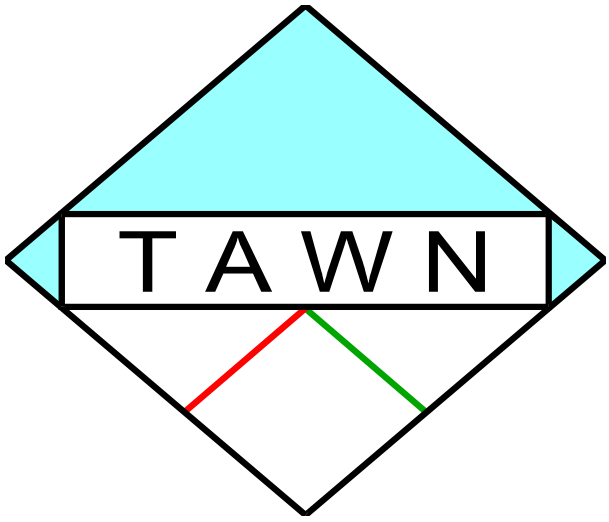
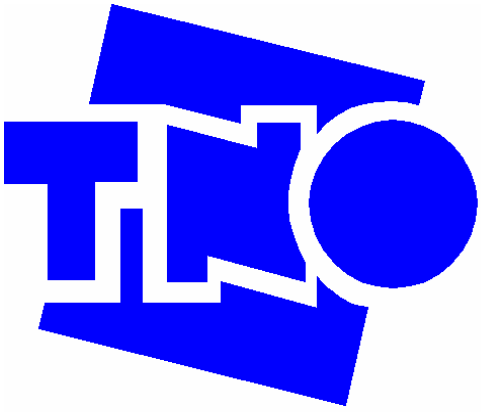


3 – Days Thermal Analysis Joint Conference of TAWN and GEFTA

05 – 07 October 2005

TNO-Defence, Security and Safety

Rijswijk, The Netherlands



Introduction by Dr. P.J. van Ekeren, president of TAWN

Dear members of GEFTA and TAWN, and others interested in Thermal Analysis and Calorimetry,

We are now facing the second symposium on thermal analysis and calorimetry that is organized by the GEFTA and the TAWN cooperatively. The first one was back in 1981 in Aachen, now, in 2005, we are in Rijswijk.

Since both societies are active in the field and located in neighbouring countries one can ask "Why are these joint meetings so scarce?".

We believe that this is caused by a significant difference in the character of the membership. In Holland most of the members are working in industry. Many of them are educated at higher vocational level and are interested mainly in practical issues. Furthermore, they make few trips to symposia across the border: we see only few TAWN-members at ICTAC and ESTAC conferences.
In Germany, on the other hand, a relatively large number of members are working at universities and educated at academic level. They are interested in scientific issues.

However, this is of course a generalisation, and even then there also must be a lot of mutual interest. Considering the number of participants this meeting is very successful. Let's hope that the participants enjoy the meeting and the programme.

Furthermore I hope that we find the mutual interests and then, in a couple of years time, possibly we can look forward to the third joint GEFTA-TAWN thermal analysis meeting!

Paul van Ekeren,
TAWN president.

Introduction by Dr. M. Feist, president of GEFTA

Dear members and friends of TAWN and GEFTA,

it is a well established GEFTA tradition to organize from time to time joint symposia with the national scientific societies for Thermal analysis and Calorimetry of our neighbouring countries. During the last decade, we get together with our colleagues from Hungary (Sopron, 1995), France (Freiburg, 1996), and from Poland (Dresden, 2000).

It is, therefore, with great pleasure that German scientists being engaged in Thermal analysis and Calorimetry will have the opportunity this year to come to Rijswijk to meet their Dutch colleagues - 24 years after the first joint symposium held in Aachen. On behalf of the GEFTA board, I feel deeply indebted to the board of TAWN, especially to Paul van Ekeren and Wim de Klerk, for having taken the charge of local organization.

24 years - really a too long term, but European collaboration and scientific exchange did not interrupt in that period as we had the opportunity to meet at ESTAC or ICTAC conferences or other symposia focused on more special issues. On the other hand, it is quite clear that smaller joint symposia such as our annual conferences should be organized more often in order to better know each other, to promote scientific exchange, and to learn about actual trends as in industry as in university research.

Let us, therefore, benefit as much as possible from our meeting here in Rijswijk, at the widely known and well reputed TNO research institute. We appreciate very much the hospitality of the TNO institute and are grateful for the possibility to meet here.

Michael Feist
GEFTA chairman

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Program for TAWN-GEFTA meeting

05 - 07 October 2005,
TNO Defense, Security and Safety,
Rijswijk, The Netherlands

Wednesday 5th October 2005

12.00 hrs Start of registration for joint TAWN – GEFTA meeting

12.30 hrs Lunch at the conference venue

Conference chairman:

13.20 hrs **Opening of the conference by conference chairman**
Ing. Wim de Klerk *(TNO-Defence, Security and Safety, Rijswijk)*

Opening by chairman of Dutch Thermal Analysis Society (TAWN)
Dr. Paul van Ekeren *(University Utrecht, Utrecht, The Netherlands)*

Opening by chairman of GEFTA
Dr. Michael Feist *(Humboldt University, Berlin, Germany)*

13.40 hrs **Welcome by representative of management of TNO DSS,**
location Rijswijk
Dr. Louk Absil, Business Unit Manager BU-3 (TNO DSS)

14.05 hrs Remarks and notices for conference location

Wednesday 5th October 2005

Session chairman : Dr. Jens Fischer *(University of Bern)*

14.15 hrs	Keynote lecture: Prof. Dr. Crisan Popescu *(German Wool Institute Aachen, Germany)* Title : Thermal denaturation of wool
15.00 hrs	Presentation 1 Dr. Ena Smidt (*University of Vienna, Vienna, Austria)* Title: What can thermal analysis tells us about waste materials
15.25 hrs	Presentation 2 Ing. Erik Bevers (*Utrecht University, Utrecht, The Netherlands)* Title: Thermal properties of solid ammonia complexes for use in a high-lift chemical heat pump
15.50 hrs	Coffee / tea / softdrinks / Poster session and instrument exhibition
16.10 hrs	Presentation 3 Dr. Katja Emmerich Title: The classification of montmorilllonites with the help of STA
16.35 hrs	Presentation 4 Dr. Heiko Huth *(Institut fur Physik, University of Rostock, Germany)* Title: High sensitive AC chip calorimetry for nanogram samples
17.00 hrs	Remarks of first day / closing of first day by conference chairman
17.05	Annual member meeting TAWN and GEFTA (in separate rooms)
18.00	End of first day

Thursday 6th October 2005

08.50 hrs opening of the second day by conference chairman

Session chairman : Prof. Dr. Crisan Popescu *(German Wool Institute Aachen)*

09.00 hrs Keynote lecture:
Dr. Jens Fischer *(Dental School, University of Bern, Switzerland)*
Title: Thermal compatibility as a key factor for the success of ceramic laminates in dentistry

09.45 hrs Presentation 5
Mr. Martin Ottaway *(Benelux Scientific, Tiel, The Netherlands)*
Title: Pharmaceutical Applications of MicroReaction Calorimetry

10.10 hrs Presentation 6
Dr. Hubert Rahier *(Vrije Universiteit, Brussel, Belgium)*
Title: Thermal analysis used to study phosphorous based cements

10.35 hrs Coffee / tea / softdrinks / Poster session and instrument exhibition

11.00 hrs Presentation 7
Dr. Mark Phipps *(Triton Technology, United Kingdom)*
Title: Use of Dynamic Mechanical Analysis for investigation of powdered materials

11.25 hrs Presentation 8
Ing. Gertjan Herder *(TNO-DSS, Rijswijk, The Netherlands)*
Title: Measurement of the Relaxation Transitions of Nitrocellulose Based Gunpowder

11.50 hrs Presentation 9
Dr. Jurgen Schawe *(Mettler Toledo GmbH, Schwerzenbach, Switzerland)*
Title: TOPEM-the latest innovation in temperature modulated DSC

12.15 hrs Lunch / Poster session and instrument exhibition

Thursday 6th October 2005

12.15 hrs Lunch / poster exhibition / equipment exhibition

Session chairman : Dr. Paul van Ekeren *(University of Utrecht)*

13.15 hrs Keynote lecture:
Dr. Dirk Walter *(Technical University Berlin, Berlin, Germany)*
Title: The mechanism of the thermal transformation from synthetic goethite to hematite

14.00 hrs Presentation 10
Geert vd Poel *(University of Leuven, Leuven, Belgium)*
Title: High Performance Differential Scanning Calorimetry (Hper DSC): calibration and Applications to Polymers

14.25 hrs Poster session
(poster titles see separate section)

14.50 hrs Remarks of second day

15.00 hrs Coffee / tea / softdrinks / Poster session and instrument exhibition

15.25 hrs Start of city tour through Delft

18.30 hrs Conference dinner in Delft

Friday 7th October 2005

08.50 hrs opening of the third day by conference chairman

Session chairman : Dr. Dirk Walter (*Technical University Berlin, Berlin, Germany)*

09.00 hrs Keynote lecture:
Prof. Dr. Ir. Guy Van Assche, *(Vrije Universiteit Brussel, Belgium)*
Title: Modulated Temperature DSC and its use for studying reaction kinetics and (reaction-induced) phase separation

09.45 hrs Presentation 11
Dr. Uwe Hess *(ProSense GmbH, Germany)*
Title: The true heat flow principle: A new and fast method beyond calorimetry for process characterization

10.10 hrs Presentation 12
Mr. Dirk Waehlisch *(TU-Bergakademie Freiberg, Germany)*
Title: Thermodynamics of enantioselectivity in modified dextrines

10.35 hrs Coffee / tea / softdrinks / Poster session and instrument exhibition

11.00 hrs Presentation 13
Dr. Frieder Dreisbach *(Rubotherm, Germany)*
Title: Thermogravimetric Measurements in Supercritical Water Using a New High Pressure High Temperature Magnetic Suspension Balance

11.25 hrs Presentation 14
Ing. Erik vd Ven *(University of Twente, Enschede, The Netherlands)*
Title: Crystallization kinetics of poly-phenylenesulfone

11.50 hrs Presentation 15
Dr. Erwin Kaisersberger *(Netzsch Geratebau GmbH, Selb, Germany)*
Title: Determination of Characteristic Specifications of the New DSC 200 F3 Maia® and their Influence on Projected Applications

12.15 hrs Postersession
(poster titles see separate section)

12.45 hrs Lunch / poster exhibition / equipment exhibition

Friday 7th October 2005

12.45 hrs Lunch / poster exhibition / equipment exhibition

Session chairman : Dr. Michael Feist *(Humboldt University Berlin, Germany)*

13.45 hrs Presentation 16
Mrs. Maraija Matovic *(Utrecht University, Utrecht, The Netherlands)*
Title: Studying Crystallization and Polymorphism by Adiabatic and Differential Scanning Calorimetry

14.10 hrs Presentation 17
Dr. Michael Feist *(Humboldt University, Berlin, Berlin, Germany)*
Title: Application of Pulse TA to the investigation of Fluorides. An attempt to calibrate HF

14.35 hrs Presentation 18
Mr. Thijs Pijpers and Prof. Vincent Mathot *(KU Leuven, Leuven, Belgie)*
Title: Applications of High Performance DSC in polymer research: Advantages and limitations

15.00 hrs Closing the conference by the conference chairman

15.10 hrs Reception and farewell

Postersession

POSTER-1
Anja Neumann *(Technical University of Berlin, Germany)*
Title: Thermal stability of nitrogen doped VO_2(B)

POSTER-2
Dr. Daniela Merz *(Forschungscentrum Karlsruhe, Germany)*
Title: DTA-FTIR of Abalone shell - exploring the chemicals behind DTA signals

POSTER-3
Dr. Erwin Kaisersberger *(NETZSCH-Geratebau GmbH, Selb, Germany)*
Title: Applications of thermal analysis in nanotechnology

POSTER-4
Matthias Weil and Ekkehard Füglein (*TU-Wien, Institut für Chemische Technologien und Analytik, Wien, Austria & NETZSCH Gerätebau GmbH, Selb, Germany)*
Title: Characterisation and Thermal Behaviour of Ag_2PO_3F
Presented by Dr. Erwin Kaisersberger (NETZSCH-Geratebau GmbH, Selb, Germany)

POSTER-5
Dr. Elke Hempel *(Martin-Luther-Universitat Halle-Wittenberg, Germany)*
Title: Side Chain crystallization in micro-phase-separated poly(styrene block -Octadecylmethacrylate) Copolymers

POSTER-6
Dr. Jan Heeg *(University of Rostock, Institut fur Physik, Rostock, Germany)*
Title: Kinetics of isothermal crystallization and melting-recrystallization of iPP, IPS, PET and PBT

POSTER-7
Dr. Pascale De Meuter *(Vrije Universiteit Brussel, Brussel, Belgium)*
Title: Phase behavior of aqueous solutions of poly(vinyl methylether)s with different chain-end functionalities

POSTER-8
B. Rimez *(Vrije Universiteit Brussel, Brussel, Belgium)*
Title: Influence of ammonium polyphosphate on the thermal stability of poly(vinylacetate) and poly(ethylenen-co-vinylacetate); cone calorimetry and TGA study

POSTER-9
Patricia Heussen *(Unilever Research Vlaardingen, The Netherlands)*
Title: Practical applications of Differential Scanning Calorimetry within Unilever

POSTER-10
Jeroen vd Bergh *(Philips Research, Eindhoven, The Netherlands)*
Title: Characterisation of industrial materials and processes with TGA.

POSTER-11
Dr. Els Verdonck *(TA Instruments, Zelik, Belgium)*
Title: Design and Applications of a Powder and Liquid Holder for DMA

POSTER-12
Dr. Els Verdonck *(TA Instruments, Zelik, Belgium)*
Title: The Q5000 TGA's for Fast Heating Rate TGA and Sorption Analysis: Design and Applications

POSTER-13
Ing. Nik Boer *(Perkin Elmer,The Netherlands)*
Title: HyperDSC , A breakthrough method for materials characterization. Higher Sensitivity at Greater Speeds

POSTER-14
Dr. Uwe Hess *(Prosense GmbH, Konstanz, Germany)*
Title: Rapid Process Initiation Studied by Reaction Calorimetry

POSTER-15
Claus Linseis *(Linseis Messgerate GmbH,Selb, Germany)*
Title: Laser dilatometer Pico series 0,3 nm

POSTER-16
Thomas Lemke *(C3 Prozess- und Analysetechnik GmbH, Haar b. Munchen, Germany)*
Title: New systems for safety calorimetry - Overview

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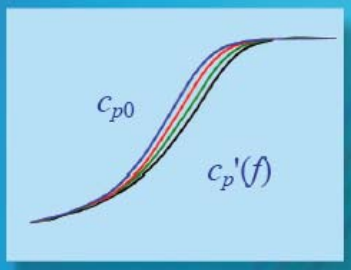

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ABSTRACTS

FOR

LECTURES

Thermal denaturation of wool

C. Popescu

DWI an der RWTH e.V., Pauwelsstrasse 8, 52056 Aachen, Germany

The investigation of the detailed structure of wool fibre reveals always interesting things not only for the textilists but also for those working in cosmetics, and biopolymer fields. Few are aware that wool, besides being one of the oldest textile fibre known by the mankind, has been also the first protein on which the X-ray diffraction studies were carried out and for which the α-helix model has been imagined. With such a glorious scientific past, it seems unlikely that wool still hides interesting facts.

The keratin proteins are among the most thermostable ones, able to keep their properties at temperatures up to 200-210°C. The picture accepted so far for keratin fibres is of a two-phase filament – matrix model. In this model the microfibrils, that are the helical fraction of the intermediate filaments, are considered as the crystalline phase and the matrix, which includes all the other morphological components, and has a high amount of cystine, and therefore is heavily crosslinked, is the amorphous phase. The matrix is considered to control kinetically the unfolding of α-helix and, therefore, the stability of the protein. The interaction of crystalline intermediate filaments (IFs) with the amorphous part and the role the viscosity of the amorphous matrix plays for the stability of a composite protein like keratin, is a topic of several studies.

Although it seems that α-keratins are similar to any other protein, the melting (folding) behaviour of the α-helix exhibits a major difference: while the melting of the α-helix in soluble proteins is a reversible one-step first-order transition, the helix-coil transition is irreversible at insoluble keratins.

The DSC peak assigned to the denaturation process is found to be around 230-240^{0}C for dry wool, and shifts with the water content, or with the nature of the treatment. Sometime it is also observed a split of the peak and the heating rate, and pressure plays also a role. The split of the temperature peak with increasing pressure, or at high water content, is attributed to the small difference existing between the two cells composing wool, ortho and para, respectively, in terms of organisation. The two cells are slightly different in terms of cystine amounts, and therefore the viscosity of the ortho and para matrices surrounding the intermediate filaments differs as well. Altering the viscosity in one strand of cells, while keeping the other strand less changed, leads to a half denaturated wool and gives information on how viscosity hinders the process.

The thermal denaturation of wool can give, thus, important hints on the thermal stability of the proteins and on the role of the matrix for this stability.

The present paper discusses some of the DSC results obtained by our group with keratin fibres, pointing out the consequences for understanding the fine structure of keratins and documenting them with SEM photos and X-ray diffraction data.

What can thermal analysis tell us about waste materials?

Smidt Ena

Institute of Waste Management, Department of Water, Atmosphere and Environment, Muthgasse 107, 1190 Vienna BOKU – University of Natural Resources and Applied Life Sciences, Vienna

Stabilization of waste materials before landfilling is a target to be reached due to the required reduction of reactivity and emissions. Thermal methods provide the fast assessment of waste organic matter stability. The stage of organic matter degradation in waste materials is related to the energy content of the material and therefore to their thermal behavior. Different waste materials (municipal solid waste, compost, abandoned landfill materials, sewage sludge) were investigated using an instrument for simultaneous thermal analysis coupled with mass spectrometry (Netzsch STA 409 CD Skimmer).

With regard to the complexity of waste materials the use of the entire sample is proved to be advantageous. The thermal behavior of complex samples reveals chemical transformation during process operation or under changing environmental conditions. Mineralization and other stabilization effects like humification and interaction with mineral components are reflected by the thermogram and the DSC curves. Some investigations have been carried out to assess stability of composts (Dell'Abate et al. 2000, Melis and Castaldi 2004) and sewage sludge (Otero et al. 2002).

Several examples presented illustrate the influence of waste treatment on thermal features of the material. Combustion of composts and municipal solid waste is characterized by 3 to 4 peaks of the DTG curve. The first peak can be assigned to the loss of water. Two peaks at about 315 °C and 475 °C, respectively, indicate the combustion of organic matter. The peak > 650 °C is caused by the decay of carbonates that are in most cases a main mineral component of waste materials. Due to degradation higher temperatures are required to achieve the same mass losses. A peak shift of the DTG, DSC, and CO_2 ion current curves towards higher temperatures is observed. As a result of decomposition the energy content of the material decreases. It is indicated by the decrease of the exothermic DSC peaks at about 315 °C and 475 °C. However, enrichment of recalcitrant molecules and humification can effect a slight increase of the DSC peak at about 475°C. Apart from process monitoring the assessment of final products is possible because of characteristic thermal patterns.

Humification contributes to organic matter stability of waste materials. The long-term behavior of waste humic substances that are "young" compared to soils is not well-known. Changes of humic substances during the composting process and under anaerobic conditions were revealed by the thermal behavior.

For practical use a quick and simple procedure is necessary to assess stability. An approach for samples of biologically treated municipal solid waste is suggested.

Sewage sludge changes considerably during the biological treatment with respect to composition and stability. Thermal characteristics are presented for primary, activated, and anaerobically digested sludge.

Process control and quality assessment of the final product are requirements for the biological waste treatment. Abandoned landfills are an additional field of responsibility for waste management. Determination of the current status and result checking of in situ remediation can be carried out by thermal characterization. Different areas of an abandoned landfill were evaluated using the curves of DTG and CO2 ion current. Compartments of the landfill can be distinguished by different composition. Construction residues show a prominent peak >650 °C due to the decay of carbonates. Organic matter that had been enclosed for two decades between tight clayey layers still has a strong peak of mass loss at around 310 °C.

Municipal solid waste of an abandoned landfill was aerated in lab-scale reactors. Mineralization of organic matter was monitored by the DTG curve and the CO_2 ion current.

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Thermal properties of solid ammonia complexes for use in a high-lift chemical heat pump

E.R.T.Bevers[1], Dr. P.J. van Ekeren[1], G.J.K.van den Berg[1], Dr. W.Haije[2]

[1] *Chemical Thermodynamics Group, Utrecht University*

[2] *Energy research Centre of the Netherlands, Energy Efficiency in Industry (EEI)*

This research projects is based on the development of a chemical heat pump (CHP), which is capable to convert industrial heat waste, which is released at a temperature between 80°C -150°C, to a usable level (230°C).

The principle of this kind of CHP is based on the reversible formation and decomposition of solid ammonia-salt complexes.

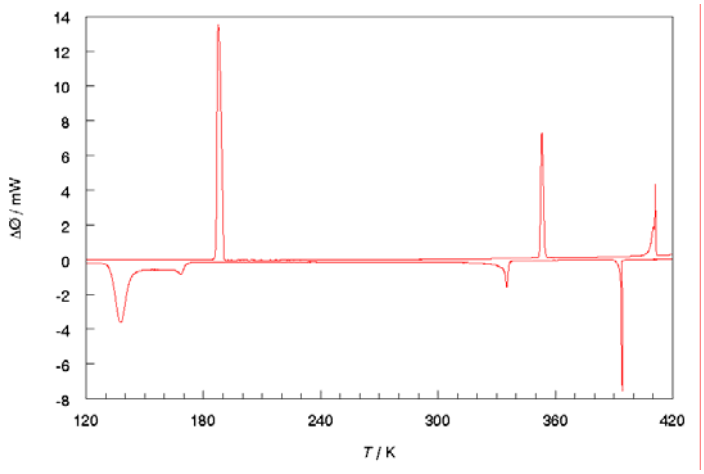
The general reaction that takes place in the CHP reactor is of the following form:

$$MZ(s) + x\ NH_3(g) \Leftrightarrow M(NH_3)xZ(s) + \Delta H$$

Possible candidate salts concerning this research were among others, $MgCl_2$ and LiCl. The thermodynamic and kinetic properties of the formation and decomposition reactions of these ammonia complexes were measured by using a High-Pressure Differential Scanning Calorimeter (HPDSC). By plotting the obtained data in a Clausius-Clapeyron diagram, various characteristics of the CHP can be obtained as well as predicted.

The sample was submitted to a temperature program at constant pressure. During this temperature program thermal effects were observed as shown in the figure. As a result of these measurements at several pressures a phase diagram could be derived.

For a better understanding of the thermodynamic data, neutron diffraction measurements were performed at ILL as well as at ISIS.



Typical example of the transitions of $MgCl_2$ and NH_3 at p=5.0 bar, diagram constructed with a heating rate of 1 K min-1, endothermic effects plotted upwards.

The classification of montmorillonites with the help of STA

Katja Emmerich[1,2] and Felicitas Wolters[3]

1) IMG, University Karlsruhe; 2) FZK, ITC-WGT, PO Box 3640, 76021 Karlsruhe,
3) IfG, Sohnstr. 70, 40237 Düsseldorf, Germany

Montmorillonites belong to smectites, which are swellable dioctahedral 2:1 layer silicates. Smectite layers consist of two tetrahedral sheets and one sandwiched octahedral sheet. Dioctahedral means, that two out of three octahedral positions are occupied by trivalent cations. According to the arrangement of hydroxyl groups we distinguish two cis- and one trans-positions. At the trans-octahedron the two hydroxyl groups are positioned at opposite corners. The two cis-octahedra share the two OH-groups at a common edge. Substitution by divalent cations causes a permanent negative layer charge that is balanced by cations in the interlayers. Those minerals display four characteristic thermal reactions: dehydration, dehydroxylation, decomposition and recrystallisation. During dehydroxylation structural water from two hydroxyl groups migrate out of the mineral structure according to $2(OH) \rightarrow H_2O + Or$ (r..residual).

Smectites expose a wide variety in chemistry and structure and their characterisation is a difficult task. Turbostratic disorder prevents the analysis of the structure of the octahedral sheet. Drits et al. [1] showed that the dehydroxylation behaviour of aluminous dioctahedral 2:1 layer silicates is related to the distribution of metal ions and vacancies over available sites in the octahedral sheet. Therefore, the dehydroxylation temperature can be used to determine the structure of octahedral sheet. Trans-vacant minerals dehydroxylate at 500°C and cis-vacant varieties at 700°C. Mixed types also exist with two dehydroxylation peaks. Thus, the cis- or trans-vacant character of montmorillonites can be determined by Thermal Analysis. To observe the evolved water a TG/DSC equipment linked to a Quadrupole mass spectrometer (Fa. Netzsch Gerätebau) (Simultaneous Thermal Analysis..STA) was used because superimposing reactions prevented peak deconvolution in DSC curves.

We proved the reliability of the border between trans- and cis-vacant varieties at 600°C with respect to PA-curves [2]. It might be expected, that dehydroxylation temperature decreases for low concentrations of one type of octahedral vacancies. Mixtures of a mostly trans-vacant and a cis-vacant montmorillonite revealed, that even small amounts of cis-vacancies dehydroxylated above 600°C because the overall amount of hydroxyl groups is nearly equal for all montmorillonites.

In addition layer charge determination bears a potential source of error for the description of a smectite. It was proved, that the measured layer charge is necessary for calculation of the stoichiometric composition of smectites as proposed by Köster [3].

The aim of the presentation is to present the new classification of montmorillonites based on the results from STA. The new system consists of trivial and systematic names. Trivial names are based on common classifications [4-6]. Systematic names include information on all structural features.

High sensitive AC chip calorimetry for nanogram samples

Heiko Huth, Alexander A. Minakov, Christoph Schick

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Calorimetry is known as a very powerful tool for the characterization of a wide variety of materials and their transitions. There is an ongoing interest in improving the technique in order to achieve high sensitivity and precision. High sensitive differential scanning calorimeters are developed mainly to measure biological samples showing small effects in highly diluted systems, e.g. (1). For reduced sample masses AC-calorimetric techniques are used in this field too (2). For more than 30 years, AC-calorimetry has been known as a sensitive technique to measure thermo physical properties of small sized samples. To further increase sensitivity a differential AC-calorimeter was developed too (3).

In order to allow measurements on sub micron films addenda heat capacity has to be reduced dramatically. The combination of silicon technology and calorimetry opens up new possibilities in this research area as demonstrated recently (4). The thin membrane allows a good ratio between sample and addenda heat capacity for sub micron films. Different chip calorimeters as from Xensor Integrations, NL are used for samples in the microgram range, but also specialized home made sensors for nanogram samples (5). Using chip calorimeter in high vacuum under essentially adiabatic conditions the glass transition in polymer films down to 3 nm is measured (5). This is realized using a fast scanning calorimeter at heating rates up to 1 000 000 K/s. Also differential setups are possible with this technique. Because of the essentially adiabatic conditions only measurements at rapid heating are possible.

Thin film calorimeter operated under non-adiabatic conditions allow heating as well as cooling at rates up to 10.000 K/s (6) and possibly faster. Using such high rates yield often non-equilibrium states of the sample under investigation. As an example, for several fast crystallizing polymers it is possible to prevent crystallization on cooling totally and to reach the amorphous glassy state (6). But often one would prefer to measure thermal properties of small samples at or at least close to thermodynamic equilibrium. This can be achieved by a combination of chip calorimetry and AC calorimetry (4). As common in AC calorimetry a small periodic heat flow is provided and the resulting complex temperature amplitude is measured. The measurements are done at slow scanning or at constant bath temperature. The frequency chosen provides a well defined time scale of the experiment. In several cases, e.g. at glass transition, a direct comparison with results from other dynamic methods like dielectric spectroscopy is possible. Such an AC-chip calorimeter for small samples using a single commercially available sensor under non-adiabatic conditions is described in (7). The sensitivity of this system is about 10 nJ/K at room temperature. This setup would allow measuring the glass transition of polymer films down to 500 nm thickness. For measuring the glass transition of much thinner polymer films the sensitivity of the calorimeter has to be enhanced.

Based on a differential AC-calorimeter we show an improved experimental setup combining the advantages of the different methods already described (8). The differential AC chip calorimeter is based on a commercially available chip sensor from Xensor Integrations, NL, which was already used in (7, 9) for AC and in (6, 10) for fast scanning calorimetry. Due to the differential setup we achieve a sensitive in the pico Joule per Kelvin range allowing to measure samples below one nanogram. Consequently films down to 1 nm thickness can be measured. Because of the small total heat capacity (addenda + sample) not only a high sensitivity is achieved but AC measurements at relative high frequencies are possible too (9). The calorimeter allows heat capacity measurements in the frequency range 1 Hz to 1 kHz.

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Thermal compatibility as a key factor for the success of ceramic laminates in dentistry

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Patients increasingly demand for beautiful teeth. Therefore more and more teeth with severe loss of dental hard tissue as well as poorly aligned teeth are restored with crowns. Feldspathic ceramic offers esthetical properties comparable to those of dentin and enamel. But the mechanical strength is too low to fabricate all ceramic crowns or bridges. Therefore a reinforcing framework has to be used, which, for esthetical reasons, is veneered with the feldspathic ceramic. Developed in the early 60's, the metal-ceramic technique was successfully used in the past decades. A metal framework is cast, using a gold-based alloy and a veneering ceramic is fired onto the substructure. During cooling tensions between ceramic and metal framework occur. The coefficients of thermal expansion (CTE) of both materials have to be matched in a way that the ceramic is slightly under pressure. Thus the strength of the ceramic is increased and the risk of fractures is lowered. As a thumb rule the CTE of the ceramic has to be 10% below that of the metal.

The Au-based alloys contain high melting components such as Pt and Pd. Due to economical reasons Au and Pt were replaced by Pd. Clinical problems with these alloys led to the assumption that Pd is not biocompatible. Therefore the trend changed and Pd free alloys were developed. But dental technicians complained about the bad fit of frameworks fabricated with these alloys. The reason was a thermal creep. While firing the ceramic, temperatures of more than 900°C are reached. At these temperatures the shrinkage of the ceramic caused by the sintering induces forces on the metal, resulting in the distortion of the framework. A bad fit of the restoration leads to secondary caries and to the loss of the restoration and the tooth. Creep measurements of the alloys at high temperatures showed a dependency of the flexure under a constant load and the content of Pt and Pd (Fig. 1).

Nowadays instead of metal the high strength ceramic zirconia is more and more used. Zirconia offers the option to make not only single crowns but to fabricate all ceramic bridges to replace missing teeth, which is an advantage in regard to esthetics. The ceramic framework is far more rigid than a metal substructure. Therefore the coefficient of thermal expansion of the veneering ceramic has to be well adapted to that of zirconia. In a simple thermal shock test it can be demonstrated that lower tensions occur when the CTE of the veneering ceramic is closer to that of zirconia (Fig. 2). In this test veneered crowns are heated to elevated temperatures in steps of 15K and quenched in ice water. The veneering ceramic is examined for cracks. Surviving crowns are heated to the next level. In this case the CTE of ceramic 2 was a little closer to that of zirconia and in the result comparable to a well proven metal-ceramic system.

For good clinical results and high success rates not only the mechanical but also the thermal properties of the materials have to be considered.

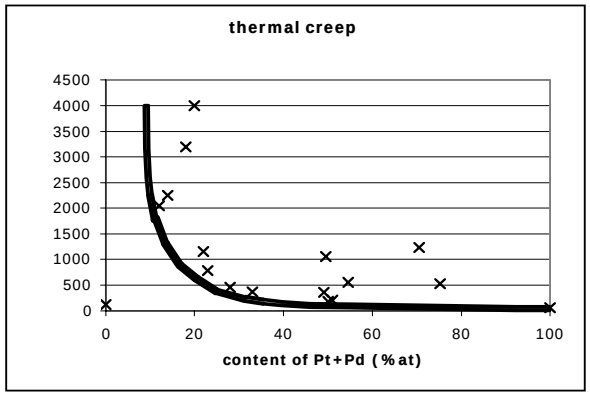

Fig. 1: Thermal creep of precious metal alloys plotted against the content of high melting components.

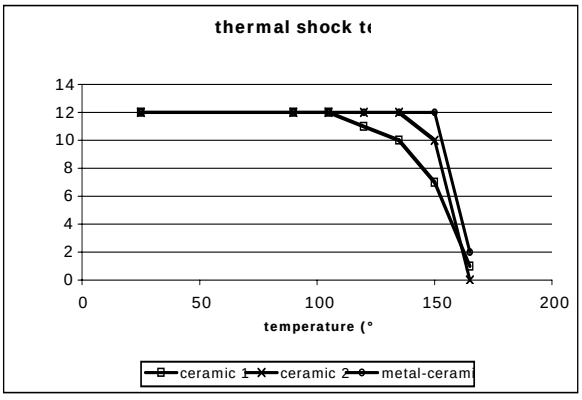

Fig. 2: Thermal shock test with 2 different veneering ceramics and a metal-ceramic system.

Pharmaceutical Applications of MicroReaction Calorimetry

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The trend to smaller sample sizes in instrumentation is not evident with the first generation of reaction calorimeters. However these large volume systems give good process simulation and have a variety of applications especially within the pharmaceutical industry. With recently available technology, the scaling down 1000 times to samples sizes from 100-1500µl has been shown to allow design of a versatile calorimeter system that is both simple and rapid in use. New application areas are possible and there is potential for such a calorimeter to be used in many more industries and academia. Information on MicroReaction Calorimetry, the instrument, data and introductory applications is available elsewhere [1] and will not be the subject of this presentation.

Detailed here are applications chosen are from the pharmaceutical industry – but it will be clear that such application can be extended to other many areas of chemical interest.

- Product development by small-scale simulation of the desired reaction is the first application. The measurement of heat of reaction, speed of reaction, effect of catalyst, temperature, feed rate and impurity
- Compatibility in mixing – a simple but important application especially in waste streams.
- Fermentation studies – heat output from micro-organisms
- Excipient compatibility – a key issue in drug formulation
- Specific heat measurement – traditionally difficult to do with multiphase samples
- Kinetic applications of pharmaceutical reactions
- Stability and unfolding of macromolecules

Thermal analysis used to study phosphorous based cements

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There is a growing interest in fast setting materials and materials for high tech applications. Because of their fast hardening reaction, phosphate cements can be a usable solution. Depending on the composition, magnesium phosphates, zinc phosphates, aluminium phosphates and calcium phosphates can be distinguished. They all exhibit different properties and hence can be used for different applications. These phosphate materials can be made by sintering at high temperatures or at low temperatures by mixing a solid phase (cement) with a liquid phase. By addition of accelerators and / or retarders in the solid – liquid mixture, the hardening time can be adjusted to the desired value.

Contrary to ordinary cements (e.g. Portland cement), these phosphate cements solidify in acid rather than in alkaline environment. At the Vrije Universiteit Brussel (VUB) a new type of phosphate cement has been developed by reaction of a calciumsilicate (wollastonite: $CaSiO_3$) with a phosphoric acid solution containing some metal ions. The big advantage of this material is that starting from a suspension with low pH, the hardened material has a neutral pH. The low to neutral pH during and after hardening in combination with a short reaction time implicates that ordinary E-glass fibre can be used in the matrix material without being attacked. By implementing E-glass fibre mats in the matrix material, the tensile strength of the cement can be increased from 10 MPa (for pure matrix) to 45 MPa (matrix combined with glass mats with a random orientation) or to 90MPa (matrix combined with glass mats with a unidirectional orientation). Another great advantage of the system is that the material seems to have a good heat resistance. This allows high temperature applications. The fundamental chemistry of this reaction is however not well known, but is at present under study.

Keywords: phosphate cements, molecular characterisation, reaction kinetics, modulated temperature DSC

Use of Dynamic Mechanical Analysis for Investigation of Powdered Materials

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Dynamic Mechanical Analysis (DMA) is a traditional thermal analysis technique historically used, predominantly, to investigate the molecular relaxation processes that occur in polymeric materials. Many publications and presentations using this technique have been presented in the past. This paper focuses on the development of a new sample holding mechanism developed by Triton Technology which for the first time, conveniently and reproducibly, enables the mechanical properties of powdered materials to be investigated by DMA.

A DMA instrument measures the stiffness of a material as a function of temperature (sometimes frequency or RH as well). A sinusoidal load (stress) is applied to a sample and both the distance the sample is displaced (strain) and the phase shift between the stress and strain (damping or δ) is measured. As the stiffness of a material (and its damping behaviour) changes dramatically when going through a relaxation like a Tg, DMA is an excellent instrument to monitor these events. The modulus of the material is also calculated.

A conventional DMA can operate in different modes depending on the stiffness of the material, the specific sample dimensions and what parameters are required. Most operational modes require a bar or a film of the material under test. The Triton Technology Materials Pocket is a piece of stainless steel that is folded with the powdered material "sandwiched" in the fold. When run in bending mode, (Figure 1), the two sides of the pocket will deform in slightly different ways producing a shearing action on the powdered material. As steel does not show any relaxations over the temperature range of the instrument and its modulus remains constant, any signals generated by the instrument are from the powder.

This technique has been applied to various systems that demonstrate the effectiveness of the Materials Pocket. A polymer will be shown where the sample was run as a bar in conventional single cantilever bending and then the same material was run as a powder in the Materials Pocket. This experiment demonstrates that the same relaxation information is obtained from the powdered material as from the bar sample. It is often inconvenient or difficult to obtain uniform bar geometries from samples so this ability is particularly relevant for looking at moulded products.

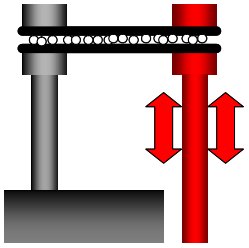

Figure 1, Single Cantilever Bending of a Materials Pocket

As a simple example, freeze dried coffee was run using this technique and the complex nature of the experiment will be shown.

More recently, pharmaceutical applications have been investigated both at Triton Technology and at collaborative universities. Data will be shown that demonstrates that amorphicity can be quantified for powdered pharmaceutical materials in a very precise and reproducible way.

Measurement of the Relaxation Transitions of Nitrocellulose Based Gunpowder

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Department Energetic Materials

Many applications of energetic materials give rise to problems in investigating the mechanical properties as a function of frequency or temperature. The cause of these problems have several origins: difficult sample preparation because of the energetic nature of the material, very small transitions and non-linear behaviour are some of the causes of complications during investigation of these materials. Nitrocellulose is one of the often-used energetic materials which is difficult to characterise, partly because of its rigid nature at room temperature and its small changes in modulus during the relaxation transitions.

In order to be able to perform a complete characterisation of nitrocellulose, as a subject of a surveillance program for the MoD, several experiments were performed, attempting to measure the different thermal transitions in nitrocellulose gunpowder, as well as the coefficient of thermal expansion. Different techniques, like Differential Scanning Calorimetry (DSC), Thermal Mechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA) were compared to investigate these mechanical properties. The sample preparation in this investigation is fully discussed. With DMA the shear mode and the bending mode were applied, trying to indicate the-, ß-, (and possibly γ-) transition. Also an attempt was made to measure the frequency dependency of these transitions by performing several isothermal frequency sweeps and constructing a master-curve from these curves. During this investigation several problems in sample preparation and measurements were encountered and evaluated.

A clear conclusion could be drawn from these experiments about the optimal technique to measure the relaxation behaviour, as well as the possibility to establish the frequency dependant behaviour and about the possibility to use this characterisation in a surveillance program. Also some recommendations are given in order to perform a correct and safe sample preparation method.

TOPEM® - the latest innovation in temperature modulated DSC

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Temperature modulated DSC (TMDSC) techniques consist of a temperature program with a linear temperature ramp and a superimposed small temperature perturbation. For this modulation different signal shapes are used:

- step-wise temperature changes followed by isothermal segments [1],
- single frequency sinusoidal modulations [2] and
- multi-frequency periodic modulations by superposition of multiple sinusoidal functions [3] or the use of non-sinusoidal modulation functions [4].

TMDSC is used for heat capacity measurements, determination of the kinetic contribution to the DSC signal [2], and separation of different components in the heat flow signal and the measurement of the frequency dependence of the heat capacity. One advantage of temperature modulated DSC in general is the possibility to measure heat capacity changes also during ongoing excess heat production processes (reaction, crystallization, evaporation etc.). This is achieved by separation of the measured sample response signal (heat flow) into the so called "reversing" and "non-reversing" heat flow components.

TOPEM® is a novel temperature modulated DSC technique where a non-periodic stochastic temperature perturbation is superimposed to a conventional DSC temperature program. Using an advanced evaluation procedure both, the quasi static material properties as well as the frequency dependency of thermal processes can be simultaneously analyzed in one single measurement. Using quasi-static properties improves the separation possibilities of temperature modulated DSC considerably. The frequency dependence of thermal processes can be used to get more insight in molecular dynamics and allows an easier identification of thermal events. These possibilities are shown on typical examples.

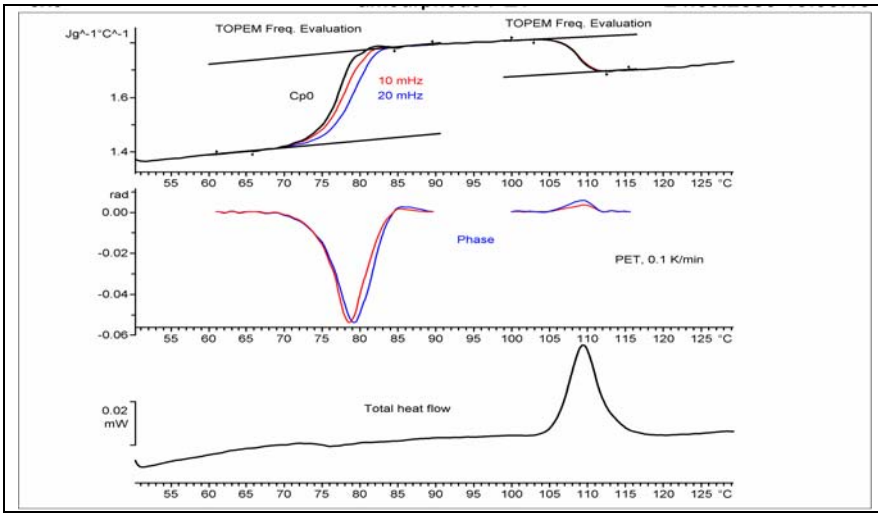

Figure: Example of one TOPEM® measurement of amorphous PET resulting in several curves. The glass transition step is shifted to higher temperatures with increasing frequency, whereas in the crystallization region the frequency curves are identical.

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The mechanism of the thermal transformation from synthetic goethite to hematite

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Synthetic pigments of goethite (Bayferrox®) of different particle size were investigated by thermal analysis (DTA; TG; DSC), infrared spectroskopie (IR), and X-ray diffraction (XRD) measurements. It follows that a so called 'hydrohematite' ($Fe_{2-x}O_{3-3x}(OH)_{3x}$; x= 0: α-Fe_2O_3; x = 1: $Fe(OH)_3$) described in the literature [1] does not exist as a discrete intermediate [2,3] during the dehydration course from goethite to hematite. Instead a dependence of the dehydration mechanism on the particle size was observed [4]. Transformation enthalpies and activation energies [5] for the dehydration process will be given.

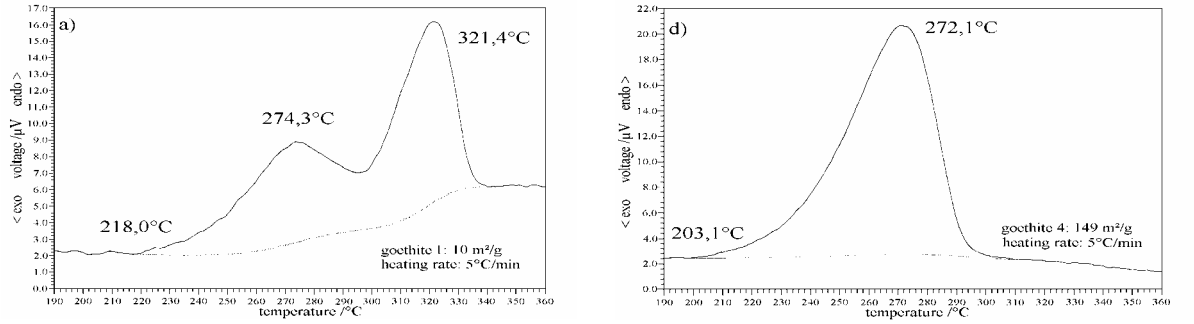

Figure 1 DTA of goethite samples of different particle size. Left, goethite 1 (10 $m^2\ g^{-1}$); right, goethite 4 (149 $m^2\ g^{-1}$).

Based on the assumption that the thermal dehydration proceeds from the crystal surface to the centre of the goethite needles the following model is developed for the mechanism of the dehydration process: at an early stage of the dehydration, water leaves the crystal lattice in the [010] direction of the crystal by developing dehydration channels parallel to the crystallographic c-axis [001]. The matrix between the channels is formed by hematite.
In case of greater crystal dimensions the dehydration channels within the outer crystal regions begin to grow together, forming a compact hematite layer at the crystal surface, whereas the dehydration front within the needle has not reached the crystal centre, i.e. the dehydration process is not finished yet.
The compact surface hematite layer acts like a barrier, which hampers the further extension of the dehydration zone, because an additional amount of enthalpy must be provided to overcome the dehydration barrier and thus allow the dehydration front to proceed into the needle centre, until the dehydration has finished. Experimental evidence for this model consists of the second peak in the DTA plots of goethite samples, for example goethite 1 (Fig. 1).
In case of very small needle dimensions (goethite sample 4; Fig. 1) the dehydration is finished before the surface hematite layer reaches a "critical" thickness, thus a dehydration barrier can not form. The thickness of the critical hematite layer postulated here increases with the size of the goethite needles. The dehydration mechanism, which is compatible with the DTA/DSC results, is confirmed by TEM investigations.

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High Speed/High Performance Differential Scanning Calorimetry (HPer DSC): Temperature Calibration in the Heating and Cooling Mode and Minimization of Thermal Lag

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The temperature calibration of High Performance DSC in the heating and cooling mode is discussed. Several primary and secondary calibration standards are studied at different sample masses and various heating and cooling rates. The experimental onset and peak temperatures of Indium with different sample masses are measured at different heating rates and the two related correction factors are presented. The symmetry of the HPer DSC with respect to the cooling and the heating modes is checked and found to be good. The liquid crystals M24, HP-53 and BCH-52, being substances with no or very small supercoolings, are recommended as secondary standards for temperature calibration in both the cooling and heating mode. In order to verify whether the proposed correction factors of Indium can also be used in the cooling mode, the melting behavior of Indium and the phase transition temperatures of the secondary standards obtained in heating are compared, and it turns out that the latter are usable as well. Finally, recommendations for both an extensive temperature calibration and a rather quick calibration procedure of scanning calorimeters in the heating and the cooling mode for various sample masses and various rates are given. The calibration procedure developed for HPer DSC facilitates making the right choices to minimize the thermal lag with respect to the sample mass and scan rates at the start of the measurement, instead of just making corrections afterwards.

Modulated Temperature DSC and its use for studying reaction kinetics and (reaction-induced) phase separation

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During the polymerization of thermosetting polymers, the chemorheology of the reacting system changes considerably. After a gradual increase in molar mass and an increasing extent of branching, gelation occurs when a (macroscopic) network is formed, which still contains a soluble fraction. Further reaction increases the crosslink density of the network. Along this structural evolution, vitrification occurs when the material changes to a glassy state due the increase of the glass transition temperature up to or above the cure temperature. The resulting strong decrease in molecular or segmental diffusion can affect the polymerization rate, making it diffusion or mobility controlled, and often prematurely halts the reaction, thus strongly influencing the final material properties.

Modulated temperature differential scanning calorimetry (MTDSC) has proven to be a valuable technique for the characterization of reacting polymer systems. In this technique the evolution of the polymerization reaction and the degree of vitrification can be quantitatively studied using the simultaneously measured heat flow and heat capacity signals, respectively. The effects of isothermal, non-isothermal, and combined cure paths on the polymerization reaction and the vitrification can be studied using a limited number of MTDSC experiments. For amine-cured epoxy resins, the gradual rise in heat capacity before vitrification can be attributed to the consumption of primary and secondary amine functional units. Therefore, both heat flow and heat capacity evolutions can be used to study the reaction kinetics.

Using MTDSC, the result of mobility restrictions on the reaction steps can be studied. For step-growth polymerization epoxy-amine systems, the reaction rate and the heat capacity decrease almost simultaneously, an indication that similar molecular or segmental mobilities are involved. In contrast, for the free radical cross-linking copolymerization of an unsaturated polyester resin, an autoacceleration is observed closely before the onset of vitrification. For these systems, the onset of diffusion control is specific for the different types of reactions in the mechanism (e.g., termination versus propagation), and can be influenced by the size of the molecules involved.

Predicting the influence of cure cycles requires cure kinetics modelling, especially, e.g., for extending experimental diagrams to time-temperature conditions that cannot be assessed experimentally. Moreover, mechanistic kinetic modelling can aid in the prediction of the influence off-stoichiometric compositions, thermoplastic modifiers, or impurities, on the cure kinetics. For thermoplast-modified amine-cured epoxy systems, the formation of reactive and unreactive complexes has important effects on the reaction kinetics. If the thermoplast is not fully miscible with the final epoxy-amine network, reaction-induced phase separation occurs. The concurrent appearance of an excess heat capacity contribution enables one to detect reaction-induced phase separation in thermoplast-modified systems.

The excess heat capacity contribution arising from demixing and mixing phenomena is also observed upon phase separation or remixing of partially miscible polymer blends and solutions. It enables one to get in situ information about the kinetics of the mixing/demixing processes and the morphology evolution.

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The True Heat Flow Principle: A new and fast method beyond calorimetry for process characterization

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ChemiSens Int AB, Lund, Sweden,

The True Heat Flow principle is a method to obtain most reliable calorimetric data of chemical reactions or phase transitions without the need for calibrations. Therefore, the method is fast and ideally suited for measurements under changing conditions like increasing reaction volumes, changing stirring rates or viscosities. Measurements are performed in volumes between 10 and 180ml. All kinds of peripherical devices for dosing, sampling and probing can be connected to the system. An exceptionally stable baseline allows the investigation of long term reactions.

Thermodynamics of temperature dependent enantioslectivity in cyclodextrins

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Recently, thermopile-chip based heat flow sensors were successfully used for the detection of volatile organic compounds in chemical sensing [1]. The low time constant makes a resolution in the area of nanojoules and, consequently, low detection limits possible. The further development towards quantitative chip-calorimetry and the combination with a quartz crystal microbalance (QCM) enabled the determination of thermodynamic data for absorption processes into thin receptor layers, for example chiral recognition of enantiomers in cyclodextrines [2]. In both applications the measurements benefit from the excellent performance of chip-calorimeters for the quantitative detection of fast absorption processes in thin receptor films (small time constant, fast mass transfer inside films).

From gaschromatographic measurements a decrease of the enantioselectivity with increasing temperature is known. In some cases also a non linearity of the van't Hoff plot of the chiral separation factor was observed. The reason for this behaviour is probably a change in the mechanism of chiral interaction with temperature [3; 4]. Thermodynamic data for the recognition processes can contribute to a better understanding of such effects and provide a deeper insight into the mechanism of enantioselectivity. However, the widely used gaschromatographic method for the determination of thermodynamic data is not reliable in the case of non linear van't Hoff plots. This contribution focuses on the presentation and discussion of temperature dependent chip-calorimetric and QCM measurements of chiral recognition processes in cyclodextrines. This combination of methods avoids the problems of the van't Hoff method by direct measurement of absorption enthalpies and absorption isotherms and provides the relevant thermodynamic data as well as additional information on the concentration dependence of enantioselectivity.

The absorption of the enantiomers of methyl lactate into Lipodex E® was used as the chemical test system. This system has been extensively studied by gaschromatography and a change of enantioselectivity was reported near 60°C [3]. Chip-calorimetric and QCM measurements were performed in the temperature interval from 5 to 60 °C. By fitting a thermodynamic absorption model to all the experimental data, the absorption process could be separated into a non-specific, achiral and a specific, chiral contribution and the thermodynamic data for both contributions were calculated. The thermodynamic data were determined in the temperature range of 5 – 60°C, discussed in relation to the enantioselectivity and compared to available literature data.

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Thermogravimetric Measurements in Supercritical Water Using a New High Pressure High Temperature Magnetic Suspension Balance

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In the last 10 years supercritical water (SCW) got more attention and many processes were developed using SCW as process fluid. SCW is widely used in processes in the recycling and disposal industry. SCW is for example able to decompose substances that are biologically difficult to break down. Another example for a process with SCW is the cracking of high polymers in order to make them recyclable. For the design of such processes the thermophysical properties and the reaction behaviour of SCW have to be known.

Experimental data of mass transfer and decomposition processes can be directly detected in thermogravimetric experiments. Here the change of the mass of a sample in dependency of temperature and pressure is observed by means of a microbalance.

In conventional measuring systems there is a direct contact between the microbalance the measuring fluid. For this reason the applications of the gravimetric method have been limited in the past to low pressures, moderate temperatures and non-corrosive fluids.

Using magnetic suspension balances investigations under almost every condition are possible. For more than 15 years Rubotherm produces magnetic suspension balances for different kinds of applications which are successfully applied in research and development. Until recently the maximum operating temperature of the high pressure magnetic suspension balance was limited to 250°C. However, sample temperatures can be much higher.

Especially for processes with SCW Rubotherm developed a new magnetic suspension balance with a larger range of operation (500 bar and 500°C). This is clearly above the critical point of water and as a result of that condensation of water vapour even at high pressures up to 500 bar is avoided. Using this new magnetic suspension balance an automatic installation for the investigation of mass transfer processes in SCW was developed.

The measurement principle, the new instrument and the experimental installation will be described in detail. In addition, the measurement procedure and experimental data referring to the decomposition of a polymer in supercritical water will be presented and discussed to a certain extent**.**

Crystallization kinetics of Polyphenylenesulfone

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Differential Scanning Calorimetry is often used to study crystallization kinetics. Most of the non -isothermal experiments are performed under heating conditions and the results are fitted using a Kissinger like method.
Here we propose a method to study crystallization behavior of (poly)phenylsulfone (PPS) while cooling.
The aim is to obtain a description of the crystallization kinetics at cooling rates approximating actual process conditions.
Experiments were performed with different cooling rates, starting from a PPS melt at 320°C.

We assume an iso-kinetic process where the crystallization rate $\dot{x}$ is a function of both the temperature T and the crystallization degree x such that $\dot{x} = f(x)/\tau(T)$. The function $\tau(T)$ we call the kinetic model, $f(x)$ is called transformation model.

1) Determination of the kinetic model, the time constant τ(T)

The temperature belonging to 50% conversion is denoted as T½. Each cooling rate β will give a different T½.

The time constant τ(T) is estimated from: $\tau_{1/2} = \frac{dT_{1/2}}{d\beta}$.

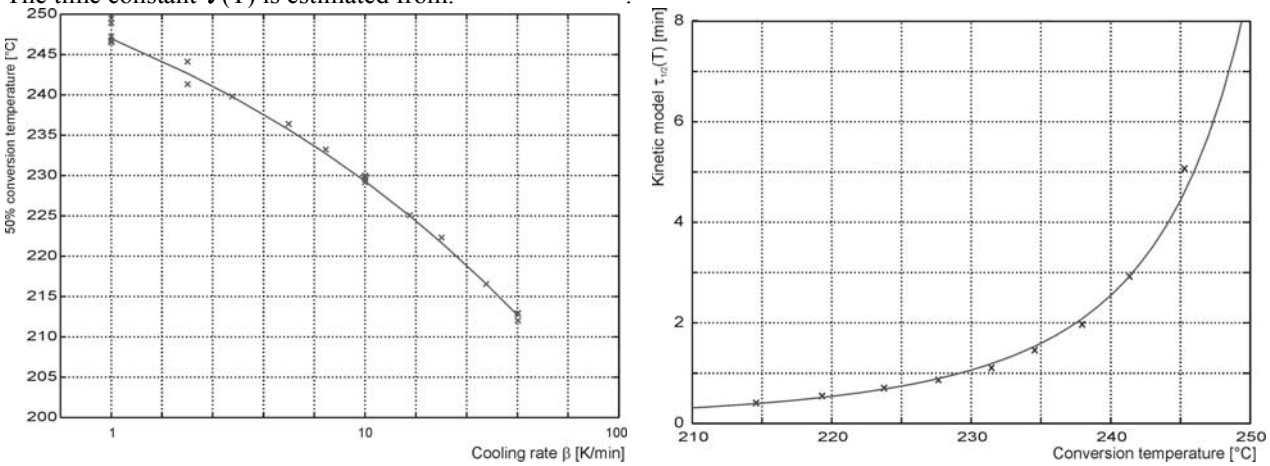

Figure 1: a) 50% conversion vs. cooling rate, b) estimated time constant for 50% conversion

2) Determination of the transformation model f(x).

The transformation is fitted with a generalized Avrami model: $\dot{x} = (1-x)^r \frac{n}{\tau}\left(\frac{t}{\tau}\right)^{n-1}$, where the saturation exponent r has been added to describe impingement of growing crystals. The Avrami exponent n is determined by an Avrami plot: $\log((1-x)^{r-1}-1)$ vs. log S , where for each experiment the kinetic strength S is defined as:

$S = \int_0^t \frac{dt}{\tau} = \frac{1}{\beta}\int_T^{T_c} \frac{dT}{\tau(T)}$, where the onset of crystallization is assumed at Tc .

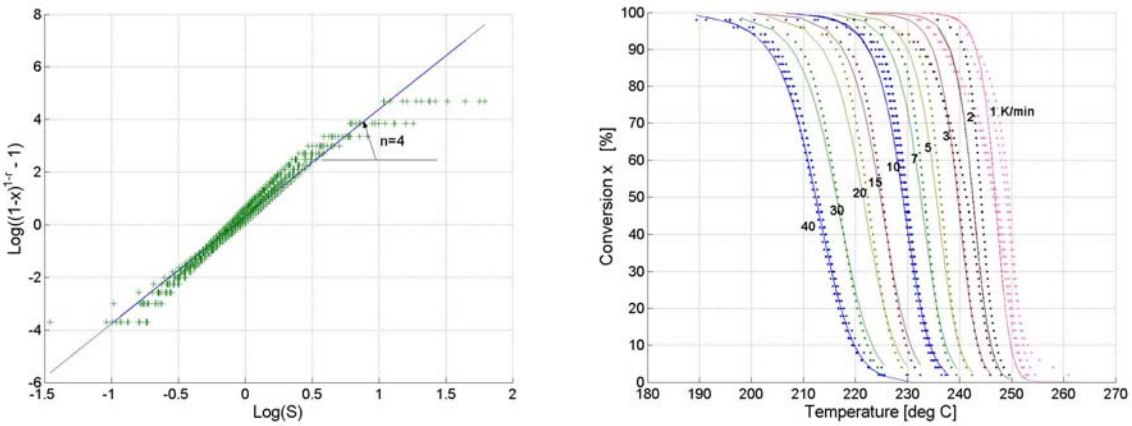

Figure 2: a) Avrami plot, b) simulated conversion vs. experiments

3) Results and discussion

The function fit of the kinetic model clearly shows that this process is not thermally activated. Kissinger like methods are not applicable.
The Avrami plot yields fit values n = 4. and r = 2.2. These have been used to simulate the continuous cooling experiments. The fit appears valid for cooling rates in a range of 5 to 40 K/min.
The iso-kinetic model appears to be not applicable for description of conversion at temperatures not far below the onset of crystallization. The experiments using low cooling rates (β < 5 K/min) show bad reproducibility, probably due to secondary recrystallization effects.

Determination of Characteristic Specifications of the New DSC 200 F3 Maia® and their Influence on Projected Applications

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There is a well-introduced frame of procedures for the characterization of the properties of a DSC for comparative technical and application estimations. Important parameters for a comprehensive technical description are the calorimetric sensitivity [1], often expressed by the digital detection limit in the signal for the heat flow rate, and the resolution [1, 2] as the ability to separate partly overlapping thermal events; the resolution is strongly influenced by the thermal resistance and the time constants of the DSC signal. Further the noise of the signal and the stability and reproducibility of the DSC baseline are included in characteristic specifications. The accuracy of the evaluation results is determined by the calibration possibilities offered for the hard-and software, and here especially the quality of the temperature, heat and heat flow calibrations influences the overall accuracy of the DSC.
The procedures for determination of the characteristic specifications will be discussed and the individual parameters will be correlated with general design features of a DSC, and specifically of the new DSC model.
The new value-line DSC 200 F3 Maia® is developed for quality control applications in the polymer industry, including also the polymer-related applications in the film, packaging, food and pharmaceutical industries. With discussion of application results it will be demonstrated, how the technical specifications of the DSC fit to the focused applications and where results reflect the direct influence of an individual technical parameter.
The application of Advanced Software for further signal treatments will be discussed with respect to the quality control and failure analysis applications in the polymer industry.

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Studying Crystallization and Polymorphism by Adiabatic and Differential Scanning Calorimetry

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Calorimetric techniques can very successfully determine the physical and chemical properties of a substance, a mixture and/or reaction mixture, as a function of time or temperature. These techniques are often used to analyse thermal behaviour of a material [1, 2, 3] by exposing it to a controlled temperature program, involving heating, cooling or isothermal periods, during which the material will undergo physical or chemical changes. Here we focus on phase transitions and first we will demonstrate the usage of adiabatic calorimetry in investigation of the crystallization of binary mixture of 1,4-dichlorobenzene and 1,4-dibromobenzene. Previous studies of the mixtures that tend to form solid solution, like the mixture of 1,4-dichlorobenzene and 1,4-dibromo benzene, point to difficulties in experimental determination of the equilibrium phase diagram. This comes from more reasons, such as the uncertainty about whether the system has reached the equilibrium during measurements or homogeneity of the solid phase is questionable [4, 5].
During the melting and crystallization of solid solutions, the overall equilibrium between entire amounts of solid and liquid phase is prevented by very low diffusion rates in the solid phase. Therefore, the result of crystallization will be an inhomogeneous state of solid, containing composition gradients in its bulk. In our work we focused on the crystallization of the issued mixture in an adiabatic calorimeter, by analysing the enthalpy change of the mixture, experimentally obtained by cooling the melt under the rate of 0.1 K·min-1. Accordingly, we developed a kinetic model that describes the crystallization process and is based on the assumption that at slow cooling rate equilibrium is established between the surface of the growing solid phase and the existing liquid phase along the cooling path. Moreover, the application of the kinetic model is extended to the determination of excess thermodynamic properties of the solid phase that enable the calculation of the phase diagram. The advantage of proposed kinetic model over the traditional equilibrium approach for the determination of excess properties is that it is not based on the unjustified assumption that the system is in complete equilibrium.
Hereafter, we will present the results of measuring one of the monoacid triacylglycerides, tristearin, in differential scanning and adiabatic calorimeter. Although the polymorphism of tristearin has been quite exhaustively studied [6, 7, 8], we believe that the combination of these two calorimetric techniques can give more precise data and better insight in the crystallization processes.

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Application of *PulseTA*® to the investigation of Fluorides. An attempt to calibrate HF

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PulseTA© has been developed as an extension of the hyphenated techniques in thermal analysis (TA-MS, TA-FTIR) and is applicable to various capillary or skimmer coupled TA equipment [1]. It is based on the quantitative calibration of ion current (IC) or IR signals which can be performed *on line* by injecting permanent gases into the purge gas stream or *off line* by a preceding separate TA run of a suitable calibration substance (e.g. $NaHCO_3$ or $CaC_2O_4 \cdot H_2O$ for the calibration of the water IC signal m/z 18).

The solid state chemistry of fluorides or fluorometalate complexes is directly related to the exact knowledge of the role and the extent of pyrohydrolysis which occurs if fluorides were subjected to heating processes. Therefore, the quantitative description of HF evolution during thermal processes is of crucial importance for understanding the high temperature chemistry of fluorides. Further complication results from the fact that, in most cases, water is simultaneously released.
$NaHF_2 \cdot nH_2O$ (*i.e.* a non-defined stoichiometric form) was successfully used as calibrating substance for HF [2]. It is due to the fact that NaF, the product of the simultaneous release of HF and H_2O, represents a suitable weighing form thus allowing the determination of the precise water content in the same single calibration run after having precedingly calibrated the IC for m/e 18.

The considerable advantages of *Skimmer*® systems [3,4] are weakened by the unavoidable disadvantage that the IC signals become temperature-dependent. This is due to the constructive conception allowing the gas sampling for MS through the orifice system at the sample temperature (!) and which goes up to 1500°C. Therefore, the calibration is exactly valid only for the temperature range where the calibration run was made, *i.e.* approximately 150-220°C in the case of $NaHF_2 \cdot nH_2O$. Consequently, a precise determination of evolved species by using the method of *PulseTA*® yields reliable results only via a temperature-dependent calibration. This does not represent a problem when injecting usual permanent gases but is extremely complicated, if not impossible, in the case of HF due to its known corrosive properties.
The proposed method is based on the measurement of the temperature-dependent intensity decrease for several permanent gases or liquids such as Ar, CO_2, O_2, H_2O, and an extrapolation to the behaviour of HF. The decrease of the integral intensity revealed to be less important than expected and amounts, *e.g.* to 84% for CO_2 at 950°C, to 78% for Ar, respectively. The injection of liquids meets more difficulties and yields less precise values. Quite surprisingly, the intensity decrease for m/z 18 amounts to only 98% at 950°C. This means that water determination by *PulseTA*® is possible without temperature-dependent calibration. The area change for the HF calibration is estimated at 90% for the range 600-700°C, and 85% for 900°C, respectively. Several examples will be elucidated.

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Applications of High Performance DSC in polymer research: Advantages and limitations

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In practice, like during processing, high cooling rates are common. Therefore, it is of interest to study crystallisation behavior at the same cooling rates. During heating many materials – especially polymers – reorganize (e.g. by cold crystallization, recrystallization etc.) and in principle it is possible to hinder this by the application of high scanning rates1. High Performance DSC (HyperDSC) is a powerful analytical tool for analysing polymers by providing high and constant cooling and heating rates. By using the high-speed capabilities of HPer DSC, it is possible to perform quantitative measurements within very short time on sample masses down to the microgram level.

HyperDSC has been applied to study crystallization and melting behavior of polyolefin's at high and constant cooling and heating rates. In addition, with the fast-response sensor of the Diamond, even higher (but not-constant) scanning rates have been realized with average rates of 1000 °C/min, to temperatures as low as -180ºC. The deviation of the sensor temperature measured from the programmed temperature is 1 °C at maximum, thanks to the power compensation principle.

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ABSTRACTS

FOR

POSTERS

Thermal stability of nitrogen doped VO_2(B)

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Institut für Chemie der Technischen Universität, Straße des 17. Juni 135, D-10623 Berlin

VO_2 is a promising material for optical applications and it's properties possibly can be enhanced by incorporation of nitrogen. Several modifications of VO_2 are known. The rutile type is observed at ambient temperature. Previous studies [1, 2] reported a reversible phase transition (semiconductor↔metal) from monoclinic VO_2(M1) to tetragonal VO_2(R) at 68°C. This structural transition is associated with a significant variation of several physical properties including an increase of the electrical conductivity and a decrease of optical transmittance in the near infrared region down to virtually zero [3]. Another modification, monoclinic VO_2(B) [4], is derived structurally from V_6O_{13} [5].

Starting from ammonium vanadate (NH_4VO_3), $V(O,N)_2$(B) was formed by reduction in a NH_3/H_2O gas mixture through a reaction time of 9 hours at 300 - 350°C. 0,24 - 1,44 mass% nitrogen was incorporated in $V(O,N)_2$(B), determined by hot gas extraction.

$V(O,N)_2$(M1) (rutile type, 0,08 mass% nitrogen) was obtained by heating $V(O,N)_2$(B) in nitrogen atmosphere at 400 - 450°C. A mass change was not detected. Oxidation of $V(O,N)_2$(B) (mass increase; exothermic effect) is observed in air at ~335°C (figure 1). The oxidation product (V_2O_5) was characterized by X-ray diffraction (XRD). A previous phase transition to $V(O,N)_2$ (rutile type) as seen in nitrogen atmosphere was not observed.

An oxidation process of VO_2(M1) to V_2O_5 is detected at ~605°C (figure 2). The melting point (heating) as well as the crystallization point (cooling) of V_2O_5 is observed in a profile of hysteresis, respectively.

Furthermore particle geometry and surface structure of nitrogen doped VO_2(B) were characterized by electron microscopy (SEM).

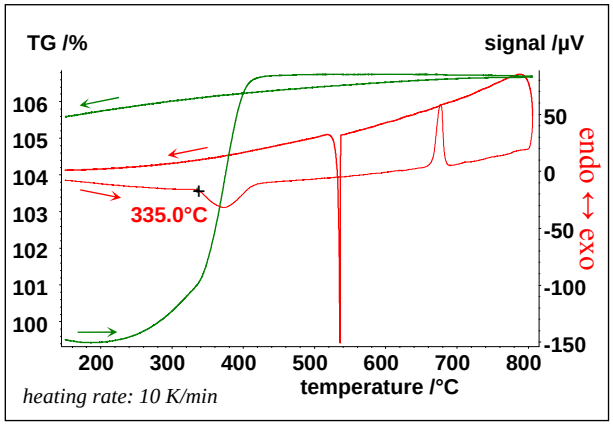

Fig. 1. DTA/TG of $V(O,N)_2$(B) in oxygen atmosphere

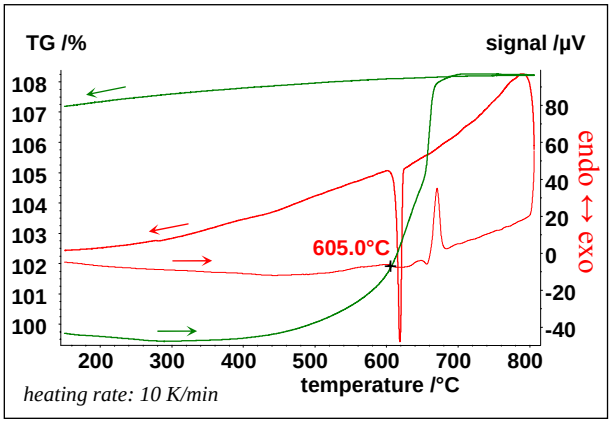

Fig. 2. DTA/TG of VO_2(M1) in oxygen atmosphere

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DTA-FTIR of Abalone Shell – Exploring the Chemistry behind DTA Signals

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Differential Thermal Analysis (DTA) is widely used to study enthalpic changes during thermal treatment by recording the difference in temperature between a sample and a reference material against either time or temperature. In investigating complex mixtures or composites, the coupling of DTA to FTIR (Fourier Transform Infrared Spectroscopy) can be extremely useful. The FTIR spectra of the volatile released products are measured simultaneously and thus are directly linked to the observed DTA signals. We applied a DTA-FTIR method to investigate the characteristics of a fascinating biocomposite: the nacre of the Abalone shell (Haliotis laevigata).

The nacreous layer of the Abalone shell is known to be an extraordinary composite material. It is composed of a regular arrangement of 500 nm thick aragonite-plates within an organic matrix of protein and chitin molecules [1-4]. Because of this unique building concept, the mechanical properties outmatch those of the individual materials of the composite. Based on that observation, the exact composition of Abalone shell is investigated to develop new artificial materials with similar qualities.

In this investigation, we carried out DTA measurements of mineral aragonite in comparison to Abalone shell. During dynamic thermal treatment of mineral aragonite in air, we observed an endothermic signal at 490°C, interval [470…510°C], due to the phase transformation of aragonite to calcite [5]. Treating Abalone shell under similar conditions, REM and XRD results showed the same phase transformation of Abalone aragonite into calcite. However, the DTA curve turned out to be completely different: An endothermic signal at 275°C was observed, and a very strong exothermal signal at 460°C, interval [430…510°C]. Additionally, we measured a mass loss at both temperatures. We speculated, that these significant differences might be caused by the embedded organic compounds.

By means of DTA-FTIR we were able to prove this theory for Abalone nacre in detail:

At both DTA steps of the thermal treatment of Abalone in air we determined characteristic protein decomposition products. At 275°C, the major products ammonia, CO and hydrocarbons related to protein pyrolysis were observed. Since most of the pyrolysis reactions are endothermic, this is plausible with the observed DTA data. At 460°C, we detected the characteristic combustion products of proteins [6], which typically are ammonia, CO_2, HCN, and water (NO at detection limit). Since a combustion process is an exothermal reaction, we conclude, that the strong observed exothermic DTA signal at 460°C is caused by the combustion of the imbedded organic molecules. In the overall enthalpy balance shown by the DTA data, this strong exothermic signal supercompensates the simultaneous endothermic reaction caused by phase transformation of aragonite into calcite.

In nitrogen atmosphere, the DTA curve of Abalone shell shows two endothermic signals – a signal at 275 °C and a broad signal with a maximum at 440 °C. At both temperature intervals, the characteristic pyrolysis products of proteins are detected. In contrary to the air atmosphere, only low concentrations of CO_2 are observed, but higher concentrations on hydrocarbons. Additionally, the residue at 900 °C shows a grey colour, probably due to left-over coke mixed into the white CaO, which is the only residue in air atmosphere. Mineral aragonite, on the other hand, shows similar DTA signals at 490 °C in air and nitrogen atmosphere, representing the phase transformation of aragonite into calcite.

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Applications of Thermal Analysis in Nanotechnology

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Thermal Analysis methods find broad application for the characterization of nanomaterials during synthesis, part preparation and control of final product properties. Different thermoanalytical techniques were applied to characterize the melting and transition temperatures, the sintering, synthesis and decomposition of various nano-sized powders and nano-dispersed materials. The aim was to demonstrate that the sensitivity of modern thermoanalytical methods is well suited for general applications on materials with a reduced particle size into the sub-micrometer range and that the results provide important parameters for the thermal characterization of organic and inorganic nanomaterials. Calorimetric methods, like DSC and High Pressure DSC are applied to study melting of nanosized materials, their temperature-induced reactions and the stability ranges. DSC and simultaneous TG-DSC techniques can be applied to prepare materials in the nano-size range, like shown for example in literature for aluminum and aluminum nitride particles [1, 2] and for the demonstration of the influence of the particle size on melting temperatures for aluminum [1], for silver clusters in nickel [3] and transition temperatures from goethite to hematite [4, 5]. Electro-ceramic materials show a strong dependence of the mechanical and electrical properties upon the sintering process. Barium titanate ceramic powders were grinded in the NETZSCH disk agitator ball mill to nanosized powders. Specially prepared sample tablets were measured in the dilatometer up to the end of the sintering process. The tablets pressed from nanosized powders show a much earlier completion of the densification in the sintering step compared to materials with grain size in the micrometer range. Details about the sintering process of nano-crystalline zirconia are described in [6] and the simulation of the sintering of high tech ceramics by the kinetic analysis of dilatometer experiments is discussed in [7]. Polymer coated ceramic and metal powders were analyzed by coupled techniques (TG-FTIR) to show the type, amount and decomposition ranges of the coatings.

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CHARACTERISATION AND THERMAL BEHAVIOUR OF Ag_2PO_3F

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Monofluorophosphates(V) are important materials used as toothpaste additives, wood preservatives, corrosion inhibitors or as intermediates during biomineralisation of fluoroapatite. Possible preparation routes of these materials include solid state reactions using metalfluoride/-phosphate melts, or conversion of the readily soluble $(NH_4)_2PO_3F$ and metal salts in aqueous solutions. A more convenient method makes use of the metathesis reaction Ag_2PO_3F + 2 M^ICl / ($M^{II}Cl_2$) → $M^I_2PO_3F$ / ($M^{II}PO_3F$) + 2 AgCl. However, no detailed structural information on the starting material Ag_2PO_3F is known so far.

Single crystals of Ag_2PO_3F were grown by slow evaporation of a diluted aqueous solution of $(NH_4)_2PO_3F$ and $AgNO_3$. The crystal structure (*C2/c*, Z = 8, a = 9.2456(8), b = 5.5854(5), c = 14.7840(13) Å, β = 90.178(2)°, 1165 structure factors, 67 parameters, $R[F^2 > 2\sigma(F^2)]$ = 0.027) is made up of PO_3F tetrahedra and distorted $[AgO_4]$ and $[AgO_6]$ polyhedra as the main building units.

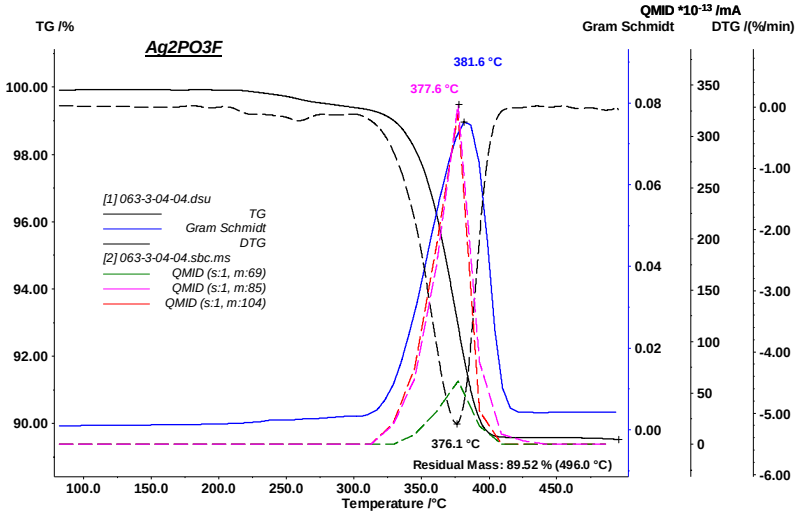

Fig: 1: Temperature-dependent behaviour of Ag_2PO_3F

Ag_2PO_3F was further characterised by infrared spectroscopy and ^{19}F- and ^{31}P-NMR spectroscopy. The thermal behaviour of Ag_2PO_3F was investigated by means of Simultaneous Thermal Analysis (STA) coupled to both Fourier Transform Infrared Spectroscopy (FTIR) and Mass Spectrometry (MS). No mass changes are detected up to 200°C. Decomposition of Ag_2PO_3F is observed during heating to 500°C. Release of POF_3 forms a mixture of $Ag_4P_2O_7$ and Ag_3PO_4.

Side chain crystallization in microphase separated poly(styrene-block-octadecylmethacrylate) copolymers

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The crystallization behavior of two microphase-separated poly(styrene-*block*-octadecylmethacrylate) block copolymers with lamellar and cylindrical morphology is studied by DSC. The findings are compared with results for a polyoctadecylmetharcylate (PODMA) homopolymer. The situation in the block copolymers is characterized by the occurrence of a confined side chain crystallization in small PODMA domains surrounded by a glassy polystyrene phase. The strength of confinement effects depends significantly on the block copolymer morphology. The crystallization behavior of PODMA lamellae with a thickness of about 10nm is practically unaffected and similar to the situation in the homopolymer. In cylindrical PODMA domains with a diameter of about 10nm strong confinement effects are observed: The degree of crystallinity is 50% reduced and the crystallization kinetics slows down. The Avrami coefficient changes from $n \approx 3$ for the homopolymer and PODMA lamellae to $n \approx 1$ for PODMA cylinders. These findings indicate a transition from three- to one-dimensional growth and/or a change from heterogeneous and homogeneous nucleation having similar consequences. Additional x-ray scattering data are presented and a speculative picture explaining qualitatively the differences in the crystallization behavior of PODMA lamellae and cylinders in a glassy polystyrene matrix is discussed.

Kinetics of isothermal crystallisation and melting-recrystallisation of iPP, iPS, PET and PBT

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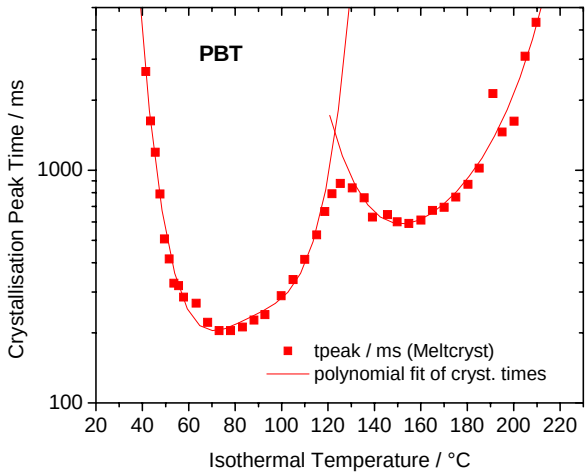
Isothermal crystallisation and melting-recrystallisation were investigated by the help of Fast Scanning Chip Calorimetry and DSC (Differential Scanning Calorimetry). For the purpose of fast scanning a commercially available chip calorimeter was used. The implanted heater in combination with non-adiabatic operation gave the possibility for both controlled fast heating and cooling /1/.
Crystallization kinetics of the slowly crystallising iPS and PET were studied on a PerkinElmer PYRIS 1 DSC. PBT and iPP were investigated with the fast scanning chip calorimeter.
In the case of iPP, in accordance with de Santis /2/, two minima in isothermal melt crystallisation half time were observed. These can be explained by the formation of two different phases in iPP. Namely, the crystalline α-modification and the mesomorphic phase. Additionally isothermal cold crystallisation experiments gave no evidence for preferring a certain crystallising temperature in case of the α-modification. Only the mesomorphic phase gave again a pronounced peak in crystallisation half time.
Suprisingly, for PBT two minima in crystallisation half time were found too, for both melt and cold crystallisation. The reason for this is not yet understood.



The figure shows the time of the maximum of the crystallization peak for PBT as a function of crystallization time for melt crystallization.

Beside crystallization kinetics recrystallization kinetics will be discussed too.

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PHASE BEHAVIOR OF AQUEOUS SOLUTIONS OF POLY(VINYL METHYLETHER)S WITH DIFFERENT CHAIN-END FUNCTIONALITIES

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A range of hydrophilic polymers was synthesized by living cationic polymerization of vinyl methylether (VME), having different hydrophilic or hydrophobic chain-end functionalities [1]. The introduction of dissimilar end-groups largely influences the solubility behavior of the polymer under investigation, examined by Modulated Temperature DSC (MTDSC). Terminal-modification with a hydroxyl function improves the solubility, whereas a large Br-containing end-group causes the polymer to be insoluble in water at room temperature, even though the special type III lower critical solution temperature (LCST) demixing behavior is maintained [2]. By decreasing the polymer molar mass, the end-group effect enlarges, by which the solubility becomes even worse.
Exploiting the MTDSC methodology, several predictions for the low-temperature phase behavior of PVME/water solutions, based on extensions made to the general theory of Wertheim, were evaluated [3]. The predicted peculiar shape of the melting curve, suddenly dropping at high PVME content could be reconstructed by partial integration of the melting peak observed. Moreover, the existence of an upper critical solution temperature (UCST)-type of demixing at sub-zero temperature was confirmed experimentally by MTDSC, using both its sensitivity for detecting glass transitions and the ability to perform quasi-isothermal demixing experiments.

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Influence of Ammonium Polyphosphate on the Thermal Stability and Degradation Pathway of Poly(Vinylacetate) and Poly(ethylene-co-vinylacetate): Cone Calorimetry and TGA Study.

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For fire-protection of surfaces thin coatings composed of blends of polymer emulsions or dispersions and flame retardants with a thickness ranging between 50 and 200 μm are used. From environmental and health aspect [1], in recent years the international standards require specific development towards the elimination of toxic flame retardants such as halogen flame retardants (halogen FR) like bromine containing biphenyl derivatives in all types of applications and fields: automotive, public transport, etc. The required halogen-free FR's usually act as intumescent systems upon combustion: degradation of the protective layer results in the creation of a char, inhibiting the flame to reach fuel underneath, whilst halogen FR's act as radical capturing molecules in the gaseous phase [1-4].

In this study, composites of water-based emulsions of poly(vinylacetate) (PVAc) and poly(ethylene-co-vinylacetate) with weight percentages of vinylacetate of 70 and 85 (noted as EVA70 and EVA85 respectively) and ammonium polyphosphate were coated on woven textile for tape applications. By means of the automotive FMVSS 302 test and cone calorimetry with a heat flux of 30 $kW.m^{-2}$, self-extinguishing coatings with a clear lower rate of heat release during combustion are obtained with low filling levels of APP, with an efficiency depending on the amount of vinylacetate present in the (co)polymer.

The degradation mechanism of these composites in oxidative environment was established using TGA-MS, isothermal TGA experiments and solid state NMR measurements on partially degraded products. It was seen that during the autocatalytic deacetylation process of the (co)polymers, the ammonium polyphosphate breaks into monomer or dimer and subsequently fully crosslinks with the polymer backbone, accelerating the deacetylation of the polymer, highly stabilising the charred structure. This charred structure degrades at elevated temperatures with low degradation velocity, indicating their efficient activity as flame retardant composites. [5,6].

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Practical Applications of differential scanning calorimetry (DSC) within unilever

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Background
Within Unilever DSC is an essential tool to reveal the underlying
phase-compositional principles of functional properties of food and detergent systems. For systems with a clearly established phase-composition-functionality relation, DSC can be used to enhance the development of novel products. Furthermore, DSC can be deployed to establish such relations, often in combination with other measurement techniques.

Instrument
The equipment used for the DSC analysis is the Perkin Elmer power compensated Pyris-1 equipped with a controlled cooling accessory using liquid nitrogen as cooling agent.

Types of samples analysed
Oils and fats, are analysed to obtain information about the onset and endset temperature of the individual melting fractions, heat of fusion (ΔH) and polymorphic transitions.

Spreads are analysed to obtain information about the crystallisation of the oils and fats in the end product. This information is used to control the production process.
Additional information that can be obtained is the crystallisation of the water in the spreads. Depending on the composition glass transitions of the sugars in addition to denaturation peaks of the proteins can be observed.

Packaging materials are frequently analysed to solve problems in a factory.

Rice granules can be analysed to obtain information about the gelatinization temperature of the processed rice. This information is valuable for instant rice food products.

Dry food products with sugars will absorb water when stored in a high humidity environment. The determination of the glass transition temperature of such products give information about the shelf life.

Liquid detergents are analysed by DSC to obtain information about there melting habits. Frequently the heat capacity (ΔCp) is determined to calculate the cooling capacity necessary at a factory.

Characterisation of industrial materials and processes with TGA.

Jeroen van den Berg and Piet Rommers

Philips Research, Materials Analysis department

The characterisation of industrial materials and processes is essential for manufacturing products. TGA can be used to investigate properties and stability of new materials and to optimise production processes. Two examples are shown in this poster.

Materials used in the production of devices can contain additives and impurities that influence the reactivity and stability of the material. Often this leads to problems like unwanted deposits on products. Characterisation of such materials with TGA can prevent such problems. This is shown for materials used for isolation. In this case TGA is also a valuable tool to optimise subsequent GC-MS analyses.

In production processes, gas purity can be critical. For instance, when carbon parts in a reactor are heated at high temperatures, the presence of oxygen can decrease the lifetime of these parts. With TGA it is possible to determine what oxygen concentration can be tolerated without degrading the carbon parts. To do so, the combustion rate of carbon was determined at a specific temperature and with various oxygen concentrations.

Design and Applications of a Powder and Liquid Holder for DMA

Nick Hawkins, Els Verdonck

TA Instruments

A powder holder for use with the TA Instruments DMA has been developed in response to the growing need to be able to measure transitions in powders. The main application area is to study pharmaceuticals. The amorphous phase in the active component or excipient acts as a site for water absorption and influences e.g. the solubility of the drug. DMA is an excellent tool to study the amorphous phase of the material as it is more sensitive to measure Tg than is DSC and it allows monitoring of sub-Tg relaxations. Other areas where DMA study of powders could be important include food (sugars, sweeteners), powder coatings, fine chemicals (pigment additives, binders), ink toners, …
The presented design of powder holder is used in the dual cantilever clamp configuration.
Applications in various areas are presented in this poster.

The Q5000 TGA's for Fast Heating Rate TGA and Sorption Analysis: Design and Applications

Els Verdonck, Rudolf Mollema

TA Instruments

The new Q5000 IR (IR heating) is designed to meet the most demanding research applications. It delivers extremely flat baselines, high sensitivity, and operation at controlled heating rates as fast as 500°C/min. This results in the capability to quantitatively measure very low levels of volatiles in small samples, and increased productivity. The autosampler allows opening sealed sample cups just prior to the analysis, this being especially useful for moisture sensitive samples. Another feature includes greatly simplified automated Curie point temperature calibration. Hi-res and MTGA are included. High Resolution™ TGA is a patented furnace control technology that improves, compared to standard TGA, the separation of closely occurring decomposition events. It includes constant reaction rate, auto-stepwise isothermal and dynamic rate method. Modulated™ TGA facilitates study of material decomposition by producing continuous model-free kinetic data .

The new Q5000 SA (Sorption Analysis) is designed for high performance sorption analysis of materials under controlled conditions of temperature and humidity.
The new software includes automatic calibration / verification / diagnostic capability.
Design and applications of these TGA's are presented.

HyperDSC , A breakthrough method for materials characterization. Higher Sensitivity at Greater Speeds.

M.Divito[1], S.Goth[1], N. Boer[2]

PerkinElmer Business Unit Shelton USA[1], PerkinElmer The Netherlands[2]

Obtain additional, previously undetected information, in seconds rather than minutes.
HyperDSC™ is the premier fastscan DSC technique. It provides the ability to perform valid heat flow measurements while heating or cooling a sample with fast linear controlled rates, up to 500°C/min. Measurements are made with 1000 Hz. DSC output is measured in Mw (J/sec) ; HyperDSC gives increasing sensitivity with decreasing scanning time.
The technique allows you to obtain additional, often crucial information, in seconds rather than minutes and is only available on the Diamond DSC from PerkinElmer.
Many of the world's leading pharmaceutical and polymer R&D laboratories and university's have adopted the technique because of it's ability to provide information that previously may have gone undetected.

Benefits:
In addition to increased sensitivity, HyperDSC™ offers many benefits including:

- The ability to analyse materials as received without inducing changes such as annealing, re-organization and re-crystallization, incidences that are typically included at slow scanning rates (10°C - 20°C/min.) and that frequency lead to misinterpretation of results and sample properties.
- Increased sensitivity for detection of weak transitions.
- Measurements can be performed under process conditions.
- Very small samples up to ug levels can be measured.
- Overlapping events can be separated based on their differing kinetics.
- Complements conventional DSC.
- HyperDSC experiments are fast – up to 20 times faster, gives dramatically increased sample throughput.
- HyperDSC is simple, without complicated math or calibration required, so anyone with basic DSCskills can perform HyperDSC experiments.

Applications;
Pharmaceutical:The HyperDSC technique makes it easier to study polymorphism in pharmaceuticals, detection of low level amorphous content (> 1%), suppress decomposition for more complete characterisation. Polymer/Chemical: HyperDSC realistically simulate polymer/chemical processing conditions in injection molding that were previously complicated with conventional DSC. Detection of low energy transitions, analyze reorganisation effects, separate overlapping events.
In addition Scientists are also exploring the use of HyperDSC in protein analysis.

Rapid Process Initiation Studied by Reaction Calorimetry

Uwe Hess

Prosense GmbH, Konstanz, Germany

Rapidly controllable redox initiator systems are frequently used in emulsion polymerisation reactions. Reaction calorimetry based on the True Heat Flow principle, (THF), can be used for on-line studies of rapid redox initiations and the optimisation of large-scale production processes.

Instrumental
The experiments were performed with a ChemiSens CPA202 reaction calorimeter, a small-volume, plug & play instrument that requires no calibration and delivers extremely reliable results. For dosing of the reagents, which were preheated in the thermostat liquid, a high precision syringe motor pump was used.

True Heat Flow principle (THF)
The heat flow is restricted to a well defined thermal path through the reactor base plate and is controlled by a Peltier element. Possible heat losses are effectively suppressed by a thermostat bath, in which the reactor is completely immersed. The calorimeter can be run in various modes like isothermal, scanning or adiabatic.

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Claus Linseis & Florian Linsesis

Linseis Messgerate GmbH, Selb, Germany

Linseis presents the new Laser Dilatometer L75/LASER, which was developed with the University of Dresden. This highest precision dilatometer works with a Michelson Interferometer and thus delivers unbeaten performance in respect to resolution and repeatability.

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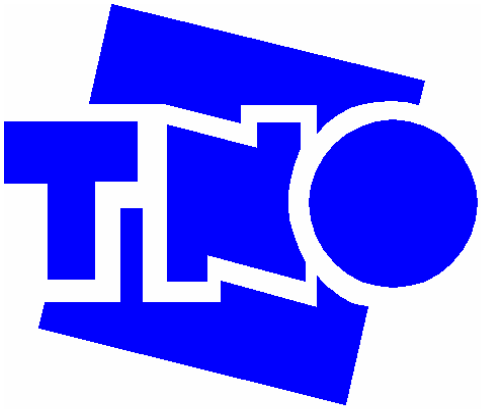

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