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Alternating thermal analysis techniques¹

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Abstract

Existing thermal analysis techniques, e.g. DSC, TMA and TGA are applied to obtain information using normally constant or linear changing experimental parameters, i.e. heating rate, probe load or purge gas flow. Superimposed on the constant parameter or linear changing variable, a dynamic part (e.g. a dynamic load, a changing purge gas composition or non monotonous temperature gradient) reveals additional information on the nature of the samples and ongoing simultaneous effects compared to standard applications, without much longer investigation time. The well known dynamic load TMA (DLTMA) adds to the expansion of the information on the elastic behavior, and the new alternating DSC technique (ADSC) gives insight into the sensible heat flow and the latent heat flow, i.e. the respective heat flow signals related to a change of temperature and to an uptake or loss of heat which can be recorded only once.

Keywords: TA; Alternating TA; Temperature modulation

1. Introduction to the concept of alternating thermal analysis

In DSC, TGA and TMA, the physical or chemical properties of a sample are measured as a function of constant or linearly changing temperature under constant surrounding conditions, such as furnace atmosphere or other measuring conditions [1]. Alternating TA techniques superimpose on the “constant” techniques, as described before, a regular changing parameter (or even independent variable) in a way in which the parameter alternates between two values (e.g. load in TMA [2]) or where the temperature (as the in-

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dependent variable) is programmed in a non-monotonous way (e.g. isothermal steps for purity analysis [3] or isothermal step method (ISM) [4]). The first mentioned alternating technique (dynamic load TMA or DLTMA) is used to reveal changes in E -modulus, the latter, for example, to detect critical thermal decompositions in safety investigations.

1.1. Measurement of length changes

In DLTMA with its typical alternating load to the sample the E -modulus (or Young's modulus) is calculated as follows:

$$E = \text{stress/strain} = (\Delta F/A)/(\Delta L/L_0) \quad (1)$$

where A is the cross sectional area of the specimen, ΔF is the change of force to the measuring probe ($F_{\text{high}} - F_{\text{low}}$), ΔL is the length change due to change in probe force (alternating length), corrected by the respective blank length change and L_0 is the initial length of the specimen.

The alternating length (ΔL) is superimposed on the thermal expansion (Δl) which correlates to the temperature change (ΔT) as follows:

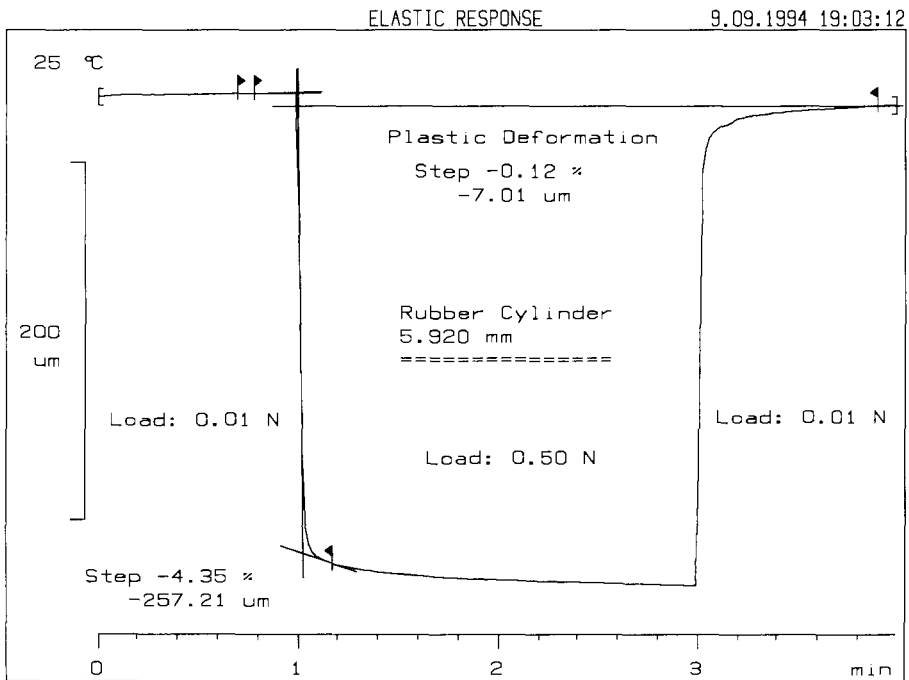


Fig. 1. Elastic response of a soft rubber cylinder of 6 mm diameter measured by loading and unloading 0.49 N and recording the length change by TMA. Between probe and specimen an alox-disc of 1 mm thickness and of 6 mm diameter was used to spread the load equally over the full cross section of the cylinder.

$$\Delta l = \alpha \times \Delta T \times L_0 \quad (2)$$

or in differential form

$$dl/dT = (dl/dt)/\beta = \alpha \times L_0 \quad (3)$$

where α is the expansivity (linear expansion coefficient) and β is the heating rate.

Hence, the DLTMA curve (e.g. Fig. 2) represents in the average the expansion behavior for a mean load and with the difference of the extremes of the up-and-down curve, the envelopes, the elastic behavior.

1.2. Measurement of heat flow

In the isothermal step method using DSC, the temperature is gradually increased specially to trigger autocatalytic effects or to gradually melt an impure substance, but “suppressing” heat capacity effects (e.g. Fig. 3).

The heat capacity and its change with time or temperature can only be measured by

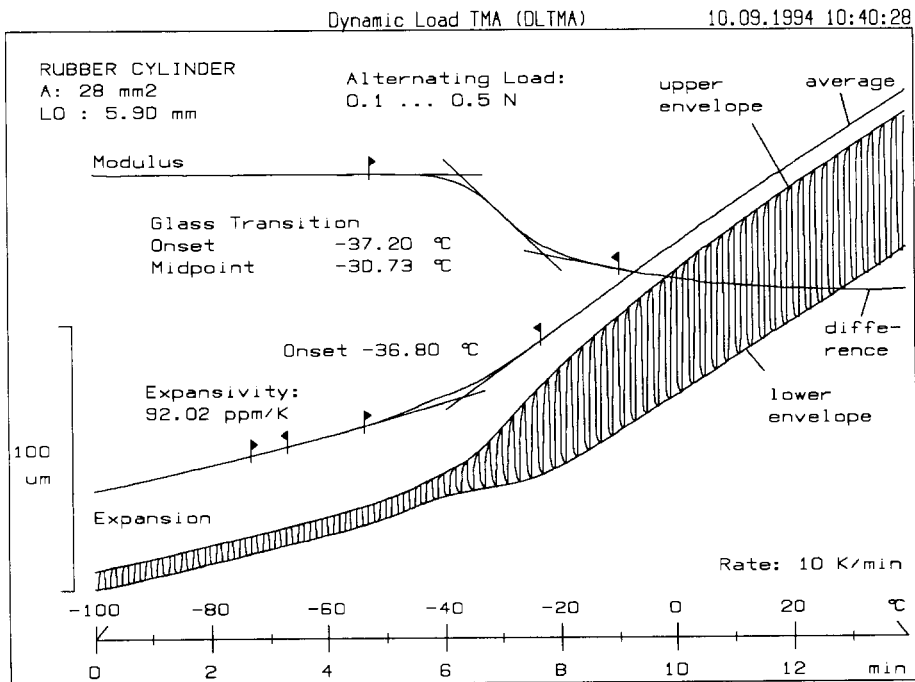


Fig. 2. Expansion and elastic response of a rubber cylinder with 6 mm diameter by DLTMA. The load alternates between 0.1 and 0.5 N at a frequency of 1/12 Hz during the heating from -100 to 40°C . Heating rate 10 K min^{-1} . The average of the envelopes represents the expansion due to heating, the difference of the envelopes is proportional to the E -modulus. From both curves the glass transition temperature is calculated as an onset point.

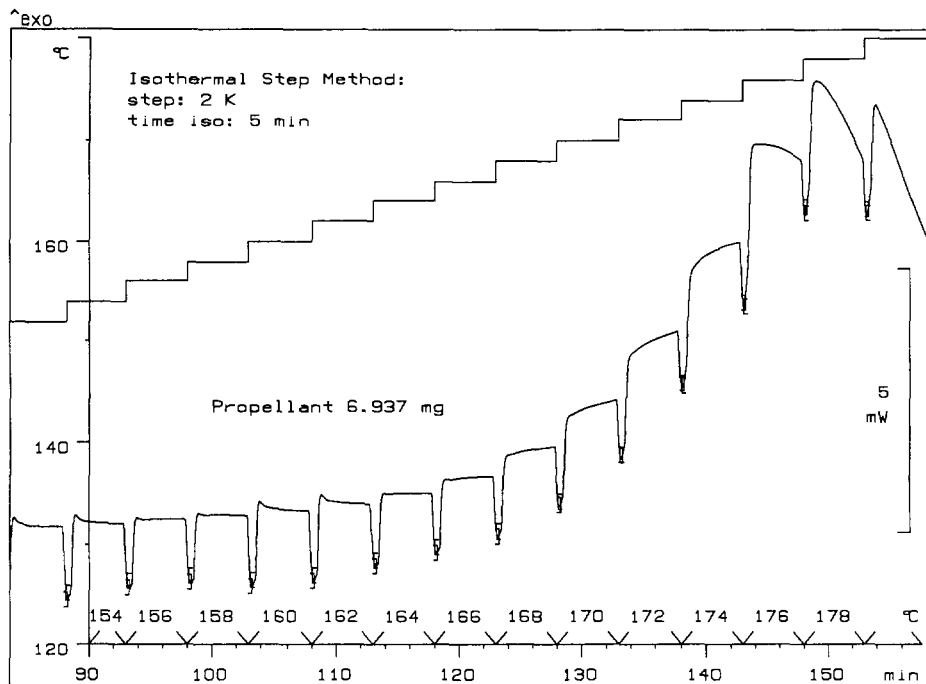


Fig. 3. Some small pieces of a propellant are heated stepwise, as the temperature curve shows, in an aluminum pan with small hole in the lid. Purge gas flow 80 ml min^{-1} . Under these conditions the decomposition is completed at 250°C and the respective energy output is 2520 J g^{-1} .

changing the temperature of the sample and monitoring the respective heat exchanged with the surroundings as defined in Eq. (4):

$$\Delta H = m_0 \times C_p \times \Delta T \quad (4)$$

where ΔH is the enthalpy change due to temperature change (without additional effects), m_0 is the mass of the specimen, C_p is the specific heat capacity of the sample and ΔT is the temperature increase or decrease by heat input or output. Eq. (4) is a good and practical approximation of the thermodynamic function for small temperature changes.

In addition to the heat flow due to heat capacity, other energy changes are usually recorded, i.e. the power of a chemical reaction or heat changes due to physical transitions – the thermal effects of interest for DSC measurements.

Hence, in calorimetry (e.g. in DSC) all the effects add up to the resulting measuring signal:

$$Q = m_0 \times C_p \times \beta + Q_r + Q_t + Q_b \quad (5)$$

where Q is the heat flow measured by DSC (or other calorimetric systems), Q_r is the power related to chemical reactions, Q_t is the heat flow related to physical transitions and

Q_b is the drift of the measuring signal (heat flow of blank curve, usually measured separately).

Eq. (5) can be expressed in terms of the “nature” of the energy involved and be split up into a part in which the energy exchange leads to temperature change, so-called sensible heat (ΔH_s), and into another part, the so-called latent heat (ΔH_l), in which heat input does not increase the temperature, as known from the heat of fusion:

$$\Delta H = \Delta H_s + \Delta H_l \quad (6)$$

or with respect to time, expressed as heat flow

$$Q = Q_s + Q_l \quad (7)$$

with

$$\text{sensible heat flow: } Q_s = m_0 \times C_p \times \beta + Q_b \quad (8)$$

after initial deflection, at constant heating or cooling,

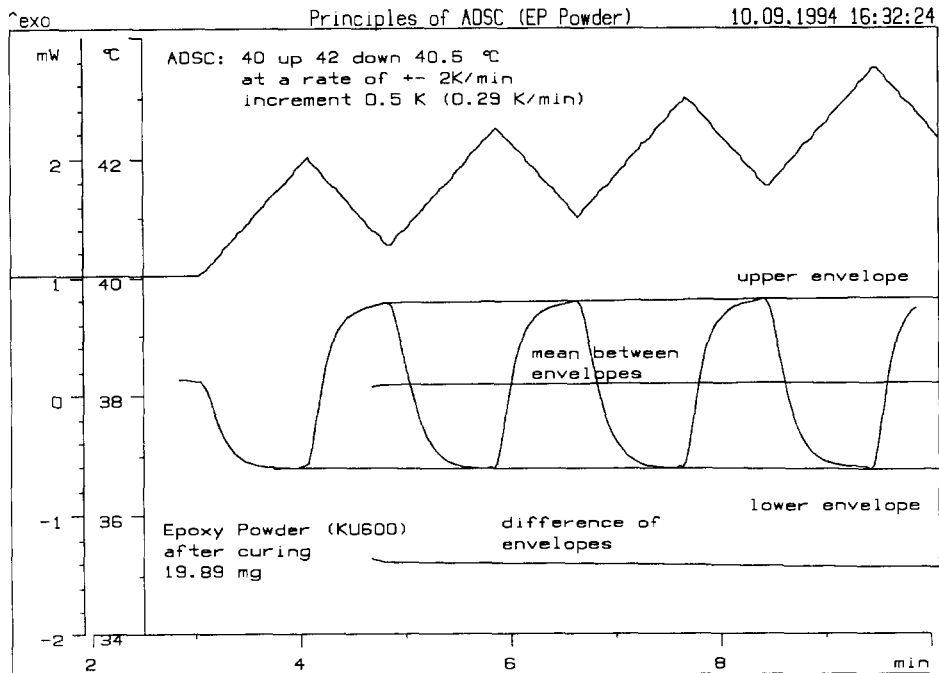


Fig. 4. The temperature program and DSC curve of an ADSC measurement shown with the envelopes to the peaks and with their respective average and difference curves. Cured epoxy powder KU600 from Ciba-Geigy as the specimen in a sealed aluminum crucible.

$$\text{latent heat flow: } Q_l = Q_r + Q_t \quad (9)$$

Eq. (8) is used to determine C_p . The initial deflections in DSC curves for the switch over from isothermal to heating or cooling at a constant rate (β) (see e.g. Fig. 4) directly represent the heat capacity ($m_0 \times C_p$). Hence, many of such initial deflections spread over time and/or temperature will show the heat capacity profile. This is determined by the difference of the envelopes to the many initial full deflections. This can be achieved by alternating the temperature (as the influencing variable) in pieces of small ramps, as will be used in the new alternating DSC (ADSC) technique. Hence, the sensible heat flow is defined to represent the behavior of the heat capacity and is determined as the half value of the difference between the envelopes of the ADSC curve.

It can be assumed, that an ongoing reaction is not greatly affected in rate by small alternating temperatures. In addition, the heat capacity shows also no important change during such a small temperature change (Q_s being constant). Therefore, applying the ADSC technique, the heat flow due to the reaction, the latent heat flow, can be measured by Eq. (7) as the average of the upper and lower envelope to the ADSC curve.

From this discussion it can be concluded that alternating DSC is able to monitor inde-

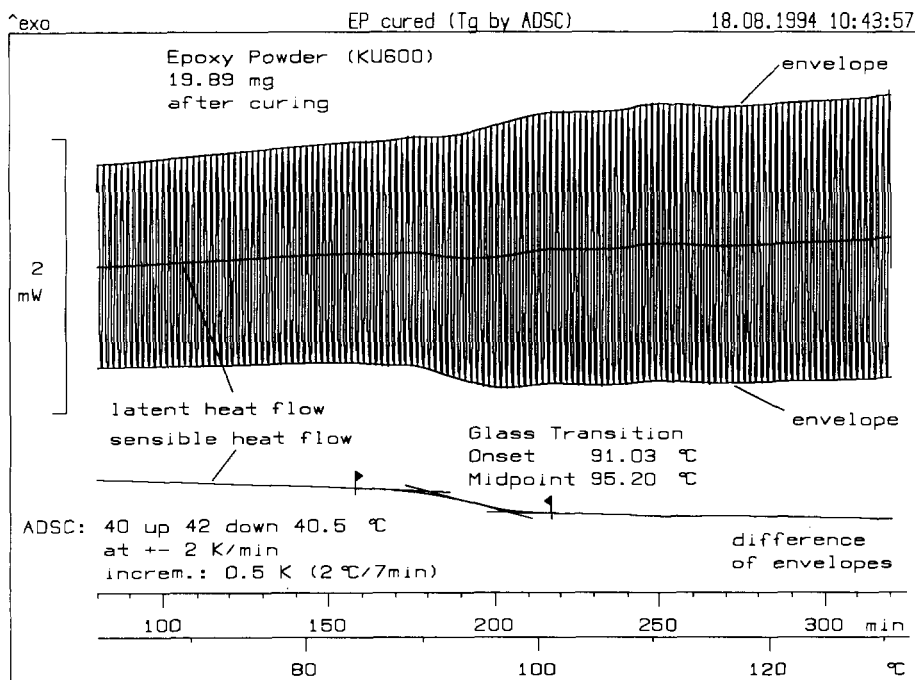


Fig. 5. Cured epoxy powder KU600 (specimen as in Fig. 4) measured by ADSC technique in the range of the glass transition of 95°C. The broadening of the bandwidth of the initial deflections clearly indicates the C_p change, represented by the sensible heat flow. The average curve (latent heat flow) shows only a very small heat relaxation.

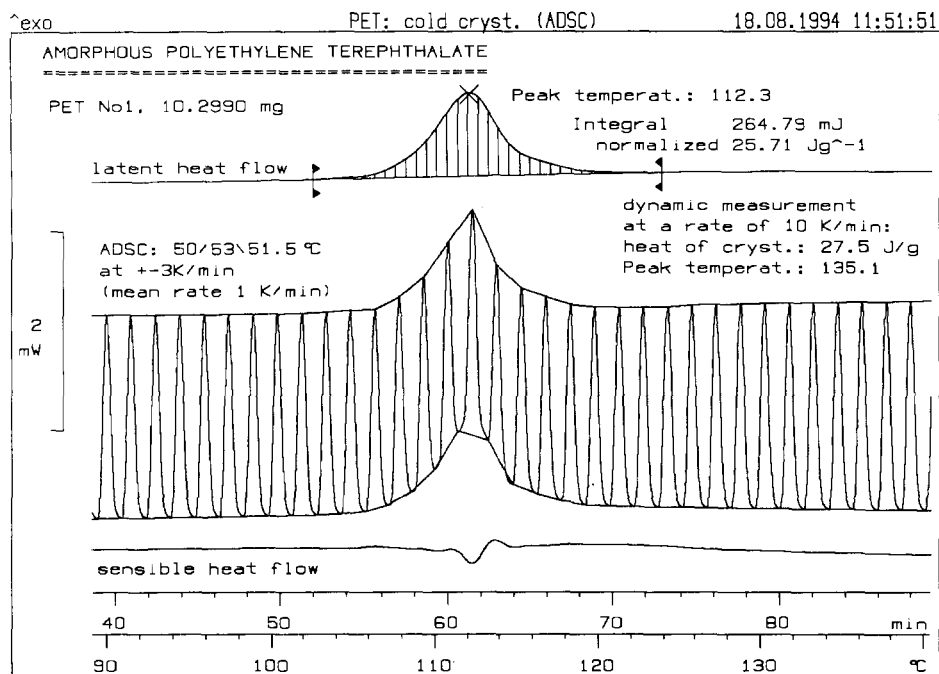


Fig. 6. Cold crystallization of amorphous polyethylene terephthalate (PET) by ADSC. 10 mg in a sealed aluminum crucible. One temperature cycle is done within 1.5 min to reach 1.5°C temperature increase (average rate 1 K min⁻¹).

pendently the sensible and the latent heat flow of simultaneous thermal effects such as relaxation and evaporation effects during glass transition, or chemical and physical transitions with enthalpy and C_p change.

2. Experimental

Experiments have been performed to illustrate the concept and the power of alternating TA techniques. The samples used are described in the results. The measurements and evaluations as well as the figure printouts were performed on a Mettler TA8000 system with TMA40 and DSC820 measuring cells.

3. Results and discussion

3.1. Alternating TMA (DLTMA)

Alternating the load during TMA experiments reveals plastic and elastic deformation during expansion. The procedure to measure an elastic response is shown in Fig. 1 where the load is increased and decreased from 0.01 to 0.5 N. The soft rubber cylinder does not

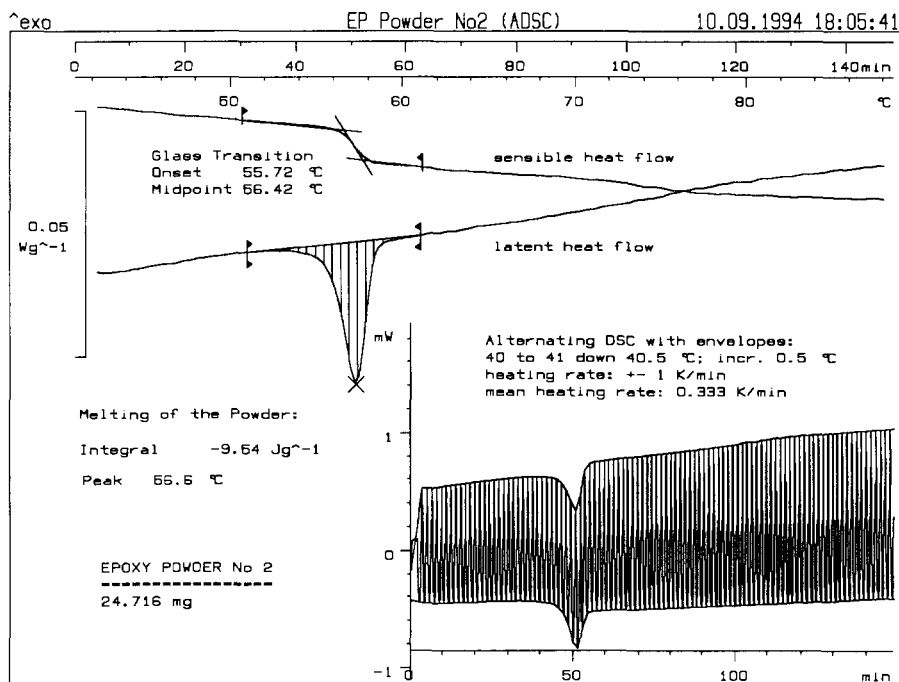


Fig. 7. "Fusion" of epoxy powder particles of KU600. The ADSC temperature program starts at 40–41°C and is lowered to 40.5°C within 1.5 min and incremented to give an average heating rate of 0.333 K min⁻¹. Sample preparation: aluminum pan filled with powder and sealed hermetically.

recover fully and a plastic deformation of 0.12% remains. The *E*-modulus by compression is 0.4 N mm⁻².

The rubber cylinder shows a glass transition at -37°C (Fig. 2). During this glass transition the expansivity increases by a factor of 2.7 while the *E*-modulus decreases by a factor of 20 (37 to 1.8 N mm⁻²) as calculated from the curve in Fig. 2.

3.2. Isothermal step DSC

To detect autoacceleration of a decomposition reaction by temperature increase, the isothermal step method with 2°C steps and 5 min waiting was used. As Fig. 3 shows, an exothermal reaction can be detected at 160°C under the given conditions. Due to the accelerated reaction, the DSC signal is getting more exothermal during the isothermal periods, as can be clearly seen for 170, 172 and 174°C. Towards the end of the reaction the rate is only increased by the temperature increase, but finally goes back to zero with full decomposition.

3.3. Alternating DSC (ADSC)

The principle of the alternating heating rate with the resulting initial deflections in the

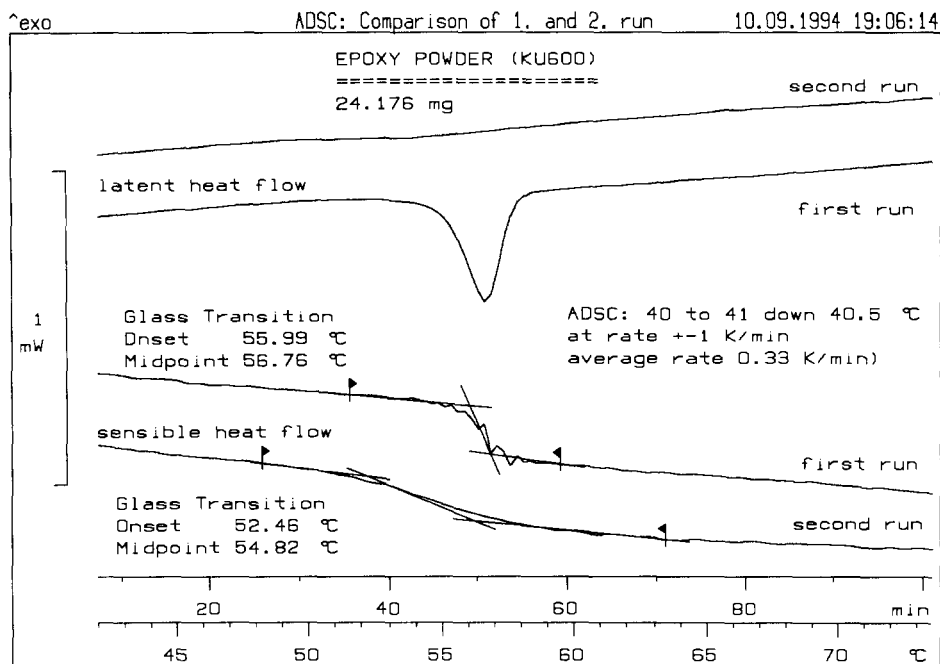


Fig. 8. Comparison of sensible and latent heat flow of first and second ADSC run of the epoxy powder specimen as given in Fig. 7.

DSC curve is demonstrated in Fig. 4. As the temperature program curve shows, the temperature is increased from the isothermal 40°C at the beginning to 42°C at a rate of 2 K min⁻¹ and immediately decreased to 40.5°C with the same but negative rate. This up and down cycle of 1.75 min is repeated in a loop but with a starting point increment of 0.5°C. Therefore the average heating rate amounts to 0.29 K min⁻¹. The envelopes to the endo and exo peaks are drawn. From these the average curve (sum of the curves divided by two) as the latent heat flow and the sensible heat flow (lower minus upper envelope) is calculated. The heat capacity is calculated from this curve by division of twice the heating rate ($2 \times \beta$).

The full ADSC curve up to 130°C is shown in Fig. 5 revealing the expected glass transition at 95°C by a step-like change of the sensible heat flow (as in a normal DSC curve) but without other effects.

The next example (Fig. 6) has been selected to have predominantly a one-way physical reaction but no change in heat capacity. The signal deflection acting like a ribbon keeps its width during the exothermal cold crystallization of an amorphous PET. The heat of crystallization taken from the latent heat flow is 25.7 J g⁻¹, a value which compares well with the value of 27.5 J g⁻¹ found from a normal DSC curve. But, in DSC the peak temperature is shifted upwards to 135°C by the 10 times higher heating rate, compared to 112°C by the ADSC measurement. The sensible heat flow keeps approximately constant during this process.

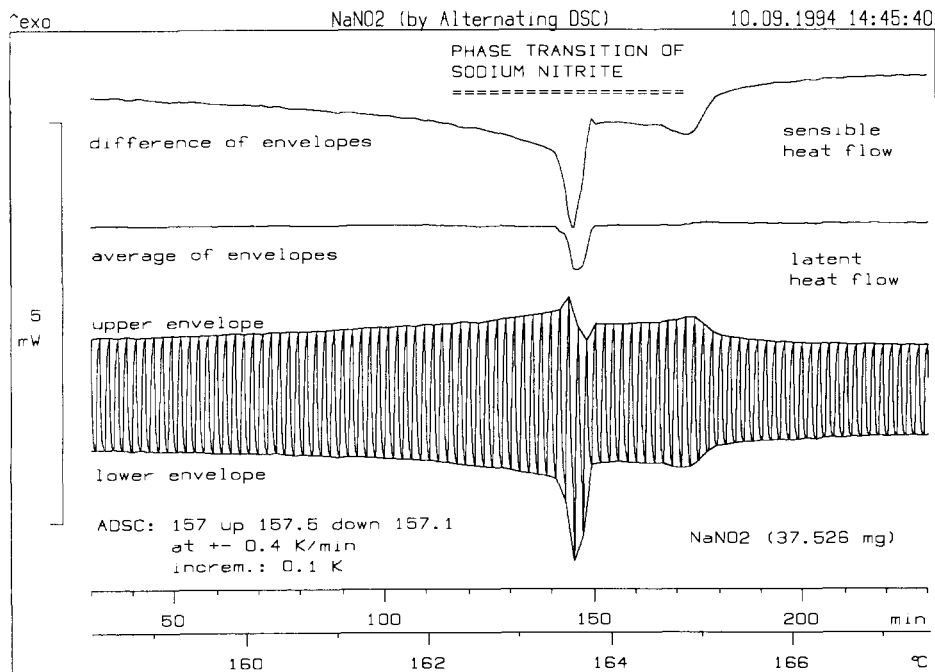


Fig. 9. Phase transition of sodium nitrite at 163.6°C measured by ADSC with average heating rate of 0.044 K min⁻¹.

The examples shown before revealed individual thermal effects, i.e. change in heat capacity or heat of a one-way reaction. The power of ADSC is demonstrated in the next example, where the fusion of the new epoxy powder particles by increasing temperature is measured (Fig. 7).

The increase of the heat capacity goes along with an uptake of latent heat of fusion, very similar to the heat of relaxation at the glass transition. But, the jump in heat capacity seen during this fusion is afterwards found to be 10°C lower than measured with DSC at a heating rate of 10 K min⁻¹. The comparison of the first and the second ADSC heating gives a decrease in glass transition temperature of 2°C and a broadening of the range (Fig. 8).

The ADSC technique is able to increase the average temperature very slowly, but still reveals overlapping effects. Sodium nitrite, analyzed in this way, shows small endothermal heat of transition at 163.6°C, but shows also peaks in heat capacity revealed by the sensible heat flow curve (Fig. 9). In normal DSC, two endothermal peaks can be seen, if the sample is heated slowly (e.g. 0.5 K min⁻¹) but these effects could be mis-interpreted as two separate amounts of heat of transition.

A change in heat capacity can be based on a change in the specific heat capacity (as in glass transitions) or by a change of the amount of sample. This effect is met during evaporation of water; its C_p changes only from 2384 to 2255 J g⁻¹ over the broad range from 50 to 100°C. Fig. 10 shows the resulting curves of the ADSC measurement of the

evaporation of water through a small pinhole in the lid during slow heating. Integrating the average of the envelopes (latent heat flow) using the zero baseline gives a heat of evaporation of 2361 J g^{-1} . The difference in envelopes divided by $C_p \times 2 \times \beta$ (see Eq. (8)) gives the weight loss curve going down from 20 to 0 mg.

Polyamides also absorb moisture which is evaporated during heating. The moisture affects the glass transition temperature. With DSC this glass transition is usually hidden by the evaporation peak. PA 6 pellets absorb up to 5% of moisture as measured by TGA. ADSC measurements differentiate between the sensible heat flow (heat capacity) and the latent heat flow (evaporation) in this case. As given in Fig. 11 the glass transition is found to be at 9.7°C evaluating the sensible heat flow curve; the water acts as softening agent to lower the dry transition temperature of 40°C . Integration of the moisture desorption peak monitored by the latent heat flow curve and relating it to the heat of evaporation at 50°C defines a moisture content of 4.0%, the same value as found by DSC measurement at a rate of 5 K min^{-1} . The pronounced increase of the latent heat flow at 28°C is an indication of sample history, i.e. the storage temperature.

4. Conclusion

The techniques of alternating thermal analysis have been generally defined, and the

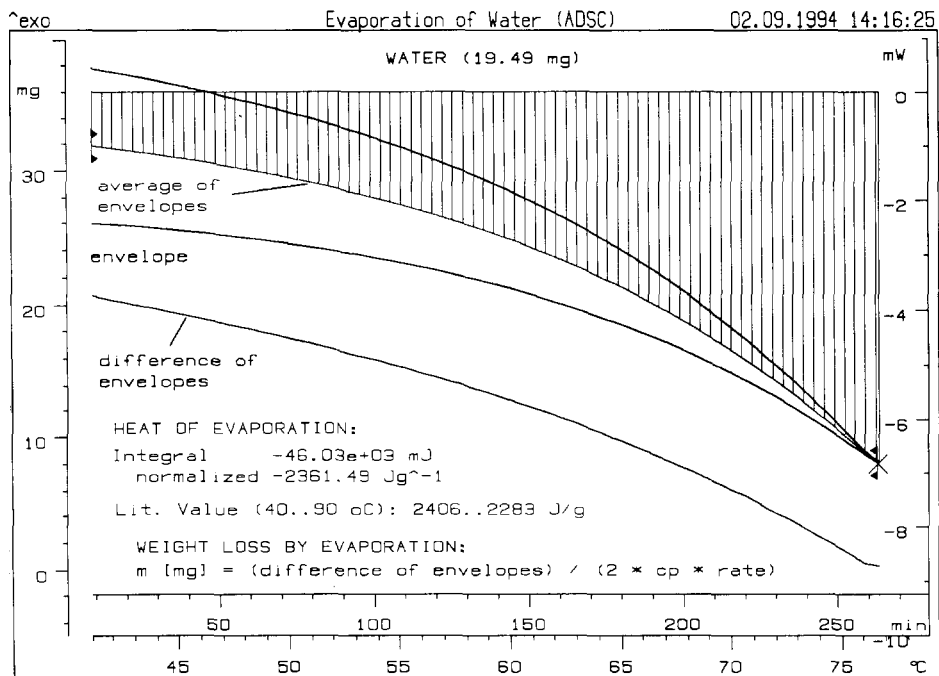


Fig. 10. Evaporation of water measured by ADSC. Alternating temperature program: $40\text{--}42^\circ\text{C}$ and back to 40.5 at a rate of $\pm 1 \text{ K min}^{-1}$. The evaporation through the 0.5 mm pin hole ends at 77°C .

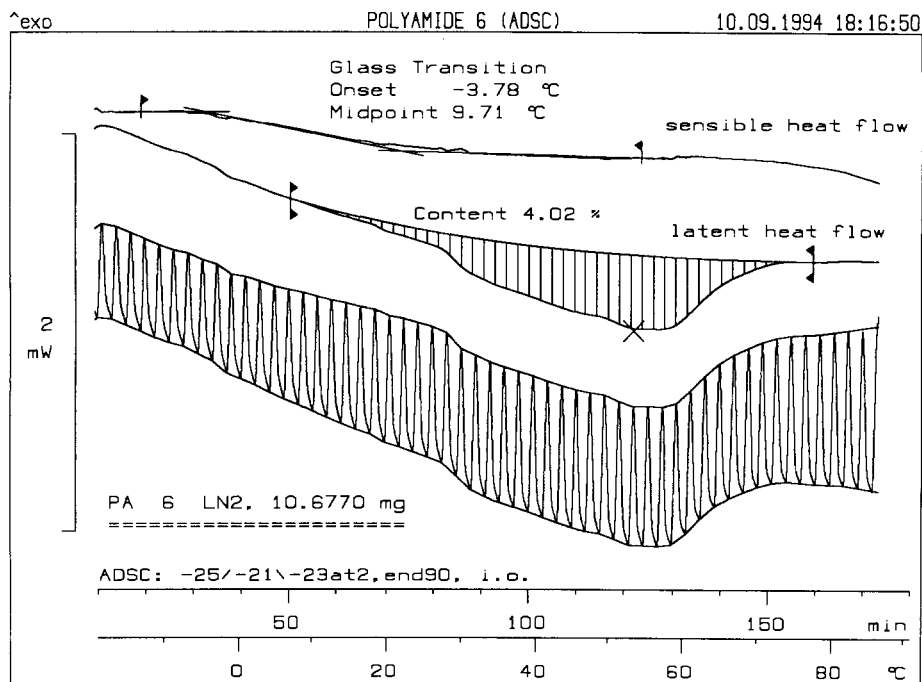


Fig. 11. ADSC of polyamide 6 using a repetitive temperature loop from -25 up to -21 and back to -23°C at a rate of 1 K min^{-1} giving an average heating rate of 0.66 K min^{-1} . A 10.67 mg pellet was flattened and packed in an aluminum pan with a pinhole in the lid. To calculate the content of moisture, heat of evaporation of 2384 J g^{-1} (50°C) is taken as a reference value.

new terms of sensible and latent heat flow have been introduced. These new terms describe the signals derived from alternating DSC (defined as ADSC), a technique easy to apply, which uses the repeated short linear heating and cooling of a sample to monitor the change of heat capacity overlapped by an exo- or endothermal chemical or physical reaction power. Hence, alternating TA techniques such as DLTMA or ADSC provide in a very comprehensive way information on simultaneous changing physical properties such as expansion and modulus or heat capacity and heat relaxation during glass transitions. Alternating a normally constant parameter of a TA experiment reveals much more information on a sample during one scan. But, only one measuring technique, e.g. TMA or DSC, is applied. The experimental method can easily be created and the measuring curves evaluated by simply drawing the envelopes.

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