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Education

A PRACTICAL THERMAL ANALYSIS COURSE

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Abstract

A practical Thermal Analysis Course is described, lasting one full week, in which the students are performing at least 10 experiments from different kinds, covering a broad range of possible applications. In combination with the elaboration of the experiments a number of lectures is given about the practice of thermal analysis. So a course is obtained, in which the students learn a lot of the possibilities (and impossibilities) of thermal analysis techniques, particularly by experiments, performed by their own.

Keywords: evaluation of TA experiments, influence of gas phase, practical TA course, TA experiments for students

Introduction

Since many years, a practical Thermal Analysis Course is given at Delft University. This course is intended for participants, coming from universities and industrial laboratories, in order to get experience with a broad range of thermal analysis techniques and applications.

During a full week the students are performing about 10 different experiments, using TG, TG/MS, DTA, DSC and TMA/DMA instruments. The experiments must be clear and instructive, covering different areas like inorganics, minerals, organics, pharmaceuticals, polymers and environments. They are used for the determination of kinetics, purity, polymeric properties, phase equilibria, the influence of the gas composition on decomposition reactions and analysis of complex compounds.

Further lectures are given about more theoretical aspects, like the principle of the different techniques, the operation and calibration of different instruments and the elaboration of the experiments.

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Upset of the course

The participants arrive at Monday 9.00 a.m. Groups of 2 or 3 persons are formed. The experiments are performed by the students themselves, coached by an instructor, who discusses before starting the upset and purpose of the experiment. Every day there are two experimental sessions of about 2–3 hours each, and a theory session of about 1 hour. During these theory sessions the experiments are discussed and compared, and lectures are given about a number of aspects of Thermal Analysis, such as:

- The operation of instruments and the applicability of TG, DTA, DSC, EGA and TMA techniques.
- The influence of temperature and gas phase.
- Special problems in the analysis of polymers, organics, inorganics and catalysts.
- Determination of the degree of reaction (α) from TG and DSC curves. Construction of baselines in DTA and DSC.
- Kinetics by TG and DSC, purity analysis and phase diagrams.
- Calibration of TG, DTA and DSC instruments.

All these aspects come back in the practical experiments.

At last, after 41/2 days of experiments and discussions, the whole Friday afternoon is devoted to the finishing touch: comparison of the results of the experiments, done by the different student groups, mentioning of useful literature (books, journals and proceedings of conferences), local activities (TAWN [the Dutch Thermal Analysis Society], ESTAC and ICTAC) as well as local and international meetings and conferences.

Last but not least, information is given about the instruments of the different manufacturers (performance and price). Also documentation is distributed, provided by these manufacturers.

Discussion of the experiments

Instruments

The most important part of this course consists of practical experimentation, performed on different types of instruments.

The applied instruments are:

TG: self built thermobalances and the high temperature micro-thermobalance from Stanton Redcroft (now: Rheometric Scientific).

DSC: Gold Cell from Rheometric Scientific DSC 910 from DuPont (now: TA Instruments). DSC-4 from Perkin Elmer. The "student" DSC from Mettler-Toledo.

DTA: High temperature DTA, provided by Perkin Elmer during the course.

TMA: Perkin Elmer.

EGA: Mass Spectrometer IQ-200 from Leybold-Hereaus, coupled to a (self-built) thermobalance.

The Perkin Elmer instruments are belonging to the Laboratory for Polymers Research of the Chemistry Department at the Delft University.

Experiments

During the last four years the following experiments were included in the courses [1, 2].

1. The DSC measurements of PETP-wires (Polyethylene Tere Phtalate). (Fig. 1) [1].

The difference between amorphous and crystalline polymers is learnt: the amorphous unstretched polymer shows a glass transition and a cold crystallization next to a melting peak, while the crystalline PETP (second run after slow cooling, or a new experiment with stretched wires) only shows the melting peak.

From the heats of crystallization and melting the amorphous/crystalline proportion of the samples can be determined.

2. Measurement of the glass transition temperature of a polystyrene coffee spoon by DSC and TMA [1].

Experimental conditions: DSC 10.580 mg, 20 K min^{-1}; TMA (penetration), sample height 0.732 mm, 5 K min^{-1}.

The T_g, measured by DSC corresponds well with the onset temperature in TMA (both measured for the second run), namely 109.8 and 108.1°C, respectively. The students learn that a reproducible second run can be made after a first run up to 140°C, because in the first run a lot of stress relaxation appears.

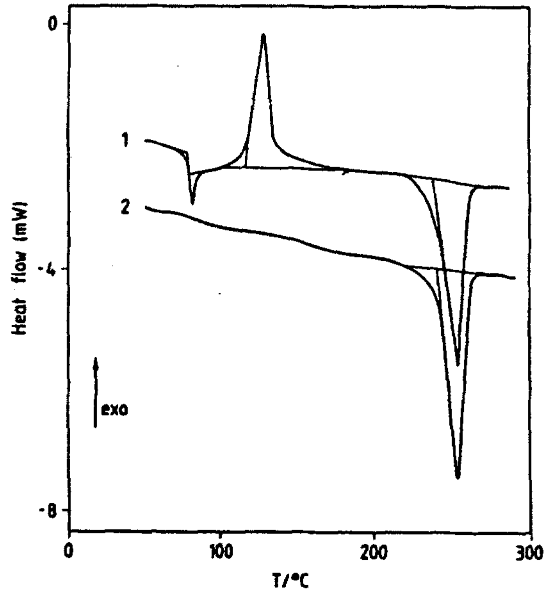

Fig. 1 DSC curves of 3.50 mg PETP wires at 20 K min^{-1}). 1. First run of an amorphous (unstretched) sample showing glass transition (T_g=77.8°C), cold crystallization (T_0=116.4°C, Ht=–28.62 J g^{-1}) and melting (T_0=240.6°C, Ht=35.90 J g^{-1}).
2. Second run of the same sample after cooling down with about 20 K min^{-1}, only showing the melting peak (T_0=241.9°C, Ht=38.92 J g^{-1})

3. Curing of an epoxy resin (Fig. 2) aged at 50°C [1].

From the peak areas the conversion degree α can be determined resulting into calculation of the rate of conversion at 50°C.

The DSC peak of the fresh sample also can be used for calculation of the kinetics according to the Borchardt-Daniels method. Now the students can make a comparison of both methods for determination of the curing kinetics.

4. Proximate analysis of 73.30 mg rubber by TG (Fig. 3) [2].

The students calculate the exact composition: water 0.14 wt%, rubber 63.17 wt%, carbon 32.33 wt% and mineral residue 4.36 wt%.

5. TG analysis of catalyst pellets, consisting of Ni, NiO, H_2O and Al_2O_3 (Fig. 4).

This is a more complicated analysis with several gas changes: $N_2 \rightarrow H_2 \rightarrow N_2 \rightarrow$ air.

The students learn to work safely with hydrogen at high temperatures.

The analysis results into the determination of the composition of the original catalyst: water content 8.5 wt%, NiO 46.6 wt%, Ni 28.5 wt% and Al_2O_3 16.4 wt%.

6. TG measurement of the decomposition of dolomite ($Ca_xMg_{1-x}CO_3$) in air or CO_2 (Fig. 5) [2].

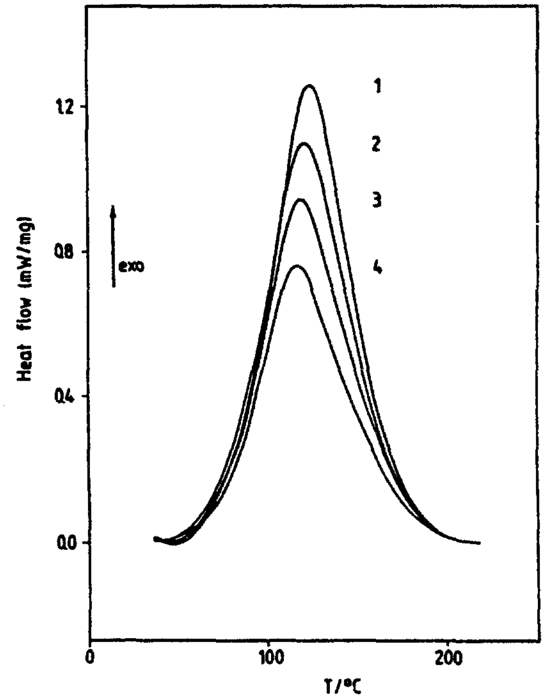

Fig. 2 DSC curves of the curing of an epoxy resin (two-component glue, slow version), aged at 50°C. Sample size 5–10 mg in an open pan. Heating rate 20 K min^{-1} from 20–250°C. 1. Aged 0 min, Ht=218 J g^{-1}; 2. Aged 20 min, Ht=195 J g^{-1}; 3. Aged 40 min, Ht=169 J g^{-1}; 4. Aged 60 min, Ht=136 J g^{-1}

In air nearly no separation can be seen between both reactions, but in CO_2 the $CaCO_3$ decomposition shifts to higher temperatures, resulting into a complete sepa-

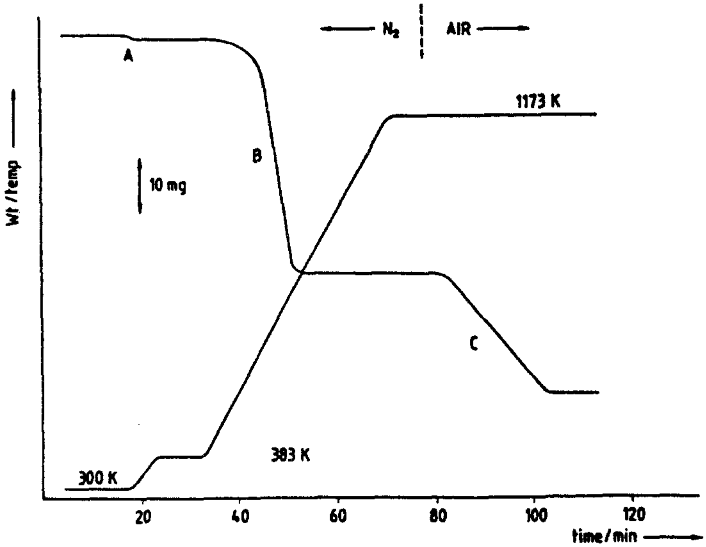

Fig. 3 Proximate analysis by TG of 73.3 mg rubber (Dunlop tire). Program: N_2, 20 K min^{-1}, 300 → 383 K; iso at 383 K for 20 min; heating at 20 K min^{-1}, 383 → 1173 K; iso at 1173 K. Change of N_2 into air at 1173 K. Mass changes: A=0.1 mg (water), B=46.3 mg (rubber) and C=23.7 mg (carbon)

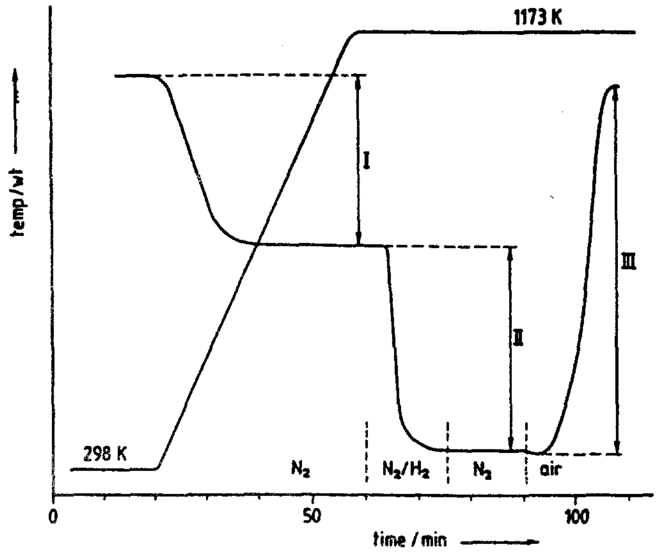

Fig. 4 TG analysis of 75.50 mg of catalyst pellets, containing Ni, NiO, H_2O and Al_2O_3 in varying gas phases. Heating rate 20 K min^{-1} from 298 → 1173 K. Mass changes: I=6.40 mg (volatiles), II=7.54 mg (NiO → Ni) and III=13.40 mg (all Ni → NiO)

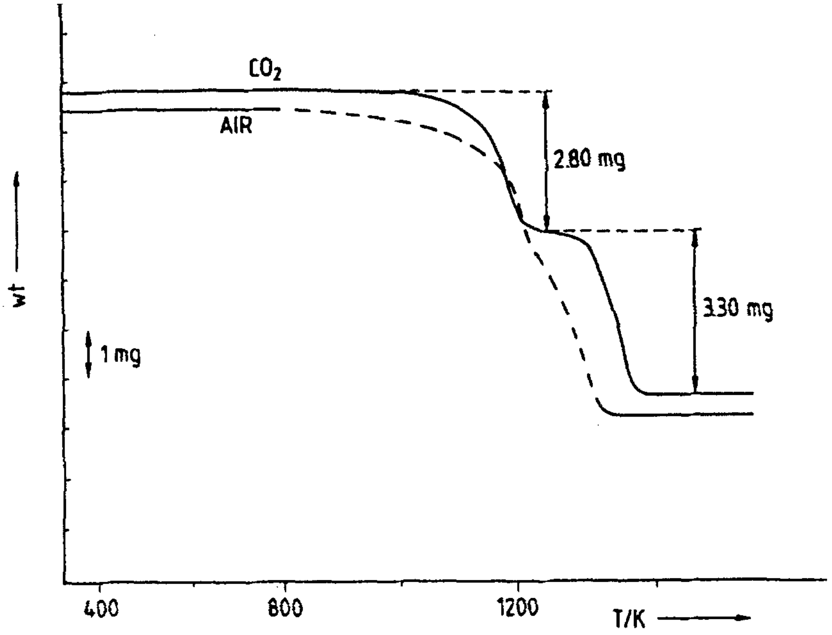

Fig. 5 TG measurement of a piece of natural dolomite at a heating rate of 50 K min^{-1}. In air: mass 13.0 mg, total mass loss 6.10 mg. In CO_2: mass 13.4 mg, total mass loss 6.10 mg

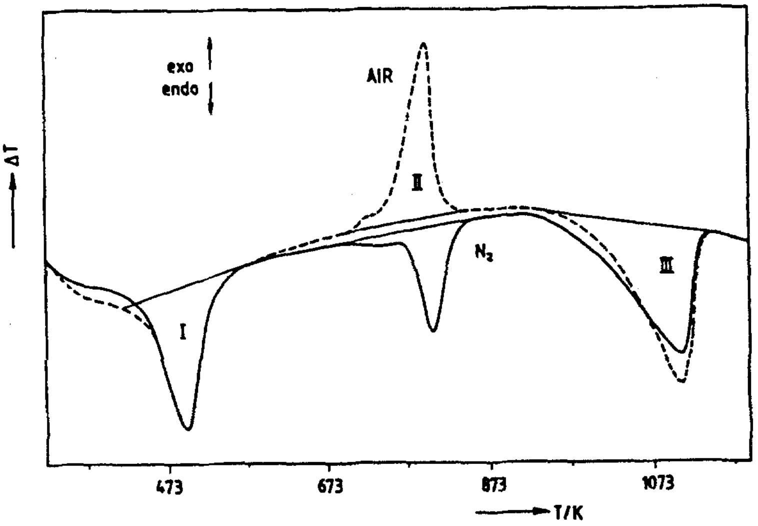

Fig. 6 DTA measurement of the decomposition of calciumoxalate monohydrate powder, at a heating rate of 20 K min^{-1}. In nitrogen, showing three endothermic peaks, and in air, showing the second peak being exothermic

ration between both reactions. Now the composition of this natural product can be calculated: $MgCO_3$ 39.9 wt%c, $CaCO_3$ 56.0 wt% and non reacting minerals 4.1 wt%.

Furthermore the students are confrontated with a kinetic problem: why doesn't the $MgCO_3$ decomposition shift to higher temperatures, going from inert gas to CO_2 ? This can only be explained if the rate determining step is not the reaction of $MgCO_3$ into $MgO+CO_2$, but a solid state reaction: dolomite → $MgCO_3$ +$CaCO_3$, followed by a fast decomposition of $MgCO_3$ [3].

7. DTA measurements of the decomposition of $CaC_2O_4 \cdot H_2O$ in air or N_2 (Fig. 6) [2].

It is not possible to use a DSC instrument for this experiment, because the applied temperatures are too high for DSC. Therefore the high temperature DTA of PE was used (for temperatures up to 1500°C).

Three peaks are visible in the DTA curve: loss of water vapour (I), loss of CO (II) and loss of CO_2 (III). In N_2 all three peaks are endothermic, but in air or oxygen the second peak (II) becomes strongly exothermic, because CO is oxidized into CO_2.

When the DTA instrument should be correctly calibrated, also the heats of reaction could be measured [4].

The heat measured for peak III, corresponding to the decomposition of $CaCO_3$ into $CaO+CO_2$, amounts to be 1026 J g^{-1}. The literature value should be 1170 J g^{-1} calciumoxalatemonohydrate, so the preceding calibration with Al and Au is not satisfactory.

8. Determination of a Phase Diagram (Pb/Sn) with DSC (Fig. 7). The samples are previously prepared by melting Pb and Sn together [1].

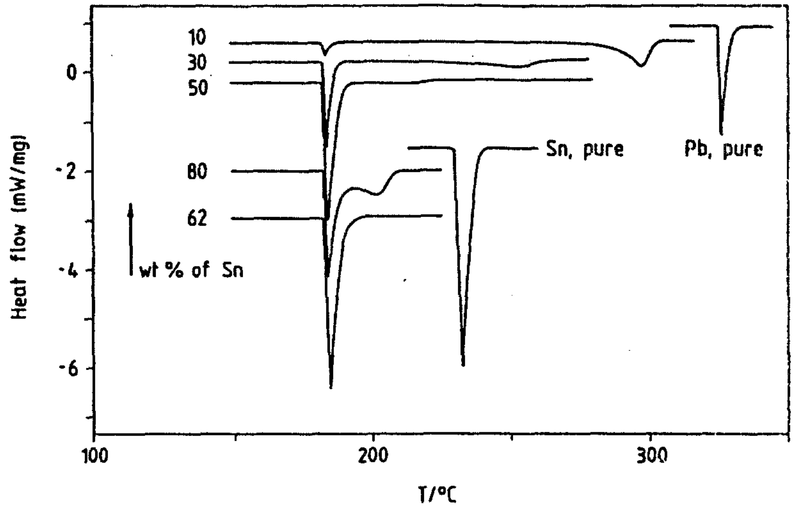

Fig. 7 DSC measurement of the Pb/Sn phase diagram, measured in flowing N_2. Sample weight about 5 mg, heating rate 20 K min^{-1}. All mixtures show an eutectic temperature (T_0 about 183°C) and a liquidus temperature varying according to the phase diagram

According to the equilibrium phase diagram [5], all characteristic points (the temperatures of the eutectic and the liquidus) can be measured. Of course, the use of much slower heating rates (1 K min^{-1}, instead of 20 K min^{-1}) would be better, since the establishment of the equilibrium needs time, but even with 20 K min^{-1} a good insight is given in the determination of a phase diagram.

9. TG/MS measurement of the decomposition of calciumoxalatemonohydrate in a Helium atmosphere [1].

The problems are discussed how to connect a thermobalance to a mass spectrometer. The students see that the successive decomposition reactions of calciumoxalate hydrate indeed produce H_2O, CO and CO_2 in the gasphase.

10. Temperature calibration of a thermobalance [1]

This is done by heating a set of magnetic metals with different Curie temperatures in a magnetic field (Ref. [1]). The set consists of Alumel (163°C), Nickel (354°C), Perkalloy (596°C), Iron (780°C) and Hisat50 (1000°C).

One of the problems is how to make a good magnetic field: if it is too strong, the sample will stick to the furnace wall, while a too weak magnetic field gives very small signals.

Particularly the heating at 50 K min^{-1} in a N_2 atmosphere (just like the dolomite experiment) shows great differences (up to 70°C) between the measured and the real temperature values.

11. Calibration of a DSC instrument.

The low temperature region of a DSC instrument (–100 to +200°C) is calibrated, using In (+156.60°C, 28.62 J g^{-1}), Hg (–38.87°C, 11.62 J g^{-1}) and Adamantane (–64.56°C, 24.78 J g^{-1}) [6]. Both temperature and DSC signals are calibrated.

12. Purity analysis of several compounds, measured by DSC [1].

Several compounds, like benzoic acid and stilbene are measured. The purity is calculated using the DSC purity programme.

The students learn to work with this type of investigations. They see that benzoic acid gives problems because of evaporation during the melting reaction. This can be explained by comparison of the boiling and melting temperatures: for benzoic acid 249 and 122°C, and for stilbene 308 and 125°C, respectively.

It is clear that benzoic acid, compared to stilbene, has a higher vapour pressure at its melting temperature.

13. Testing of the performance of a DSC instrument with the TAWN test, using 4,4′-Azoxyanisole [7].

This compound shows two transitions: Solid → Liquid Crystal at 118°C, with a great heat effect (about 108 J g^{-1}) and Liquid Cystal → Liquid at 135°C, with a very small heat effect (about 2 J g^{-1}).

The resolution is measured by heating a large amount of sample with a fast heating rate (5 mg, 20 K min^{-1}), vhile the sensitivity is measured by heating a small amount of sample with a slow heating rate (0.25 mg, 0.1 or 1 K min^{-1}).

Final remarks

Not all the experiments are done during every course. So, in the last course (June 1996) the TG/MS experiment was not included. Likewise, during some sessions two fast experiments were combined, for instance 10 and 11.

At the end of the course the students know how to work with different kinds of instruments (TG, DSC, DTA, etc.) and they got insight in the possible applications and limitations of the different techniques.

Also the influence of the gas phase is very important, in particular for analytical purposes. They did learn something about kinetics, as well in TG as in DSC experiments. They also learnt to handle the relevant computer program for elaboration of the experiments, calculation of the purity and kinetics, and calibration of the instruments.

They got knowledge about the different manufacturers, instruments, performances and prices.

Last but not least they learn how to proceed in developing their thermal analytical knowledge (literature, societies, conferences, etc. etc.).

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References

1 M. E. Brown, Introduction to Thermal Analysis, Chapman and Hall, London 1988, Chapters 3, 4, 13 and 14 (ISBN 0-412-30230-6).
2 S. St. J. Warne, in Thermal Analysis - Techniques and Applications, Eds E. L. Charsley and S. B. Warrington 1991, p. 231 (ISBN 0-8516-375-2).
3 G. Hakvoort, "Influence of the gasphase on the rate of decomposition reactions", in: Proc. 26th Int. Conf. Vac. Microbalance Techn., Marrakesh, 1995, M'bark Ben Chanaa (Ed), p. 13-20.
4 G. Hakvoort, Thermal Analysis, Proc. 4th ICTA, Budapest, 1974, Vol. 1, p. 469.
5 Gmelins Handbuch der Anorganischen Chemie, 8ste Auflage, 1971, Tl. C4 (Pb), p. 1487.
6 G. Hakvoort, J. Thermal Anal., 41 (1994) 1551.
7 P. J. van Ekeren, C. M. Hol and A. J. Witteveen, Proc. 11th ICTAC, J. Thermal Anal., 49 (1997).