

Quality Assurance and Failure Analysis

DSC Analysis. Compared with other materials, plastics react very sensitively to changed parameters such as composition, temperature, or nature and duration of a load. When trying to discover the reason for failure in cases of damage or quality variations, differential scanning calorimetry (DSC) permits conclusions to be drawn regarding physico-chemical reactions of materials as a function of temperature.

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Differential scanning calorimetry in accordance with ISO 11357 or DIN 51007 permits polymer testing laboratories to carry out phase change measurements such as glass transitions, melting, and crystallization of thermoplastics as well as cross-linking reactions of thermosets and rubbers. Numerous practice-related application examples are given in [1, 2, 3]. In addition, the DSC method is used to determine the specific heat capacity at a constant pressure as a function of temperature.

Crystallization and Melting

Typical DSC application areas for semi-crystalline thermoplastics are determining of the peak melting temperature as a means of material identification, and measuring the required melting heat (in J/g), from which the degree of crystallinity can be calculated [2, 3, 4]. Just as important for the plastics processor, however, is the information on crystallization behavior. For example, knowing at which temperature the melt starts to crystallize is useful when injection molding thin-walled parts, so that mold cooling can be adjusted accordingly in order to ensure complete cavity filling.

Figure 1 shows the different cooling curves of three polytetrafluoroethylene (PTFE) films. Whilst the white-pigmented film (yellow DSC curve) only starts to set at 313 °C (extrapolated endset) and no more than 33 J/g of crystallization heat is released, crystallization of the violet film (red curve) starts already at a higher tem-

perature (317 °C). It is also considerably faster, as indicated by a higher slope of the larger crystallization peak (38 J/g). Completely different is the crystallization behavior of the black PTFE film (black curve).

The 2-stage, considerably slower solidification starts at 320 °C. Here, only 11 J/g of crystallization heat are released, which suggests a far higher pigment content (and therefore a lower polymer proportion).

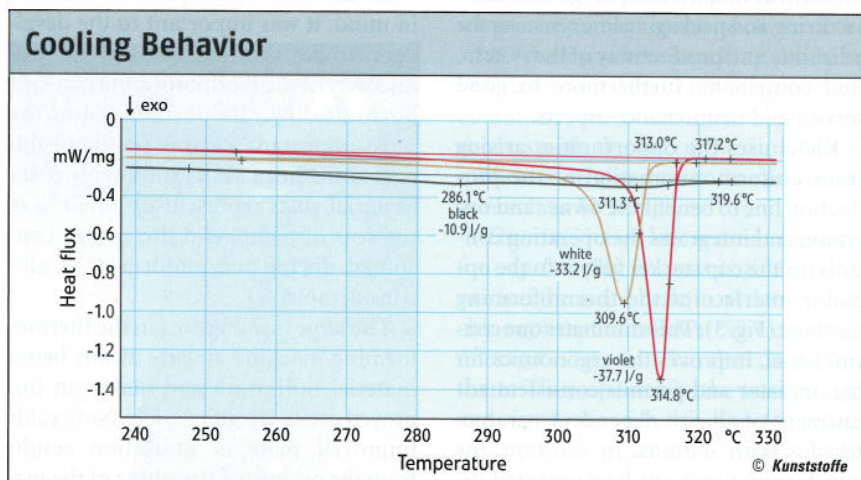


Fig. 1. The analysis of controlled cooling at a cooling rate of 10 K/min of various PTFE films shows clear differences caused by the color pigment content

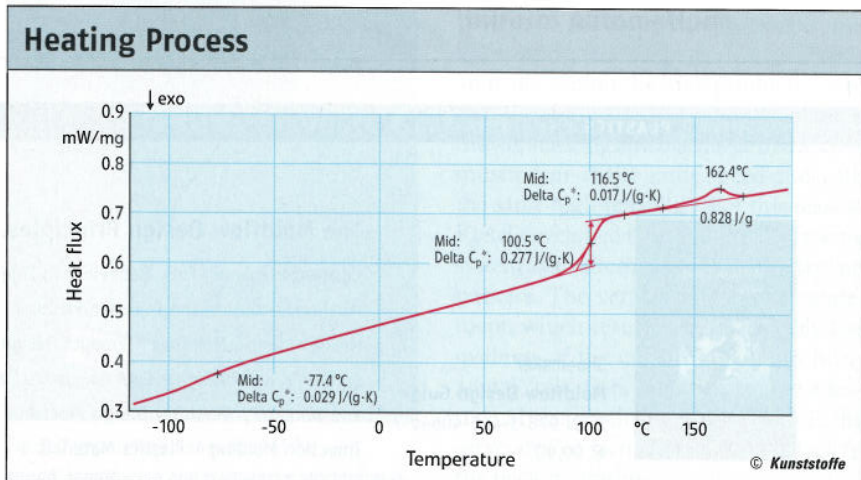


Fig. 2. Apart from the three glass transitions in ABS components during heating of ABS/PP the melting process of the PP content is also shown

Translated from Kunststoffe 9/2007, pp. 224–226

Thermal Measurement Value	Deducible Material Property
Glass transition temperature T_g	Softening temperature, dimensional stability under heat, low-temperature behavior with rubber
Melting peak temperature T_m	Melting behavior
Crystallization temperature T_c	Solidifying behavior
Reaction temperature T_r	Curing with thermosets, vulcanization with rubbers
Endothermic melting heat Δh_m	Information on the energy relationships (intermolecular forces) between the material's molecules during changes of the aggregation state
Exothermic crystallization heat Δh_c	
Exothermic reaction heat Δh_r	
Specific heat capacity c_p	Relationship between energy absorption and temperature increase
Degree of crystallinity	Correlation of tightness and stiffness
Crystallite size distribution	Molecular weight distribution (from the curve shape of the melting peak)
Crystallization behavior	Influence of nucleating agents, recyclates
Oxidation stability	"Oxidation induction time (O.I.T.); following a gas change from nitrogen to oxygen atmosphere, e.g. acc. to DIN EN 728)

Table 1. Relationship between thermal measurement values and material properties

Amorphous thermoplastics have only one glass transition, which is measured with DSC as an endothermically progressing step. These T_g steps can also be detected with blends or copolymers. The acrylonitrile butadiene styrene (ABS) copolymer examined in Figure 2 exhibits the three expected glass transitions for polybutadiene (B) at -77°C , polystyrene (S) at 101°C , and acrylonitrile (A) at 117°C . In addition, a further component melts at 162°C . Due to the position of its melting peak, the component must be the semi-crystalline polypropylene (PP) in the form of foreign material. Admittedly, PP can increase crystallinity and therefore the tightness of the normally tough, amorphous ABS material, but it can also lead to brittle fracturing.

Both examples demonstrate the application possibilities for DSC involving thermoplastics in the field of quality assurance and failure analysis. The relationships between DSC and traditional mechanical testing methods such as tensile test, chromatography or microscopy are explained in [1]. Moreover, reference [3] shows the correlations between the crystallization behavior of semi-crystalline thermoplastics and the viscosity number and molecular weight. By comparing the thermal measurement values and the material properties that can be deduced from them, it is possible to illustrate the performance of DSC analysis (Table 1).

DSC has also proved its value in the field of thermosets for determining the

degree of curing. Hereby, standard tasks include measurement of exothermal curing reactions, residual exothermics for post curing, as well as glass transition shifts with increasing degrees of cross-linking. For elastomers, caoutchoucs, and rubbers, DSC serves to measure the glass transition in the low temperature range and the vulcanization behavior (exothermal cross-linking).

Highly Significant Data

Particularly high demands on the quality of polymer materials are placed by the automotive industry, their suppliers, and the electrical/electronic sector. Therefore, the DSC method is also used for further testing of material and component properties [4, 5].

Apart from the identification of material types, this analysis method is also capable of determining differences in materials and even lots, whereby the simultaneous determination of batches and the detection of processing materials such as fillers or additives are possible. In the case of failure analyses, impurities and foreign components are detected reliably. In the field of blending technology, the compatibility of different polymer components can be tested, or the influence of plasticizers and other additives determined. By comparing the analysis results of different material modifications, it is not only possible to illustrate the effect of varying proportions of recycled or re-generated components in the material,

but also the effects of external influences such as storage in different media (oil, acid, lye, etc.), tempering, ageing or thermal and hydrolytic damage. Similarly, DSC analysis can also assist during process optimization and mold design, as the influence of the gate and unfavorable wall-thickness ratios can be determined, and analysis results provide information on the required mold temperature, cooling time, or melt temperature. In addition, the distribution of filler materials in complex molded parts and possible elastomer modifications can be examined.

Customized Analytical Equipments

To some extent, the physico-chemical properties of different material groups such as melt or crystallization temperature differ widely. For this reason, Netzsch-Gerätebau GmbH, Selb, Germany, has developed a DSC system for polymer analyses (type: DSC 200 F3 Maia; Fig. 3), which is specially adapted for routine applications in quality assurance, failure analysis, and process optimization with polymers.

Modern DSC equipments for polymer applications operate in a temperature range between -170°C and 600°C , and ensures a stable base line. Usual heating and cooling rates are 10 K/min or 20 K/min, although the DSC furnaces can work considerably faster, e.g. in case just a short check is required for quality control. The decisive criterion hereby is whether the polymer sample is able to follow a high heating rate, as one normally attempts to maintain thermodynamic equilibrium.

Software-controlled gas-flow control systems with programmable gas changes, different cooling systems (compressed air, intracooler or liquid nitrogen) with linear cooling rates, as well as the use of different crucibles are the current state of the art. Nowadays, practically all thermally-related questions regarding polymers can be handled by varying these parameters.

Depending on the application area, modifications or extensive additions are available for the differential calorimeter.

By means of **automatic sample changer systems** and macro recorders that are programmed by the operator, samples can also be analyzed overnight or during the weekend according to individual measurement and evaluation routines. Interruption of a previously programmed and running test series to car-

ry out unforeseen measurements during daily operations is also possible at any time.

With **pressure DSC (P-DSC)**, the DSC cell is placed in an autoclave and subjected to gas pressure, for example to examine the curing of phenolic resins at a constant pressure, or the effect of anti-oxidants under high oxygen pressure.

Photo DSC is used to examine samples of UV or VIS light-sensitive resins, adhesives or paints (mostly acrylate-based) regarding their reaction after exposure to the light source.

With **TM-DSC**, temperature modulation and a special measurement and evaluation software are used to separate overlapping thermodynamic (reversing) and kinetic (non-reversing) processes.



Fig. 3. The DSC 200 F3 Maia with automatic sample changer was designed specifically for the analysis of polymer samples

An extended application is provided by **DSC-FTIR/MS**: Fourier transform IR spectrometers or mass spectrometers are coupled to the DSC cell in order to identify released gases, e.g. as occur during the curing of polycondensation materials or paints and coatings.

Conclusions

Differential scanning calorimetry (DSC) is an extraordinary analysis method for detailed investigation of the physico-chemical properties of polymers. Regarding damage analysis, it must always be remembered that faults are not always caused by material defects, but that material failure is frequently due to incorrect

design or changed machine parameters during production.

For quality assurance, however, the DSC method is suitable without any restrictions, as no other analysis method permits so many conclusions to be drawn about material compositions and the influences of additives. ■

REFERENCES

- 1 Möhler, H.; Knappe, S.: Focus on Thermal Analysis for Polymers. Netzsch-Gerätebau GmbH, Selb, 1998
- 2 Ehrenstein, G. W.; Riedel, G.; Trawiel, P.: Praxis der Thermischen Analyse von Kunststoffen. Carl Hanser Verlag, München, Wien, 1998
- 3 Frick, A., Stern, C.: DSC-Prüfung in der Anwendung. Carl Hanser Verlag, München, Wien, 2006
- 4 Harenbrock, M.; Knappe, S.: Zuverlässig für die Automobilindustrie; Saugrohrfertigung bei Mann + Hummel – DSC sichert Qualität. Kunststoffberater (1999) 6
- 5 Knappe S., Mayo C.: Thermal Analysis – Integrated into QA Systems of Automotive Suppliers. Kunststoffe plast europe 85 (1995) 12, pp. 16–18

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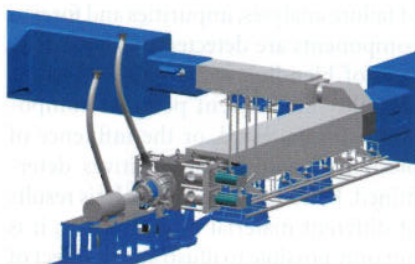
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Flying Start with New Process Technology

Pelletising. Coperion Werner & Pfleiderer GmbH & Co. KG, Stuttgart, Germany, have already taken four orders for their newly developed ultra large ZSK-NT plant which is intended for processing polyolefins. Two of these will run with a throughput of over 50 t/h. The first of these units is going to be taken into production in 2007. The ZSK-NT has already been qualified by several licensors for the preparation of bimodal film and pipe grades.

The ZSK-NT is a two stage processing system that comprises two twin screw ZSK Megacomponent extruders each with relatively short processing units. In the first stage a relatively small, at least

in comparison to the throughput, but fast running twin screw extruder carries out the melting of the polymer powder. This could for example be a ZSK 250 Mc with 250 mm diameter screws that run



Sensitive materials are subjected to lower thermal loadings in the ZSK-NT (photo: Coperion)

at up to 600 min⁻¹. In the second stage a larger ZSK extruder running at a lower screw speed, but with a high fill level performs the homogenisation and pelletising of the melt. The decoupling of the processing steps allows each of the various tasks to be performed with optimised screw configurations and process parameters. According to the manufacturer the end result is exceptionally good homogeneity, particularly with difficult products, since energy input and therefore thermal loading of the melt is lower in comparison to machines with longer processing units and larger diameters.

► www.coperion.com