ONset

NETZSCH

CUSTOMER MAGAZINE

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Dear Reader:

Today, I have several reasons to be happy to present you with our latest issue of **on**set. For one thing, the **on**set is presenting itself for the first time in a new design. First published in May 1990 as a four-paged leaflet informing readers about new instruments and activities at NETZSCH-Gerätebau, it has since become a customer magazine with a fresh, modern layout and many interesting articles. Many thanks to all authors who were involved in this issue of **on**set.

For another thing, NETZSCH-Gerätebau was able to inaugurate its new production, development and logistics center in Selb at the beginning of October. With additional floor space of over 6500 m^2, the company is now ideally set up for the future. Impressions from the new building and its inauguration can be found in the lead article.

This issue of **on**set, however, offers a lot more yet:

Kinetics Neo is an advanced development of the successful NETZSCH *Thermokinetics* program for the kinetic evaluation of thermoanalytical data. It allows for predictions based on calculations and the optimization of processes that would otherwise require time-consuming tests. It features a new, intuitive user interface along with a series of unique analysis possibilities. More about that on page 6.

The two interesting customer articles focus on the thermal behavior of carbon fiber-reinforced composites. Prof. Dr. Sebastian Eibl from the Bundeswehr Research Institute for Materials, Fuels and Lubricants in Erding, Germany, reports about how chemometric methods can considerably enhance the significance of thermogravimetric investigations. Dr. Pauline Tranchard and Prof. Dr. Serge Bourbigot from the University of Lille, France, give insight into the thermal properties (in particular, specific heat capacity and thermal diffusivity) of virgin and degraded laminates

Based on the example of the amoxicillin trihydrate antibiotic, the article on pages 18 and 19 demonstrates the influence of the hole size of crucible lids on DSC curves during evaporation processes.

Finally, the contribution starting on page 20 introduces a new sample holder for the determination of thermal diffusivity which allows for a defined sample thickness particularly for samples in the liquid state, and thus also for precise results from metal measurement into the melt.

Enjoy your browse through this 17th issue of **on**set!

Dr. Gabriele Kaiser
Scientific & Technical Communication

Opening Ceremony at NETZSCH-Gerätebau

Yann Jeschke, Marketing

From left to right: Dr. Jürgen Blumm, Dr. Hanns-Peter Ohl, District Administrator Dr. Karl Döhler, Dr. Thomas Denner, District Vice President Robert Engel, Dr. Claudia Netzsch, Selb Mayor Ulrich Pötzsch, Moritz Netzsch, Member of the Bavarian Government Martin Schöffel, Christian Netzsch and Dietmar Bolkart

On October 9, 2017 – after a construction period of only 12 months – the new production facility at NETZSCH-Gerätebau at the Selb site was officially inaugurated.

In chilly October weather, the new building was put into operation by Dr. Thomas Denner, Managing Director of the Business Unit, along with numerous staff, neighbors, members of the Netzsch family, shareholders, representatives from the political sphere and upper NETZSCH management.

District Vice President Thomas Engel, District Administrator Dr. Karl Döhler and Selb Mayor Ulrich Pötzsch commemorated the successful development of this tradition-rich company in their speeches. They expressed their delight that NETZSCH has again decided in favor of the Selb site – which reflects very positively both inside and outside our region.

People Take Center Stage

With the construction of this new production hall, another important milestone for growth has been laid: Capacities at NETZSCH-Gerätebau GmbH have now increased by 60%. Already today, 20% more instruments are being manufactured than in the old premises.

A View ....


... into the new production facility


... of a work station in the new production facility


... into the "social area" – an inviting space for employees to get together during breaks and lunch time

Even with a state-of-the-art new manufacturing and logistics concept, it is still people at center stage. Dr. Thomas Denner, Managing Director of the Business Unit, says: "For us, digitalization in production does not mean automation. It can't, since we do not produce in series but rather design each instrument individually according to our customers' needs. We concentrate instead on an efficient interface between people and IT."

Investment in Staff

It is true that simpler activities will increasingly be eliminated in the years to come and the demand for qualified specialists will continue to rise. In order to qualify all NETZSCH employees to face this new challenging world of work, the company invests in regular training sessions and continued education. This involves not only professional qualification but also a basic understanding of digital processes, openness to new solutions and a willingness to acquire new skills – and also employ them.

Together with Managing Director Dr. Jürgen Blumm, the two Managing Directors of the Erich NETZSCH Holding Dr. Hanns-Peter Ohl and Dietmar Bolkart, and shareholders Dr. Claudia Netzsch, Moritz Netzsch and Christian Netzsch, the ribbon was cut by Dr. Denner, after which the construction team gave the official green light for successful work in the new premises.

After that, all attendees had the opportunity to take a closer look at the new production hall, the new offices and the stylish "social area" – and the NETZSCH staff present was happy to answer their questions. The evening ended with a delicious barbecue and cool drinks in a cozy atmosphere.

KINETICS NEO

Analysis and Prediction of Your Chemical Process

Dr. Elena Moukhina, Research & Development

How Fast is Your Process at a New Temperature?

If we are aware or not, everybody uses chemical processes or their results in everyday life. Therefore, it is very important to have an idea how long such processes will take. For example, if we stick two things together, it is crucial to know when we will have a rigid joint: in several seconds or in several hours. The duration of many processes is temperature-dependent: e.g., baking at low temperatures requires much more time than baking at higher temperatures. Or, if we stay in the kitchen: What temperature and what amount of time is necessary to fry chips in order to get the best result in the shortest time?

The same questions about the optimal temperature program and process duration are very common in industry as well, for example, for the curing of paints or epoxy resins in the automotive industry.

Or sintering of ceramics occurs faster at higher temperatures, and this saves production time. High temperatures, however, can lead to a non-uniform heating and production of micro cracks, which are decreasing the quality of the product. This leads to the question: How high can the temperature be increased in order to save time and maintain the high quality of the product?

These questions are usually answered by trial-and-error tests, which require a lot of time. Moreover, mistakes in the kitchen lead only to ruined food, but errors in industry can be very dangerous and can lead to accidents with damages. Therefore, process predictions and simulations should be carried out prior to the actual production process before the real production should be started.

The new Kinetics Neo software can help answer these questions, find the optimal temperature program, and time duration for chemical processes.

Kinetics Neo Always by Your Side

- Determine the amount of time needed for paint to cure
- Optimize production time for high-quality ceramics
- Maximize the quality of metal powder product during polymer burnout
- Optimize a material's synthesis process when using a new catalyst
- Find out the curing time for a dental filling

Lifetime Predictions

The second group of challenges where the process duration is very important are questions related to lifetime prediction and safety storage. For example, it is known that some pharmaceuticals must be stored in cold places, because they can at worst lose their activity if the cold chain is interrupted. How long may we store these substances at the given temperature to keep them active? The insulation of electrical wires works well at room temperature, but electrical equipment features sometimes higher temperatures where already degradation of the insulation can occur. How long may we use the electrical insulation at the enhanced temperature without a short-circuit? If the process duration is about days or months, then these questions can be answered by common experiments.

Sometimes, however, the duration of a process is about years or decades, such as the degradation of water pipelines. So far, direct experiments have been impossible. Therefore, the only way is to perform short experiments to initialize the degradation process at high temperatures, and then to extrapolate the data by using software.

Some hazards are dangerous in storage and could lead to thermal explosions. Therefore, it is very important to know, how long and at what temperature they may be safely stored or transported.

NETZSCH Kinetics Neo

Kinetics Neo can overcome all issues where the intensity and duration of the chemical process depends on temperature.

Kinetics Neo: All in One

NETZSCH Kinetics Neo is a new software for the analysis of the experimental rate of chemical reactions at different temperature conditions and the determination of kinetic parameters of reactions such as:

- Activation energy
- Reaction orders
- Number of individual steps

Kinetics Neo delivers the user the knowledge to determine the optimum temperature program for industrial processes in order to get a high-quality product at shortest time and minimum energy costs.

Additionally, it allows for prediction of the reaction rate and reaction duration of a chemical process at conditions, which are different from the experiment, for example, concerning decades for pipeline degradation or seconds for the thermal explosions of hazards.

There are two approaches in kinetic analysis of chemical processes: model free and model based.
Kinetics Neo offers both possibilities. Both kinetic results can be used for predictions and optimization.

Model-Free Approach: Fast for Simple Reactions

Advantage of the model-free method is its quickness; one of the reasons why it is often found in literature. It is used when it is assumed that the chemical process can be described by only one kinetic equation, where the activation energy is only the function of degree of conversion. Therefore, this approach works not only fast and well for single-step reactions but also for processes, which have no competitive or independent reaction steps.

Kinetics Neo includes 7 different model-free methods, three of them are set up according to ASTM standards, three others (Friedman, OFW, KAS) are widely used in modern literature on kinetic analysis. The 7th powerful method is the numerical method performing numerical finding of the activation energy and the pre-exponential factor functions of conversion to get the best model-free solution with the best agreement between the simulation and experiment.

- Analysis
  - Model-free
    - ASTM E698
    - ASTM E2890
    - ASTM E1641
    - Friedman
    - Ozawa-Flynn-Wall (OFW)
    - Kissinger-Akahira-Sunose (KAS)
    - Numeric Optimization

Model-Based Approach: Powerful for Complex Reactions

However, not all chemical processes are single-step ones or having only consecutive steps. Even for a mixture of two substances decomposing independently, the model-free approach cannot be applied anymore, because for each independent decomposition in this mixture, an independent kinetic equation is necessary. Generally, the number of kinetic equations must be equal to the number of individual reaction steps of the whole process. For independent reaction steps, these equations must also be independent. For the dependent reaction steps such as consecutive or competitive, the equations are interconnected in the system. This kinetic approach is called model-based. It requires the user's knowledge about the individual reaction steps. The advantage of this approach is the fact that it can describe any chemical process, including very complex ones with any number of kinetic steps in any combination. This analysis is unique and worldwide only realized by NETZSCH.

NETZSCH Kinetics Neo

The Kinetics Neo software allows the user to create the desired kinetic model visually by adding independent, competitive or consecutive reaction steps into the existing model to any position. The number of reaction steps and their combinations are not limited. Each reaction step can be one of 18 different reaction types including nth order reaction, phase boundary reactions, diffusion, autocatalysis and nucleation.

Model-free and model-based results can be compared in the software statistically in order to select the best result, which can later be used for predictions and optimization.

Predictions and Process Optimization

Based on the kinetic model (model free or model based), the software simulates the signal, conversion rate and conversion for user-defined temperature program. This allows for the prediction of sample properties for temperature conditions which differ from the conditions originally used during measurement(s).

Another possibility is process optimization. It allows for the simulation of data once the experimental data is described by model-free or model-based kinetics. The temperature profile can be calculated and optimized taking into account defined boundary conditions; e.g., constant conversion rate, constant signal rate, temperature range and range of heating rates.

Predictions

Isothermal

Dynamic

Multiple step

Step iso

Modulated isothermal

Modulated dynamic

Adiabatic

Time-Temperature-Transition (TTT)

Optimization

Conversion rate

Signal rate (rate-controlled mass loss (RCM) for thermogravimetry and rate-controlled sintering (RCS) for dilatometry)

What Makes Kinetics Neo So Valuable ...

- Completely new software, rewritten from scratch, based on the latest technologies
- Fast and easy-to-operate user interface
- Includes all model-free and model-base methods; statistical comparison of the results from all methods
- New: Powerful numerical model-free method for fast determination of the best model-free solution
- Predictions and optimizations by means of both model-free and model-based methods
- Fast and easy visual creation of a kinetic model using the model-based method
- Unlimited number of kinetic models
- Any number of individual reaction steps in any desired combination by simply adding, eliminating, or changing the reaction step
- Adaption of individual reaction steps at any time
- Optimization of an individual step or the entire kinetic model with just a click of the mouse
- Formal concentration of each reactant and reaction rate for each reaction step as a function of time or temperature
- Analysis and prediction of isothermal crystallization reactions

NETZSCH Kinetics Neo

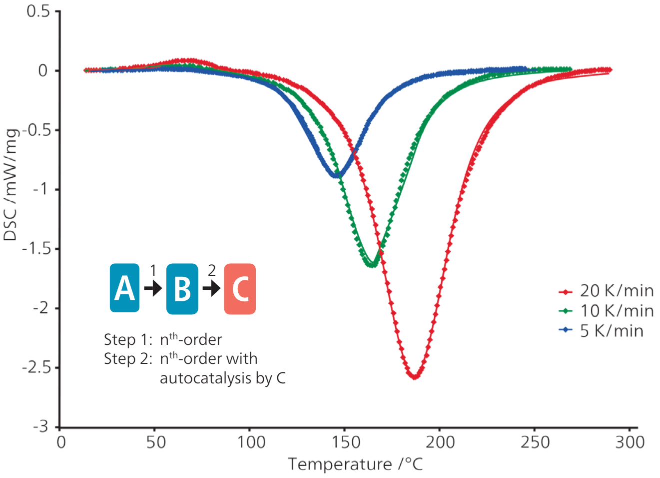

Fig. 1. Model-based; DSC measurements; sample masses approx. 20 mg

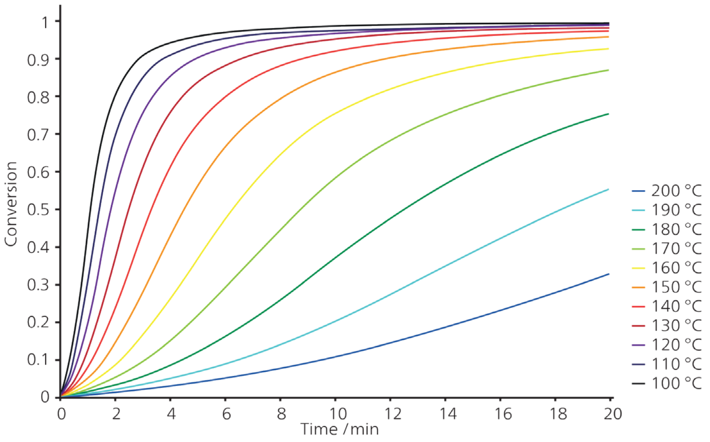

Fig. 2. Predictions for different isothermal conditions. Sigmoidal course is typical for autocatalytical reactions.

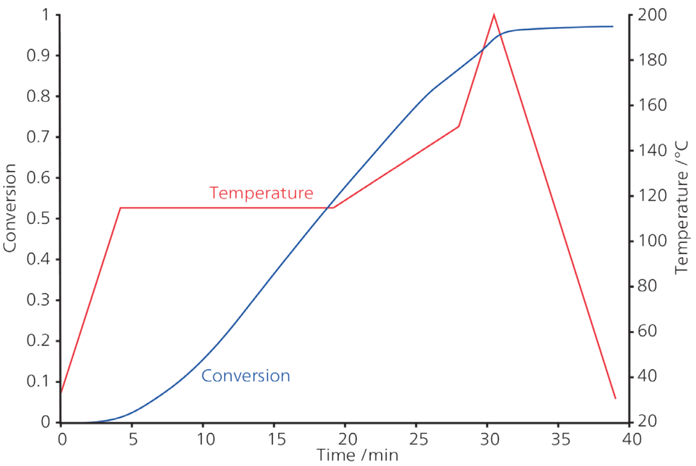

Fig. 3. Prediction according to a user-defined temperature profile including heating and isothermal steps

Analysis and Predictions of the Curing Behavior

The curing behavior of epoxy-based adhesives raises many questions, including:

- What is the minimum temperature needed for a specified curve over a given duration of time?
- What is the degree of curing for a given temperature program?

Figure 1 shows the experimental DSC data (points) of a curing process at three different heating rates. The process includes reaction steps of different directions: endothermal melting at approx. 60°C and exothermal curing between 120°C and 200°C. For these kinds of processes, an analysis based on model free kinetics fails. The plot includes the simulations of the curing process (solid lines) created using the kinetic model displayed. This kinetic model can now be used for the calculation of various predictions, and process optimization can be derived from them.

Figure 2 depicts the curing behavior for many isothermal conditions. For example, a 95% curing level is achieved at 150°C after16.4 min, at 170°C after 9.2 min and at 200°C after 4.2 min.

Figure 3 shows the degree of curing for a user-defined profile.

For more information and download options, please see under https://kinetics.netzsch.com/en/.

Expanding the Informative Power of Thermogravimetry Using Chemometric Methods

Prof. Dr. Sebastian Eibl, Bundeswehr Research Institute for Materials, Fuels and Lubricants, Erding, Germany

Introduction

Thermogravimetric Analysis (TGA) is a very well established procedure for characterizing a great variety of material types. In the area of polymer analysis, for example, the thermal stability, filler content and so forth can be characterized. It is also possible to expand the informative power of thermogravimetry through multivariate (chemometric) data analysis. Using carbon fiber-reinforced plastics (CFRPs) with pre-existing thermal damage, this example will show how TGA allows for the determination of the residual strength and of the duration and temperature of the load on a sample with an unknown thermal history.

Carbon Fiber-Reinforced Plastics

CFRPs are used in all modern aircraft. They are characterized by excellent strength and low weight. Their disadvantage in comparison with metal structures is their comparatively low thermal stability due to their polymer content. In the field of aviation, epoxy resins are typically used as a polymer matrix; these may contain a thermoplastic toughener that is stable at high temperatures such as, in this case, a polyether sulfone.

For a failure analysis with high informative power, test procedures need to be capable of quantifying thermal damage and, for example, of determining the temperature that had been reached.

Chemometric Analysis

Chemometric analysis is a procedure that enables the determination of material properties, typically on the basis of spectroscopic data. To this end, a large number of samples with different known properties is analyzed at first. This calibration set is then used for multivariate data analysis in order to determine the properties of an unknown sample using its spectrum. In the following example, CFRP samples under thermal load are stored at various temperatures, their strength is determined and a thermogravimetric analysis is carried out.

Chemometric evaluation of the TGA curves allows for subsequent prediction of specific values with regard to the duration and temperature of storage as well as residual strength.

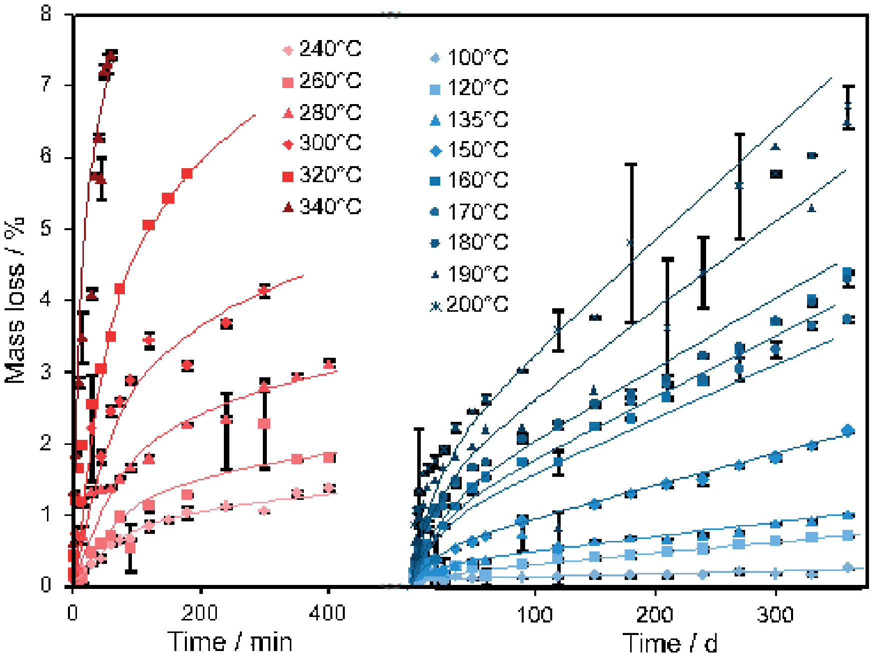

Fig. 1. Storage conditions for CFRP under thermal load, shown on the basis of the relative mass loss resulting from the differing durations of storage between 100°C and 340°C

Figure 1 shows all of the stored CFRP samples on the basis of the determined mass losses.

Thermogravimetric Analysis

From the set of samples, 120 were selected and each analyzed on the basis of repeat determination (heating rate: 10°C/min; flow: 50 ml/min nitrogen, weight: 20 mg). Figure 2 shows the TGA analysis for selected CFRP samples under thermal load. At around 350°C, an inflection point for the mass loss ensues which can be attributed to the degradation of the polymer matrix. The residue is composed of pyrolysis residuals of the resin and the carbon fiber portion. The fiber portion of the intact CFRP is 65%

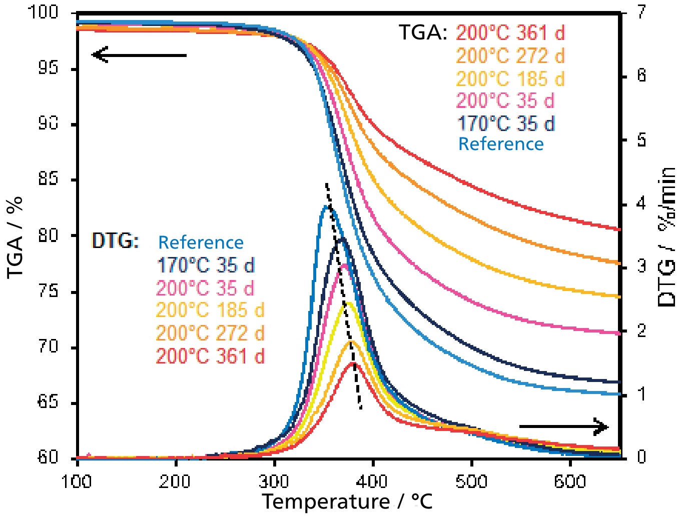

Fig. 2. Thermogravimetric analysis of CFRP samples under differing thermal load; reference without prior thermal load; increasing thermal load from blue to red.

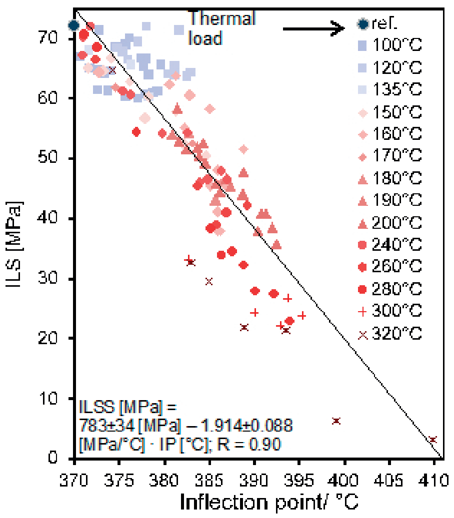

Fig. 3. Empirical correlation of the inflection point of the resin degradation with the residual strength (interlaminar shear strength, ILS)

With increasing prior thermal load, one sees a shift of the polymer decomposition to higher temperatures and an increase in the residue. Both observations can be explained by the fact that, already during preliminary thermal storage, components of the polymer matrix that were relatively more prone to degradation were removed. In the TGA analysis, the more thermally stable portions degrade afterward at higher temperatures. Samples with pre-existing thermal damage thereby exhibit lower polymer content, which can be seen in the relatively higher residues with the TGA. For this reason, the sum of the mass loss through the prior thermal load (figure 1) and the thermogravimetric analysis is similar for all samples.

In order to counteract any influence of differences in composition with regard to fiber and polymer content in the samples analyzed, all of them were ground prior to analysis.

Empirical Correlation

The temperature of the inflection point which is characteristic for the polymer degradation exhibits – as is to be expected – a correlation with the residual strength of the samples (compare figure 3).

This correlation can be used to determine the residual strength from the TGA analyses. The temperature of the thermal load, however, cannot be determined this way, since the degree of thermal damage formally constitutes a function of load time and temperature.

Also, as residue increases, a clear interrelation with the strength ensues (not shown). Due to the fact that the fiber and matrix portion is not always constant for the intact sample material and to the fact that a relatively small amount of sample material is used for the TGA, however, this correlation is less precise.

Chemometric Analysis of TGA Curves

A separate determination of the load duration and temperature, as well as of the residual strength, can take place using the chemometric analysis of the TGA data. Thereby, all data points of the TGA curve, without any additional pre-processing of data, are incorporated into the calculation of what is known as a “Partial Least Squares Regression” (PLS).

Customers for Customers

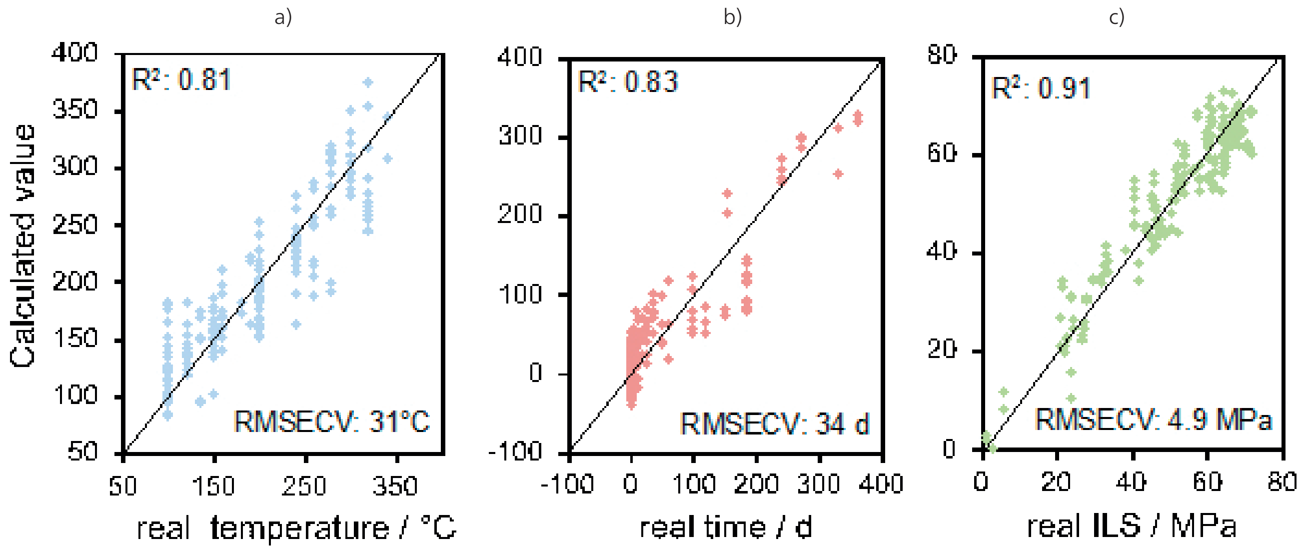

Fig. 4. Comparison of the real temperature and time of storage as well as the residual strength with the values calculated from the TGA curves using a PLS (root mean square error of cross validation, RMSECV)

Figure 4 depicts the prediction accuracy for the load temperature by juxtaposing real storage temperature to the temperatures determined using the TGA curves.

The mean deviation of a data point from the real value (root mean square error of cross validation, RMSECV) is about 15°C in the best case. Corresponding deviations for the duration of the thermal load as well as the residual strength can be seen in table 2.

While the determination of the residual strength (4c) and of the load temperature (4a) can take place with sufficient precision, the specific duration (4b) of the thermal load is to be viewed as imprecise. This is due to the inhomogeneous distribution of the data points, whereby a multitude of samples that were stored only briefly creates an imbalance. In order to enable a more precise determination, the data set can be divided into samples that were stored for a long period and those that were stored only briefly. This method increases the prediction accuracy significantly.

Tab. 1. Mean deviations (RMSECV) of the values determined for the chemometric analysis

	Temperature [°]	Time	ILS [MPa]
Short-term data	15	49 d	4.0
Long-term data	10.1	70 min	3.3
All data	31.4	34 d	4.9

Short-term data: 1min-600 min. 240°C-340°C. 0-70 MPa; 80 TGA curves, long-term data: 1d-360 d. 100°C-200°C. 35-70 MPa; 160 TGA curves
All data: 1min-360 d. 100°C-340°C. 0-70 MPa; 240 TGA curves

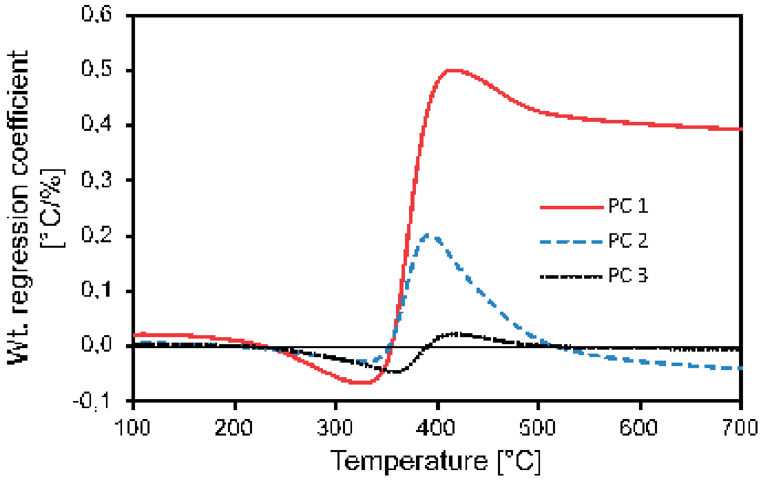

Fig. 5. Weighted regression coefficients of the first three principal components (PC 1-3) for prediction of the temperature of the prior thermal load

The Author

Prof. Dr. Sebastian Eibl studied chemistry at the LMU Munich, where he also received his doctoral degree.

Since 1999, he has been head of the laboratory in the area of analytical chemistry at the Bundeswehr Research Institute for Materials, Fuels and Lubricants (WIWEB) in Erding, Germany.

In 2014, he received an honorary professorship at the University of the German Federal Armed Forces in Munich.

Regression Coeffficient of Chemometric Analysis

In order to calculate the temperature ranges from which the chemometric analysis gains information from the TGA curves for the determination of specific values, the regression coefficients can be used. Multiplication of the regression coefficient with the corresponding value from the TGA curve thereby yields the determined value, after adding together all values of the TGA curve. If, for example, positive regression coefficients ensue in a temperature range, this means that the calculated value is thereby increased. Figure 5 shows the regression coefficients of the first three principal components for the determination of the load temperature, which cover a total variance for the data set of 60%.

From the plot, it becomes evident that a high load temperature is calculated on the basis of the TGA curve, primarily in the temperature range over 400°C. In this range, the high residues of samples with heavy thermal damage have an effect, especially in the form of the first principal component. With the second principal component, high temperatures are calculated primarily in samples for which the inflection point lies at comparatively high temperatures. Additional regression coefficients, especially those of higher principal components, cannot be attributed directly to any given degradation process that is thermogravimetrically ascertainable and therefore cannot be readily interpreted.

Summary

A detailed evaluation of TGA curves based on chemometric methods can expand the informative power of thermogravimetry. Slight differences in the curve progressions of CFRP samples which were subjected to differing levels of prior thermal load allow, in the example presented here, for the determination of values which would otherwise not be possible to ascertain.

Details in:

Eibl S. Comparison of surface and bulk analytical techniques for the distinct quantification of a moderate thermal pre-load on a carbon fibre reinforced plastic material, Polymer Degradation and Stability, 10.1016/j.polymdegradstab. 2016.11.015

High Temperature-Dependent Thermal Properties of a Carbon-Fiber Epoxy Composite

Dr. Pauline Tranchard and Prof. Dr. Serge Bourbigot, University of Lille, Unité Matériaux et Transformation

With the increased use of composite materials in aircraft structure, the need to model the detailed behavior of laminates under fire conditions has arisen. One of the main issues is to succeed in determining input data used for the fire models that are developed. Notably, it is necessary to characterise the high-temperature dependent properties of the material such as the specific heat capacity and the thermal diffusivity.

The present work is focused on the development of methods of characterising the thermal properties of laminates. The specific heat capacity and thermal diffusivity of an aeronautical carbon fibre/epoxy laminate (Isotropic T700/M21 [1]) were measured as a function of the temperature and of the decomposition degree. One of the main issues is to succeed in measuring these properties without losing the physical meaning of the measurement.

Heat of Decomposition (Non-Reversing Signal)

Specific heat capacity and heats of decomposition were determined based on the modulated signal (TM-DSC) obtained using simultaneous thermal analysis (STA) from NETZSCH (STA ***F1*** *Jupiter*®). TM-DSC measurements were performed instead of classical differential scanning calorimetry to obtain better accuracy and precision in the specific heat capacity values. It permits the separation of non-reproducible experimental artefacts from the measurement. The measurements under inert atmosphere were performed on a degraded sample to obtain a baseline and on a virgin sample during its decomposition. Using the two curves, heats of decomposition can be determined by integrating the area of decomposition peaks. Results of the non-reversing specific heat capacity and the remaining mass are presented in Figure 1.

The first peak is an exothermic peak with a heat of decomposition of $2.6 \cdot 10^5$ J/kg (315°C to 425°C) and the second one is endothermic with a heat of decomposition of $1.5 \cdot 10^5$ J/kg (425°C to 545°C). It is evident that the first peak is unusual because material decomposition is generally endothermic in an inert atmosphere. These phenomena are assigned to several processes such as bond dissociation, new bond formation and gas evaporation. Some materials can produce an exothermic reaction under an inert atmosphere [2]. Notably, PAN and bisphenol C polyacrylate (extremely flame-resistant polymers) exhibit a high exothermic decomposition reaction. Most polymers with exothermic decomposition (under nitrogen) contain either halogens or some unsaturated double or triple bonds, which can lead to char formation by cross-linking or cyclization reactions.

This explanation can be linked to the decomposition mechanism of epoxy resins presented in previous works [1, 3]. The decomposition occurs through cyclization of aliphatic chain ends and it explains the exothermic decomposition identified in our case.

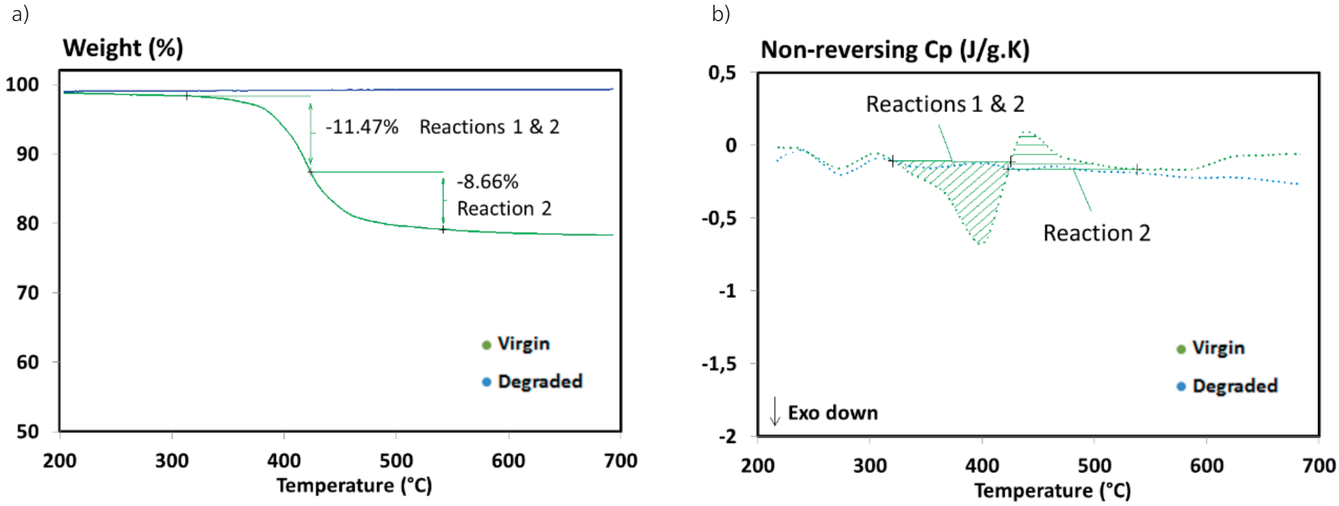

Figure 1. (a) Remaining mass and; (b) non-reversing specific heat capacity obtained during an STA test carried out under nitrogen to determine the heats of decomposition of T700/M21 [1]

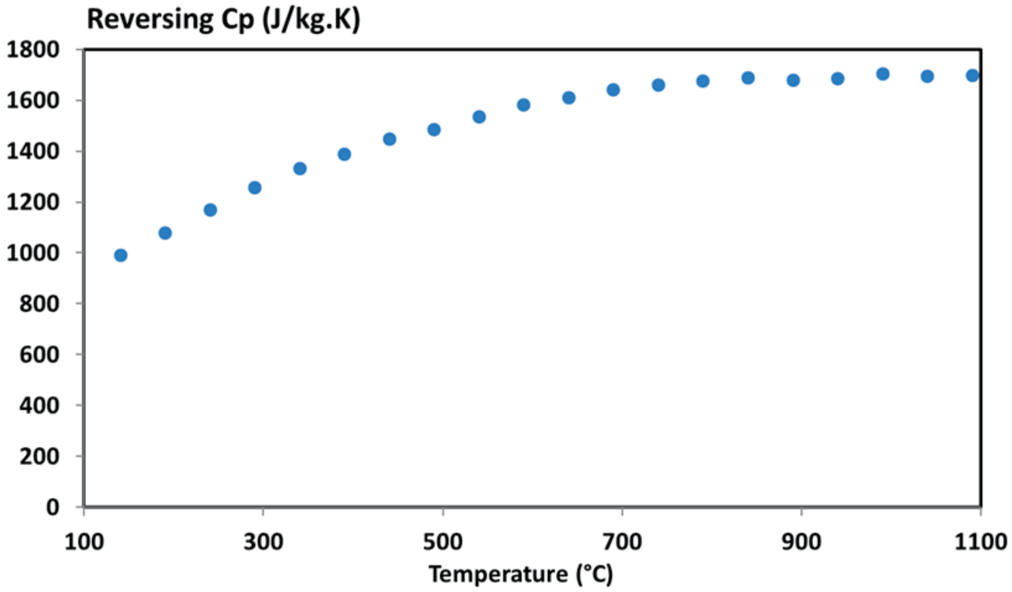

Fig. 2. Specific heat capacity of the degraded materials obtained with STA ***F1*** measurements [1]

Similar results were recently reported by McKinnon et al. [4] where a carbon fibre/epoxy composite also exhibited exothermic and endothermic reactions

Effective Specific Heat Capacity (Reversing Signal)

The specific heat capacities of the degraded materials were obtained with TM-DSC up to 1100°C. As far as we know, it is the first time such a method was applied on an anisotropic carbon fibre/epoxy laminate [1]. The reversing signal measurements obtained on the degraded materials are presented in Figure 2.

In both cases, an increasing specific heat capacity with increasing temperature is observed. The specific heat capacity of the non-degraded sample is close to the values found in literature for similar materials [6-7]. The degraded sample shows an increase in its specific heat capacity up to 1600 J/(kg·K) at 1000°C. It has been reported [8] that the specific heat capacity of carbon fiber/carbon composite can reach a value of 2020 J/(kg·K) at 1230°C.

Determination of Thermal Diffusivity

A Light Flash Apparatus from NETZSCH (LFA 467 *HyperFlash®*) was used to measure the thermal diffusivity of the sample in the through-thickness and in-plane directions. The thermal diffusivity tensor was measured up to 450°C on virgin and degraded materials. This composite has an anisotropic structure, so measurements are needed in the three main directions of the composite. However, the thermal diffusivities in the two in-plane directions are assumed to be equal for the isotropic T700/M21 laminate (assumption of homogeneous interlayers).

Test bodies were exposed to the fire test developed by Tranchard et al. [9] for 150s and 300s to get a measurement as a function of the decomposition degree – i.e., half-degraded and degraded. The thermal diffusivities of virgin, half-degraded and degraded coupons were measured as a function of temperature and their results presented in Figure 3.

The thermal diffusivity of the virgin material decreases linearly up to 350°C and then suddenly decreases sharply. This temperature (350°C) is close to the temperature of decomposition of the composite. The formation of cracks and thermal delamination seems to be responsible for this decrease. These phenomena increase the thickness of the sample (considered to be constant during the measurements) and hence the measured thermal diffusivity decreases. The half-degraded and degraded samples show a much lower thermal diffusivity at low temperatures and then a weaker dependence on the temperature. The two degraded materials have quite different thermal diffusivities due to their different thermal histories. The thermal diffusivity of the degraded sample increases slightly above 300°C, which is most probably due to further structural changes and increasing radiation within the sample. At high temperatures (>400°C), the virgin sample has a thermal diffusivity 2-3 times lower than the burnt material. This difference can be explained by differences in material thickness, decomposition state, and thus also of thermal history.

The in-plane thermal diffusivity of the virgin and half-degraded samples were measured up to 250°C (it was difficult to cut sample strips from coupons that were too degraded and thus measurement on the completely degraded sample was not possible). The results differ from the results obtained from the transverse measurement (Figure 3b). Only one direction was measured on the isotropic composite (symmetric stacking). These results show, in Figure 3, that the in-plane thermal diffusivity is approx. 15 times higher than the through-plane, which confirms the thermal anisotropy of this material. Small differences between the virgin and half-degraded samples were detected. These are attributed to heat transfer in the horizontal direction which is more or less independent of the degree of decomposition (but more investigations are necessary). On the other hand, the virgin and half-degraded materials have the same mass fraction of fibre which is not degraded [9], but differing mass fractions of resin and of carbonaceous residue.

Conclusion

The specific heat capacity, heats of decomposition and thermal diffusivity of a carbon fibre/epoxy composite were determined as a function of the temperature and of the decomposition degree. These properties and the associated protocols permit the feeding of a public database [10] necessary for providing information on a laminate exposed to fire or to high temperature. These properties are specific to a carbon fibre/epoxy composite applied to aircraft structure. As a bonus, the properties are used for such applications as modelling laminate in fire for fire safety engineering.

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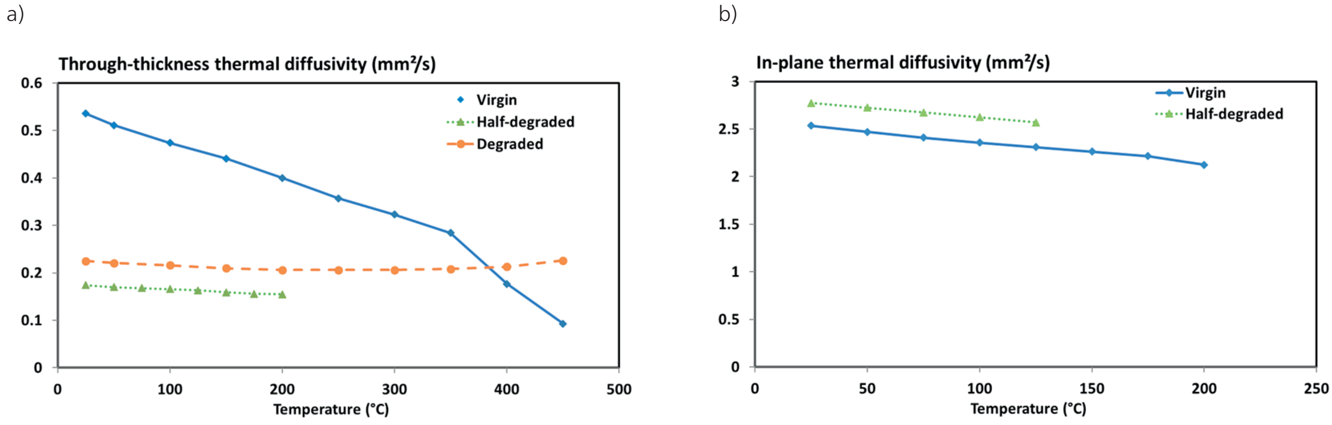

Fig 3. a) Through-thickness and; b) In-plane thermal diffusivities of the T700/M21 composite (virgin, half-degraded and degraded states) as a function of temperature [1]

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Dr. Pauline Tranchard obtained her Master's degree in 2011 in Thermal and Energy Sciences at the Engineering School "Ecole Polytechnique de l'Université de Nantes". She joined the Airbus Company in Toulouse (France) in 2011 as a thermal research engineer to work on the modelling of composites in fire. She continued her research with a PhD thesis in collaboration with the R_2Fire group (reaction and resistance to fire) and with the Airbus thermal team as part of an industrial research agreement (CIFRE). She was conferred her PhD in 2015 and joined the R_2Fire group as a researcher. Her research interests include the understanding of fire's effects on the behavior of materials, the characterization of thermophysical properties at high temperature and the modelling of the behavior of materials subjected to fire.

The Author

Prof. Serge Bourbigot obtained his PhD in 1993 and joined ENSCL as an assistant professor in 1993. He passed his French "Habilitation à Diriger des Recherches" in chemical engineering at the University of Lille in 1998. He earned a position as an associate professor in chemical engineering at ENSAIT in 1999. In 2002, Prof. Bourbigot left his laboratory to spend a year on sabbatical leave at NIST (Gaithersburg, MD, USA). In 2003, ENSCL offered him a position as full professor in flame retardancy (ULille). He is head of research at ENSCL and he is the leader of the R_2Fire group (reaction and resistance to fire). His research interests include the reaction and resistance to fire of polymeric materials including thermoplastics, thermosets, textiles and coatings, with special emphasis on solid-state NMR and heat transfer modelling.

What is the Influence of Crucible Lids on the Thermal Behavior of Hydrates?

Dr. Gabriele Kaiser and Claire Strasser, Scientific & Technical Communication

Introduction

Hydrates are a group of crystalline solids which release their crystal water when heated. The release temperature is dependent, for one, on the binding energy with which the water is bound into the structure. This provides the opportunity to obtain information on the bonding relationships in the crystal structure by means of thermal analysis. The release temperature, however, is also influenced by the crucible system used. It is to be expected that the diameter of the hole in the crucible lid will influence the release temperature. Effects in the DSC or TGA curves which can be traced back to the same release of water from a hydrate can therefore vary widely in terms of their temperature position, based only upon the measurement conditions selected.

With the following example of amoxicillin trihydrate, it will be shown which effects come into play for DSC curves.

Amoxicillin is an antibiotic employed for humans and animals for the treatment of bacterial infections, such as middle ear infections, bronchitis or skin diseases. The substance is not attacked by stomach acid and can therefore be administered not only as an infusion or injection but also as a tablet or suspension. Oral pharmaceutical forms mostly contain amoxicillin in the trihydrate form, a white crystalline powder [1].

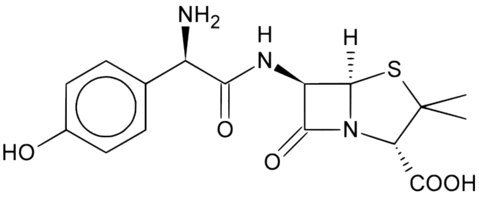


Fig. 1. Structure of amoxicillin

Pre-Investigations by Means of TGA-FT-IR

In order to verify that the release of water by amoxicillin is not overlapped by decomposition of the substance, a

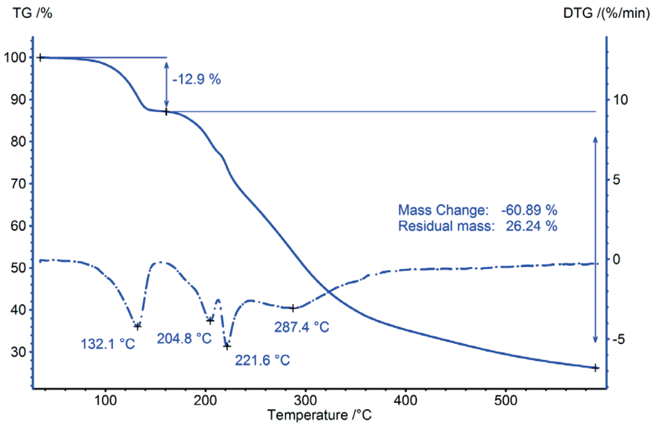


Fig. 2. TGA measurement on amoxicillin trihydrate, depicted here are the TGA (solid line) and DTG (dashed-dotted line) curves; sample weight: 3.5 mg, crucible: Al crucible (lids manually pierced), heating rate: 10 K/min, atmosphere: N_2
The curve progressions (TGA and DTG) in the range between approx. 170°C and 250°C are probably influenced by the fact that the hole size is quite small (decomposition products are not able to escape the crucible fast enough).

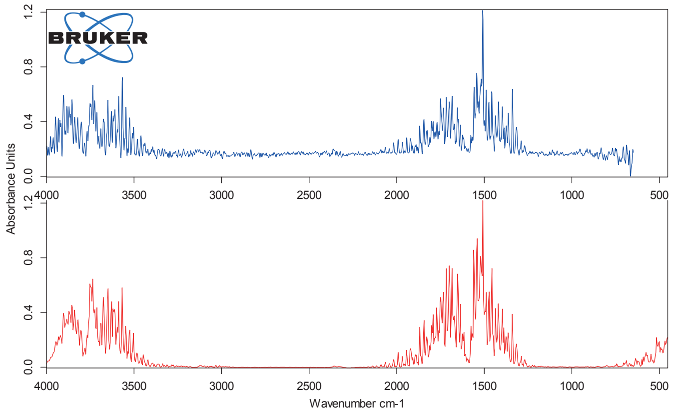
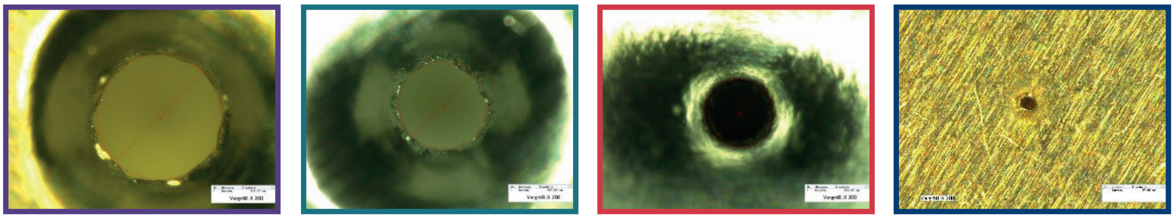


Fig. 3. FT-IR spectrum of the gas released at 133°C (blue, top) in comparison with the library spectrum (EPA library) of water (red, bottom)



727 µm 507 µm 386 µm 63 µm

Fig. 4. Microscopic photographs of the lids with holes of varying size; since the holes are not perfectly round, the diameters indicated are approximate values.

thermogravimetric measurement in combination with a Bruker FT-IR was first carried out, the result of which is depicted in figure 2.

The sample exhibits several mass changes during heating to 600°C. The first step with a DTG peak temperature of 132°C corresponds to a mass loss of 12.9%. This value is in good agreement with the theoretical mass loss of 12.88%, which can be calculated based on the molar mass of amoxicillin trihydrate at 419 g/mol and the release of all three water molecules.

Figure 3 confirms that the gas released is indeed exclusively water.

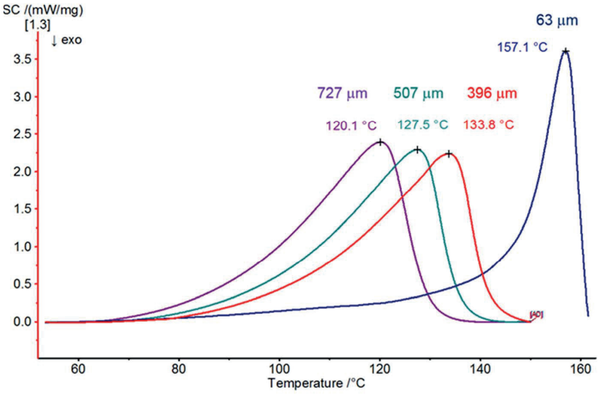


Fig. 5. DSC measurement on amoxicillin trihydrate; sample weight: approx. 2.25 mg, crucible: *Concavus*® (Al) – holes of differing size, heating rate: 10 K/min, atmosphere: N_2
The DSC measurement with the smallest-diameter hole (dark blue) was interrupted at 165°C so as to not enter the decomposition range.

DSC Investigation with Differently Pierced Crucible Lids

Samples with a mass of 2.25 mg each were weighed into Concavus® aluminum crucibles and the crucibles were sealed with differently pierced lids. Pictures of the prepared holes are presented in figure 4.

The water release appears in the DSC curves as an endothermic peak. As can clearly be seen in figure 5, both the start of the peak and, in particular, the top of each corresponding peak are shifted to higher temperatures as the hole size decreases. A reduction of the hole diameter by a factor of 11.5 (from approx. 727 µm to approx. 63 µm) results in a shift in the peak temperature of 37 K. Additionally, the form of the peak changes: the smaller the hole in the lid, the narrower and steeper the peak.

Summary

When aluminum crucibles with pierced lids are used for the testing of organic and inorganic hydrates, the size of the hole has a significant influence on the temperature position of the resulting endothermal evaporation peak. Good reproducibility of the DSC measurement results can only be achieved when the identical measurement conditions employed also include identical hole size. Likewise, similar behavior is to be expected for all reactions in which gases are released, such as combustion or decomposition reactions.

Literature

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New LFA 467 *HT HyperFlash*® Sample Holder – Dedicated to Liquid Metals

Dr. André Lindemann, Applications Lab, and Dr. Elisabeth Kapsch, Scientific & Technical Communication

Fig. 1. Design of the new sample holder for liquid metals; stainless steel (order no. LFA46700B96.040-00) and SiC version (order no. LFA46700B96.041-00)

Introduction

For LFA measurements, a defined sample thickness is required because the thermal diffusivity (a) is proportional to the square of the sample thickness (d): $a \sim d^2$. This demands high precision to obtain the exact thickness value. In addition, the heat flow through the outer container walls in the axial direction can be critical for sample holders for liquids. Furthermore, it should be considered that measurements on metals into the melt could easily destroy the sample holder.

In order to address these critical issues, NETZSCH developed a new sample holder for measurements on metals which need to be carried out at temperatures above the melting point (figure 1). The special design, with some parts made of stainless steel or SiC and inner parts made of sapphire, allows for measurements with excellent IR-detector signals and therefore high precision. Measurements can be performed up to 750°C in the sapphire/stainless steel combination and up to 1250°C in the sapphire/SiC combination.

The sample (i.e., the metal) is placed in a sapphire crucible which is closed with a sapphire lid on top. The defined sample thickness in the melt is realized by placing an additional mass on top of the sapphire lid. This ensures flexible positioning of the lid in terms of height and prevents any damage to the sapphire part resulting from axial thermal expansion of the metal.

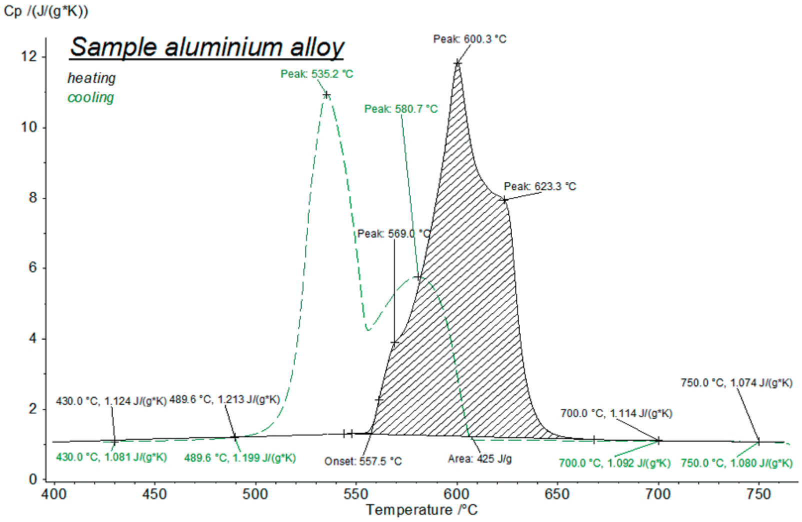

Fig. 2. Apparent specific heat capacity including energetic effects of an aluminum alloy during heating (solid black line) and cooling (dashed green line; DSC measurement)

Test Conditions

For the determination of the specific heat capacity (c_p) and thermal diffusivity (a), an aluminum alloy was tested in the temperature range between 450°C and 750°C using the LFA 467 *HT HyperFlash*® and DSC 404 ***F1*** *Pegasus*®. The sample thickness amounted to 1.5 mm; the sample surface preparation included a graphite coating. The new sample holder for liquids in the sapphire and stainless steel version was used.

PRECISE PRACTICE

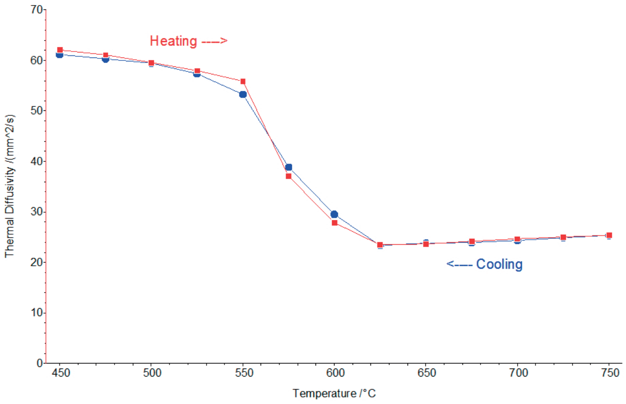

Fig. 3. Thermal diffusivity of the tested aluminum alloy between 450°C and 750°C; phase transitions solid → liquid → solid during heating (red curve) and cooling (blue curve)

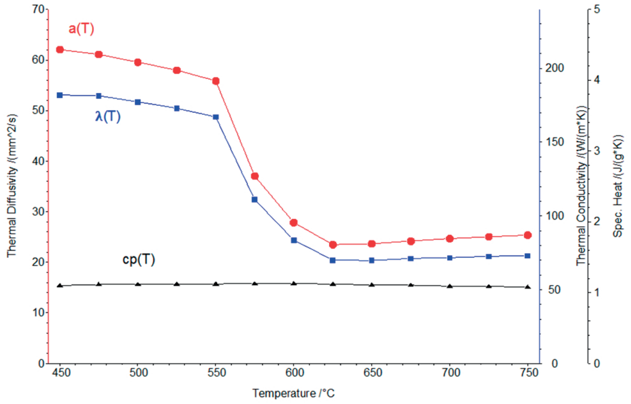

Fig. 4. Thermal diffusivity (red cuve), thermal conductivity (blue curve) and specific heat capacity (black curve) for the phase transition solid → liquid

Measurement Results

The suitability of the new LFA sample holder for liquids was checked by means of a series of measurements on the aluminum alloy with additional DSC measurements prior to the LFA tests. Figure 2 depicts the phase transition during heating and cooling detected in the DSC. During heating (black curve), multi-step melting of the alloy starts at 558°C (onset, solidus temperature) with peak temperatures at 569°C and 600°C. The last step is finished at 623°C (liquidus temperature). The DSC records a slight sub-cooling effect in the cooling curve (dashed green line). The crystallizing process starts between 610°C and 600°C, approximately 10 to 15 K below the liquidus temperature determined during heating. The crystallization ends at 535°C.

Depicted in figure 3 is the thermal diffusivity of the aluminum alloy during heating and cooling (LFA measurements). The values during melting and crystallization are in very good agreement, which indicates that the IR-detector has excellent signal stability and that conditions are stable both within and outside of the phase transitions (e.g., constant thickness of liquid/solid metal film). The solidus temperature is detected between 550°C and 575°C (by comparison, DSC: 558°C) and the liquidus temperature between 600°C and 625°C (by comparison, DSC: 623°C). The good agreement between the two independent methods demonstrates the high temperature accuracy of the LFA 467 *HT HyperFlash*®.

Figure 4 presents the thermophysical properties of the aluminum alloy including the calculated thermal conductivity (λ) and specific heat capacity (c_p) for the solid-liquid phase transition. The determination of the "true" specific heat capacity is based on the DSC measurement, under subtraction of the phase change enthalpy:

$$c_p \, dT = c_p \cdot dT - dh_{phase}$$

Summary

For the NETZSCH LFA 467 *HT HyperFlash*®, a new sample holder for liquids is available in two versions; one can be used up to 750°C and the other up to 1250°C. Measurements on a liquid aluminum alloy clearly demonstrate the high reproducibility of the results during heating (melting) and cooling (crystallization). The special design of the sample holder ensures constant sample thickness during the melt. At the same time, it prevents mechanical pressure on sapphire parts resulting from thermal expansion. The excellent signal stability is expressed in the high precision with low scatter. Additional DSC measurements confirm the LFA test results.

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Events

Exhibitions

	Date	Location
IEX 2017 – Insulation Expo USA	Dec 12 - 13, 2017	Houston, TX, USA
CAMX 2017 – Composites and Advanced Materials Expo	Dec 12 - 14, 2017	Orlando, FL, USA
Nepal Lab Expo 2017	Dec 14 - 16, 2017	Kathmandu, Nepal
Isranalytica 2018	Jan 22 - 23, 2018	Tel Aviv, Israel
Plastindia 2018	Feb 7 - 12, 2018	Ahmedabad/Gujarat, India
Nano Tech 2018	Feb 14 - 16, 2018	Tokyo, Japan
Tire Technology 2018	Feb 20 - 22, 2018	Hanover, Germany
Composite Expo 2018	Feb 27 - Mar 1, 2018	Moscow, Russia
JEC World 2018	Mar 6 - 8, 2018	Paris, France
Foam Expo 2018	Mar 6 - 8, 2018	Novi, MI, USA
Indian Ceramics 2018	Mar 7 - 9, 2018	Gujarat, India
Eurolab 2018	Mar 14 - 16, 2018	Warsaw, Poland
ARABLAB 2018	Mar 18 - 21, 2018	Dubai, UAE
analytica 2018	Apr 10 - 13, 2018	Munich, Germany
ceramitec 2018	Apr 10 - 13, 2018	Munich, Germany
Analitika Expo Moscow 2018	Apr 24 - 26, 2018	Moscow, Russia
Ceramics Expo 2018	May 1 - 3, 2018	Cleveland, OH, USA
NPE 2018 – The Plastics Show	May 7 - 11, 2018	Orlando, FL, USA
IEX Europe 2018	May 16 - 17, 2018	Cologne, Germany
Plast Milano 2018	May 29 - Jun 6, 2018	Milan, Italy
ACHEMA 2018	Jun 11 - 15, 2018	Frankfurt, Germany
PDM 2018	Jun 19 - 20, 2018	Telford, UK

Webinars

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Events

Conferences

	Date	Location
GCC 2018 – Gulf Coast Conference	Jan 17 - 18, 2018	Houston, TX, USA
ICACC 2018	Jan 21 - 26, 2018	Daytona, FL, USA
AABC Europe 2018	Jan 29 - Feb 1, 2018	Mainz, Germany
PITTCON 2018	Feb 26 - Mar 1, 2018	Orlando, FL, USA
FSHTC – Fuel Cell and Hydrogen Technology Conference	Mar 14, 2018	Birmingham, UK
TAC 2018	Mar 27 - 28, 2018	Belfast, UK
Swerea SICOMP Conference	Jun 1 - 2, 2018	Stockholm, Sweden
Praxistage für Höchsttemperatur- und Nuklearanwendungen	June 6, 2018	Dresden, Germany
ECCM-18	Jun 25 - 28, 2018	Athens, Greece

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