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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

ADJUSTMENT OF HEATING RATE FOR MAXIMUM RESOLUTION IN TG AND TMA (MaxRes)

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Abstract

Conventional thermogravimetric analysis (TG) uses constant heating rates to determine decomposition rates of a material and compositional analysis. Often, the decomposition steps can not be separated clearly enough due to parallel or consecutive reactions. If the reaction rates and the respective activation energies are enough different the TG resolution can be much enhanced by lowering the heating rate during the decomposition steps. The automated discrete adjustment of the heating rate is controlled by a set of parameters, such as threshold values, waiting times and rate factors. This technique, called MaxRes, allows for faster compositional analysis without loss of resolution. The same technique is also applicable to thermomechanical analysis (TMA) if time/temperature dependent events such as softening are to be separated.

Keywords: compositional analysis, event separation, heating rate, MaxRes, softening, TG, TMA

Introduction

Thermogravimetric compositional analysis and decomposition studies use most often constant heating over the interesting temperature range. While this method is often satisfactory, there are many situations in which mass losses occur in overlapping temperature regions. But, already many years ago, it has been noticed that adaptation of the heating rate is essential for investigation of thermal decomposition reactions [1–4]. This procedure also helped to separate overlapping slow dehydration steps and allowed for quasi-isothermal conditions during the main reactions. Nowadays, the control of such necessary heating rate changes is handled by microprocessor software routines that require adjustment of only a few control parameters.

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Methods

Based on the changes of the mass (TG signal) or nowadays also of the length (TMA signal) of a sample, the heating rate is automatically lowered or raised. Generally speaking, the heating rate is reduced during a thermoanalytical event giving a significant signal change.

This serves to increase in TG the resolution of decomposition measurement because effects which lie close to each other no longer overlap at a low heating rate. This overlapping can readily be seen on the 1st derivative of the TG signal (i.e. differential thermogravimetric curve, DTG). With poorly resolved events, the signal between two DTG-peaks does not return to the baseline, or one of the events appears as a shoulder-like signal. To enhance the separation, one could run the entire measurement with a very slow heating rate, but then the time needed for such measurement would be much longer. To control the adaptation of the heating rate in function of the DTG signal the following parameters are available in the function called 'MaxRes':

- minimum and maximum heating rate
- high threshold (derivative of the signal) to lower of the heating rate
- low threshold (derivative of the signal) to increase of the heating rate
- time-out and factor

Such a MaxRes measurement usually starts with the maximum heating rate selected. As soon as the absolute value of the first derivative goes above the upper threshold, the heating rate is lowered by the factor given. After the time-out occurs, the DTG signal is reassessed and, if it is still greater than the upper threshold, the heating rate is again reduced by the factor. This continues until the minimum heating rate is achieved. Once the DTG signal falls below the lower threshold, the heating rate is raised by the factor. The rate will continue to increase as long as the DTG is below the lower threshold, until the maximum heating rate is again achieved.

The resulting temperature program is consequently composed of discrete dynamic segments. A second sample could then be measured using a manually programmed temperature profile exactly following the temperature profile with the main rate changes as resulting from the MaxRes measurement. This would not be possible with a continuously changing heating rate method. In this way, a MaxRes method can be optimized and then used as a routine analytical program. Hence, the MaxRes program may also be used as a learn procedure for optimal temperature programming.

All heating rate-based resolution enhancement techniques suffer from limitations. The most important factor is the activation energies of the overlapping decompositions. If the activation energy of the second reaction is much larger than that of the first, the events can not be separated simply by lowering the heating rate. In such cases other procedures, such as a change of gas composition or pressure may help to enhance the resolution.

Experimental

The thermoanalytical measurements were performed in the STAR^e-system with the measuring cells for thermogravimetry (TGA/SDTA851^e) and thermomechanical analysis (TMA/SDTA840) from Mettler-Toledo. Temperature calibration of the measuring cells were performed following the preprogrammed standard procedures with indium and zinc melting points.

A selection of various samples were measured under both constant heating rate and MaxRes temperature control. Heating rates varied from 0.5 to 50 K min^{-1} and are specified in the discussions for the individual experiments. Air was used as purge gas, except as noted. The constant heating rate experiments are performed not only for comparison purposes but also as screening methods to determine realistic parameters for the MaxRes experiments. The standard parameter settings used for the MaxRes measurements are listed in Table 1 and have been used, if not otherwise specified.

Evaluations and result presentation were performed using the corresponding STAR^e-software. MaxRes curves and measurements with constant heating rate have been put to the same diagrams for comparison purposes.

Table 1 Standard parameter settings for the MaxRes measurements

Parameter	TG	TMA
Minimum heating rate	5%	10% of maximum heating rate
Maximum heating rate	see the respective measurements	
High threshold	3 μg s^{-1}	12 nm s^{-1}
Low threshold	1 μg s^{-1}	4 nm s^{-1}
Time-out	6 s	18 s
Factor	2	1.5

Results

TG application examples of MaxRes

Figure 1 demonstrates different ways of enhancing resolution in TG using coppersulfate pentahydrate. In all three curves, the mass loss regimes are apparent to the 85.5, 71 and 64% level, corresponding to losses of 2, 2 and 1 waters of hydration, respectively. At the high rate of 25 K min^{-1}, the first and second mass loss step are poorly resolved, so that it is difficult to clearly define where the first mass loss ends and the second begins. At a heating rate of 5 K min^{-1} the steps are well separated but the experiment lasts five times longer. With the MaxRes method the required measuring time for a complete step separation is halved compared to a constant slow heating for good event separation.

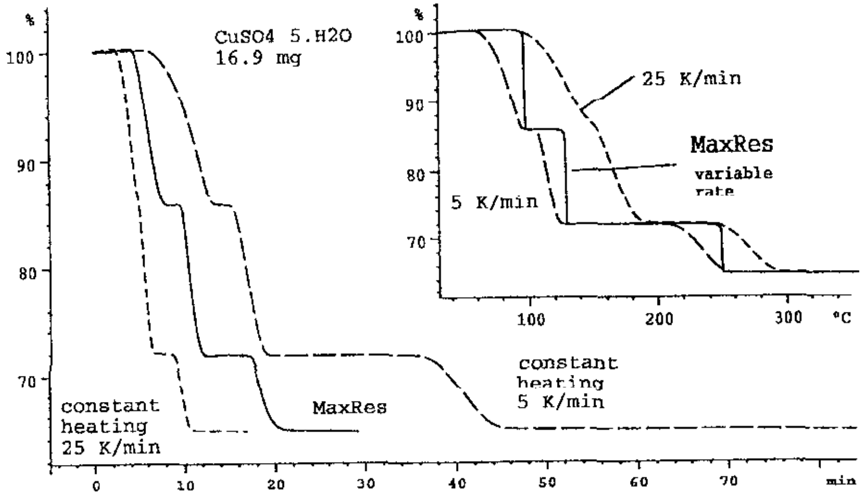

Fig. 1 Decomposition of coppersulfate pentahydrate with loss of water of crystallization in three steps. The left diagram (normalized sample mass in function of time) shows the two TG curves with constant heating at 25 and 5 K min^{-1} respectively (dashed lines) and the MaxRes curve (solid line; standard parameters, variable rates, changing between 25 and 0.5 K min^{-1}). The right diagram shows the same measurements but with the sample mass in function of sample temperature. Specimen masses 16 to 17 mg, 30 ml min^{-1} air as purge gas flow

Similar findings are shown in Fig. 2 for samples from building materials research. The decomposition of a reaction product of calcium hydroxide, calcium sulfate, aluminum oxide, and water is compared for a measurement at 10 K min^{-1} and a measurement with MaxRes control. The derivative curves (DTG) clearly demonstrate the difference in resolution between the two methods especially at the dehydration steps up to 200°C. Furthermore, the sneaking mass loss between 350 and 500°C is resolved by MaxRes into two well pronounced steps below and above 400°C. The enhanced quality of the data easily justifies the extra time associated with the MaxRes experiment (approx. 40 min longer).

In rubber analysis the temerature of elastomer decomposition depends strongly on the heating rate. Due to kinetic effects, slow heating apparently shifts the individual decompositions to lower temperatures. This is obvious if the constant heating rate curves of TG measurements of a typical rubber sample are compared (Fig. 3). Table 2 summarizes the respective contents of the rubber components determined by the TG mass losses. As these results show, the separation of the rubber components depend on the heating rate. Using automatic adjustment of the heating rate by MaxRes three decomposition steps are detected (Fig. 3) due to the complex reaction kinetics and also due to the selected combination of MaxRes parameters. This demonstrates the necessity to optimize the control parameters of MaxRes for a given task in order to avoid artificial mass loss steps.

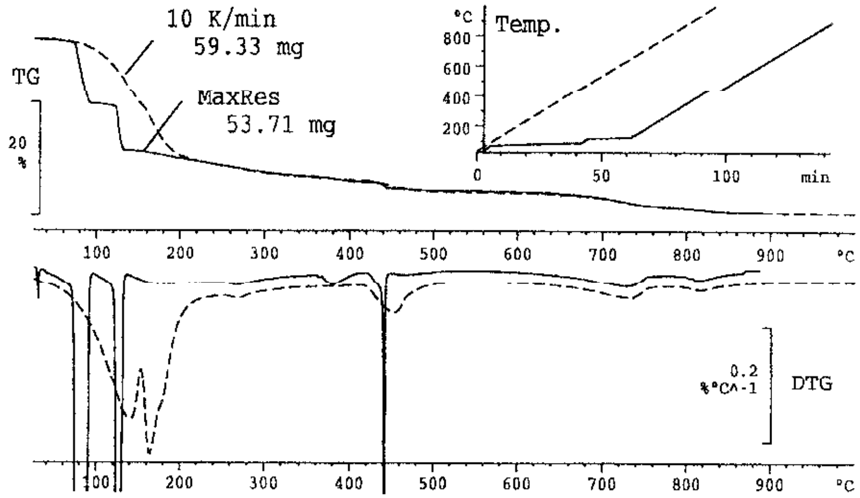

Fig. 2 Decomposition of a reaction product of $Ca(OH)_2$, $CaSO_4 \cdot 0.5H_2O$, $Al(OH)_3$ and H_2O (Etringit) in 30 ml min^{-1} air purge gas flow. In the three coordinate systems (TG, DTG, Temperature), the measurement with constant heating (dashed line) is compared to the MaxRes analysis (solid line). In the diagram temperature *vs.* time, the rate changes by MaxRes between 10 and 0.5 K min^{-1} are graphically displayed. MaxRes with standard parameters

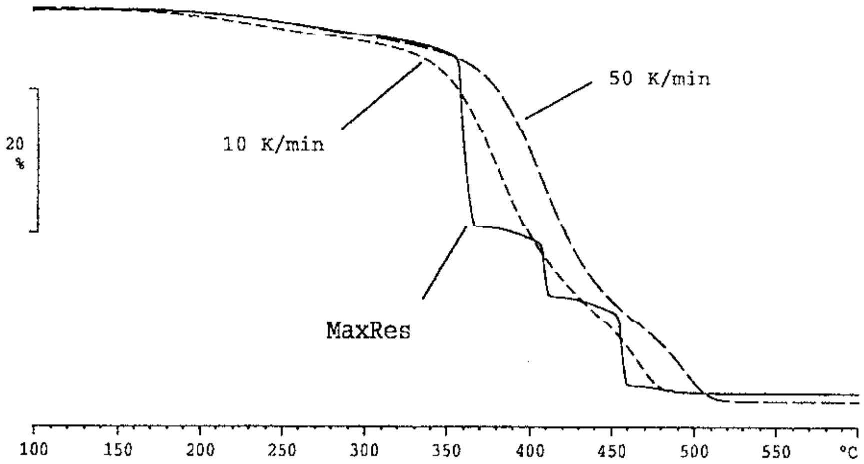

Fig. 3 Rubber analysis by TG showing decomposition of the elastomer components using constant (dashed lines) and rate adapted (solid line) heating. Standard parameters setting for MaxRes analysis with rates between 50 and 2.5 K min^{-1}. Pyrolytic furnace atmosphere: 50 ml min^{-1} nitrogen purge

Table 2 Compositional analysis of the rubber sample

Method	Natural Rubber	EPDM
Mixture given	40.9%	10.2%
Measured	mass loss %	mass loss %
50 K min^{-1}	39.3	10.9
10 K min^{-1}	37.7	10.8
MaxRes	37.9	10.4
	2 first steps	3^{rd} step

All available control parameters of MaxRes can be changed individually to optimize the event separation and the experiment duration. As an illustrative example Fig. 4 shows the influence of the threshold values on the separation of the two dehydration steps of coppersulfate pentahydrate up to 120°C (Fig. 1).

The influences can be summarized as follows: Lowering the high threshold limit reduction of the heating rate starts at lower temperatures often leading to better separation without much extension of experiment duration. A not too small low threshold guarantees for the accelerated heating after an event and shortened experiment time. Lowering generally the heating rates (min. and max. values) usually enhances the resolution of events but extends the duration of the experiment.

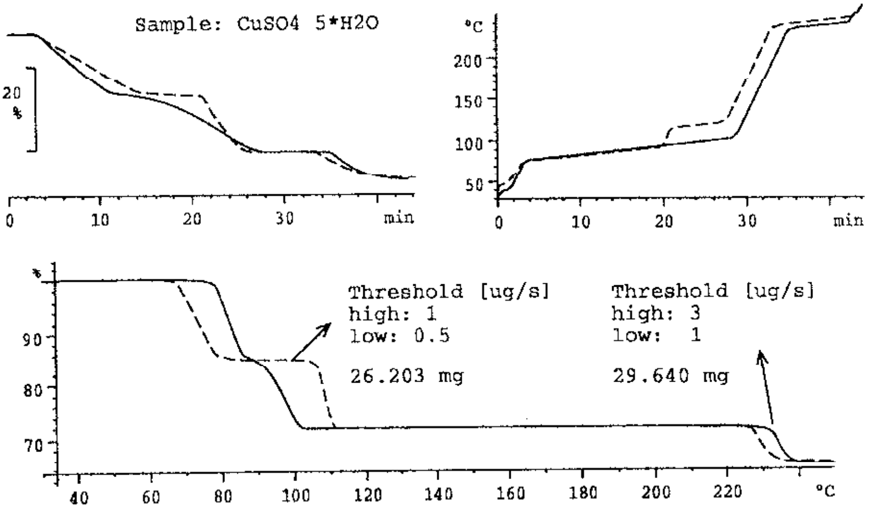

Fig. 4 Dehydration of $CuSO_4 \cdot 5H_2O$ using TG with MaxRes heating rate control. One measurement was performed with standard parameter setting (25 K min^{-1} max. heating rate; solid line), the comparison measurement (dashed line) used 1 and 0.5 μg s^{-1} for high and low threshold values, respectively

The other parameters in Table 1 are not much influencing the rate adaptation behavior. Time out and factor only control the speed of rate adaptation, i.e. with slow decomposition reactions a smooth rate change is preferred for less disturbance of the furnace temperature control. In most experiments performed, the heating rates changed between the maximum and minimum value (Figs 2 and 4).

Not only decomposition kinetics can be separated by the MaxRes technique. Also physical evaporation can be split off from an overlapping decomposition reaction. To achieve this separation, a higher heating rate is often applied to shift the reaction towards higher temperatures. But, the compositional analysis of plasticizer in PVC needs an other approach: the pressure of the furnace atmosphere is lowered to shift the evaporation temperature down to a value where PVC does not decompose. The diffusion of the plasticizer out of the PVC/NBR blend is time controlled and therefore a lowering of heating rate allows for a complete evaporation before the PVC decomposition starts. In this example approximately 10% additional experiment time is needed for better event separation (Fig. 5).

The temperature profile found by the MaxRes experiment was used as a guide to establish a fixed method for a repetitive content analysis. The fixed method was set to have approximately the same temperature program (see temperature/time diagram in Fig. 6). The TG curves in Fig. 6 show, that the MaxRes ex-

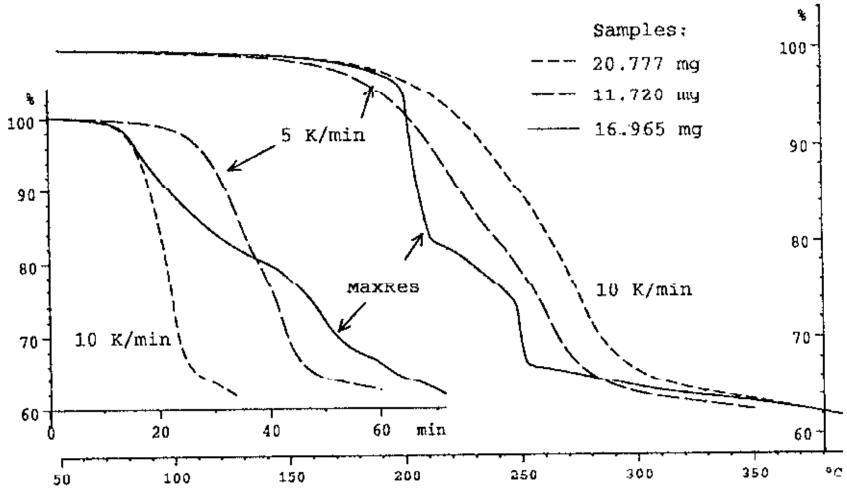

Fig. 5 Separation of plasticizer evaporation from PVC decomposition in a vacuum TG experiment to determine the content of each component. Furnace atmosphere: 4 mbar pressure with small nitrogen gas flow to purge out decomposition products (e. g. HCl). A MaxRes experiment (with standard parameters, 10 K min^{-1} max. rate; solid line) is compared with constant heating rate experiments (5 and 10 K min^{-1}; dashed lines). The mass loss in the MaxRes curve up to 212°C corresponds to the given plasticizer content of 19%. Accurate determination of this content would be nearly impossible by the measurement at constant 10 K min^{-1}

periment (as in Fig. 5) and the fixed method experiment gave the same event resolution.

TMA application example of MaxRes

Penetration of a TMA probe into layers of coatings due to softening of these layers is also a temperature and time/viscosity dependent effect. Therefore, determination of the softening behavior of two layers can be enhanced by heating rate control using MaxRes technique, in analogy to the TG examples discussed above [5]. Using constant heating rate in TMA the indentation of the probe into two layers is resulting in two overlapping length changes (similar to overlapping mass changes in thermogravimetry). In such a case, the MaxRes technique reduces the heating rate during the first indentation so that the temperature for the softening of the second layer is not reached before the indentation of the first comes to an end. The amount of indentation is governed also by the shape of the probe tip and force acting on it, therefore, the length change by the indentation (length change step) does not necessarily represent the layer thickness. The TMA curves in Fig. 7 show, that the MaxRes experiment allows for a better identification of the two layers by subsequent penetration, compared to the linear heating experiments. Independent of the heating rate, all curves show the overlapping two-step indentation. The measurements demonstrate that the slower the

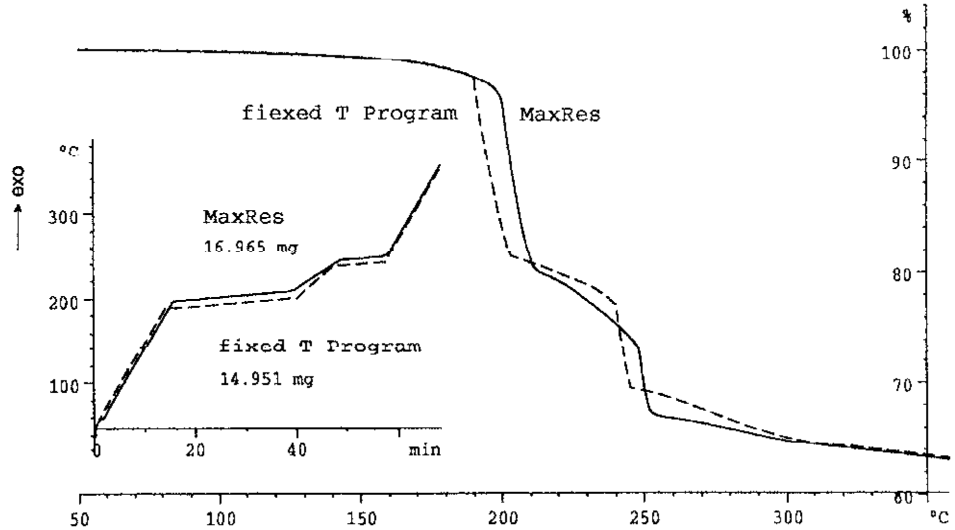

Fig. 6 TG measurement of a plasticizer/PVC/NBR mixture under 4 mbar vacuum. The MaxRes experiment (same as in Fig. 5; solid line) defined the temperature profile for the fixed temperature program for the subsequent compositional analysis. Fixed T program (dashed line): 50 to 190°C at 10 K min^{-1}, to 202°C at 0.5 K min^{-1}, to 240°C at 5 K min^{-1}, to 245°C at 0.5 K min^{-1}, to 400°C at 10 K min^{-1}

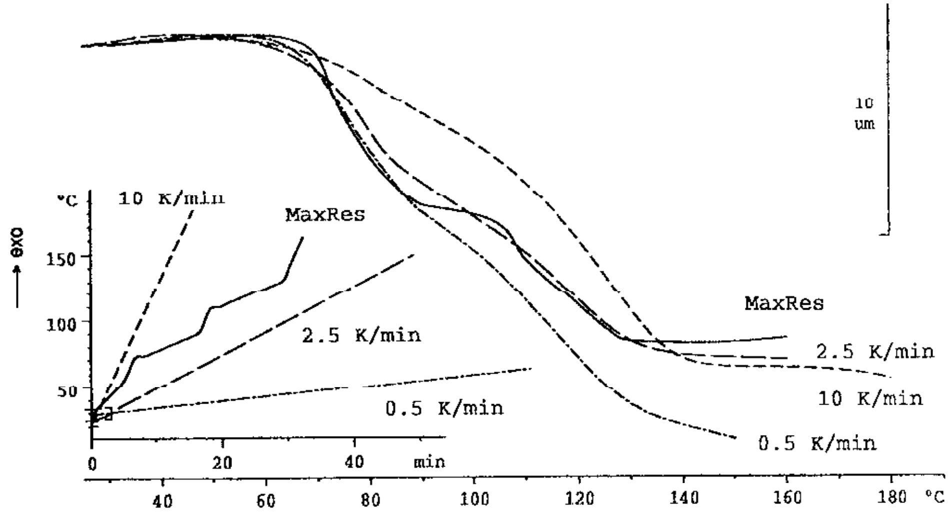

Fig. 7 TMA measurements of the softening behavior of polyurethane coatings. TMA probe with hemispherical tip (radius 1.5 mm) and load of 0.05 N to the surface. Sample thickness (substrate and coatings): 0.5 mm. Experiments with constant heating (dashed lines; 0.5, 2.5 and 10 K min^{-1}) are compared to a MaxRes experiment (solid line; standard parameters, max. rate: 10 K min^{-1}, min. rate: 2 K min^{-1})

heating, the more penetration occurs during the first softening. The MaxRes experiment approaches this behavior but uses less time. The inserted diagram in Fig. 7 gives the temperature-time profiles of the respective measurements. The extrapolated onset of the change from fast to slow heating in the MaxRes temperature profile could be used to define the softening temperature, i.e. 69 and 105°C for the coating investigated.

Conclusions

Often, the decomposition steps in thermogravimetry can not be separated clearly enough due to parallel or consecutive reactions.

With a special software program built into the TG and TMA system the heating rate can be decreased (or increased again) depending on the recorded mass or dimension changes. This technique, called MaxRes, allows for shorter analysis times and/or for better resolution between overlapping events. A set of control parameters allows for optimization of the experimental conditions and sample dependent rate adjustment.

A similar method for rate control on the basis of the temperature difference signal (SDTA) is available and will be further developed.

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