Thermogravimetry. The material composition of polymers is an important quality criterion. The relative amounts of the constituents present can be determined by means of thermogravimetric analysis, which also provides information on the thermal stability of these compounds.

Is the Formulation Right?

STEPHAN KNAPPE

While differential scanning calorimetry (DSC) may be the best-known thermoanalytical measurement method in the polymer world [1], thermogravimetic analyis (TGA or TG, thermogravimetry) as defined in ISO 11358 or DIN 51006 is used primarily in the rubber industry. There, the plasticizer, elastomer and carbon black contents, for example, are determined quantitatively by means of the mass loss as a function of temperature or time [2].

TGA also finds use for analysis of the material composition and thermal stability of thermoplastics and thermosets, especially in the case of blends, filled and unfilled compounds [3, 4].

With TGA, a sample is placed in a refractory crucible of inert material (e.g. alumina) in a defined environment (heating rate, gas atmosphere, flow rate, type of crucible, etc.) and heated in a controlled manner, with the composition of the sample ultimately being established through comparison of mass loss, temperature and time. The sample holder is connected to a micro balance that records mass changes during heating. The temperature is measured by means of a thermocouple positioned very close to the crucible. Table 1 presents an overview of the material characteristics that can be determined using TGA.

Additional Functions

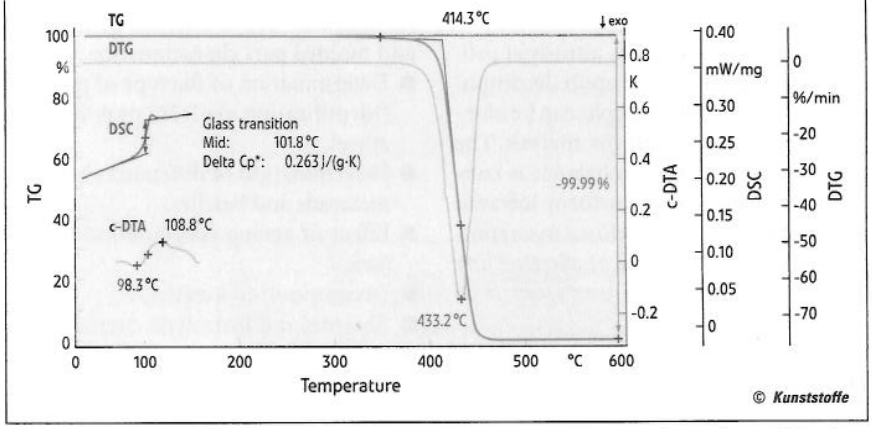
Depending on the field of application, the functionality of the thermobalance may also be expanded through incorporation of additional software and connection to various equipments. In addition to analytical instruments in general, Netzsch-Gerätebau GmbH, Selb, Germany, produces and markets the appropriate accessories for expanded capabilities.

Using an automatic sample changer, the operator can also analyze the specimens overnight or on the weekend with the aid of a programmed macro-recorder in accordance with specific measurement and evaluation routines. Incorporating unforeseen measurements that arise in the course of daily business into an already programmed and running series of measurements poses no difficulty.

In measuring systems with a thermocouple near the specimen, e.g. thermobalances and dilatometers, it is possible by using c-DTA (calculated differen- ▶

Translated from Kunststoffe 10/2007, pp. 255–257

Decomposition Behavior



PE104011

Fig. 1. Decomposition behavior of a polystyrene sample with a c-DTA signal (orange) and DSC reference curve (black) for the glass transition at 102 °C; heating rate 20 K/min

Comparison of Samples

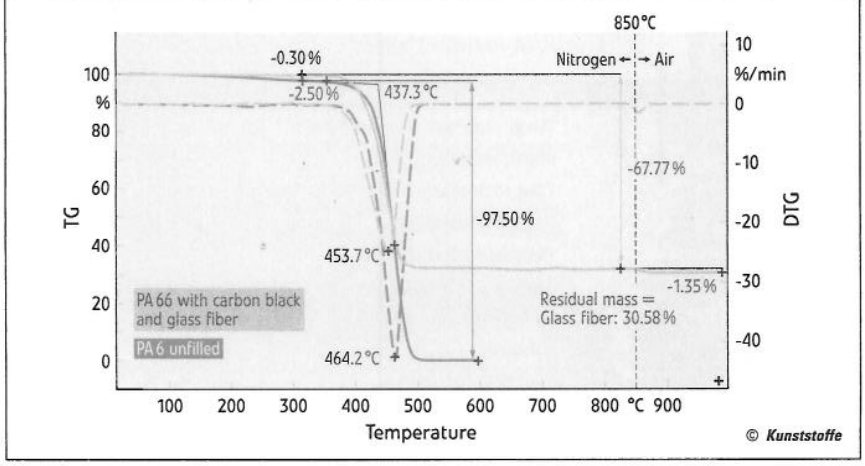


Fig. 2. Comparison of the decomposition curves of unfilled PA6 (red) and glass fiber-reinforced, carbon black-filled PA66 (beige); heating rate 20 K/min for each

tial thermal analysis) software to obtain information on endothermic (e.g. vaporization accompanied by mass loss or melting without mass loss) and exothermic processes (e.g. curing) in addition to signals associated with mass or dimensional changes. Usually, simultaneous thermal analysis instruments (STA) that have a DSC head for the sample and reference are implemented in this case.

If the thermobalance is evacuated by means of a vacuum pump and subsequently filled with nitrogen, a pure atmosphere for pyrolysis of the sample can be created. Oxidation is largely prevented. Moreover, by measuring in vacuum, the boiling point of low volatiles in the polymer mixture is reduced, thus achieving better separation during the subsequent decomposition of the polymer.

In order to obtain an event-dependent heating rate with special software (type: Super-Res), the operator specifies threshold values in relation to the mass loss rate. This ensures better separation of overlapping mass loss steps and thus makes higher resolution possible.

The gases released, e.g. already at processing temperatures or upon decomposition of the polymer sample, can be identified via coupling with gas analysis. The gas outlet on the thermobalance is connected to a Fourier transform infrared spectrometer (FT-IR) and/or a mass spectrometer (MS) by means of a heated line or capillary, thus permitting analysis of the gases.

Ensuring Material Quality

Modern thermobalances for polymer applications operate over a wide range of temperatures extending from room temperature to 1,000 °C and exhibit minimal buoyancy and drift that can be corrected by performing a measurement under identical conditions (heating rate, atmosphere) with an empty crucible. The heating rate is generally 10 K/min or 20 K/min, although the thermo-micro furnaces can heat considerably faster if only a quick check for quality purposes is involved. Software-controlled gas flow control systems with a programmable change of gas from an inert atmosphere (usually nitrogen) to an oxidizing atmosphere (usually air or oxygen), the ability to evacuate the sample cell and measurement in vacuum as well as use of different crucible types are standard features.

The automotive industry sets very stringent requirements regarding the quality of polymeric materials for its suppliers as do the electrical and electronics industries. Accordingly, TGA is employed for more in-depth analysis of material and molded part characteristics:

- Determination of the type of material (identification via DTG peak temperature),
- Determination of differences between materials and batches,
- Effect of ageing (degradation behavior),
- Decomposition kinetics,
- Thermal and hydrolytic degradation,
- Effect of exposure to diverse media (oils, acids, bases),
- Effect of recycled material and regrind amount,
- Effect of various plasticizer types (and other additives),
- Detection of impurities and foreign components,
- Determination of an elastomer modification (rubber component),
- Determination of drying times (evaporation) and
- Filler distribution in complex molded parts.

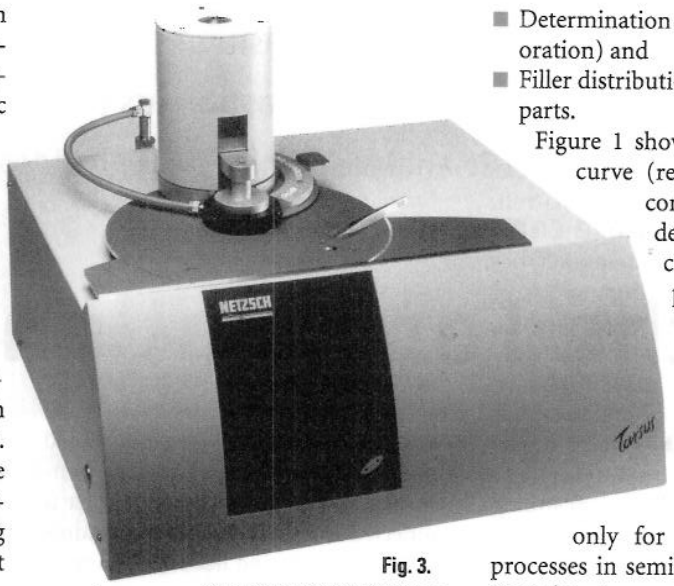


Fig. 3. The Model TG 209 F3 Tarsus thermobalance with upgradeable automatic sample changer has been designed specifically for testing plastics

Figure 1 shows the horizontal TG curve (red) that precedes decomposition and its 1st derivative (derivated TG curve, DTG, beige) for a polystyrene (PS) sample. PS decomposes in a nitrogen atmosphere at 414 °C, which has been evaluated here as the onset temperature. The c-DTA signal can be used not only for macro-scale melting processes in semi-crystalline materials. Even the micro-scale glass transition step (orange) within the amorphous PS between 98 °C and 108 °C can be detected. It exhibits good agreement with the midpoint at 102 °C from a separate DSC measurement (DSC curve, black).

Figure 2 illustrates the different decomposition behavior of two polyamide samples. The unfilled PA 6 (red curve) has a higher moisture content, which is indicated at the first mass loss step (2.5 %). Decomposition in a nitrogen atmosphere begins at 437 °C (extrapolated onset temperature) and is complete at about 500 °C (mass loss 97.5 %).

In contrast, the reinforced, black-pigmented PA 66 (beige curve) contains considerably less moisture (only 0.3 %). Decomposition (mass loss 67.8 %) begins earlier, i.e. at a lower temperature (about 418 °C). After switching to an air atmosphere at 850 °C, the incorporated carbon black burns to form carbon dioxide (1.35 %). The residue that remains is attributable to the glass fiber content of about 30.6 %.

These two examples demonstrate the possible uses of a thermobalance in the

Thermal quantity	Associated material characteristic
Mass loss Δm	Water / moisture / solvent content
	Plasticizer content
	Filler content (e.g. carbon black, chalk, glass fibers)
	Polymer content
	Residual mass (ash content)
	Stability with respect to oxidation (oxidation induction time or temperature; O.I.T. in oxygen)
Mass gain Δm	Oxidation
Extrapolated onset temperature T_0^E	Start of decomposition
Shape of the DTG curve	Decomposition behavior
	Decomposition rate

Table 1. Relationship between the most important thermal quantities and the material characteristics that can be derived from them

thermoplastics sector in the course of product development, quality assurance and failure analysis (Fig. 3). Characterization of stabilizers and processing aids with the help of TG-FTIR coupling is explained in [4] using PVC mixtures for pipe extrusion as examples.

Conclusion

Thermogravimetric analysis (TGA) is a very easy to use and exact measurement technique that provides information on the composition and thermal stability of polymers. In addition, stabilizer decomposition and the age of the resin specimen being tested can be assessed with the aid of TGA. Moreover, the results of the analysis permit conclusions to be drawn about the material characteristics, e. g. effects of media or moisture uptake. This method of analysis is thus well-suited for quality assurance testing or failure analysis and represents an ideal supplement to DSC tests. ■

REFERENCES

1 Knappe, S.: Quality Assurance and Failure Analysis. Kunststoffe international 97 (2007) 9, pp. 142–144

2 Knappe, S.; Urso, C.: Applications of thermal analysis in the rubber industry; Thermochimica Acta, 227, Elsevier Science Publishers B.V. Amsterdam, 1993

3 Ehrenstein, G. W.; Riedel, G.; Trawiel, P.: Praxis der Thermischen Analyse von Kunststoffen; Carl Hanser Verlag, München, Wien, 1998

4 Möhler, H.; Knappe, S.: Focus on Thermal Analysis for Polymers. Netzsch-Gerätebau GmbH, Selb, 1998

THE AUTHOR

STEPHAN KNAPPE, born in 1960, is Sales & Applications Support Manager at Netzsch Gerätebau GmbH, Selb, Germany; stephan.knappe@netzsch.com