Matthias Wagner

Thermal Analysis in Practice

Fundamental Aspects

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Preface

Thermal analysis is the name given to a group of techniques used to determine the physical or chemical properties of a substance as it is heated, cooled or held at constant temperature. The fascination of thermal analysis lies in its dual character: In addition to its purely analytical functions, it can be used as an engineering tool. Heat treatment applied to a sample in the first measurement may cause physical and chemical changes. Such effects can be investigated by cooling the sample and measuring it a second time in the same instrument.

The aim of *Thermal Analysis in Practice* is to provide practical help to newcomers, inexperienced users or in fact anyone who is interested in learning more about practical aspects of thermal analysis. It gives an overview of the DSC, TGA, TMA, and DMA techniques and shows how they can be used to measure different kinds of thermal events. The work presented in this handbook was performed using METTLER TOLEDO instruments, and the results were evaluated using METTLER TOLEDO's **STAR**^{e} software, but since DSC, TGA, TMA, and DMA are industry-standard techniques, readers using equipment from other manufacturers will also benefit greatly from the information presented.

Many modern thermal analysis instruments can be equipped with additional options such as connections to FTIR and MS equipment, humidity generators, UV/VIS light sources, or microscopy. These are covered in this book, as well as more recent developments in instrumentation, such as Flash DSC (fast scanning calorimetry) and connection to GC/MS.

Most of the chapters were written by Georg Widmann. Further contributions were made by Dr. Rudolf Riesen, Dr. Jürgen Schawe, Dr. Markus Schubnell and Dr. Matthias Wagner. We would like to thank everyone involved especially Dr. Vincent Dudler for the chapter on chemiluminescence. We also thank Dr. Angela Hammer for proofreading the original German manuscript. The text was reviewed and translated by Dr. Dudley May, Greifensee, and further reviewed by John Arthur, Australia. I would like to thank Dr. Klaus Könnecke for his contribution to the standards chapter.

Schwerzenbach, April 2017

Dr. Matthias Wagner, Editor

Contents

1 Introduction to Thermal Analysis

1.1 Definitions

An earlier definition proposed by the **ICTAC**, the International Confederation for Thermal Analysis and Calorimetry, was:

> "Thermal analysis covers a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample is programmed. The sample is kept in a specified atmosphere.
>
> The **temperature program** may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these."

Various objections were later raised and various recommendations put forward to clarify certain points. For example:

- The distinction between a thermoanalytical technique and a thermoanalytical procedure. Thermal analysis means the whole thermoanalytical method. It covers both the thermoanalytical technique (measurement of a change in a sample property) and the thermoanalytical investigation procedure (evaluation and interpretation of the measured values).
- Analysis therefore means more than just monitoring.
- In many cases, the change in the sample property is monitored and not the sample property itself.
- In most cases, the temperature of the environment is programmed rather than the temperature of the sample.
- Atmosphere is an operational parameter and is not essential for the definition.

This finally led to the most recent ICTAC definition of thermal analysis put forward in 2014.
This defines thermal analysis simply as:

> "Thermal analysis (TA) is the study of the relationship between a sample property and its temperature as the sample is heated or cooled in a controlled manner."

The definition clarifies key words used in this definition as follows:

- **Study** – implies that time is an integral part of the thermal analysis experiment and the total experiment, and the interpretation and discussion of the measured data are included.
- **Relationship** – implies that either the sample property can be measured as a function of temperature (controlled-temperature program), or the temperature can be measured as a function of the sample's property (sample-controlled heating).
- **Sample** – the material under study during the entire experiment (starting material, intermediates and final products) and its close atmosphere. This is equivalent to the thermodynamic system.
- **Property** – any physical or chemical property of the sample.
- **Temperature** – which can be directly programmed by the user, or controlled by a property of the sample. The program may include an increase, or decrease in temperature, a periodic change, or a constant temperature or any combination of these.

The data produced in a thermal analysis experiment is displayed as a thermoanalytical curve in a thermoanalytical diagram. Frequently, several different measured signals are displayed at the same time (referred to as **simultaneous measurement**).

The thermoanalyst is usually interested in so-called **thermal effects** in which the measured signal changes more or less abruptly.

Often the objective is to measure physical quantities outside thermal effects, for example the specific heat capacity, the expansion coefficient or the elastic modulus.

Note: The term "thermogram" is dated and should not be used. It is nowadays reserved for the graphical representation of the surface temperature distribution of objects.

The terms currently used are thermoanalytical curve or diagram, measurement curve, for example a DSC curve, a TMA diagram, etc.

1.2 A Brief Explanation of Important Thermal Analysis Techniques

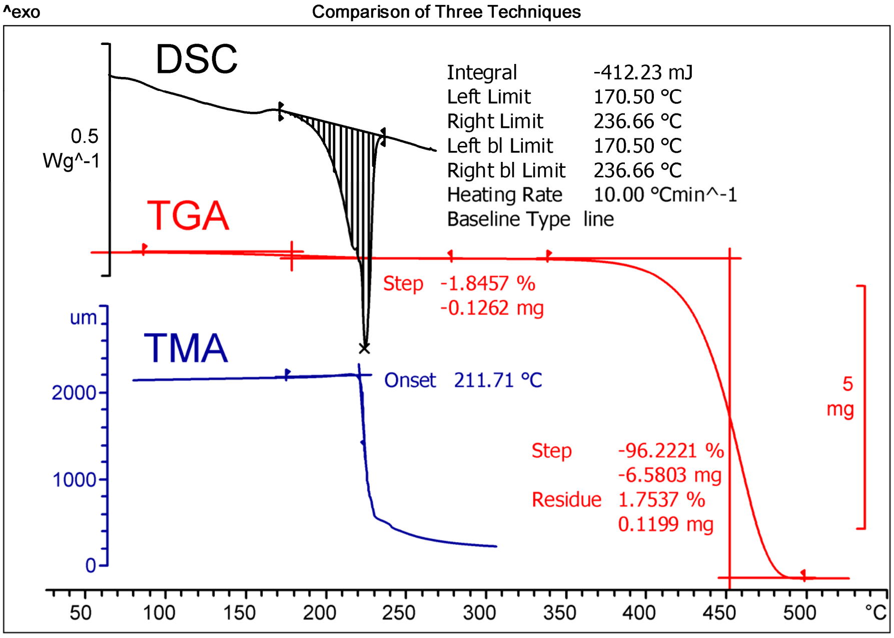

Figure 1.1. The three techniques used to measure polyamide 6 show different thermal effects. DSC: melting peak of the crystalline part; TGA: drying and decomposition step; TMA: softening under load.

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, only the thermocouple voltage in mV or µV was displayed.

SDTA, Single DTA. This term was patented by METTLER TOLEDO and is a variation of classical DTA that is particularly useful when used simultaneously with thermogravimetric analysis. The measurement signal represents the temperature difference between the sample and a previously measured and stored blank sample.

DTA (and SDTA) allows you

- to detect endothermic and exothermic effects, and
- to determine temperatures that characterize thermal effects.

DSC, Differential Scanning Calorimetry. In DSC, the heat flow in and out of a sample and a reference material is measured as a function of temperature as the sample is heated, cooled or held isothermally 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,
- determine peak areas (transition and reaction enthalpies),
- determine temperatures that characterize a peak or other effects, and
- measure specific heat capacity.

TGA, Thermogravimetric Analysis. TGA measures the weight and hence mass of a sample as a function of temperature. The acronym **TG** was previously used. Nowadays TGA is preferred in order to avoid confusion with T_g, the glass transition temperature.

TGA allows you to

- detect changes in sample mass (gain or loss),
- determine 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.

DTG, Differential Thermogravimetry corresponds to the 1st derivative of the TGA curve.

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. Important analysis techniques are mass spectrometry and infrared spectrometry. EGA is most often used in combination with a TGA because volatile compounds are eliminated in every TGA effect (mass loss).

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,
- determine deformation step heights, and
- to measure expansion coefficients.

DMA, Dynamic Mechanical Analysis. In DMA, the sample is subjected to a sinusoidal mechanical stress and the force amplitude, displacement (deformation) amplitude and phase shift are determined.

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.

TOA, Thermooptical Analysis. By TOA we mean the visual observation of or the measurement of the optical transmission of a sample, for example in a thermo-microscope. Typical applications are the investigation of crystallization and melting processes as well as polymorphic transitions.

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

1.3 Application Overview

Property, application	DSC	DTA	TGA	TMA	DMA	TOA	TCL	EGA
Specific heat capacity	●●●	●						
Enthalpy changes, enthalpy of conversion	●●●	●						
Melting enthalpy, crystallinity	●●●	●						
Melting point, melting behavior (liquid fraction)	●●●	●		●		●●●		
Purity of crystalline nonpolymers	●●●		●●●			●		
Crystallization behavior, supercooling	●●●	●				●●●		
Vaporization, sublimation, desorption	●●●	●	●●●			●●●		●●●
Solid–Solid–transitions, polymorphism	●●●	●●●		●		●●●		
Glass transition, amorphous softening	●●●	●		●●●	●●●	●		
Thermal decomposition, pyrolysis, depolymerization, 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				●	●●●			

Table 1.1. Application overview showing the thermoanalytical techniques that can be used to study particular properties or perform certain applications. ●●● means "very suitable", ● means "less suitable".

1.4 The Temperature Program

A sample is subjected to a temperature program in order to **measure** the processes that occur or to subject the sample to defined **thermal treatment**, for example annealing, erasing thermal history or creating a defined thermal history.

According to ICTAC, the **temperature program**

> "may involve heating or cooling at a fixed rate of temperature change, or holding the temperature constant, or any sequence of these".

The elements making up such sequences are called **segments**.

The temperature program usually begins at the start temperature from a state of isothermal equilibrium in which no measurement data is collected. As soon as the start temperature is reached, the measurement begins with the first segment of the temperature program.

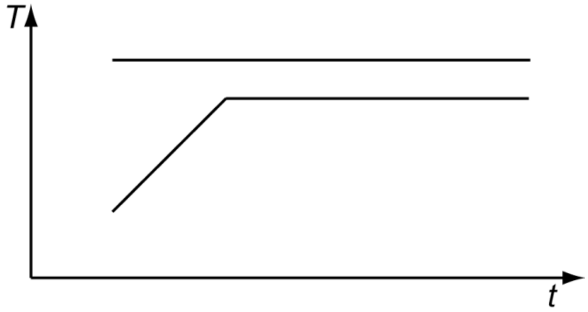

Figure 1.2. Isothermal measurement. Above: Insertion of the sample into the measurement cell that has already been programmed to the isothermal temperature (purely isothermal program). Below: Insertion of the sample at room temperature followed by dynamic heating (or cooling) to the measurement temperature.

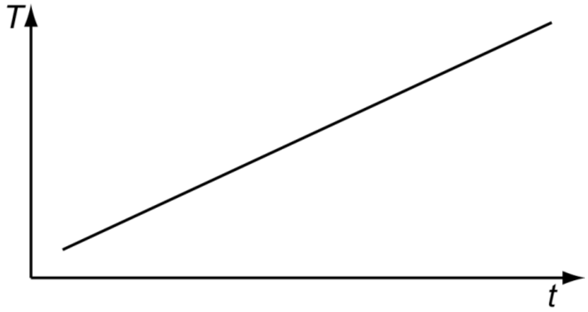

Figure 1.3. Dynamic measurement at a constant heating rate. This is the usual operating mode for most measurements. With DSC, low heating rates result in good temperature resolution but small effects, whereas high heating rates give poor temperature resolution and large effects. Low heating rates are 0.5 to 5 K/min, medium rates 5 to 20 K/min, and high rates >20 K/min.

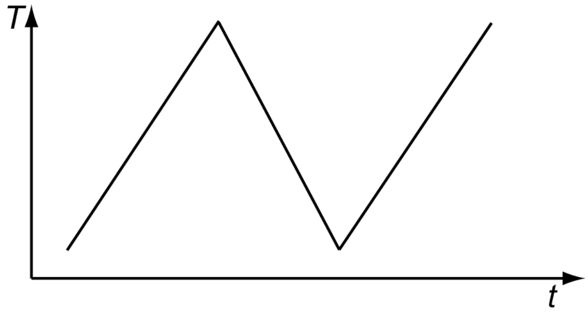

Figure 1.4. Dynamic heating, followed by cooling and a second heating segment. This is often very useful for interpreting measurement curves.

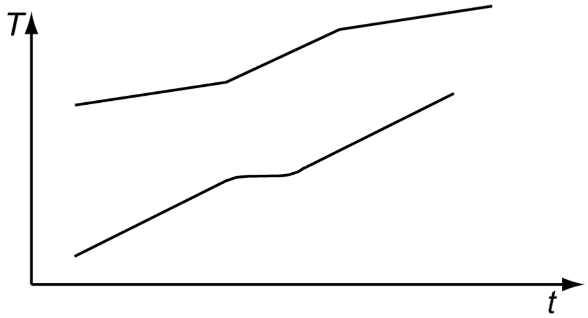

Figure 1.5. Dynamic measurements at different heating rates to save time. Above: A DSC In-Al check.
Below: MaxRes® used with TGA: The resolution remains good - the heating rate is automatically decreased parallel to the increasing reaction rate of the sample. As soon as the reaction rate slows, the heating rate increases again.

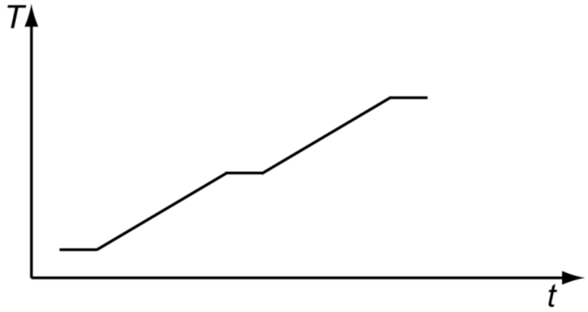

Figure 1.6. The isothermal-dynamic-isothermal temperature program is mainly used for the measurement of the specific heat capacity with DSC and for IsoStep®.

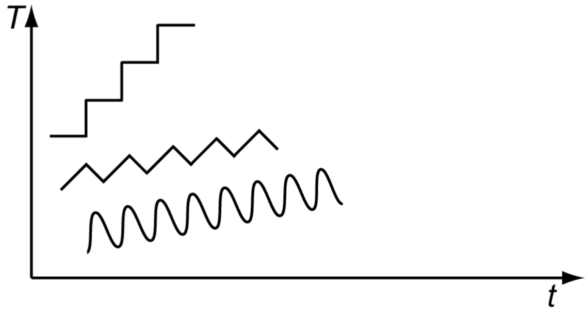

Figure 1.7. Periodic temperature programs. Top: A series of isothermal steps, mainly for safety investigations of chemical reactions, for equilibrium-melting, and for IsoStep®.
Middle: The saw-tooth program illustrates a version of alternating DSC (ADSC).
Bottom: The sinusoidal modulation (below) is the current version of our ADSC technique. ADSC can separate certain effects. The phase shift that occurs between the heating rate and the heat flow is an additional piece of information.

The heating rate chosen applies to a so-called reference position*) because the real sample can exhibit first order phase changes (e.g. melting) in which the heating rate cannot be controlled. This type of temperature control of the sample environment is known as **isoperibolic**. In fact, the temperature of the sample advances compared to that of the reference during exothermic processes and lags behind in endothermic processes. Depending on the thermal contact of the sample (thermal resistance), the sample temperature can deviate from the reference temperature by several tenths to several °C (K).

*) In the case of TGA/SDTA, DMA/SDTA and TMA/SDTA, this corresponds to a fictive inert sample during the blank run, whereas in DSC it is a reference crucible during the measurement.

References and Further Reading

[1] ICTAC Nomenclature of Thermal Analysis, at http://www.ictac.org

2 A Brief History of Thermal Analysis

Thermal methods were used long before anyone talked about chemistry or material sciences. Even in antiquity, many substances were subjected to a "heat test" to verify their identity and authenticity.

Nowadays, most of these tests have been replaced by other physical-chemical test methods.

In the 18th century, thermometers and temperature scales were developed, for example that of Anders Celsius in 1742. The thermal expansion of materials was used to indicate the temperature. Conversely, measurements of the change in length of materials as a function of temperature (dilatometry) had already been performed at this time.

The manufacture of ceramic products is closely connected with the development of thermal analysis. For example, even today, so-called Seger cones are still used to indicate the temperature reached at the position in the furnace where they are placed. A set of these consists of several triangular pyramids cones made of clay and oxide mixtures of increasing softening temperature. When they reach a particular temperature, they deform under the influence of their weight.

In the 19th century, it became possible to measure heat quantities. This was after the difference between temperature and heat content or enthalpy had been clarified using thermodynamic principles.

In 1887, Le Chatelier [1] performed the first actual thermoanalytical measurements as we understand them by putting a thermocouple in a sample of clay and heating the sample in a furnace. The heating curve was recorded on a photographic plate using a mirror galvanometer.

In 1899, Roberts-Austen [2] significantly improved the sensitivity and meaningfulness of such measurements through the introduction of two differential thermocouples connected in opposition. This allowed him to measure the temperature difference between the sample and an inert reference. He is therefore regarded as the inventor of differential thermal analysis, DTA.

In 1915, Honda [3] published the first thermogravimetric measurements in which the mass of the sample was almost continuously measured. Before this, it had only been possible to measure the mass difference after a thermal experiment by back-weighing.

In 1955, Boersma [4] invented the present-day heat flow DSC with his idea of placing the thermal resistance outside the crucible. The development of power-compensated DSC was first described in a publication by Watson et al. [5] in 1964.

Dynamic mechanical measurements with a constant selectable frequency have only recently become possible. Before this, similar measurements were performed using a torsion pendulum at resonance frequencies.

Robert MacKenzie [6] studied the history of thermal analysis in great depth and published many articles on this subject.

In more recent years, thermal analysis has profited greatly from the availability of powerful computer hardware and software. This has had an enormous influence on the development of thermoanalytical methods. Before 1980, measurement curves were recorded with linear pen recorders and evaluated manually. Selection of the wrong measurement range meant that the measurement had to be repeated using a more suitable range. Nowadays, the measured curve is saved, then displayed in an optimal fashion for interpretation and if necessary automatically evaluated.

2.1 Thermal Analysis at METTLER TOLEDO

Erhard Mettler, the founder of the company, had been very successful with his analytical and precision balances. In 1960, he began looking for possible additions to expand the range of products.

TA1: Hans-Georg Wiedemann came forward with his ideas for the commercialization of his "thermobalance" just at the right time. A development group was quickly set up to modify the purely mechanical semi-micro balance using electromagnetic force compensation so that the balance signal could be recorded graphically on a pen recorder. At the same time, furnaces, temperature sensors and controllers were developed to enable temperature programs to be performed. Vacuum technology also had to be developed before in 1964 the first TA1 "recording vacuum thermoanalyzer" was introduced. The TA1 Thermal Analysis System could simultaneously perform TGA, DTG and DTA measurements. Soon any reputable laboratory engaged in materials science research had to have a TA1 even though the cost of such a system at that time was very high, about 120,000 to 200,000 Swiss Francs, depending on the particular version. The most important application areas of the TA1 were inorganic compounds and ceramic materials.

FP1: At about the same time, an instrument for the automatic determination of the melting point of organic substances was developed. An additional measuring cell for the dropping point of edible oils and lubricant greases and a hot stage for the observation of samples under the microscope completed the system.

TA2000: In 1971, an instrument followed for quantitative differential thermal analysis, as the earlier versions of the present-day heat flow DSC were called at the time. Soon a temperature range of -170 to +500 °C was available, which was ideal for the investigation of organic compounds and the increasingly important polymer plastic materials. At the same time, the first successful trials began with computer (PDP11) evaluation techniques following digitization of the analog measurement data. From 1973 onward, the first programmable desk top computers appeared on the market and automatic evaluations became an economical proposition for normal customers.

TA3000: 1981 saw the introduction of the TA3000 System with its new method concept. This was the first commercial instrument for the automatic measurement and evaluation of thermoanalytical data. Routine measurements enabled efficient quality control tasks to be performed. In addition to the DSC and TGA measuring cells, the **TMA40** Thermomechanical Analyzer was introduced. This was revolutionary at the time because its programmable sample load enabled dynamic load TMA (DLTMA) to be performed for the first time.

STAR^{e} concept: Thermal analysis has benefited enormously from the availability of powerful but inexpensive personal computers. The **STAR**^{e} System was the result of the development of the **TA4000** (1987) and then the completely new **TA8000** (1992). Some of its most important features were its

- modular design,
- excellent measurement performance,
- unique calibration with FlexCal^{TM},
- fully automatic through to result assessment, and
- integrated relational database.

The innovative **DMA/SDTA861**^{e} Dynamic Mechanical Analyzer was introduced in 2002. Its modular design means that additional measuring modules can be developed in the future as required and integrated into the system using the **STAR**^{e} software.

2007 saw the introduction of the Thermal Analysis Excellence line comprising the TGA/DSC 1 with its innovative SDTA, DTA and DSC sensors sample holders and the DSC 1.

Both the performance and the operating convenience of the instruments were greatly improved. High priority was given to ergonomics and optimum ease of use. For example, the instruments could be operated using the intuitive touchscreen display or by actuating the hands-free SmartSens infrared sensors.

The new TGA and DSC models offered a choice of several different detectors. The TGA-DSC sensors simultaneously detect both weight and enthalpy changes with great accuracy. They differ in their maximum sample size and performance. The unique TGA-DSC sensor measures heat flow using six thermocouples and is very sensitive.

The instruments can be connected to a computer directly via TCP/IP, or via a network. This is an important advantage in a larger laboratory where several analysts operate different instruments and computers.

In 2009 the HP DSC 1 replaced the HP DSC 827^e. It could be equipped with a PC10 gas controller which allowed the cell pressure to be controlled. DSC microscopy was now available for both high-pressure DSC and standard DSC.

The Flash DSC 1 was introduced in 2010. It is the first commercially available high speed calorimenter which allows heating with up to 2,400,000 K/min and cooling with up to 240,000 K/min making it ideal for characterization of modern materials and optimization of production processes. This innovative instrument was presented an R&D 100 Award and included in the R&D 100 Editor's Choice.

2012 saw the market introduction of the DMA 1, a new DMA for QC applications with a versatile rotatable measurement head which even can be used for submersion measurements and measurements at controlled humidity.

2013 the TGA 1 a dedicated TGA was added to the portfolio. It uses the latest ultramicrobalance technology and provided very accurate and precise weighing results thaks to its innovative thermostating principle. At the same time new hot stages HS82 and HS84 were introduced. HS84 uses now the FRS 5 sensor and the resulting DSC curves are evaluated with the **STA**R^e software.

In 2014 the TMA/SDTAs 840/841 were replaced by the TMA/SDTA 1 which is offered in 4 different models: Liquid Nitrogen cooled, Intracooler, Large Furnace and even high temperature offering measurements up to 1600 °C. At the same time the new features of the TGA 1 were implemented in the TGA/DSC which then became the TGA/DSC 2. Last but not least the DSC 2 became available which benefited from an improved sensor technology resulting in superior longterm reproducibility.

In 2015, DSC, HP DSC, TGA and TGA/DSC received a major update offering now a new graphical user interface including One Click Shortcuts on all major products. Except the HP DSC all of them are available with integrated gas supply with mass flow controllers. TGA and TGA/DSC offer now automatic buoyancy compensation making recording blind curves obsolete.

Finally, in 2016 the TMA/SDTA 2+ replaced the TMA/SDTA 1+. At the same time **STA**R^e software version 15 was released. It has a completely new icon based user interface.

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[6] R. C. Mackenzie, Thermochim. Acta, 73 (1984), 249.

3 Polymers

3.1 Introduction

Polymers (or macromolecules) are extremely large organic molecules made up of very many smaller units (monomers). They are widely used in materials such as rubber, plastics, and adhesives to name a few. The length of an individual macromolecule is typically 10 nm to 1000 nm and the molar mass is more than 10,000 g/mol. Polymers always consist of mixtures of macromolecules of different size and are therefore characterized by their average molar mass.

At low temperatures, polymers are glassy solids. Above their glass transition temperature, they become more or less soft and elastic. There are several ways to classify polymers, for example based on the polymerization process used to produce them, on their structure (linear, branched, or network) or as below on their properties (thermoplastics, elastomers or thermosets).

- **Thermoplastics** are linear or branched uncrosslinked molecules. The thread-like macromolecules are joined together through entanglement and intermolecular forces. Thermoplastics soften or melt on heating and can therefore be molded and recycled. On cooling they may form a glass below the glass transition temperature. If the polymer chains are uniformly built up and mostly free of side chains, they may partially crystallize, giving rise to amorphous (non-crystalline) and crystalline regions. Above the crystallite melting temperature they melt and are liquid. Many linear polymers are soluble in certain solvents and can be cast as films from solution.
- **Thermosets** are network polymers that are heavily crosslinked to form a dense three-dimensional network. Thermosets cannot melt on heating and decompose at higher temperatures. They are therefore normally rigid and cannot be plastically molded or dissolved. Their starting materials are more or less liquid and cure to the finished polymer during the molding process. Above the glass transition temperature, they become somewhat rubbery and soft.
- **Elastomers** are network polymers that are lightly cross-linked. On cooling, elastomers become glassy. On heating, they cannot melt or flow because of their crosslinks. If their glass temperature is below room temperature, they are soft and rubbery at normal temperatures. Under mechanical stress, elastomers undergo marked deformation, but regain their original shape almost completely when the stress is removed. Since the polymer chains are chemically linked through crosslinking (vulcanization), elastomers cannot be molded or dissolved. Molding is therefore performed prior to vulcanization of the thermoplastic starting material.

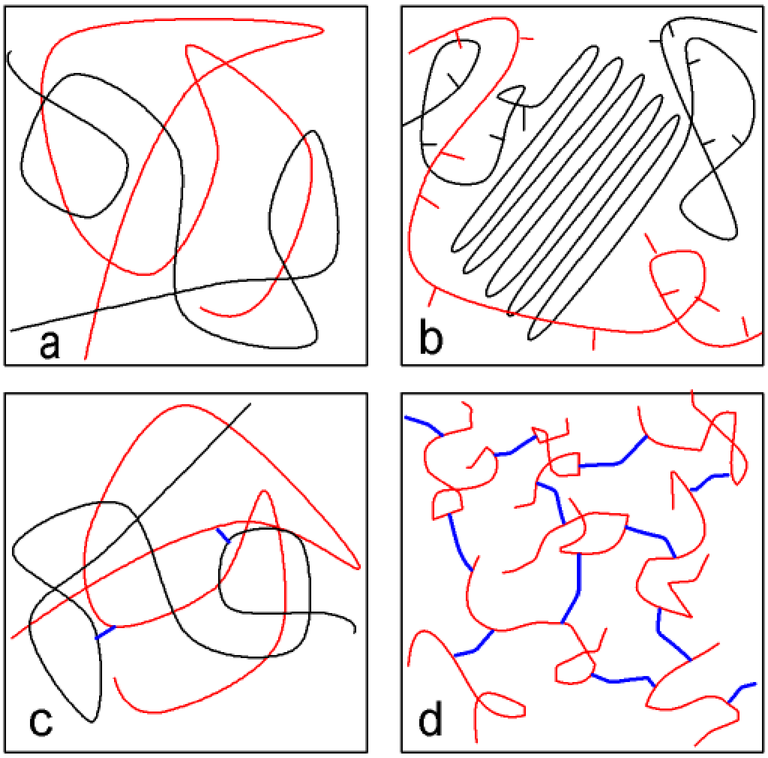


Figure 3.1. Schematic diagrams of different polymer molecules.
a: Amorphous thermoplastic. The two macromolecules are shown in different colors in order to distinguish them more easily.
b: Semicrystalline thermoplastic. In the center of the diagram is a chain folded crystallite. The remainder of the molecule and the red colored molecule are not able to crystallize because of the randomly occurring side groups.
c: Elastomer. The two macromolecules are linked at two points (colored blue).
d: Thermoset. The red molecules (resin) are three-dimensionally crosslinked by the blue curing agent.

3.2 Synthesis of Polymers

Polymers are formed when very many (up to several thousand) monomer units are linked together end to end by covalent bonds. The monomer units are reactive molecules that possess at least one bond that can be relatively easily cleaved. This allows the monomer units to be joined together through a chemical reaction.

Polymerization

In polymerization, the macromolecules are produced through successive linking of the same or similar individual monomer molecules to form a chain molecule. If there is only one type of chemical repeat unit (monomer) the corresponding polymer is a homopolymer; if more than one type of monomer is involved, it is a copolymer. A typical example is the formation of polyethylene, which has one of the simplest molecular structures. The basic monomer unit for polyethylene is the ethylene molecule (C_2H_4), whose two carbon atoms are joined through a covalent double bond. Under favorable conditions of pressure and temperature and in the presence of a suitable free-radical initiator such as benzoyl peroxide, the double bond of the C atoms is transformed into a single bond, leaving each C atom with an unpaired electron. As a free radical it can then form a bond with another ethylene molecule.

$$H_2C{=}CH_2 \longrightarrow H_2C_{.}\text{-}C_{.}H_2$$

$$H_2C_{.}\text{-}C_{.}H_2 + H_2C{=}CH_2 \longrightarrow H_2C_{.}\text{-}CH_2 - CH_2\text{-}C_{.}H_2$$

As can be seen, the resulting dimer is also a free radical so that further monomers can become attached.

Although the most important chain reactions are those involving free radicals, there are also other mechanisms. The reactive center at the growing end of a polymer can be ionic in character. Ionic polymerization is subdivided into cationic and anionic mechanisms. If the monomer has a non-organic atom (e.g. vinyl chloride $CH_2=CHCl$) or a side group (e.g. propylene $CH_3\text{-}CH=CH_2$), the side groups can occur randomly in the macromolecule (atactic polymer, little tendency for crystallization) or stereoregular (syndiotactic, on alternate sides; or isotactic, on the same side).

Copolymers: The properties of a copolymer depend not only on the content of the individual monomer units but also on their distribution. A random copolymer exhibits only one glass transition, whereas block and especially graft copolymers show transitions that correspond to the constituent homopolymers.

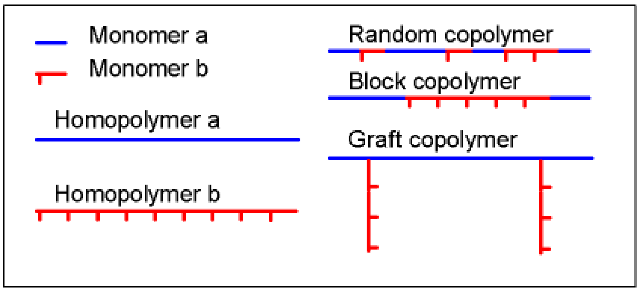
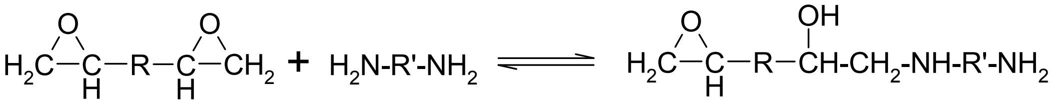


Figure 3.2. The monomers can be randomly distributed in the copolymer molecule or be present in blocks. Side chains can also be grafted onto the main chain.

Polyaddition

In polyaddition polymerization reactions, macromolecules are produced through the chemical reaction of low molecular weight compounds with reactive groups, such as hydroxyl, amino, acid, isocyanate or epoxy groups. The monomers are joined to each other by means of the oxygen or nitrogen atoms. For example, the reaction of an epoxy resin with an amine begins according to the following equation:



$$H_2C{-}\underset{H}{C}{-}R{-}\underset{H}{C}{-}CH_2 + H_2N\text{-}R'\text{-}NH_2 \rightleftharpoons H_2C{-}\underset{H}{C}{-}R{-}\overset{OH}{CH}\text{-}CH_2\text{-}NH\text{-}R'\text{-}NH_2$$

The reaction continues without stopping due to the remaining reactive group of each monomer. Three-dimensional crosslinking to form a thermoset is only possible because the secondary amine hydrogen can also react with an epoxy group. Each molecule of the amine therefore has four possible points of attachment.

In general, molecules with two points of attachment form linear polymers, and those with three or more points of attachment, three-dimensional crosslinked polymers.

Polycondensation

In polycondensation polymerization reactions, the same or different types of monomer molecules are joined together with the elimination of a substance of low molecular mass (usually water). A well-known example is the polymerization reaction of hexamethylenediamine (1,6-diaminohexane) and adipic acid (hexanedioic acid) to form polyamide 66 (PA 66) or nylon 66.

As shown in Figure 3.3, an H atom of the hexamethylenediamine reacts with an OH group of the adipic acid thereby eliminating a molecule of water. The reaction continues at both ends of the new molecule and leads to the formation of a long chain. The numbers in the name polyamide 66 (nylon 66) refer to the number of carbon atoms in the two monomers.

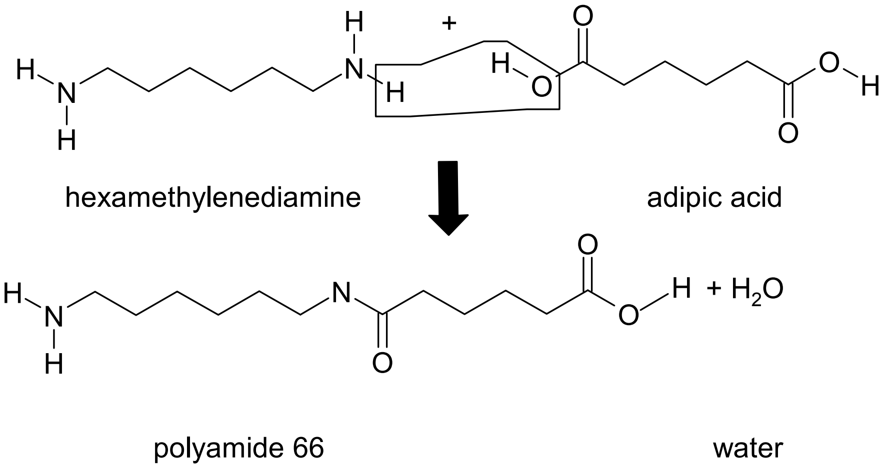


Figure 3.3. Polycondensation of hexamethylenediamine and adipic acid to polyamide 66.

3.3 Thermoplastics

In thermoplastics, the polymer chains are held together by weak bonding forces (van der Waals forces) and entanglement; there are no crosslinks. The chains can therefore easily turn and stretch under load. Semicrystalline thermoplastics contain both amorphous and crystalline regions. The latter disappear on melting. The properties of thermoplastics are very temperature dependent.

Below the glass transition temperature (T_g), thermoplastics are rigid glass-like materials. At the T_g, the thermoplastic becomes leathery, at higher temperatures rubbery, and finally more or less fluid. For this reason, many thermoplastics are easy to mold and can be recycled. The influence of temperature on the elastic modulus (Young's modulus) of an amorphous thermoplastic is shown schematically in Figure 3.4. The melting and glass transition temperatures of a number of different thermoplastics are summarized in Table 3.1.

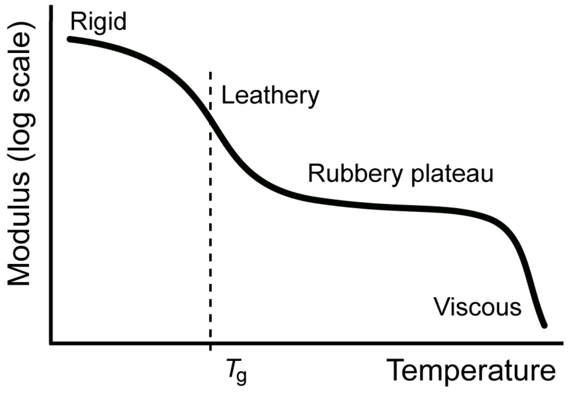


Figure 3.4. Influence of temperature on the elastic modulus and the behavior of a thermoplastic.

Polymer	Glass transition temperature	Melting temperature
Polyethylene (low density)	-120 °C	115 °C
Polyethylene (high density)	-120 °C	137 °C
Polyvinylchloride (PVC)	87 °C	175–212 °C
Polystyrene (PS)	85–125 °C	240 °C
Polypropylene (PP)	-16 °C	168–176 °C
Polyester (PET)	75 °C	255 °C
Polyamide (PA 66)	50 °C	265 °C

Table 3.1. Glass transition temperature and melting temperatures of various thermoplastics.

Some semicrystalline thermoplastics are polymorphous and can exist in different crystalline forms (e.g. PTFE). The degree of crystallinity of a thermoplastic depends on a number of factors. Simple polymers such as polyethylene crystallize most easily because there are no bulky groups present to prevent regular arrangement in a lattice. The degree of crystallinity of a thermoplastic also depends on how the material has been cooled from the melt. Slow cooling allows the macromolecules sufficient time to form a crystal lattice and leads to a high degree of crystallinity. On the other hand, shock-cooled polymers tend to retain an amorphous structure.

Deformation behavior of thermoplastics

Thermoplastics undergo both elastic and plastic deformation under the action of mechanical force. The deformation depends on the duration of the stress and on the rate at which the stress is applied. Figure 3.5 shows a typical tensile stress–strain curve for polyamide 66.

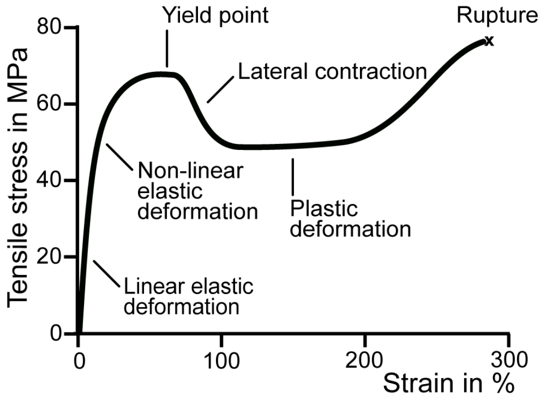


Figure 3.5. Typical tensile stress–strain curve of polyamide 66.

In the region of elastic deformation, two main mechanisms are in effect. On the one hand, the entangled chains are elastically stretched and return to their original position again after the tensile stress has been removed. On the other hand, entire sections of the chains can be shifted with respect to one another. These shifts are reversible in the elastic deformation region but the characteristic time constants for the relaxation can be hours or even months. This behavior, which is known as viscoelasticity, determines the deformation in the non-linear region of elastic deformation. If the polymer is subjected to a tensile stress above the yield point (elastic limit) the phenomenon of cold drawing occurs. The molecular structure changes permanently and permanent plastic deformation occurs. The chains are partially disentangled, stretched and simultaneously oriented parallel to each other. This process of cold drawing leads to localized lateral contraction or the formation of a neck (so-called necking). The neck region spreads until the entire specimen has been drawn into the new shape. Once the polymer is fully drawn, it is stronger than during the necking propagation. The chains are now aligned and more densely packed. This leads to an increase of the effective bonding forces between the chains and thus to a final upswing in the stress-strain curve. When the maximum tensile strength that the material can withstand is reached, it ruptures or breaks.

Viscous behavior and viscoelasticity

Polymeric materials behave both as viscous fluids and elastic solids; they are viscoelastic materials and their mechanical properties depend on time and temperature. The extent to which mechanical stresses cause chain slippage and plastic deformation depends on the temperature and the rate at which the stress is applied. If the stress increases slowly or at high temperatures, the chains react and adapt to the force exerted on them. If the stress is exerted rapidly or at low temperatures, the slipping and stretching process does not have sufficient time to adapt to the stress and the material becomes brittle and breaks. The viscosity of the polymer is a measure of the slippage of its chains and is therefore a property that characterizes deformation behavior of the material. In the case of thermoplastics, a marked temperature dependence of the viscosity according to the equation $\eta = \eta_0 \exp(Q_A/RT)$ is observed. Here Q_A is the activation energy for the slipping process of the chains and η_0 a constant.

The time-dependent deformation of a material under an applied stress is called creep [1]. A purely elastic material responds instantaneously to the stress and recovers its initial shape when the stress is removed. A viscous liquid, however, will deform as long as the stress is applied. The response of a viscoelastic material is in between the two. In amorphous thermoplastics, the activation energy of chain slippage and the viscosity are relatively small; the polymer undergoes deformation even with low stresses. At constant tensile stress, the polymer first of all reacts with rapid stretching. In contrast to metals, the expansion does not attain a constant end value. Rather the polymer continues to stretch slowly. This creeping of the material increases with increasing stress and with increasing temperature.

Another phenomenon that is also due to the viscoelastic properties of polymers is the stress relief in polymers that have been stretched by a fixed amount. For example, the stress in a rubber band that has been placed around a pile of books used to hold them together decreases with time.

Thermoplastic elastomers

Thermoplastic elastomers are a subgroup of thermoplastics that have been developed to combine the processing advantages of thermoplastics with the properties of elastomers. The elastic behavior of thermoplastic elastomers is however not due to crosslinking (as with elastomers) but is a result of the special segmented chain structure of the macromolecule. This consists of alternate, mutually incompatible, hard and soft segments or blocks. The hard blocks tend to aggregate in domains that act as crosslinking points. The crosslinking usually takes place through thermally labile physical interactions. The result is that thermoplastic elastomers flow at elevated temperatures and can be processed and molded in the same way as thermoplastics.

Further information on thermoplastics can be found in the METTLER TOLEDO “Thermoplastics” Handbook [2].

3.4 Thermosets

Thermosets are heavily crosslinked, close-meshed, three-dimensional polymers. Because of their close-meshed crosslinking, thermosets as a whole resemble a single giant molecule rather than a material made up of individual macromolecules. In fact, the individual macromolecules can hardly move. The result is that thermosets are hard and brittle materials with great structural strength. Fillers are often added to influence their mechanical properties. Thermosets are insoluble but can swell. Once thermosets have been crosslinked (cured) they can no longer be thermally molded. They do not melt and cannot be recycled.

Important types of thermosets are

- phenolic resins for electric insulation boards (printed circuit boards) and tubing,
- melamine-formaldehyde resins for furniture,
- unsaturated polyester resins for boots, travel trailers, aircraft parts and car bodies, and
- epoxy resins for molding and adhesive resins, as well as for printed circuit boards.

Thermosets are mostly used as composites. The addition of glass fibers, or even better, carbon fibers, yields very stiff components of low density, such as are used in Formula 1 racing cars.

Further information on thermosets can be found in the METTLER TOLEDO “Thermosets” Handbook [3].

3.5 Elastomers

Elastomers are lightly crosslinked linear chain molecules that form a wide-meshed three-dimensional network. Elastomers are also glass-like and brittle at low temperatures (i.e. in the range -10 °C to -80 °C). At higher temperatures, they largely retain their shape thanks to the crosslinking. They do not melt but begin to degrade and decompose if the temperature is too high. For this reason they cannot be recycled.

Elastomers are amorphous and show very little crystallization during processing. They can be elastically stretched without permanent plastic deformation occurring.

The starting material for the production of elastomers is natural rubber (caoutchouc) or synthetic rubber. By rubber, we mean an uncrosslinked polymer that can be crosslinked in a process called vulcanization and which has certain rubbery elastic properties and can undergo plastic deformation. Crosslinking is achieved using a vulcanizing agent. This reacts at suitable positions on the macromolecules and joins different chains together (see Figure 3.1c). The oldest and most widely used vulcanizing agent is sulfur.

The hardness or modulus of the elastomer can be influenced by the amount of vulcanizing agent used: small amounts of sulfur (typically 1%) lead to soft elastomers. Larger amounts of sulfur produce a hard elastomer.

The composition of an individual elastomer is very complex and is matched to the specific demands put on the material. Besides the actual rubber, an elastomer contains numerous ingredients such as vulcanizing agents, vulcanizing accelerators, activators, vulcanizing retarders, fillers, plasticizers, stabilizers, oxidation inhibitors, antiaging agents, pigments, and so on.

An example showing the typical composition of the tread of an automobile tire is given in Table 3.2.

Ingredient	Content in %
Natural rubber	39%
Filler (carbon black)	35.1%
Plasticizer (mineral oil)	19.4%
Processing agent	1.2%
Antiaging agent	1.5%
Vulcanizing agent (sulfur)	0.8%
Vulcanizing accelerator	0.7%
Dispersing agent (stearic acid)	0.8%
Vulcanization activator (zinc oxide)	1.5%

Table 3.2. Typical composition of the tread of an automobile tire.

Natural rubber (caoutchouc) is obtained as the milky emulsion of rubber particles known as latex from the tropical rubber tree (Hevea brasiliensis). The other ingredients are produced synthetically.

Synthetic rubbers are produced from very different starting materials such as butadiene, styrene, acrylonitrile, chloroprene, ethylene, propylene and so on.

Elastomers are classified according to the type of rubber used.

Some important elastomers are

- natural rubber, NR, for articles of daily use such as shoes, sponges, seals, automobile tires, tubing,
- styrene-butadiene-rubber, SBR, for automobile tires,
- butyl rubber, IIR, wherever low gas permeability and good heat and resistance to aging are required (e.g. automobile hoses),
- ethylene-propylene rubber, EPM/EPDM, seals,
- acrylonitrile-butadiene rubber, NBR, seals, tubing,
- fluorine elastomer, FPM, seals, molded parts, cable insulation, and
- chlorosulfonated polyethylene elastomers, CSM, wherever good stability toward light (UV), ozone, weather and fire is required.

Further information on elastomers can be found in the METTLER TOLEDO "Elastomers" Handbook [4].

3.6 Polymer Additives

Most polymers contain different types of additives that give them special properties. Some important additives are summarized below.

Fillers such as carbon black are added to rubber to increase the strength and wear resistance of tires or shoe soles. Inorganic fillers in the form of flakes or short fibers improve the mechanical stability of polymers (e.g. polyester mixed with glass fibers). Calcium carbonate, silicate or clay is often used as an extender for large volume polymeric parts of relatively low polymer content.

Pigments serve as additives for coloring polymers. They are usually in the form of fine particles that are dispersed uniformly throughout the polymer mass (e.g. TiO_2 particles for a white color).

Stabilizers counteract the decomposition of polymers under environmental influences (UV-radiation, oxygen, water, heat). For example polyvinylchloride requires heat stabilizers. Otherwise it would lose hydrogen and chlorine atoms even at room temperature with the formation of hydrochloric acid and the polymer would become brittle.

Since most polymers are poor electrical conductors, their surfaces can easily become charged with static electricity. **Antistatic agents** bind moisture from the surroundings, which leads to an increase in the surface conductivity of the polymer.

Most polymers are flammable because they are basically organic materials. **Flame retardants** usually contain chlorine, bromine or metal salts. They prevent the occurrence or the spread of polymer fires.

Plasticizers are molecules of low molecular mass that lower the glass transition temperature. They act as lubricants inside the polymer and so improve its molding properties. Plasticizers are widely used with PVC products to make the PVC soft, for example for water hoses.

3.7 Use of Thermal Analysis to Characterize Polymers

Numerous important properties of polymers can be quantitatively determined using thermoanalytical methods such as DSC, TMA, TGA, DLTMA and DMA. Table 3.3 summarizes the different types of polymer, the thermoanalytical effects, and the techniques that can be used to characterize them.

Polymer type	Effect and corresponding thermoanalytical technique
Thermoplastics	• crystallinity (DSC) • glass transition (DSC, TMA) • melting behavior (DSC) • thermal stability, oxidation stability (DSC, TGA) • elastic behavior (TMA, DLTMA, DMA) • fillers and filler content (TGA-EGA)
Thermosets	• glass transition (often lies in region of decomposition) (DSC, DMA) • curing reaction and determination of the degree of cure (DSC) • thermal expansion coefficients (TMA) • gelation time (DLTMA) • thermal stability, oxidation stability (DSC, TGA) • fillers and filler content (TGA-EGA)

Polymer type	Effect and corresponding thermoanalytical technique
Elastomers	• viscoelastic behavior (TMA, DLTMA, DMA) • thermal stability, oxidation stability (DSC, TGA) • composition (TGA) • vulcanization (DSC) • fillers and filler content (TGA-EGA)

Table 3.3. Polymer types, thermoanalytical effects and the techniques that can be used to analyze them.

References and Further Reading

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4 Basic Measurement Technology

The aim of this section is to introduce and explain different terms and expressions that a newcomer to thermal analysis might encounter.

4.1 Definition

Sensors transform the physical or chemical property being measured into an electrical signal. The signal is usually analog. The term sensor covers a wide range of different measuring devices. Ideally, the measurement signal produced by the sensor should be a unique function of the property it is measuring. Quite often, the function is non-linear (e.g. thermocouple voltage as a function of temperature). If the non-linearity of a sensor is known and is reproducible, it can be easily mathematically modeled using appropriate software.

4.2 Sensitivity

Every sensor has a certain sensitivity. This is defined as the size of the electrical signal per unit of the measured quantity. For example, a copper-constantan thermocouple at room temperature has a sensitivity of about 42 µV/K. See also detection limit.

The behavior of sensors is normally described using polynomial mathematical models.

$$y = A + Bx + Cx^2 \ldots \qquad (4.1)$$

where y is the quantity effectively measured (e.g. the electrical resistance of a resistance thermometer).

A is the ordinate intercept, B the slope (sensitivity of the sensor). C and possibly additional terms are needed to describe the non-linearity of the function. x is the true physical quantity.

4.3 Noise

Signal noise is more important than the sensitivity because modern electronics nowadays allows even very weak signals to be amplified. The noise is however also amplified. There are three main contributions to noise:

1. Real random fluctuations of the quantity (e.g. small fluctuations in temperature),
2. Noise occurring in the sensor (statistical measurement errors), and
3. Amplifier and analog-digital converter noise.