ONset

NETZSCH

CUSTOMER MAGAZINE

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Dear Reader:

The global climate, politics and economic forces are constantly changing, and we are therefore happy to be able to present you this new edition of our customer magazine as usual. In line with our new NETZSCH slogan, “Proven Excellence”, this issue of **on**set features many exciting applications and interesting tips and tricks you can use in your day-to-day work.

This time, we have put together a broad range of all sorts of thermal analysis topics for you. And speaking of a broad range – in this issue, you can learn more about the possibilities of "Commercial Testing" at NETZSCH and the newly created glossary on our homepage.

The leading article examines why a DSC measurement is sometimes not sufficient for the characterization of pharmaceutical active ingredients and excipients; on pages 8 and 9, you will learn more about the flexibility of the DMA GABO EPLEXOR®. This measuring instrument for dynamic mechanical analysis allows for different test conditions from practice to be applied in the laboratory.

This time, the customer article was provided by Dr. Andreas Kleiner, BSH Haushaltsgeräte GmbH, Giengen, Germany. He explains how our Ug measurement instrument, Uglass, can support you in testing your insulating glass with operation that’s as easy as child’s play.

In the Tips & Tricks section, you will learn why proper sample preparation is essential for obtaining clear and precise results.

Along with the Tips & Tricks, I would like to draw your attention to our calendar of events. At all of our trade fairs, conferences and other events, we offer users the opportunity to discuss questions about the thermal characterization of materials with our experts. In this context, we will give you a little preview of our plans for the upcoming K 2019, the leading trade fair for the plastics industry. We are looking forward to seeing you at our booth.

We hope you will enjoy browsing through this issue of **on**set.

Yann Jeschke
Head of Marketing

Greater Certainty in the Characterization of Pharmaceutical Active Ingredients/Excipients and Formulations

Dr. Gabriele Kaiser, Business Field for Pharmacy, Cosmetics, and Food

According to DIN 51007, Differential Scanning Calorimetry (DSC) can be used to describe the physical or chemical processes associated with a measurable heat change. The results of such an investigation include both characteristic temperature and caloric information.

Fig. 1. STA 449 ***F3*** *Nevio* with automatic sample changer

Often a DSC Measurement Alone Is Not Sufficient

If the thermal behavior of a material being investigated is already known, or if the result is a DSC diagram with just a few well separated signals, then evaluation and interpretation is generally quite simple – particularly if one employs state-of-the-art tools such as *Identify*, the curve recognition and database program by NETZSCH (see **on**set[18], page 5). With increasing complexity of the DSC curves and/or substances with unknown composition, it is more challenging to arrive at clear conclusions. One reason for this is that DSC effects can be caused not only by phase transitions and chemical reactions, but also by mass changes.

STA = Application of Two Thermoanalytical Methods to One and the Same Sample

Simultaneous Thermal Analysis (STA) combines DSC and thermogravimetric analysis (TGA) on the same sample and thus allows for the direct differentiation of certain processes such as structural changes and decomposition phenomena.

The advantage of an STA experiment over an investigation employing two separate instruments lies in the identical conditions acting on the sample in a single measurement. For separate individual measurements, on the other hand, one must ensure that the conditions are really the same and not just similar. The example of amoxicillin trihydrate in **on**set[17] on pages 18 and 19 demonstrates how, for example, variation in the hole in the aluminum lid of the crucible can influence the evaporation of hydrate water. The larger the diameter of the hole, the lower the temperatures of the water release.

Figures 2 and 3 depict the thermal behavior of diclofenac sodium. Diclofenac sodium is a painkiller that also possesses anti-inflammatory properties.

In the corresponding DSC curve (figure 2), two overlapping endothermal effects with peak temperatures of 281°C and 285°C can be seen; these immediately switch over to two exothermal effects with peak temperatures at 295°C and 336°C. According to literature (e.g., [1]), this range is to be interpreted as the melting and decomposition of diclofenac sodium. However, the question arises: At what temperature does decomposition start?

Curve Comparisons Require Identical Measurement Conditions

More information can be provided by the additional recording of a TGA curve. It must be considered, however, that comparing a DSC measurement carried out in

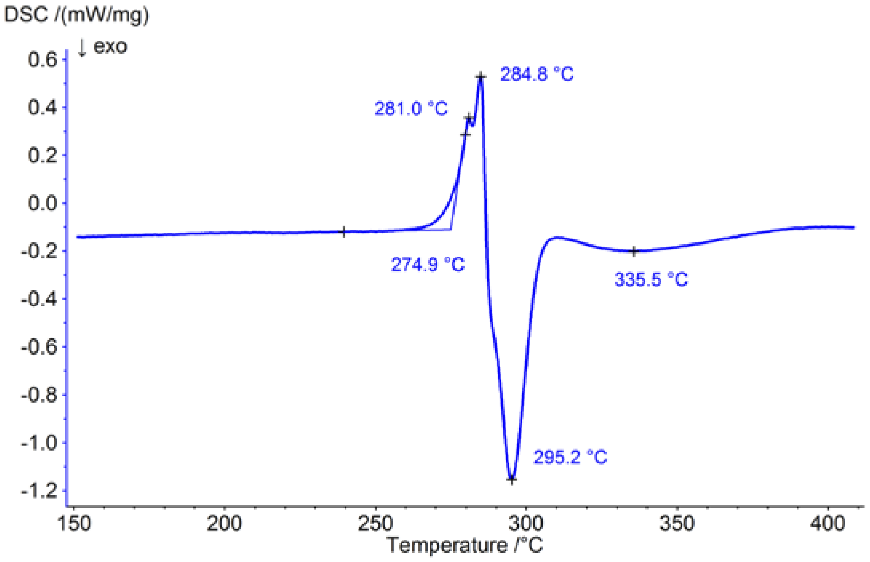


Fig. 2. DSC measurement on diclofenac sodium, sample mass: 3.26 mg, heating rate: 5 K/min Al crucible with pierced lid, N_2 atmosphere

aluminum crucibles with pierced lids to a TGA measurement which is typically conducted in open Al_2O_3 crucibles would do little to provide relevant additional information, for the reasons stated above. The contact areas between the sample and the surrounding gas atmosphere deviate from each other; in open crucibles, decomposition products may enter the gas phase sooner than in closed crucibles with pierced lids. The only method that yields the necessary results is a comparison of DSC and TGA signals that reflect the sample's behavior under exactly the same conditions – as an STA investigation does.

Simultaneous Thermal Analysis Means Identical Conditions for DSC and TGA Measurements

Along with the DSC profile (blue), figure 3 also depicts the simultaneously recorded TGA curve (green). It can clearly be seen that the sample mass begins to decrease already at approx. 263°C. To make this correlation clear, a dashed black line was additionally drawn which corresponds to the theoretical progression of the TGA curve without mass change. With reference to the DSC curve, this means that the mass change starts shortly after the beginning of the first endothermal effect or, in other words, that in this case, part of the sample starts to decompose already during melting.

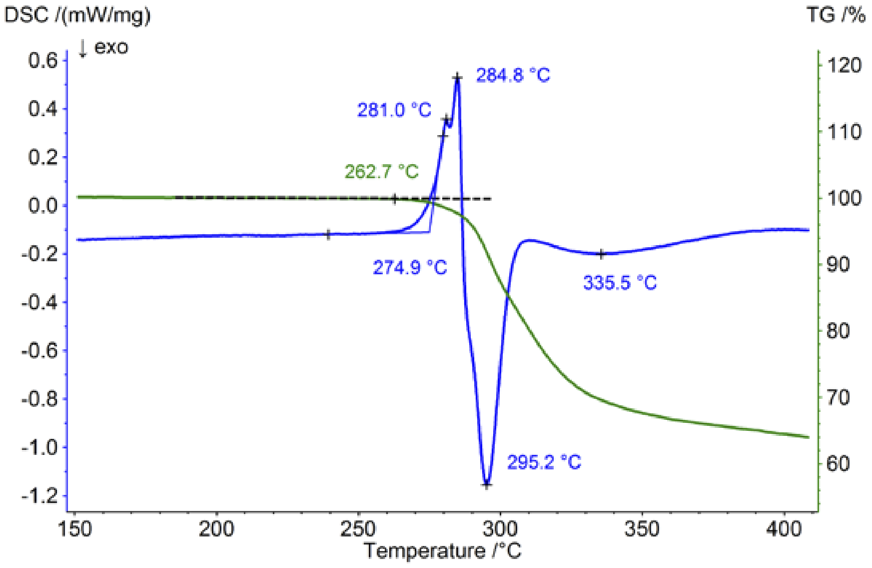


Fig. 3. DSC and TGA signals of the STA measurement on diclofenac sodium from figure 2

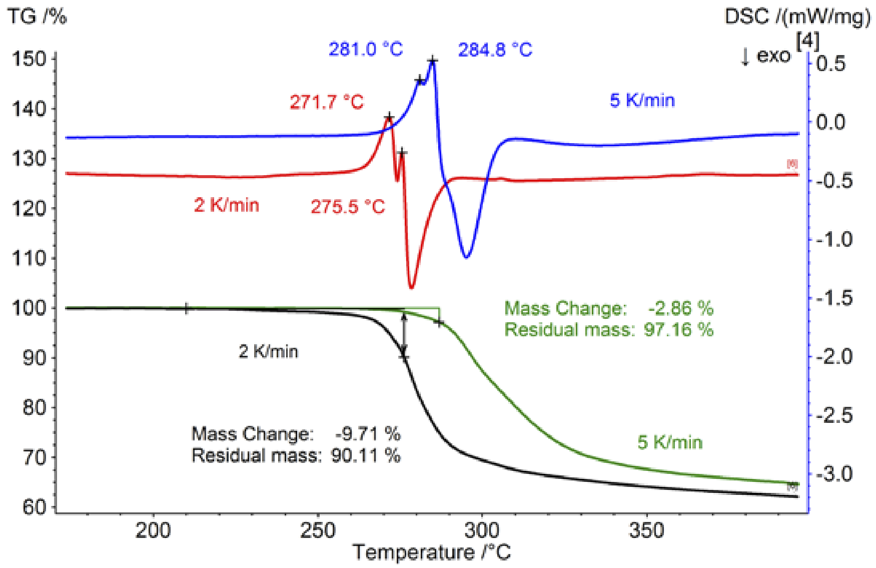


Fig. 4. STA measurement on diclofenac sodium from fig. 3 in comparison with a measurement on the same substance carried out at 2 K/min; sample mass: 3.18 mg, N_2 atmosphere, Al crucible with pierced lid, TGA: green and black, DSC: red and blue

Reducing the heating rate to 2 K/min (figure 4) causes the mass loss to start considerably earlier and also shifts the DSC effects to lower temperatures. Furthermore, the shape of the DSC signal changes. The mass change in the range of the endothermal DSC effects, at almost 10% for the measurement at 2 K/min, is considerably higher than for the measurement at 5 K/min (approx. 2.9%). This means that the DSC signal of the measurement at 2 K/min is more heavily influenced by the concurrent mass change than that of the measurement at 5 K/min.

In the measurement at 2 K/min, the first endothermal peak is smaller than the second one (in the measurement at 5 K/min, this is exactly the other way around) and the two effects are more clearly separated from each other. The corresponding peak temperatures differ by approx. 10 K. This value is greater than expected for the shift of a melting peak that only occurred due to variation of the heating rate from 5 K/min to 2 K/min.

Influence of the Heating Rate on the Decomposition Mechanism

All this indicates that changing the heating rate also changes the decomposition mechanism. Since – according to literature [2] – an intramolecular cyclization occurs when heating diclofenac sodium (and a new compound – 1-(2,6-dichlorophenyl)-indolin-2-on – is thus formed), the complex behavior of reactions above approx. 230°C is probably a combination of melting, cyclization and decomposition.

Conclusion

Simultaneous Thermal Analysis (STA) allows for a reduction in the amount of effort required to thermally characterize a substance and for an increase in the informative power of the curves by applying identical conditions to one and the same sample. The new STA 449 ***F3*** *Nevio* is specially designed for applications in the pharmaceutical, cosmetics and foods industries and offers a range of sensible complements allowing for adaptation to a wide variety of applications, such as diverse crucible materials and a humidity generator for investigations under defined humidity levels. Please contact your local representative for more information.

References

[1] B. Tita, A. Fulias, E. Marian and D. Tita, Rev. Chim (Bucureşti), 60, Nr. 5, 2009, pp 524 – 528
[2] P. Tudja, M.Z.I. Khan, E. Meštrović, M. Horvat and P. Golja, Chem. Pharm. Bull, 49 (10), 2001, pp 1245 - 1250

Finding Solutions Together – Contract Testing at NETZSCH-Gerätebau

Markus Dollinger, Marketing

Fig. 1. View into one of our specialized laboratories in Selb

If you are reading this issue of **on**set, you of course already know that we are one of the leading providers of solutions in the field of thermal analysis.

Our in-house laboratories play a central role in developing enhancements to our instruments as well as new products. We run laboratories of our own all over the world with extensive equipment for virtually any thermal analysis method.

You may not be aware, however, that our laboratories – along with all of our lab teams' know-how – are also available to you through contract testing!

Our largest laboratory is located at our headquarters in Selb. Contract testing is carried out for you by our seven laboratory subdivisions – each specializing in a different method – with a total of more than 55 instruments and over 20 laboratory experts. Our scientists from the fields of physics, chemistry and materials science then serve for the evaluation and interpretation of your measurement results.

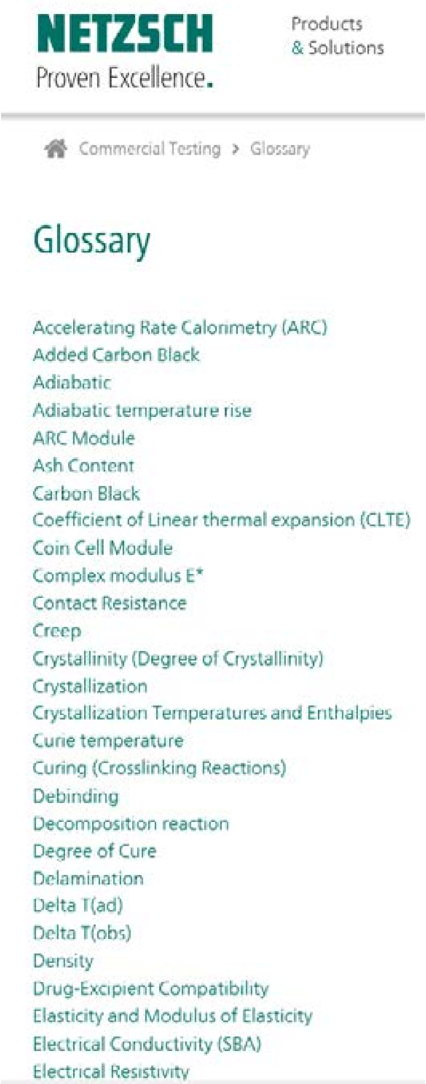
If you only need measurements using a given method on an occasional basis, contract testing is a cost-effective alternative – especially since it does not require you to have personnel of your own with the necessary knowledge for carrying out and evaluating measurements. High workloads and bottlenecks in your own laboratory can also be addressed by outsourcing measurements to us, thus preventing downtime in production or high scrap rates.

We will work together with you to find the best-suited analysis method, discover the reasons behind any production problems, prepare error analyses and work out tailor-made solutions.

Many renowned companies from the automotive, aerospace, electronics, motor sports, chemical, polymer and ceramic industries already rely on us for contract testing.

We would be happy to provide you with more information about our services. Please also feel free to take a look at the glossary on our homepage!

Contact us:
ngb_laboratory@netzsch.com



Glossary

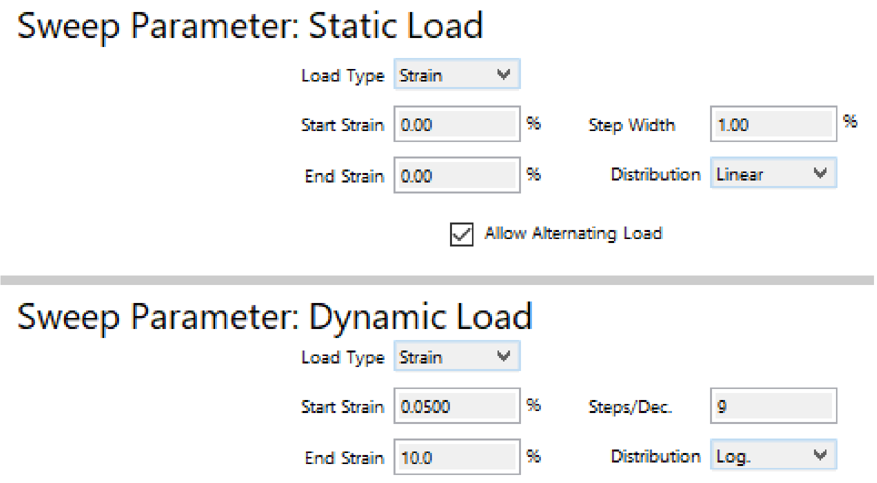
Accelerating Rate Calorimetry (ARC)
Added Carbon Black
Adiabatic
Adiabatic temperature rise
ARC Module
Ash Content
Carbon Black
Coefficient of Linear thermal expansion (CLTE)
Coin Cell Module
Complex modulus E*
Contact Resistance
Creep
Crystallinity (Degree of Crystallinity)
Crystallization
Crystallization Temperatures and Enthalpies
Curie temperature
Curing (Crosslinking Reactions)
Debinding
Decomposition reaction
Degree of Cure
Delamination
Delta T(ad)
Delta T(obs)
Density
Drug-Excipient Compatibility
Elasticity and Modulus of Elasticity
Electrical Conductivity (SBA)
Electrical Resistivity

Transferring Real Operating Conditions from Practice into the Laboratory Using the DMA GABO EPLEXOR®

Dr. Sahbi Aloui, Applications Laboratory, Permanent Establishment Ahlden, Germany

Technical Elastomers

Technical elastomers feature excellent elastic behavior. They can be repeatedly deformed and return to nearly their original length after mechanical relief. Depending on the type, technical elastomers can effectively store or dissipate, i.e., transform, mechanical energy. That is why they are used in many vibration control applications, such as in tires, vibration absorbers in motor and rail vehicles, conveyer belts, seals, hoses, etc.



Sweep Parameter: Static Load

Load Type: Strain
Start Strain: 0.00 %
End Strain: 0.00 %
Step Width: 1.00 %
Distribution: Linear
☑ Allow Alternating Load

Sweep Parameter: Dynamic Load

Load Type: Strain
Start Strain: 0.0500 %
End Strain: 10.0 %
Steps/Dec.: 9
Distribution: Log.

Fig. 1. Independent adjustment of the static and dynamic load with the "Allow Alternating Load" function. At a static deformation of 0%, the dynamic deformation may increase from 0.05% to 10%.

Visco-Elastic Behavior

Technical elastomers can be loaded either statically or dynamically or both at the same time. In the case of a static load, the load is constant over time and often commensurate with its own weight. The dynamic load, however, is a function of time and is either externally imposed (passive) or defined by a drive (active). Dynamic loads are caused, for example, by external influences such as earthquakes, sea waves or strong winds. They also occur in a large number of technical systems as a result of periodically moving masses.

The visco-elastic properties of the elastomer composites at different temperatures and frequencies are determined by means of dynamic-mechanical analysis (DMA). DMA systems are designed for quality control, material as well as product release and material development. For static-dynamic loads, the static loads are first set and then the dynamic load is varied for each static load. Thereby, the sample is subjected to a sinusoidally changing mechanical load of constant frequency and constant amplitude.

DMA GABO EPLEXOR® – 2 Independent Drives

The main feature of the DMA GABO EPLEXOR® systems is the independent generation/setting of static and dynamic loads. The static pre-load is generated by a servo motor and introduced into the sample via the force transducer and the sample holder. The dynamic load is generated by an electrodynamic oscillator and also transferred to the sample. Although using two independent drives requires greater technical effort, it also results in significantly higher flexibility in use.

Static and Dynamic Load

In contrast with shear experiments, it is absolutely mandatory in tension, compression and bending load tests for the static pre-load to be higher than the dynamic load. This restriction is due to the fact that a tensile sample can buckle under alternating tensile loads if the dynamic load amplitude exceeds the static load component. Alternating pressure loads result in a temporary loss of contact between the sample and the sample holder. Correct testing free of artefacts is not possible in this case.

"Allowing Alternating Load"

For some applications such as rubber conveyor belts, drive belts or rubber-metal bearings, deviations from the above rule – that the static pre-load must be higher than the actual dynamic load – may occur in practice if buckling or lifting is prevented by other technical measures. By means of the "Allow Alternating Load" parameter, the restriction that a dynamic amplitude should be smaller than the static load is removed, if required. In this mode, it is therefore also possible to exactly simulate the load situation of the respective application (see figure 1).

For such load conditions, samples that are short and thick are generally recommended as they do not tend to "bulge" as long, thin specimens do.

Payne Effect of Carbon Black-Filled SBR Vulcanisates

Figure 2 shows the example of a dynamic load sweep under tensile stress for a carbon black-filled SBR sample. The measurement was carried out at room temperature and a frequency of 10 Hz. In the first test, the dynamic deformation amplitude was increased stepwise from 0.05% to 10% (blue curve); for the second test, this was carried out in reverse and the dynamic amplitude was reduced stepwise from 10% back to the initial amplitude of 0.05% (red curve). A static pre-strain was not applied here.

The modulus of elasticity |E*| decreases with increasing deformation amplitude (figure 2, blue curve). The dependence of the storage modulus on the deformation amplitude for filled elastomers is also known as the Payne effect.

The Mullins Effect

With a decreasing deformation amplitude (figure 2, red curve), |E*| increases, but does not reach the slope of the "virgin" curve (blue curve). This effect of tension softening is known as the Mullins effect. Reversible and irreversible changes in the polymer matrix, the crosslinking structure and the filler network during load are responsible for this behavior. Some causes include desorption of adsorbed chain sections from the filler surface, breaking of the crosslinking points and/or collapse of the filler agglomeration under the influence of mechanical stress.

Summary

The flexibility of the DMA GABO EPLEXOR® through its independent drives allows for the realization of a great variety of test conditions from practical applications in a laboratory setting, as shown by the above example of dynamic deformation variation.

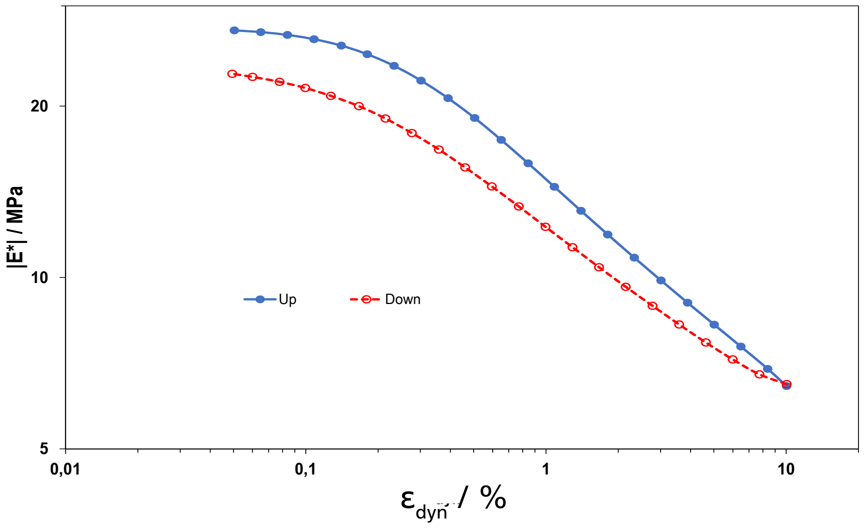


Fig. 2. Dependence of the elasticity modulus of the strain amplitude for SBR with 70 phr N 234 at room temperature and a frequency of 10 Hz. The static deformation amounts to 0% while the dynamic deformation increases from 0.05% to 10%.

Epoxy Resin Curing Investigated by Means of the DSC 214 *Polyma* and MMC 274 *Nexus*®

Dr. Ekkehard Füglein and Dr. Stefan Schmölzer, Applications Laboratory

Introduction

Epoxy resins are materials that have been widely used in a variety of applications, including the coating and coloring of bicycle lanes or crossroads, the surface-coating of floors in parking garages and warehouses, and electronics. Nowadays, epoxy resins are also used as light-weight materials for the rotor blades of windmills. Particularly this application illustrates why knowledge of the curing reaction and its kinetics is essential for the optimization of curing processes in terms of temperature, time and efficiency.

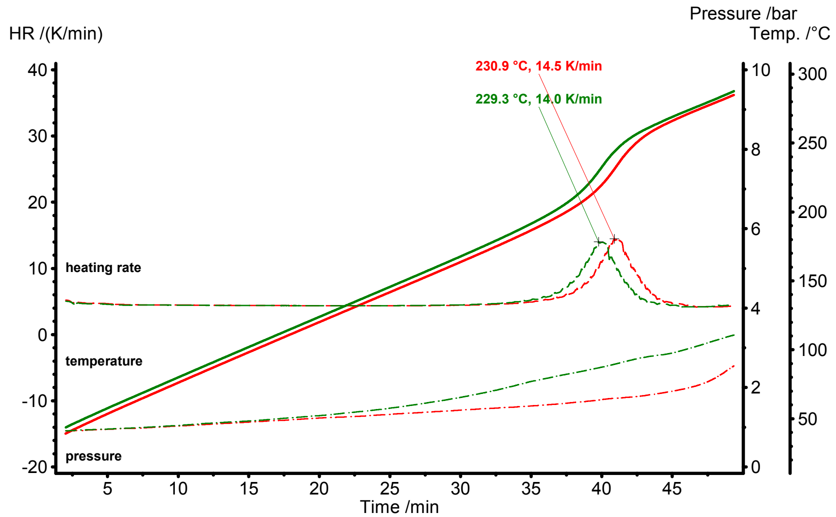


Fig. 1. MMC results of a repeat measurement of the epoxy curing showing measured sample temperature, heating rate and pressure

This article points out similarities and differences in sample preparation, measurement modes and results obtained for the curing reaction of epoxy resins using the DSC 214 *Polyma* versus the scanning module of the MMC.

Sample Preparation and Measurement Conditions MMC

In order to prevent an early reaction of the epoxy resin, it is stored in a refrigerator at -20°C and removed only shortly prior to sample preparation, for approximately one hour at room temperature.

Due to the specific heat and mass of the vessel along with the specific heat capacity and mass of the sample, the heating rate in the constant power mode will not be exactly constant. The ratio of mass and specific heat capacities is known as the Φ factor (or thermal inertia). According to ASTM E1981 [1], it can be expressed in the following equation:

$$\phi = \frac{\Delta T_{ad}}{\Delta T_{obs}} = 1 + \frac{m_V \cdot C_{p,V}}{m_S \cdot C_{p,S}}$$

T: temperature
ad: adiabatic
obs: observed
m: mass
V: vessel
c_p: specific heat capacity
S: sample

Ultimately, the resulting heating rate will be influenced by the thermal behavior of the sample itself. Since the curing of the epoxy resin is an exothermic reaction, the heat of reaction will increase the heating rate temporarily. Heat losses to the surrounding environment are suppressed by the guard heaters positioned on the sides, top and bottom of the calorimeter. These heaters will track the sample temperature independently from the constant power mode of the external heater.

Results and Discussion

Figure 1 shows the course of curing of a repeat measurement of the epoxy resin with the MMC 274 *Nexus*®. A sample mass of approx. 1000 mg and a constant power level of 1000 mW lead to a temperature increase of aprox 4.5 K/min up to 150°C. With the beginning of the curing reaction, the heat of reaction increases the heating rate up to a maximum of 14.0 K/min and 14.5 K/min, respectively. Due to this, the measured sample temperature increases much faster during the curing process.

Comparison of the Curing Reactions

Conducting a measurement along the same lines using the DSC 214 *Polyma* yields comparable results even though the two measurement modes and the sample masses are significantly different.

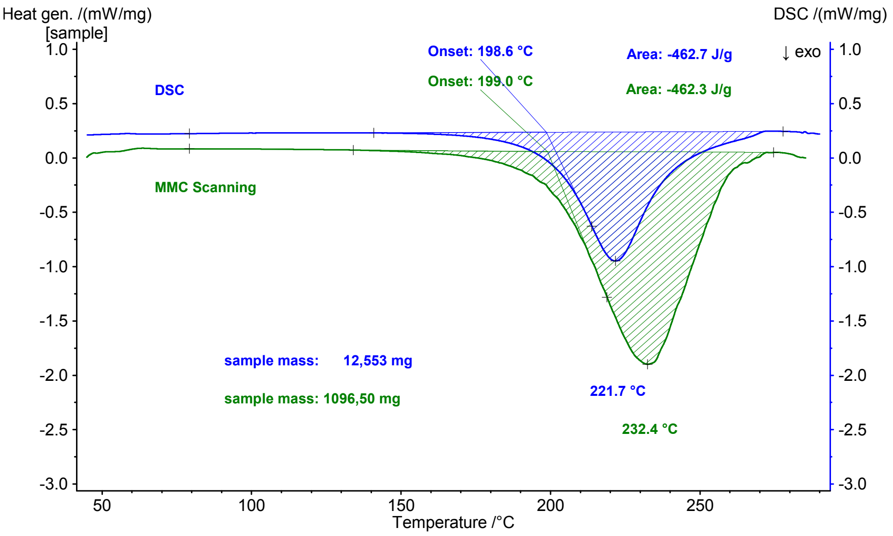


Fig. 2. Comparison of the curing reaction of the epoxy resin showing the DSC results in blue as well as the MMC results in green

Figure 2 compares the results of the measurement using the DSC 214 *Polyma* with those from the MMC 274 *Nexus*®.

The evaluated values for both the enthalpy of curing and the extrapolated onset – representing the beginning of the curing reaction – are identical for the two techniques within the uncertainty limits. The maximum peak temperature, however, differs by more than 10 K. This significant difference is due to the enormous difference in sample mass: 12.553 mg (DSC) versus 1096.5 mg (MMC). It simply takes more time to complete the reaction when the sample mass is more than 80 times higher.

Comparison of the Reaction Enthalpies

Taking into consideration that the results for both the DSC and MMC techniques are scales with the identical range of heat flow (DSC right scale, MMC left scale), the visual impression of the peak areas is different. However, the evaluated values for the extrapolated onset and reaction enthalpy are identical within the uncertainty. Temperature-scaled results of dynamic heating or cooling treatments include the heating rate; integration of DSC peak areas is calculated in terms of time and not temperature. From DSC experiments, we expect the heating rate to be constant (here 5 K/min).

For the MMC, a constant power input was used – therefore, the heating rate depends on the sample behavior. The heat of reaction during the MMC measurement more than triples the measured heating rate from 4.5 K/min prior to the reaction to 14.5 K/min during the curing reaction. This increase in heating rate let the peak area for the MMC results appear much larger than that for the DSC results (at a constant rate of 5 K/min). Since enthalpy evaluation takes the heating rate into account, the evaluated values are almost identical although the visual impression of the peak areas is different [2].

Summary

The curing reaction of epoxy resins can be investigated with various measurement techniques. DSC is certainly the most widely used technique for investigating curing reactions due to the strong exothermic heat of reaction. This work shows that in addition to differential scanning calorimetry, another caloric technique can also serve for the investigation of a curing reaction. In contrast to DSC, the scanning module of the Multiple Module Calorimeter MMC 274 *Nexus*® can study samples on the gram scale and yields comparable results.

References

[1] ASTM E1981 Reapproved (2012), “Standard Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry”, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshocken, PA 19428-2959.
[2] E. Füglein, S. Schmölzer, "Epoxy Curing Investigated by Means of the DSC 214 *Polyma* and MMC 274 *Nexus*®“, NETZSCH Application Note 130, 2019

"The NETZSCH Uglass Measurement Device Provides Support ... with Ease-of-Operation"

Dr. Andreas Kleiner, BSH Home Appliances Group, Product Division Refrigeration, Giengen, Germany

Fig. 1. Uglass – the mobile Ug-value measurement device

Europe's Leading Home Appliances Manufacturer

BSH Hausgeräte GmbH is Europe’s leading manufacturer of home appliances and is known primarily for its Bosch and Siemens brands. Our appliances are characterized by reliability, durability and quality, which means that quality control is an important factor in our development and production. The “Uglass” measuring instrument by NETZSCH (figure 1) assists in determining the thermal transmittance* of glazings installed in refrigerating appliances thanks to its very simple operation and ability to achieve results quickly.

Glass doors are widely used for refrigerated areas in supermarkets. This reduces energy consumption and maintains food quality. Mostly, single glazing is employed, and rarely, multi-pane insulated glazing. BSH Hausgeräte GmbH is also carrying out tests and trials on vacuum insulating glass.

Testing Insulating Glass

In the field of home appliances, insulating glass is used for wine and beverage refrigerators. With the “Uglass” instrument, it is possible to measure the Ug value upon delivery of the insulating glass (at incoming goods inspection) and also later in the process on the finished device, prior to packing and delivery.

Insulating glass is a mass product with reliable manufacturing processes but issues can still arise; for example, it is possible for a different low-e coating, or none at all, to have been used for a certain batch. This can be verified by random measurement with the “Uglass” device. Low-e coatings are significant contributors to a low U-value as they ideally allow only visible light to pass through and block the remaining radiation.

Vacuum Insulating Glass – Leightweight Glass for Increased Efficiency

Since refrigeration appliances are constantly in operation, it is necessary to reduce their energy consumption as much as possible by using high-performance insulation materials. A new and very promising development is vacuum insulating glass, or VIG for short. Similarly to conventional insulating glass, it consists of two glass panes separated by a gap of up to 0.5 mm. In the inter-pane cavity, however, there is no gas, but a vacuum.

In vacuum insulating glass, the heat is transferred by radiation; convection does not take place!

The vacuum eliminates convection in the inter-pane cavity (IPC) and significantly reduces heat transfer. With low-e coatings on both panes, it is possible to achieve U-values of less than 0.5 W/(m^2·K). It should be noted that these low values can only be achieved if thermally toughened glass (toughened safety glass) is used. The higher strength allows for the spacers – which are barely visible but required in the vacuum inter-cavity pane – to be positioned at a greater distance from each other, thus keeping the heat transfer through these spacers as low as possible. The spacers prevent the outer air pressure from compressing the panes. Due to an IPC of <1 mm, the total thickness of the vacuum glass is somewhere between 6 and 10 mm – depending on the glass thickness – and therefore significantly thinner than conventional insulating glass. In cooling units, this allows for a higher useable volume with simultaneously lower energy consumption.

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*also U-value, formerly k-value, indicates the heat flow through a component (e.g., wall, window or roof) with an area of one square meter, if the temperature difference between the two sides is 1 K. The SI unit of the U-value is therefore W/(m^2·K).

Fig. 2. Uglass in "action"

Uglass Detects Damage in a Very Short Time

If the edge bond leaks and air penetrates due to mechanical damage or any production errors and high temperature differences, the increase in the U-value is far more dramatic than for conventional insulating glass due to the very low distance between the panes. The problem, however, is that such defects are usually not visible.

And that is where the Uglass measuring instrument comes into play (figure 2): Within a few minutes, it is apparent whether the U-value is well below $1\ W/(m^2 \cdot K)$ as expected or whether there is a defect and a U-value of $>5\ W/(m^2 \cdot K)$ is measured.

When measuring vacuum glass, the glass thicknesses are initially measured – as for double glazings – with the GlassBuddy by BOHLE on the setting of “no ISO” (laminated glass) due to the low distance between the panes of <1 mm. In the “Uglass” software, the “Vacuum Glass” tab is selected and the glass parameters are entered. Adjustments to the software have only just been implemented and are in the trial phase.

Checking the Results with the GHP Method

In order to check the accuracy of “Uglass” even in the very low U-value range, various vacuum glasses were measured with both “Uglass” and the Guarded Hot Plate (GHP) apparatus. The values obtained are very comparable, indicating that “Uglass” can be used for all types of gas-filled or evacuated insulating glass. Due to the lack of convection in the IPC, the orientation for the U-value is not relevant for vacuum glass. For gas-filled insulation glass, measurement with a GHP in the horizontal state yields increased U-values due to convection in the IPC, so it is not possible to carry out a direct comparison. Moreover, the size and weight of insulating glass comprise a problem for many plate measuring instruments since there are often limitations with regard to sample size. The “Uglass” measuring instrument, on the other hand, can be mounted onto any insulating glass and can therefore be used more flexibly.

The Author

Dr. Andreas Kleiner

After completing his studies of physics, Dr. Andreas Kleiner received his doctorate at IBM Research, Zürich (Rüschlikon), Switzerland, with his thesis "Data Storage on Nanoscale".

Since 2012, he has been working at BSH Home Appliances Group, Giengen, in the Product Division Refrigeration, in pre-development. There, he is responsible for new and alternative insulation technologies and high-performance insulating materials, primarily for refrigeration appliances, but also in collaboration with the other BSH product lines (cooking, washing, dishwashing, small appliances) as well as with the product lines of the entire Bosch Group (since 2015, BSH has been a 100% Bosch subsidiary).

How to Avoid Incorrect Results Due to Improper Sample Preparation

Claire Strasser, Business Field for Pharmacy, Cosmetics & Food

A thermogravimetric balance measures the mass changes in a sample during a temperature/time program (DIN 51005). As a result, it is possible to determine the temperatures of chemical and physical processes that induce a mass change. The processes include vaporization, sublimation, desolvation, and thermal and oxidative decomposition, among others.

It is well known that the thermogravimetric curve is influenced by the following factors:

- Heating rate
- Sample geometry
- Sample mass

If, for example, the heating rate and the sample mass are increased, the detected TGA effects are also shifted to higher temperatures. However, it is also possible to play with the factors heating rate and sample mass, in order to obtain as much information as possible from the measurement curve: better separation of overlapped effects by variation of the heating rate and/or sample mass, magnification of small-scale effects by increasing them, etc.

Improper sample preparation can be the cause of more than just a shift of the mass losses monitored by the TGA: It can lead to significantly different results. With thermogravimetry, solid specimens can be measured as a powder or a piece of a tablet; liquids can be measured as well. However, one should be aware that reproducible TGA curves can only be obtained by consistently using the same sample preparation (sample form) and measurement conditions. In particular, the sample surface influences certain processes, which can be seen in the evaporation of solvents or in oxidative decomposition (combustion). As a consequence, these effects are associated with different temperatures depending on weather the investigated sample is a powder or composed of a single piece.

In the following, thermogravimetric measurements are used to carry out kinetic analysis of the reaction. This example demonstrates how crucial sample preparation can be to draw the correct deductions..

TGA-FT-IR Measurements on Ibuprofen Tablet

The measurements were carried out on an ibuprofen tablet, Ibu 400 akut, marketed by 1A Pharma®. This tablet contains ibuprofen as an API (Active Pharmaceutical Ingredient); this is one of the most frequently used non-steroidal anti-inflammatory drugs (NSAIDs). Furthermore, it also includes excipients that act as fillers, lubricants, disintegrants, etc.

Measurements were performed at different heating rates between 5 and 20 K/min with the TG 209 ***F1*** *Nevio* thermobalance in a dynamic nitrogen atmosphere. Aluminum oxide crucibles were used. The sample masses ranged from 9.93 mg to 10.09 mg. The gases evolved during heating were directly transferred into the gas cell of the FT-IR spectrometer by Bruker Optics.

Figure 1 displays the TGA measurement on the commercial ibuprofen tablet at a heating rate of 10 K/min along with the DTG curve (first derivative of the TGA curve). Additionally, the calculated DTA signal (c-*DTA*®, the difference between furnace and sample temperature) is displayed between 70°C and 100°C (blue curve).

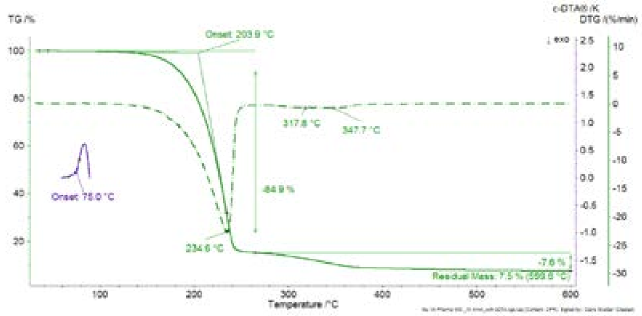

Fig. 1. TGA measurement on the commercial ibuprofen tablet at 10 K/min (green solid curve), DTG curve (green dashed dotted line) and c-*DTA*® signal (blue curve)

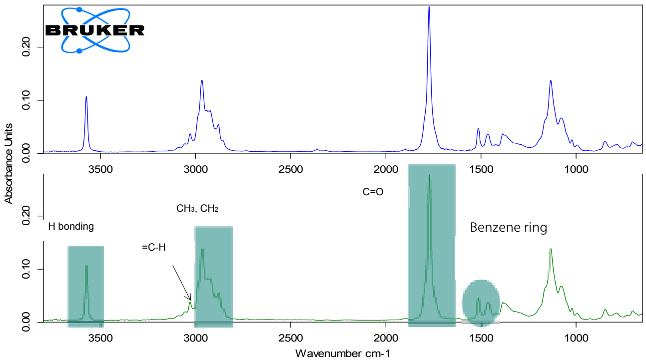

Fig. 2. FT-IR spectra of the gases released at 231°C from pure ibuprofen (top) and from the investigated ibuprofen tablet, Ibu 400 akut (bottom)

For better readability of the plot, the c-*DTA*® signal was only displayed in the temperature range of the ibuprofen melting. The peak detected at 75°C (extrapolated onset temperature) is not associated with a mass loss; it does not result from decomposition or evaporation, which would induce mass changes in the TGA curve, but from the melting of ibuprofen.

The first mass loss with an extrapolated onset temperature of 204°C amounts to 85%. It indicates the decomposition or the evaporation of a component present in the tablet, most probably, the evaporation of the active ingredient, ibuprofen [1]. For verification purposes, pure ibuprofen was also measured by means of TGA-FT-IR (figure 2). The spectra of the gases released at 232°C are very similar for the two materials.

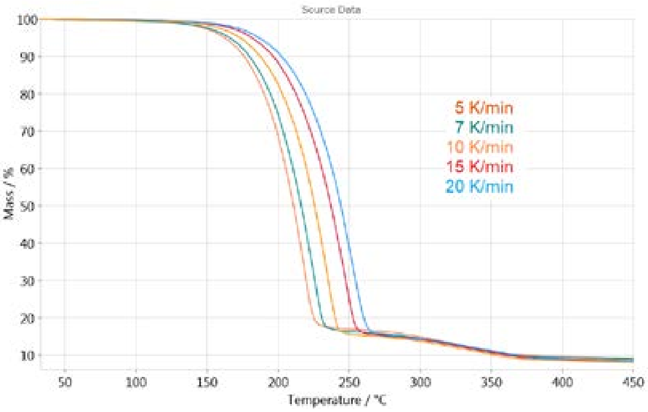

Fig. 3. TGA measurements on the commercial ibuprofen tablet at different heating rates (plot created with the NETZSCH Kinetics Neo software)

This proves that the mass loss detected at 235°C (DTG peak, figure 1) in Ibu 400 akut actually results from the evaporation of the active ingredient (ibuprofen) and is not due to the decomposition of an excipient.

In figure 1, Ibu 400 akut exhibits two further mass-loss steps between 250°C and 400°C which are partially overlapped. They are probably due to the thermal decomposition of excipients present in the tablet as microcrystalline cellulose or magnesium stearate [2].

Figure 3 shows the TGA measurements at different heating rates. The effects are shifted to higher temperatures as heating rates increase. This dependence of the TGA curve on the heating rate allows for determination of the reaction kinetics.

Determination of the Reaction Kinetics by Means of Kinetics Neo

The TGA curves obtained are the basis for the kinetic evaluation of the reactions occurring in the measured temperature range. For this, the NETZSCH Kinetics Neo software was used. It allows for modelling the kinetics of single- to multi-step reactions.

This software can assign each individual step to different reaction types with kinetic parameters of their own, such as activation energy, order of reaction, and pre-exponential factor. Based on the results, Kinetics Neo is able to simulate the reaction(s) for user-specified temperature programs.

Tips & Tricks

To implement, the thermogravimetric curves are first imported into the Kinetics Neo software. Then, a reaction model is selected for each step (for example: n^{th} order reaction). Based on the reaction model chosen, the software calculates thermogravimetric curves. The pertinence of the model is assessed via the correlation coefficient between the measured and calculated curves.

For the first mass loss, the software calculates a curve with a one-step reaction model, A → B. The sample behavior in the temperature range from 250°C to 450°C is described with three independent steps (C→D, E→F and G→H) because this is the best fit for the measured data in this temperature range.

Figure 4 displays a comparison of the measured and calculated curves for such a model. With a correlation coefficient of higher than 0.999, the kinetic model describes the reaction process very well.

For each reaction step, Kinetics Neo calculates the kinetic parameters: activation energy, reaction order, contribution of the step to the global process, etc. Table 1 presents them for all four steps.

Validation of the Kinetic Model

Even when the agreement between measured and calculated curves is very high, the reliability of a model should always be checked by comparing the kinetic results with an additional TGA measurement carried out under different conditions, for example, during an isothermal segment.

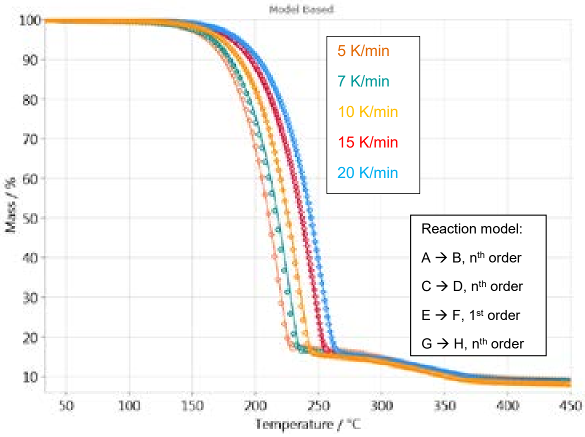

Fig. 4. Comparison of the measured curves (dots) and calculated curves (continuous lines) for a 4-step reaction model

For this test, a commercial ibuprofen tablet was crushed and this powder was measured in an open aluminum oxide crucible by heating to 200°C at 10 K/min. After that, the temperature remained isothermal for 25 minutes. The results are given in figure 5. It is immediately evident that this TGA measurement is not in agreement with the TGA curve calculated by Kinetics Neo, which then begs the question: Is the calculation incorrect?

Tab. 1. Kinetic parameters for the four steps

Reaction	A → B	C → D	E → F	G →H
Reaction type	n^{th} order	n^{th} order	1st order	n^{th} order
Activation energy [kJ/mol]	77.823	181.866	148.941	460.643
Log(PreExp) [Log(1/s)]	6.814	14.911	10.511	38.543
Reaction Order	0.286	1.332	1	13.410
Contribution	0.912	0.022	0.034	0.033

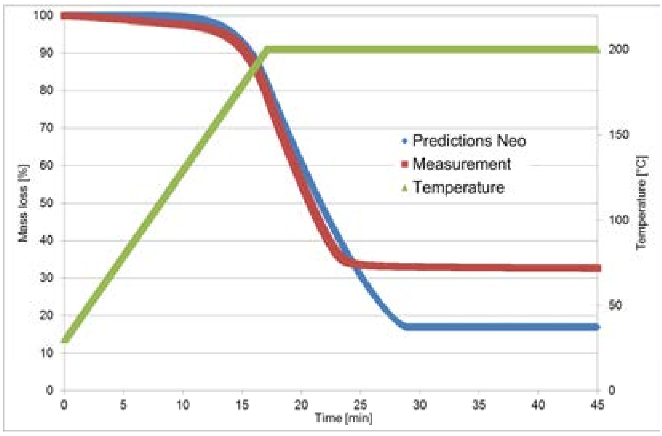

Fig. 5. TGA measurement on a commercial ibuprofen tablet (crushed) during heating to 200°C, followed by an isothermal step (red curve); comparison with the data calculated by Kinetics Neo for the same temperature program (blue curve)

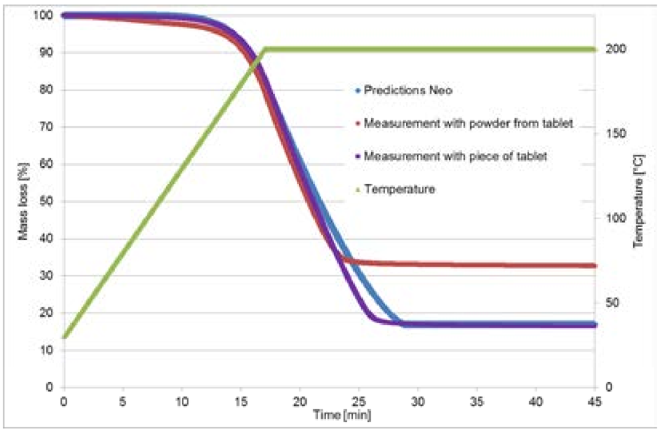

Fig. 6. TGA measurement on a commercial Ibuprofen tablet during heating to 200 °C and isothermal (powder from tablet: red curve; piece of tablet: violet curve), comparison with the data calculated by Kinetics Neo for the same temperature range (blue curve)

What Is the Reason for the Difference Observed?

The thermogravimetric measurements used for calculation in Kinetics Neo were carried out on a piece of an Ibu 400 akut tablet. In contrast with that, the validation measurement was carried out on a powder produced by crushing the tablet.

As mentioned before, the first mass-loss step is due to the evaporation of ibuprofen, which is dependent on the sample surface [1]. One can expect the larger sample surface associated with the crushed material to have a heavy influence on the TGA curve.

In a second experiment, the previous measurement (heating to 200°C and isothermal) was carried out again, but this time using a piece of the tablet. The new thermogravimetric curve now corresponds very well to the one calculated by Kinetics Neo! (See figure 6.)

Conclusion

TGA measurements were carried out on an ibuprofen tablet (commercial name: Ibu 400): one on a solid piece and one on a powder. FT-IR measurements were able to demonstrate that the first mass-loss step results from the evaporation of the active ingredient. In addition, this process is highly dependent on the sample surface, so the results of measurements carried out on a piece of the tablet differ from those carried out on the powder. This also has a great impact on the kinetic analysis. Such a kinetic analysis is particularly useful when investigating the thermal stability of a pharmaceutical.

References

[1] A thermal analysis study of ibuprofen, S. Lerd-kanchanaporn and D. Dollimore, Journal of Thermal Analysis, Vol. 49 (1997), Issue 2, pp 879-886

[2] NETZSCH Application Note 120: Compatibility Studies on Diclofenac Sodium – Fast and Easy with Thermal Analysis; Figures 5 and 9

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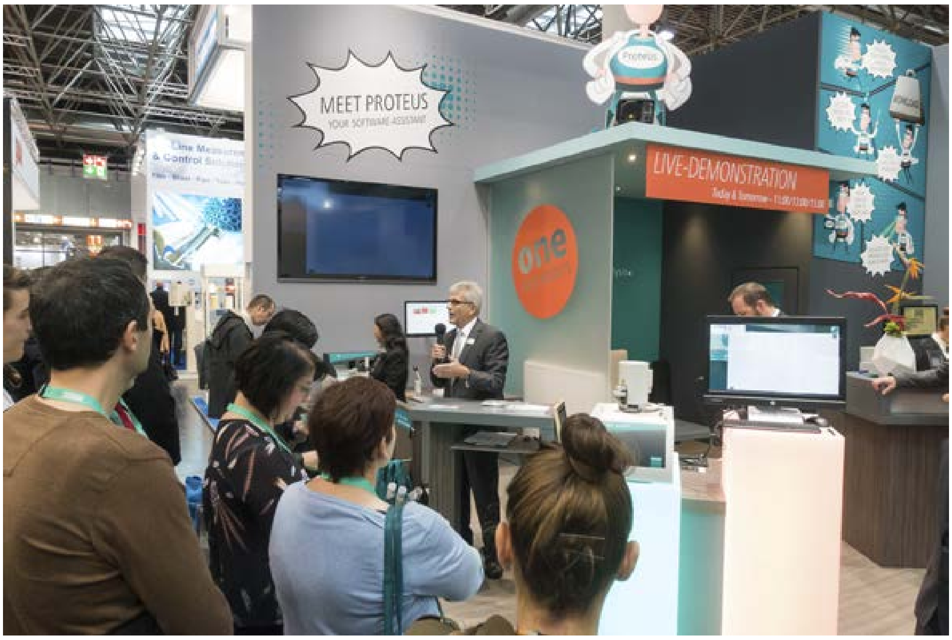
SAMPE	May 20 - 23, 2019	Charlotte, NC, USA
Chinaplas	May 21 - 24, 2019	Guangzhou, China
Plastic 2019	May 22 - 24, 2019	Osaka, Japan
Plastpol	May 28 - 31, 2019	Kielce, Poland
Asean Ceramics	Aug 28 - 30, 2019	Thailand, Bangkok
Composites Europe 2019	Sep 10 - 12, 2019	Stuttgart, Germany
Foam Expo Europe 2019	Sep 10 - 12, 2019	Stuttgart, Germany
Analitika Latin America	Sep 24 - 26, 2019	Sao Paulo, Brazil
K 2019	Oct 16 - 23, 2019	Dusseldorf, Germany

Events



Conferences

	Date	Location
28. Kunststoffkolloquium Leoben	Apr 25 - 26, 2019	Leoben, Austria
DKG-Tagung Leoben 2019	May 5 - 9, 2019	Leoben, Austria
10. Duroplasttagung	May 8 - 9, 2019	Iserlohn, Germany
11th International Heat Flow Calorimetry Symposium on Energetic Materials	May 13 - 16, 2019	Pfinztal-Berghausen, Germany
23. Kalorimetrietage	Jun 12 - 14, 2019	Braunschweig, Germany
ECerS	Jun 16 - 20, 2019	Turin, Italy
ITCC and ITES 2019	Jun 17 - 20, 2019	Wilmington, NC, USA
ICT 2019	Jun 6 - July 4, 2019	Gyeonju, Korea
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