow relaxation. The storage modulus 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.

7.3 Overview of effects and applications

Table 4 summarizes the typical effects of elastomers that can be measured by different thermal techniques.

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

7.4 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.

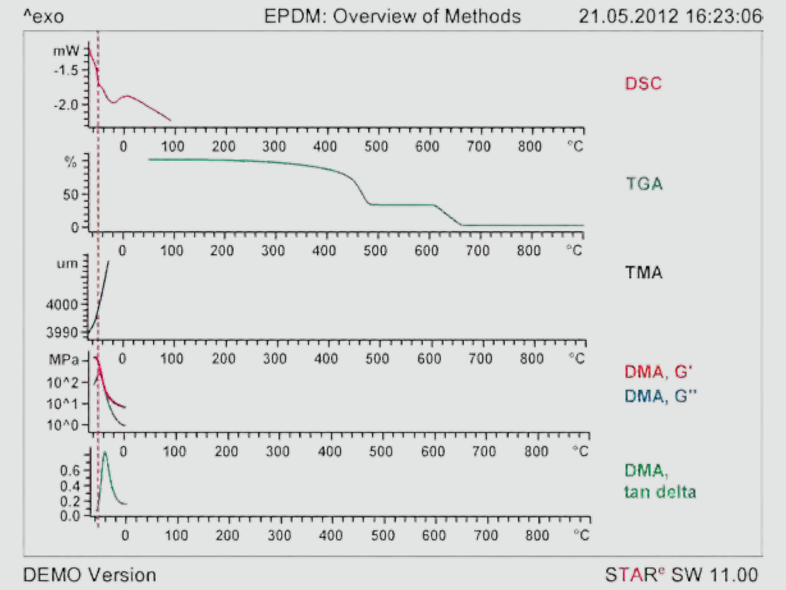

Figure 48.
Overview of effects and comparison of results. The glass transition temperature is shown by a vertical dashed line.

7.5 References

[1] Ni Jing, A. Hammer, Thermal analysis of polymers, Part 5: DSC and TGA of elastomers, UserCom 35, 1–5.

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

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[4] Ni Jing, Elastomer seals: Creep behavior and glass transition by TMA, UserCom 28, 13–16.

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