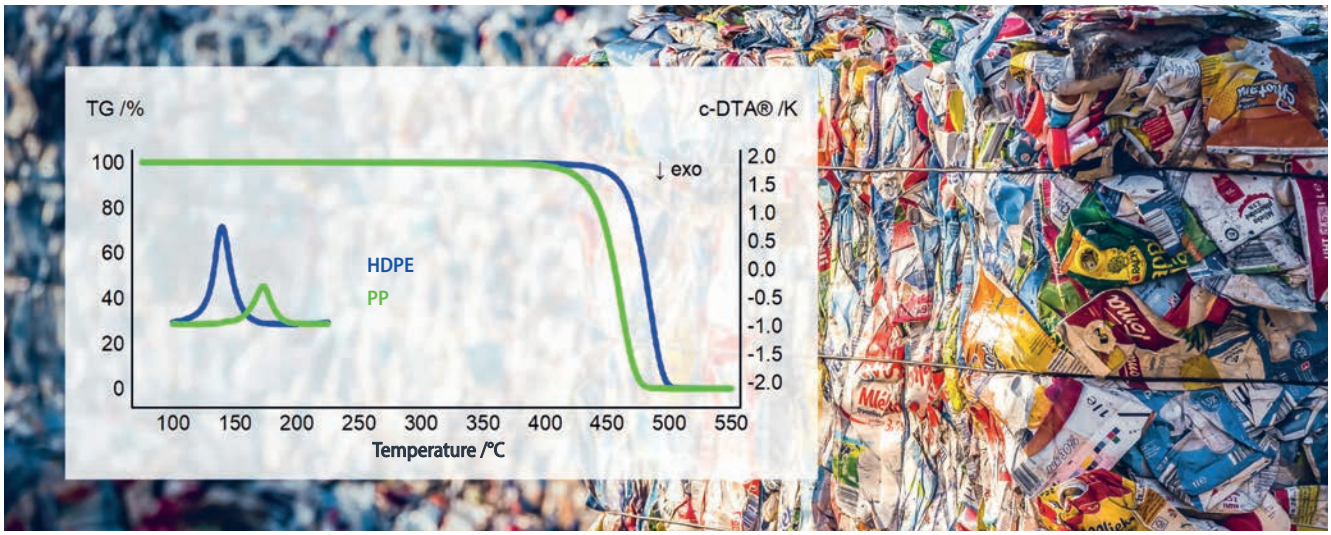
DSC and TGA: Insights into Methods and Applications for Polymer Blends

High-Quality Recyclates and Increased Yields through Thermal Analysis

Thermal analysis methods such as DSC and TGA allow for precise analysis of polymer blends derived from post-consumer waste. DSC distinguishes and quantifies polymers through specific melting enthalpies, while TGA determines decomposition temperatures and identifies non-polymer contaminations. Together, these methods provide an efficient solution for identifying and optimizing recyclates, even in complex material systems.



Ready for recycling: Compressed beverage carton bales. Polymer blends from post-consumer waste can be precisely analyzed using DSC and TGA.

With the increasing demand for high-quality plastic recyclates, the use of sophisticated analytical methods is essential. This is particularly relevant in light of standards such as DIN SPEC 91446, which defines quality standards for plastic recyclates to ensure the availability of high-quality materials for technical applications. Furthermore, regulatory requirements, such as the EU's Packaging and Packaging Waste Regulation (PPWR) and the End-of-Life Vehicles (ELV) Directive, increase the pressure on the recycling industry to improve the quality and yield of recovered materials. These standards promote the use of high-quality recyclates and compel the industry to adopt precise methods for analyzing the composition of plastic waste.

Traditional IR-based methods, such as Near-Infrared Spectroscopy (NIR) and Fourier-Transform Infrared Spectroscopy (FTIR), commonly used for quick identification of plastics, face limitations when analyzing complex polymer blends, heavily pigmented, or dark-colored materials. Thermal analysis methods like Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) provide deeper insights into thermal properties, making them particularly effective for determining the composition of recyclates.

Method Comparison: DSC

DSC measures the rate of heat flow in a sample compared to a reference in order to identify phase transitions such as melting and glass transitions. These thermal transitions are characteristic of specific polymers and can be used to identify the components in a mixture and quantify their proportions. In polymer blends, such as those often found in recycling streams, these thermal effects may overlap. The "Peak Separation" function of the Netzsch Proteus software allows these peaks to be mathematically separated for precise analysis.

A concrete example (**Fig. 1**): A measurement of a blend of LDPE with 20 wt % PP was performed with DSC (instrument: DSC 300 Caliris; manufacturer: Netzsch Analyzing & Testing) from –20 °C to 250 °C (shown here only from 30 °C to 200 °C) under a nitrogen atmosphere. The DSC heat flow signal (blue) shows two distinct peaks. Using the Peak Separation function, the two peaks were separated (green, orange). In a second step, the separated peaks were analyzed using the Identify function to determine that the first peak at 110 °C corresponds to LDPE

$$w_{polymer} = \frac{\Delta H_{m\_blend}}{\Delta H_{m\_pure\ polymer}} \cdot 100\,\% \qquad [1]$$

$$w_{polymer} = \frac{\Delta H_{m\_blend}}{\Delta H^{0}_{m\_pure\ polymer} \cdot X_c} \cdot 100\,\% \qquad [2]$$

$w_{polymer}$	Polymer content in a blend, expressed as a percentage
ΔH_{m_blend}	Measured melting enthalpy of a polymer fraction in the blend
$\Delta H_{m\_pure\ polymer}$	Measured melting enthalpy of the pure polymer
$\Delta H^{0}_{m\_pure\ polymer}$	Melting enthalpy of a 100 % crystalline polymer
X_c	Assumed crystallization degree of the polymer

and the second peak at 163 °C to PP (here, only the identification of LDPE is shown).

An important aspect of DSC analysis is that the percentage of each polymer can be calculated based on the measured melting enthalpy. This value is compared to reference enthalpies (specific melting enthalpies) of the pure polymers. The crystallinity of the polymer plays a crucial role because the melting enthalpy is directly related to the amount and crystallinity of the polymer. By separating the peaks and calculating the corresponding areas, the exact composition of the polymer blend can be determined. Two approaches are used here.

First approach: If the pure material is known, the polymer content can be calculated from the ratio of the measured melting enthalpies of the blend and the pure material (**Equation 1**).

Second approach: In recycling streams, it is rare to know the composition of the pure material. Under these conditions, one must use the 100 % enthalpy of the polymers and assume a typical crystallinity for the material in the blend (**Equation 2**).

The melting enthalpy of a 100 % crystalline polymer is known for many plastics and is, for example, 207 J/g for PP and 293 J/g for PE.

When applied to the two separated peaks in **Figure 1**, method 1 yields a polymer content of 78 wt % for LDPE and 18 wt % for PP, compared to the actual values of 80 % and 20 %, respectively. The missing 4 % arises from the mathematical fitting of the curve, where small portions of the enthalpy are not included.

Method Comparison: TGA

Thermogravimetric Analysis (TGA) complements DSC by monitoring the mass changes of a sample as a function of temperature. This is particularly useful for determining thermal stability and identifying decomposition processes. Netzsch's c-DTA technology (Differential Thermal Analysis) enables precise temperature calibration and the detection of exothermic and endothermic reactions, allowing the calculation of a DSC signal, which can then be used with the Identify database for identification purposes.

An example shows a TGA measurement (instrument: TGA 309 Libra; manufacturer: Netzsch Analyzing & Testing) on PP, HDPE, LDPE, and a blend of HDPE with 30 wt % PP (**Fig. 2**). The mass of all samples remains constant until about 420 °C, above which all four materials »

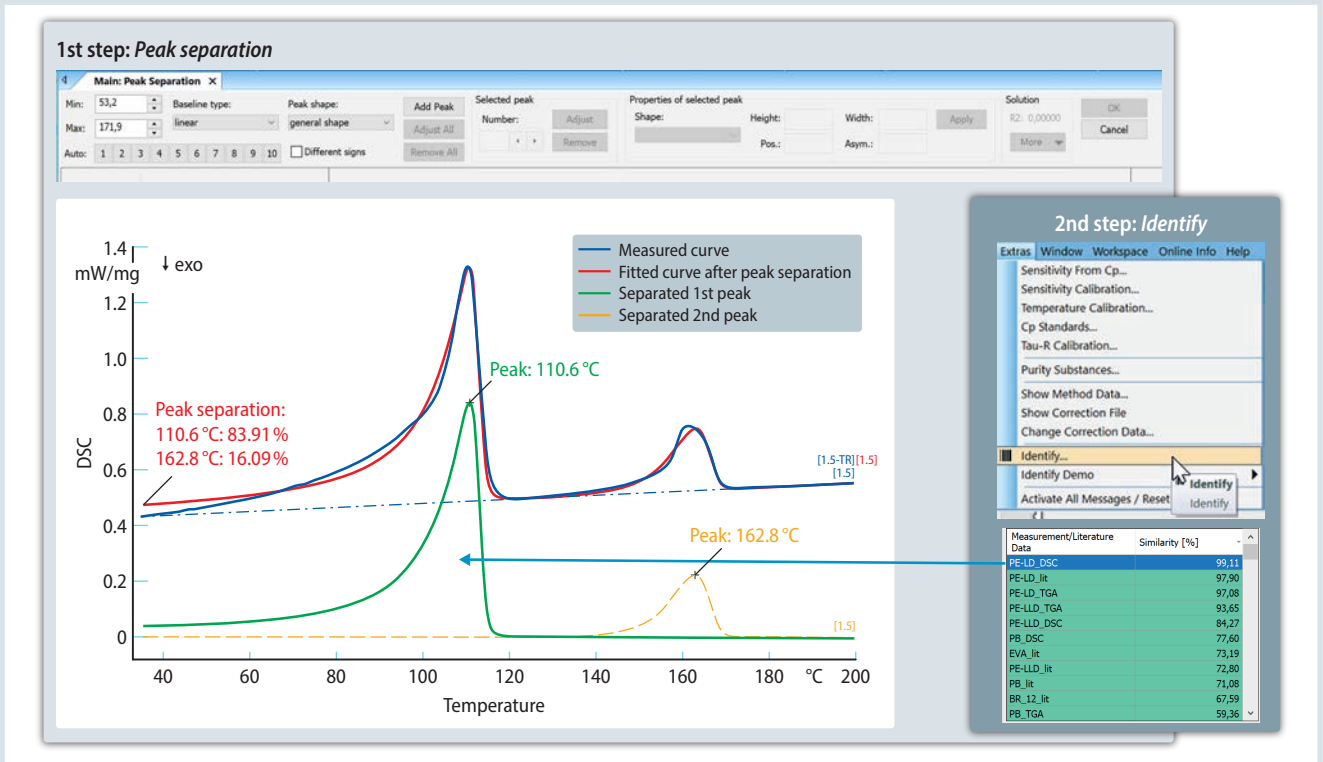


Fig. 1. In the DSC measurement of a polyolefin blend, the heat flow signal (blue) shows two distinct peaks. Using software, these two peaks can be separated (green, orange), analyzed, and thus used for material characterization. Source: Netzsch; graphic: © Hanser

begin to decompose. The pure materials are easily distinguished during decomposition. However, the decomposition of the blend closely resembles that of LDPE. To achieve greater differentiation, the c-DTA signal is used (left side of the figure), representing a calculated DSC signal. This allows a comparison of the melting behavior of the four materials, revealing a clear difference between LDPE and the blend.

Additionally, two overlapping peaks can be observed in the blend. In a subsequent step, these melting peaks can be cross-referenced with the Identify database and identified as HDPE and PP. It is also possible to separate the peaks in the signal. However, in most cases, the calculated c-DTA signal is not used for quantification based on the peak area. For this purpose, it is recommended to combine the analysis with a DSC measurement.

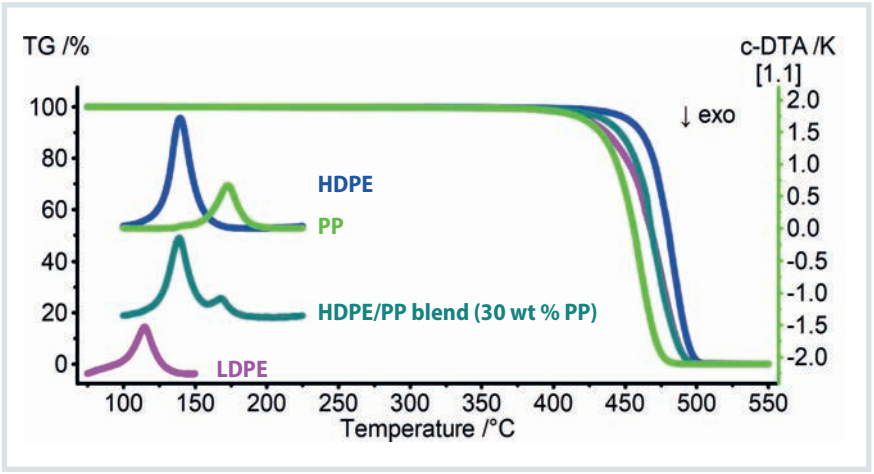


Fig. 2. TGA measurement from room temperature to 550 °C in a nitrogen atmosphere of HDPE, PP, LDPE, and a blend. The decomposition curve of the blend overlaps with that of LDPE, but the c-DTA signal allows for clear differentiation. © Netzsch

IR-based Methods: NIR and FTIR

Near-infrared spectroscopy (NIR) and Fourier-transform infrared spectroscopy (FTIR) are widely used methods for the rapid identification of polymers. They utilize specific absorption spectra, which serve as fingerprints for the materials. NIR is particularly effective in sorting plastics in recycling streams, as it provides quick results and is easy to apply. FTIR offers a more detailed spectral analysis and can provide deeper insights into the chemical structure of polymers.

However, IR-based methods face significant challenges when analyzing complex polymer blends. A particularly difficult issue arises when analyzing polyolefins, such as polyethylene (PE) and polypropylene (PP), as these polymers have similar chemical structures. This results in overlapping absorption bands, making reliable differentiation difficult. Specifically, a quantitative distinction between LDPE, HDPE, and LLDPE is nearly impossible using IR-based methods. Furthermore, IR-based methods are generally unsuitable for analyzing dark or black plastics because these materials strongly absorb infrared light, leading to inaccurate or even no measurement results.

In comparison, DSC and TGA offer deeper insights into the thermal and physical properties of polymers and can be used to quantify polymer content in blends. A significant advantage of thermal analysis methods is that they are independent of the color of the plastics, making them particularly useful for analyzing dark or black polymers. However, these methods are considerably slower. For example, a relevant DSC measurement can take 2 to 2.5 hours. As a result, it cannot be used inline in the process, unlike NIR measurements, and is instead limited to quality control laboratories. In practice, small sample sizes of 10 mg provide reliable results for homogenized samples, such as compounds, but a larger number of samples is necessary for flakes. Methods like the DSC-based Madscan technology from Veridis Technologies B.V. (Netherlands) are well-suited for this purpose, as they can measure 30 g at once.

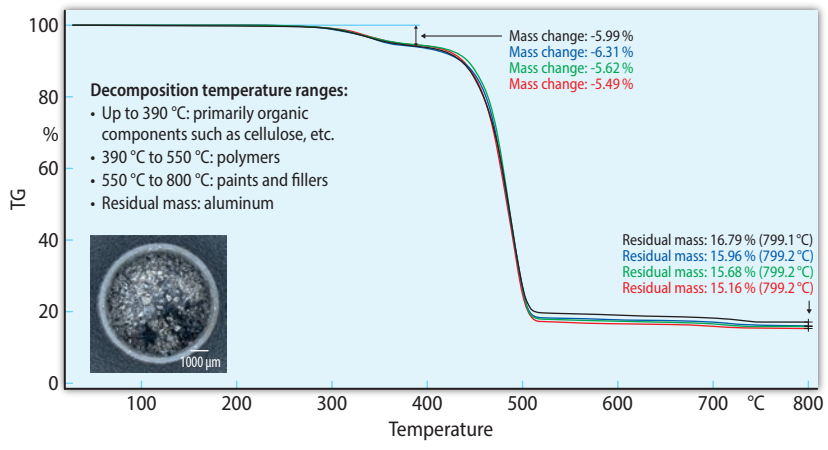


Fig. 3. TGA measurement of a beverage carton fraction with a sample weight of 20 mg; temperature settings: 25 to 800 °C (20 K/min), gas: N_2 (23 ml/min). Source: IPT; graphic: © Hanser

Results: Application to PCR from Beverage Cartons

A case study demonstrating the application of these thermal analysis methods in industry-focused research is provided by the Institute for Polymer and Production Technologies (IPT). The IPT works closely with the recycling industry and specializes in the analysis and optimization of post-consumer and post-industrial recyclates (PCR and PIR, respectively).

For a PCR sample derived from the mechanical recycling process of beverage carton fractions from the dual system, the goal was to determine the composition of the plastic. The main

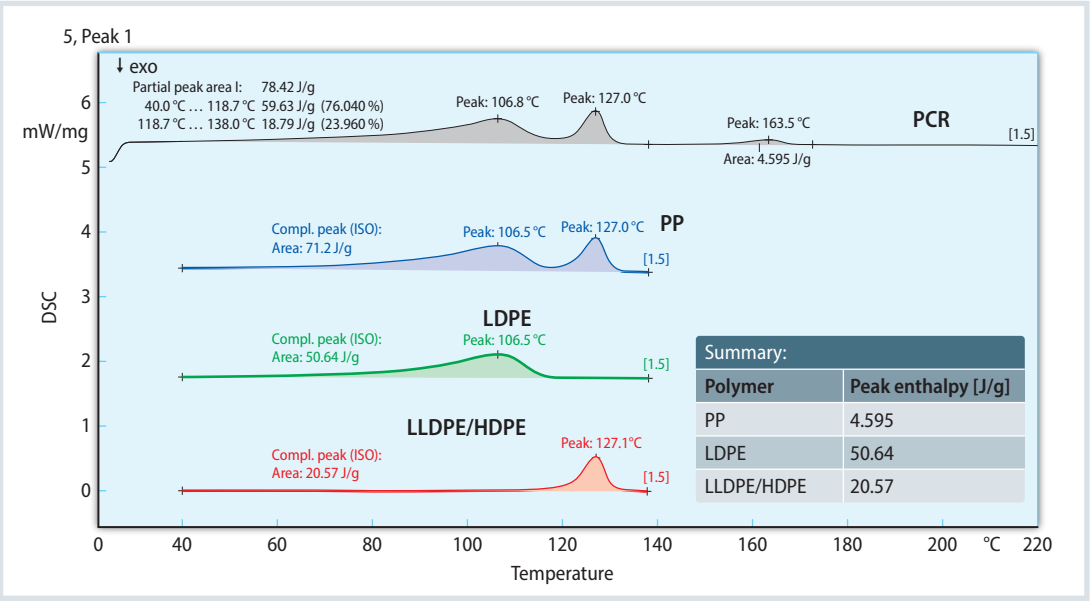


Fig. 4. DSC measurement of the beverage carton blend fraction with a sample weight of 5 mg (crucible: Concavus Al, perforated lid); temperature settings: 25 to 220 °C (10 K/min), gas: N_2 (40 ml/min).
Source: IPT; graphic: © Hanser

component of such recyclates is LDPE. However, other polymers like PP and PET, as well as organic and inorganic residues, such as cellulose fibers and aluminum particles, are also present. The DSC analysis showed a peak for PP and overlapping peaks for LDPE and LLDPE/HDPE, which were separated using the Peak Separation function. (LLDPE and HDPE are compatible and, after homogenization in a compounder, appear as a single peak.) The quantification of polymer fractions based on the calculated enthalpies of fusion is significantly more accurate than what could be achieved using IR methods.

The TGA analysis (instrument: TG 209 F1 Libra; manufacturer: Netzsch Analyzing & Testing) identified the decomposition temperatures of the various components as follows: cellulose decomposed at temperatures below 390 °C, while polyolefins such as PP and LDPE decomposed between 390 °C and 550 °C. Aluminum and other inorganic materials, which do not thermally degrade, remained as residue after switching to oxygen at temperatures above 800 °C (**Fig. 3**). This detailed analysis not only allows for the identification of components but also potentially maximizes yield. The results indicated approximately 9 % organic degradable components, such as fiber residues, and 17 % inorganic materials, primarily aluminum.

From the melting enthalpies measured in the DSC (instrument: DSC 214 Polyma; manufacturer: Netzsch Analyzing & Testing) and after "Peak Separation" (**Fig. 4**) , the weight fractions of the individual components were calculated using equation [2], taking into account the TGA results (sample mass correction). The results showed weight fractions of 43 % for LDPE, 17 % for LLDPE/HDPE, and 5 % for PP. When all identifiable components of the PCR are combined:

- Semi-crystalline polymers: 65 %,
- fiber residues: 9 % and
- aluminum: 17 %.

This leaves a residual weight fraction of approximately 9 %, which consists of unknown substances and measurement inaccuracies.

Indispensable Tool for the Recycling Industry

The results show that the combination of DSC and TGA is particularly effective for analyzing polymer blends. DSC's ability to accurately measure the enthalpy of fusion and precisely quantify the components of a blend makes it an indispensable tool for the recycling industry. TGA complements this analysis by providing detailed information about decomposition temperatures, thermal stability, and the proportions of non-melting material components.

As mentioned, these thermal analysis techniques also excel because they are independent of color, making them suitable for analyzing black polymers. The application of these methods to the example of beverage cartons demonstrates how precise and effective the determination of polymer content can be, ultimately contributing to maximizing the yield of valuable recyclates.

Outlook

The ongoing development of thermal analysis techniques is expected to yield even more precise and efficient methods for analyzing polymer blends. Future innovations may focus on shortening measurement times, increasing sample quantities, and integrating with other analytical techniques to enable even more comprehensive characterization of recyclates. Continuous improvement of these methods will be essential to meet the growing demands for the quality and purity of recyclates in a sustainable circular economy. ■

Info

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