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OnSet 16

News, Facts and Professional Solutions for Thermal Analysis

New DSC 204 ***F1*** *Phoenix*® and TG 209 ***F1*** *Libra*® with Unique Automatic Sample Changer

Dr. Thilo Hilpert, Research & Development

In this Edition:

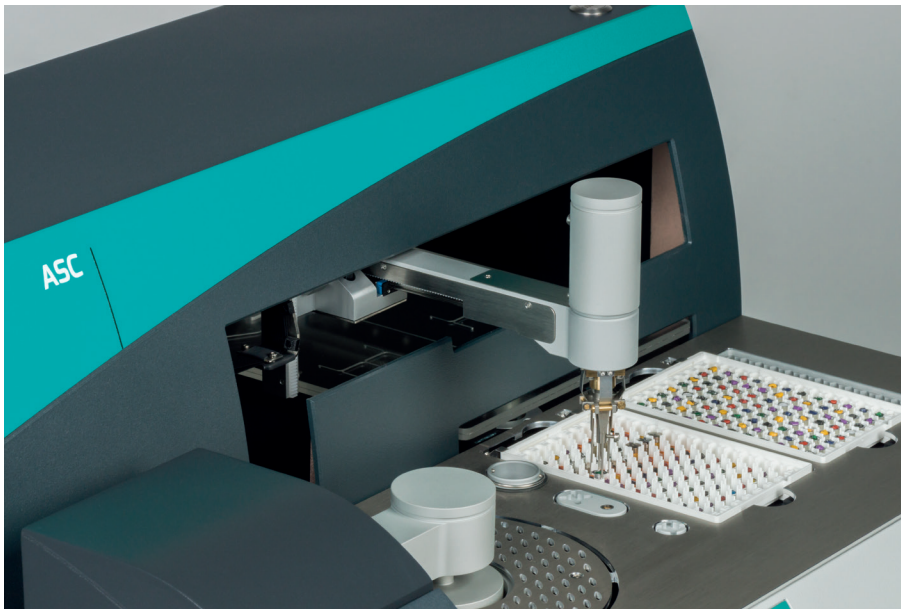

Fig. 1. DSC 204 ***F1*** *Phoenix*® with automatic sample changer (ASC)

Automatic sample changers (ASCs) allow for measurements around the clock and thereby increase sample throughput. With a cutting-edge workflow design allowing for even greater efficiency, this brand new ASC by NETZSCH has been newly developed with a view to the *3in1* trays for the DSC 204 ***F1*** *Phoenix*® and TG 209 ***F1*** *Libra*®.

The portal design with five stepper motor axes – three for moving the gripper, one for opening the gripper and one for covering the tray – offers a completely new level of flexibility and accuracy. Up to two of the *3in1* trays in the 96-MicroPlate format can be inserted; scanners identify these clearly via the label.

Editorial

Dear Reader:

Over the years, thermal analysis has established itself as a purposeful method in many areas. However, new application fields are always arising and instrument technology is continuously undergoing further development. Efficiency, sample throughput, ease-of-operation and automatic evaluation support are the topics gaining in importance. Particularly high demands are placed on the analytical software.

I'm therefore happy that we are able to introduce three innovations in this edition of On**Set** that – each in its own way – can be of great help in your day-to-day work. The new automatic sample changer for the DSC 204 ***F1*** *Phoenix*® and TGA 209 ***F1*** *Libra*® offers not only an unparalleled number of measurement positions, but also a variety of extremely practical features with the potential to redefine the term "efficiency".

Identify – the system for curve recognition, interpretation and classification that is unique in the field of thermal analysis – has had its functions expanded. DSC, TGA, DIL/TMA and c_p measurements can now be analyzed and – along with the comprehensive NETZSCH libraries which are included in the standard delivery – the KIMW database for polymers can now also be included. Thanks to our collaboration with the Kunststoff-Institut Lüdenscheid (KIMW), Germany, it was possible to integrate a material database into *Identify* containing the DSC data for 600 commercially available polymers and blends.

In many cases, the HFM (Heat Flow Meter) technique has become standard for determining the thermal conductivity of insulating materials in quality assurance and research & development. For this kind of application, NETZSCH has various systems in the product line that conform to relevant standards in this field: One of them is the HFM 446 *Lambda*^{5}, which was first introduced only a few months ago. It is specially designed for sample sizes of 200 mm x 200 mm and features a series of technical innovations.

I would like to warmly recommend the article contributed by Daniela Jahn of the Institute for Bioplastics and Biocomposites in Hanover, Germany. She investigated the influence of a hydrolysis stabilizer in different concentrations on a semi-crystalline PLA (polylactide) homopolymer by means of DSC and compared it to the thermomechanical properties of the material.

In line with the topic of DSC on polymers, the article in our *PRECISE PRACTICE* series focuses on how multi-layer packaging films can be investigated with regard to their composition by means of DSC and the NETZSCH *PeakSeparation* Advanced Software Package.

Last but not least, my warmest congratulations go to the newly elected GEFTA board (German Society for Thermal Analysis), under the chair of Dr. Dr. Dirk Walter.

I hope you'll enjoy your browse through our On**Set**[16]!

Yours truly,

Dr. Gabriele Kaiser
Head "Scientific & Technical Communication"

Continued from Page 1

Concavus Crucible of Al

Concavus Lid of Al

Inner height to lid	2.25	mm	Add. height due to lid	0.12	mm
Outer height	2.6	mm	Delta height	0.38	mm
Inner diameter	4.7	mm	Outer diameter	6.9	mm
Outer diameter	7.0	mm	defined hole	-	mm
Inner bottom diameter	4.4	mm	Avg. mass	12.1	mg
Outer bottom diameter	4.6	mm	purity	99.5	%
Avg. mass	39.5	mg	Max. temperature	600	°C
Purity	99.5	%	Delta volume (down)	-6.2	µl
Max. temperature	600	°C	Delta volume (up)	6.0	µl
Nom. volume	35	µl	Cold weldable	yes	
Cold weldable	yes				

Fig. 2. *Concavus* crucibles and lids in the crucible database

The new gripper with concentric 4-pin movement – in conjunction with the new crucible database (see figure 2) – allows for *SafeTouch* functionality for the adaptive gripping of any crucible/lid combination. Gripping force and level as well as the different depths of the *3in1* trays are automatically adjusted.

The *3in1* trays offer advantages in terms of packaging, preparation and archiving; the unique serial number allows for reliable identification, even when reusing in the future. Compatibility with the MicroPlate format also allows for direct filling with pipetting robots.

Along with the fixed strip for 12 calibration and reference crucibles, respectively, up to 204 positions are possible.

The automatically maneuvered tray cover with integrated gas purging reliably protects the samples from environmental influences such as dust, humidity and atmospheric oxygen. The samples and trays are visible at all times. The cover can be manually opened and closed for such tasks as changing out the tray and samples. An automatic closing function ensures that the samples remain continuously protected to the greatest possible extent. The lids on particularly sensitive samples can also be pierced immediately prior to insertion into the measuring cell with a needle which can be optionally integrated into the gripper.

Fig. 3. Sample changer with half-open tray cover

The *Proteus*® 7.2 software enables a cutting-edge workflow design and even greater efficiency – particularly for longer measurement series. Reference crucibles and one calibration set can remain in the ASC at any given time; there, they are protected by the tray cover. References are suggested by the software; automatic calibration can also be run over the weekend. The measurement can be defined as desired for either any given crucible position in the tray, any rows/columns, or the entire tray in one step. Selection of a measurement rule (method) is just as easy.

Anticipatory optimization allows for dynamic and fluid maneuvering and also reduces changing times by up to 20 s or 25%.

The crucible is detected in the gripper via a modulated laser beam and a photo diode as it passes by the detection position. This elegant solution saves time and is unaffected by intense light sources or solar radiation.

Fig. 4. Labels of two *3in1* trays with 2D code – they include type, content and serial number and can be read automatically

Along with readable information such as the order number, content and serial number, the label of the *3in1* trays (shown in figure 4) also contains a DataMatrix 2D code which is read upon insertion by the cameras installed in the ASC.

All currently available coupling options for gas analysis can also be delivered for the new ASC; the *PERSEUS* coupling has been adjusted.

Summary

Having a cutting-edge workflow design with even greater efficiency, the new automatic sample changer by NETZSCH plays in a higher league. Features such as the *3in1* trays in MicroPlate format, rinsable tray cover, and *SafeTouch* (operating by means of a 4-pin gripper and crucible database) all allow for successful application in areas outside quality assurance as well.

Crucible Database: This includes all NETZSCH crucibles, lids and liners (altogether approx. 120 pieces) with pictures, order info, dimensions, material and dependencies – such as ASC and sample carrier compatibility and much more.

As an example, figure 2 shows a set comprised of a *Concavus* crucible and lid with features from the crucible database. *SafeTouch* makes use of this data in order to ensure that all crucibles are gripped safely and gently. The measurement definition uses previously defined sets consisting of crucible, optional lid and liner as well as properties like cold-welded or pierced.

Customer-specific crucibles, lids and liners can also be defined and applied.

2016 Annual Meeting of GEFTA

Dr. Ekkehard Füglein, Applications Laboratory

Dr. Michael Feist (left) and Dr.Dr. Dirk Walter (right)

The work group of Dr. Mario Beiner, Scientific Head of the Polymer Applications Business Field at the Fraunhofer Institute for the Microstructure of Materials and Systems (IMWS) in Halle, Germany, hosted this year's annual meeting of the German Society for Thermal Analysis (GEFTA).

In his welcoming speech, Dr. Beiner noted that the GEFTA annual meeting is the most important forum in the German-speaking world for discussing important trends with expert colleagues and learning about new methods. Over the course of two-and-a-half days, the around 40 participants had plenty of opportunity to do just that, during 20 lectures, a moderated poster presentation and an excursion to the Fraunhofer Pilot Plant Center in Schkopau, Germany.

On the occasion of the general meeting, the GEFTA members were called on to elect a new chairman. After eighteen years in this position, the presiding chairman, Dr. Michael Feist from the Humboldt University of Berlin, was no longer available for this function.

His successor, Dr.Dr. Dirk Walter from the Justus-Liebig University in Gießen, thanked him cordially for his excellent work as head of GEFTA and highlighted his tireless commitment in past years as well as his special skills in organizing and conducting multilateral conferences with the neighboring European Societies for Thermal Analysis and Calorimetry.

Dr. Feist will remain an active member of the GEFTA board and will support his successor in his new position to the best of his ability.

Along with Dr. Feist and Dr. Walter, Dr. Steffen Neuenfeld, Dr. Wolfgang Hohenauer and Dr. Christoph Schick will also be part of this newly elected board.

Polymer Identification by Means of KIMW Database and *Identify*

Dr. Alexander Schindler, Research & Development, Dr. Tobias Pflock, Business Field Management Polymers
Martin Doedt, KIMW Prüf- und Analyse GmbH, Lüdenscheid, Germany

Over the years, the Kunststoff-Institut Lüdenscheid [1] – an experienced contact for any question regarding plastics – has built up a materials database which currently contains DSC curves for more than 600 commercially available polymers. Thanks to collaboration between the Kunststoff-Institut and NETZSCH-Gerätebau GmbH, this extensive database has now been integrated into the *Identify* curve identification software within *Proteus*® analysis. In conjunction with *AutoEvaluation*'s automatic, user-independent evaluation of DSC measurements, this not only simplifies polymer analysis with regard to such issues as identification, failure analysis and quality control, but also makes the results more meaningful [2].

Search Libraries:

Library	Entries
Alloys Poster NETZSCH	42
Ceramics Poster NETZSCH	32
Ceramics_Inorganics NETZSCH	255
Elements Poster NETZSCH	104
Metals_Alloys NETZSCH	135
Organics_Food_Pharma NETZSCH	309
Polymers DSC KIMW	600
Polymers NETZSCH	176
Polymers Poster NETZSCH	70

Fig 1. Libraries within *Identify* (Status December 2016)

What Does *Identify* Offer?

The *Identify* database system was introduced for direct comparison and thus classification and interpretation of DSC curves, but can now also be employed for $\Delta L/L_0$ measurements stemming from DIL and TMA instruments (see also pages 8 to 10), for c_p-data from DSC instruments and, most recently, also for TGA measurements [3]. Once *Identify* is available within *Proteus*®, it can automatically be used for all signal types of any of the supported instruments. The user always has access to the entire database with all of its possibilities, such as overlaying of the current measurement curve with any database curves – including those of different data types.

The entire NETZSCH part of the database comprises more than 1,100 entries from the fields of polymers, organics, food and pharma, ceramics and inorganics, and metals and alloys as well as chemical elements (see figure 1). These entries are composed of measurements and literature data of different data types (DSC, TGA, DIL/TMA and c_p). Users can, of course, create or expand libraries with their own measurements and literature data, and these can simultaneously be shared with other users via the computer network.

Basically, *Identify* offers different search algorithms; the database search can be limited to certain temperature ranges and the results can be filtered according to various criteria, such as the measurement conditions.

The Advantages of the KIMW Database

While the NETZSCH part of the *Identify* database forms a solid foundation due to its large variety of materials and methods, the optional KIMW part additionally features previously unachieved depth in the area of DSC on polymers: It includes 600 DSC measurements on different commercially available polymers and blends, reflecting about 130 different polymer types. This means that for many polymer types there are measurements on different products of the same type present which may exhibit significantly different DSC profiles. In addition to the multitude of DSC curves, there is the advantage that for each of the 600 polymers, the exact trade name and manufacturer are stored, along with color and filler content.

In summary, their integration into *Identify* allows the 600 DSC curves of the KIMW database to be used directly and intelligently – either via a purely visual comparison or

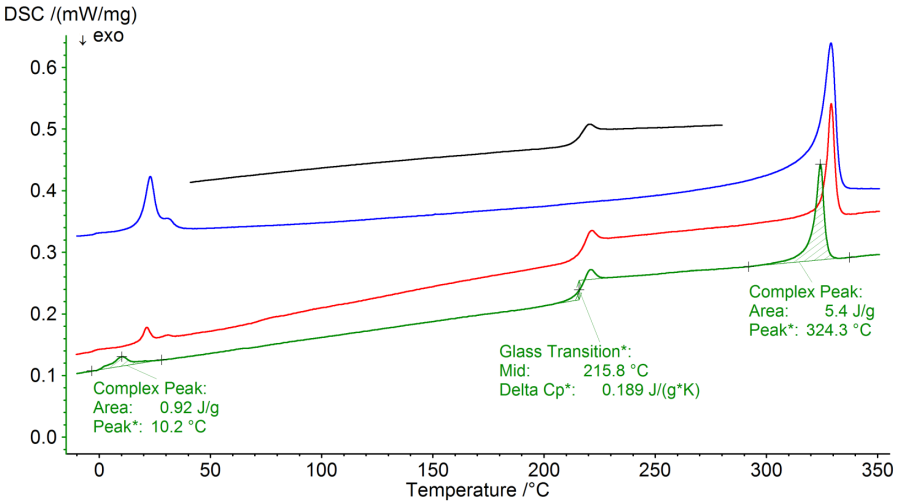

Fig. 2a. Comparison of the DSC curves for the "PEI-PTFE Ultem 4001" polmyer blend (green) with the database curve for "PEI-PTFE Luvocom 11067223" (red) and with typical database curves for PTFE (blue) and PEI (black). For better illustration, the curves were offset in relation to each other in the y-direction.

for automatic identification of a polymer as shown with the following example:

Identification of a Polymer Blend

Figures 2a and 2b illustrate an exemplary database search where a measurement on the polymer blend "PEI-PTFE Ultem 4001", which is already available in the KIMW database, serves as an input curve. The *AutoEvaluation* and *Identify* results appear with a single click: First, automatic detection and evaluation of the effects were carried out; in this case, an endothermic effect was found in the temperature range between approximately 0°C and 30°C, as well as a glass transition at approximately 216°C and another endothermic (melting) effect at a peak temperature of 324°C. The database search yielded the same curve as the most similar hit along with another PEI-PTFE blend, but also measurements on pure PTFE and PEI (see figure 2b).

In contrast, the DSC curves of most of the other polymer types had a much lower similarity so that they could be ruled out. For more details such as measurement conditions or interpretation of the effects, please see reference [2].

Results:

Measurement/Literature Data	Similarity [%]
PEI-PTFE_Ultem_4001_DSC	100,00
PEI-PTFE_Luvocom_1106-72...	66,31
PTFE_5-15G_DSC	54,09
PTFE_1-24G_DSC	53,74
PESU-PTFE_Ultrason_KR_41...	48,40
PTFE_Algoflon_L203_DSC	44,88
PEI_Ultem_1000_DSC	43,74
PEI_Ultem_2312_GP30_DSC	43,68

Class	Similarity [%]
PEI-PTFE (2)	83,15
PTFE (3)	50,90
PESU-PTFE (1)	48,40
PEBA (2)	37,98
PPA-PTFE (1)	35,00
LCP-PTFE (1)	30,40
EVM (1)	29,95
PEEK-PTFE (1)	29,37
PEI (14)	27,92

Fig. 2b. Results of the *Identify* database search with regard to the "PEI-PTFE Ultem 4001" sample. The hist list on the left shows comparisons with individual measurements; the hit list on the right, with classes; i.e., defined groupings (the number in parentheses always indicates the number of measurements in the class).

Summary

The KIMW database integrated into *Identify* allows for direct comparison of a measurement with many hundred DSC curves on commercially available polymers. This makes polymer identification not only easier, but also more reliable!

Literature

[1] http://kunststoff-institut-luedenscheid.de/en/
[2] M. Doedt, A. Schindler, T. Pflock. DSC-Auswertung mit einem Klick – Datenbank-Integration und Evaluationssoftware vereinfachen Polymeridentifizierung. Kunststoffe 10/2016. S.189-191
[3] A. Schindler, C. Strasser, S. Schmölzer, M. Bodek, R. Seniuta, X. Wang. Database-Supported Thermal Analysis Involving Automatic Evaluation, Identification and Classification of Measurement Curves. Journal of Thermal Analysis and Calorimetry, DOI 10.1007/s10973-015-5026-x
To the Article

Identify for Fast and Easy Classification of a Zero-Expansion Material

Michael Thelen and Dr. Gabriele Kaiser, Scientific & Technical Communication

ZERODUR® is, for example, used for telescope mirrors in observatories

One important aspect of quality assurance is the determination of specific material properties. This is done in order to guarantee consistency with regard to product quality. Material batches which do not correspond to the desired specifications can thus be identified and filtered out.

With the introduction of measuring methods and the *Identify* thermoanalytical database, the NETZSCH *Proteus*® software now features two tools allowing for fast and easy evaluation of routine measurements. Measurement methods ensure that the same measurement parameters are always being employed. In such a method, also evaluation steps can be integrated, which can always be carried out, automatically and in an identical manner, following a measurement. This way, one can quickly see whether the respective quality characteristics have been fulfilled [1]. In order to also be able to assess a measurement without prior evaluation, *Identify* offers the possibility of comparing a measuring curve with the references stored in the

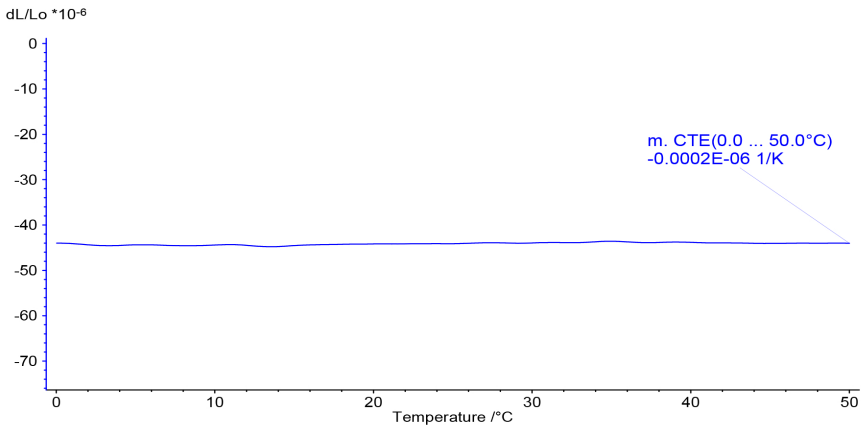

Fig 1. Evaluated measurement of the ZERODUR® DK1 reference sample

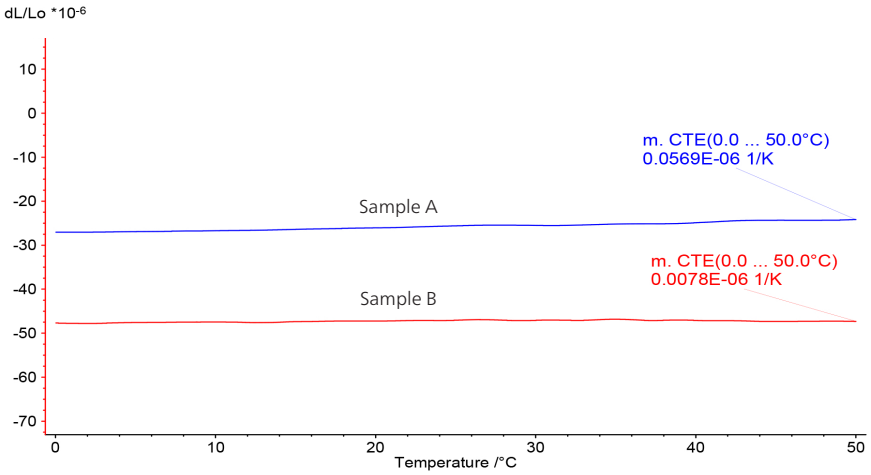

Fig. 2. Measurement of two ZERODUR® DK1 samples (A and B) from different batches with corresponding evaluation

database. In the case of DIL or TMA curves, this curve comparison is independent of the evaluation steps carried out. Through previously set tolerances, *Identify* is even able to assess a sample with regard to its quality criteria. Thanks to the possibility of expanding the database with one's own measurements, the database can be adjusted to individual requirements at any time [2, 3].

A characteristic value to be determined within the scope of quality control can be, for example, the mean coefficient of thermal expansion, m.CTE. It describes the length change of a material during temperature change within a certain temperature interval. The mean linear coefficient of thermal expansion can be determined with the help of a dilatometer or a thermomechanical analyzer (TMA).

Zero Expansion = Mean Coefficient of Thermal Expansion of 0 K^{-1}

ZERODUR® is a lithium alumosilicate glass ceramic by Schott AG with an extremely low coefficient of thermal expansion. The low thermal expansion property is realized by virtue of the fact that, during heating, the substances added to the glass melt form seed crystals on which tiny crystals grow; these crystals contract when they are heated [4]. ZERODUR® is used in various high-tech applications such as high-precision measurement technology, astronomy (e.g., for telescope mirrors) or LCD lithography [5]. ZERODUR® DK1 (expansion class 1), which was employed for these measurements, has an m.CTE of 0 K^{-1} in the temperature interval between 0°C and 50°C. The specified tolerance is $0.0500 \cdot 10^{-6}$ K^{-1}. For the measurement of such small changes in length, a dilatometer with high sensitivity is required. The NETZSCH DIL 402 *Expedis Supreme*, which features a particularly high resolution, was therefore the ideal instrument for this task.

***Identify* – No Prior Evaluation Needed for Classification**

For the dilatometer experiments, cylindrical samples with a length of 25 mm and a diameter of 6 mm were prepared. The measurements were carried out under a helium atmosphere (gas flow: 50 ml/min) in the temperature range from -100°C to 100°C at a heating rate of 2 K/min with probe contact pressure of 250 mN using a fused silica sample holder.

In the first step, a reference sample of ZERODUR® DK1 was measured and the mean coefficient of thermal expansion was determined in the interval from 0°C to 50°C). Figure 1 shows the evaluation of the reference measurement. Based on this measurement, a method was then created which included the applied evaluation steps (method including evaluation). A method such as this – including evaluation – is capable of such tasks as automatic determination of the coefficient of thermal expansion and presentation of the graph in the predefined scaling following the end of the respective measurement without the operator's intervention.

The *Identify* database was simultaneously expanded by the measurement of the reference sample. In order to use the entry for quality control, it must be assigned to a defined class. Such a class is comprised of all of the measurements assigned to it and can be annotated with tolerances.

All in all, different batches of ZERODUR® DK1 were investigated by means of both the previously described method including evaluation and a pure measurement method (with the same measurement parameters). The results of two measurements A and B, obtained with the method includ-

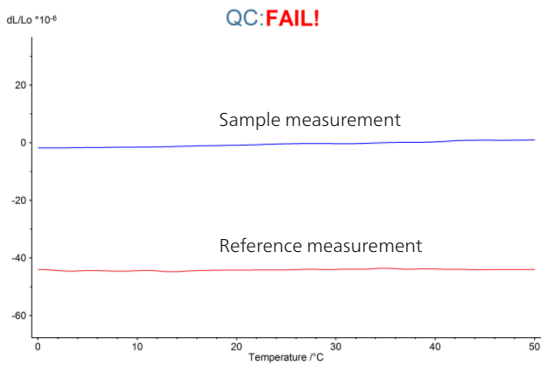

Fig. 3. Measurement of a sample from a batch that does not fulfill quality requirements

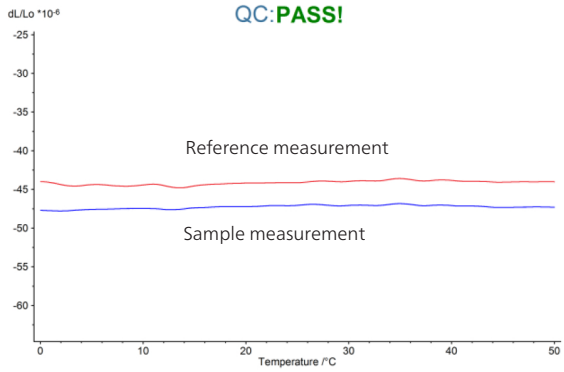

Fig. 4. Measurement of a sample that fulfills quality criteria

ing evaluation, in the temperature range between 0°C and 50°C are depicted in figure 2. It can be seen at first glance that sample A (blue) with an m.CTE of $0.0569 \cdot 10^{-6}\ K^{-1}$ is beyond the tolerance of $0.0500 \cdot 10^{-6}\ K^{-1}$.

Sample B (red), in contrast, has an m.CTE of $0.0078 \cdot 10^{-6}\ K^{-1}$ and does fulfill the requirements.

Quality assessment of the samples investigated with the pure measurement method was carried out with the help of *Identify*. Manual evaluation was therefore not necessary. Figure 3 presents the result of the database comparison for a measurement which is beyond the permissible tolerance. This is clearly expressed by the automatic diagram label, "QC: FAIL!". The blue curve here represents the measurement of the sample; the red curve, that of the stored reference. If the requirements are fulfilled, on the other hand, the label reads "QC: PASS!" (see figure 4). Also here, the blue curve corresponds to the sample measurement; the red curve to the reference.

Summary

The NETZSCH *Proteus*® software – along with the *Identify* thermoanalytical database and the methods – features two modules which are of great help in day-to-day routine work. The use of measuring methods ensures that measurement conditions are always identical, while *Identify* supports the operator in classifying the results. This allows even newcomers to thermal analysis to immediately carry out sample measurements and assess them in term of whether they fulfill quality criteria.

Literature

[1] E. Füglein, Application Note 083
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[5] http://www.us.schott.com

Quality Assurance of Insulating Materials in Next to No Time

Alexander Frenzl, Business Segment Management Glass, Ceramics and Building Materials

Fig. 1. Heat flow meter NETZSCH HFM 446 *Lambda*^{S}

Thermal insulation produced so as to be in accordance with current guidelines and regulations can only function correctly if the material properties declared by the manufacturer are regularly checked on a random basis by both the manufacturer (in-plant monitoring) and neutral testing institutes (third-party monitoring). One such material property is thermal conductivity, which can be determined by the methods described in ISO 8301 and ASTM C518.

Standard Method for Quality Assurance

While the standards ISO 8302 and ASTM C177 describe absolute methods employing the guarded hot plate and require – over wide temperature ranges – relatively long measurement times at high measuring precision, the standards ISO 8301 and ASTM C518 cover the heat-flow method.

This method can be traced back to the international thermal conductivity reference materials NIST SRM 1450 and IRMM-440 and is characterized by very efficient measurement times. In addition to this, the instruments can be calibrated for a variety of materials of known thermal conductivity. That's why they have become standard not only in the field of quality assurance but also in research and development.

Materials can be measured directly following production in different plate sizes.

For many years now, NETZSCH has offered measuring instruments which are employed in both material development and quality assurance for the determination of thermal conductivity across a very wide temperature spectrum. Particularly in the field of building materials, where the decisive operating temperatures are around room temperature, the heat-flow method is ideally suited.

In this method, two plates are used to create a temperature gradient through the sample to be measured (see figure 2). Once the heat flow generated through the gradient and the thermal conductivity calculated from it are stable within defined limits, a temperature-dependent thermal conductivity measurement value can be recorded (figure 3).

Intuitive Operating Concept

At NETZSCH, we view ourselves as a solution provider. In recent years, we have worked hard on optimizing our instrument operation through software to provide users with the greatest possible ease in handling routine tasks. For quality assurance in the production of insulating materials, NETZSCH now offers a user-friendly, clear solution in the current HFM 436 *Lambda* and HFM 446 *Lambda*^{S} (figure 1) and the accompanying *SmartMode* software. The clearly structured, touchscreen-capable software runs under all current Windows operating systems and is designed, per present-day expectations, to accept inputs not only via mouse or keyboard but also directly via touchscreen or a Windows tablet PC.

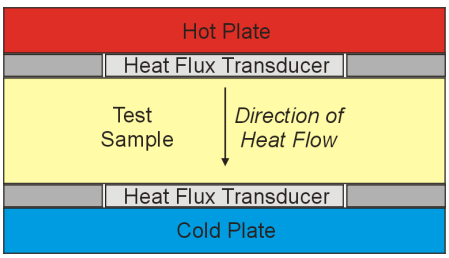

Fig. 2. Measuring principle of a heat flow meter

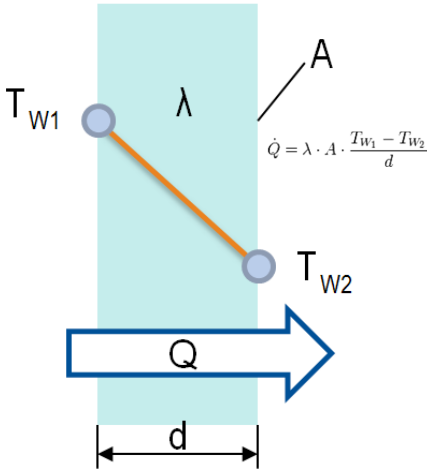

Fig. 3. Schematic of heat transfer through a stationary solid body

The current status of all connected instruments can be seen at a glance (figure 4). Under "Favorites", you can choose recurring measurement definitions (methods) with just one click. The "User Methods" section administers all measurement specifications defined and saved by the user, which are known as 'methods'. You can mark the methods for your Favorites section with just the tap of a finger. The "Wizard" guides you in defining a new method according to your specifications. You just take care of the essentials, such as naming the measurement, designating the material, or specifying your sample's dimensions. After selecting the appropriate calibration, just set the temperature points of interest to you and the measurement can be started. Once a "User Method" is set up, all you still need to do is enter a sample ID and you can start a new measurement within a measurement series in a matter of seconds.

Evaluation of the Measurement Is as Easy as Child's Play

All instrument signals are displayed in clearly-structured graphs during the entire measurement. Information on the current temperatures of both of the plates as well as the sample can be seen at a glance. The current signals of the heat-flow sensors and the currently calculated thermal conductivity can also be seen in the graphs (see figure 5).

At the end of the measurement, the thermal conductivity is presented as a function of temperature in both graphic and tabular form in the "Results" overview.

Just One Click to a Standard-Compliant Report

For your internal documentation, a variety of reporting functions are available. With a single mouse click, you may select from among three predefined templates: either the short report, the expanded report with additional instrument information or the report in accordance with ASTM C518 that – along with general measurement information – also includes information on calibration and measurement uncertainty.

The report is immediately loaded into Word; from there, it can be printed, saved or converted into a PDF. In addition to that, one can export to Excel a complete report depicting, in individually prepared tables, all of the metadata of the measurement along with the measurement results and all graphs. This way, the data can also be very easily embedded into existing QM systems.

Of course, you can also easily customize the report templates to your company's CI.

Statistics: $\lambda_{90/90}$

The integrated $\lambda_{90/90}$ calculation is of particular advantage. The $\lambda_{90/90}$ value is the basis for determination of the declared value of the thermal conductivity within the realm of CE declarations of building materials. It is calculated from a measurement series of at least 10 measurements and states which thermal conductivity values to a probability of 90%, can be achieved for 90% of the output production volume. This value is widespread as a common statistical value in classical quality assurance and is applied in all European production of insulating materials. Aging materials, such as PU foam for example, can additionally be fur-

Fig. 4. *SmartMode* – clearly and logically structured

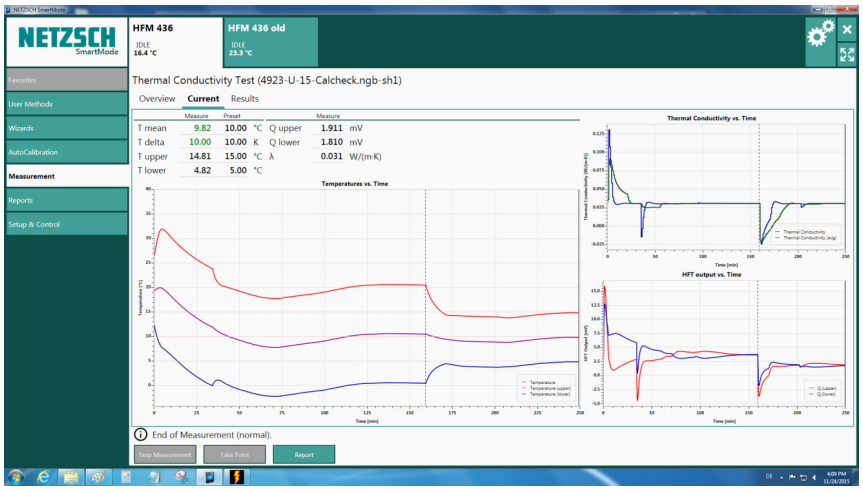

Fig. 5. Presentation of the current measurement – to the report in just one click

nished with the normatively defined extra aging supplements within the scope of the calculation. This makes the NETZSCH HFM instrument series to a very valuable tool in the realm of in-process production control.

Add-Ons and Accessories

Particularly for fiber materials such as glass or rock wool, the thermal conductivity is heavily dependent on the sample's degree of compression. With the optional load device, the thermal conductivity of fiber materials or compressible foams can be measured as a function of compression. To that end, the pressure to be applied to the sample during the measurement can be defined. This allows the true installation situation to be readjusted very easily. Hard samples or samples with rough surfaces and comparatively high thermal conductivities make it particularly challenging to correctly measure the thermal conductivity. While soft or compressible samples most often exhibit good contact with the plates, in hard or rough samples the smallest of gaps may form between the sample and measuring plates. This contact resistance can falsify the measurement result. By means of the optional instrumentation kit consisting of two additional thermocouples and two silicone pads, even samples such as this can be measured correctly. The silicone pads, which are positioned between the sample and plates, allow for good contact and homogeneous heat flow. Additionally, the thermocouples are applied to the lower and upper sample surfaces in order to be able to measure the exact surface temperature of the sample.

For gritty materials or powders, a special measuring framework is available. This can be filled manually and pared back with a ruler. After insertion, the gritty material can be measured just like any other solid sample structure.

With the latest addition to the NETZSCH HFM family, the HFM 446 *Lambda*^{S}, this instrument series has been expanded by a very useful instrument. With a plate size of 200 x 200 mm, this device features very compact dimensions and is particularly well suited for material development in the field of polymers and any kind of foams or materials such as aerogels. The possibility of measuring the specific heat capacity is of special interest. Particularly in the quality assurance of phase-change materials (PCMs) or PCM-containing building materials, the operating ranges and storage capacities of such materials can now be investigated.

Conclusion

With the NETZSCH HFM instrument series and the brand-new *SmartMode* software, your measuring efforts need not extend beyond the essentials of physical handling. Since the introduction of iPad and Co., software masks requiring explanations have become a thing of the past. Take advantage of the intuitive Wizard, create and save your own User Methods and draw from your pool of recurring Favorites with no more than a tap of the finger. Create comprehensive reports for your internal documentation with a single click and benefit from the many years of experience behind our employees' application know-how.

Long-term Stability of Bio-Based Plastics –

Investigation of the Effectiveness of Hydrolysis Stabilizers by Means of DSC

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Institute for Bioplastics and Biocomposites

Introduction

Plastic components are exposed to various environmental influences during their service life which can significantly change their material properties and reduce their life cycle [1]. These influences are classified as "internal" factors (chemical degradation, physical structure, etc.) or "external" factors (temperature, atmospheric and biological burdens, etc.) [2].

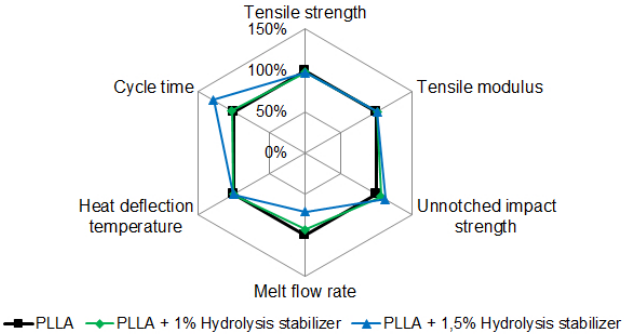

Fig. 2. Influence of stablization on the thermal properties

Generally, multiple factors come into play at the same time. Plastics are chemically and thermomechanically stressed by, e.g., temperature and humidity, both during production/processing and later operating directly on the component. This may result in oxidative and/or hydrolytic chain degradation of the materials. The change in chemical structure may cause changes in mechanical, thermal and rheological property; rigidity, impact strength, thermal and chemical stability, and the elasticity of a material will be reduced [3]. Particularly plastics containing ester groups, such as bio-based PLA, are prone to a hydrolytic degradation process (figure 1). Via cleavage of the molecular chains, reactive acid end-groups are developed which are then responsible for further chain reactions.

In order to prevent premature failure of a component, stabilizers are often employed in plastics processing that improve long-term stability in relation to external influences [4]. Such additives, however, also mean higher costs for material manufacturers and ultimately also for the product itself.

Information on the effectiveness of stabilizers is therefore crucial for material development and the target-oriented application of additives [5]. Already slight differences in concentration can change the properties and determine the price of the material depending on the application field.

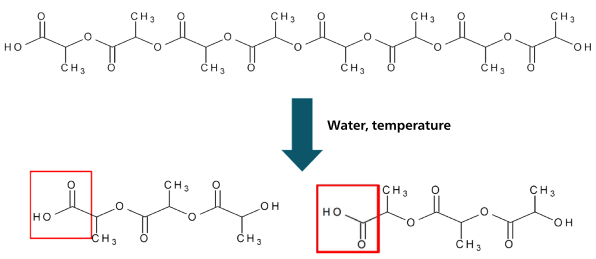

Fig. 1. Material degradation of polylactide (PLA, also known as polyactic acid)

Experimental

In order to analyze the influence of various levels of PLA hydrolysis stabilizer concentration, several modified PLA compounds were manufactured, characterized and subjected to aging tests.

The material used was a semi-crystalline PLA homopolymer (PLLA) to which additives were added in different concentrations (1% / 1.5 wt%) for protection against hydrolysis during extrusion. The additive thus protects the biobased plastic from molecular chain degradation both during processing and in the finished product. The hydrolysis stabilizer reacts with the acid end groups of the PLLA and so prevents the acid-catalyzed ester hydrolysis [5].

The recorded thermomechanical properties are presented and compared in figure 2. Hydrolysis protection (1 - 1.5 wt%) has no influence on the tensile strength, tensile modulus or heat deflection temperature. The impact strength rises with increasing concentra-

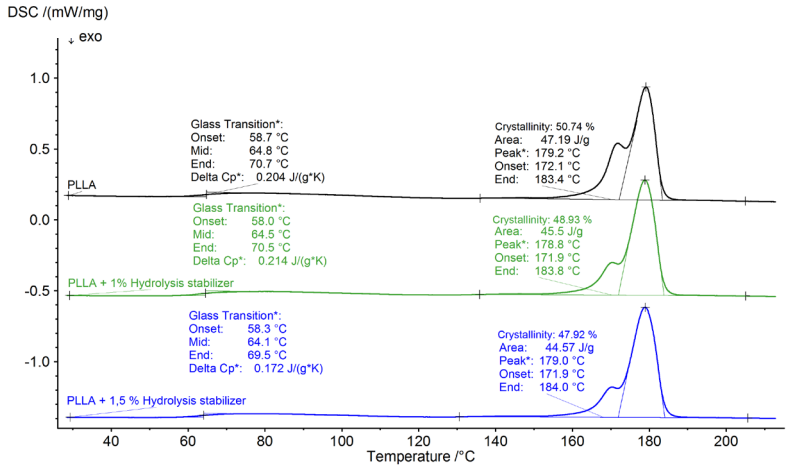

Fig. 3.Influence of stabilization on the thermal properties

tion of the stabilizer, indicating a change in crystal structure. The flowability is reduced by 1.5 wt/% due to the cross-linking effect of the additive, what might have a negative impact on the cycle time. This also suggests a reduction in the degree of crystallization [6].

In order to be able to judge the influence of the additive on crystallization, the materials were analyzed by means of DSC (NETZSCH DSC 204 ***F1*** *Phoenix*®). The samples were dynamically heated (heating/cooling rate: 10 K/min) in a closed aluminum crucible (approx. 7 mg) under a nitrogen atmosphere (flow rate: 20 ml/min) to a temperature above the melting point (T_m = 170°C).

As can be seen from the 2nd heating curves (figure 3), the melting enthalpy (ΔH_m) is reduced as the concentration of the hydrolysis stabilizer increases. Less energy is required for melting the crystalline portions of the material. On the basis of ΔH_m and the literature value for a completely crystallized PLA ($\Delta H_{Lit.}$ = 93 J/g [7, 8, 9]), the degree of crystallization (K) can be calculated using the formula:

$$K = \frac{\Delta H_m}{\Delta H_{Lit.}} \cdot 100\ \%$$

[10, 11].

K defines the stiffness as a function of the crystal structure. It is generally the case that the higher the value for K, the stiffer and more brittle a material is. In comparison with PLLA, there is a tendency for decline in the degree of crystallization of the stabilized samples. This might be a reason for the increase of impact strength as well as of the cycle time (figure 2).

Resistance to Water

In a water immersion test, all samples were continuously aged at 65°C over a period of 750 hours.

By means of DSC, the melting ranges of the materials were recorded in order to draw conclusions about the degradation behavior. Molecular chain degradation generally yields shorter chain segments that melt at lower temperature and thus result in a lowered melting point, evaluated as maximum peak of the melting effects (T_m).

With the 2nd DSC heating curve (closed Al crucible, sample masses: 5.5 - 6 mg, N_2 flow rate: 20 ml/min, heating/cooling rate: 10 K/min), hydrolytic degradation of the material becomes noticeable (figure 4).

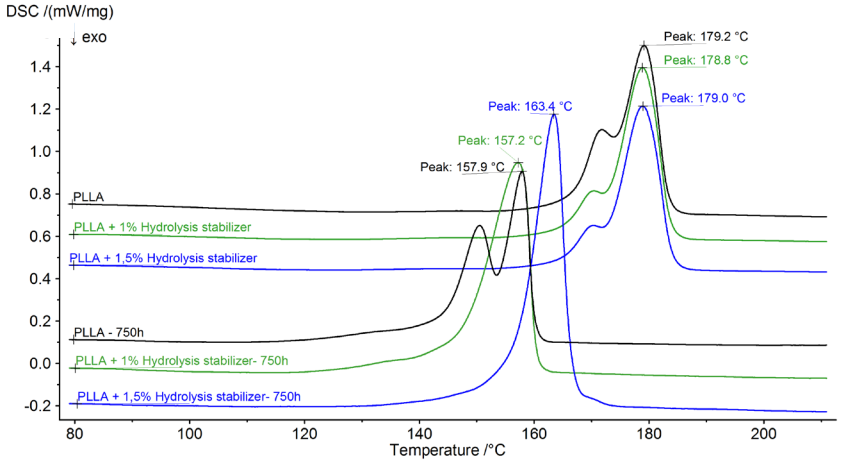

Fig. 4. Influence of stabilization on T_m (0/750 h water storage) – DSC

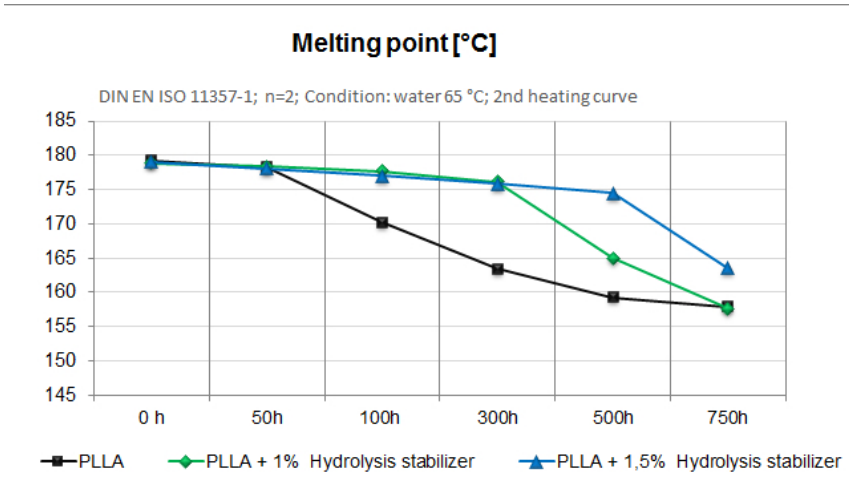

Fig. 5. Influence of stabilization on T_m (0 - 750 h water immersion)

The samples exposed to water exhibit a shift of T_m to lower temperatures (max. $\Delta T = 21°C$) after 750 h. As follows, a higher concentration of the stabilizer offers longer protection against material degradation (1.5 wt%, $\Delta T = 15°C$).

The influence of the water immersion test on T_m from 0 - 750 h (figure 5) illustrates that the PLLA already exhibits a drastic degradation of the molar mass after 50 h in H_2O. This means a complete loss of the material's properties and functional failure of a component. The stabilized PLLAs exhibit the beginning of material degradation after 300 h (1 wt%) and 500 h (1.5 %wt%), whereby the long-term resistance to H_2O is significantly improved.

Resistance to Oxygen, O_2

In order to be able to make any declarations about the stabilizer's effect and the concentration with respect to O_2, isothermal and dynamic OIT measurements were carried out comparatively using the DSC (204 ***F1*** *Phoenix*®). These in turn should allow for conclusions to be drawn about the oxidation behavior due to exothermal reactions with oxygen [1, 10, 11].

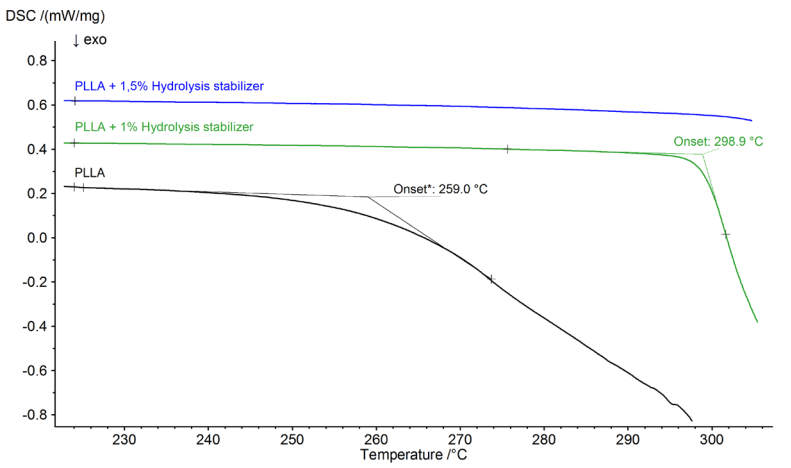

Fig. 6. Influence of stabilization on the Oxidation Induction Temperature

Dynamic OIT

For determination of the Oxidation Induction Temperature (OIT), the sample was initially heated to 200°C (10 K/min) in an open aluminum crucible (sample mass: 13 mg) under a nitrogen atmosphere (flow rate: 20 ml/min). Following an isothermal phase (5 min), the purge gas was switched to O_2 and the sample was dynamically heated to 330°C (10 K/min) at a flow rate of 50 ml/min.

As the exothermal reaction (figure 6) shows, the non-stabilized PLLA is irreparably damaged at a significantly lower temperature (< 260°C). In contrast, the stabilized samples react with oxygen at a temperature >290°C. The subtle differences between concentrations of 1 wt% (> 290°C) and 1.5 wt% (> 310°C) can clearly be seen. This means that the PLLA has been successfully stabilized.

Isothermal OIT

For determination of the Oxidation Induction Time, the samples (15 mg) were dynamically heated to a temperature over T_m (10 K/min) in an open aluminum crucible under a nitrogen atmosphere (flow rate: 20 ml/min) and, beginning at 225°C, isothermally purged with O_2 (flow rate: 50 ml/min, 50 min). The time from the first contact

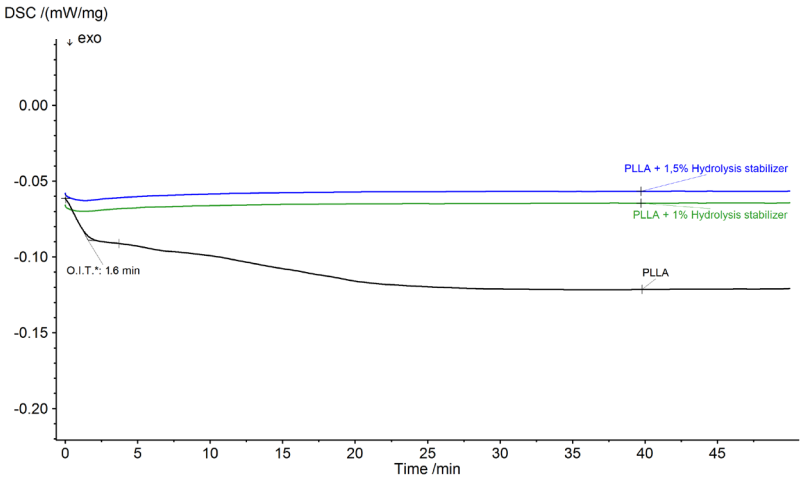

Fig. 7. Influence of stabilization on the Oxidation Induction Time

with O_2 until the start of oxidation was measured [2].

Fig. 7 shows that the performance of pure PLLA against O_2 can be improved by using hydrolysis stabilizers. Compared to the stabilized samples, PLLA exhibits an oxidative reaction already after a short time (OIT = 1.6 min) and is irreparably damaged.

The two stabilized samples (1 - 1.5 wt%), in contrast, exhibit no oxidative reaction.

Summary

The resistance of PLLA to O_2 and H_2O can be prolonged with the help of hydrolysis stabilizers. The additive protects a material – when subjected to external factors – against molecular degradation and therefore also against the loss of material's properties. Even the smallest of differences in concentration (0.5 wt%) can influence the material properties (impact strength, flowability, degree of crystallization) and determine the long-term stability and the life span depending on the application. Target-oriented metering of expensive additives additionally offers possible savings in terms of material costs.

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Fast, Simple and Precise: DSC and *Peak Separation* for the Identification of Polymers in Packaging Films

Claire Strasser, Scientific & Technical Communication

Fig. 1. *Concavus* crucibles with slide-in lids, which ensures optimum contact between sample and crucible

From transparent rigid films that keep sliced sausage and cheese fresh for longer, to stable yogurt cups to colorful, flexible coffee packaging, composite films have become indispensable in the packaging industry. Depending on the application, these highly developed products may need to be oxygen-tight, transparent or printable and possess a certain flexibility and/or stability. Such properties can only be achieved through the use of a variety of components, such as multiple polymer layers. To this end, polymers are in turn selected according to their own properties.

For the identification of individual polymers in a multi-layer film, DSC has proven itself in the packaging industry as a fast and easily accessible method.

In the following example, a commercially available composite film was investigated by means of the DSC 204 ***F1*** *Phoenix*®. The sample was prepared in the *Concavus* crucible and evenly pressed onto the crucible bottom by means of a slide-in lid (figure 1) which was specially developed for measurements on very thin samples such as films.

Figure 2 shows the results of the DSC measurement from the 1st and 2nd heating runs. In both heating runs, multiple overlapped peaks were detected between 108°C and 121°C. This indicates the presence of different polymers; the temperature range here is typical for various low-density polyethylene types.

In the 1st heating, a peak at 176°C was additionally detected which indicates the presence of EVOH (polyethylene vinyl alcohol). EVOH is also known as a barrier plastic, and is widely used in the packaging industry due to its good impermeability to substances such as oxygen. Its melting temperature is dependent on its ethylene content; a melting temperature of 176°C corresponds to an ethylene content of between 35 mol-% and 38 mol-% [1]. In the 2nd heating, the peak at 176°C is shifted to a lower temperature (159°C). This shift is probably due to the melting of a mixed phase formed between polyethylene and EVOH. The broad effect between 230°C and 280°C will be investigated in more detail in the following.

For this, the composite film was separated into two layers: a flexible, aluminum-colored film and a second, thinner, printed film (see figure 3). Between the two layers was an additional paper layer.

The two films on either side of the paper layer were measured separately from one another. The DSC curves are presented in figure 4.

The printed film (blue curve) – except for the peak at 254°C (figure 2) – exhibits the same effects as the composite material as a whole. In contrast, the aluminum-colored film (black curve) produces only one peak, at 255°C (1st heating) and 248°C (2nd heating), respectively. This temperature range is typical for the melting of PET.

With these results, the following can be concluded about the composition of the composite film: The thinner, printed film consists of different polyethylene types as well as EVOH; the aluminum-colored one is PET. The appearance of the PET layer in terms of color indicates an aluminum coating which may be used, for example, as a light shield in packaging [2]. The aluminum melting peak (660.4°C) is outside the measured temperature range and was therefore not detected.

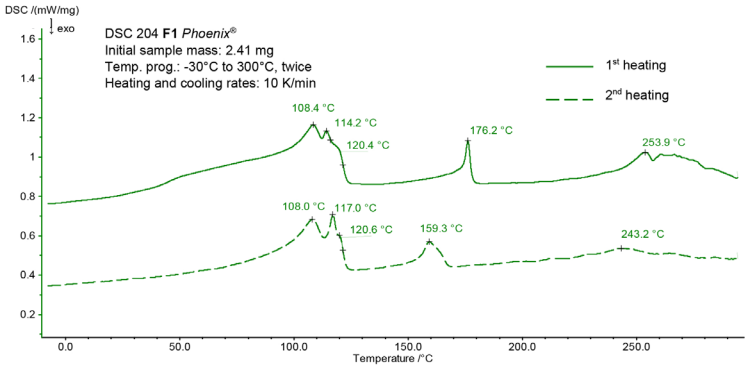

Fig. 2. DSC measurement on a commecially available packaging film (all layers) to 300°C

Fig. 3. Individual films from the multi-layer film

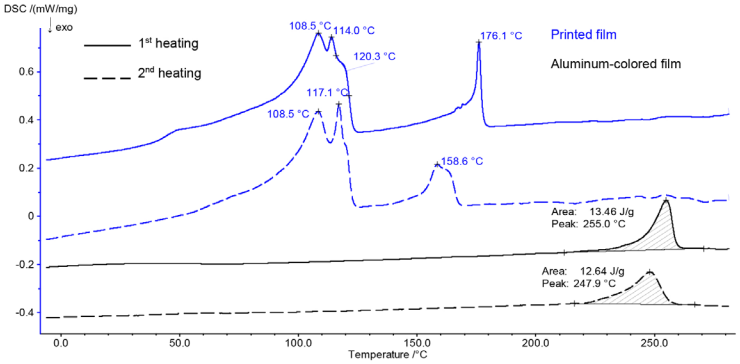

Fig. 4. DSC measurement on the individual films of the multi-layer film. Each individual film was heated twice between -30°C and 300°C at 10 K/min.

In order to be able to clearly identify the three overlapping peaks between 108°C and 121°C, the DSC curve from the 2nd heating (figure 4, dotted line) was imported in the *Peak Separation* software program. *Peak Separation* allows for the presentation of experimental data in the form of the additive overlapping of peaks. This program offers different curves types such as Pearson, Gauß, Cauchy, etc. Here, the Fraser-Suzuki curve progression along with a mixture of the Fraser-Suzuki- and asymetrical Cauchy curve progresssion was selected. By applying these profiles to the measured DSC curve, it becomes possible to mathematically separate the overlapping peaks.

Figure 5 shows the results of the peak separation. Four calculated peaks can be related to the experiment's DSC curve (blue dotted line). The peaks at 108°C, 118°C and 120°C are typical for different low-density polyethylene types (PE-LD, PE-LLD).

An additional peak at 92°C (orange curve) can be attributed to the melting of small crystallites.

The correlation coefficient between the sum of the four calculated curves and the measured curve is determined to be 0.999 and thus confirms the good fit of the calculated endothermal peaks to the measured data.

Summary

DSC measurements yield valuable information on the composition of packaging films. These complex materials consist of different layers, which can sometimes be identified with just a single DSC measurement. The packaging shown in our example consists, at a minimum, of PET, EVOH and several polyethylene types of different densities.

The melting ranges of the different polymers often lie close together. However, complete separation of the peaks and/or precise material characterization can be achieved by means of careful sample preparation and the application of the *Peak Separation* software.

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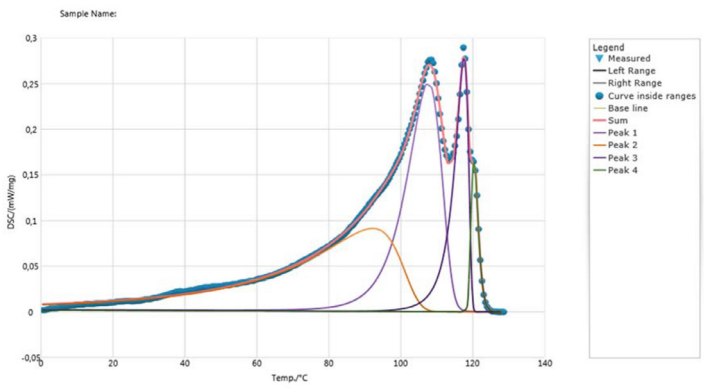

Fig. 5. Peak separation of the 2nd heating curves. Dotted blue curve: measured data, red curve: sum of the four calculated curves (light purple, orange, dark purple and green curves).

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Event	Date	Location
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Thermal Analysis Conference TAC 2017	Apr 10 - 12, 2017	Lincoln, UK
Analitika Expo 2017	Apr 11 - 13, 2017	Moscow, Russia
26. Kunststoffkolloquium Leoben 2017	Apr 20 - 21, 2017	Leoben, Austria
Ceramics Expo 2017	Apr 25 - 27, 2017	Cleveland, OH, USA
ANTEC 2017	May 8 - 10, 2017	Anaheim, CA, USA
Dispersion Days 2017	May 15 - 17, 2017	Selb, Germany
2nd Int. Conf. on Technical Ceramics	May 16 - 18, 2017	Teheran, Iran
Plastpol 2017	May 17 - 20, 2017	Kielce, Poland
SAMPE 2017	May 22 - 25, 2017	Seattle, WA, USA
SICOMP 2017	Jun 1 - 2, 2017	Piteå, Sweden
JTACC-V4	Jun 6 - 9, 2017	Budapest, Hungary
22. Kalorimetrietage Braunschweig	Jun 7 - 9, 2017	Braunschweig, Germany
FIP 2017	Jun 13 - 16, 2017	Lyon, France
ICMAT 2017	Jun 18 - 23, 2017	Suntec City, Singapore
SECAT 2017	Jun 26 - 28, 2017	Oviedo, Spain
PPS 2017	Jun 26 - 29, 2017	Dresden, Germany
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ECCMR 2017	Aug 28 - 31, 2017	Munich, Germany
Composites Europe 2017	Sep 19 - 21, 2017	Stuttgart, Germany

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