WHITE PAPER

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Powerful Database Allows for Polymer Identification by Means of DSC with a Single Click

Martin Doedt, Dr. Alexander Schindler and Dr. Tobias Pflock

DSC (Differential Scanning Calorimetry) is one of the most frequently employed methods in polymer analysis and is used for identification, failure analysis and quality control for all plastics available on the market. Through the integration of a comprehensive material database by the Kunststoff-Institut Lüdenscheid, Germany – with the DSC curves for currently 600 commercially available polymers – into the novel *Identify* curve recognition software, these polymer applications have now been significantly simplified for DSC users. Along with automatic, user-independent evaluation of DSC measurements by means of *AutoEvaluation*, this yields considerable advantages like faster classification and more meaningful interpretation of the measurement results.

DSC analyses have been used for identification of unknown materials for many years [1]. Comparison of thermal property values such as glass transition temperatures and melting temperatures is usually carried out by means of literature values. This is often time-consuming and yields less information than a direct comparison of DSC curves.

In many other analytical fields, such as infrared spectroscopy or mass spectroscopy, it has been customary for decades to automatically identify unknown samples or impurities by comparison with reference spectra from databases with the help of evaluation software. Such possibilities had not been available in DSC analysis so far. This is because, first of all, there are less features available for identification than there are in, for example, an IR spectrum; and secondly, because of the fact, that the thermal property values of plastics vary with their structure and composition, even if the base polymer is nominally the same.

With the continuous development of new polymers and polymer blends, the number of overlapping thermal property values also increases. That is why the comparison of not only numerical values but also of curve shapes is gaining more and more importance. Simultaneously, there is a growing need for automatic evaluation of measurement results and automatic release or blocking of charges in the routine application of analytical instruments; for example, for incoming goods inspection. For both automated procedures and individual interpretations of thermograms by trained and experienced users, significant simplifications can be expected through the use of databases, thus saving time and money.

Such a database for the polymer field has now been developed at the Kunststoff-Institut Lüdenscheid (KIMW [2]), allowing for easier, differentiated comparison of DSC curves for known and unknown polymers with the reference curves for currently 600 commercially available polymers [3]. It can be integrated into the *Identify* [4, 5] curve recognition system within the *Proteus*® software by NETZSCH Gerätebau GmbH. This allows for faster and more accurate determination in the analysis of unknown samples.

Figures 1a and 1b demonstrate how a DSC curve for an unknown polymer is identified by means of *Identify* and the KIMW database: First, autonomous evaluation of the curve by means of *AutoEvaluation* [4, 5] is carried out without any intervention on the operator's part, followed by the clear identification based on the detected effects of glass transition (at approximately 30°C) and melting (peak temperature at 179.2°C). The hit list shown on the left of figure 1b refers to measurement and literature data from the database, where the calculated "similarity" – which ranges from 0% to 100% – serves as a relative measure

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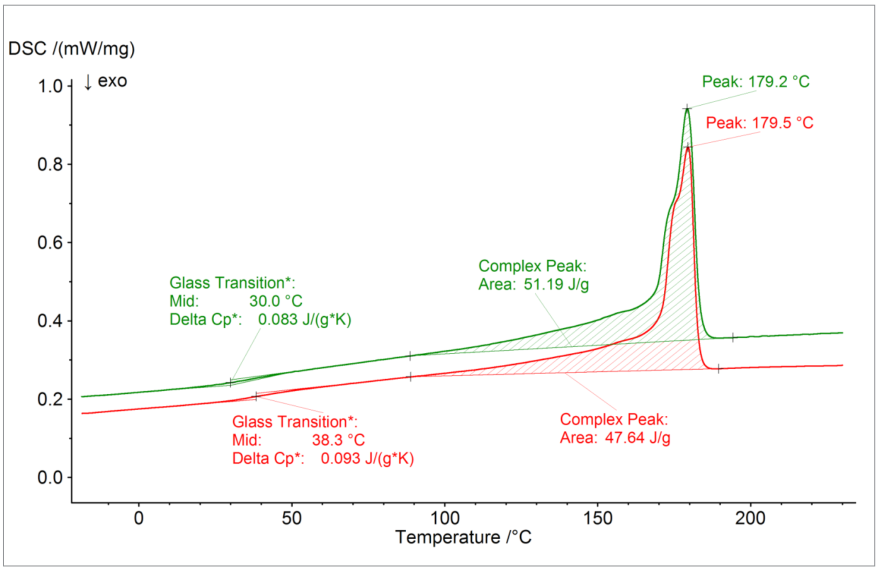
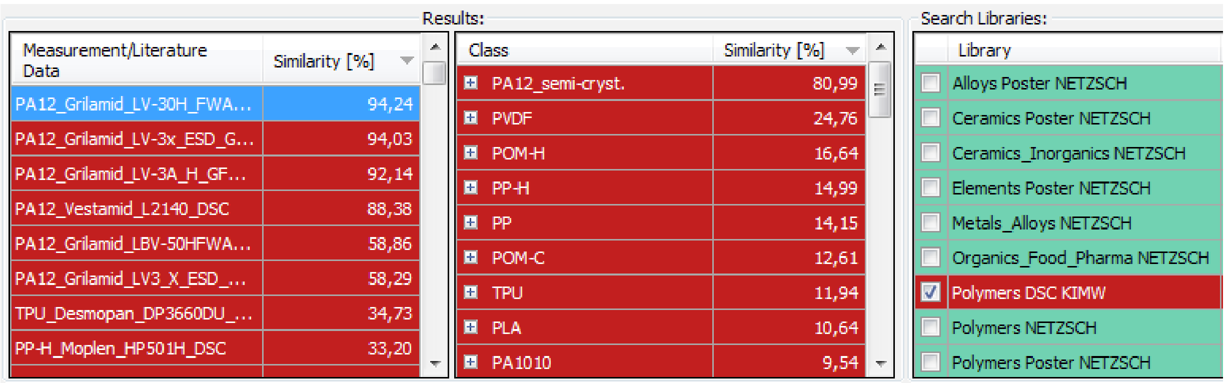


1a Comparison of the DSC curve of an unknown polymer (green) with the most similar database curve (red) which represents a measurement of "PA12 Grilamid LV-30H FWA GF30" (see figure 1b).



Results:

Measurement/Literature Data	Similarity [%]
PA12_Grilamid_LV-30H_FWA...	94,24
PA12_Grilamid_LV-3x_ESD_G...	94,03
PA12_Grilamid_LV-3A_H_GF...	92,14
PA12_Vestamid_L2140_DSC	88,38
PA12_Grilamid_LBV-50HFWA...	58,86
PA12_Grilamid_LV3_X_ESD_...	58,29
TPU_Desmopan_DP3660DU_...	34,73
PP-H_Moplen_HP501H_DSC	33,20

Class	Similarity [%]
PA12_semi-cryst.	80,99
PVDF	24,76
POM-H	16,64
PP-H	14,99
PP	14,15
POM-C	12,61
TPU	11,94
PLA	10,64
PA1010	9,54

Search Libraries:

Library
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1b Results of the *Identify* database search for the unknown polmyer from figure 1a (left and middle column); for explanation see text). The selection of librariers can be seen on the right.

for resemblance. Additionally, there are comparisons with classes; i.e., defined groupings of database entries (see middle of figure 1b). It can clearly be seen that the unknown polymer is a semi-crystalline polyamide of type PA12, whereupon the similarity values also reflect considerable differences between different representatives of the same type. It is significantly less likely to be any other polymer type than PA12.

Generally, it should be noted that all DSC curves were heated at 10 K/min to above the melting point, cooled back at 10 K/min and then reheated at 10 K/min to above the melting point [6]. Since the results of the second heatings are the most meaningful due to the defined thermal history [1], only these DSC curves were included. The masses of all polymer samples amounted to approximately 10 mg; all DSC measurements were carried out with the DSC 214 *Polyma*.

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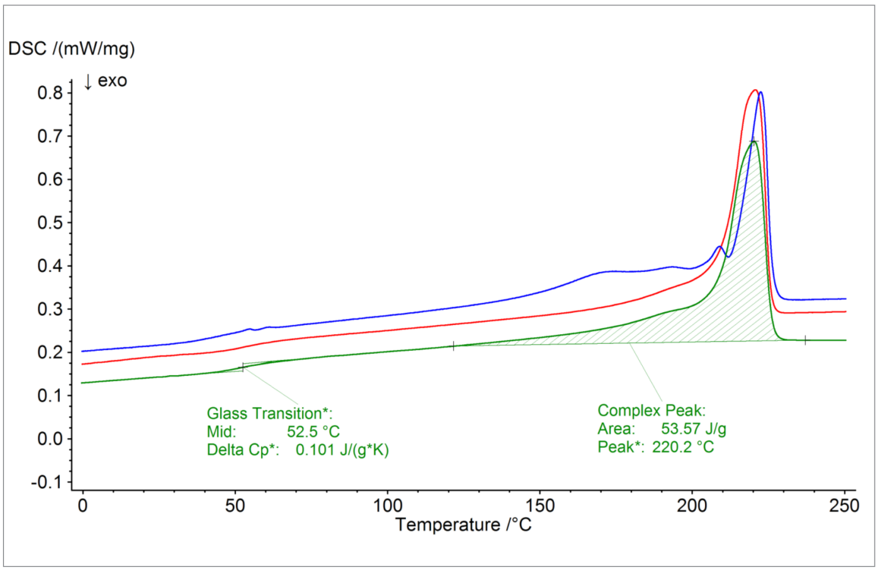
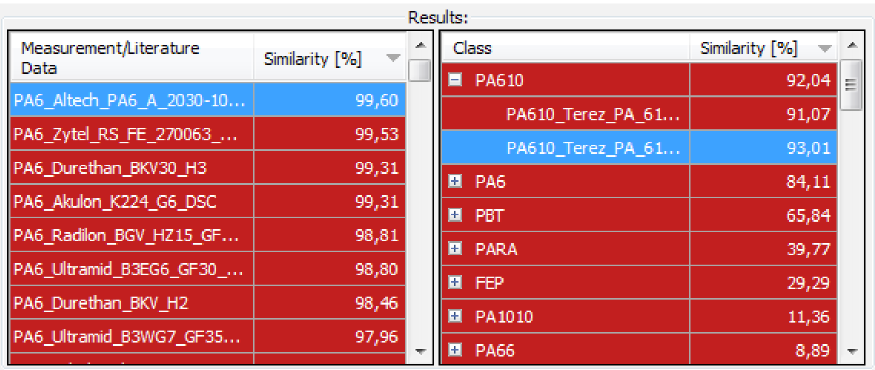


2a Comparison of the DSC curve of an unknown polymer (green) with the most similar database curve (red; measurement of "PA6 Altech PA6 A 2030-109 GF30") and the database curve of "PA610 Terez PA610 GF30 H ECO" (blue), see figure 2b.



Results:

Measurement/Literature Data	Similarity [%]
PA6_Altech_PA6_A_2030-10...	99,60
PA6_Zytel_RS_FE_270063_...	99,53
PA6_Durethan_BKV30_H3	99,31
PA6_Akulon_K224_G6_DSC	99,31
PA6_Radilon_BGV_HZ15_GF...	98,81
PA6_Ultramid_B3EG6_GF30_...	98,80
PA6_Durethan_BKV_H2	98,46
PA6_Ultramid_B3WG7_GF35...	97,96

Class	Similarity [%]
PA610	92,04
PA610_Terez_PA_61...	91,07
PA610_Terez_PA_61...	93,01
PA6	84,11
PBT	65,84
PARA	39,77
FEP	29,29
PA1010	11,36
PA66	8,89

2b Results of the *Identify* database search for the unknown polymer from figure 2a.

The second example demonstrates that, due to its efficient, effect-based algorithms, *Identify* is even capable of distinguishing between polymers with very similar characteristic temperatures: The database comparison with the unknown DSC curve shown in figure 2a yields as a result some DSC curves measured on PA6 which exhibit a very high similarity to the unknown DSC curve (see figure 2b). The PA610 curves which are also listed in the database show lower similarity values due to slightly different glass transition temperatures and melting peak temperatures. In addition, database curves can be very easily retrieved and overlapped within the user interface in *Identify*, allowing for a purely visual comparison. This extra information is particularly revealing in the case of the PA6 and PA610 curves: In contrast with PA6, the PA610 curves exhibit a distinct shoulder at approximately 170°C along with an additional small melting peak at approximately 210°C.

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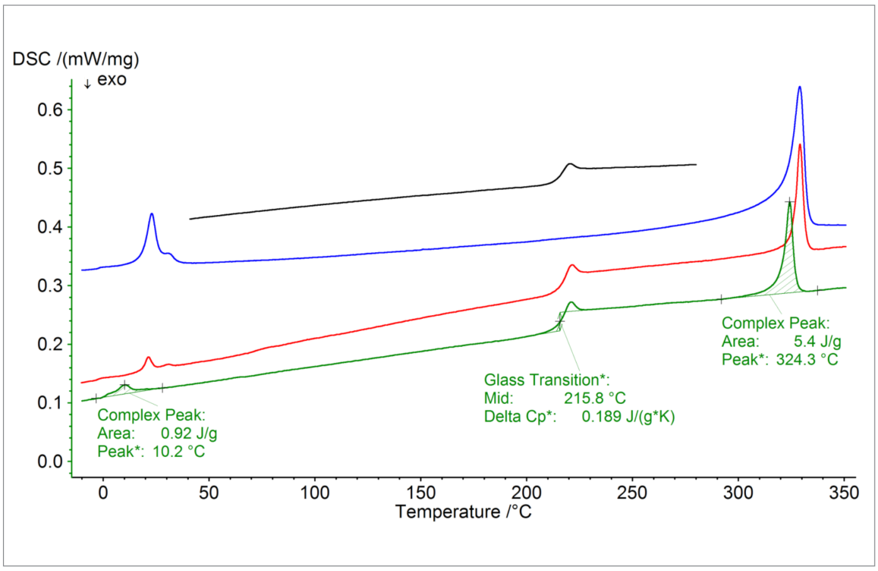

3a Comparison of the DSC curve of an unknown polymer (green) with the most similar database curve (red, measurement of "PEI-PTFE Luvocom 11067223", see figure 3b), and with typical database curves for PTFE (blue) and PEI (black). The curves were staggered in the y-direction for better illustration.

Results:

Measurement/Literature Data	Similarity [%]
PEI-PTFE_Luvocom_1106-72...	66,72
PTFE_5-15G_DSC	54,51
PTFE_1-24G_DSC	54,14
PESU-PTFE_Ultrason_KR_41...	48,28
PTFE_Algoflon_L203_DSC	45,35
PEI_Ultem_1000_DSC	43,75
PEI_Ultem_2312_GP30_DSC	43,72
PEI_Ultem_AUT_200_DSC	42,98

Class	Similarity [%]
PTFE	51,33
PEI	27,98
SEBS	18,99
PA6-6T	17,78
PPA	17,31
PESU	15,70
LCP	14,44
PEEK	13,40
TPS	11,90

3b Results of the *Identify* database search with regard to the unknown polymer from figure 3a (see text)

The third example clearly demonstrates how measurements on polymer blends can also be automatically evaluated, interpreted and classified with the help of *Identify* and the KIMW database. In the unknown DSC curve, three effects were automatically detected and evaluated (see figure 3a): An endothermal effect in the temperature range between approximately 0°C and 30°C, a glass transition at approximately 216°C and another endothermal (melting) effect at a peak temperature of 324°C. The database search yields a PEI-PTFE polymer blend as the most similar hit and furthermore, that the unknown DSC curve approximately corresponds to a superposition of the DSC curves of the pure PEI and PTFE polymers (see figure 3b). The latter can be handled by *Identify* by adjustment of the algorithm [3] that users can also select themselves. Further, the database search can be limited to, for example, certain temperature ranges and the results can be filtered according to various criteria such as measurement conditions. Incidentally, the endothermal effect in the range of room temperature shown in figure 3a can be attributed to a structural transition of PTFE, while the glass transition of PTFE, which takes place at approximately 120°C to 130°C, can typically not be seen in the DSC signal.

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Since adding DSC curves to one's own libraries and classes is very easy, *Identify* can be applied not only for material recognition and failure analysis, but also for quality control [4, 5]. For these applications, deviations in the characteristic effects such as temperature shift, or the presence of additional effects – as with the example shown in figure 3 – allow for the clear classification of DSC curves and also recognition of possible extraneous phases. Furthermore, fillers, which are often contained in polymers, result in changes to the DSC signal: Although fillers typically exhibit no characteristic DSC effects of their own, they do change the magnitude of the effects in the polymer portion (e.g., the mass-specific melting enthalpy), which *Identify* can also use for distinguishing DSC curves.

The comprehensive polymer database of the Kunststoff-Institut Lüdenscheid and the new *Identify* database software by NETZSCH-Gerätebau thus open the door to a new level of thermal analysis: The knowledge from several hundred database measurements becomes accessible to a wide group of users – and the application of DSC technology becomes even more prevalent and further simplified.

Literature

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The Authors

Martin Doedt has built up the material database for different analytical methods at the Kunststoff-Institut Lüdenscheid, where he is manager of the department material and failure analyses.

Dr. Alexander Schindler has worked in the fields of experimental physics, thermal analysis and thermophysical properties for over 18 years. At NETZSCH, he has been employed in the Applications Laboratory as well as in the Hardware and Software Development. He is a known expert in thermal characterization methods and their applications.

Dr. Tobias Pflock has been responsible for the business development of the polymer market at NGB. He has a PhD in physics and a strong background in dynamic mechanical analysis as well as other analytical techniques for polymer testing.

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