ONset NETZSCH
CUSTOMER MAGAZINE
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NETZSCH
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Just in Time for Our 150th Anniversary: We Present the Future

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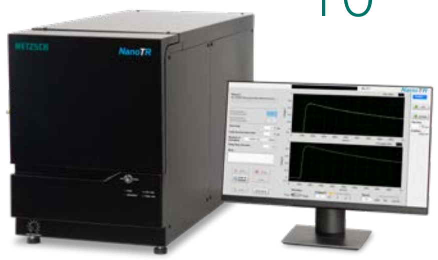

Dear Reader:

It's a great pleasure to be able to inform you about a very special event in this issue of our customer magazine: We are celebrating the 150th anniversary of our company! 150 years of Proven Excellence. We have celebrated with our employees all over the world at six great international events.

For 150 years, it's been our mission to provide our customers with quality, reliability and innovative solutions. Today, we would like to celebrate this wonderful achievement with you and thank you, our long-time companions, for your support and loyalty. You have helped us to become what we are today. Without you, we would not have any anniversary to celebrate or successful past to look back upon.

In our history of 150 years, we have experienced many ups and downs, but one thing has remained constant: our commitment to excellence and continuous development in order to always meet and exceed your needs. It fills me with great pride to see where we are today and to be optimistic about the next 150 years.

One reason for our continued success is our ability to develop new products and technologies that meet the changing requirements of our customers. In this issue, we would therefore like to proudly present our new generation of dynamic-mechanical analysis. The new innovative *Eplexor*® series offers even more efficient and powerful solutions to handle your most sophisticated demands.

Furthermore, we would like to introduce the *NanoTR* and *PicoTR* Time Domain Thermoreflectance analyzers. This revolutionary technology takes the determination of thermal diffusivity to a new level. It opens up completely new ways for you to optimize your processes and further drive your success.

Along with these exciting new products, we also present interesting contributions from the areas of software innovations and *TIPS & TRICKS*. Our objective is not only to offer you high-quality products, but also to provide you with the necessary knowledge and tools to make your work more effective and efficient. Our experts are happy to share their expertise and experience to make your day-to-day work easier.

We are looking forward to continuing to be at your side over the next 150 years and working with you to achieve new milestones.

With this in mind, I hope you enjoy your browse through this edition of **on**set!

Moritz Netzsch
Member of the Executive Board
NETZSCH Group

The New Generation of Dynamic-Mechanical Analysis – The DMA 303 *Eplexor*®

Dr. Wiebold Wurpts, Product Line Management for DMA, TMA and DIL

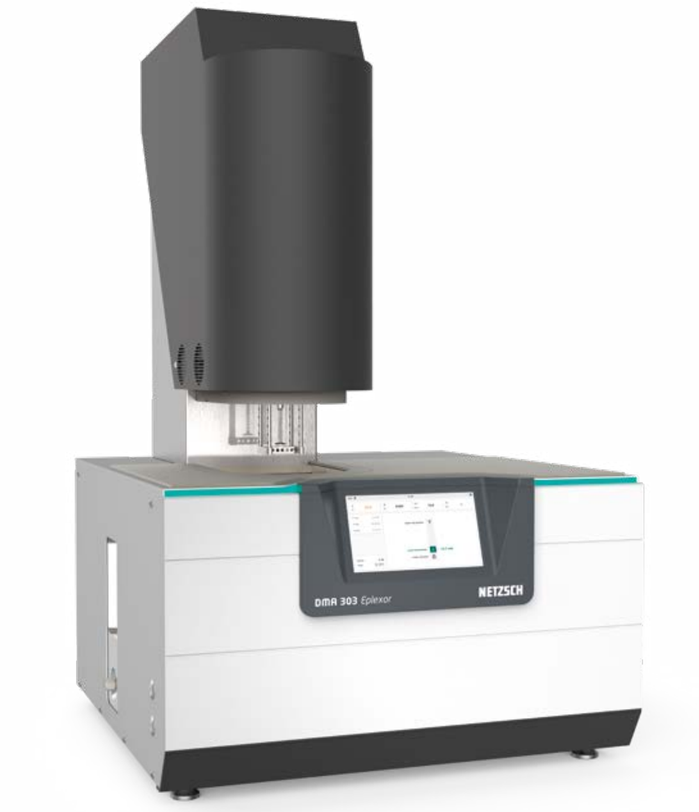

Fig 1. The new DMA 303 *Eplexor*®

With the activities in the polymer sector at the beginning of the 1990s, the first instrument for dynamic-mechanical analysis (DMA) was developed alongside the methods of DSC and TGA for the comprehensive analysis of polymers.

This DMA model is primarily intended for applications in the lower force range, in the automobile industry with its suppliers, as well as in the electrical industry.

After initial groundbreaking features, such as multi-frequency measurement for calculation of the master curve, more and more innovations were added, until in 2015 the application range was again considerably expanded due to the acquisition of GABO's high-force DMAs.

With the new DMA 303 *Eplexor*® (Figure 1), the objective of our new development hit the bull's eye: To combine ease-of-use and extraordinary force, displacement and temperature ranges into one desktop DMA.

Highest Force

The new DMA 303 *Eplexor*® is based on the measurement concept of an electrodynamical shaker (yellow in Figure 2) for oscillation excitation and an additional stepper motor (orange) for start-up of the sample. The folded structure of the force-driving parts (dark green) allows for a compact design. This concept further includes optical displacement sensors (light green) with a position resolution of 1 nm. To keep the setup as compact as possible, the current is measured directly via the current of the shaker.

The new electronics facilitate a low noise level, so measurements with very low force levels of 1 mN are also feasible (see table 1).

Table 1. Specifications for the DMA 303 *Eplexor*®

Force range	0.001 N to 50 N
Temperature range	-170°C to 800°C
Maximum dynamic amplitude	± 2.5 mm
Maximum static deformation	30 mm
Frequency range	0.001 Hz to 150 Hz

At the same time, the maximum force increases to 50 N without switching the measurement range. For measurements that do not require a static preload, e.g., in cantilever and shear, up to 50 N can be applied to the sample. For measurements that require a static preload, e.g., in tension, 3-point bending and compression/penetration, the force range (50 N) can be divided into a static and dynamic component. Due to the increased force range, larger deformations can now be achieved, even for measurements on stiff samples, and thus meaningful results can be obtained.

Furthermore, the dynamic amplitude was increased up to ± 2.5 mm. The stepper motor allows for quasi-static deformations of up to 30 mm. To take advantage of this, the Universal Test or tensile test was added as a new measurement type.

DMA 303 *Eplexor*®

Wide Temperature Range

The new DMA 303 *Eplexor*® also achieves temperatures as low as -170°C by means of liquid nitrogen cooling as well as -70°C with an air intracooler. In order to be able to also measure metals or glass in a high-temperature range, the maximum measurement temperature is now 800°C. However, to protect the shaker from overheating, a heat pipe ensures that a constant temperature is maintained for the shaker (blue in Figure 2).

Homogeneous Temperature Distribution

If different material effects occur in the same temperature range, a sharp resolution is often difficult. Therefore, the sample is placed in a closed pot, heated (and coolable) from all sides. To minimize remaining temperature differences as much as possible, the air in the furnace is circulated by a fan wheel. The sample holder is ideally made of a titanium alloy (optional) with low thermal conductivity.

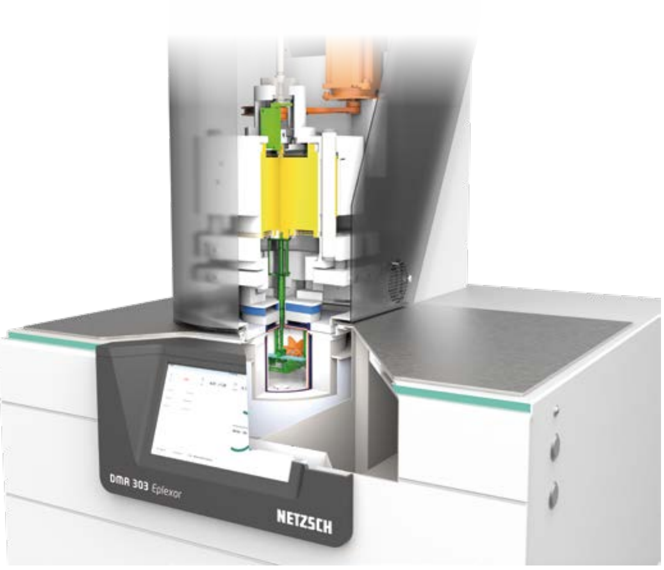

Fig. 2. Quarter section of the measuring cell of the the new DMA 303 *Eplexor*®

Easy Height Adjusment for Furnace

During development, special attention was paid to user-friendly and ergonomic operation. The movable furnace catches the eye: The working height can always be adjusted individually (see Figure 3); even delicate samples are thus much easier for the operator to load, whether while standing or sitting. The standard sample illumination (see Figure 4) is very beneficial for checking correct sample positioning (which can have an influence on the measurement results).

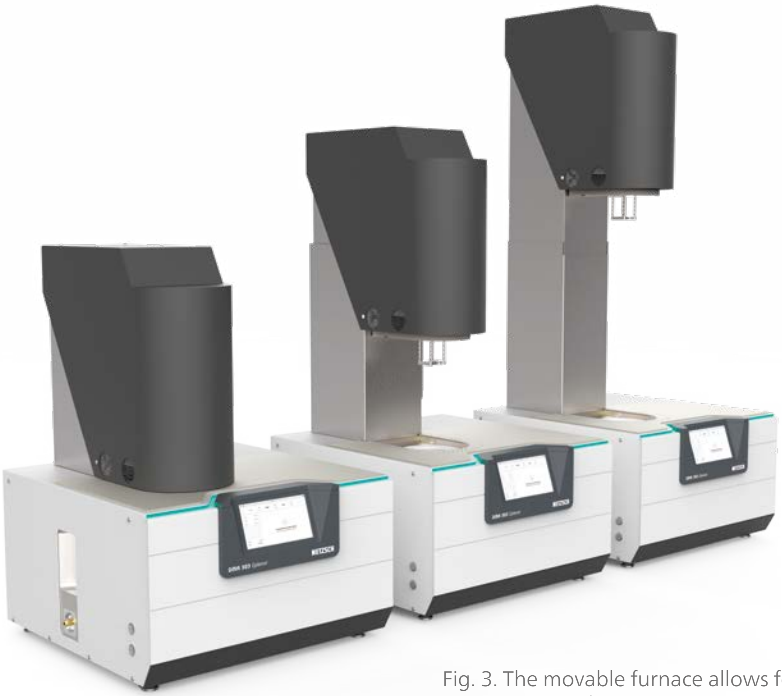

Fig. 3. The movable furnace allows for ergonomic working in any position

Fig. 4. Optimum illumination of the sample

Display: All Important Information at a Glance

The new display always shows the current force and deformation. This way, the operator always has the applied force in view, even when manually moving and inserting the sample. If the sample is to additionally be pre-conditioned prior to the measurement, thermally or mechanically, this is done in manual mode via the new DMA Proteus® software; meanwhile, the operator can still put the necessary settings for the measurement into place. As soon as the measurement is running, the current status of the measurement is also displayed on the LED strip on the housing – and is visible from afar. This makes it easy to detect the end of the measurement, even if you are not standing directly in front of the instrument.

Automatic Sample Holder Detection

The sample holders form the heart of the DMA. For the bending holder shown in Figure 5, the highest possible reproducibility of results is achieved thanks to the particularly flexible bearing. Along with this function, however, the operation is also consistently simplified here. Sample holders, for example, are changed out without any tools: The lower holder is clamped on by a lever, while the probe is conveniently fixated by hand with a knurled nut. The RFID chip automatically detects the sample holder, thus ensuring that mix-ups do not occur and the operator can fully concentrate on the measuring task.

After installation of a new sample holder, a reference run to a gauge block is first carried out, to measure the spacing of the sample holder and to carry out a routine check on additional instrument functions. Then, the instrument is ready for measurement: The user can now load a pre-defined measurement or a self-created favorite, or alternatively can define entirely new measurements. To this end, various measurement types are available which can be linked as desired to form a measurement list (as with the familiar segment program). As is also the case with other NETZSCH instruments, the results can be monitored during the measurement and can then be compared with other measurements and methods in the *Proteus®* analysis software. The measurements can be displayed with any signals on the x-axis – this is, for example, necessary for a tensile test or load sweep, where strain is typically displayed on the x-axis. In addition, the measurements can also be automatically evaluated with the optional *AutoEvaluation* function or managed with the *Proteus® Search Engine* (see article on pages 24 to 26) using keywords.

Fig. 5. Bending sample holder with RFID detection

Application Example: Silicone

Figure 6 shows the DMA measurement on a silicone strip in the temperature range from -180°C to -20°C. The sample with a cross-section of 6.4 mm x 0.96 mm was measured in the tensile direction. The course of the elastic storage modulus, E', loss modulus, E'', and loss factor, tan δ, is shown. In this measurement, it was possible to cool the furnace down to below the specified minimum temperature of -170°C.

As is usual for polymers, the storage modulus (and thus the stiffness) is many times higher in the cold range than in the warm range. While the storage modulus at -140°C is still at approx. 3000 MPa, the modulus decreases to approx. 300 MPa by -110°C. In this transition, material damping typically reaches a maximum. Above -110°C, the material crystallizes, and the stiffness increases temporarily. Starting at an onset temperature of -62°C, the crystals melt and the silicone exhibits the familiar pasty behavior which makes it so well-suited for so many applications.

DMA can be employed for the detection of the application limits of materials. Moreover, the material can be studied even more closely in the cold range, in order to develop detailed understanding of the material.

Summary

With the DMA 303 *Eplexor®*, NETZSCH meets all of the expectations for a DMA in a handy desktop format: The unique temperature and force range allows for new applications, and an improved resolution enables measurements on even the thinnest of films in the softening range. Last but not least, the instrument offers ease-of-use through such features as sample illumination and the movable furnace.

For more information, please go to:

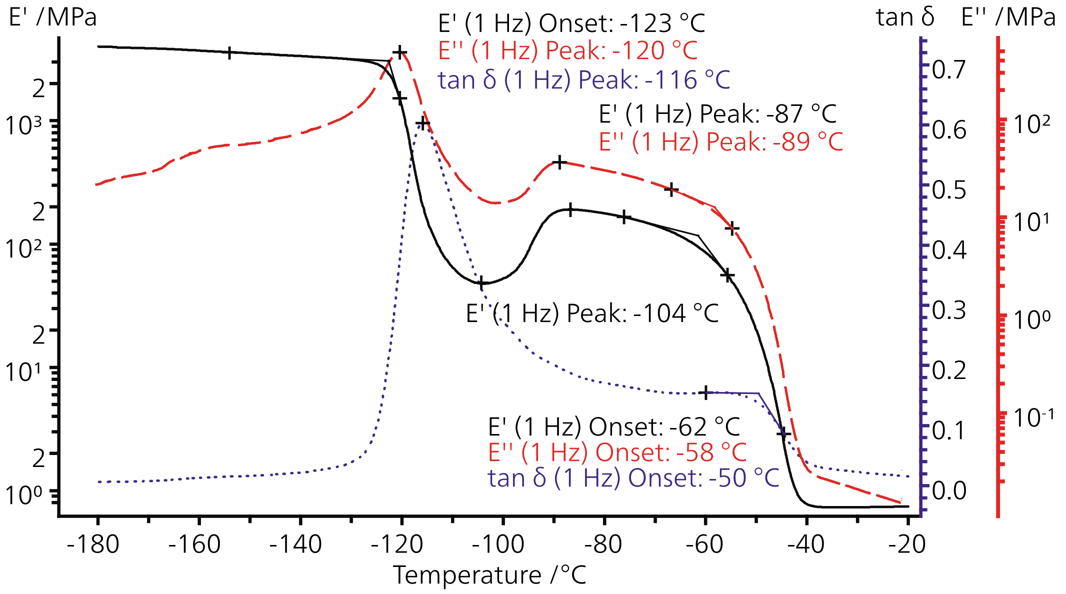

Fig. 6. DMA measurement on a silicone sample

Fancy the Future – NETZSCH Celebrates 150 Years of Excellence

Svenja Fröhlich, Corporate Communications Erich NETZSCH GmbH und Co. Holding KG

Fig. 1. Managing Directors of the NETZSCH Group Paul Netzsch, Jens Niessner and Moritz Netzsch (from left)

From a small workshop in Selb to an internationally successful mechanical engineering group: More than 4,000 employees worldwide are celebrating NETZSCH's 150th anniversary year.

The beginning was marked by start-up flair: Two brothers set up their own business in 1873 and develop a quality product in a small workshop in Selb that impresses the local fire brigades. The fire extinguishers by "Gebrüder NETZSCH Maschinenfabrik" become a bestseller. Thomas Netzsch is a locksmith; his younger brother, Christian Netzsch, an engineer – the machines they end up later developing for ceramic production are also renowned for their quality. In line with the boom of the porcelain industry in the Fichtel Mountains in northeast Bavaria, the company finally focuses entirely on the production of such machines.

This is how, 150 years ago, the success story began of a family-owned company that today spans the globe. With our three business units, "Pumps & Systems", "Grinding & Dispersing" and "Analyzing & Testing", we offer products such as the progressing cavity pump, mills for wet and dry milling, thermal analysis instruments, rheometers, and fire testing systems, operating with more than 4,100 employees at around 210 production and sales locations worldwide. Today, the group is again headed by two brothers from Selb: Moritz and Paul Netzsch. As the fifth generation of the Netzsch family, they run the company together with CFO Jens Niessner.

"Our History Provides Answers"

What began in 1873 in a workshop in Selb has long since outgrown its infancy. But NETZSCH wants to remain true to its family values and roots. In this anniversary year, Moritz Netzsch emphasizes: "It is important to me that we have continued stable development of what we do today. My wish is that, with all the reflection, with the necessary rethinking and new thinking, we grow organically and take the company into the next generation stronger than ever."

The look to the past is not only based on values and success, but also reveals the precision of fit for a customer solution value proposition. "Our history provides the answers as to why we have existed for such a long time. Our 'Proven Excellence' slogan is not just an empty phrase. We can prove our excellence based on our history. It is possible to observe how NETZSCH has actively shaped entire industries over many years. But also how we have always been capable of adapting to radical changes in the corporate world or markets. This sometimes also meant that we had to drastically reposition ourselves," says Paul Netzsch. After the Second World War, for example, potato washing machines were built, and during the heyday of the porcelain industry, NETZSCH built complete factories for the ceramic industry. All of these developments ultimately led to NETZSCH positioning itself very successfully in the market with the "Analyzing & Testing", "Grinding & Dispersing" and "Pumps & Systems" business units. "We would like to also transfer this historically grown adaptability to the future," explains Moritz Netzsch.

Success from Generation to Generation

Looking back also has a personal component, particularly for cases in which important milestones in the company's history can be attributed to Erich Netzsch (1903-1990) and Thomas Netzsch (1946-2010). The two managing directors each shaped the company in their own distinctive way and brought it forward with landmark decisions. The discovery and continued development of the Mohno pump under Erich Netzsch and the intensive internationalization under Thomas Netzsch are just two examples to mention. The company still benefits today from the formative positions taken by these leaders. The same is true of the insights into values and quality, which for generations have focused not only on the company's own products and customers, but also on its employees. 25 or even 40 years of employment – also internationally – are therefore nothing unusual at NETZSCH. The average length of service of the international staff at NETZSCH is high, at 10.6 years.

CFO Jens Niessner is convinced: "You can feel our NETZSCH spirit at every location. Our values, the economic success, the perspective for the employees – this combination sparks a radiance that makes us competitive even in places where other companies that are well-known internationally are based."

"Our Mission"

The vision for the future has been set: In 2022, the company launched a new strategy for the three business units. "We drive industrial progress to sustain a successful eco-system through generations" – the new mission reveals a strengthened will at NETZSCH to shape the future. Since 2019, employees have participated in the development of futuristic ideas – such as NETZSCH's own NEDGEX innovation incubator – of course, always in search of potential new business fields. In 2021, NEDGEX was awarded the Digital Lab Award by Infront Consulting and Capital business magazine as one of the best digital innovation labs in Germany.

In its 2023 anniversary year, NETZSCH has planned extensive celebrations – also at all major international locations. The company will share the various facets of its history with its employees, customers, and partners, as well as with the interested public, in a magazine and anniversary blog.

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DMA on Biomaterials: Seeing the Invisible!

Prof. Dr. Michael Gasik, Aalto University Helsinki, Finland

Introduction

Many biomaterial types are presently available for use in different implants, especially in orthopedic and dental cases. Metallic alloys, ceramics and composites are used, be it with or without live cells. There is a growing application field of different scaffolds used in tissue engineering applications to support and promote the formation of new tissues, and many of these are being made by 3D (bio)printing.

Biological tissue regeneration is known to be one of the most demanding challenges, requiring biomaterial structures with correct biomechanical properties [1] that mimic in vivo behavior [2]. Proper biomaterials assist the body in rebuilding the damaged tissue and minimize the associated pain and healing time [3].

This article presents a new application of the dynamic-mechanical analysis technique (DMA), called BEST (Biomaterials Enhanced Simulation Testing) for the characaterization and improvement of biomaterials and medical devices that goes beyond the well-known classical viscoelastic analyses.

Challenges

Numerous studies were already carried out and clinical data was collected regarding the shape, design, and surface state of biomaterials, as well as the geometry of implants and their suitability for the different tissues' quality and location. Significant differences were also reported for implanted materials that were seemingly identical but originated from different sources [4].

Biomechanical characterization of bone and soft tissues is more problematic than for metallic, ceramic and polymer materials. Published datasets are often not based on comparable measurement protocols and conditions, leading to a lack of consistency. Generalization of these data is very difficult or almost impossible when it comes to providing simple, robust and relevant information.

For biomechanical characterization, one usually reverts to assuming a material as being a type of elastic or viscoelastic matter in order to approximate the properties into individual numbers, usually referred to as "elastic modulus". This, however, fits only with linear elastic materials for very small deformations, and the NPL guidelines [5] list nine methods for calculating the elastic modulus which can lead to different values. The vast majority of biomaterials and tissues are clearly not elastic ones, so it is a significant oversimplification to try to artificially reduce data to some fixed numbers: What, for example, would be the benefit of knowing the "elastic modulus of mucosa" spanning from 0.1 to 680 MPa by different sources?

Unfortunately, issues related to inertia effects (high frequencies) or instrument limits (low frequencies) are not always sufficiently documented in the test protocols published. Even if instrument inertia is eliminated, the sample itself will always have finite inertia, which can produce artefacts from momentum diffusion, visco-elastic waves, and secondary flows – all of which can violate the assumption of homogeneous and linear deformation [6]. More sophisticated models have a substantial number of artificial fitting parameters, and there are great experimental difficulties in carrying out such tests within existing standards, protocols, and ad hoc test methods [7].

For processes like 3D bioprinting, there are several challenges which must be overcome, such as controlling properties of the bioinks, managing flow and its effect on the cells' viability, and ensuring optimal biophysical properties of the constructs after printing and upon implantation [8].

Higher resolution and speed with control in the 3D microenvironment are required, and an optimal combination of mechanical and transport properties must be achieved within the space and time scale; these are needed in particular for diffusion-limited vascularization. New Medical Device Regulations (2017/745) demand that proper mechanical evaluation should be carried out, resulting in adherence to the Health Technology Assessment Regulations (2021/2282).

Unfortunately, many different methods of biophysical testing yield rather different outcomes, and it is not easy to obtain realistic, true properties. There are many reasons for the differences – uneven contact, phase state, inertia and elastic instability effects, fitting with improperly assumed models, limitation in strain definition, lack of proper loading history assessment, etc. Hence, it is very important to have a robust approach which can quantify both a biomaterial's behavior and its performance in the process rather than just generating some specific numbers.

The BEST Concept

To address these challenges, we have developed the patented BEST method (Biomaterials Enhanced Simulation Testing). It can be applied for many hard and soft biomaterials, including hydrogels, 3D-printed constructs, and controlled drug delivery. BEST solutions are targeting problems caused especially by improper and fragmented testing, and are established on an integrated approach based on a fundamental causality principle: "*There was no response by the specimen before the stimulus was applied*."

BEST is performed under controlled conditions with required coherent stimuli in the DMA environment. It assesses changes in the specimen's properties in time, phase and stimulus domains [9]. In post-processing, BEST integrates the data, convolutes the specimen's history, and extracts unknown values, all without requiring the user to select the model of material (data analysis is essentially model-free). Invariant parameters obtained with a proprietary quantum regression algorithm incorporate the specimen history, showing the position and direction of the development of a biomaterial [10].

The key BEST feature is invariant processing of DMA data, which usually remains unexplored by the user. This new method overcomes common limitations in the linearity of tissue properties in many models, namely a scaling property (homogeneity) and a superposition property (additivity), which are not generally held for Fourier transformation used in linear viscoelasticity.

Hence, BEST applies a correct testing protocol and uses idempotent methods to extract parameters from a single specimen/test, resulting in high output data without the use of complex math (no need in complex moduli) or the assumption of linearity, and is capable of reprocessing also other rheology data in such a way as to not lose their value.

DMA Application Example

In the example shown here, the method described above was deployed based on measurements performed with a NETZSCH DMA to characterize the properties of acrylic hydrogel for 3D bioprinting without using an assumed model. The gel was placed into a 1-mL syringe with a 29G needle and set up in the customized DMA sample holder which is usually used for bending; it was tested in stepwise creep mode at 25°C.

Figure 1 shows the experimental data for the gel amount extruded (µL) via a defined needle nozzle, normalized per applied local pressure (kPa). This data clearly reveals non-linearity of the flow kinetics with time and applied pressure, and there is no straightforward way to select any material model to describe these dependencies.

From this data, the BEST method extracted time-invariant values for the viscous stiffness of the gel under these injection conditions as well as its memory value [9,10] (fig. 2). Here, the curves are almost linear, and the slopes of the lines are nearly constant for all applied pressures (numbers in kPa). This means that the gel, despite exhibiting non-Newtonian behavior, is linear in terms of model-free invariant values. It can also be seen that numeric values are changing with the applied pressure in a non-monotonic way, disclosing that there might be different limiting phenomena affecting the flow. In order to see the effect of the flow development, the plot of memory values vs. applied pressure is shown in Figure 3. This map shows that the gel in the syringe faces friction, flow resistance and possibly no-slip effects at low pressures when memory values are much lower than unity. After about 65 kPa – the onset – these values jump up, signaling that the gel achieves a more developed flow.

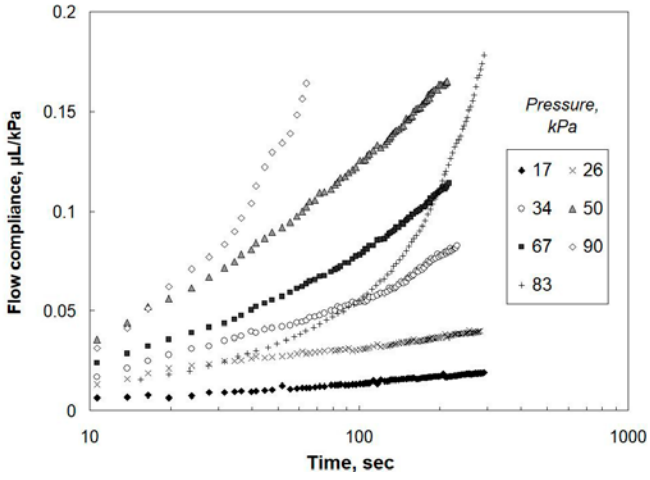

Fig. 1. Normalized extruded gel volume (µL) per applied pressure (kPa) for acrylic gel

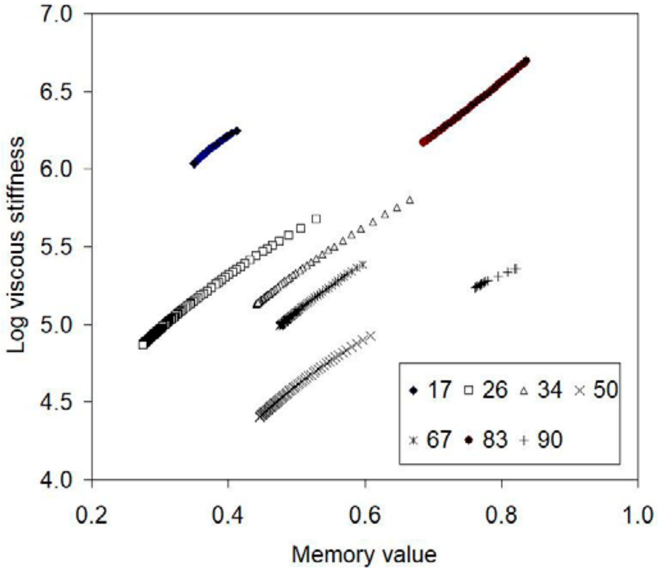

Fig. 2. Logarithm of viscous stiffness of the gel in the syringe vs. invariant material memory values

The presented method can determine invariant values and use them in the model-free prediction of 3D bioprinting processes, depending on the nozzle, geometry, pressure, time and other process conditions, without the need to determine the ink rheological parameters separately. The BEST method generates "first-hand" data for further predictive modeling of the 3D printing process and applies the same philosophy for characterization of the 3D-printed tissues and constructs.

Summary

The developed approach demonstrates the capability to “see invisible” features of the materials and their interactions with the stimuli and environment. This way,

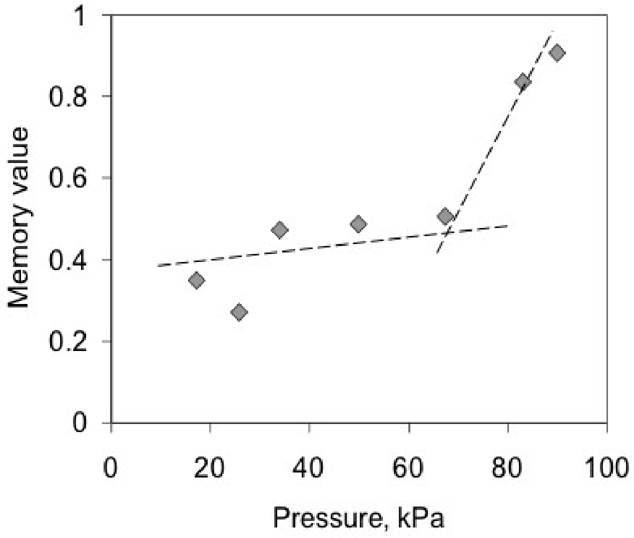

Fig. 3. Steady memory value of the gel vs. applied injection pressure

dynamic-mechanical analysis (DMA) can provide much more information than the elastic moduli and loss tangent. Using BEST processing, one can obtain many readouts for various purposes (in some cases, even from a single specimen or test). For example, it is possible to obtain the aggregate modulus; characteristic Deborah time; creeping compliance; effective fluid diffusivity and permeability/permittivity; equivalent channel size for the fluid flow in dynamics; material memory value; swelling pressure; and more within a single experiment. And this goes beyond just biomaterials, as the BEST application is model-free and does not require any fitting parameters; further, it can also be applied to test data already created.

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The Author

Prof. Dr. Michael Gasik from Aalto University in Finland (Department of Chemical and Metallurgical Engineering) began working in thermal analysis applications in 1985 and has been collaborating with NETZSCH-Gerätebau GmbH for almost that long.

His focus has been on materials for high-temperature applications and for hydrogen technology. Since 2000, he has been actively working with biomaterials, medical devices and regenerative medicine applications. In 2019, he was appointed as the Ambassador of the European Orthopedic Research Society.

Prof. Michael Gasik is a co-founder of Seqvera Ltd. and inventor of the BEST method – Biomaterials Enhanced Simulation Testing – which has been implemented for the first time in NETZSCH DMA equipment.

One focus point of the research activities of Prof. Gasik is the determination of the mechanial properties of biomaterials. In this context, he uses DMA data generated with a NETZSCH DMA as a basis for further calculations to characterize these materials.

Safety First! – During the Production, Transport and Storage of Chemicals

Dr. Gabriele Kaiser, Business Field Management for Pharmacy, Cosmetics & Food

Fig. 1. ARC® 305

Wherever larger amounts of chemicals are handled, thermal events may occur under unfavorable conditions, resulting in fires, deflagrations or even explosions. Detailed risk analysis of the methods and production plant is therefore very important, in order to identify and assess such risks and thus derive suitable measures for minimizing them.

In chemical process safety, it is mainly adiabatic calorimeters that are used to measure undesired reactions such as the degradation of reactants or the unintentionally fast progression of a reaction. The newly revised ARC® 305 (Figure 1) by NETZSCH offers comprehensive possibilities to this end.

Exothermal Reactions Release Heat

Chemical reactions always proceed of their own accord when their energy balance – starting from the reactants – is negative overall. In other words, after overcoming an energy barrier – the so-called activation energy, or E_a – the products are at a lower energy level than the reactants. Catalysts (situation 2 in Figure 2) usually lower the activation energy. If the excess energy produced is released in the form of heat, the corresponding process must be cooled.

What Happens if the Generated Heat Cannot be Entirely Discharged?

If the heat of reaction generated within a vessel (synthesis reactor, silo, etc.) cannot be dissipated quickly enough to the environment – due, for example, to a failure of the cooling system – there will be a risk of local overheating. As a result, the speed of the reaction taking place is increased which, in turn, produces more heat and further increases the speed of reaction, etc. This process is called thermal runaway and has been responsible for a number of accidents in the chemical industry over past decades. In China alone, 271 events due to thermal runaway reaction were recorded between 1984 and 2019 [1].

Worst-Case-Scenario

In order to experimentally determine the hazard potential of a substance, measurements are carried out under adiabatic conditions; i.e., under conditions that do not allow for any (or almost any) heat exchange with the environment. Such tests under the "worst" possible circumstances can be used to simulate the situation of, for example, a beginnng decomposition reaction inside a tanker.

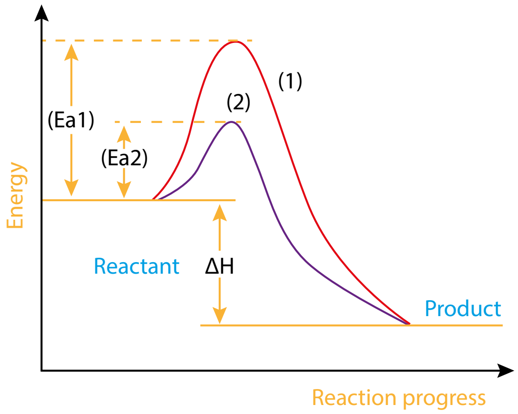

Fig. 2. Schematic course of an exothermal reaction (1) without catalyst and (2) with catalyst

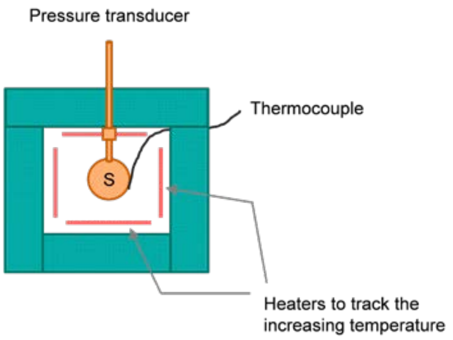

Fig. 3. Schematic setup of an adiabatic calorimeter

ARC® = Accelerating Rate Calorimeter

Accelerating Rate Calorimeters are capable of realizing such near-adiabatic conditions. To this end, the sample container with the sample is located in a closed chamber which is equipped with heaters on the bottom, on the side walls and on the lid. These heaters ensure that the temperature inside the calorimeter (within the green area in Figure 3) matches the temperature measured on the outside of the sample container. The crucial term in this relationship is temperature tracking: If the temperature in the sample vessel increases, the temperature of the environment must also increase.

Since the temperature increase in the sample during thermal runaway occurs very quickly, the heaters must be capable – with the aid of a sophisticated control system – of reacting very quickly and also of increasing the temperature correspondingly quickly. The ARC® 305 is capable of tracking up to 200 K/min.

Key Parameters Like TMR and T_{D24} as a Result

Accelerating Rate Calorimeters by NETZSCH can be employed for the thermal analysis of solid or liquid substances as well as for gas/liquid, liquid/liquid, gas/solid and liquid/solid mixtures; also, they can be used for the process simulation of batch and semi-batch reactions or fire exposure, and for the measurement of physical properties.

In connection with safety investigations, it is primarily Heat-Wait-Search tests (Figure 4) that are applied. This refers to the stepwise heating of the sample (each followed by a waiting and verification phase of the sample temperature) until the self-heating rate exceeds a defined threshold. The system then switches to the adiabatic mode. The temperature and pressure development are recorded. With the help of the temperature increase observed, ΔT_{obs}*, the ideal temperature increase in the adiabatic case, ΔT_{ad}, can be determined, taking the thermal inertia (also called Φ factor) into account. If the specific heat capacity of the sample is known, the heat of reaction (e.g., decomposition enthalpy) can be calculated [2].

TMR stands for Time-to-Maximum-Rate and refers to the time between the start of the thermal runaway and the maximum reaction rate (the maximum self-heating rate). In order to adapt the experimental results as closely as possbile to real conditions, the influence of the sample container must be eliminated to the greatest possible extent. This can either be done experimentally or mathematically (with the NETZSCH *Proteus®* software) by reducing the thermal inertia to 1. T_{D24} ultimately specifies the temperature at which the TMR value is 24 hours.

Literature

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[2] ASTM E1981-22, Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry

*The index obs stands for observed

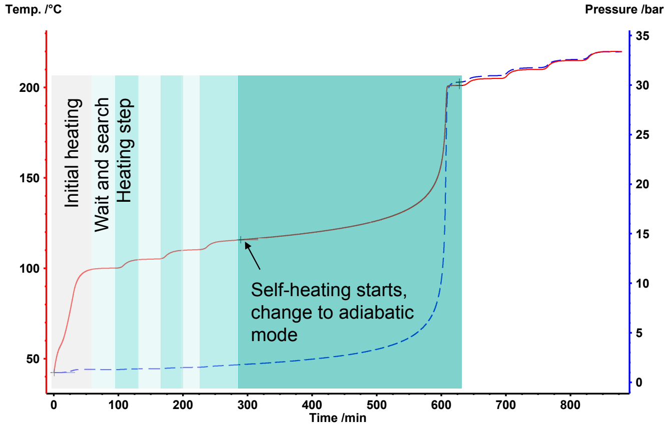

Fig. 4. Heat-wait-search test

Thermophysical Property Evaluation Techniques for Thin Films and Interfaces

Kazuko Ishikawa, Nano Technology Business Field Manager

Fig. 1. Thermal analysis systems for thin films *NanoTR*

Heat is looming ever larger over IoT. Heat from highly integrated and fast electronics threatens electronics with failure, malfunctions, and shorter life spans. In order to realize higher performance, longer life, lower energy consumption, and improved reliability and stability of devices, it is important to optimize thermal design and simulation by understanding the flow, spread, and temperature distribution of heat generated inside. Since state-of-the-art electronics and electronic devices are composed of multilayer thin films, it is essential to measure the thermophysical properties of such thin films.

Our *NanoTR* and *PicoTR* thermal analysis systems for thin films are the world's first analyzers to provide high-precision measurements of the thermophysical properties of metallic, oxide, organic and other films. These analyzers enable rapid and highly precise measurements of

- thermal diffusivity
- thermal effusivity
- thermal conductivity
- and interfacial thermal resistance

for films ranging from several nanometers to several tens of micrometers in thickness, formed on any substrate.

Our advanced measurement technologies are commercial versions of technologies developed by the National Metrology Institute of Japan (NMIJ) of the National Institute of Advanced Industrial Science and Technology (AIST).

Pulsed Light Heating Thermoreflectance Method

The pulsed light heating thermoreflectance method is a measurement technique for determining the thermal diffusivity or thermal effusivity of a thin film in the direction of the film thickness by instantaneously heating a thin film sample on a substrate with a pulsed laser and measuring the rate of increase in back surface temperature or decrease in surface temperature due to heat diffusion inside the film.

The response speed is an order of magnitude faster than thermocouples, resistance thermometers, and radiation thermometers and ultra-fast temperature measurement, close to the pulse width of laser light, can be realized.

Thermal Analysis System for Thin Films: *NanoTR* and *PicoTR*

The *NanoTR* is shown in Figure 1 and the *PicoTR* is shown in Figure 2. *NanoTR* uses nanosecond pulsed light, while *PicoTR* uses femtosecond pulsed light to instantaneously heat one side of the thin film and observe the induced ultrafast temperature response, which can be measured with a time resolution of 1 picosecond (for *PicoTR*). Both systems are equipped with two modes of the pulse light heating thermoreflectance method: rear heating / front detection (RF) mode and front heating / front detection (FF) mode, making it possible to measure various thin films formed on any substrate.

Fig. 2. Thermal analysis systems for thin films *PicoTR*

NanoTR and *PicoTR*

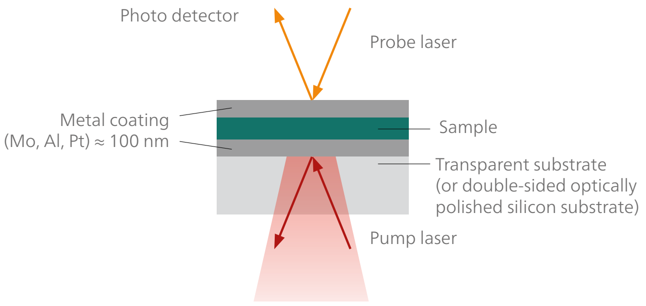

Fig. 3 a). RF mode

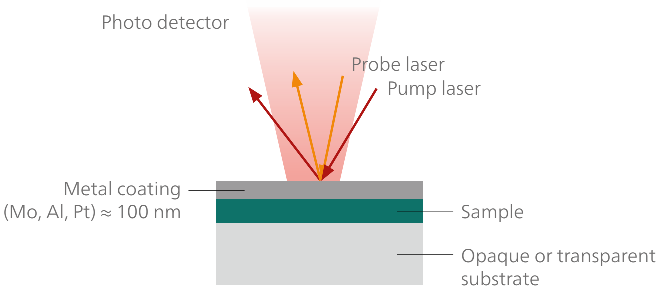

Fig. 3b). FF mode

RF and FF Modes

Figures 3a) and b) show the configuration of the RF mode and FF mode. The RF mode is used to measure thin films deposited on transparent substrates such as glass substrates or silicon wafers that are optically polished on both sides. This arrangement is, in principle, identical to the laser flash method, which is the standard method for measuring the thermal diffusivity of bulk materials. By measuring the heat diffusion time in the film thickness direction of the thin film, the thermal diffusivity can be obtained with low uncertainty.

On the other hand, for thin films on opaque substrates that cannot be heated from the back, the FF mode can be used to measure the thermal effusivity from the surface temperature drop.

Traceability to National Standards and Establishment of JIS Standards

The reliability of this measurement has been verified by NMIJ CRM5808-a (400-nm Molybdenum film) and CRM5810-a (500-nm Titanium Nitride film), which are certified reference materials supplied by AIST as national standards. In 2011, JIS* standards (JIS R 1689 and JIS R 1690) were also established for these measurement techniques.

Thermophysical Properties of AlN Films

Aluminum nitride (AlN) is a material with excellent electrical insulation properties and very high thermal conductivity comparable to metals; it is expected to be applied as a thin film for heat dissipation in thin-film devices.

Figure 4 shows a two-layer sample of AlN film coated with 100 nm Molybdenum (Mo) on quartz glass, measured in the FF mode of the *PicoTR*; the thickness of the AlN film was varied from 100 nm to 400 nm. For the FF mode analysis, the *PicoTR* thermal simulator is used, which can analyze the thermophysical properties of up to three-layer structures and take into consideration the interface thermal resistance of each layer and the thermal conductivity of the substrate.

*Japanese Industrial Standard

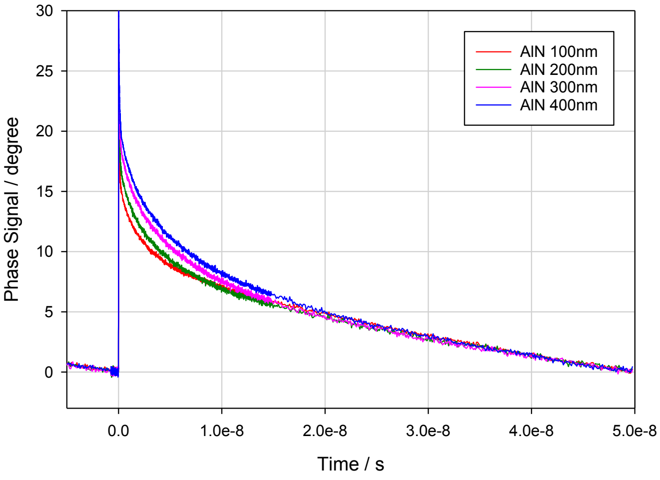

Fig. 4. Measurement result for the AlN film (measured by *PicoTR* in FF mode)

NanoTR and PicoTR

Table 1. Analysis results for the AlN film measurements

Sample	Mo / AlN Interfacial thermal resistance $R_{m\text{-}f}$ $m^2·K/W$	AlN Thermal effusivity b_f $J/(m^2s^{0.5}K)$	AlN Effective thermal conductivity λ $W/(m·K)$	AlN/Glass Interfacial thermal resistance $R_{f\text{-}s}$ $m^2·K/W$
AlN 100 nm	2.0×10^{-9}	3268	4.9	1.0×10^{-9}
AlN 200 nm	2.0×10^{-9}	3367	5.2	1.0×10^{-9}
AlN 300 nm	2.5×10^{-9}	3399	5.3	1.0×10^{-9}
AlN 400 nm	2.5×10^{-9}	3464	5.5	1.0×10^{-9}

The results of the analysis are shown in table 1. It can be seen that there is a contribution of interfacial thermal resistance between the Mo and AlN films. A slight thickness dependence of the AlN film was also observed.

Evaluation of Interfacial Resistance Between Mo and ITO

To evaluate the interface that occurs at the contact surface of different materials, it is possible to calculate the interfacial thermal resistance between the layers by measuring multiple three-layer samples with different thicknesses of the film.

For example, in Mo/ITO*/Mo three-layer samples deposited on a quartz glass substrate, samples are prepared by changing the thickness of the ITO film to 10 nm, 20 nm, and 30 nm. The thickness of the Mo film on both sides is 100 nm. ITO is an essential material for liquid crystal displays and touch panels. It is a conductive thin film material with 80% transmittance in the visible range.

Each sample is measured by the RF method of *PicoTR*, and the heat diffusion time of the entire three-layer film is obtained. Figure 5 shows the results for the measurement of each sample. The temperature history curves obtained were fitted with a theoretical equation to obtain the heat diffusion time of the entire three-layer film, and the thermal diffusivity of the ITO film and

*Indium Tin Oxide

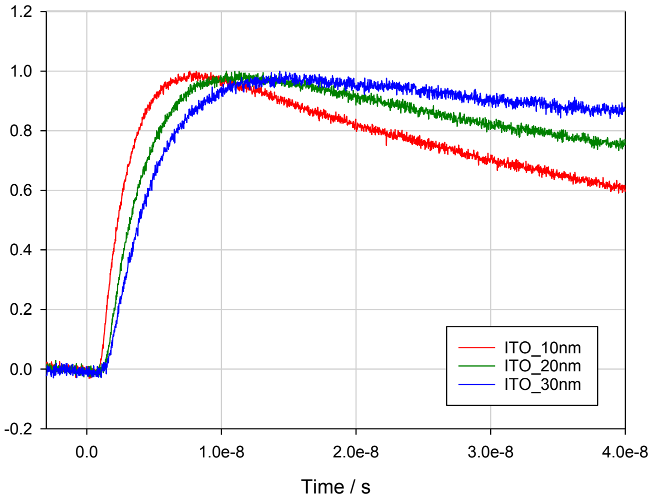

Fig. 5. Measurement result for Indium Tin Oxide, ITO film (measured by *PicoTR* in RF mode)

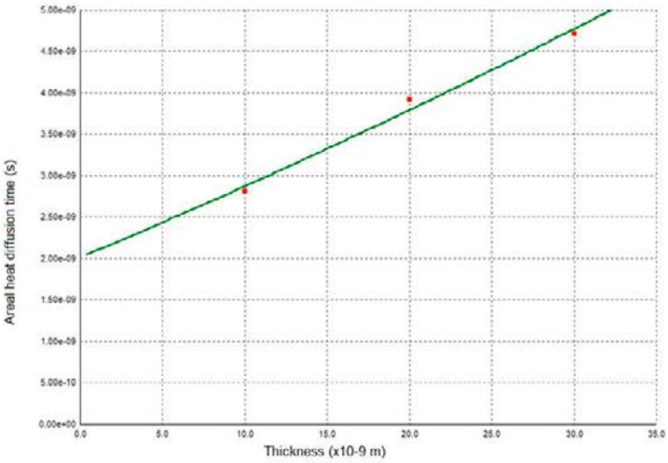

Fig. 6. Relationship between the thickness of the ITO layer and areal heat diffusion time

Table 2. Analysis results for the ITO film measurements

	Mo / ITO / Mo	**ITO**	**ITO**	**Mo / ITO**
Sample	**Areal heat diffusion time** τ_f **s**	**Thermal diffusivity** k_z $\mathbf{m^2/s}$	**Effective thermal conductivity** λ **W/(m·K)**	**Interfacial thermal resistance** R_z $\mathbf{m^2 \cdot K/W}$
ITO 10 nm	2.81×10^{-9}	7.03×10^{-7}	1.7	6.36×10^{-9}
ITO 20 nm	3.93×10^{-9}			
ITO 30 nm	4.71×10^{-9}			

interfacial thermal resistance between the ITO and Mo films were calculated by three-layer film analysis of the area using the heat diffusion time method. From Figure 6, the thermal diffusivity of the ITO film was calculated to be 7.0×10^{-7} m²/s, and the interface thermal resistance between the ITO and Mo films was 6.4×10^{-9} m²·K/W (table 2).

The FF mode of the *PicoTR* measurement mode can also be used to evaluate the interfacial thermal resistance between the thin film and the substrate.

Summary

The pulsed light heating thermoreflectance method is one of the time-domain thermoreflectance (TDTR) methods. The *NanoTR* and *PicoTR* are equipped with an electrical delay system, which allows for a longer observation time than optical delay systems using an optical stage. Moreover, by using two high-speed pulsed lasers, ultrafast thermal diffusion phenomena can be observed and quantitatively evaluated. Both systems can measure a wide range of thin-film samples with low thermal conductivity to those with high thermal conductivity as introduced in this article.

We will continue to provide thermal solutions through reliable thermal measurement and analysis technology at the national standard level as well as the SI-traceable calibration technology.

References

[1] Analytical equations for rear heating/front detection using pulse thermoreflectance
Progress in Heat Transfer, New Series, Vol. 3 (The Japan Society of Mechanical Engineers), pp. 185, equation (3.70) (in Japanese)
[2] T. Baba, Jpn. J. Appl. Phys., 48 (2009) 05EB04-5, equation (24)
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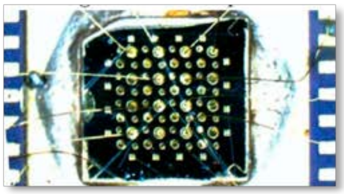
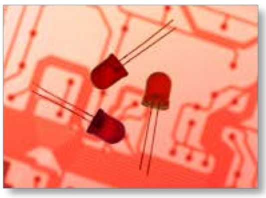
[4] T. Yagi et al., Proc.35th Jpn. Symp. Thermophys.Prop., (2014)
[5] T. Yagi et al., Proc.38th Jpn. Symp. Thermophys.Prop., (2017)





Next-Generation Energy Materials

Benchmarking Storage and Conversion Properties Using Thermal Analysis (Part 3)

Andrew Gillen, NETZSCH Australia Pty Ltd., and Dr. Michael Schöneich, Applications Laboratory

Introduction

In parts 1 (**on**set^{23}) and 2 (**on**set^{24}) of this series, we introduced Simultaneous Thermal Analysis and Evolved Gas Analysis, both conventional thermal analysis (TA) techniques for studying reactants and reaction products, widely applicable for applications in the energy materials sector.

Conventional TA is widely used for studying gas-solid reactions; however, it has the restriction of being limited mostly to isothermal or linear temperature segments. This approach cannot accurately describe the initial part of the reaction as the solid-gas interaction may begin during the dynamic heating step. Another difficulty met with conventional thermal analysis is interpreting experimental data where simultaneous reactions occur, or where the sample of interest contains a low percentage of reactive components. For example, oxide catalysts for solar thermal applications often lose weight upon heating due to reduction and dehydration processes.

*Pulse*TA

The Pulse Thermal Analysis method, *PulseTA* (see setup in Figure 1 and schematic in Figure 2) was introduced in the late 1990s by NETZSCH Analyzing & Testing to overcome many of the aforementioned difficulties

Fig. 1. *PulseTA* setup with a NETZSCH STA 449 ***F5** Jupiter*® and QMS 403 *Aëolos® Quadro*

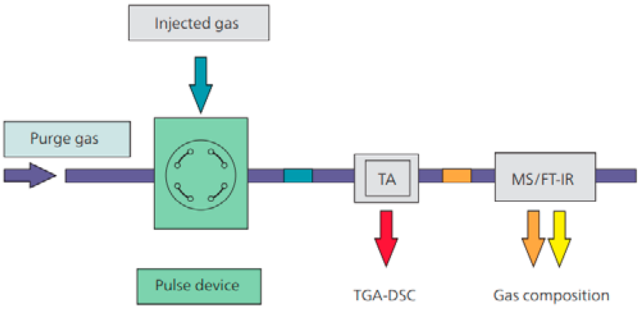
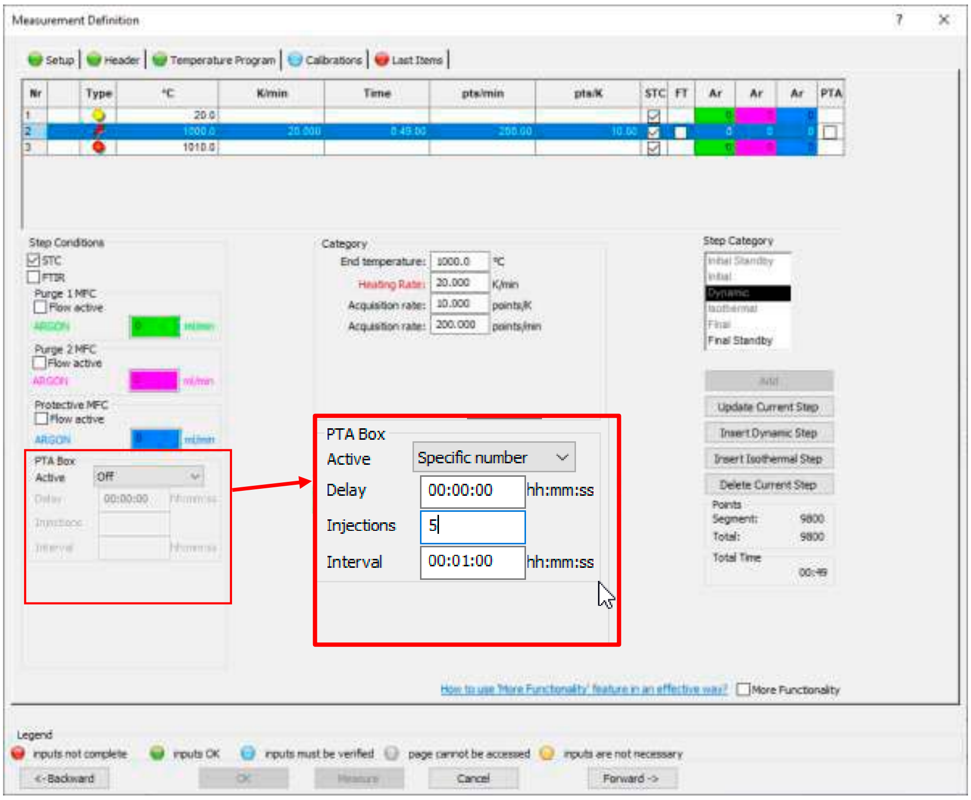


Fig. 2. NETZSCH *Pulse*TA schematic diagram



Nr		Type	°C	K/min	Time	pts/min	pts/K	STC	FT	Ar	Ar	Ar	PTA
1		●	20.0					☑		0	0	0	
2			1000.0	20.000	0:49:00	200.00	10.00	☑	☐	0	0	0	☐
3		●	1010.0					☑		0	0	0	

Step Conditions
☑ STC
☐ FTIR
Purge 1 MFC
☐ Flow active
ARGON 0 ml/min
Purge 2 MFC
☐ Flow active
ARGON 0 ml/min
Protective MFC
☐ Flow active
ARGON 0 ml/min
PTA Box
Active Off
Delay 00:00:00 hh:mm:ss
Injections
Interval hh:mm:ss

Category
End temperature: 1000.0 °C
Heating Rate: 20.000 K/min
Acquisition rate: 10.000 points/K
Acquisition rate: 200.000 points/min

PTA Box
Active Specific number
Delay 00:00:00 hh:mm:ss
Injections 5
Interval 00:01:00 hh:mm:ss

Step Category
Initial Standby
Initial
Dynamic
Isothermal
Final
Final Standby

Points
Segment: 9800
Total: 9800
Total Time 00:49

Fig. 3. *PulseTA* is particularly advantageous for energy materials research, providing simultaneous mass change, gas identification and quantification capabilities.

The method, developed by Dr. Marek Maciejewski and Prof. Alfons Baiker [1], significantly increases the sensitivity of thermoanalytical measurements and is based on the injection of a specific amount of the gaseous reactant into an inert carrier gas stream. Changes of mass, enthalpy and gas composition resulting from the reaction progress are monitored throughout the experiment. The setup can be programmed to allow the desired reaction temperature to be reached and maintained under inert atmosphere. Well-defined pulses of reactive gas (e.g., hydrogen) can be introduced as desired, controlled by the NETZSCH *Proteus®* software (ref. Figure 3). Between gas pulses the reaction stops, thus providing the opportunity for ex-situ analysis of sample properties as the reaction progresses (e.g., by powder X-ray diffraction) [1].

*Pulse*TA is particularly advantageous for energy materials research, as it provides simultaneous mass change and gas composition data when examining adsorption / desorption processes. This allows quantification of the gas adsorbed, determination of the temperature range of the desorption and the identification of the desorbed species. Separation of simultaneously occurring reactions can be achieved by programming specific temperatures for the chemical reaction. Applications fields include catalysis (TPR, TPO, TPD)*, redox looping, kinetic analyses and more. The *Pulse*TA method can also be used for calibrating the MS signal, thereby making it possible to have accurate quantification of TA-MS signals (<0.01wt%).

Today, STA 449 *Jupiter®*, STA 2500 *Regulus* and TG 209 ***F1** Libra®* instruments can be equipped with the *Pulse*TA coupling extension for FT-IR or mass spectrometer (e.g., *Aëolos® Quadro*).

*TPR: Temperature Programmed Reduction
*TPO: Temperature Programmed Oxidation
*TPD: Temperature Programmed Desorption

*Pulse*TA

Example 1: Temperature-Programmed Reduction of a Metal Oxide by *Pulse*TA

Temperature programmed reduction (TPR) is a technique used to study the reduction behavior of metal oxides with a reducing gas like hydrogen. In this process, the metal oxide is heated to a high temperature while being exposed to a flow of hydrogen gas. The temperature is then gradually increased while monitoring the mass change and gas composition to determine the temperature at which reduction of the metal oxide occurs. This kind of dynamic approach often lacks in the possibility to see small changes within the kinetic processes, especially at the beginning of the reduction process. In this case, the *Pulse*TA technique can provide valuable information about the kinetics of gas-solid reactions and the reaction mechanisms involved.

For example, let's consider the reduction of natural iron oxide with hydrogen gas at 1000°C (refer to Figure 4). At the beginning of the experiment, a sample of Fe_2O_3 is loaded into an STA and heated to 1000°C under a flow of inert argon gas. The initial heating of the sample leads to the decomposition of impurities such as hydroxides.

Once the sample reaches 1000°C, small pulses of hydrogen gas (1 ml each) are periodically injected into the STA (black curve). These gas pulses result in periodic changes in the gas composition, eventually leading to a stepwise reduction of the iron oxide. This leads to distinct mass loss steps (green curve) accompanied by the release of the generated water (blue curve).

Each step can be considered as an individual solid-gas reaction, providing valuable insights into each reaction step's distinct behavior. It enables the observation and analysis of even subtle signal variations, for example, mass change differences as small as 0.01%. This allows even minor changes in the reaction kinetics, such as surface layer passivation, to be observed and studied.

Example 2: Quantification of CO_2 Release in a Reaction Using *Pulse*TA

*Pulse*TA is an effective tool for performing a rapid and uncomplicated calibration of gas analyzers such as mass spectrometers. This is accomplished by injecting a precise volume of calibration gas into the gas flow of the thermal analyzer using *Pulse*TA, which is then detected by the gas analyzer. By knowing the amount injected and measuring the signal response, it is straightforward to establish a signal correlation that serves as the foundation for quantifying unknown amounts that are released during the reaction.

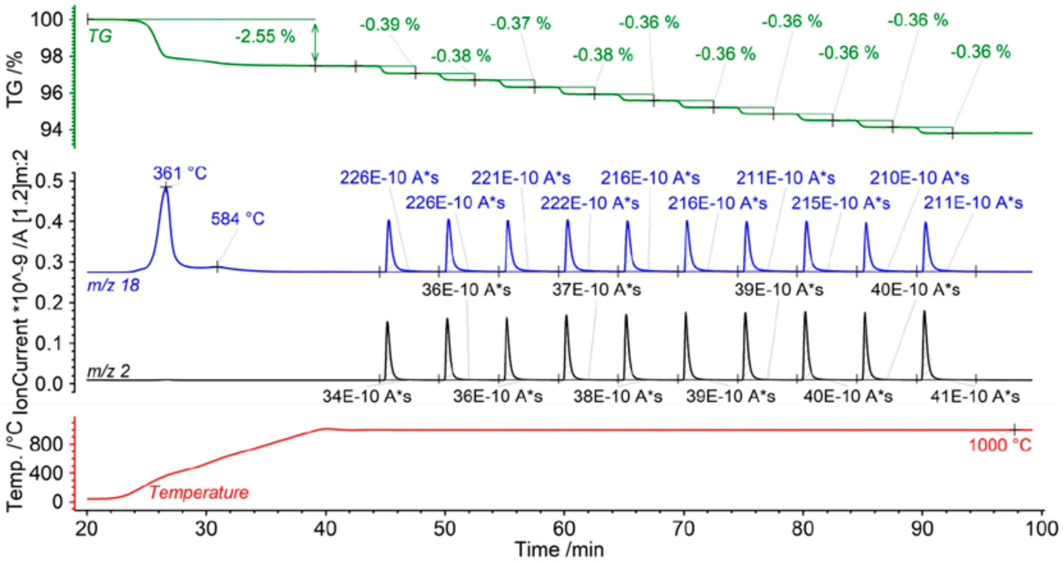


Fig. 4. STA and *Pulse*TA measurements on an Fe_2O_3 sample

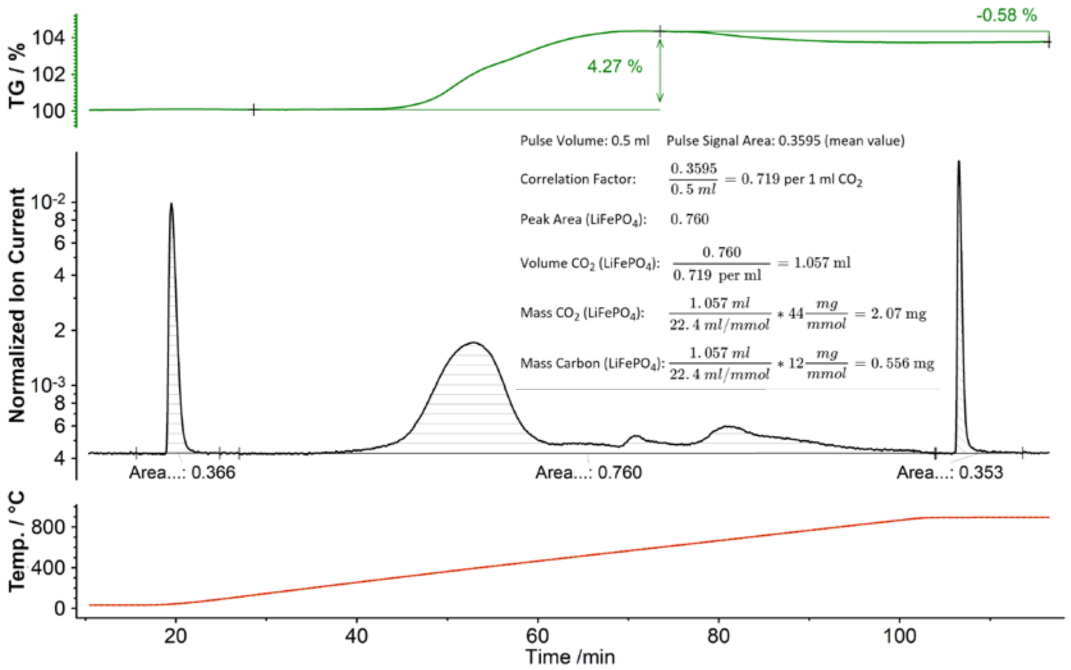


Fig. 5. TGA and *Pulse*TA measurement on an $LiFePO_4$ sample; see details in our application Note 240

For instance, in the case of $LiFePO_4$ materials with carbon-based surface coatings, the oxidative nature of $LiFePO_4$ material makes it impossible to determine the carbon content by a simple TGA analysis under an air atmosphere (Figure 5). The reason for this is that the oxidation of the $LiFePO_4$ material overlaps with the burning of the carbon surface coating, which prevents precise determination of the carbon-related mass loss (green curve in Figure 5) .

However, due to the nature of the sample, the ion current signal of m/z 44 (black curve) can be uniquely attributed to carbon dioxide, providing a basis for quantifying the carbon content. With the assistance of *Pulse*TA, a simple correlation between the signal response of a single pulse and its CO_2 content can be established. This approach can even be integrated within the sample measurement like an internal standard. By applying the obtained correlation factor to the signal response of the $LiFePO_4$ material, the CO_2 release amount can be calculated, which can then be used to determine the carbon content.

Conclusion

In **on**set[23] and **on**set[24], we demonstrated the benefits of using conventional thermal analysis and evolved gas analysis methods for benchmarking energy materials. In this section, we noted several limitations of conventional TA approaches, and how the *Pulse*TA approach can be used to overcome these.

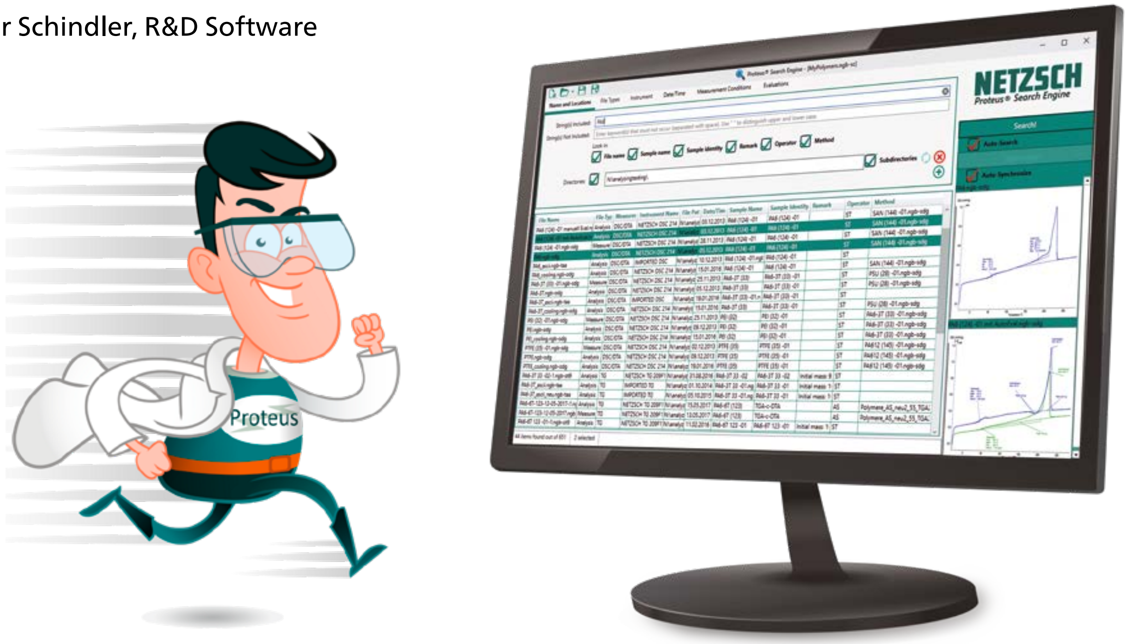
Namely, for solid-gas reactions, *Pulse*TA eliminates the chance of the reaction starting on the heating segment prior to reaching the isothermal segment. *Pulse*TA also improves the sensitivity of thermoanalytical measurements, particularly important in cases where there are low volumes of reactants present in the sample. Finally, *Pulse*TA is a convenient, easy-to-use platform for calibrating evolved gas analyzers (e.g., QMS 403 *Aëolos® Quadro*) and quantifying gaseous reaction products, as described in example 2.

References

[1] . M. Maciejewski et al., Thermochimica Acta 295 (1997), 167

Powerful Data Management with *Proteus® Search Engine*

Dr. Alexander Schindler, R&D Software



Do you carry out lots of measurements and create numerous analysis states – maybe even for many different projects? One way or another, quick and selective access to your data is the key to powerful data management. *Proteus® Search Engine* (*PSE*) is a new tool with which to efficiently search for and quickly find your measurements and analysis states in the file system – either locally or in the network!

What Is *Proteus® Search Engine*?

The *PSE* application can be regarded as a special and powerful file explorer for NETZSCH thermal analysis measurements and analysis states. Currently, measurements of type DSC/DTA, TGA, STA, DIL/TMA, DMA and DEA are supported. This tool is available beginning with *Proteus®* 9.0 and is started from the "Assistant" as the central launcher for NETZSCH *Proteus®* applications. As can be seen from the screenshot shown in Figure 1, file names are clearly displayed in a list according to directories and filter criteria selected by the user.

These user-defined properties can be stored as a "search". Users can create custom searches, for example "MyPolymers", "AllMyLocalFiles", "MyProjects_2023", etc., and can switch easily between different existing searches.

Files shown can be sorted alphabetically by such categories as file or sample name. Graphs of measurements or analysis states can be displayed as a small preview or – with a single click – enlarged in a separate window. The corresponding folders in the file system, where the selected data is located, can also be opened with a single click. It is also possible to directly open selected files in *Proteus®* analysis via the right mouse button.

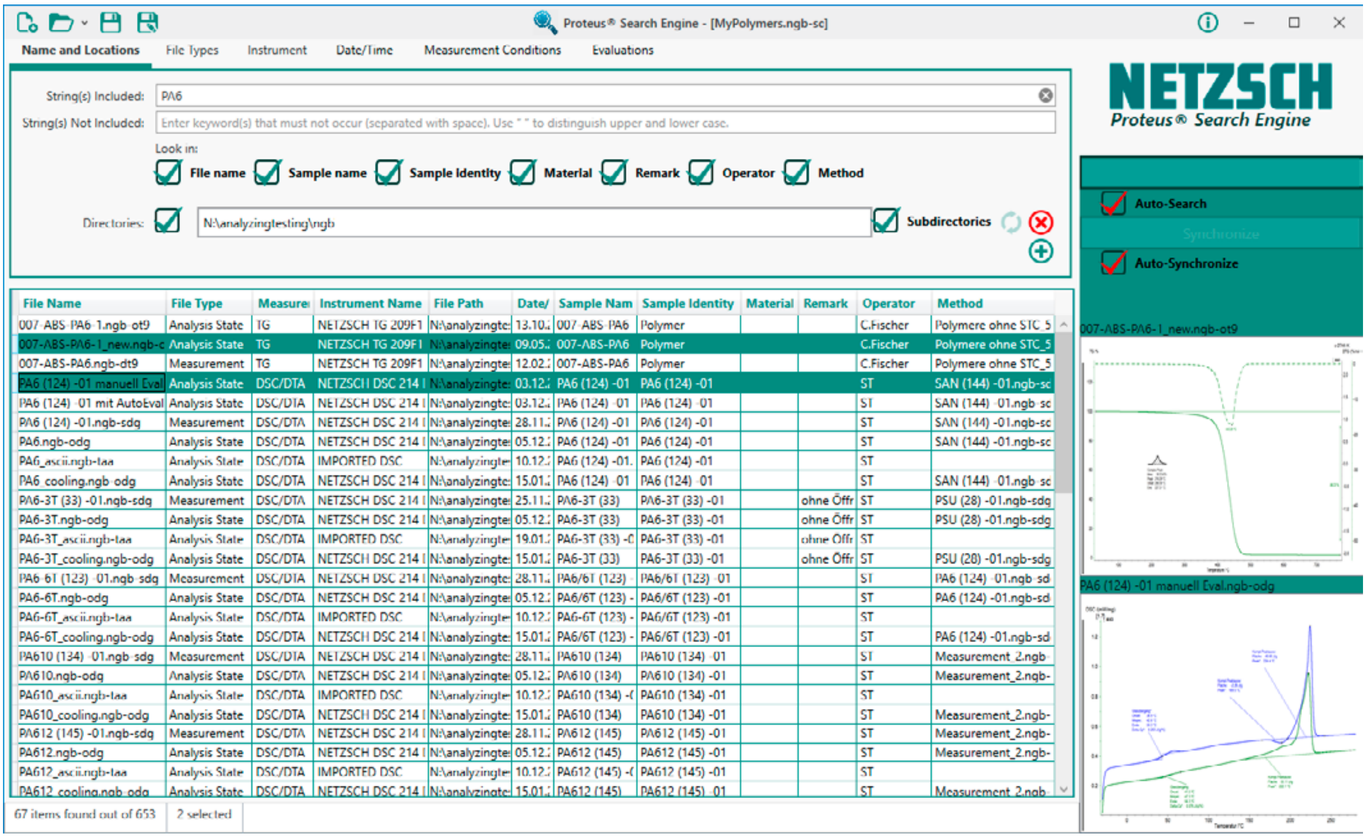
Synchronization Lends Speed

Unlike a conventional file explorer, *PSE* synchronizes with the selected search directories and uses database technology in the background. Once the directories are synchronized, all information required for searching and finding is available in-situ. This allows the search results to be shown immediately – even after switching to a completely different search. Full synchronization of, for example, a new directory can be carried out on demand in the background, and Auto-Synchronization makes sure that any changes such as additional measurements are detected automatically.

Proteus® Search Engine

Filtering Lends Power

When working with measurement and evaluation data for different materials and different measurement setups, it is tremendously helpful to be able to sort data by certain filter criteria. Those filter criteria are "strings" (sets of keywords) – for example, in file names, sample names/identity, material, remarks, and operator. The string "PA6" was used for the search shown in Figure 1. But other items can also serve as filter criteria, including file types (see Figure 2), instrument names, a range of date and time, and measurement conditions such as heating rate or sample mass.



String(s) Included: PA6

String(s) Not Included: Enter keyword(s) that must not occur (separated with space). Use " " to distinguish upper and lower case.

Look in: ☑ File name ☑ Sample name ☑ Sample Identity ☑ Material ☑ Remark ☑ Operator ☑ Method

Directories: ☑ N:\analyzingtesting\ngb ☑ Subdirectories

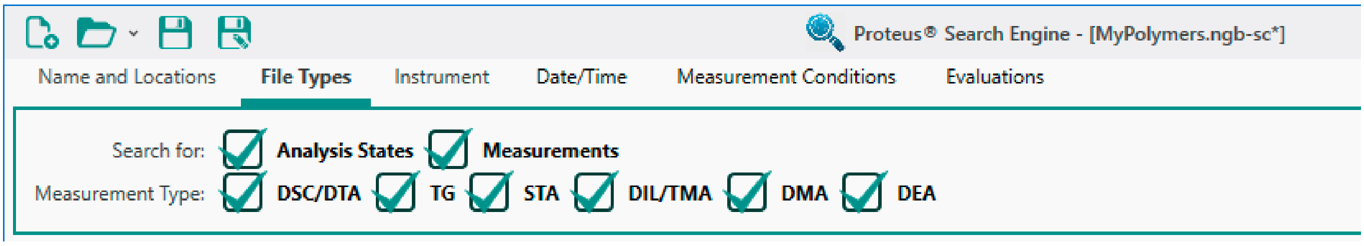
☑ Auto-Search

☑ Auto-Synchronize

File Name	File Type	Measure	Instrument Name	File Path	Date/	Sample Nam	Sample Identity	Material	Remark	Operator	Method
007-ABS-PA6-1.ngb-ot9	Analysis State	TG	NETZSCH TG 209F1	N:\analyzingte	13.10.	007-ABS-PA6	Polymer			C.Fischer	Polymere ohne STC_5
007-ABS-PA6-1_new.ngb-c	Analysis State	TG	NETZSCH TG 209F1	N:\analyzingte	09.05.	007-ABS-PA6	Polymer			C.Fischer	Polymere ohne STC_5
007-ABS-PA6.ngb-dt9	Measurement	TG	NETZSCH TG 209F1	N:\analyzingte	12.02.	007-ABS-PA6	Polymer			C.Fischer	Polymere ohne STC_5
PA6 (124) -01 manuell Eval	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	03.12.	PA6 (124) -01	PA6 (124) -01			ST	SAN (144) -01.ngb-sc
PA6 (124) -01 mit AutoEval	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	03.12.	PA6 (124) -01	PA6 (124) -01			ST	SAN (144) -01.ngb-sc
PA6 (124) -01.ngb-sdg	Measurement	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	28.11.	PA6 (124) -01	PA6 (124) -01			ST	SAN (144) -01.ngb-sc
PA6.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	05.12.	PA6 (124) -01	PA6 (124) -01			ST	SAN (144) -01.ngb-sc
PA6_ascii.ngb-taa	Analysis State	DSC/DTA	IMPORTED DSC	N:\analyzingte	10.12.	PA6 (124) -01.	PA6 (124) -01			ST	
PA6_cooling.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	15.01.	PA6 (124) -01	PA6 (124) -01			ST	SAN (144) -01.ngb-sc
PA6-3T (33) -01.ngb-sdg	Measurement	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	25.11.	PA6-3T (33)	PA6-3T (33) -01		ohne Öffr	ST	PSU (28) -01.ngb-sdg
PA6-3T.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	05.12.	PA6-3T (33)	PA6-3T (33) -01		ohne Öffr	ST	PSU (28) -01.ngb-sdg
PA6-3T_ascii.ngb-taa	Analysis State	DSC/DTA	IMPORTED DSC	N:\analyzingte	19.01.	PA6-3T (33) -0	PA6-3T (33) -01		ohne Öffr	ST	
PA6-3T_cooling.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	15.01.	PA6-3T (33)	PA6-3T (33) -01		ohne Öffr	ST	PSU (28) -01.ngb-sdg
PA6-6T (123) -01.ngb-sdg	Measurement	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	28.11.	PA6/6T (123)	PA6/6T (123) -01			ST	PA6 (124) -01.ngb-sd
PA6-6T.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	05.12.	PA6/6T (123) -	PA6/6T (123) -01			ST	PA6 (124) -01.ngb-sd
PA6-6T_ascii.ngb-taa	Analysis State	DSC/DTA	IMPORTED DSC	N:\analyzingte	10.12.	PA6-6T (123) -	PA6/6T (123) -01			ST	
PA6-6T_cooling.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	15.01.	PA6/6T (123) -	PA6/6T (123) -01			ST	PA6 (124) -01.ngb-sd
PA610 (134) -01.ngb-sdg	Measurement	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	28.11.	PA610 (134)	PA610 (134) -01			ST	Measurement_2.ngb-
PA610.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	05.12.	PA610 (134)	PA610 (134) -01			ST	Measurement_2.ngb-
PA610_ascii.ngb-taa	Analysis State	DSC/DTA	IMPORTED DSC	N:\analyzingte	10.12.	PA610 (134) -(	PA610 (134) -01			ST	
PA610_cooling.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	15.01.	PA610 (134)	PA610 (134) -01			ST	Measurement_2.ngb-
PA612 (145) -01.ngb-sdg	Measurement	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	28.11.	PA612 (145)	PA612 (145) -01			ST	Measurement_2.ngb-
PA612.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	05.12.	PA612 (145)	PA612 (145) -01			ST	Measurement_2.ngb-
PA612_ascii.ngb-taa	Analysis State	DSC/DTA	IMPORTED DSC	N:\analyzingte	10.12.	PA612 (145) -(	PA612 (145) -01			ST	
PA612_cooling.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214 I	N:\analyzingte	15.01.	PA612 (145)	PA612 (145) -01			ST	Measurement_2.ngb-

67 items found out of 653 | 2 selected

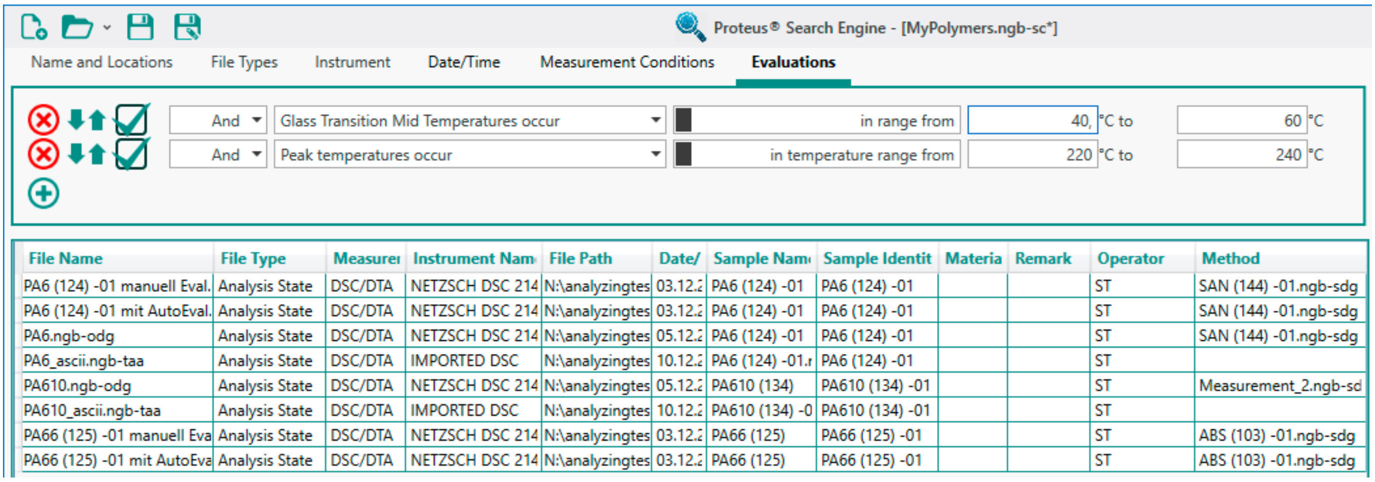
Fig. 1. Typical search result obtained with *Proteus® Search Engine*



Search for: ☑ Analysis States ☑ Measurements

Measurement Type: ☑ DSC/DTA ☑ TG ☑ STA ☑ DIL/TMA ☑ DMA ☑ DEA

Fig. 2. Filter criteria (here file and measurement types) of *Proteus® Search Engine*



Proteus® Search Engine - [MyPolymers.ngb-sc*]

And | Glass Transition Mid Temperatures occur | in range from 40, °C to 60 °C

And | Peak temperatures occur | in temperature range from 220 °C to 240 °C

File Name	File Type	Measurer	Instrument Nam	File Path	Date/	Sample Nam	Sample Identit	Materia	Remark	Operator	Method
PA6 (124) -01 manuell Eval.	Analysis State	DSC/DTA	NETZSCH DSC 214	N:\analyzingtes	03.12.2	PA6 (124) -01	PA6 (124) -01			ST	SAN (144) -01.ngb-sdg
PA6 (124) -01 mit AutoEval.	Analysis State	DSC/DTA	NETZSCH DSC 214	N:\analyzingtes	03.12.2	PA6 (124) -01	PA6 (124) -01			ST	SAN (144) -01.ngb-sdg
PA6.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214	N:\analyzingtes	05.12.2	PA6 (124) -01	PA6 (124) -01			ST	SAN (144) -01.ngb-sdg
PA6_ascii.ngb-taa	Analysis State	DSC/DTA	IMPORTED DSC	N:\analyzingtes	10.12.2	PA6 (124) -01.r	PA6 (124) -01			ST	
PA610.ngb-odg	Analysis State	DSC/DTA	NETZSCH DSC 214	N:\analyzingtes	05.12.2	PA610 (134)	PA610 (134) -01			ST	Measurement_2.ngb-sd
PA610_ascii.ngb-taa	Analysis State	DSC/DTA	IMPORTED DSC	N:\analyzingtes	10.12.2	PA610 (134) -0	PA610 (134) -01			ST	
PA66 (125) -01 manuell Eva	Analysis State	DSC/DTA	NETZSCH DSC 214	N:\analyzingtes	03.12.2	PA66 (125)	PA66 (125) -01			ST	ABS (103) -01.ngb-sdg
PA66 (125) -01 mit AutoEva	Analysis State	DSC/DTA	NETZSCH DSC 214	N:\analyzingtes	03.12.2	PA66 (125)	PA66 (125) -01			ST	ABS (103) -01.ngb-sdg

Fig. 3. Filter criteria (here specific evaluation results) of *Proteus® Search Engine*

And filtering according to evaluation results existing in analysis states allows one to search for particular measurements; for example, those originating from a particular material. This can be seen in Figure 3, where the occurrence of the glass transition and peak temperatures in certain temperature ranges reveals analysis states with measurements on the polymers PA6, PA610 and PA66 as search results.

Additional evaluations currently available are endo- and exothermic effects, peak areas and onset temperatures. Users can also define whether evaluations should be outside of defined temperature ranges; such outlier detection can serve as a tool for quality control!

What's the Difference between This and *Identify*?

Both *PSE* and the known *Identify* database system are tools for the searching and fast finding of measurements. However, whereas *PSE* incorporates only the user's data (found in the file system via synchronization), *Identify* contains user-added data as well as NETZSCH libraries with currenty up to 2500 measurements and literature data from various application fields.

Furthermore, only *Identify* offers automatic recognition of new "input" measurement curves. Both applications allow for sophisticated filtering and viewing of the measurement curves, but the overlaying of different curves is only possible in *Identify*. Another difference between *PSE* and *Identify* is that *PSE* is an independent *Proteus®* application, whereas *Identify* is incorporated into *Proteus®* analysis.

Summary

Finally, it should be noted that for each PC, the installation of a single instrument having the *Proteus® Search Engine* option is sufficient in order to fully use all its capabilities for all file types supported. This is the same philosophy as for *Identify*.

Influence of Sample Preparation on TGA Measurements with the Example of Copper Sulfate Pentahydrate

Martin Mühlbach, Technical Sales

Generally, a thermogravimetric measurement for determination of temperature-dependent mass changes is carried out according to the following sequences:

Sample preparation
→ Measurement
→ Data Evaluation
→ Interpretation

Sample handling and sample preparation can both influence the measurement and hence also the result. Such issues may include the way the sample is transported or stored, and the sample's state as well as the ways in which this state might be changed in preparation for the measurement. Furthermore, the chemical structure as well as the material's morphology can significantly influence the measurement process. It is therefore advantageous to have a lot of preliminary information about the substance to be tested in order to prepare samples correctly and to determine the measurement parameters.

Example: Copper Sulfate Pentahydrate

Copper sulfate pentahydrate, a copper salt of sulfuric acid, belongs to the sulfate group of substances. Five molecules of water are bound in its crystal structure. As crystal water-containing copper sulfate, it has a characteristic deep blue color.

When heated, the water molecules are released in several steps, leaving the colorless copper sulfate anhydrate or, in the higher temperature range, the reddish-brown copper(I) oxide (see Figure 1).

Measurement Results

Figure 2 shows the result of a thermogravimetric analysis in the temperature range between 30°C and 1000°C along with the 1st derivative of the TGA signal according to time (DTG).

Up to approximately 250°C, three mass-loss steps can be determined. The first two steps exhibit similar mass loss (around 14%), whereas the third step is only about half as high in comparison (7.5%). Looking at the substance's stoichiometry, it can be concluded that the first two steps are each due to the release of two molecules of water and the third step is due to the release of one molecule of water.

Mass-loss steps four and five, at approx. 730°C and 890°C, are due to the split-off of SO_3 as well as O_2.

$$CuSO_4 \cdot 5H_2O \xrightarrow{5H_2O\nearrow} CuSO_4 \xrightarrow{SO_3\nearrow} CuO \xrightarrow{O_2\nearrow} Cu_2O$$

Fig. 1. Release of the water molecules during heating of copper sulfate pentahydrate

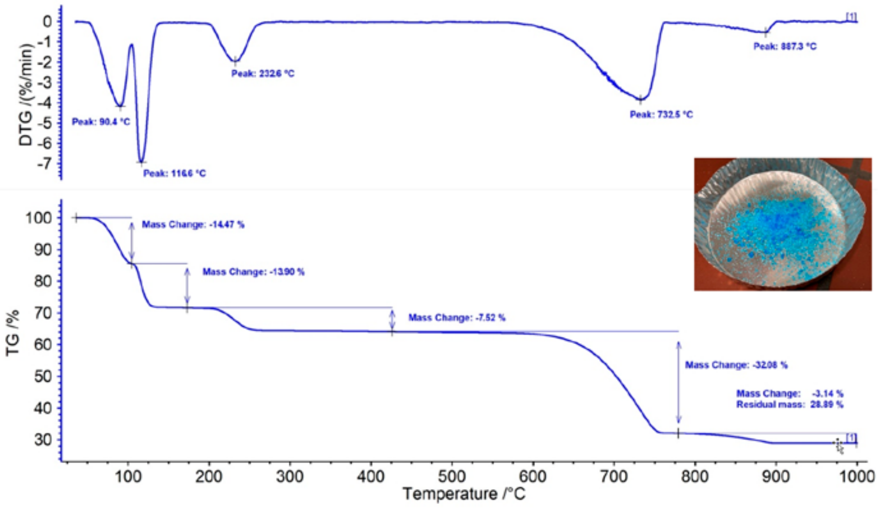


Fig. 2. TGA and DTG signals for copper sulfate pentahydrate, temperature range: 30°C to 1000°C; sample mass: 10 mg, heating rate: 10 K/min, atmosphere: nitrogen, measured with the TG 209 ***F1*** *Libra®*

Fig. 3. a) and b): Starting material of copper sulfate pentahydrate and c) as crushed powder in a mortar bowl

The material employed is a commercially available product supplied as crystalline granules with different particle sizes. Coarse particles > 1 mm are dark blue; fine particles < 1 mm are light blue (Fig. 3a) and b)). For TGA measurements, only a few milligrams are required, which makes it difficult to weigh in a representative quantity from the starting material. In these cases, dry grinding using a mortar is the best way to obtain homogeneous samples (Figure 3c)).

The optical differences are reflected in the TGA curves, depending on the particle size (Figure 4).

The evaluation of the thermograms shows a shift in the DTG peak toward lower temperatures with decreasing particle size. While the onset of the steps remains nearly the same, the temperature range of the mass-loss steps is reduced while their height remains the same. This means that the same amount of water is released much faster the smaller the particle size; or in other words, the smaller the crystals, the larger the free surface and the better the water molecules can be released.

This comparison shows how the sample amount, type of sampling and sample handling have an impact on the measurement result. Good and well-planned sample preparation is therefore always recommended.

Use of the Automatic Sample Changer

Whether your day-to-day lab work involves repetitive measurements for quality control or the processing of a variety of measurement orders, an automatic sample changer (ASC) offers much in the way of advantages and convenience. After preparation of the samples and definition of the measurement criteria, the measurements on the samples in the magazine are run completely autonomously. Both the ability to close the cover of the ASC magazine and the ability to purge with nitrogen can greatly reduce the influence of oxygen and humidity on the samples. However, what happens to samples that contain moisture, solvents or other volatile substances?

The following measurements were repeated on five samples (each approx. 11 mg, taken from the material in crushed form) by means of the ASC without purging

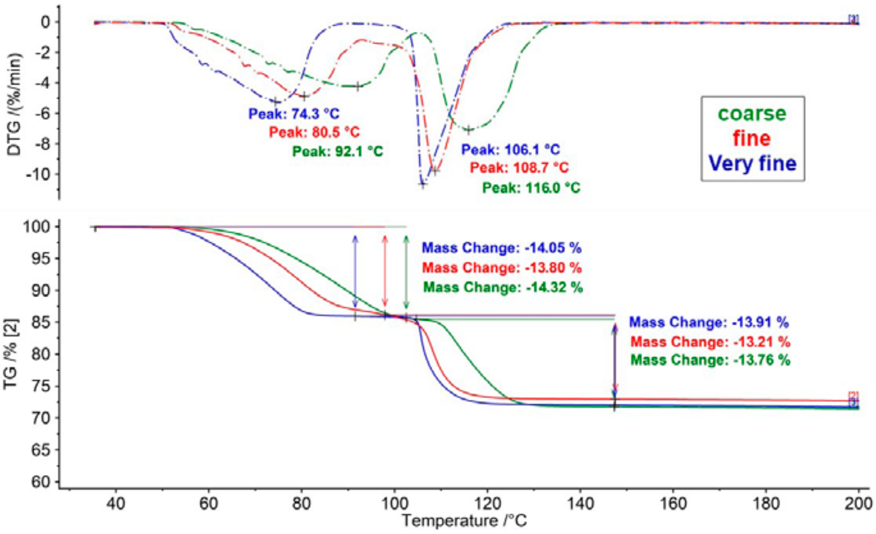


Fig. 4. TGA and DTG curves of the three samples with different particle size; coarse particles: green; fine particles: red; very fine particles (mortared): blue; temperature range: up to 200°C; atmosphere: nitrogen (40 ml/min); TG 209 ***F1*** *Libra*®

the ASC chamber. A comparison of the TGA curves reveals differences in the first mass-loss step in each case (Figure 5).

While the first sample (no. 1, green) exhibits a mass loss of 14%, the last sample (no. 5, purple), which was measured 8 hours after the first sample, shows a mass loss of only another approx. 3%. All subsequent steps are the same.

Since all five samples were prepared at the same time and positioned in the ASC, this indicates that an increased storage time leads to a reduction of the first mass-loss step. Associated with this, the DTG peak of the first step is shifted to lower temperatures, since the lower residual amount of water can be released faster (Figure 6).

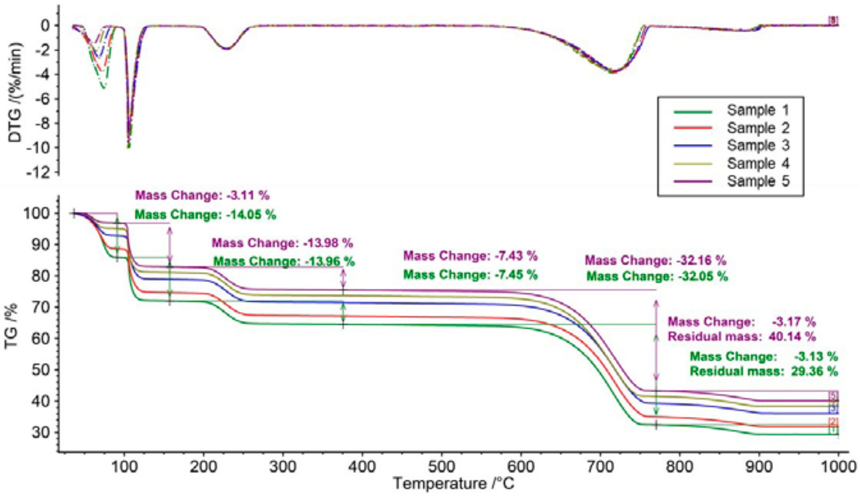


Fig. 5. TGA and DTG curves on five consecutively measured samples; measured up to 1000°C; sample mass: 11 mg; heating rate: 10 K/min; atmosphere: nitrogen (40 ml/min); TG 209 ***F1*** *Libra®* with ASC

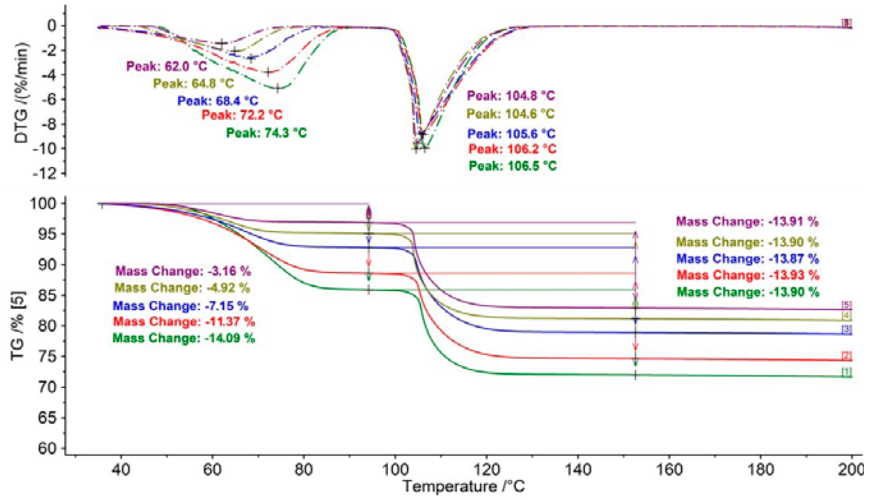


Fig. 6. TGA signals and DTG curves of five samples measured; temperature range: 30°C to 200°C; sample mass: 11 mg; heating rate: 10 K/min; atmosphere: nitrogen (40 ml/min); TG 209 ***F1*** *Libra®* with ASC.

This effect was only observed with the material crushed in the mortar. Repetitive measurements with the crystal particles of the starting material did not yield any difference over time. This confirms that crushing the material results in a continuous release of water molecules from the crystal structure at the particle surface.

Summary

Simple investigations can show the influence of the various effects of sample preparation, sample handling and material composition on the measurement result and help improve sample preparation.

We are happy to provide support in preparing SOPs (Standard Operating Procedures) and sample preparation. Contact us at ngb_laboratory@netzsch.com.

30 Years of NETZSCH-BRUKER

Thermal Analysis and FT-IR Spectroscopy – A Success Story for 30 Years

30 YEARS COOPERATION
NETZSCH
BRUKER

Fig. 1. Coupling of the STA 449 ***F1*** *Jupiter*® with the BRUKER *INVENIO*

The combination of thermal analysis and FT-IR (Fourier Transform Infrared) spectroscopy is an absolute must, especially in the polymer-producing, chemical and pharmaceutical industries. NETZSCH has been collaborating with the leading manufacturer of FT-IR spectrometers, Bruker Optics, since 1993. It all started with a customer inquiry from Australia. Today, there is a close partnership that can be seen in the numerous further developments over the years.

As early as 2003, Bruker Optics and NETZSCH Analyzing & Testing jointly developed a communication interface for mutual data exchange. In addition to importing and exporting various data, it was possible for the first time to exchange live data and synchronize the two measurements during a running experiment. This meant that the two measurements could be started simultaneously via the *Proteus*® software – having to operate only one PC already meant significantly simplified handling for the operator.

Further development steps were taken by the direct coupling without transfer line, PERSEUS®, as well as the possibility to use automatic sample changers. Lowest space requirements, high sample throughput, flexibility in the selection of coupling devices, almost integrated solutions and progressive automation have made the NETZSCH-Bruker FT-IR coupling particularly well known in quality control.

Today, higher temperatures in the gas cell up to 370°C as well as in the transfer line and adapter head up to 400°C make it possible to examine even higher-boiling gases that are released from the sample. Optimization of the transfer path also helps gases find their way into the gas cell for detection, which, in turn, has increased detection sensitivity.

Here, you can find the link to our image video:

LFA Lamellar Sample Holder for Anisotropic Materials – Now Also Available for the Higher Temperature Range to 600°C

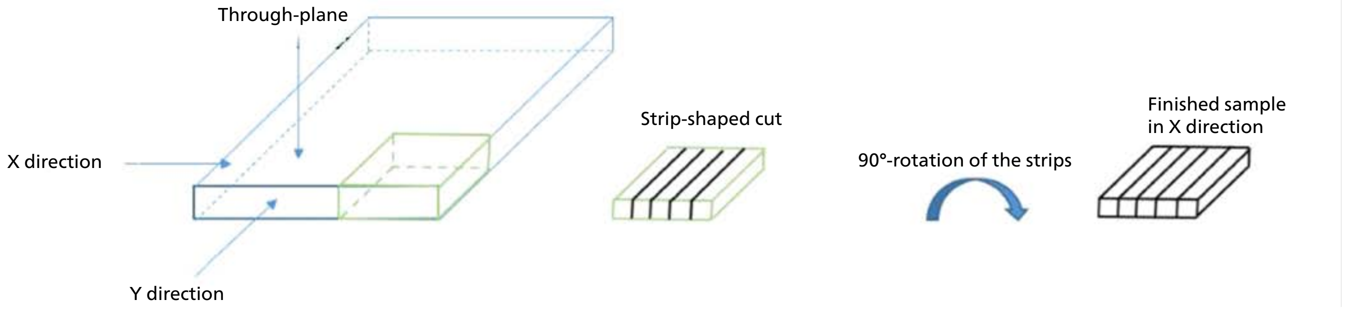


Fig. 1. Sample preparation of a CFRP sample for use in the lamellar sample holder of the LFA 467 *HT*

With a special LFA sample holder of stainless steel, measurements on anisotropic samples exhibiting different thermal diffusivities in the x-/y-direction (in-plane) can now also be carried out with the LFA 467 *HT HyperFlash*® to 600°C.

For measurements with the so-called lamellar sample holder of the LFA 467 *HT HyperFlash*®, strip-shaped samples are inserted into the sample holder, fixated with set screws and thereby centered. Ideally, the sample will consist of 2-mm-thick strips with parallel surfaces. Careful sample preparation and precise determination of the thickness minimize uncertainty in the measurement results. For easier sample preparation, a preparation tool is optionally available.

For comparison, a CFRP sample was investigated between 25°C and 105°C (in steps of 10 K) with the respective lamellar sample holders in the standard version of the LFA 467 *HyperFlash*® (up to 500°C) and also in the high-temperature version (HT).

Figure 2 depicts the thermal diffusivity of the CFRP sample in the x-direction, whereby the results for the sample measured with the standard version of the LFA 467 *HyperFlash*® are shown in black opposite the results from the LFA 467 *HT HyperFlash*®. Evaluation of the thermal diffusivity shows that the maximum deviations are in the range of ± 3% compared to the LFA 467 *HyperFlash*® data.

This means that it is now possible to carry out direction-dependent measurements with the high-temperature model, the LFA 467 *HT HyperFlash*®, as well.

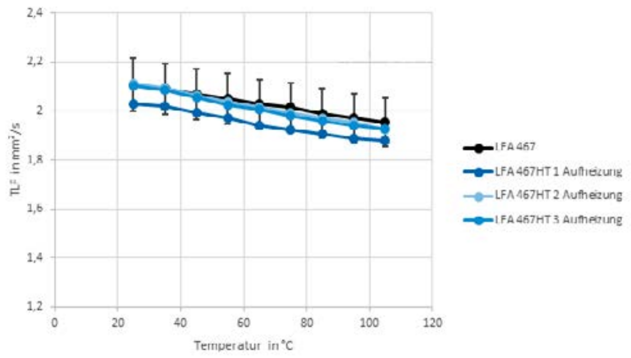


Fig. 2. Measurements on a CFRP sample with the lamellar sample holder for the LFA 467 *HT*

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Imprint

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