Tracking Down a Powder Coating Based on PUR

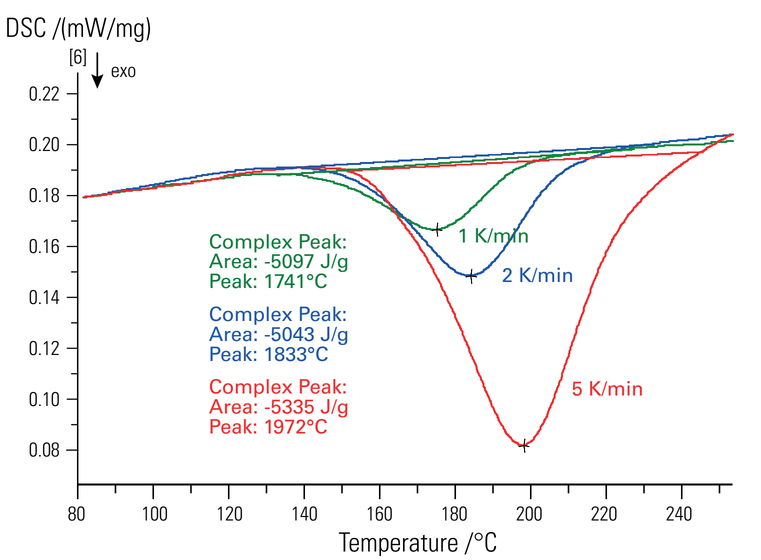
Application Note M64

Introduction

Powder coatings are increasingly employed in the automotive industry. They meet ecological requirements to release the possible pollution during curing. Prior to using them, it should be guaranteed that they have a homogeneous gleaming lacquer coating depending on particle-size distribution and the powder distribution on the surface.

DSC and Reaction Kinetics

DSC (Differential Scanning Calorimetry) measurements offer a fast and accurate description of a reaction system. The exothermal curing reaction of a powder coating based on PUR is influenced by the heating rate (Fig. 1). For a reaction kinetic evaluation of DSC measurements, the thermo analytical data at different heating rates are integrated in the software program Thermokinetics. Besides a model-free estimation of the activation energy, the analysis of multiple-step reactions is possible.



TG-FT-IR

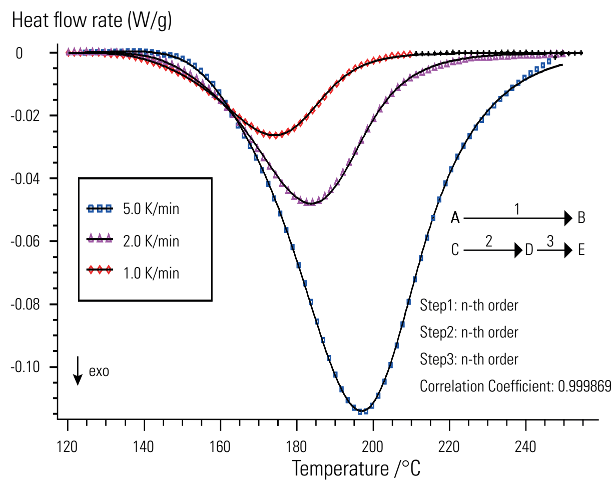
- Easy-to-use, powerful, integrated software
- Optimized low volume design
- Vacuum compatible to remove oxygen, eliminate carryover, and lowering boiling points
- Easy maintenance of gas cell and transfer line
- Optional 64 position automatic sample changer

Application Areas

- Outgasing of Materials
- Detection of Residues
- Analysis of Additives
- Analysis of Aging Processes
- Competitive Analysis
- Characterization of Natural and Raw Materials
- Desorption Behavior
- Analysis of Synthesis Processes
- Analysis of Decomposition Processes

Fig. 1
Heating rate comparison DSC measurement.

The curve fitting is obtained by using non-linear regression (Fig. 2). Engineering graphics allow predictions on the isothermal behavior of the powder coating investigated by non-linear regression (Fig. 3).



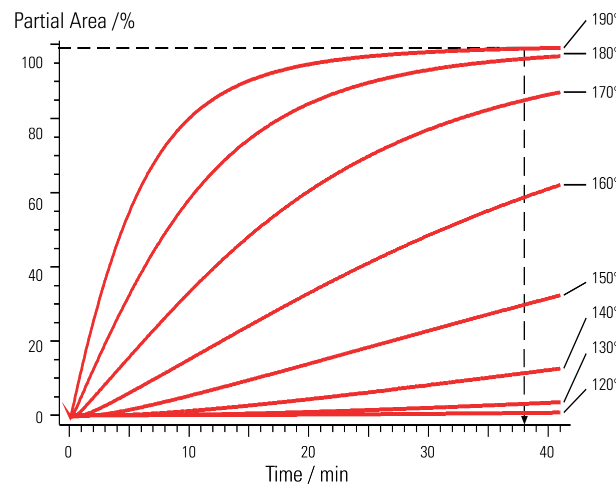


Fig. 2 (left)
Curve fit of the DSC heat rate comparison to a three step reaction of n-th order.

Fig. 3 (right)
Prediction of the isothermal behavior for different temperatures.

TG-FT-IR

Simultaneous TG-FT-IR (Thermogravimetry - Fourier Transform Infrared Spectroscopy) measurements deliver additional information to the curing reaction, temperature stability and decomposition behavior. A quantitative and qualitative characterization of the evolved gases can be obtained with a single measurement investigating the same sample under identical conditions. Thermogravimetry (TG) is a well established method for the investigation of organic substances. It follows mass changes as a function of time and/or temperature and gives information about characteristic decomposition temperatures and quantitative composition (e.g. softener content) of the investigated material [DIN 51006]. An identification of gases released directly from the sample during thermal treatment cannot be performed just by thermal analysis.

Infrared spectroscopy (IR) is an widespread method in the fields of polymers and organic chemistry. It gives, with the exception of homonuclear diatomics and noble gases, a characteristic spectrum for each substance. The FT-technique adds the sensitivity and speed to accurate follow rapid decomposition steps. Due to small molecular interaction in the gas phase, gas mixtures can be resolved into their single components by subtracting away library spectra of the corresponding pure compounds. Digital libraries are available, considerably simplifying identification of the evolved gases. Combined with thermogravimetry, IR-spectroscopy gives exact information about which substances are formed at which temperature (on-line analysis). Thus, the TG-FT-IR coupling (method) gives a deep insight into the course of decomposition reactions and yields information about the physical-chemical nature of the observed process.

Experimental

The investigation of the powder coating based on PUR was carried out with a Netzsch thermal analyzer coupled to a Bruker FT-IR spectrometer (e.g. with the INVENIO platform). The thermo balance and FT-IR spectrometer are connected via a heated transfer line (370°C), adjusted to both systems. The transfer line opens in a heated (370°C) gas cell with optimized volume/path length ratio. On account of the small volume in the thermo micro balance, transfer line and gas cell, a very low transfer gas flow can be used.

This guarantees a high concentration of the released gases, transported in the gas cell, and thus a maximum sensitivity. The measurement was carried out in a nitrogen atmosphere at a gas flow of 10 ml/min. Because of the vacuum-tight construction of the thermo micro balance and the gas cell, both systems can be evacuated together prior to the measurement in order to minimize the influence of residual gases (e.g. oxygen) on the pyrolytic decomposition.

The measurements were conducted from room temperature to 500°C at a heating rate of 5 K/min. The transfer line and the gas cell were adjusted to 200°C. For the simultaneous FT-IR measurement, a resolution of 4 cm^{-1}, in the spectral range 650 - 5.000 cm^{-1} at a time resolution of approx. 15 sec. was selected. Electronic triggering of both analysis procedures enables the same start and end temperature. Therefore, an exact correspondence of the gases identified by IR spectroscopy to the decomposition temperature measured thermogravimetrically is possible. The TG measurement of the powder coating based on PUR depicts Fig. 9. Before the two-step decomposition at 353°C and 411°C two small mass losses can be observed at the maximum decomposition rate temperature (DTG peaks) at 85°C and 203°C. These two mass losses amount to 1% and correlate with the curing reaction of the material (see Fig. 1 and Fig. 2). Single FT-IR spectra were taken at the maximum decomposition rate temperatures (DTG peaks) for evaluation of the evolved gases.

The single FT-IR spectra at 85°C (Fig. 4) already indicate small emissions of methacrylic acid. The emission correspond to a mass loss of 0.2%. At 203°C carbon dioxide and an isocyanic acid can be clearly identified by a library search (Fig. 5).

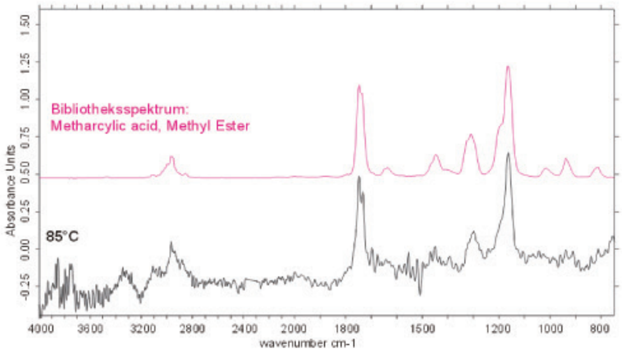


Fig. 4 (left)
Library search result of the FT-IR spectrum at 85°C.

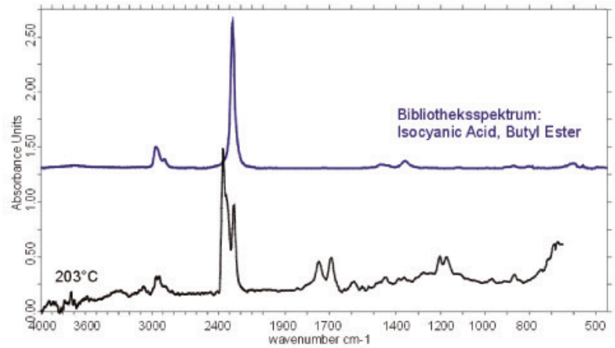


Fig. 5 (right)
Library search result of the FT-IR spectrum at 203°C.

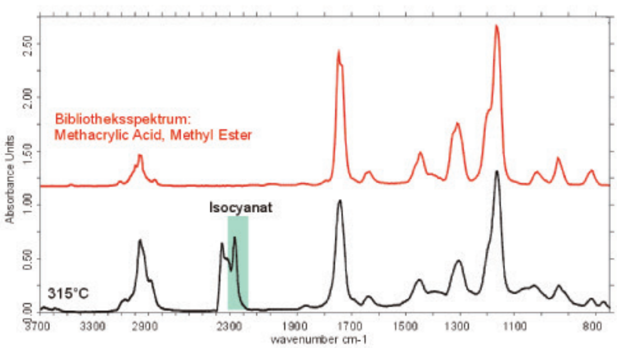


Fig. 6 (left)
Library search result of the FT-IR spectrum at 315°C.

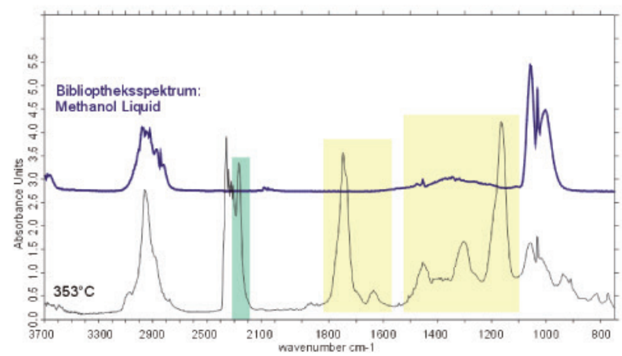
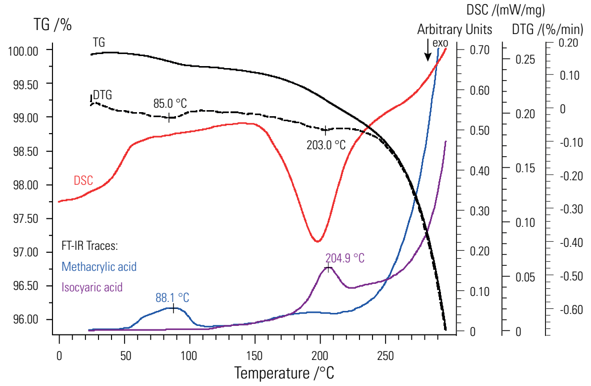


Fig. 7 (right)
Library search result of the FT-IR spectrum at 353°C.

The FT-IR spectrum at 315°C indicates methacrylic acid and still sub-ordinated isocyanic acid (Fig. 6). At 353°C the gas phase mainly consists of methacrylic acid and a maximum emission of methanol can be detected (Fig. 7).

The calculated FT-IR traces of methacrylic acid and isocyanic acid correlate with the first small mass losses (DTG peaks at 85°C and 203°C; Fig. 8). The release of methacrylic acid cannot be observed in the DSC curve. Isocyanic acid is released during the exothermal curing reaction. The release of isocyanic acid is finished after the main mass-loss step (Fig. 9). Methacrylic acid evolves during the two-step decomposition of the powder coating and is accompanied by the release of carbon dioxide. The decomposition product methanol is detected between 300°C and 430°C.



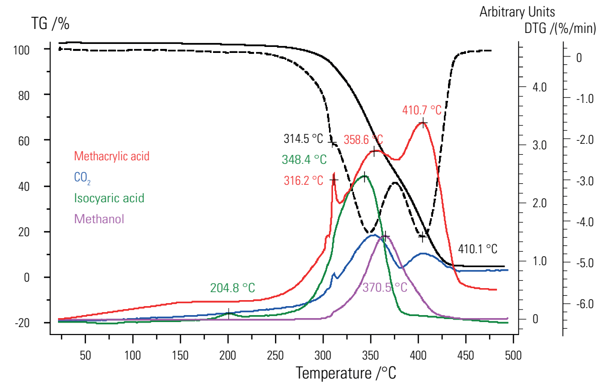


Fig. 8 (left)
DSC result.

Fig. 9 (right)
TGA result.

Summary

The DSC method allows the description of powder coating systems. The glass transition and the exothermal curing reaction as well as the degree of cross-linking can be determined. Kinetic analysis allows the determination of reaction model. Reliable predictions of the curing behavior can be taken from engineering graphics. TG-FT-IR coupling monitors the thermo-gravimetrical behavior and identifies the evolved gases during curing. Both results correlate, this means the released gases can be referred to the mass loss. Before the curing of the here investigated powder coating a release of methacrylic acid can be clearly detected. During the polyaddition reaction isocyanic acid evolves. This indicates encapsulated molecules or a steric hindering of the isocyanic acid which cannot take part on the reaction.

TG-FT-IR is based on a coorperation with

NETZSCH

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