Measuring Cell Enables Characterization of Fast-Reacting Polyurethanes and Epoxy Resins

Sharp Look at Reactive Resins

The processing of highly reactive resin systems requires a detailed understanding of the material behavior during component manufacture. The characterization of systems using DSC to date has reached its limits, especially in the case of polyurethanes. A specially developed measuring cell, on the other hand, delivers better results.

Reactive resin systems such as polyurethanes (PU) or epoxides (EP) are used as matrix materials in fiber-reinforced composites (FRP) or processed into compact molded parts in the transportation and automotive industries, the construction sector, aerospace, medical technology, or in the field of regenerative energy production [1–3]. Industrial developments focus on highly reactive systems with reaction times of a few minutes or even seconds [4, 5]. Although these systems enable short cycle times, they pose a major challenge for robust process design.

Detailed knowledge of the thermal and rheological material behavior in the mold is essential for determining stable process parameters. A large number of models for describing the reaction progress can be found in literature [6, 7]. The most common method for characterizing reactive materials and determining input data for numerical models is Differential Scanning Calorimetry (DSC) [6]. However, the behavior of highly reactive resin systems with reaction times of a few minutes can only be measured to a limited extent, since sample preparation can take more than two minutes and measurement speeds are limited. In addition, the influence of the process parameters can often not be taken into account with conventional analysis methods. As a result, there is a lack of fundamental data for model development of these materials, which can be used for process design and simulation.

At the Institute of Plastics Processing in Industry and Craft at RWTH Aachen University (IKV), Germany, possibilities for analyzing thermal reaction behavior were therefore investigated in a publicly funded research project, and a measuring cell was developed for characterizing highly reactive resin systems under process-related conditions. Based on the data obtained, models are then determined to describe the reaction process.

Characterization of Highly Reactive Polymers

To analyze the influence of the reaction time on the characterization of the reaction behavior of PU and EP resins, taking into account the sample preparation, three materials of different reactivity were investigated in a DSC Q2000 of the manufacturer TA Instruments (**Table 1**). In addition to an EP, whose processing or gel time allows a complete characterization, two polyurethanes were also selected, whose curing reaction cannot be completely recorded by conventional DSC. The measurement data generated serves as reference values for the validation of the measuring cell developed at IKV.

For sample preparation, the starting components were weighed and mixed manually for at least 15 s. A drop (approx. 20 µl) of the material was then placed in an aluminum DSC crucible and positioned in the DSC. The preparation time was measured for each test and ranged from 120 to 130 s. The weight of the samples ranged from 20 to 23 mg.

Difficulties of PU Characterization

Figure 1 shows the measured heat flux versus temperature in the thermogram of the non-isothermal DSC measurements of the three investigated material systems for an exemplary system-dependent heating rate in each case. The

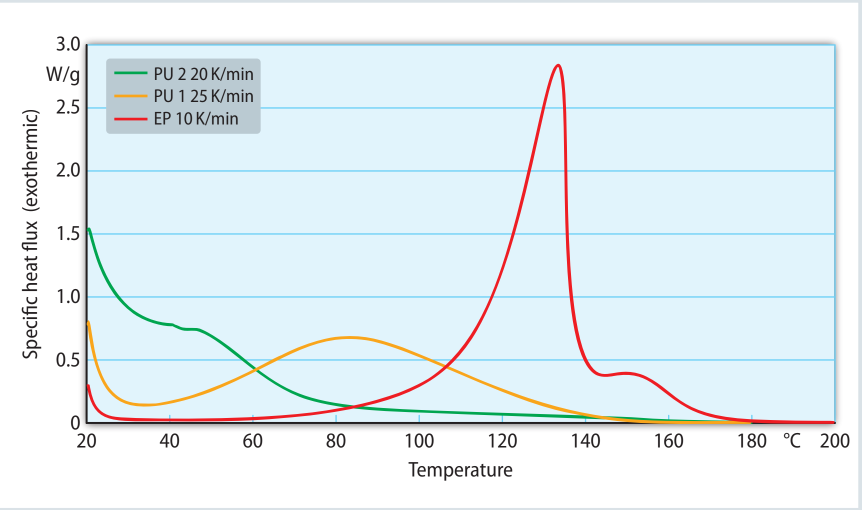

Fig. 1. Thermograms of the reactions of an EP and two polyurethanes under non-isothermal conditions: the EP could be fully characterized. This is not the case for the PU. Source: IKV; graphic: © Hanser

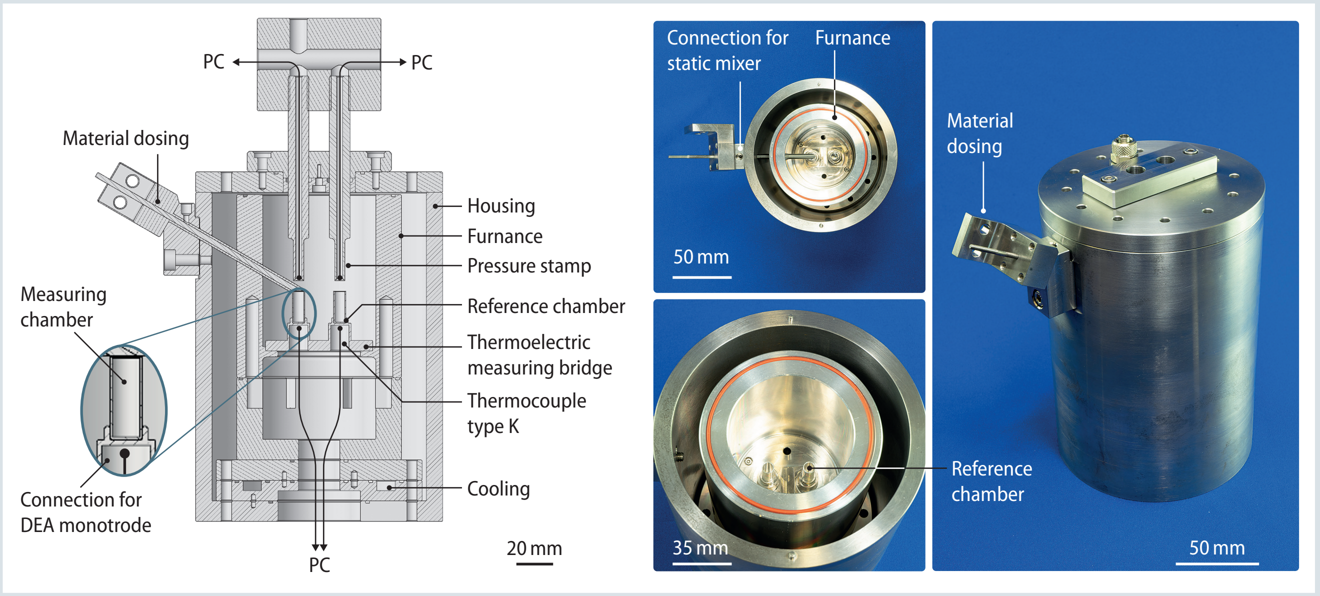

Fig. 2. Measuring cell for thermal characterization of highly reactive resin systems: In contrast to DSC, the reactive material is dosed directly into the measuring chamber. Source: IKV; graphic: © Hanser

curves of the EP and the first PU show the typical exothermic peak, although this is only fully developed in the case of the EP and previously shows a steady-state region with constant heat flux. In the case of the EP, a complete characterization is thus obtained, which can be used to derive models for process design.

In the case of the first PU, the reaction starts even before a steady-state measuring region with constant heat flux is set. The resulting temperature distortion due to the rapid reaction of the PU system prevents the complete analysis of the sample. An extrapolation of the thermogram shows that the reaction already begins well below 20 °C. However, an exact starting temperature cannot be determined. Furthermore, a complete characterization of the reaction enthalpy is not possible, which is why material data cannot be determined. Finally, an even more reactive material was investigated with the second PU system. The course of the curve deviates considerably from the typical reaction course. Therefore, no statements can be derived for the reaction enthalpy and characteristic values, such as the reaction start temperature, since the setting of the steady-state measuring region is superimposed on the exothermic heat flux of the reaction.

The investigations show that a complete and reproducible characterization of the reaction behavior of crosslinking polymers by means of DSC becomes more difficult with increasing reaction rates due to the time-consuming experimental preparation of the samples and a limited measuring speed of the analytical method. Basically, two types of highly reactive systems can be distinguished. On the one hand, there are systems that cure at room temperature in less than 120 s and on the other hand, systems whose reaction starts well below room temperature.

Name	Material	Supplier	Application	Gel time at 25 °C	Measuring range DSC/ heating rate
EP	Epikote 04976	Hexion	Production of FRP by the winding and pultrusion process	24 h	20 – 200 °C, 10 K/min
PU 1	Puropreg 185 L IT	Rühl Puromer	Production of FRP using the RTM process	550 s	20 – 180 °C, 25 K/min
PU 2	Puroclear 3098/4 IT	Rühl Puromer	Lightfast cast elastomer systems	80 s	20 – 180 °C, 20 K/min

Table 1. Overview of EP and PU characterized by DSC Source: IKV

Measuring Cell for the Analysis of Highly Reactive Resin Systems

In order to better understand the reaction behavior of highly reactive material systems, the influence of pressure, temperature and material conditioning on crosslinking are analyzed at IKV. These factors are the focus of the investigations, as experience has shown that they are of particular importance for the processing of the materials under investigation.

For this purpose, a novel, automatable measuring cell based on the principle of DSC (**Fig. 2**) was developed. The cell consists of an aluminum furnace in which a measurement chamber and a reference chamber are symmetrically arranged on a bridge. Therefore, heat fluxes from the furnace flow equally into both chambers. The setup allows quantitative measurement of exothermic effects in the sample for isothermal conditions as well as for heating rates between 2 and 50 K/min. The bridge consists of a nickel-copper alloy whose thermoelectric properties are constant in the temperature range considered. Thermocouples are positioned at the junctions between the bridge and the two cells to record the incoming and outgoing heat fluxes. The different behavior of the sample and the reference allows the thermal properties of the sample to be determined. »

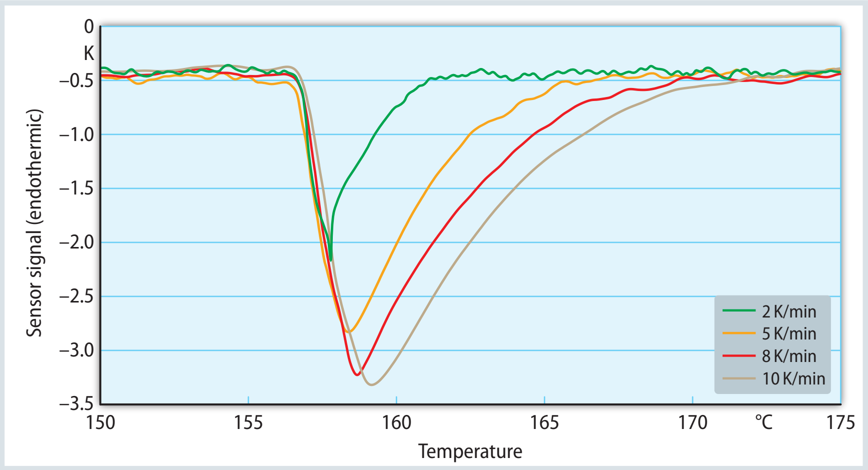

Fig. 3. Thermograms of the melting process of indium for four heating rates and a sample mass of 300 mg: the measurements strongly correspond to the melting temperatures reported in literature. Source: IKV; graphic: © Hanser

Direct Dosing of the Reactive Material into the Measuring Chamber

Unlike conventional DSC, the reactive material is dosed directly into the preheated measuring chamber (T = 10 – 200 °C). The enthalpy of reaction can therefore be measured as early as 10 s after mixing. The dosing is carried out by a piston dosing unit with static mixer developed at IKV, which allows the dosing of sample quantities below 1 g. To increase the mixing quality and reproducibility, a dosing adapter was also developed which reduces the material flow of an industrial high-pressure dosing unit to less than 1 g/s and can be connected directly to the measuring cell.

A cooling channel in the bottom of the measuring cell creates a constant heat sink, which is intended to minimize thermal fluctuations and increase measuring accuracy. In addition, defined cooling rates can be set in this way and measurement temperatures below 10 °C can be realized. A measuring pressure of ≤=100 bar can be applied via mechanical stamps in order to characterize the reaction behavior under process-related conditions. The heat fluxes flowing off via the stamps are quantified by additional thermocouples. Furthermore, a dielectric monotrode can be installed into the bottom of the measuring cell to determine the curing state of the reactive material by measuring the ion viscosity. This setup allows the simultaneous correlation of thermal and dielectric measured quantities to describe the reaction behavior of highly reactive plastics in real manufacturing processes.

In addition, the thermal characterization of foaming materials using DSC-based methods is to be investigated for the first time with the developed measuring cell. For this reason, both crucibles with a height of 5 mm and variants with a height of 10 mm can be used in the measuring cell. However, for the measurements it must be taken into account that there is an increase in the heat transfer area during foam expansion and consequently a falsification of the sensor signal. The consideration of this influence is part of future investigations.

Measurement Results Agree with Known Values

The commissioning of the measuring cell includes both a temperature cali-

Heating rate [K/min]	Minima [K]	Normalized area [K·s]	Correction factor [J/(K·s)]
2	-2.17	-112.21515	$7.59 \cdot 10^{-2}$
5	-2.83	-109.65812	$7.77 \cdot 10^{-2}$
8	-3.23	-110.33923	$7.72 \cdot 10^{-2}$
10	-3.32	-111.00993	$7.67 \cdot 10^{-2}$

Table 2. Evaluation of the indium calibration of the developed measuring cell. Source: IKV

Info

Text

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References & Digital Version

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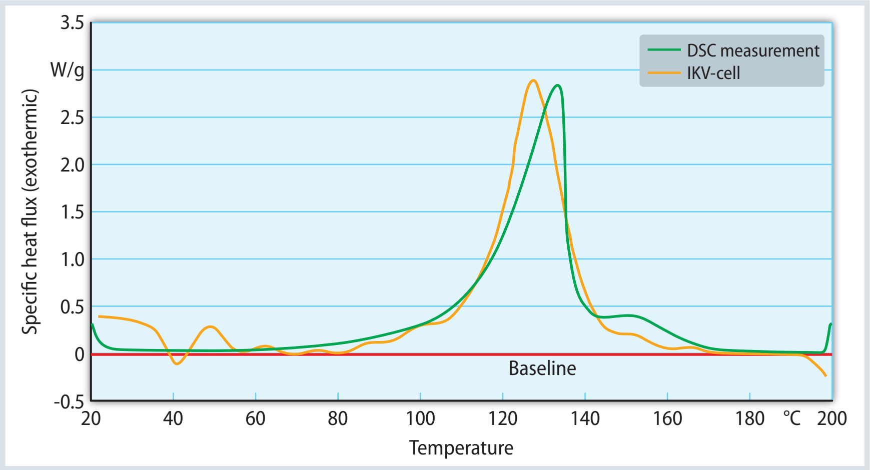

Fig. 4. Comparison of the exothermic reaction of the epoxy resin Epicote 04976 in a DSC measurement and in the IKV measuring cell: the values strongly agree. The choice of the baseline has a great influence on the result of the measurement. Source: IKV; graphic: © Hanser

bration and a heat flux calibration. During temperature calibration, the temperature measured with the measuring cell is compared with a temperature of a chemical or physical transition known from the technical literature. Heat flux calibration determines a proportionality factor between the actual heat flux occurring and the voltage generated in the sensor. A large number of different reference materials with a defined phase transition described in literature are available. However, only materials that exhibit a melting process in the temperature range between 10 and 200 °C can be considered for the developed measuring cell. Under these boundary conditions, indium with a purity of 99.99 % from the company Strategic Elements was chosen for the investigations. The medium has a melting temperature of 156.6 °C and an enthalpy of fusion of 28.5 J/g [8].

Calibration was performed at four heating rates of 2, 5, 8 and 10 K/min. The sample mass was 300 mg for all measurements. It can be seen that with increasing heating rate, the minima of the curves decrease and shift to higher temperatures (**Fig. 3**). This dependence on the selected heating rate must be taken into account during temperature calibration. All measurements show good agreement with the melting temperature described in literature. Based on the determined areas under the measured curves, the calibration factor for calculating the heat flux is determined according to equation 1. The areas increase with the heating rate and must be normalized to the respective heating rate for calibration of the measuring cell.

$$k(T, p) = \left| \frac{m \cdot \Delta_S^l H_m (T, p)}{A(T, p) \cdot M} \right|$$

m = Weighing-in of the calibration substance

$\Delta_S^l H_m$ = Molar enthalpy of fusion of the calibration substance

A = Measured area normalized to the heating rate

M = Molar mass of the calibration substance

This calibration results in the correction factors listed in **Table 2** for the heating rates considered.

To validate the calibrated measuring cell, EP was measured as before in the DSC at a heating rate of 10 K/min. The test preparation was analogous to the measurement with the conventional DSC. The sample weight was 70 mg.

Choice of Baseline Still Decisive

The thermogram determined with the measuring cell shows the typical exothermic reaction course of an EP resin and is comparable to the DSC measurement (**Fig. 4**). However, it is noticeable that the peak of the thermogram of the measuring cell is tilted to the left compared to the DSC measurement and shows a fundamental oscillation in the curve. The measuring cell measures a maximum heat flux of 2.92 W/g at 128.28 °C. From the peak area, the reaction enthalpy is 365.8 J/g. The relative deviation of the enthalpy from the DSC measurement is thus 4.5 % on average.

The choice of the baseline, the parameter-specific heat flux curve of a measurement without specimen (**Fig. 4**), still has a significant influence on the determined area at the current stage of development and is complicated by the fundamental oscillation. The fundamental oscillation is the result of an unstable furnace control system, which is to be completely avoided by optimized control parameters within the scope of current work. It is assumed that this fundamental oscillation in interaction with the increased sample mass is causal for the shifted peak area. Further measurements of the exothermy of the epoxy resin with optimized control parameters and at varying heating rates as well as sample masses will provide a better understanding of the observations.

Conclusion and Outlook

Using three representative reaction systems, it was shown to what extent the reaction rate is crucial for the complete characterization of the reaction course in DSC. Based on the difficulties identified, a measuring cell for the characterization of highly reactive non-foaming polymers was developed, which reduces the time delay between the start of the reaction and the start of the measurement by direct and automated dosing of the sample into the measuring chamber. Pressure stamps as well as a temperature control allow the setting of measurement conditions close to the production process (1 to 100 bar, 10 to 200 °C). The characterization of a slow-reacting epoxy resin demonstrates the suitability of the cell for quantified measurements of the reaction enthalpy. Based on this, further work will be carried out on fast-reacting polymer systems such as PU.

The measurement data obtained are then used to determine model parameters, and the reproducibility of the measurements and the quality of the parameters determined are evaluated by comparing the thermal reaction models with real components. For this purpose, components produced with an industrial dosing unit are demolded after defined curing times and the reaction conversion achieved is analyzed on the basis of the residual reaction enthalpy. ■