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Short Communication

COMPARISON OF ACTIVATION ENERGIES OBTAINED FROM MODULATED AND CONVENTIONAL NON-MODULATED TG

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Abstract

Recently, model free kinetic analysis of sinusoidal modulated TG-curves has been presented. In this contribution we compare the activation energies resulting from model free analysis of modulated TG-curves and from Vyazovkin's model free kinetic analysis of non-modulated TG-curves. We used polytetrafluorethylene and manganese oxide as samples. As a result we find, that both methods deliver similar activation energies for polytetrafluorethylene. However, the activation energies of manganese oxide deviate substantially.

The main purpose of kinetic analysis is its potential for predictions of the temporal behavior of materials under certain thermal conditions. Analysis of modulated TG-curves allows a model free determination of the temperature dependence of the activation energy. However, in order to make predictions, one still has to rely on kinetic models such as e.g. first order kinetics. This is in contrast to Vyazovkin's approach, which allows a model free description of kinetic processes in terms of a conversion dependent activation energy. This function can then be used to make kinetic predictions without any further assumptions with respect to reaction models. In this paper we further discuss this fundamental difference.

Keywords: activation energy, modulated TG, model free kinetics

Introduction

In the early seventies Flynn proposed kinetic analysis of modulated thermogravimetric data [1]. In modulated thermogravimetry (MTG) a periodic temperature mod-

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ulation is superimposed on a non-modulated dynamic temperature scan with a constant heating rate. Using a sinusoidal modulation, characterized by a modulation amplitude A_T and a period P, results in a general temperature program according to

$$T=T_0+\beta t+A_T\sin(\omega t)$$

where T_0 is the initial start temperature, β denotes the average or underlying heating rate and ω is the period P divided by 2π. The relation derived by Flynn delivers a model free expression for a temperature dependent activation energy

$$E=\frac{RL(T^2-A^2)}{2A}$$

where R is the gas constant, T the average temperature during a modulation cycle, A the amplitude of the modulation and L the natural logarithm of the ratio of the maximum and the minimum conversion rate during a cycle. This equation can be applied to any periodic temperature program presumed the period of the modulation is sufficiently long to ensure equilibrium between the mass loss rate and the temperature.

Recently, this scheme has been applied using sinusoidal temperature modulations [2, 3]. In this contribution we compare the results of model free kinetic analysis of MTG-curves with a model free analysis of non-modulated thermogravimetric experiments. Model free kinetic analysis is generally based on the isoconversional principle, according to which the reaction rate, $d\alpha/dt$, at a given extent of conversion, α, is a function of the temperature only, i.e.

$$\left[\frac{d\ln\frac{d\alpha}{dt}}{dT}\right]_\alpha=-\frac{E_\alpha}{R}$$

Several authors have developed different isoconversional methods [4, 5]. For our purpose we used the non-linear model free kinetics suggested by Vyazovkin [6, 7]. As samples we used polytetrafluorethylene (Teflon®, PTFE) and powdered manganese oxide, MnO_2.

Experimental

Measurements were performed with a Mettler Toledo TGA/SDTA851^e, equipped with the large furnace. To ensure close coupling between the sample, the furnace and the temperature sensor helium was used as purge gas (70 ml min^{-1}). For the MTG experiments an underlying heating rate of 2 K min^{-1} was applied and the parameters of the sinusoidal modulation were set to 5 K (amplitude) and 240 s (period). The conventional experiments were performed at heating rates of 2, 5 and 10 K min^{-1}, respectively. For all experiments standard 70 µl alumina crucibles were used. Typical sample masses were around 14 mg.

The evaluation of the modulated TG-curve was done by applying a discrete Fourier analysis to the 1st derivative of the modulated TG-signal. Afterwards, the envelopes to the first derivative were constructed using the results of the discrete Fourier analysis. The ratio of the envelopes was then used to calculate the activation energy according to Eq. (1). Vyazovkin's modelfree kinetic analysis of non-modulated TG-experiments is optionally available in the Mettler Toledo STAR^e software which also operates the TGA/SDTA851^e. Note that the analysis of modulated TG-curves cannot be done within STAR^e.

Results

Example 1: Polytetrafluorethylene, PTFE

Figure 1 displays the modulated TG curve and its first derivative as a function of time and temperature. As expected the conversion rate slows down during cooling half cycles. In Fig. 2 we show the activation energy as a function of the temperature of PTFE resulting from the MTG experiment shown in Fig. 1. When there is no or only a small mass loss unreasonable values for L result. Reliable data are, therefore, limited to the temperature interval between about 470 and 550°C.

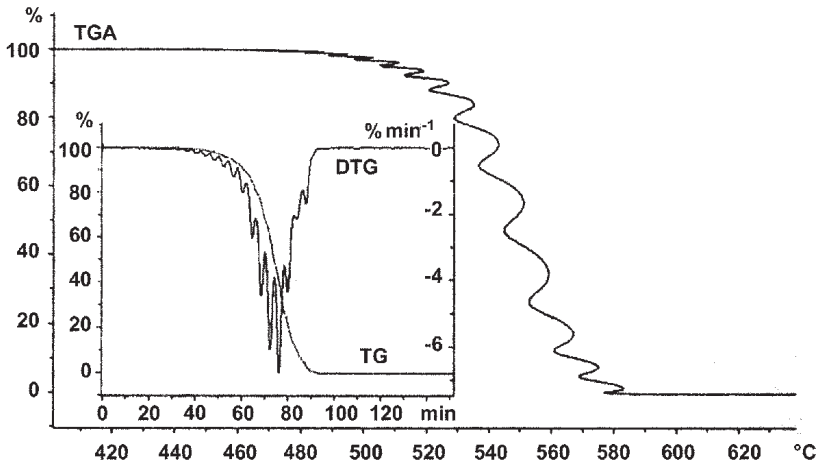

Fig. 1 TG and DTG modulated thermogravimetric curves for PTFE. Note the difference between the TG-curve plotted *vs.* time and temperature, respectively. Modulation parameters: amplitude 5 K, period 4 min, underlying heating rate 2 K min^{-1}

Typical results of a model free analysis of conventional data are given in Fig. 3. Apart from the original TG-curves it shows the conversion for the different heating rates and the resulting activation energy as a function of the conversion.

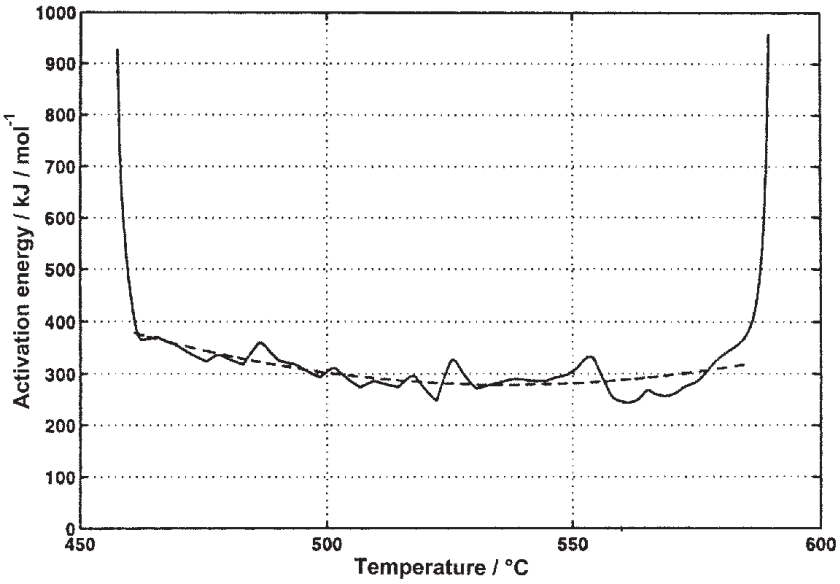

Fig. 2 Activation energy as a function of temperature for PTFE using model free kinetic analysis of a modulated TG-experiment. Dotted: 2nd order polynomial fit

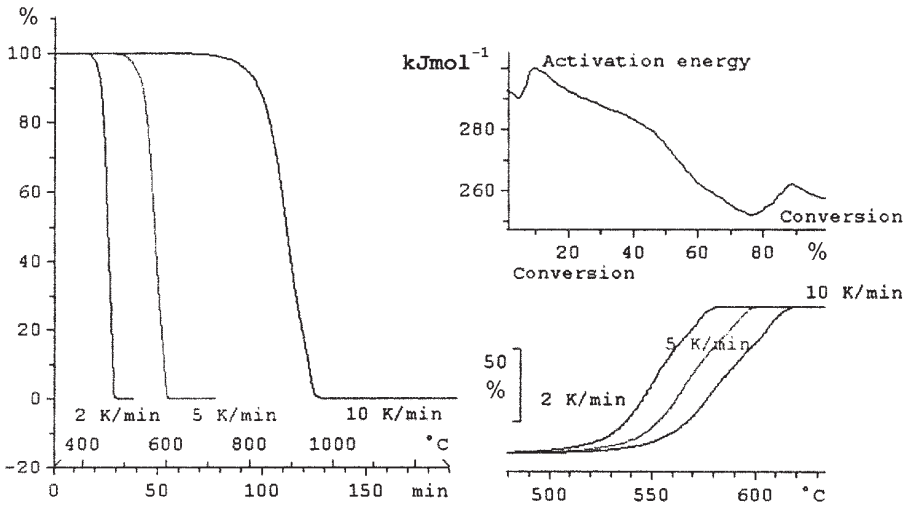

Fig. 3 Modelfree kinetic analysis of Teflon (PTFE). At least 3 curves are required. The calculation of the activation energy is based on the respective conversion curves of the TG-traces

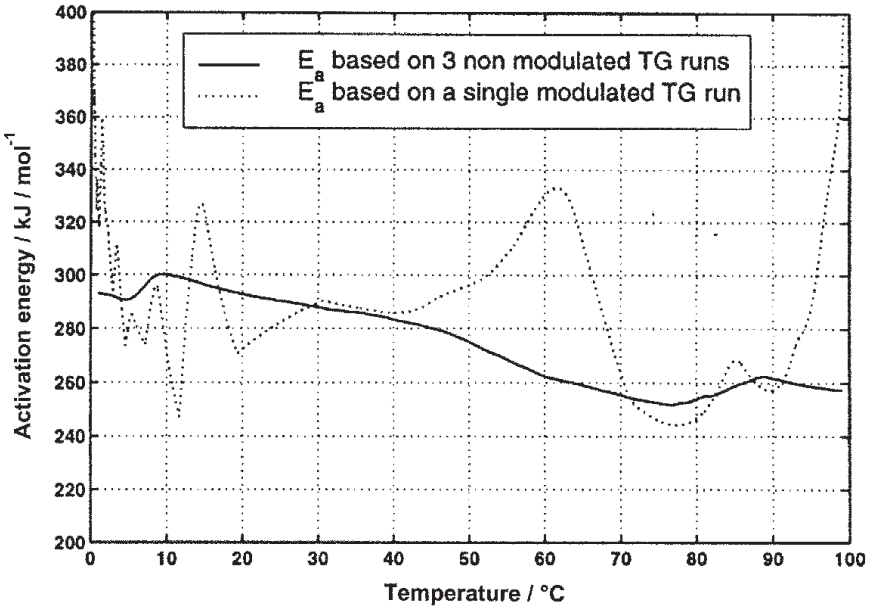

Fig. 4 Comparison of the activation energy resulting from modulated TG and conventional TG

To compare the activation energy functions resulting from the two methods, we converted the temperature axis in Fig. 2 in a conversion axis and plotted the activation energies of the modulated and the conventional analysis in Fig. 4 as a function of conversion. It shows reasonable agreement of both types of analysis.

Example 2: Manganese oxide, MnO_2

Kinetic analysis of MnO_2 is much more demanding since the reduction of MnO_2 occurs in several steps:

$$4\ MnO_2 \rightarrow 2\ Mn_2O_3 + O_2 \quad (650°C) \quad (I)$$
$$6\ Mn_2O_3 \rightarrow 4\ Mn_3O_4 + O_2 \quad (990°C) \quad (II)$$
$$2\ Mn_3O_4 \rightarrow 6\ MnO + O_2 \quad (1600°C) \quad (III)$$

Furthermore, several solid–solid transitions occur, leading to non-stoichiometric intermediary phases [8]. The TG-curve of MnO_2 therefore shows much more steps than expected from the 3 stoichiometric reactions shown above. This can be seen in Fig. 5 which shows a TG-curve at 2 K min^{-1} and its first derivative.

The comparison of the activation energies evaluated with model free techniques applied to modulated and non-modulated TG-experiments is shown in Fig. 6. For reference we have also included the TG-curve. Between ~750 and ~950°C the activation energy cannot be calculated since there is hardly no reaction in this temperature re-

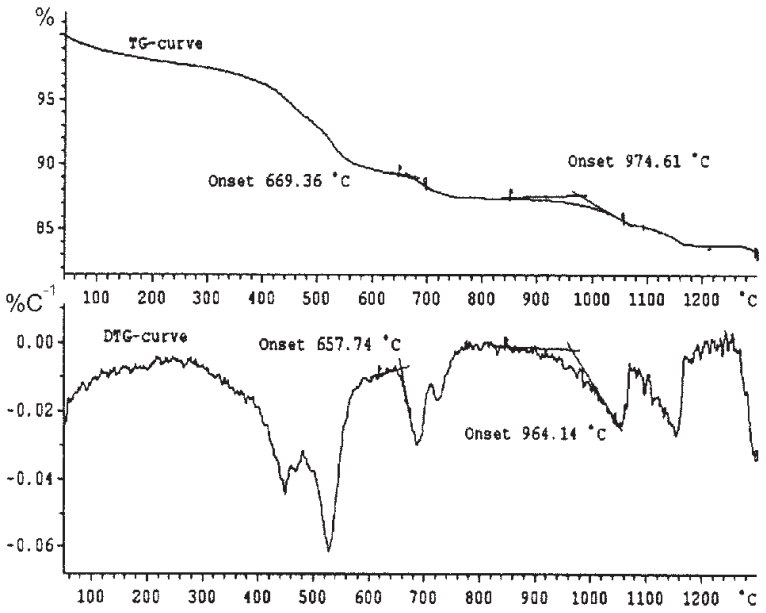

Fig. 5 Non-modulated TG-analysis of MnO_2 at 2 K min^{-1} and its first derivative. Details see text

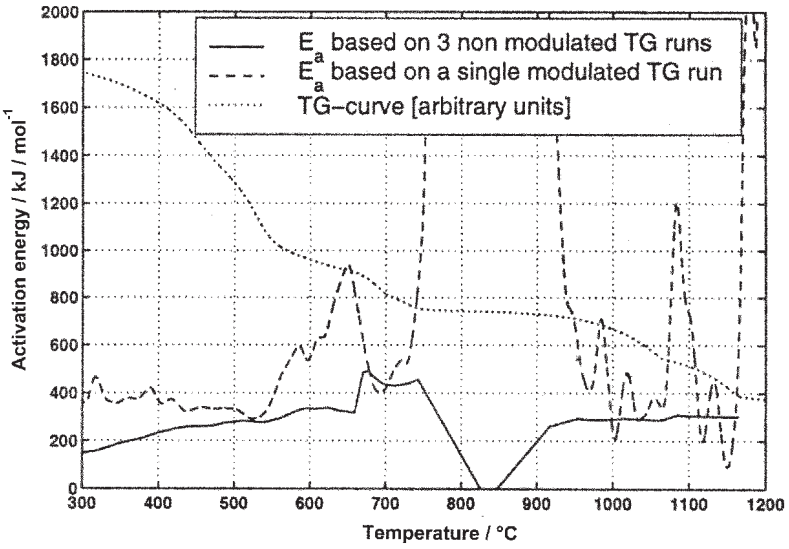

Fig. 6 Activation energy as a function of energy evaluated from modulated and conventional TG data. The TG-curve is plotted in arbitrary units for reference

gime. Below 550°C, the activation energy based on the modulated scans is generally significantly higher than the results based on the non-modulated curves. Above 550°C the activation energy found from the modulated experiment shows considerable fluctuations, which are difficult to understand. We therefore conclude, that in this case the analysis of modulated TG-curves delivers rather doubtful results.

In contrast, activation energies resulting from Vyazovkin's approach are much more consistent and credible. Furthermore, comparison of the TG-curve and the activation energy shows a good correlation of different reaction steps in the TG-curve and distinct levels of the activation energy. Thus, different reaction energies may be attributed to different reaction steps.

Discussion and conclusions

The main purpose of kinetic analysis usually is its potential to make predictions on the temporal behavior of a sample when it is subjected to certain thermal conditions. Analysis of modulated TG-curves delivers a model free determination of the temperature dependence of the activation energy. However, in order to make predictions one still has to make use of kinetic models such as e.g., first order kinetics since in the scheme of modulated TG-analysis the reaction is described by the general rate equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = f(\alpha)\exp\left(\frac{-E(T)}{RT}\right)$$

where $f(\alpha)$ describes the reaction model (e.g., in case of n^{th} order kinetics $f(\alpha)=(1-\alpha)^n$). Therefore the interesting aspect of modulated TG is not that it is modelfree but lies in the fact, that the temperature dependence of the activation energy may be established under certain conditions. In contrast, model free kinetics as suggested by Vyazovkin is a true model free description of kinetic processes in terms of a conversion dependent activation energy which can be used to make predictions without any further assumptions with respect to reaction models.

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