

APPLICATION NOTE

Polymer Mixtures – Identify

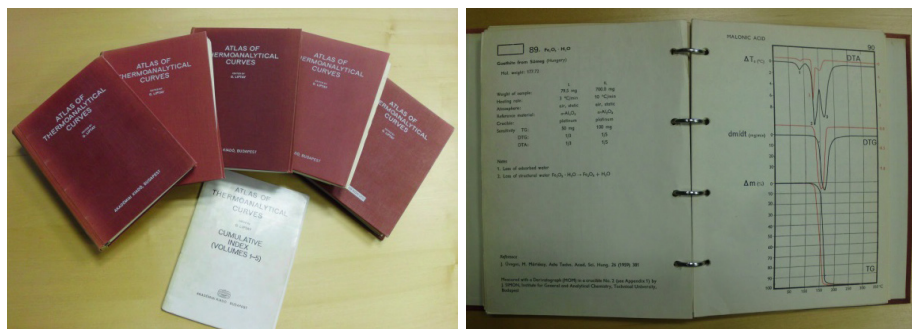


Identification of Polymer Mixtures (PE/PP) by Means of *Identify*

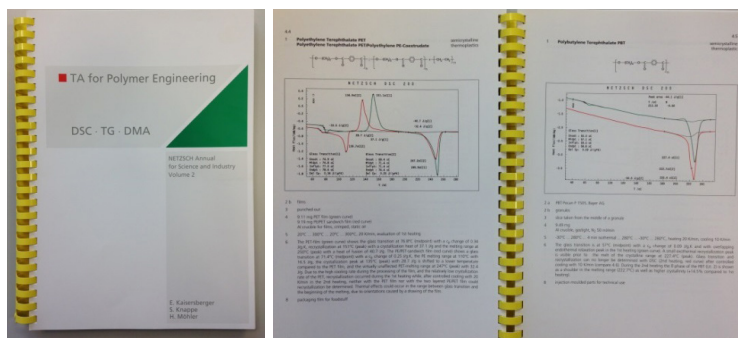
Dr. Ekkehard Füglein and Erwin Kaisersberger

Introduction

Comparison of one's own measurement results with results well known from literature has always been an important part of scientific work for analysts; that is why such comparisons have, of course, also been practiced in thermal analysis – long before the increased use of computers and the existence of on-line databases. In the 1970s, G. Liptay and colleagues, among them Judit Simon, created the five-volume "Atlas of Thermoanalytical Curves" (figure 1), in which more than 400 inorganic and organic solids were investigated and the results published along with the measurement conditions and a brief interpretation [1].

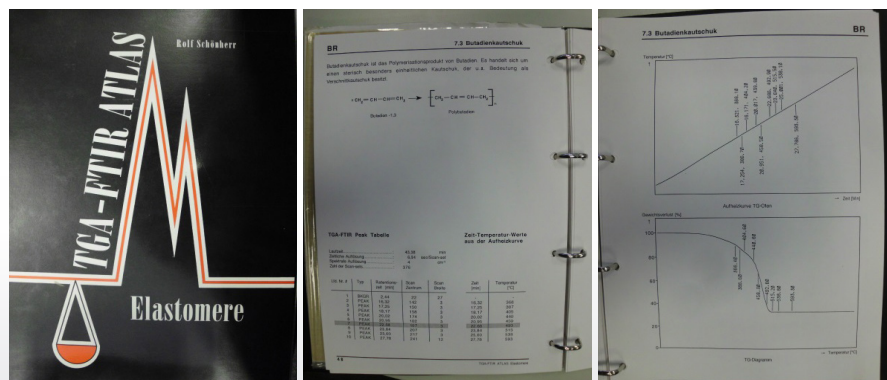


1 G. Liptay, "Atlas of Thermoanalytical Curves"



2 H. Möhler et. al., "NETZSCH Annuals for Polymer Characterization"

In the early 1990s, H. Möhler et al. [2] published several volumes as a compilation of measurement results using various thermoanalytical methods for polymer characterization (figure 2).



3 R. Schönherr, "TGA-FTIR-Atlas – Elastomers"

In 1996, R. Schönherr introduced an atlas (figure 3) including thermogravimetric and infrared spectroscopic results on 20 common elastomers [3].

In addition to quantifying the gases evolved, combination of the methods of thermogravimetry and infrared spectroscopy allows for their identification due to the simultaneously registered gas spectra. Via the common time basis, the individual spectra from the infrared spectrometer can be related to the corresponding thermogravimetric mass-loss steps for any given point in time. Much like a fingerprint, the illustrative comparison can yield information on the substances released, even if the individual absorption bands cannot each be related to the corresponding chemical functionality group.

These lists of printed collections of results – which are certainly not exhaustive – have served many analysts well in the past. They all, however, have the considerable disadvantage of not allowing for a direct software-based comparison of the data. For spectroscopic methods like FT-IR or mass spectrometry (MS), such result comparisons have long been part of common evaluation routines within the software. In the field of thermal analysis, however, such library comparisons have been sorely lacking so far.

This gap can now be bridged with the latest development in the NETZSCH *Proteus*[®] software. Comparative thermo-analytical data recorded under identical measurement conditions now allows – for the first time in thermal analysis – for the software-based identification of polymers, based on a direct curve comparison and the determined characteristic glass transition or melting temperatures [4][5].

Materials and Methods

The TGA-FT-IR measurements on ethylene vinyl acetate (EVA) were carried out using a NETZSCH *Perseus* TG 209 *Libra F1* apparatus. The sample (8.750 mg) was transferred to an aluminum oxide crucible and heated at a rate of 10 K/min to 600°C. Nitrogen (5.0) was used as a carrier gas at a flow rate of 40 ml/min. The gas detection cell inside the FT-IR spectrometer was heated to 200°C and the data acquisition software of the FT-IR recorded one spectrum every 20 seconds. Identification of the evolved gases was carried out using the NIST-EPA database together with Bruker Optics OPUS software.

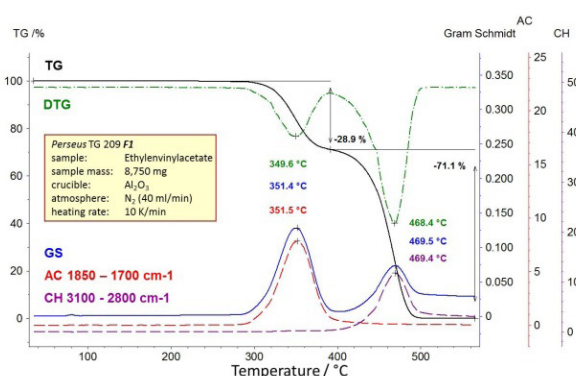
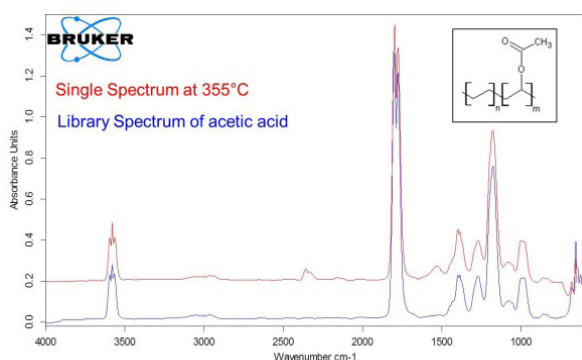
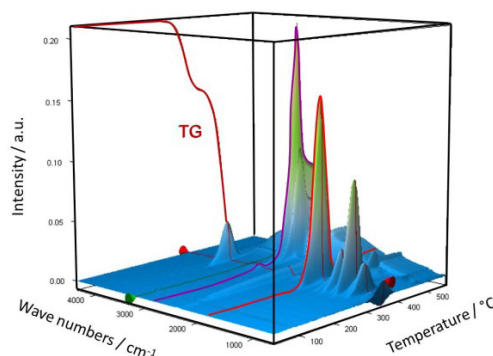
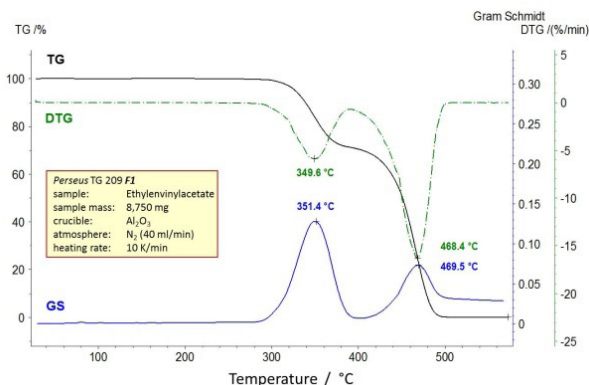
The melting behavior of the polymer samples was studied using the NETZSCH DSC 214 *Polyma*. Aluminum pans (NETZSCH *Concavus*) with pierced lids were used to heat, cool, and reheat the sample mixtures at a rate of 10 K/min. The two heating segments were each run to 200°C which is above melting of both samples, PE and PP. The second

heating for each mixture was used to evaluate the melting enthalpy. Each crucible in the series of low-density polyethylene and polypropylene mixtures was prepared using one piece from each sample in the appropriate proportions to achieve a total mass of 10.05 mg (± 0.10). Each sample of each mixture was measured using four repeat measurements. Therefore, the symbols given in figure 8 each represent mean values of five measurements.

Results and Discussion

Simultaneously to the work of R. Schönherr, Bruker Optics (Ettlingen) and NETZSCH-Gerätebau (Selb) offered a commercial solution for the TG-FT-IR coupling instrument he described. This then allowed for continuous communication between the two data acquisition systems where individual measurement data could be transferred to the measurement software for the other instrument and also evaluated there. Thanks to this software communication, the temperature program of the thermobalance now served as a common basis for data. This yielded a considerable benefit to the user: It was no longer necessary to conduct a time-consuming conversion of the gases' point of release in the thermobalance and correlate this with the point in time that the corresponding IR spectra were detected. Both datasets can be presented and evaluated scaled to temperature. As an example, figure 4 shows the individual steps for evaluation of the measured data for the pyrolysis of ethylene vinyl acetate (EVA) and for identification of the gases released. The signal known as the Gram-Schmidt trace is transferred into the thermogravimetric software from the spectrometer software, reflecting the changes in the total absorption intensities (top left quadrant in figure 4). Shown on the top right of figure 4 is a three-dimensional temperature-scaled presentation of all IR spectra. The corresponding mass-loss curve are superimposed onto the back surface of the cube. To characterize the substances released, individual spectra are extracted from this 3-dimensional presentation and compared with reference spectra from gas phase libraries.

The result of the library comparison of the IR spectrum detected at 355°C is shown on the bottom left in figure 4. The measured spectrum (red) is in quite good agreement with the absorption bands for acetic acid. By integrating the characteristic absorption range for acetic acid from 1700 to 1850 cm^{-1} – i.e., by slicing the three-dimensional presentation parallel to the temperature axis – one obtains the temperature-dependent course of these absorption intensities. By directing this trace back into the



4 Pyrolysis of ethylene vinyl acetate (EVA):
 top left: TGA-DTG measurement results (black and green) with the additional Gram-Schmidt trace (GS, blue)
 top right: temperature-scaled three-dimensional presentation of all IR spectra with the additional TGA curve
 bottom left: comparison of individual spectrum (red) measured at 355°C with the library spectrum of acetic acid (blue)
 bottom right: TGA-DTG-GS results with the traces for the absorption area 1700 - 1850 cm⁻¹ (acetic acid) and the absorption area 2800-3100 cm⁻¹ (hydrocarbon chain)

thermogravimetric software (figure 4, bottom right), it can be confirmed that the mass-loss step at 350°C (DTG) is due solely to the release of acetic acid (dashed red curve) while in the second mass-loss step at 468°C, gases are formed as would be expected for degradation of unbranched hydrocarbon chains (dashed violet curve). This was confirmed by means of a reference spectrum for polyethylene (PE) from a self-established database (not shown here). The maximum absorption intensities for this are in the range from 2800 to 3100 cm⁻¹. The two mass-loss steps add up to 100%; therefore, the entire polymer sample underwent pyrolysis without any residues.

This example shows how a complete thermogravimetric analysis combined with spectroscopic identification of the gases released can be realized. The gaseous products released from the sample in both mass-loss steps can each be related to one component; the temperature-dependent intensity course of these components (the trace) proves that no overlapping or mixing is occurring and therefore each mass-loss step can be exclusively related to the

identified species. The gases released can thus be quantified by means of the thermobalance and identified with the help of infrared spectroscopy.

As already mentioned, such comparisons of one's own results with the reference spectra in databases or spectra libraries have been commonplace for many years in a lot of analytical areas. The example discussed above clearly showed how helpful and targeted such software comparisons can be. These were, however, limited in the above example to the spectroscopic portion of the evaluation; analogous database comparisons for the methods of thermal analysis had not yet existed. There were various reasons for this. While, for example, in infrared spectroscopy the wave numbers of an absorption band are characteristic for a certain type of bond, the corresponding length of bond and their chemical environment, the results of a thermoanalytical measurement are heavily influenced by sample preparation, sample amount, crucible material, heating rate and purge gas atmosphere.

APPLICATIONNOTE Identification of Polymer Mixtures (PE/PP) by Means of *Identify*

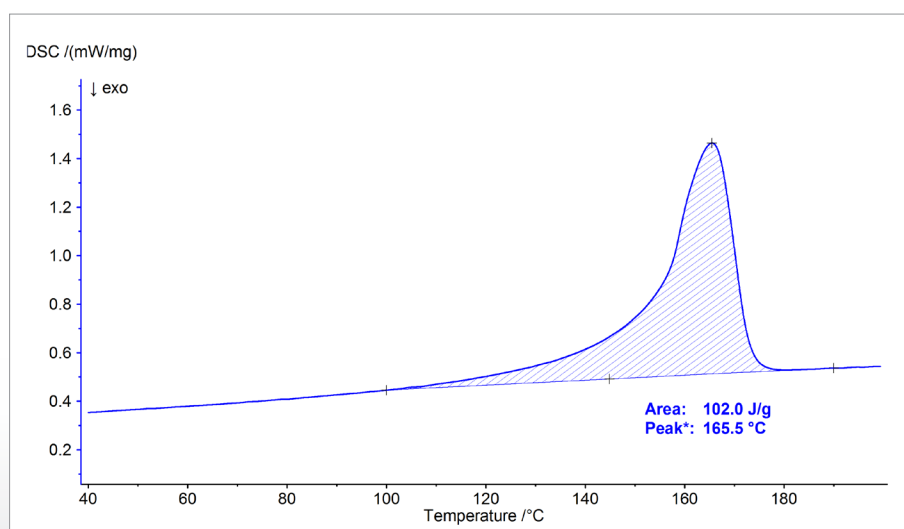
Thermal analysis comprises a variety of standardized measuring techniques and methods. A well-known introduction to the methods of thermal analysis can be found in W.F. Hemminger and H.K. Cammenga [6]. Recommendations on the use and definition of the individual methods are summarized in DIN 51005 [7]. The most widespread and most often used method is differential scanning calorimetry (DSC) and shall be given a closer look in consideration of database comparisons. Please refer to the corresponding literature [6][8] for operational function and setup; a compilation of numerous measuring instructions can be found in DIN EN ISO 11357 [9].

Polymer analysis is probably the application field in which the DSC method can most often be found. Qualification of material batches, production control based on determination of the melting and crystallization behavior, the degree of crystallinity, the oxidation behavior, the detection of impurities or foreign admixtures, and the development of new material compositions are only some of the issues in polymer applications to which thermal analysis can be applied. Especially for the detection of extraneous materials or for the control of mixtures with targeted manufacturing specifications, the ability to conduct comparisons with databases established especially for this purpose would be very helpful.

A novel database, *Identify* – part of the NETZSCH *Proteus*® evaluation software – shall be introduced here by means

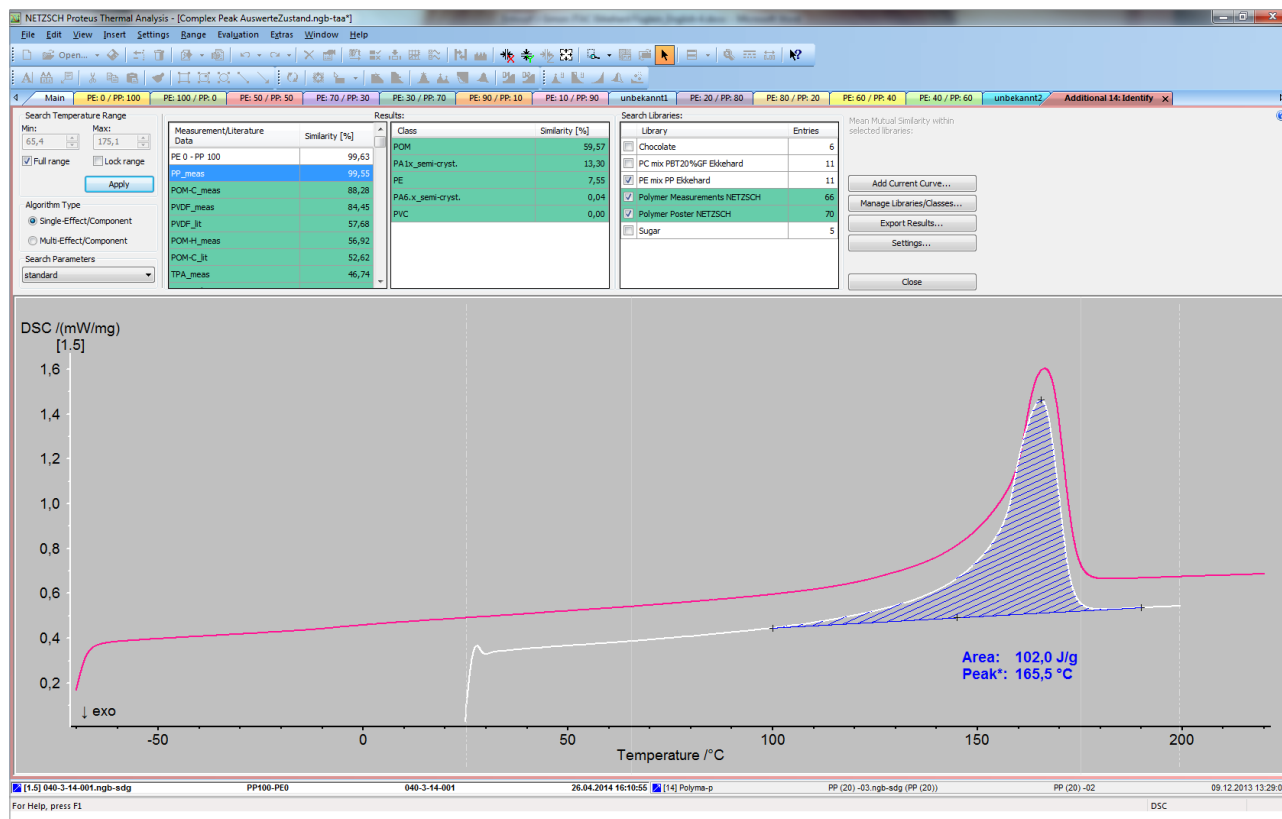
of two examples from the field of polymer analysis. A compilation of important thermoanalytical data such as melting temperature, specific heat capacity, thermal expansion coefficient, density, thermal conductivity and some others is already available for 66 of the most often-used thermoplastic materials, in the form of posters [10], as a book [11] but also as applications for smartphones [12]. The DSC measurement results for these polymer samples form, among others, the basis for the *Identify* database.

The results of a DSC measurement on a polypropylene sample (PP) are depicted in figure 5. Here, 10.125 mg of a PP granulate was inserted into a pierced aluminum crucible and measured in the DSC 214 *Polyma* in two cycles under a nitrogen atmosphere at 10 K/min from 25°C to 200°C each. Shown is the second heating segment, in which the peak area was evaluated along with the peak temperature (165.5°C). It yields the melting enthalpy of the crystalline portions of the semi-crystalline sample at 102.0 J/g. Based on these measurement results, the available results were qualified in a comparison with the *Identify* database and presented with regard to their similarity. The result of this comparison is presented in figure 6. The measured curve (white with blue hatched area) is visually compared with the measurement data available in the database. The magenta-colored curve corresponds to the database entry with the next-highest similarity to the measured curve.



5 DSC results on polypropylene (PP)

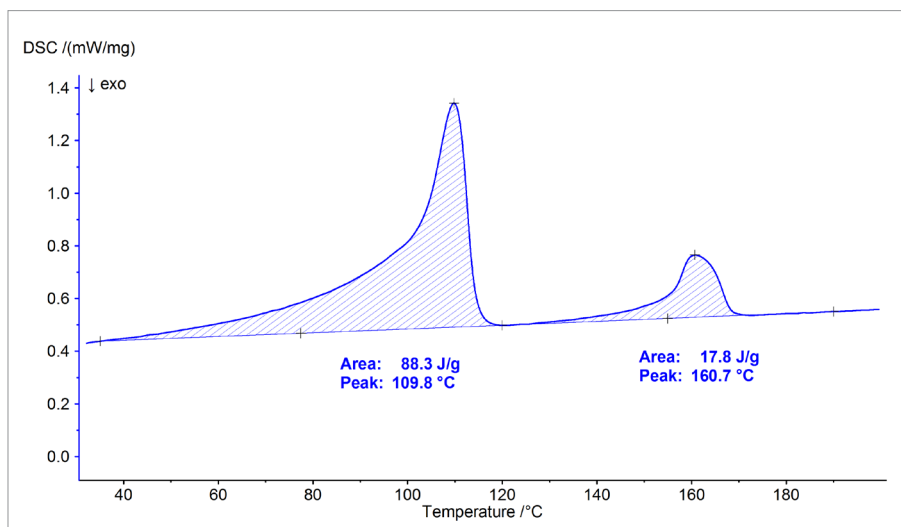
APPLICATIONNOTE Identification of Polymer Mixtures (PE/PP) by Means of *Identify*



6 Comparison of DSC measurement results with the *Identify* database

The most similar measurements are additionally qualified in a list (figure 6, top left). As can be seen, the measured sample has a similarity of over 99% with the datasets of two stored measurements on polypropylene. The following items in this list include further polymers like polyoxymethylene (POM) and polyvinylidene fluoride (PVDF), showing similarities of 88% and 84%, respectively. The similarities are graded primarily on the basis of the values determined. For example, peak temperatures of 168.2°C for POM and of 172.0°C for PVDF are the measurement values stored in the database, which reflects the trend of the aforementioned similarities in comparison with the polypropylene samples (165.5°C) measured here. Along with the peak temperature, also the peak areas (enthalpy), the extrapolated onset, the extrapolated endset, the peak shape, the existence of a glass transition and its step height contribute to the grading of this similarity comparison. Additionally, five different weightings of the measurement data used in the comparison can be carried out.

In the above example, it was shown that the measured polypropylene sample could be identified as such in a comparison with the *Identify* database. In the following example, it shall be shown that the database comparison can be applied not only to single-phase samples but also to sample mixtures. For such purposes, of course, the thermoanalytical impacts on the measured data for various mixtures must be entered into the database. For the determination of an "unknown" mixture ratio of polyethylene (PE) and polypropylene (PP) by means of such a database comparison, eleven mixtures in 10% grading increments (100:0; 90:10; 80:20; etc.) were therefore produced.

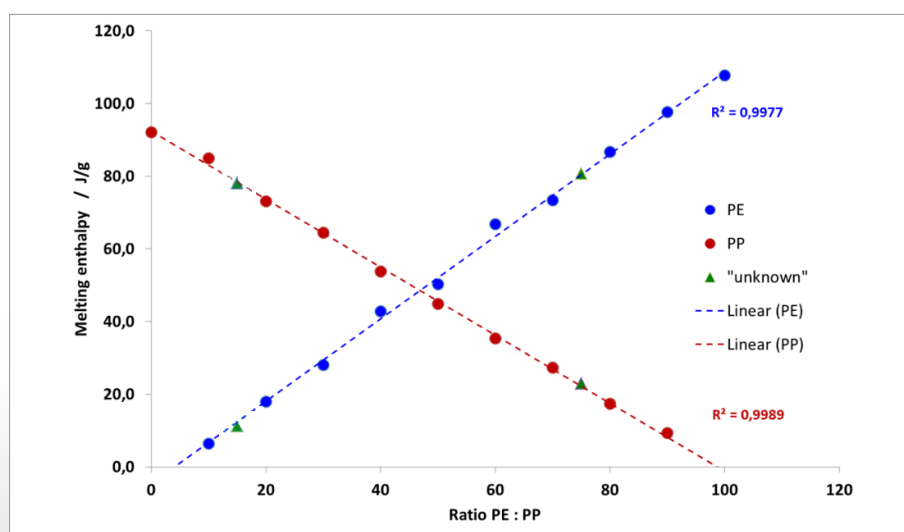


7 DSC results of the melting behavior of a polyethylene-polypropylene mixture at a ratio of 80:20

Figure 7 depicts the results of a DSC measurement on the PE80:PP20 mixture. The melting enthalpy in the temperature range around 110°C represents the polyethylene portion, and the peak area in the temperature range around 160°C represents the polypropylene portion. Corresponding to the change in the mixture ratio, it can be expected that the melting enthalpy in the range around 160°C increases as the polypropylene portion increases, and that the melting enthalpy of polyethylene in the range around 110°C decreases proportionately. The corresponding correlation of the mixture ratio and the melting enthalpy is graphically summarized in figure 8. The symbols each represent a mean value of five measurements.

The thermoanalytical evaluations for all mixture ratios were carried out in grading intervals of 10% and the results were stored in the *Identify* database. For two “unknown” PE-PP mixture ratios of 15:85 and 75:25 (marked as green triangles in figure 8), the relationship discussed above with regard to the melting enthalpy also applies.

A database comparison of the measurement results of the samples with ratios of 15:85 and 75:25 should therefore yield the next-closest two mixture ratios of 10:90 and 20:80 or 70:30 and 80:20 with the highest similarity values.



8 Correlation of the melting enthalpy with the PE:PP mixture ratio (“unknown” mixture ratios marked with triangle symbols at 15:85 and 72:25)

NGB · Application Note 078 · E · 09/24 · Technical Specifications are subject to change.

APPLICATIONNOTE Identification of Polymer Mixtures (PE/PP) by Means of *Identify*

Measurement/Literature Data	Similarity [%]
PE 70 - PP 30	99,04
PE 80 - PP 20	96,82
PE 60 - PP 40	95,73
PE 50 - PP 50	88,75
PE 90 - PP 10	86,78
PE 40 - PP 60	81,59
PE 30 - PP 70	70,36
PE 20 - PP 80	59,90

Measurement/Literature Data	Similarity [%]
PE 20 - PP 80	96,83
PE 10 - PP 90	93,93
PE 30 - PP 70	88,19
PE 40 - PP 60	77,41
PE 50 - PP 50	71,86
PE 60 - PP 40	62,76
PE 70 - PP 30	57,39
PE 80 - PP 20	45,12

9 Results of the database comparison for identification of two PE-PP samples with "unknown" mixture ratios

In figure 9, exactly this expectation was confirmed, thus demonstrating that the *Identify* database can recognize and qualify not only individual substances but also sample mixtures such as the two semi-crystalline samples, low-density polyethylene and polypropylene.

Conclusion

There has long existed a demand for an online database capable of comparing measured thermoanalytical data with library data or values. But no options other than printed collections of thermoanalytical results had ever existed until now.

This work introduced *Identify*, the first thermoanalytical software offering an online comparison of measured DSC data with literature values or data stored in a library.

To demonstrate their high performance, a series of polymer mixtures were created and measured using a differential scanning calorimeter (DSC). The evaluated values for melting enthalpy were used as identification and quantification criteria. A linear correlation was drawn between the polymer content inside the mixtures and the melting enthalpy. Based on this, *Identify* was able to recognize the next-closest mixture ratios from the database with the highest similarity values. It was thereby demonstrated that *Identify* is not only capable of identifying unknown samples by means of a library comparison, but it can also identify the ratio of mixtures.

References

- [1] "Atlas of Thermoanalytical Curves" (TG-, DTG-, DTA-Curves measured simultaneously), Edited by G. Liptay, Akadémiai Kiadó, Budapest, 1976
- [2] (a) "DSC on Polymeric Materials", E. Kaisersberger, H. Möhler, NETZSCH Annual for Science and Industry, Volume 1, @NETZSCH-Gerätebau GmbH, D-8672 Selb, 1991

- (b) "TA for Polymer Engineering", E. Kaisersberger, S. Knappe, H. Möhler, NETZSCH Annual for Science and Industry, Volume 2, ©NETZSCH-Gerätebau GmbH, D-8672 Selb, 1993

- (c) "TA for Polymer Engineering", E. Kaisersberger, S. Knappe, H. Möhler, S. Rahner, NETZSCH Annual for Science and Industry, Volume 3, ©NETZSCH-Gerätebau GmbH, D-8672 Selb, 1994

- [3] "TGA-FTIR Atlas Elastomere", R. Schönherr, Verlag W.K. Schönherr, D-Burgdorf, 1996

- [4] (a) A. Schindler, "Automatic Evaluation and Identification of DSC Curves", *Plastics Engineering*, 2014

<http://www.plasticsengineering.org/ProductFocus/productfocus.aspx?ItemNumber=20498>

- (b) A. Schindler, NETZSCH Application Note 059, "Analysis of 200 Unknown DSC Curves by Means of Identify Using its Polymer Libraries", 2014

- (c) A. Schindler, C. Strasser, Application Note 060, "Stability of *Identify* Database Search Results with Regard to Sample Mass and Heating Rate", 2014

- (d) A. Schindler, NETZSCH Application Note 061, "The *Identify* Database as an Archive for NETZSCH and User Data", 2014

- [5] Füglein E, Kaisersberger E. "About the development of databases in thermal analysis" *J. Therm. Anal. Calorim.* DOI: 10.1007/s10973-014-4381-3

- [6] W.F. Hemminger and H.K. Cammenga, "Methoden der Thermischen Analyse", Springer Verlag Berlin Heidelberg, 1989

- [7] Deutsches Institut für Normung, DIN 51005, "Thermische Analyse (TA) – Begriffe"

- [8] E. Füglein and A. Léon, in "Hydrogen Technology - Mobile and Portable Applications", A. Léon (ed.), Springer-Verlag Berlin Heidelberg, 2008, 501-521

- [9] Deutsches Institut für Normung, DIN EN ISO 11357, "Kunststoffe – Dynamische Differenz-Thermoanalyse (DSC)", parts 1 through 8

- [10] Thermal Properties of Polymers, www.netzsch.com/TPoP

- [11] G. Kaiser, S. Schmölder, S. Pohland, S. Turan, "Handbook Differential Scanning Calorimetry (DSC) on Polymers", @ NETZSCH-Gerätebau GmbH, D-95100 Selb, 2015

- [12] Thermal Properties of Polymers App, www.netzsch-thermal-analysis.com/de/materialien-applikationen/polymere/erste-netzsch-app.html