

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.

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).

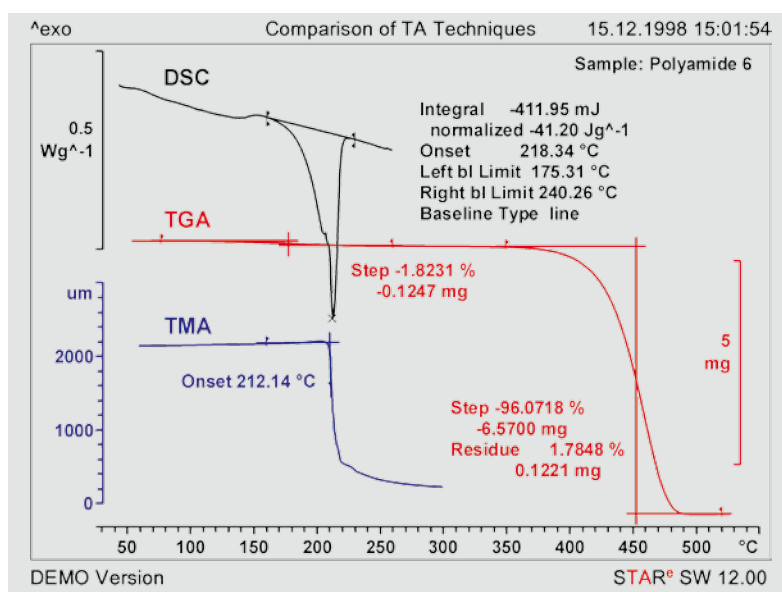
1.8 TMA

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

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.



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 function of temperature or frequency. DMA allows you to detect thermal effects based on changes in the modulus or damping behavior.

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

1.10 TOA

Thermo-optical Analysis

By TOA we mean the visual observation of a sample using transmitted or reflected light, or the measurement of its opti-

cal 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**[®] software. PET samples weighing about 3 to 10 mg were prepared and pretreated depending on the application. In general, samples should have a flat surface and make good contact with the crucible. The bottom of the crucible should not be deformed by the sample material when it is sealed.

2.3 Measurements and results

Differential scanning calorimetry

DSC is a technique that measures the heat flow of samples as a function of temperature or time. The method allows

physical transitions and chemical reactions to be quantitatively measured [2].

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

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

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

Glass transition

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

Figure 2. Structural formula of PET.

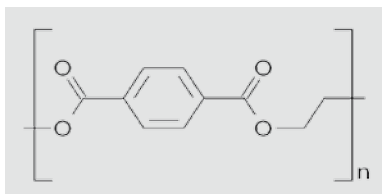
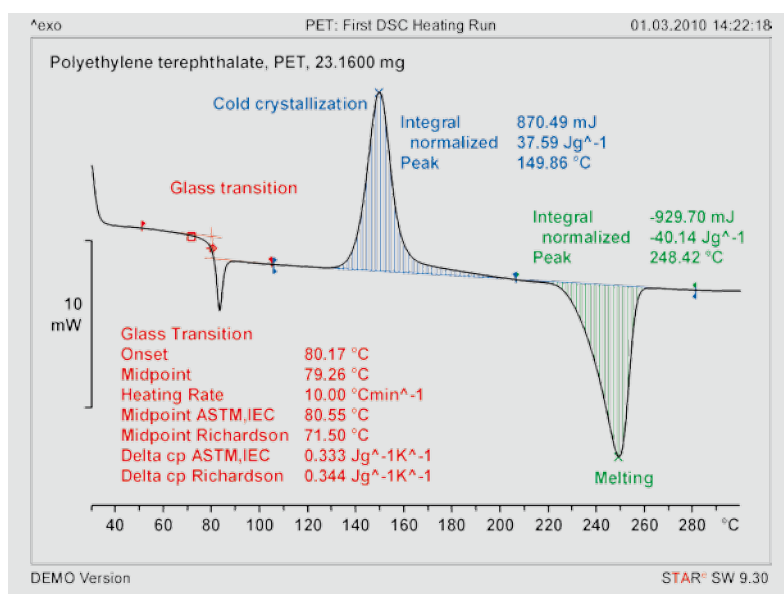


Figure 3. The main effects measured by DSC using PET as a sample. Temperature range 30–300 °C; heating rate 20 K/min; purge gas nitrogen at 50 mL/min.



plastically deformed or molded without breaking. This behavior is one of the properties that makes plastics so useful.

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

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

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

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

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

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

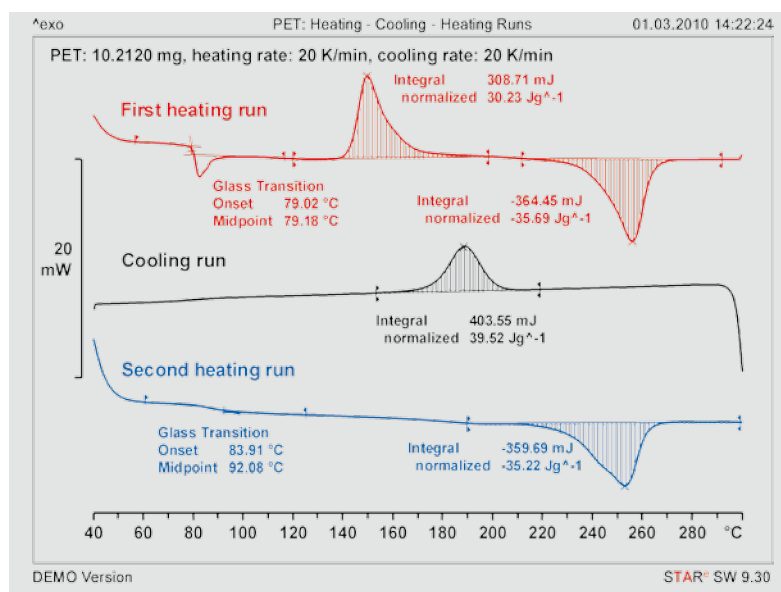


Figure 4. First and second heating runs and the cooling curve demonstrate differences regarding relaxation at the glass transition and the disappearance of cold crystallization.