

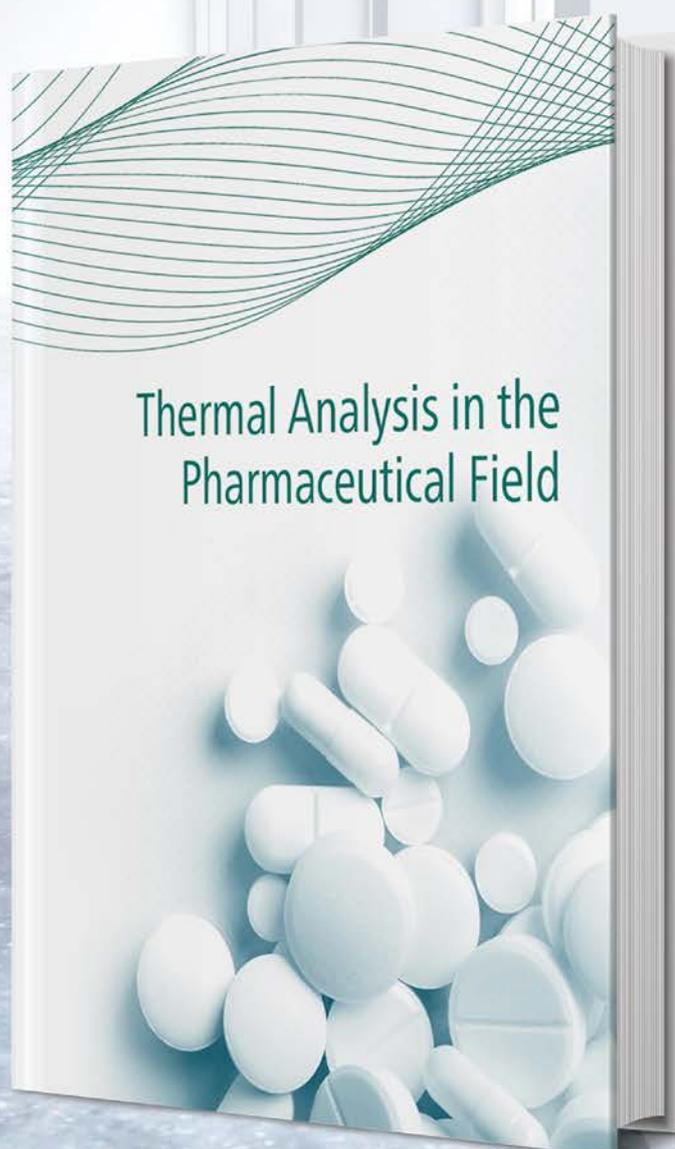
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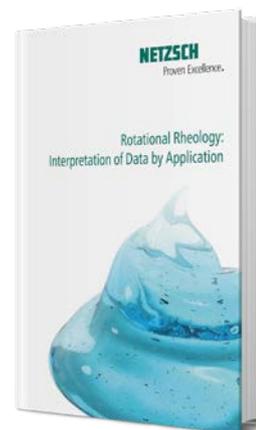
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Thermal Analysis in the
Pharmaceutical Field

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Dear Reader:

I'm pleased to be informing you about the latest news from the world of thermal analysis. I'm particularly proud to present our latest application book, "Thermal Analysis in the Pharmaceutical Field" – a reference guide for pharmaceutical applications that supports you with a lot of helpful information and practical examples.

Starting on page 6, we introduce our new TCC 918 Cone Calorimeter by NETZSCH TAURUS Instruments GmbH, which is considered one of the most important instruments in the field of fire testing and fire safety engineering – an area that will become increasingly significant in the future.

How thermal analysis can contribute to the extraction of hygroscopic salts as water and heat reservoirs is described by the research group headed by Prof. Fröba, Uta Sazama and Dr. Paul Kallenberger of the Institute of Inorganic & Applied Chemistry at the University of Hamburg. Read more about this leading-edge topic starting on page 10.

Our article under "*Tips&Tricks*" on the subject of rheology shows how important information on the desired behavior of hand cream can be obtained by means of measurements with the Kinexus rotational rheometer – all simply and clearly explained, so as to be accessible even for those who have only little experience in the field of rheology so far.

On page 19, we give you some brief insights into our collaboration with Malvern Panalytical and demonstrate how it can be beneficial for you as well.

Interested in the topic of "Material Science in Additive Manufacturing"? Then we are sure that you will be thrilled by our new articles and video series in which all aspects of this technology and a lot more are very clearly explained. Learn more about this starting on page 20, where you will also find all links to the aforementioned videos and articles.

Finally, we would like to inform you about sensXPERT, a new start-up developed in cooperation with NEDGEX, the digital unit of the NETZSCH Group. The use of sensors and artificial intelligence (AI) results in intelligent production that can take your manufacturing plant to a new level.

And last but not least, I would like to present another book on the interpretation of measurements with rotational rheometers which we can heartily recommend as a guide in the field of rotational rheology.

Interested? Then I hope you enjoy the read.

Warmly,



Doris Forst
Member of **onset** editorial staff



Achieve Your Goal Faster with the New NETZSCH Reference Book for Applications in the Pharmaceutical Field

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



Even in the era of the Internet, the search for information can be time-consuming and complex. Our new book "Thermal Analysis in the Pharmaceutical Field" in English now offers the opportunity to shorten this lengthy process. Presented in a compact manner, this reference book gives you expert insights into the measurement, evaluation and interpretation of active pharmaceutical ingredients, excipients and physical mixtures.

The book covers a broad spectrum. It has a total of eight chapters entitled as follows:

- Methods
- Characterization of amorphous and crystalline phases
- Purity
- Thermal stability
- Oxidative stability
- Storage conditions and shelf life
- Polymorphism
- Compatibility

The book uses a variety of specific application examples to illustrate how the corresponding experiments are to be carried out and what conclusions can be drawn from the results. An introduction preceding each topic describes the necessary methods and definitions addressed within and establishes the connection to pharmaceutical issues. Appendices to various chapters provide further information; for example, following the polymorphism chapter, there is a section dealing with the relationship between polymorphism and thermodynamics.

The methods used are:

- Differential Scanning Calorimetry (DSC)
- Thermogravimetric Analysis (TGA)
- Simultaneous Thermal Analysis (STA)
- Coupling of Gas Analysis Systems such as FT-IR or GC-MS to TGA/STA.

The samples used are all solids.

An Essential Guide for Research/Development, Quality Control and Teaching

Whether you are new to thermal analysis or have been involved with it for quite some time, this reference book has interesting aspects in store for each and every one of you. Along with practical tips on how to perform experiments, the measurement results are discussed and interpreted in detail. As a result, "Thermal Analysis in the Pharmaceutical Field" provides valuable support for everyday work in both the industrial and academic environments.

With its clear structure, the book also offers an overview of the many possible applications of thermal analysis in pharmaceuticals. It is not necessary to read through each chapter from the first to the last page. The book is structured in such a way that you can selectively pick out individual examples without overlooking important items. Where it makes sense to consult other chapters, appropriate cross references are provided.

On 263 pages, 28 different substances are covered, from acetylsalicylic acid to urea – in part as individual samples and in part (for compatibility studies) as mixture components. The majority of the

measurements were carried out in a dry inert gas atmosphere (usually nitrogen); however, the chapter "Storage Conditions and Shelf Life" also covers the influence of humidity on active ingredients and excipients.

See for Yourself!

Please visit our Internet page at the following address

www.netzsch.com/pharma-application

There, you will have the opportunity to get a first impression of the structure and content of the book. As a reading sample, you will find the introduction to the chapter "Thermal Stability" as well as the thermal behavior of aspartame. The pages describing the experimental examples are always structured the same. After some basic information on the sample material and the measurement parameters, the measurement curves (in this case, TGA-FT-IR) are presented and analyzed, and if possible, the results are compared with literature data.

We wish you many interesting discoveries in your reading!



The Brand New TCC 918 Cone Calorimeter for Fire Testing and Fire Safety Engineering

Dr. André Lindemann, NETZSCH TAURUS Instruments GmbH, Weimar, Germany



Fig. 1. TCC 918 Cone Calorimeter

Fire has unpredictable power. The fire behavior of a material is an extremely important factor in assuring private and public safety. To this end, fire testing ensures that materials, products and processes are always safe, of high quality, compliant and suitable for the intended purpose.

The TCC 918 Cone Calorimeter (figure 1, schematic diagram in figure 2) is considered one of the most significant instruments in fire testing. The specimens are irradiated, ignited by sparks and thereby combusted. This apparatus analyzes the combustion gases and measures the smoke produced from a test specimen that is being exposed to a certain heat flux. The principle is known as the “oxygen consumption principle” and is among the methods of calorimetry. From the oxygen concentration, the released heat is calculated.

The measurement also involves monitoring the flow rate in the exhaust pipe and the mass loss of the sample. Smoke obscuration is measured as the intensity of the laser light that is transmitted through the smoke in the flue pipe. The TCC 918 is in accordance with all nationally and internationally established standards including ISO 5660-1, ASTM E1354, ASTM E1474, ASTM E1740 and ASTM F1550.

Principle of Operation

The specimen ($100 \times 100 \times 50 \text{ mm}^3$) is positioned onto a sample holder that is placed in the load cell. The load cell monitors the sample mass during the measurement.

A conical radiant electrical heater uniformly irradiates the specimen from above. A spark igniter is located

between the specimen's surface and the cone heater. This ignites the flammable gases evolving from the specimen when it is heated. Once sufficient pyrolysis products are produced, an electric spark triggers combustion. If the entire specimen area is burning, the igniter is turned off. The combustion gases produced pass through the heating cone and are collected by an exhaust duct system with a centrifugal fan and hood. In the exhaust duct, the gas flow is measured, as are O₂, CO, and CO₂ concentrations and smoke density. A laser photometric beam determines the amount of smoke produced.

Measurement of the Gas Concentration

The measurements of gas flow and oxygen concentration are used to calculate the quantity of heat release per unit of time and surface area. The heat release rate (HRR) is expressed in J/s or W. The

development of HRR as a function of time is typically used to analyze fire properties. The analysis of the HRR curve versus time also allows for the characterization of time of ignition (TOI or TTI) and time of combustion or extinction (TOF). The system is equipped with the Siemens ULTRAMAT/OXYMAT 6E for the detection of two infrared components, CO and CO₂, as well as for the detection of O₂ in accordance with the standards.

Smoke Density Measurements

Between the gas sampling ring and fan, there is an optical measurement system. The transmission of laser light (HeNe laser) through the smoke is used as a measure for the amount of smoke produced and is the basis for determination of the smoke release over time and total smoke release (TSR). The optical device has electronics optimized for stable and safe operation.

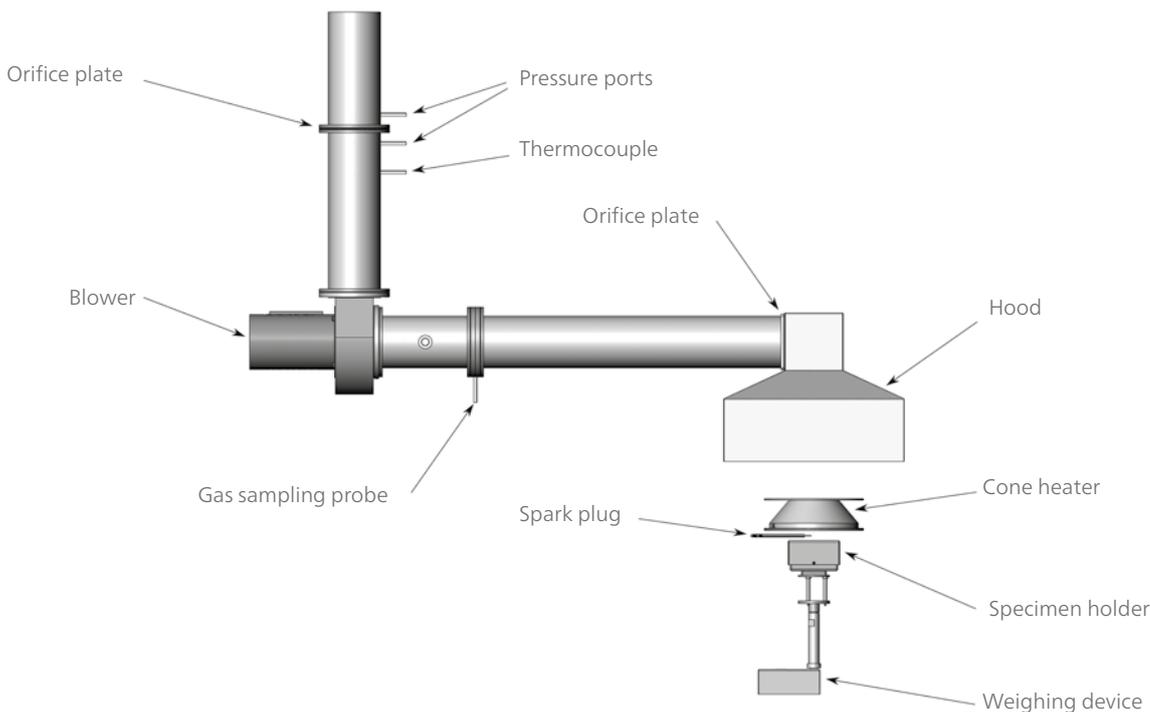


Fig. 2. Schematic diagram of the TCC 918 cone calorimeter

TCC 918 Cone Calorimeter

Flammability Parameters Associated with the Specimen's Burning Properties for Predicting Real-Time Fire Behavior

- Ignition time
- Mass-loss rate
- Combustion products
- Heat release rate
- Smoke production
- Effective heat of combustion
- Fire modelling
- Prediction of real-scale fire behavior
- Development of new products (pass/fail test)

Mass-Loss Measurement

During the experiment, the sample mass is detected by a load cell made by the well-known manufacturer Sartorius. It has a load capacity of 8.2 kg and a repeatability of 0.01 g.

Specimens and Sample Holder

The specimen ($100 \times 100 \times 50 \text{ mm}^3$) is positioned onto the sample holder that is placed in the load cell. The sample holder is made of stainless steel and has a holding frame and additional CaSi panels. It is horizontally open for easy sample access (depending on the specimen, sample holders with open or closed edges are available). Such easy access becomes necessary if the specimen swells during heating and forms a protective char layer. In such cases, a sample holder with

a wire mesh can be used to hold the sample in place during swelling. The distance between the specimen surface and cone heater is controlled by the software and by independent motoric hoists for cone heater and sample holder.

Operation via Touch Screen

The system comes with an internal single board computer (SBC) and two touch screen panels. The software is capable of presenting all relevant data and measurement results in the form of tables or graphs. With the help of the touch screen, the user is easily and safely guided through the program. An online evaluation takes place for a variety of parameters, including heat flow, smoke emission, mass loss, etc. Calibration processes are also simple and run automatically. The measurement report can be easily converted into a PDF or can be used as a text file.

PA 6 Measurement Example

To highlight the effect of different flame retardants on the fire behavior of PA 6, samples of the different compounds were injection-molded into $100 \times 100 \times 4 \text{ mm}^3$ plates for testing in the TCC 918.

Figure 3 shows the measurement results of neat PA 6 and the visualization in the TCC software. Figure 4 depicts the measurement results regarding mass loss, heat release rate and transmission as a function of time. The sample with graphite-based flame retardant (red curve) shows the lowest mass loss, the lowest heat and



TCC 918 Cone Calorimeter

the lowest smoke release (lowest reduction of transmission) of all samples. In comparison, the sample with non-halogenated flame retardant (green curve) behaves similarly to the neat PA 6 material (blue curve), except that the values for heat release are lower and the reaction ends faster. In the case of transmission, however, the smoke emission is significantly higher than with pure PA 6.

Summary

Investigation of the real-time fire behavior has become very useful in the field of fire safety engineering. To this end, the TCC is a state-of-the-art fire testing instrument for smaller test samples.

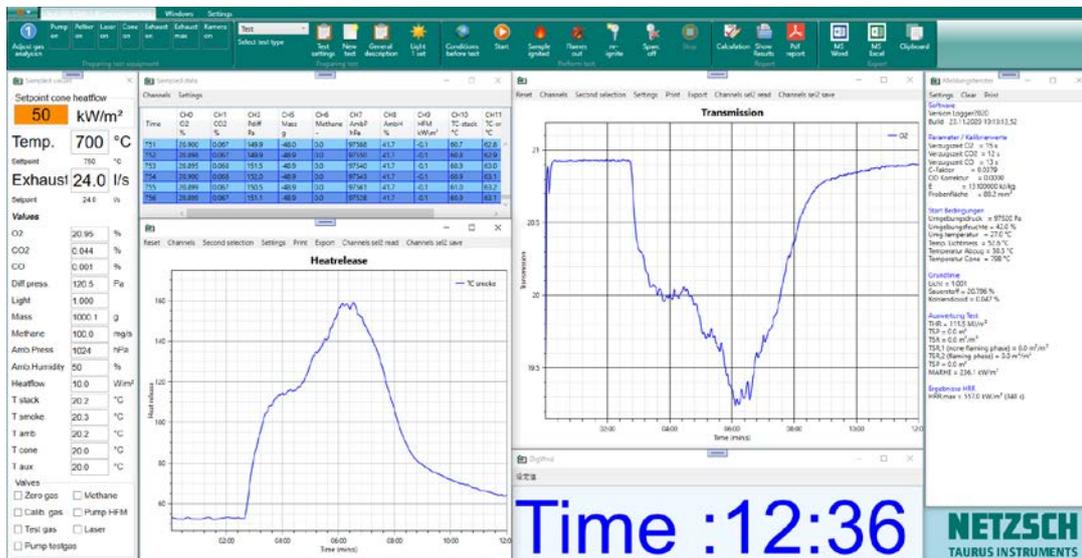


Fig. 3: Overview of TCC measurement on neat PA6 in the TCC software: Measurement input data (left column), measured values from 751 s -756 s and two exemplary measurement curves (middle columns), overview of the selected analysis values (right column).

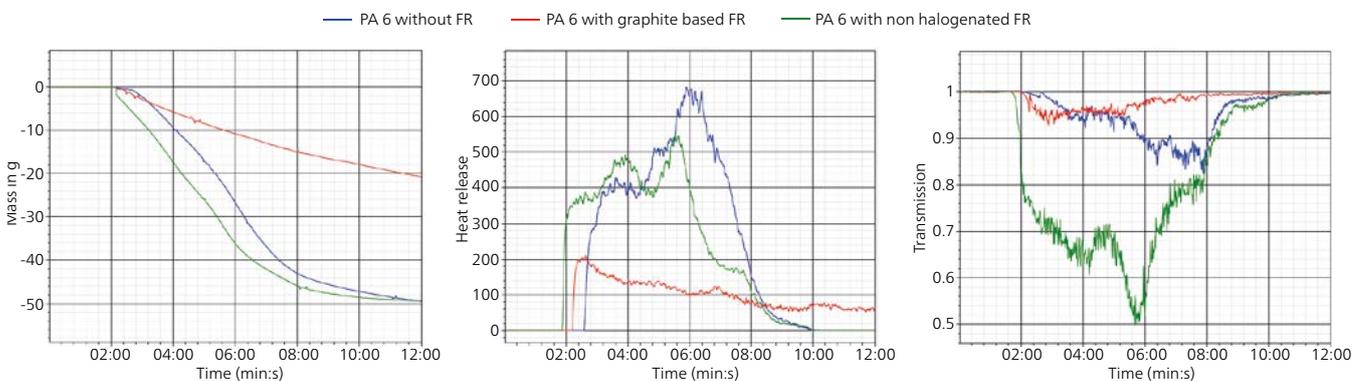


Fig. 4
Neat PA 6 (blue), PA 6 w/graphite-based flame retardant (red) and PA 6 w/non-halogenated flame retardant (green)
a) Mass loss b) Heat release rate and c) Transmission (Source: BPI)

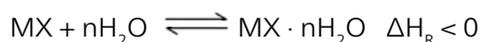
Hygroscopic Salts – A Storage for Heat and Water

Uta Sazama, Dr. Paul Kallenberger and Prof. Michael Fröba, Institute of Inorganic and Applied Chemistry, University of Hamburg, Germany

Introduction

The access to energy and freshwater becomes independently from each other increasingly a subject of a global political debate. From ethical, environmental and economic points of view, the storage of fresh water and heat from the air using alkaline earth salts can be a successful alternative.

This approach is based on the thermochemical reaction of an anhydrous salt which is able to be hydrated by absorbing water or dehydrated by releasing water.



The concept of producing drinking water by using hygroscopic alkaline-earth salts is going far beyond the common adsorption and desorption of water vapor as in zeolites or metal-organic frameworks.

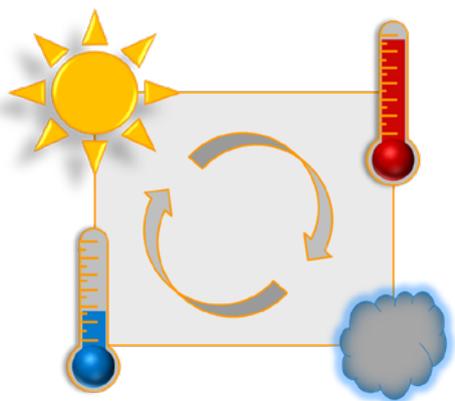


Fig. 1. Indication of the reaction cycle for energy and water production

Equal to nature, only natural atmospheric humidity and the energy of the sun light should be used as source of water and for the heat release (hydration) as well as for the regeneration of the material (dehydration).

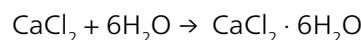
However, this approach requires that the endothermic regeneration reaction can be carried out at temperatures below 150°C. Which salt is suitable for heat storage and fresh water production by hydration and dehydration is also to be determined by the

available relative humidity. A systematic literature screening showed that especially hydrates of MgSO_4 , CaCl_2 , MgCl_2 , SrBr_2 , LaCl_3 and $\text{Al}_2(\text{SO}_4)_3$ are particularly suitable for practical investigations. [1,2,3,4]

Experimental

All investigated salts are alike in that the positive water absorption and release properties of the pure powders are significantly reduced by multiple cyclisation. The reason for this is the formation of passivation layers on the surface and an agglomeration of the salt particles, which impede the gas permeability and thus a complete hydration and dehydration, respectively. A central starting point to remedy this problem is the experimental development of a macroscopically structured support material which maintains the gas permeability of the imbedded salt particles without limiting the high volumetric as well as gravimetric water absorption and water release capacity of the salts. In this context, composites of matrix materials, which can adsorb water on their surface, and hygroscopic salts, which absorb water by hydration, have shown good and practical results. [1,5-9]

In the following, only one composite material of CaCl_2 and an alginate-based matrix, designated as A- CaCl_2 , will be described for the sake of clarity.



$$\Delta_{\text{hyd}}H = -722,2 \text{ kJ} \cdot \text{mol}^{-1}$$

Non-toxic calcium chloride is commercially available at low cost (e.g., as an industrial waste product) and has the potential to absorb more than 95% of its own weight of water and release it again at temperatures up to 100°C. It shows fast hydration kinetics at low humidities and is particularly suitable for the development of application-oriented materials which should be used for the storage of heat and fresh water.

The same applies to sodium alginate. It will be extracted from brown algae and used as a gelling, thickening and coating agent in the food industry (additive E401).

Customers for Customers

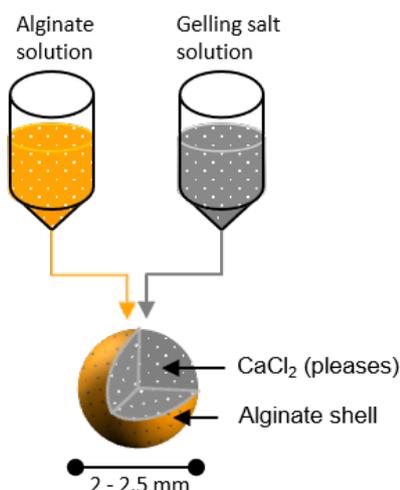


Fig. 2. Overview of the composite synthesis by salt precipitation

Figure 2 shows the synthesis of the A-CaCl₂ composite by precipitation of the gelling salt within the alginate-based matrix structure. First, hydrogel spheres are produced (Fig. 3a), which form a spherical granulate after a shape-retaining drying process up to 140°C. (Fig. 3b).

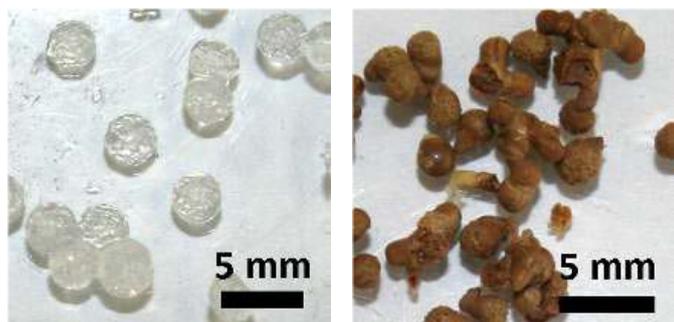


Fig. 3a. Hydrogel spheres and Fig. 3b. dried composite granules

For the application as thermochemical and hydrate storage material, a high porosity combined with a high salt content is the basis of the composite. The A-CaCl₂ composite was prepared using a gelling salt solution with a salt concentration of 6.7 mol·l⁻¹. Relative to the completely dehydrated composite, this result refers to a salt content of 70 to 78 wt%.

Thermal Analysis

Several thermochemical studies have accompanied the experimental development from a hygroscopic salt to the A-CaCl₂ composite. The focus was on the temperature range < 150°C and the conservation of the storage density with respect to water with the simultaneous suppression of an agglomeration of the calcium chloride particles.

All TGA-DTA measurements were carried out with an STA 449 **F3 Jupiter**® equipped with a silicon carbide furnace and a heating rate at 1 K·min⁻¹ using the Al₂O₃-0.3 ml DTA/TGA crucibles by NETZSCH. The used atmosphere was a mixture of argon and oxygen in a ratio of 4:1 with a flow rate of 20 ml·min⁻¹. Volatile decomposition products were qualitatively detected during thermal analysis by means of a capillary-coupled *Aëolos*® quadrupole mass spectrometer. For the sake of clarity, this data is not depicted in this article.

The thermogram (Fig. 4) shows a weight loss of 12.5% in the temperature range up to 125°C, which is due to the release of water which was adsorbed at room temperature. Furthermore, apart from the release of further residual moisture (2.4%), sodium alginate exhibits a good thermal stability up to 200°C and confirms the selection as a suitable reaction partner for the desired composite synthesis and for the intended usage.

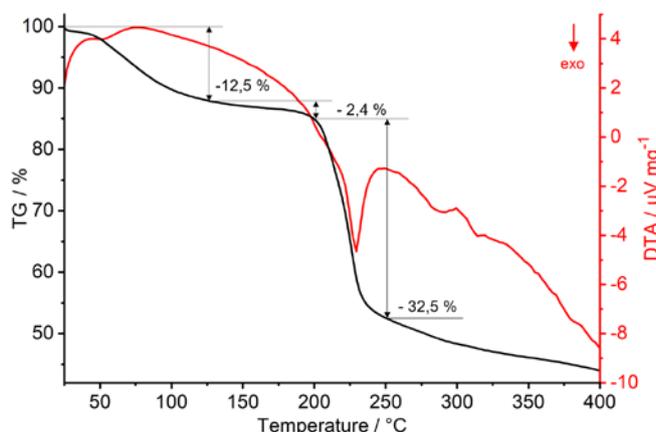


Fig 4. Simultaneous TGA-DTA of sodium alginate

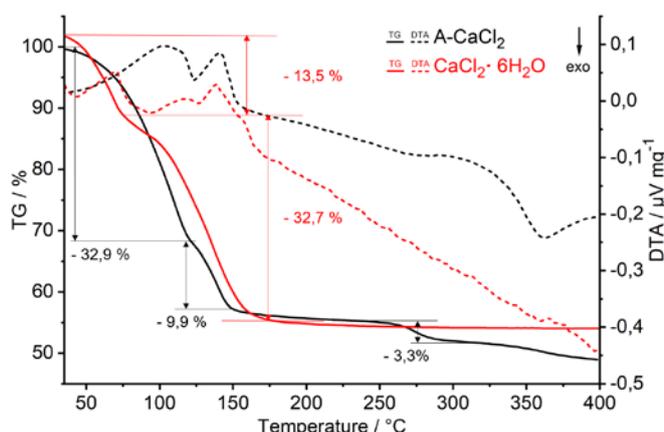


Fig. 5. Simultaneous TGA-DTA of dehydration of the A-CaCl₂ composite compared to pure CaCl₂·6H₂O salt

The complete dehydration of the pristine CaCl₂·6H₂O salt (Fig. 5, red lines) is characterized by a two-stage mass loss, which ends at a temperature of 175°C. The first mass loss up to 75°C corresponds to the dehydration from the hexahydrate to the tetrahydrate (16.9 wt% theoret.). The second mass-loss represents the complete dehydration from the tetrahydrate via the dihydrate (33.8 wt% theoret.), visible as a double peak in the DTA, to the anhydrous salt, which is stable up to 400°C.

In the presentation of the compared dehydration process, it was considered that the CaCl₂ salt absorbs water from the ambient air with very fast hydration kinetics, so that weight gain and partial deliquescence may occur already during sample preparation. This partial deliquescence leads outside of the thermobalance to vague weighed portions which require the calculation of the starting mass of the pristine salt for comparison. The initial mass of the pure salt (> 100%) was therefore calculated on the basis of the residual mass at 400°C, which was defined as the anhydrous salt. In contrast to this (Fig. 5), a calculation of the starting mass was omitted for the A-CaCl₂ composite because the matrix contributes to the delayed contact with the ambient air.

The A-CaCl₂ composite shows complete dehydration up to 150°C. In contrast to the pure salt, a mass loss occurs until 125°C, which corresponds to the forma-

tion of the dihydrate. Immediately following is a second mass loss between 125°C and 150°C, which is caused by the complete dehydration of the A-CaCl₂ composite. The parallel shifted DTA signal (black dotted line in Fig. 5) with two endothermic processes merging into each other up to 150°C suggests a reduced diffusion due to the matrix. The composite is thermally stable up to about 250°C. At higher temperatures, the combustion of the matrix material begins, which is characterized by a clearly visible mass loss around 275°C. This continues beyond 400°C (for comparison see also thermogram of sodium alginate Fig. 4).

After the complete dehydration in the temperature range between 150°C and 250°C, the difference in mass between the composite and the pure salt should become visible, which corresponds to the mass of the matrix. With complete dehydration of the pure salt, a residual mass of about 50% was expected, but a 5% higher residual mass was determined. The reason for this is the agglomeration of salt particles during hydration and the associated passivation, which prevents complete dehydration.

Tab. 1: The theoretical residual masses of the A-CaCl₂ composites when passing through the different hydrate stages. The values were normalized to the hexahydrate and calculated for a 70 wt% salt content.

Hydrate in alginate composite (CaCl ₂)	Rel. mass theoretically in %	Rel. mass TGA-DTA in %	Rel. mass TGA-DTA in °C
A-CaCl ₂ ·6H ₂ O	100	100	25
A-CaCl ₂ ·4H ₂ O	88	-	-
A-CaCl ₂ ·2H ₂ O	77	68	125
A-CaCl ₂	66	57	150

Table 1 presents a comparison of the theoretical mass losses for the dehydration of the composite, considering a salt content of 70 wt% and the values determined by thermal analysis. Minor deviations are due to sources of error such as an underestimated salt content in the composite and the hydrate steps which cannot be clearly separated in the measurement.

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In addition, the relative masses and the temperatures corresponding to the formation of the hydrates from TGA/DTA experiments (Fig. 5) are listed, too.

Thermal Analysis Under Controlled Humidity

To prove the stability of the composite material, thermoanalytical investigations were carried out not only on the thermochemical properties but also on the possible changes in the course of repeated hydration and dehydration of the salt within the matrix.

For the measurement under controlled humidity, the STA 449 **F3 Jupiter**[®] was extended with the humidity generator MHG32. The gas flow with defined humidity is generated in a mixing module, which is directly connected to the silicon carbide furnace via a heatable pipeline.

When we designed the hydration measurements, we made the decision to use cut Al_2O_3 -0.3 ml DTA/TGA crucibles. They offer the advantage over nets and slip-on plates that the spherical granules remain in place, energetic effects can still be observed and a practical accessibility of the set humidity to the material is guaranteed. (Fig. 6)



Fig. 6a. Original and 6b+c. Illustrated application of the trimmed Al_2O_3 crucible for the A- $CaCl_2$ composite granules (yellow)

To demonstrate the stability, water absorption/desorption were followed over several cycles in further thermochemical experiments.[8]

Figure 7 shows an eightfold analysis cycle, which was used to investigate the influence of repeated hydration and dehydration on the $CaCl_2$ within the alginate matrix. At the beginning of the measurement (step 1 in figure 8), the composite material is completely dehydrated to determine the relative mass for the further course of the cyclization. In the second step, hydration is carried out at 25% relative humidity (corresponding to a partial pressure of water of 10.6 mbar) for 5 h at 30°C.

The third step describes the dehydration. Under dry nitrogen, heating is carried out at 2 K/min to 150°C. In a fourth step, the desorption temperature is maintained for 5 h. In the fifth step, cooling down to 30°C at a cooling rate of about 1 K/min and subsequent equilibration for 2 h takes place. The repetition of the cycles always starts with step two.

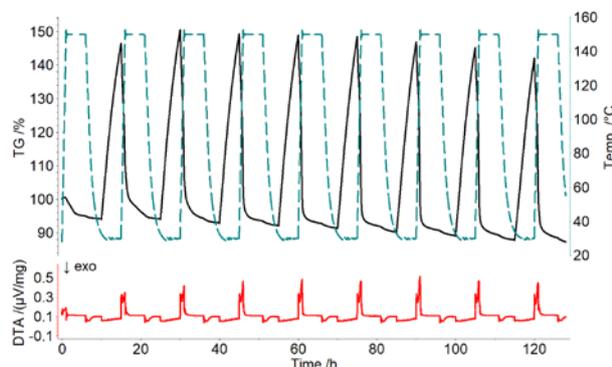


Fig. 7- Simultaneous TGA-DTA measurement of the alginate- $CaCl_2$ composites. Dehydration is carried out over eight cycles in 0% r.h. at 150°C and then re-hydrated at 30°C in 25% r.h.

During the eight cycles (5½ days), there were slightly different conditions (drift of the balance; indirect cooling of the SiC furnace), which were mathematically suppressed in the temperature-scaled display (Fig. 8) for the sake of clarity. Since the *Proteus*[®] software hides the isothermal segments in the diagram, a thermogram as shown in Fig. 8 can only be generated using a separate analysis and visualisation program (here: Origin).

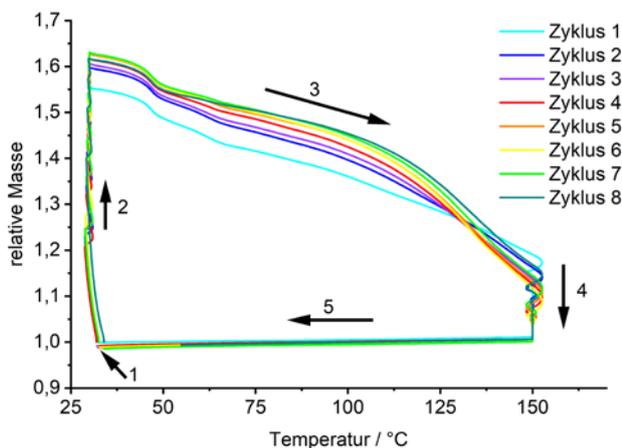


Fig. 8. Relative mass of the A-CaCl₂ composite during the cyclization process. Section 1) Completely dehydrated material at the beginning of measurement. (Starting point of the cycles.) 2) Hydration at 30°C and 25% r.h. 3) Heating to 150°C. 4) Dehydration at 150°C for 5 h. 5) Cool down to 30°C and repeat the cycle.

The unusual, because nonlinear, course of the relative mass in steps 2 and 4 (Fig. 8) is caused by a poor temperature stability due to the differential cooling of the silicon carbide furnace and is a direct result of the temperature scaled visualization of the isothermal segments that have been used.

The used material (salt content of 70% by weight) absorbs about 65 wt% of water under the conditions executed. The dehydration time selected here does not lead to complete dehydration of the entire salt species. Since neither the calculated hydrated nor the dehydrated salt corresponds to a known thermodynamically stable hydrate stage, it can be postulated that the anhydrous salt is still thermodynamically stable. The repeated cycles show that a large amount of water is reabsorbed without any problems and that an almost complete dehydration of the material is possible by heating it to 150°C.

Summary

In an open system, the thermochemical reaction naturally depends on the heating of the ambient air. However, the generation of a controlled humidity with dry nitrogen using an STA 449 **F3 Jupiter**® with the humidity generator MHG32 is indispensable for the determination and specific elaboration of reaction conditions close to practice.

With the example of an alginate-CaCl₂ composite, it could be shown that already at a relative humidity of 25% a water absorption of at least 65 wt% water can be generated. The hydration of the salt can therefore be carried out with relatively dry air. This is a great benefit for thermochemical storage applications as in most cases, no additional humidification of the air used is necessary. Because of the extremely high water absorption of the system, the investigations were extended to other fields of application such as the drying of gases and materials as well as the production of drinking water.

Literature

- [1] Dissertation Paul Kallenberger, Materialien für die thermochemische Wärmespeicherung, Universität Hamburg, 2018.
- [2] V. van Essen, L. Bleijendaal, B. Kikkert, H. Zondag, M. Bakker, P. Bach, Development of a compact heat storage system based on salt hydrates, Techn. Ber., 2010.
- [3] K. E. N'Tsoukpoe, T. Schmidt, H. U. Rammelberg, B. A. Watts, W. K. Ruck, Applied Energy 2014, 124, 1-16.
- [4] V. M. van Essen, J. Cot Gores, L. P. J. Bleijendaal, H. A. Zondag, R. Schuitema, M. Bakker, W. G. J. van Helden, ASME 2009 3rd International Conference on Energy Sustainability Volume 2 2009, 2, 825-830.
- [5] S. K. Henninger, H. A. Habib, C. Janiak, Journal of the American Chemical Society 2009, 131, 2776-2777.
- [6] M. F. De Lange, K. J. F. M. Verouden, T. J. H. Vlugt, J. Gascon, F. Kapteijn, Chemical Reviews 2015, 115, 12205-12250.
- [7] P. A. Kallenberger, F. J. Brieler, K. Posern, M. Fröba Chemie Ingenieur Technik 2016, 88, 379-384.
- [8] P. A. Kallenberger, M. Fröba Communications Chemistry 1, 28 (6 pp) (2018)
- [9] P. A. Kallenberger, K. Posern, K. Linnow, F. J. Brieler, M. Steiger, M. Fröba, Advanced Sustainable Systems 2, 1700160 (2018).

Customers for Customers

Main Authors

Uta Sazama



has worked as a technical assistant at the Institute for Inorganic and Applied Chemistry at the University of Hamburg. She started her career as a chemical laboratory assistant in 1984 with syntheses of metal organyls. A change of position brought her into contact with solid state chemistry, catalytic applications and mesostructured materials, as well as their specific functional optimization and control by means of thermoanalytical methods, from 1992 onwards.

Thanks to an evening school training as a chemical technician, she was able to become head of the thermal analysis unit in the working group of Prof. Dr. M. Fröba in 2007. In this environment, she uses her extensive professional experience for the successful processing of complex analyses and thus contributes, in dialogue with scientific employees, to the application-oriented solution of material science problems.

Dr. Paul Kallenberger



studied chemistry at the University of Göttingen and the University of Hamburg. He wrote his master thesis with the topic "Studies on the upscaling of the synthesis of nanoporous carbons" in the research group of Prof. Dr. M. Fröba. From his dissertation entitled "Materials for the thermochemical heat storage", which he carried out in the same group, several publications and a patent application came out.

Since 2018, Dr. Paul Kallenberger has been working on interface projects in the field of new technologies outside of chemical research.

The research group of **Prof. Fröba** focuses on the development of nanoporous materials for the storage of hydrogen, electricity and heat as well as on the investigation of so-called confinement effects of liquids, gases and solids in nanopores. In this context, comprehensive thermoanalytical studies will be carried out with respect to the thermodynamics and kinetics of chemical reactions and phase transitions.

Currently, Prof. Fröba is the speaker of the Energy Research Network Hamburg and a member of the board of the Hamburg Hydrogen Society as well as of the Academy of Sciences of the Free and Hanseatic City of Hamburg.

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International Patent Application
PCT/EP2018/061036, 2018
P.A. Kallenberger, M. Fröba, M. Steiger, F.J. Brieler,
K. Posern
Kompositmaterial zur Speicherung von Wasser und/
oder Wärme

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Rheology for Beginners – Determining the Viscosity of a Hand Cream



Claire Strasser, Applications Specialist Rheology, and Dr. Adrian Hill, Product Technical Specialist Rheology

Introduction

The rheological properties of a cream or lotion are closely related to different user expectations:

- Its ability to stay in the tube as long as it is not squeezed
- Its ability to stay where dispensed until it gets rubbed
- Its good flowability during rubbing.

In the following, we will show how measurements with the Kinexus rotational rheometer provide information about this desired behavior of a hand cream.

General Information

A rotational rheometer is typically made up of two parallel plates, between which the sample is loaded. The upper plate rotates, dragging along the sample. The lower plate remains fixed.

The Kinexus is typically used to carry out two types of measurements:

Viscometry:

The upper plate turns with a **defined shear rate** controlled by the gap and rotational speed. As a result,

we record the viscosity, η , of the sample, i.e., its resistance to flow.

Oscillation:

The upper plate oscillates with a **defined amplitude and frequency**. As a result, we get the viscoelastic properties of the sample, described by the elastic shear modulus, G' , the loss modulus, G'' , and the phase angle, δ (to name a few).

Viscometry – How to Quantify the Behavior of the Cream in the Tube, During Squeezing out of the Tube and During Spreading on the Hand

Figure 1 displays the viscosity curve of a commercial hand cream as a function of the applied shear rates. The material shows a shear-thinning behavior: the viscosity decreases with increasing shear rates.

The lower shear rates reflect the behavior of the cream at near rest conditions. The higher viscosity at low shear rates ensures two properties of the product: The cream will not come out of the tube without stress from outside (= squeezing of the tube). Moreover, after dispensing it on the skin, it will remain in the hand without flowing away.

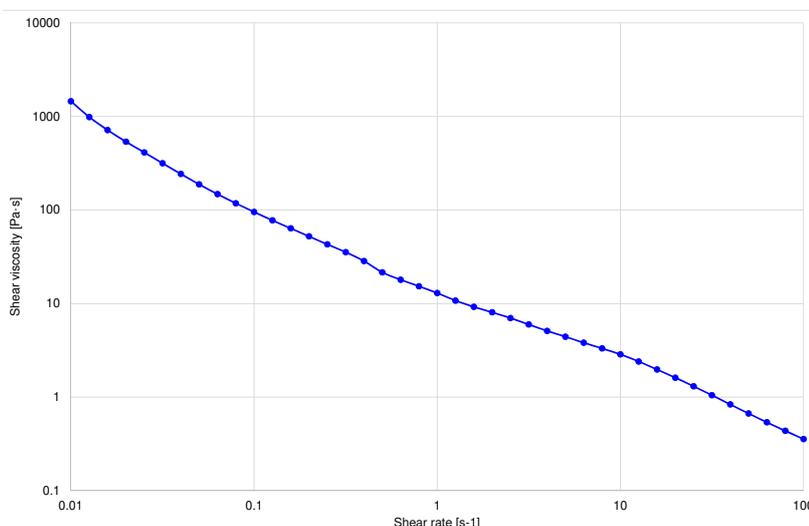


Fig. 1. Viscosity curve of hand cream as a function of the shear rates (geometry: cone-plate 1/50; measurement gap: 0.03 mm; temperature: 35°C, shear rate: 0.01 to 100 s⁻¹)

As soon as the user squeezes the tube, higher shear rates are applied to the cream. According to the resulting curve, this leads to a decrease of the product viscosity, so that it flows easily out of the tube. The higher shear rates mimic also the behavior of the cream during spreading on the skin. This process gets easier thanks to the lower viscosity, which results in a smoother feel on the skin.

In this context, an important term is the yield stress, i.e., the minimum stress that has to be applied to a material to induce its flowing.

Tips & Tricks

Figure 2 displays the yield stress measurement on the hand cream.

In the lower shear stresses range, we see an apparent increase in the viscosity coming from the sample structure stretching before yielding. The hand cream starts to flow after the peak in viscosity (see red arrow). For this example, there is another transition at higher stress, from which point the viscosity strongly decreases and is free flowing. The software calculates the yield stress value automatically: the cream would begin to flow from a shear stress of 11.7 Pa.

Oscillation – One Material, Different Behaviors ... Depending on the Time Scale of the Process

Amplitude Sweep

In an oscillation measurement, the sample has to be in the so-called linear viscoelastic region (LVER), in which the applied strain or stress doesn't lead to a breaking of the sample's associated structure. Therefore, an oscillation test with a defined frequency and a varying amplitude of deformation is carried out on the material in a first step. As a result, the maximum amplitude allowing for a non-destructive test is obtained – the stress or strain limit of the LVER.

Figure 3 depicts the curves of the elastic modulus, G' , and viscous modulus, G'' , during the amplitude sweep. The elastic modulus remains constant up to 0.2%. That means that for deformations lower than 0.2%, the substance is in the LVER.

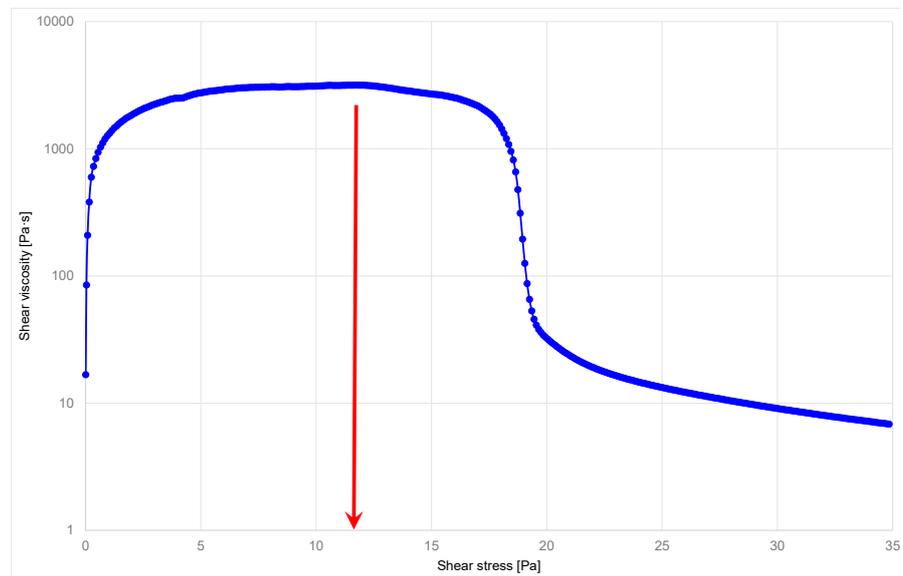


Fig. 2. Yield stress measurement (geometry: cone-plate 1/50; measurement gap: 0,03 mm; temperature: 35°C; shear stress: 0 to 200 Pa)

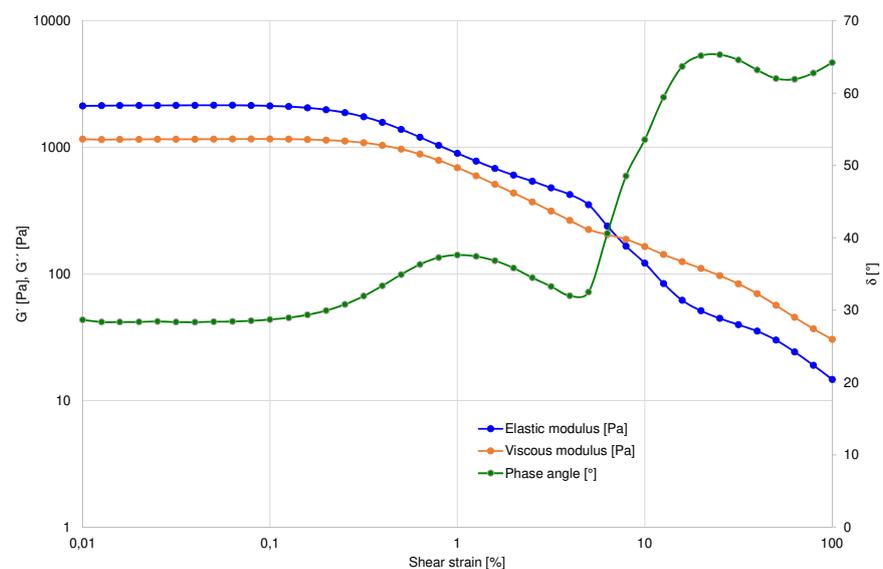


Fig. 3. Elastic modulus G' ; viscous modulus G'' , and phase angle δ during the amplitude sweep to determine the LVER (geometry: plate-plate 40 mm; measurement gap: 1.0 mm; temperature: 30°C; shear strain: 0.01 to 100% of the measurement gap)

Frequency Sweep

In the next measurement, the amplitude is set at 0.1%, while the frequency is varied to investigate the material's response over different timescales. The results are depicted in figure 4.

Over the complete measured frequency range, the G' values are larger than the G'' values: the elastic properties of the cream are more dominant than its viscous properties. The cream doesn't flow, but behaves like a solid. This can also be seen in the phase angle, which is a scale of fluidity of the sample, from zero being completely solid-like through to 90° indicating perfect liquid-like behavior. Figure 4 shows that this sample remains more solid-like (i.e., phase angle $<45^\circ$) over the whole range of frequencies tested, i.e., it doesn't flow.

Conclusion

A consumer expects from its hand cream almost contradicting behavior: It should behave like a solid to hinder it from running out of the tube before the user squeezes it, and not flow off the user's hand after being dispensed. However, it should also behave like a liquid during spreading on the skin by flowing freely.

The rheology measurements mimic these different scenarios of deformation and no deformation. The viscosity of the cream decreases with increasing shear rates: during squeezing the tube or rubbing the cream on the skin, it feels "lower viscous" than at rest – just as the user expects.

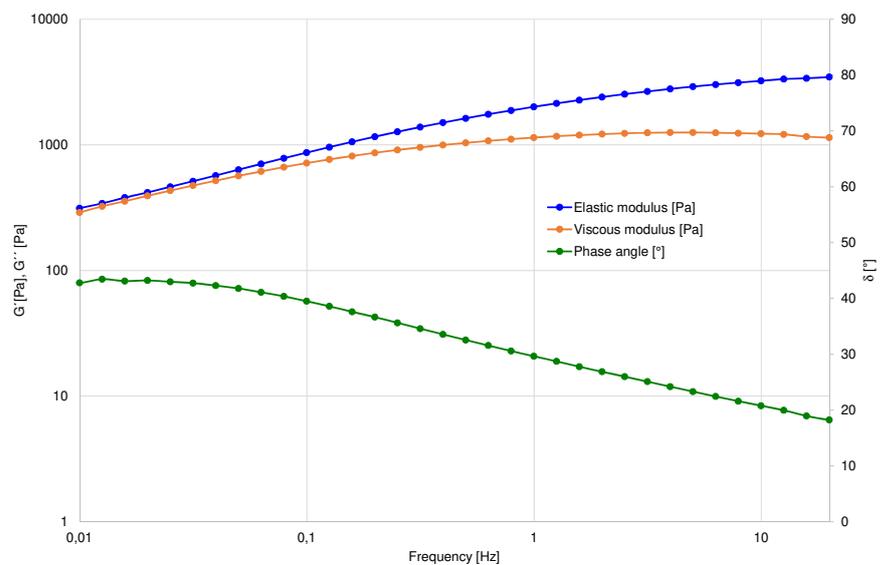


Fig. 4. Elastic modulus, G' , viscous modulus, G'' , and phase angle δ , at different frequencies (geometry: plate-plate 40 mm; measurement gap: 1.0 mm; temperature: 35°C ; shear strain: 0.1%; frequency: 0.01 to 20 Hz)



Teaming Up for Your Analysis of Pharmaceuticals

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



NETZSCH Analyzing & Testing enters into a marketing collaboration with Malvern Panalytical.

Analytical Methods That Complement Each Other

With the help of thermal analysis, a great deal of important information on active ingredients, excipients and formulations can be obtained within a short time. DSC (Differential Scanning Calorimetry) is the most often-used thermoanalytical method in this field. It is used to characterize the melting behavior of crystalline materials and the glass transition range of amorphous or semi-amorphous substances.

Since many polymorphic modifications differ from each other in their melting temperatures, DSC is frequently used for polymorphism studies. In addition, DSC offers the ability to obtain a quick overview of possible incompatibilities between active ingredients and excipients.

However, DSC is not a universal analytical method. Just like any other analytical technique, it has its limitations. DSC is capable of making temperature-induced phase changes visible, but cannot determine whether and how the structure changes. This is the strength of structure-elucidating analytical methods such as X-ray diffraction (XRD), also known as powder diffraction (PXRD) in the case of powders. Powders consist of a large number of crystallites with statistical orientation. If X-rays are irradiated at a certain angle, Θ , they are diffracted/reflected when they strike a lattice plane in the crystal lattice. The reflection is then presented as a peak in a diffractogram (intensity plotted against 2Θ).

For interpretation of the X-ray images, it is also very useful to know more about the particle size distribution of the powder. This is usually determined by means of a particle size analyzer, which works, for example, by laser diffraction. The operation principle is based on the measurement of the angle-dependent scattered light

intensity, since small particles scatter light at a greater angle than large particles.

Only when these methods are combined can a more complete picture of the material behavior be obtained. Particle size analysis, thermal analysis and X-ray diffraction complement each other perfectly. It is therefore not surprising that in many solid-state laboratories, all of these instruments can be found.

"At Malvern Panalytical, we place great emphasis on understanding our customers' workflows. This allows us to identify the multifaceted challenges and thus develop solutions for the pharmaceutical industry. In doing so, we see that the use of complementary analytical methods is often the key to solving problems. That is why we look forward to working with NETZSCH to generate new applications for advancing the development of pharmaceutical products."

Dr. Natalia Dadivanyan, Field Application Scientist X-ray Products, Application & Business Development Pharma & Food Sector Malvern Panalytical

Our Experience = Your Benefit

This partnership brings two companies together that have been successfully involved in materials analysis for many years in their respective fields. Come experience our know-how by participating in one of our joint events. The next joint webinar will take place on **May 11, 2021**. More information will be available shortly on our website www.netzsch.com/events.

Material Science in Additive Manufacturing

Milena Riedl, Marketing



Dr. Natalie Rudolph, our Business Field Manager for Polymers, will guide you through our video series

Introduction

Additive Manufacturing (AM) or 3D printing has matured over recent decades. It has become a constant in our product design and development cycles and is debuting in more and more new products. We have seen huge improvements in capabilities and output. We have a much wider range of materials and we can produce much stronger, more precise components in shorter amounts of time. These technologies are used where complex geometries are needed, at little to no additional costs over traditional methods. The ability to combine functionalities and increase complexity often also results in weight reductions, which are very valuable in many industries.

At NETZSCH Analyzing & Testing, we see more and more customers in the field of Additive Manufacturing using our equipment to select materials and optimize their processes. That is why we have been busy focusing on preparing educational video content about the different AM technologies as well as videos and articles about the material science behind them.

We aim to enable our viewers and readers to understand the basic process principles, interpret interactions

of process and material, and select suitable thermo-analytical and rheological analysis methods to answer their questions.

Our Video Series

Introduction to Additive Manufacturing

The first part of our video series is dedicated to generating a basic understanding of Additive Manufacturing (AM), its different categories and trade names, and its typical process flow.

Watch here:

www.netzsch.com/introductionAM

Following this, every week will focus on a new category, its process principles and materials, and its benefits and applications. Here are two examples:

Vat Photopolymerization

In the second part, the spotlight is on Additive Manufacturing technology Vat Photopolymerization (VP). We explain the general process principle and its variations, look at the commonly used material class of

Additive Manufacturing



UV-curing thermosets and discuss benefits and applications of the process.

Watch here

www.netzsch.com/VatPhotoP

Powder Bed Fusion

Next we move from thermosets to thermoplastics and specifically the Powder Bed Fusion process. We have a detailed look at the process principle, temperature field, materials, benefits and application of Polymer Powder Bed Fusion. Additionally, we dive into Metal Powder Bed Fusion and a variation of the technology – Multi Jet Fusion (MJF).

Watch here:

www.netzsch.com/PowderBedFusion

The videos will be complemented by articles about thermal analysis and rheology measurements on the respective materials. The articles will start with Polymer Powder Bed Fusion, often referred to as Selective Laser Sintering.

Our Articles About Selective Laser Sintering

How Does Selective Laser Sintering (SLS) Work?

Selective Laser Sintering, also categorized as Polymer Powder Bed Fusion, is one of the most frequently used Additive Manufacturing technologies for producing structural plastic parts. In this article, we explain the process principle and materials used in the SLS process.

Read here

www.netzsch.com/SLS-eng

How to Determine the Process Window for SLS Powders Using DSC

During the SLS process, the component is built up in layers in a powder bed using a laser beam that passes over the cross-section of the layer to locally melt the powder. In order to characterize a polymer powder for its suitability for SLS and to determine the possible process window, Differential Scanning Calorimetry (DSC) is used. Learn how to set up and interpret the measurements!

Read here:

www.netzsch.com/Process-Window-SLS-eng

There is more to come! Keep your eyes peeled and follow us on our social media channels to be the first to see new content about "Material Science in Additive Manufacturing".



Intelligent Plastics Production with Innovative Sensor Technology and Artificial Intelligence



NETZSCH

Dr. Alexander Chaloupka, Business Field Manager for Process Analytics

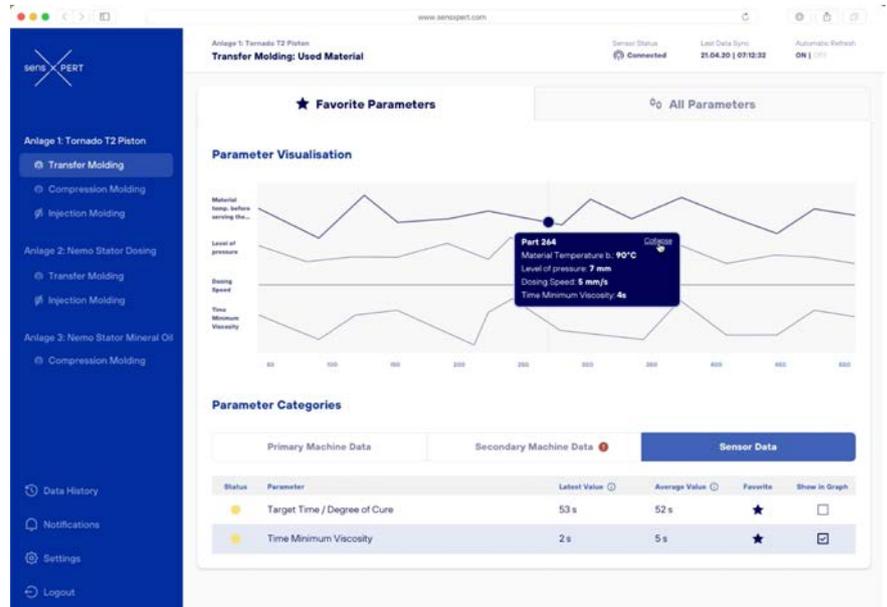
sensXPERT is being developed by NETZSCH-Gerätebau in cooperation with NEDGEX, the digital incubator of the NETZSCH group, in a start-up environment.

sensXPERT stands for easy and intelligent production of plastic parts, taking the manufacture of thermosetting plastics and fiber composites to a new level. The use of sensors and artificial intelligence (AI) with simultaneous networking of the production plant enables production in which intelligent tools measure relevant material properties and can thus influence process control.

Along with the support of dielectric sensors for material characterization (mixing ratio, curing), sensXPERT also offers the option of connecting pressure or temperature sensors and processing their signals. As a storage system including display of the process status, sensXPERT provides a cloud environment that is accessible regardless of location.

The Digital Twin of Component Manufacturing and 100% Quality Assurance

In contrast with digital twins, which provide a 3-D image of plants and components for spare parts selection, sensXPERT works with processing parameters of plastic-processing machines and data from the molding tool in which a component is molded. Machine parameters and the material response from the inside of the mold cavity are merged into a single unit. In application, this means that processes such as hot pressing,



Clearly structured user interface of the Cloud-based software

Resin Transfer Molding, vacuum infusion, and reactive injection molding are fully mapped.

Storage in the sensXPERT cloud creates transparency and makes component production traceable. In order to always keep track of the efficiency of the system, each material parameter for each component is expressed in the form of traffic light colors. The combination of the production plant and the tool made intelligent by sensXPERT enables 100% component qualification already during production and reduces bottlenecks that can arise due to downstream quality inspection. In addition, sensXPERT intervenes in the process with regard to dynamic cycle times, so the material response decides whether a component is finished or must still remain in the hot mold.

Yet sensXPERT goes even one step further: An almost unlimited number of new and existing systems can be included in the sensXPERT cloud. By means of sophisticated user management, access to individual systems can be granted or blocked for each user.

Machine Learning Meets Materials Science

sensXPERT makes it possible to experience what artificial intelligence can do in everyday work. The core of real-time quality and process control is machine learning, which is applied on the sensXPERT interface and in the cloud environment. The sensXPERT interface is the intel-

sensXPERT

ligent hardware to which the sensors are connected, which is in a state of exchange with the manufacturing plant via industrial communication protocols.

This enables all sensors already installed as well as the sensXPERT sensors to be processed by artificial intelligence in equal measure.

Machine learning by sensXPERT is based on the material science of the material to be processed: Reaction kinetic relationships are summarized together with real data from the manufacturing process in a machine learning model. The model continually develops as the number of components manufactured increases; the optimum processing parameters are thus better and better learned. The result is a continuous increase in efficiency in the manufacturing environment.

Pilot Phase in Series Production

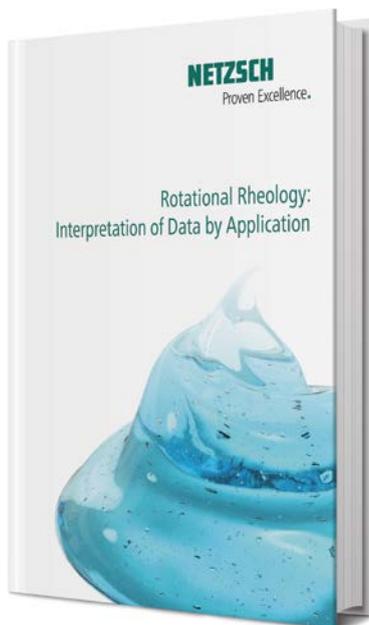


sensXPERT has already been installed at some renowned enterprises and company groups in the plastics- and composites-processing industry. From there, it has been providing valuable information which is being used for expansion of the solution. The sensXPERT team are always seeking to expand the range of applications and look forward to exchanging ideas with interested parties.

Are you facing long process times, downstream quality assurance, high scrap rates or inefficiencies? Perhaps this will lead to a collaborative venture in the test phase – even before the sales launch.

Contact us at info@sensxpert.com and become part of the sensXPERT journey!

The Mountains Flow Before the Lord ...



the scene after the end of the World War II, in one sense, it can be considered a very old science, with roots in antiquity.

What is now known as "rheology" could be traced back to the Greek philosopher Heraclitus and the Jewish prophetess Deborah (Deborah Number with the symbol De = time of relaxation/time of observation). Later, the motto "panta rhei" (everything flows) as the motto of rheology was introduced.

Rheology is as much about the deformation of solid-like materials as it is about the flow of liquid-like materials, and in particular deals with the behavior of complex visco-elastic materials that show both solid and liquid-like properties in response to force.

Soon available: New Booklet on Interpretation of Measurements with a Rotational Rheometer
www.netzsch.com/rheologybooklet

This new booklet should be helpful to understand how the flow properties of materials can be related to their rheological analysis. Even if your application isn't mentioned, hopefully you'll be inspired as to how a similar test method could be adapted to give an indication of your material's properties in a specific process."

Enjoy reading!

Philip Rolfe
Applications Specialist Rheology

... says the Book of Judges, chapter 5. Although, rheology only came to

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