

ONset

NETZSCH

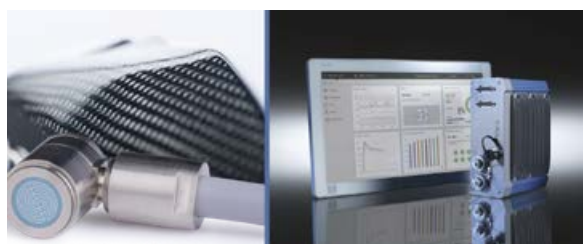
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Dear Reader:

I'm very happy that you are taking the time to inform yourself about NETZSCH and the application possibilities offered by thermal analysis in this latest edition of **onset**.

The focus of **onset**²⁰ is on extending measuring possibilities – both in the laboratory and directly in the production process. This edition builds bridges from investigations of thermal safety to the crystallization kinetics of polymers to the optimization of production processes.

Our cover story on Accelerated Rate Calorimetry (ARC) describes the measurement possibilities these calorimeters offer in order to demonstrate the hazard potential of chemicals with the help of a largely adiabatic sample environment.

On page 7, we introduce the AIC 80, an air Intracooler for the DMA 242 *Artemis*, representing a smart alternative to the use of liquid nitrogen as a cooling agent in the temperature range between -70°C and 600°C.

Based on our many years of experience with measuring instruments in a special laboratory environment, we offer some interesting insights into the use of thermal analysis instruments in "hot cells" and gloveboxes on pages 8 to 11.

Application of the Nakamura equation within the Kinetics NEO software is presented for non-isothermal crystallization using the example of polyethylene terephthalate (PET) – a material known to everybody in the form of transparent beverage bottles.

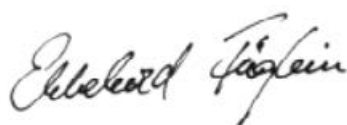
The latest generation of the *Proteus*[®] software, Version 8.0, also opens up a new chapter in the use of measuring instruments. It presents an image of the modern lab environment, the measuring instruments of which now send status reports on the progress of lab analyses to a team member's computer in their home office, for example, or to a mobile device.

As part of the collaboration between NETZSCH and KISTLER, a powerful analysis system for the on-line monitoring of injection molding machines has been developed. This contributed article explains how pressure sensors in conjunction with dielectric analysis in injection molding machines not only provide insight into the process, but can also be used to optimize it.

Practical information on how to employ cold-welded aluminum crucibles in differential scanning calorimetry (DSC) can be found on pages 20 and 21. Different crucible types made of aluminum were hermetically sealed and their deformation was investigated as a function of temperature.

Curious?

Then I wish you much enjoyment in browsing this edition of **onset**.



Dr. Ekkehard Füglein
Senior Application Scientist



The Importance of Calorimetry for Chemical Process Safety

Peter Ralbovsky, NIB, Burlington, USA



Introduction

All over the world chemical plants, large and small, operate safely and efficiently providing us with so many products that impact our life every day such as food, clothing, fuel, medicines, building materials and clean water. It would be hard to imagine our life without the support of the chemical industry. What we may not imagine is all the engineering and testing that goes into ensuring that these plants operate in a safe manner protecting the worker, their neighbors and the environment.

There are inherent risks when processing or reacting chemicals and the consequence of a failure grows as the size of the process grows. The US Chemical Safety board did a 20-year study from 1980 to 2001. They found 167 serious reactive accidents caused 108 fatalities in just US-based operations. Of these serious reactive accidents about 37% were "Thermal Runaway" reactions. What is a thermal runaway reaction and how can they be detected and prevented?

Thermal Runaway Reaction – When the Produced Heat Can No Longer Be Completely Dissipated

Thermal Runaway occurs when a reaction produces more heat than it can give off to the environment. For instance, combustion in a car engine gives off heat and to keep the engine from overheating, we have to actively cool it. If we don't do so, the heat from the combustion of the gasoline would cause the temperature to rise to the point where the engine would be damaged.

Heat that can't be removed from a reaction will cause the reaction temperature to rise. And for most reactions, an increase in temperature will cause the reaction to react faster and give off even more heat. A faster reaction leads to more heat and more heat leads to the reaction going even faster. Thermal runaway occurs whenever the heat from a reaction is larger than the heat that is lost (the cooling) to its surroundings.

Cover Story

So, to understand when a thermal runaway can happen, we have to know

(1) how much heat a reaction will produce at any temperature and

(2) how much heat a reaction can lose based on the environment around the reaction.

Calorimeters Determine the Heat of Chemical Reactions or Physical Changes

To understand (1), we use instruments known as calorimeters which will measure heat and the rate of heat output. The reaction rate and its change with temperature is a fundamental property of the reaction. We can only measure it, we can't change it. What we can do, however, is to control the temperature of the reaction and this in turn will control the rate. Many times in chemical processes, we can control the heat production by controlling how much of the reactive chemicals we add together at any time. So for instance in a "semi-batch" reactor we might add Chemical A into a pot with Chemical B but do it slowly so the heat has a chance to dissipate. Chemical engineers have a number of different tools (i.e., inhibitors, catalysts, engineering control) at their disposal to manage heat and temperature as a reaction progresses but understanding the reaction rate (kinetics) and the heat output (thermodynamics) comes from calorimetry.

Differential Scanning Calorimetry (DSC) Measures a Difference in Heat Flow

There are three basic forms of calorimetry that are used, namely scanning, isothermal, and adiabatic. By far the most used tool to measure a chemical reaction is the Differential Scanning Calorimeter (DSC). A DSC measures the differences in heat flow between a sample of interest and a known reference. A typical sample might be 10 mg of Chemical A inside a small crucible of approx. 50 μ l and the reference would be the same type of crucible but empty – no sample. If we take both pans and heat them in the same furnace the difference in heat flow between the sample crucible and the reference crucible can be measured. As the sample heats it might melt if it is a

solid and absorb heat or it might start to decompose and give off heat. Whatever chemical or physical changes are occurring in the sample, the DSC will measure the heat change in the sample compared to no change in the empty reference crucible. As a safety tool to look for potential exothermic reaction that could lead to thermal runaway the DSC has some great features. The sample size is small. So, if there is an unexpected explosion or release of toxic materials it is small and easily contained. The DSC can heat up a sample relatively quickly (10 to 20 K/min) so we can look at a lot of different chemicals quickly. From DSC data we can determine reaction rates, heats of reaction, and heat capacities which are all useful for understanding the potential for a system to go into thermal runaway.

But, of course, DSC is not the method of choice for every kind of investigation. You can't mix chemicals inside the DSC or stir materials that may be in different phases. Many chemicals produce gases when they decompose. DSC can't measure the sample pressure and it requires heavy duty crucible to handle high pressure samples. This can sometimes lead to reduced sensitivity of the tests. Small exotherms can be missed. But even small exotherms can produce enough heat to cause a thermal runaway given the right conditions.

Isothermal and Adiabatic Calorimeters

Isothermal and Adiabatic calorimeters are both often used in chemical process safety. Typically isothermal, or, as they are often called, reaction calorimeters are used to measure heat for desired reactions and are used extensively for optimization of reactions. Adiabatic calorimeters are used primarily to measure undesired reactions, whether it be a desired reaction at an undesired rate or a reaction that is completely unwanted like the decomposition of a reactant.

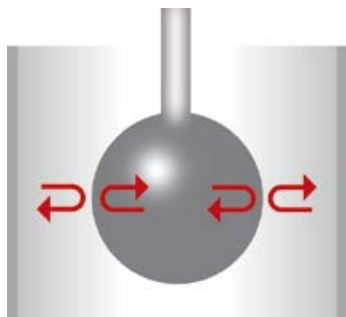
Accelerating Rate Calorimeters (ARC®) Simulate Worst-Case Scenarios

For this reason adiabatic calorimeters, such as the Accelerating Rate Calorimeter (ARC®), are built to handle unexpected reactions with high temperature and pressure rates. They are robust systems designed to protect the user and themselves from chemical

explosions. For instance, the NETZSCH ARC 254 can measure sample pressures and pressure rates and also allow for mixing of materials and injection of materials to mimic semi-batch operations. And perhaps most importantly, adiabatic calorimeters hold samples in a near-adiabatic environment. This type of testing allows the user to measure the “worst case” for thermal runaway when nearly no heat is lost to the environment. That means that an ARC 254 test conducted in a lab can replicate the near-adiabatic conditions that might exist inside a rail car whose contents are beginning exothermic decomposition.

... by Creating Near-Adiabatic Conditions

The defining characteristic of an ARC system is its ability to keep a sample in a near-adiabatic environment. This is called temperature tracking. To do this, the ARC must measure the temperature of the sample and control the environment around it so that the surrounding temperature is the same. If the sample temperature is the same as the surrounding temperature, then there is no exchange of heat and no heat loss (or gain). Any heat energy produced by the reaction will be absorbed by the sample and cause the temperature to rise. The trick then is that the calorimeter must track the temperature of the sample as it continues to increase at faster and faster rates. The ability of an ARC to track the sample temperature depends upon many factors. An ARC 254 can typically track to 200 K/min.



Adiabatic system = no heat in, no heat out

In the ARC the sample needs to be placed inside a sample vessel which can handle the temperature and pressure increase that will occur during the reaction. This might mean for instance that a 5 g sample is

placed inside a 10 g titanium vessel designed to hold the sample pressure at elevated temperatures. Some of the heat from the sample reaction will be used or lost to the sample vessel. This loss of heat to the vessel is known as thermal inertia and is a ratio of the thermal mass of the sample compared to the thermal mass of the vessel. Mathematically the higher the thermal inertia, the more heat that is lost and a thermal inertia of 1 means there is no heat lost to the container at all. High thermal inertia tests are often needed when testing energetic exotherms as the sample heat lost to the vessel helps to moderate the sample temperature and keeps the reaction rate within the capability of the instrument.

Often, the near-1 thermal inertia data can be corrected for the heat loss mathematically. However, it is possible that changes in the thermal inertia can change the reaction kinetics. In such cases no mathematical fix is possible. Instead, advanced systems such as the ARC 254 with *VariPhi*[™] can be used to run real low thermal inertia tests. This has the advantage that no correction is required at all.



Various sample vessels

Conclusion

The DSC and the ARC are excellent partners in finding and characterizing potential thermal runaway reactions. The DSC is able to quickly and safely test many samples to determine if a potential thermal hazard exists. For those systems that show some hazard potential the ARC can be used to fully characterize the temperature and pressure that may occur in a thermal runaway event. With this information, systems can be designed to prevent the thermal runaway from occurring.

AIC 80 Air Intracooler

Intracooler Based on Refrigerated Air – An Economic Solution for DMA Measurements

Dr. Georg Storch, Research & Development

Low temperatures can be more harmful to plastics than high temperatures. Serious failures may occur if material selection does not consider the low temperature properties of plastics. For this reason, many applications in the field of, for example, polymers with lower stiffness, require a measurement start below room temperature.

As an alternative to existing solutions with Vortex tube (air) and liquid nitrogen cooling (LN₂), we now offer the new compact AIC 80 air intracooler for DMA measurements. This state-of-the-art cooling device is based on a heat exchanger system and utilizes cold air.

The AIC 80 air cooling system is a compact intracooler that eliminates the need for liquid nitrogen. With this cooling system, DMA measurements can be carried out in the temperature range between -70°C and 600°C with no further efforts. In the cooling segment of a DMA measurement, the AIC 80 is activated at 300°C.

It is a compact chiller with the dimensions 38 cm x 55 cm x 80 cm (w x d x h) and a long insulated connection line of 3 m. This allows the intracooler to be placed under the table or on the side – in which way it is most convenient in your laboratory.

The valve is software-controlled and can be operated in an on/off mode in each measurement segment. An inlet for compressed air permits the connection of an air dryer (outlet dew point -70°C).



The new AIC 80 cooling system

This economic cooling system can also be connected to existing DMA 242 Artemis systems. All you need is a compressed air connection (min. 7 bar, consumption 115 l/min) or dry inert gas (min. 1 bar, consumption 50 l/min).

Contact your NETZSCH consultant or your service engineer for further details.

Expansion of the
DMA 242
Artemis
Accessories

Thermal Analysis in the Glovebox

Thomas Rampke, Global Sales Manager for General Support & Engineering Projects

Introduction

When investigating certain materials, it can be necessary to install the employed measuring instrument into what is known as a glovebox. This applies if the materials to be investigated either pose a risk to the operator of the instrument or if the materials must not be exposed to normal ambient atmosphere. These include, for example, radioactive (e.g., so-called "nuclear") or highly toxic substances as well as oxygen- or moisture-sensitive materials.

Nuclear and Chemical Gloveboxes

In light of the above, manufacturers of gloveboxes differentiate between personal and material protection. In both cases, the interior of the glovebox is hermetically sealed off from the environment. In the glovebox, a controlled, usually inert and dry gas atmosphere is employed, which is produced and maintained by appropriate gas supply, gas cleaning and circulating systems. Often, pure argon is used.

A glovebox for personal protection usually operates with a slight underpressure, while in a glovebox for material protection, there is a slight overpressure. Due to the wide array of such applications, gloveboxes for personal protection are also often called "nuclear" gloveboxes and those for material protection "chemical" gloveboxes.

Requirements for Thermoanalytical Instruments for Installation into a Glovebox

There are various measures which may be taken to prepare our thermal analysis instruments for installation in a glovebox. The effort required depends to a large extent on the type of glovebox and the intended application.

For nuclear gloveboxes, which can usually not be reopened after initial operation, the measuring part and the electronics should be separated from each other. This simplifies maintenance and servicing of the electronics,

which are located outside the glovebox. In some cases, this separation can also reduce the space required for the measuring part in the glovebox ("footprint").

Furthermore, one should keep in mind that the measurement parts located in the glovebox must be serviced with the gloves, which are often quite thick. In addition, to protect the gloves, any replacement of components should be carried out without the use of sharp or pointed tools if at all possible. For nuclear applications, the housing should be made neither of aluminum nor plastic parts and should not be painted.

Peripheral accessories such as pumps, cooling devices, thermostats, etc., are generally installed outside the glovebox. NETZSCH can also supply the hermetically sealed feedthroughs required for connecting peripheral components to the measuring instrument. Particularly for control cables and other electrical connections, it is important that these feedthroughs already be installed during production in our plant and, if necessary, that correspondingly longer cables be provided to guarantee full functionality of the instrument and its warranty.

Gas Atmosphere – Customer-Specific Solutions

In gloveboxes, an inert, dry gas atmosphere – usually argon – is used. This is a particular challenge for some components such as furnaces and vacuum tubes. Ionization of argon can lead to the formation of undesired electric arcs, and some furnace heating elements lack the oxygen required to passivate the surface. Either of these issues can lead to the destruction of the component in question.

NETZSCH takes this into consideration for the specification of glovebox instruments and offers alternative components in consultation with the customer.

Glovebox

Coupling to Gas Analysis Instruments

In addition, it is possible to couple gas analysis devices such as mass spectrometers, FT-IR or GC/MS devices which are located outside the glovebox to the thermal analyzer in the glovebox. To this end, we offer a hermetically sealed, heated coupling feedthrough for the glovebox atmosphere. This allows for the gases evolving from the samples in the thermal analyzer to be transferred via a heated transfer line to the glovebox wall, where the gas analyzer is coupled just as it would normally be coupled to the furnace of the thermal analyzer (figure 1).



Fig. 1. STA 449 **F1** Jupiter® glovebox design with heated feedthrough for coupling of the QMS 403 Aeolos®

Instrument Version for Installation in a Glovebox

NETZSCH offers specially modified versions of various instruments in the thermoanalytical and thermo-physical measurement technologies series which are primarily employed in personal-protection gloveboxes.

For example, the STA 449 **F1/F3** Jupiter® and DSC 404 **F1 Pegasus**® have a special, smaller housing for the measuring part made of unpainted stainless steel; the electronics are largely stored in a separate housing outside the glovebox (figure 2 shows the STA 449 **F3** Jupiter® representing these three instruments).

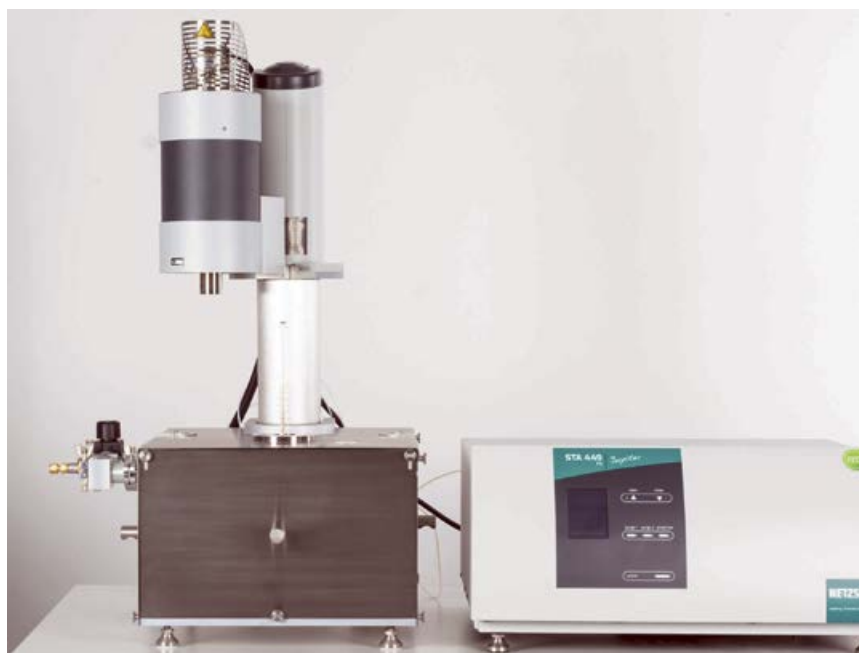


Fig. 2. STA 449 **F3** Jupiter® glovebox design with external electronics

Glovebox

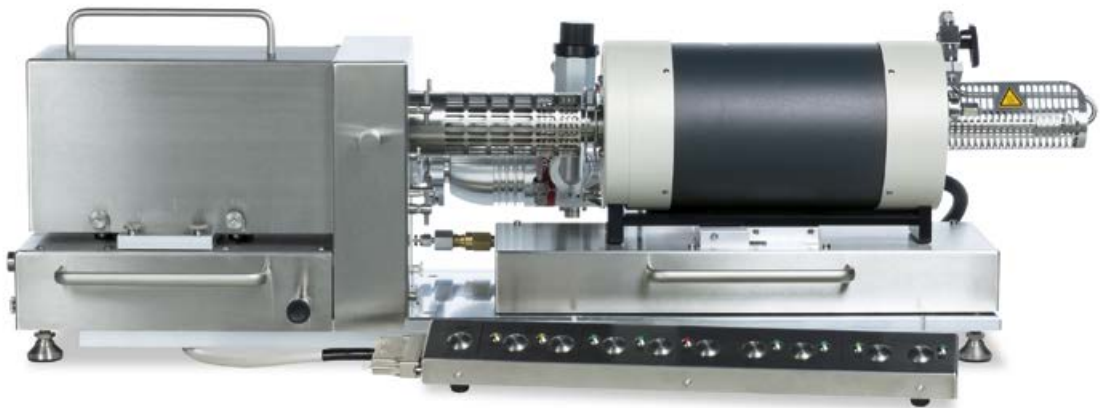


Fig. 3. Dilatometer DIL 402 *Expedis Supreme* glovebox (measuring part and remote control)

The housing parts for the measuring part can be easily removed for maintenance by means of knurled-head screws. Electronic components remaining in the measuring part are pluggable and can therefore also be changed easily and without tools.

The DIL 402 *Expedis[®] Supreme* is also available in a glovebox version with external electronics and a stainless steel housing on the measuring part (figure 3).

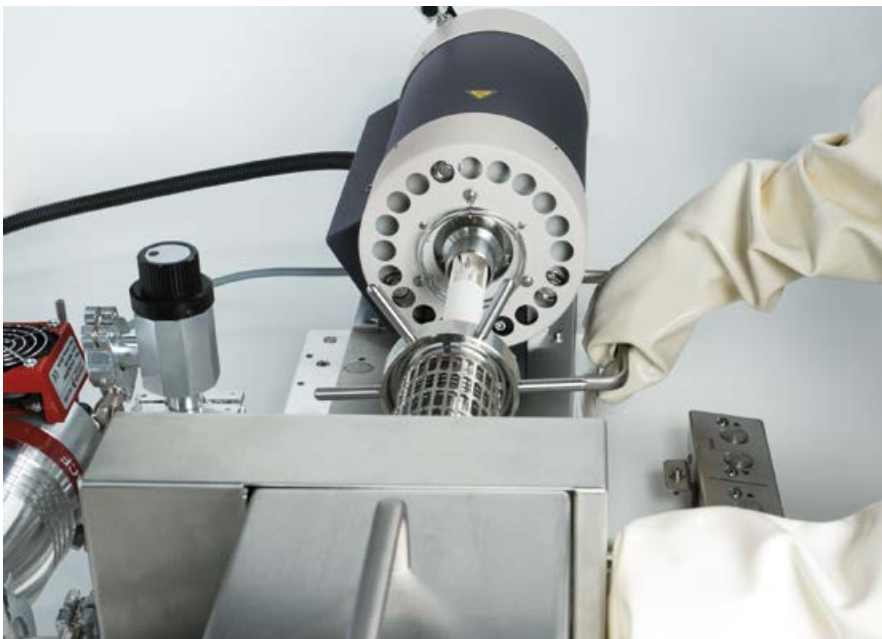


Fig. 4. Different operating aids for gloves on the DIL 402 *Expedis Supreme* GB

Easily accessible handles and star grip screws facilitate operation with gloves (figure 4). An easy-to-operate "remote control" allows for control of the furnace movement and the push rod without any need for the operator's hands to be removed from the glove.

Glovebox

In the field of LFA, the desktop version of the LFA 427 with glovebox-specific adjustments, which has already been in successful use in several laboratories, is employed: Minimalistic housing of stainless steel, pluggable electronic connections and components, gripping aids, special protection of the sample holder base against falling sample parts, a laser which is operated outside the glovebox, etc. (figure 5).

Standard Instruments in the Material-Protection Glovebox

For chemical gloveboxes, special measures such as those discussed above are often not required. Here, slightly adapted standard devices are used since such gloveboxes can be opened relatively easily for maintenance and repair work on the device after the sensitive materials have been discharged. Since peripheral devices along with the controlling PC are operated from outside the glovebox for this application for reasons including the lack of space, we also offer adapted feedthroughs for this purpose.

Summary

Special applications require special adjustments, such as is the case with the use of our instruments in a glovebox. For more than 15 years, we have been helping our customers with instruments adjusted in this way, as well as helping them communicate with glovebox manufacturers such as M. Braun Inertgas-Systeme GmbH in Garching, Germany, for the design of gloveboxes (figure 6).

The installation of thermal analysis instruments in gloveboxes requires various precautions and modifications of the instruments along with special gas-tight and/or vacuum-tight feedthroughs. In collaboration with customers, NETZSCH works out special solutions for this – thanks to the many years of experience held by our employees in development, sales and service.

For further details, please contact your local NETZSCH sales representative.



Fig. 5. Measuring part of the LFA 427 glovebox version



Fig. 6. STA 449 C Jupiter® in a material-protection glovebox at the Max-Planck-Institut CPFS Dresden (photo from "Picturebook 5", © M. Braun Inertgas-Systeme GmbH, Garching, Germany)

Nakamura Model for Polymer Crystallization Kinetics During Cooling

Dr. Elena Moukhina, Research & Development, and Dr. Stefan Schmölder, Applications Laboratory

Introduction

Thermoplastic polymers are polymers which become moldable at a certain elevated temperature. In this state, they can be molded and upon cooling, the polymer solidifies and stays in the desired shape.

For example, in the production of PET bottles, firstly the PET preform is manufactured by an injection molding process, and then PET preforms are expanded with compressed air to the bottle shape. During injection molding, thermoplastic polymers are quickly cooled down from the melt temperature to the temperature of the mold, which is typically between 20°C and 120°C. In the case of semi-crystalline polymers, crystallization starts at temperatures below the melt temperature, and the crystallization rate depends on the degree of supercooling.

On the other hand, semi-crystalline polymers also exhibit glass transitions at lower temperatures. As soon as the glass transition temperature is reached, the polymer is in the glassy state. Then no more crystallization will occur, even with high supercooling.

Crystallization under High Cooling Rates

Therefore, it is very important to know what the crystallization rate is, what fraction of the polymer becomes crystalline, and what fraction is in the glassy state at low temperatures. During the injection molding process, it is possible for cooling rates to be so high that crystallization cannot be measured with a conventional DSC. In such cases, the Kinetics Neo software can be used for predicting the crystallization process. The crystallization rate of polymers depends on two parameters: the current degree of crystallization, α , and the temperature, T .

$$\text{Crystallization rate} = f(\alpha) \cdot K(T) \quad (1)$$

The first part of Equation (1), $f(\alpha)$, depends on the degree of crystallization. In this case, the Avrami equation (nucleation type with dimension n) was considered:

$$f(\alpha) = n \cdot (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{\frac{n-1}{n}} \quad (2)$$

The second part of Equation (1), $K(T)$, is the reaction constant at the temperature T . It has a non-Arrhenius dependence on temperature.

In the simplest case of isothermal crystallization, the function $K(T)$ is a constant value, and crystallization is described just by the Avrami equation. But for crystallization during cooling, we must take into account that the crystallization rate depends on the current temperature with respect to the temperatures of melting and glass transition. Above the melting temperature, the material is in a liquid phase and no crystallization takes place. If the material temperature is below the glass transition temperature, the material is in the glassy state, where the polymer chain motion is so slow that no further crystallization occurs.

If the reaction constant $K(T)$ at the temperature T is known, then – based on Equations (1) and (2) for the cooling rate β – it is easy to obtain the Nakamura equation for the degree of crystallization α :

$$\alpha(T) = 1 - \exp\left\{-\left[\frac{1}{\beta} \int_{T(0)}^{T(t)} K(T) dT\right]^n\right\} \quad (3)$$

DIN EN ISO 11357-7:2015-12 uses this Nakamura equation for the kinetic analysis of non-isothermal crystallization during cooling.

For the analytical dependence of $K(T)$, the Hoffman-Lauritzen theory can be used:

$$K(T) = A \cdot \exp\left(\frac{-U}{R(T-T_\infty)}\right) \exp\left(\frac{K_G}{T\Delta T f}\right) \quad (4)$$

with

A : pre-exponential factor

U : activation energy of segmental jump in polymers; this parameter has a universal value of 6.3 kJ/mol

$T_\infty = T_g - 30$: temperature at which crystallization transport is finished; this temperature is 30 K below the glass transition temperature T_g .

K_G : kinetic parameter for nucleation

$\Delta T = T_m - T$: undercooling from the equilibrium melting point T_m

$f = 2T/(T_m + T)$: correction factor.

The melting temperature T_m and glass transition temperature T_g are usually known, but could be adjusted a bit during optimization. Other parameters like K_G , A , and n will be found by the Kinetics Neo software.

Crystallization Kinetics

Example of Crystallization Prediction: Polyethylene Terephthalate (PET)

Within a crystallization experiment, six measurements (figure 1) were carried out with the DSC 204 **F1 Phoenix**® at cooling rates from 1 K/min to 10 K/min. Each crystallization peak has a different crystallization enthalpy ranging from 2.5 J/g at 10 K/min to 38.4 J/g at 1 K/min due to incomplete crystallization for higher cooling rates.

For the analysis, the following known values for the glass transition temperature and for the melting temperature are taken:

$$T_g = 70^{\circ}\text{C to } 80^{\circ}\text{C}; T_m = 240^{\circ}\text{C to } 260^{\circ}\text{C}.$$

Figure 2 presents the Nakamura model; here, the experimental values are presented as rhombuses and the simulated curves in solid lines. Calculation of the simulated curves is carried out according to the Nakamura model.

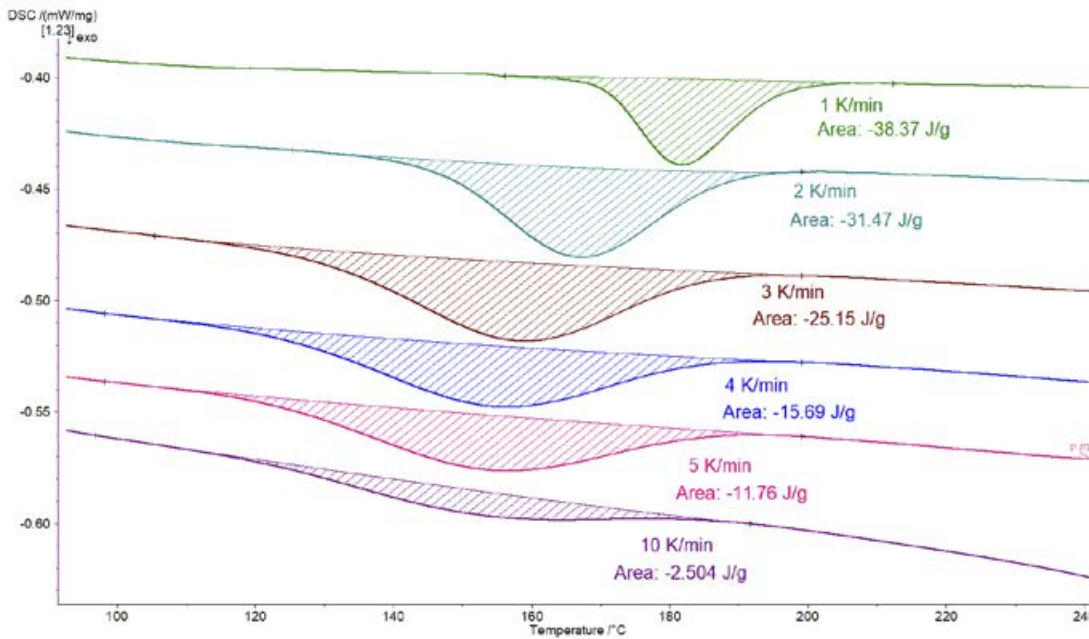


Fig. 1. Crystallization curves for polyethylene terephthalate (PET) measured at cooling rates from 1 to 10 K/min

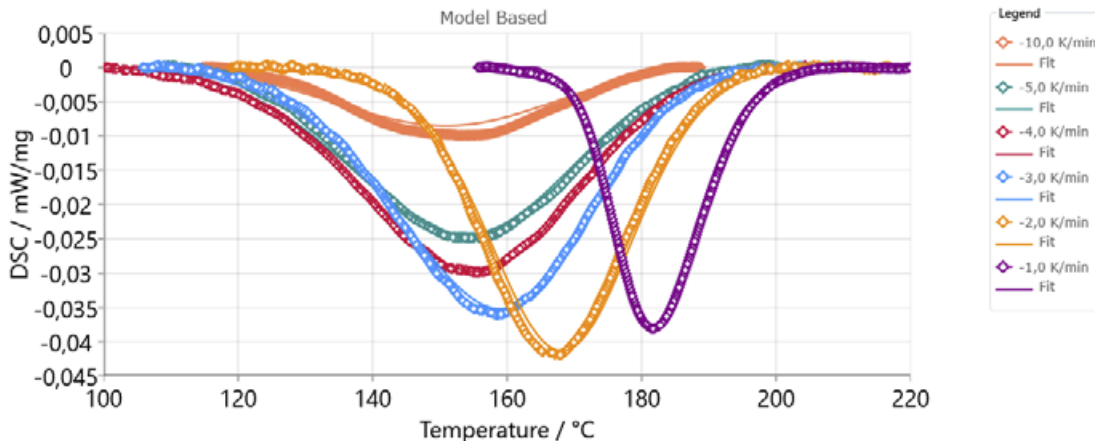


Fig. 2. Experiment and model according to Nakamura for non-isothermal crystallization during cooling

Crystallization Kinetics

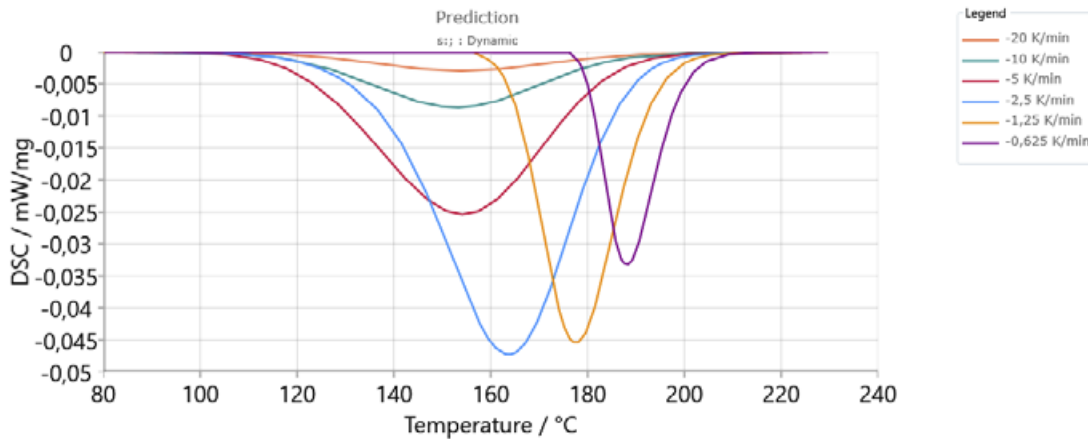


Fig. 3. Prediction of crystallization at fast cooling rates up to 20 K/min. Peak shapes and peak areas are different because of the incomplete crystallization

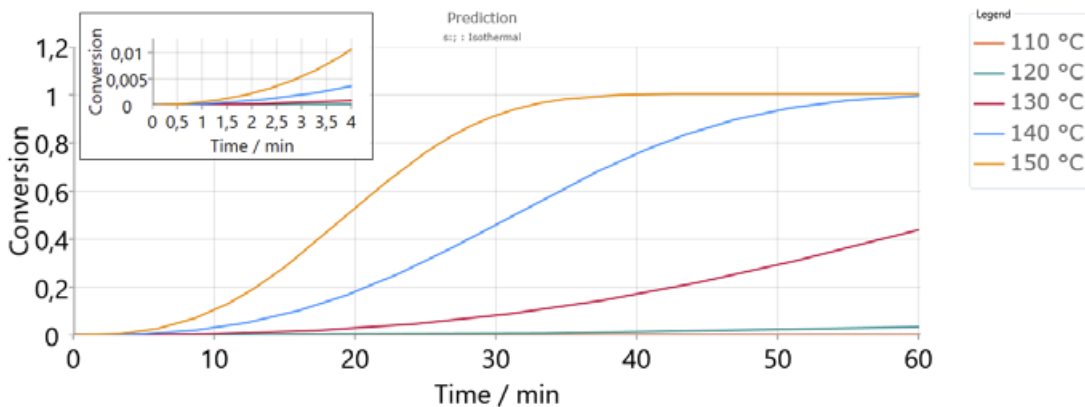


Fig. 4. Isothermal crystallization at temperatures from 110 to 140°C

In figure 3, the prediction of the crystallization process is shown. Crystallization is not complete for fast cooling because of the glass transition. Here, the polymer is partially amorphous. During injection molding, the PET preform undergoes fast cooling to 110°C and then no more crystallization will occur in the glassy state.

For the production of PET bottles, the preforms are heated and expanded with compressed air to the bottle shape (Stretch Blow Molding). Figure 4 shows the simulated crystallization during this process.

One can observe that at temperatures of 110°C to 120°C, no crystallization occurs and the bottles remain in the glassy state and transparent. If the production temperature is too high – e.g., 140°C

– then crystallization starts earlier, and the bottles get turbid.

Conclusion

Kinetics NEO is a very helpful tool for gaining an understanding of even complex production steps in polymer processing. By knowing the kinetics of the processes, as are shown here for the crystallization process, it is possible to simulate production steps. Instead of carrying out time-consuming experiments, it is possible to simulate different processing conditions in order to draw conclusions, resulting in a more efficient production of polymer parts.

You've Got Mail... From Your Measuring Instrument

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

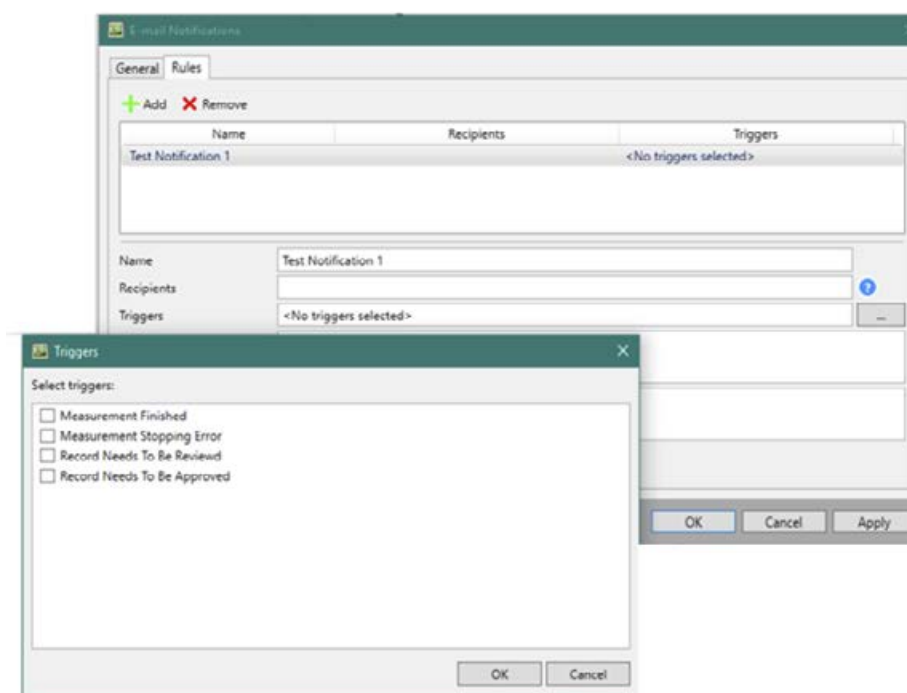


Fig. 1. Definition of an e-mail notification rule; free text for the header and footer of the notification

Beginning with software version 8.0, *Proteus*® offers the possibility – for both *Proteus*® in the standard version and for *Proteus*® *Protect* – of having messages sent by your thermal analytical device to your office computer, your computer at home (home office) or your mobile phone. These are status messages such as "Measurement has been completed" or – exclusively for *Proteus*® *Protect* – "Evaluations are ready to be signed".

Such messages can also be sent to several e-mail addresses at the same time. To do this, the different addresses must simply be entered into the 'Recipients' line in the configuration box (see figure 1), separated by semicolons. The desired trigger actions can be activated in a separate window (see also figure 1).

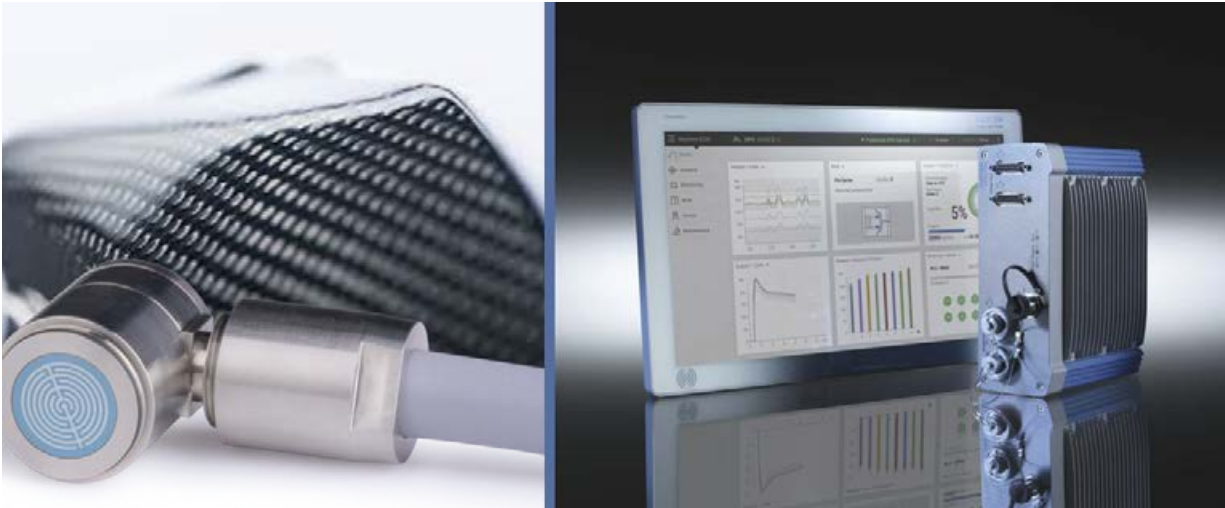
The e-mail notification feature is available for DSC, TGA, STA, DIL, TMA and LFA instruments and is part of the basic software. This feature can be applied in manual operation as well as in combination with an automatic sample changer.

For example, if you have started a comprehensive measurement series involving a sample changer on Friday afternoon and you do not hear anything from your instrument during the weekend, you can be sure that all measurements were carried out properly. In the sample changer mode, a message is sent only at the end of the measurement series or if malfunction of the operation occurs.

In manual mode, using e-mail notification dispels any need to check how far a measurement has progressed. This is particularly advantageous if the office is far from the laboratory. In manual mode, the status message "The measurement is completed" can even include the measurement file. This means that the user does not even have to set foot in the laboratory to evaluate the measurement, but – thanks to the multi-user license of the *Proteus*® software – can do this at the office or home office computer.

Optimizing Reactive Injection Molding by Means of In-line Sensors

Dr. Alexander Chaloupka, Business Field for Process Analytics



Introduction

Injection molding with thermoplastic materials has been employed for many decades and – along with industrially employed components – additionally provides us with objects we use in everyday life. Thermosets open a new chapter with regard to mechanical strength but place high demands with regard to the production of these high-performance components.

In-process sensors (in-line sensors) help the industry ensure smooth and reliable production. NETZSCH and KISTLER have joined forces to raise production to a level enabling robust manufacturing while simultaneously reducing cycle times significantly. This can be achieved by taking cavity pressure and material behavior into account with a simultaneous integrated temperature measurement. This allows for the recording of all parameters that determine the quality of a component and enables quick response in the case of deviations.

Factors Influencing Processing

Injection molders must be capable of combining fast manufacturing cycles with a high level of process stability.

However, there are many influences that can adversely affect production:

- Changes in material behavior due to different transport environments by the time it arrives at the customer's site
- Storage of the material at the customer's site
- Machine failures such as pressure loss
- Temperature deviations inside the mold between the first and last component of one batch or due to faulty heating of the mold
- Fluctuations in the individual components of a resin system

In order to be able to manufacture goods parts despite the challenges mentioned above, an appropriate time buffer must be incorporated into production planning to be on the safe side. As a result of this lengthy procedure, it is often not possible to tap the full potential of manufacturing processes. Today's commercial pressure along with the demand for faster curing cycles for maximum throughput and zero-waste production, in combination with the high complexity of the processes themselves, make it more difficult to compete on the market.

Cooperation with KISTLER

Synergy of NETZSCH and KISTLER

The partnership of NETZSCH and KISTLER offers a sensor system solution that monitors the in-mold pressure and the curing behavior during the entire injection molding process.

Sensors by KISTLER

In this system, KISTLER pressure sensors record the in-mold pressure behavior to decide whether the mold filling was successful; they can detect leakage and bubble formation in the material.

Sensors by NETZSCH

Dielectric sensors by NETZSCH monitor the cure behavior and can take on real-time quality control along with shortening of cycle times based on the material's state.

ComoNeo

In the KISTLER ComoNeo system, all sensor signals are collected: the pressure, curing and temperature signals from all dielectric and pressure sensors. The ComoNeo system is a monitoring system that can be combined with the ComoDataCenter, a browser-based storage system featuring the same functionalities for quality data analysis as those included in ComoNeo.

The Process at a Glance – Pressure and Curing Behavior in the Mold

Example: Electronic Packaging

Reactive injection molding with epoxy molding compounds (EMCs) is a frequently used method for electronic encapsulation in the automotive and aero-

Reference curve under normal process conditions:

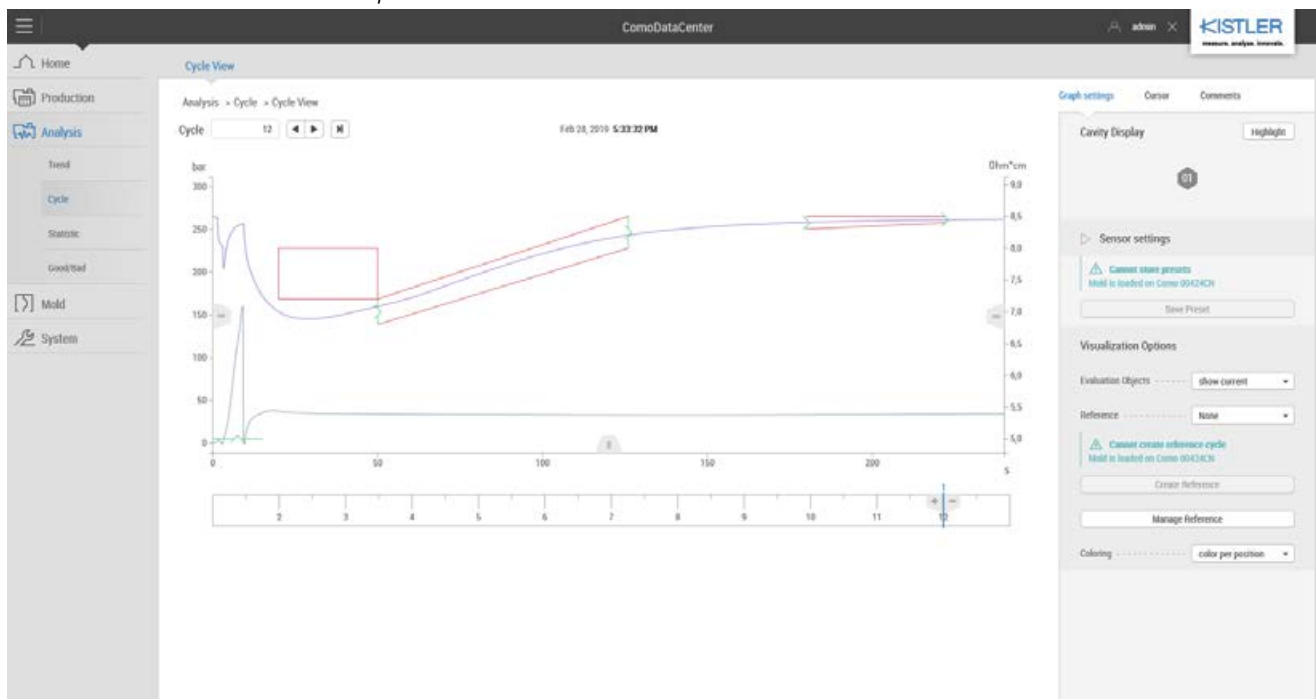


Fig. 1. Reference cycle of a reactive injection molding process for electronic packaging, recorded by NETZSCH and KISTLER sensors

Cooperation with KISTLER

space industry. One or several electrical circuit boards are placed in a closed mold and encapsulated by the epoxy molding compound which is subsequently injected into the mold; this compound softens at an elevated temperature, usually 80°C, and cures at 140 °C to 180°C. For such mass-produced articles, every cent saved through reduced reject rates and cycle times increases competitiveness. The NETZSCH-KISTLER package offers a solution that distinguishes a highly efficient manufacturer from a standard producer.

In the following, examples of a reactive injection molding process for EMCs are presented. Here, a desirable course will be compared with courses containing process deviations.

Definition of Quality Fields

Figure 1 shows a reference cycle for an electronic packaging process. In the lower half of the graph, the pressure signal from the KISTLER sensors is depicted and in the upper half, the curing signal from the NETZSCH sensors can be seen. The red boxes define areas through which – under normal conditions – the curve signal must pass (green input and output areas)

or areas which must not be exceeded (red boundary lines). The green entry which is displayed with the pressure signal describes the normal penetration of the material into the mold. For the dielectric signal, three areas have been defined from left to right:

- The minimum viscosity for the material that must be preset in order to fill the mold completely in the intended processing window
- The reactivity of the material, which must be neither too fast nor too slow (infiltration ↔ cycle time)
- Degree of cure at the end of the process

No Material in the Mold

Figure 2 shows the event where no material gets into the mold. The reason could be that the tank is empty or the auger is not working properly. Based on the sensor response, the machine control system can be informed about the missing material and the current cycle can be stopped.

Process failure – no material in the mold:

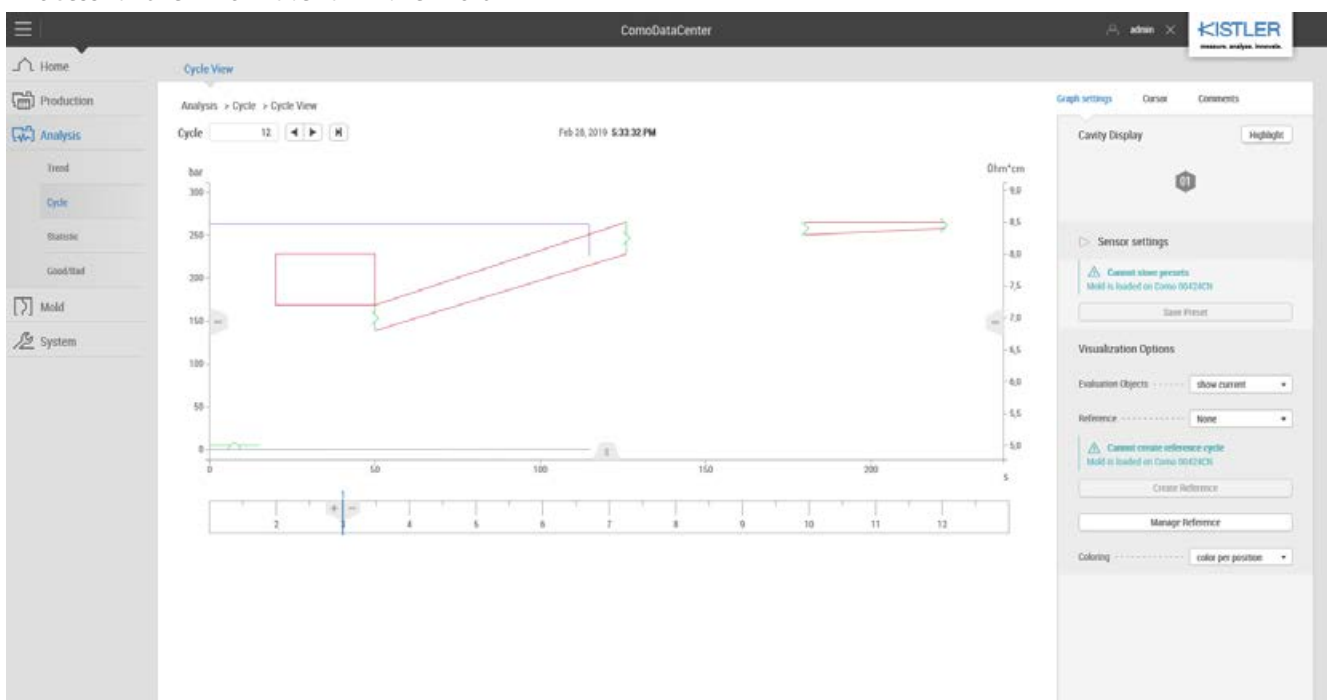


Fig. 2. No material is arriving inside the mold

Cooperation with KISTLER

Process failure – temperature of the mold is too low:

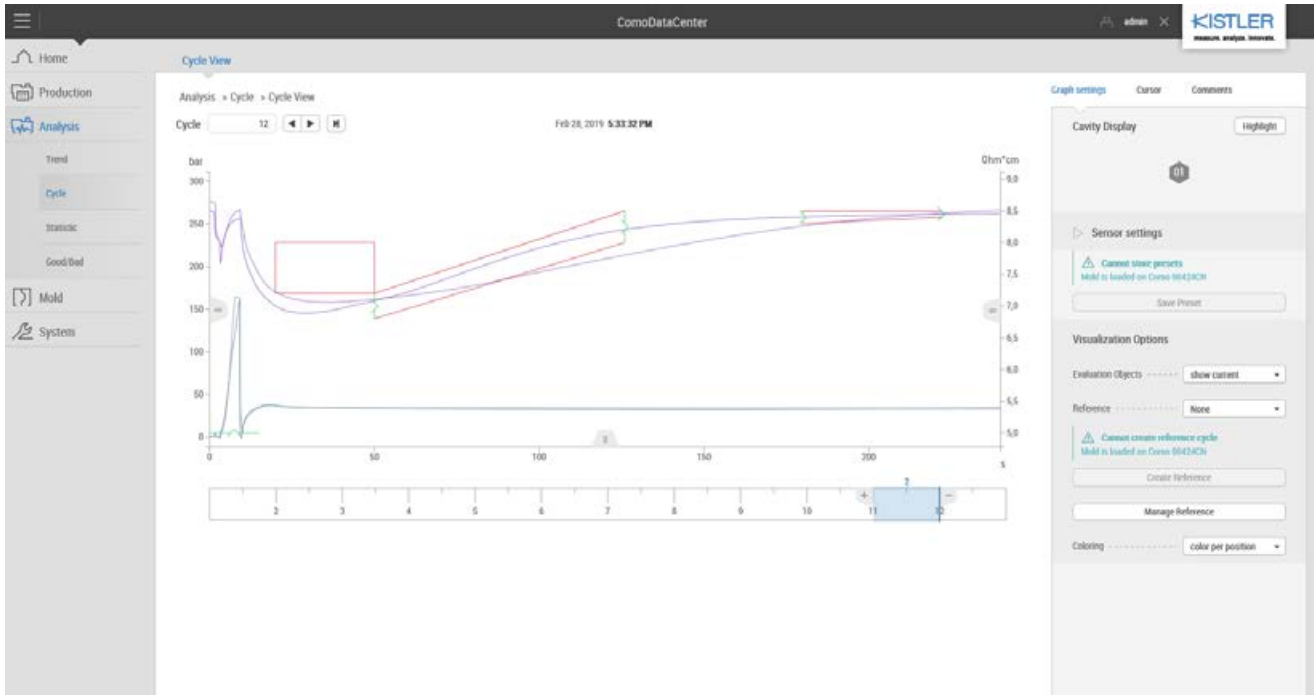


Fig.3. Temperature loss inside the mold and deviation of the material behavior compared to the reference cycle

Temperature Fluctuations in the Mold

A loss of temperature in the mold can lead to slower curing of the resin, resulting in the need to extend the cycle time. Figure 3 shows the sensor responses of the NETZSCH and KISTLER sensors in the case of a temperature loss compared to the reference cycle. The pressure signal is not affected by the temperature loss, so the reference and abnormal shot show the same behavior. The NETZSCH sensor, however, detects the slower curing due to the temperature loss in the mold and can therefore be used to adapt the process and avoid waste production. Due to the detection of the material behavior, the process can be dynamically controlled and is terminated by the sensor package only when the final level is reached.

Summary

This example impressively illustrates why the combination of pressure sensors and dielectric sensors allows for complete insight into the manufacturing process and thus for an increase in process efficiency.

Outlook

The NETZSCH-KISTLER combination offers the most powerful sensor package currently available, capable of sorting good and bad parts during production and additionally making processes more efficient, avoiding scrap production and allowing for shorter cycle times.

Up to Which Temperature Can Hermetically Sealed Aluminum Crucibles Be Employed?

Dr. Gabriele Kaiser, Business Field for Pharmacy, Cosmetics & Food and Dr. Markus Hollering, Research & Development



3in1 Box with Concavus® crucibles

Introduction

Aluminum is the standard material for DSC crucibles up to 600°C. For measurements, the crucibles and lids are typically cold-welded in a press. The lids are often pierced (usually manually), so that no pressure builds up inside the crucible during evaporation by the sample. But is a pierced lid also necessary on the reference side? And does the answer depend on the crucible type? In the following, we will be addressing questions like these.

The Experiment

Two different types of cold-welded aluminum crucibles are heated to 600°C and then visually checked for deformations.

Standard crucibles of aluminum with a diameter of 6 mm and a volume of up to 40 µl were compared with Concavus® crucibles having a diameter of 5 mm and a maximum volume of also 40 µl.

The Result

Figure 1 shows hermetically sealed standard aluminum crucibles at room temperature and after heating to temperatures between 250°C and 600°C. At about 300°C, the bottom of the crucible begins to deform and by 600°C, it exhibits only a single point of contact (in the center) with the base. The lid remains unaffected by the temperature.

The situation looks different for Concavus® crucibles (figure 2). Here, the lid bulges, while the crucible bottom exhibits no visible changes at 600°C.



Fig. 1. Hermetically sealed standard aluminum crucibles at different temperatures

Tips & Tricks



Fig. 2. Hermetically sealed *Concavus*® crucibles at RT and 600°C

In figure 3, a direct comparison of the two crucible types after temperature treatment to 600°C is presented.

The reason for the differing behavior lies in the different manufacturing processes and the associated material thicknesses. The bottom of the *Concavus*® crucibles is significantly thicker than the lid. Therefore, it is the lid rather than the bottom that deforms when the internal pressure increases (the enclosed air expands during heating). A stable bottom and particularly the small cavity, which is formed by the signature concave shape of the bottom, have a positive effect on the repeatability of the measurement curves.

The aluminum foils for the bottom and lid of the standard crucibles have approximately the same thickness and are approximately as thick as the *Concavus*® lids. Due to the geometry, the bottom (and not the lid) of the standard crucible is deformed at higher temperatures. In principle, a thinner base results in a lower level of thermal resistance between the crucible and sensor and therefore, also in higher sensitivity.

Summary

Variations in the contact area between the crucible bottom and the sensor during a measurement usually lead to effects in the associated DSC curves and should therefore be avoided. This applies to both the sample crucible and reference crucible.

If working with standard crucibles, it is advisable to use a pierced lid on the sample and reference sides beginning at approximately 250°C in order to prevent deformation of the crucible bottoms.

Concavus® crucibles are significantly more pressure-stable and could – without the sample – also be heated to 600°C when hermetically sealed. In practice, however, when sample crucibles with pierced lids are used, pierced lids are generally also used on the reference side – often, the lid on the reference side even has two holes to allow the reference crucible to be distinguished from the sample crucible.



Fig. 3. Comparison of the two crucible types after heating to 600°C

Testing. Analyzing. Optimizing.

... at K 2019 in Düsseldorf

Milena Riedl, Content Marketing Manager, Business Field for Polymers



Plastics continue to be an innovative, indispensable and future-oriented material. 225,000 visitors from 165 countries informed themselves about recycling systems, sustainable raw materials and resource-saving processes at the K 2019 show in Düsseldorf.

Leading themes of the largest fair for plastics and rubber included sustainability, recycling and automation solutions. In the conference program of VDMA, several recycling specialists further educated fair attendees on market potentials and challenges as well as applications for recycled materials. A wide range of different solutions for Industry 4.0 and automation were also presented throughout the fair.

The booth design of NETZSCH Analyzing & Testing reflected our ability to support customers along the entire process chain of the plastics manufacturing industry. In the incoming goods control of raw materials, important material properties of thermoplastics, thermosets and

elastomers as well as additives and fibers can be measured and evaluated before the material is stored, conditioned and processed. Thus, in the case of reactive injection molding, characteristic values are collected that allow for the reduction of cycle times and scrap production. Finally, analysis of the visco-elastic properties of finished parts helps check and verify the required quality.

At the NETZSCH Analyzing & Testing booth, we shared thermal analysis application stories in our hourly speed talks. Topics included failure analysis with DSC, identification and quantification of re-granulate mixtures and the analysis of hazardous combustion gases. We extend many thanks to our

expert guest speakers for taking the time to visit our booth and share thermal analysis knowledge in practical case studies.

Did you miss our talks? No problem. They are available under

<http://www.ta-netzsch.com/polymer-talks>



Events

Trade Fairs and Conferences 2020

| | Date | Location |
|---------------------------------|----------------|------------------------|
| ICACC | Jan 26 - 31 | Daytona Beach, FL, USA |
| Tire Technology Expo 2020 | Feb 25 - 27 | Hanover, Germany |
| Pittcon 2020 | Mar 1 - 5 | Chicago, IL, USA |
| JEC World 2020 | Mar 3 - 5 | Paris, France |
| ARABLAB 2020 | Mar 16 - 18 | Dubai, UAE |
| analytica 2020 | Mar 31 - Apr 3 | Munich, Germany |
| Composite-Expo 2020 | Apr 21 - 23 | Moscow, Russia |
| Chinaplas 2020 | Apr 21 - 23 | Shanghai, China |
| INTERPHEX 2020 | Apr 28 - 30 | New York, NY, USA |
| SAMPE 2020 | May 4 - 7 | Seattle, WA, USA |
| Plastic Expo Osaka | May 13 - 15 | Osaka, Japan |
| Plastpol 2020 | May 18 - 22 | Kielce, Poland |
| Polymer Testing World Expo 2020 | Nov 4 - 5 | Cleveland, OH, USA |
| analytica China 2020 | Nov 16 - 18 | Shanghai, China |

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