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OBTAINING KINETIC PARAMETERS BY MODULATED THERMOGRAVIMETRY

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Abstract

A new technique, called modulated thermogravimetry, is introduced as a tool for obtaining continuous kinetic information for decomposition and volatilization reactions. The approach makes use of an oscillatory temperature program to obtain kinetic parameters during a mass loss. MTGA™ may be used under quasi-isothermal conditions to observe a single mass loss or may be combined with linear heating rate or Hi-Res™ controlled rate thermogravimetry to scan from one mass loss region to another. Results obtained are in agreement with those obtained by other kinetic methods.

Keywords: activation energy, decomposition, kinetics, modulated temperature, thermogravimetry, volatilization

Introduction

In 1992, Reading introduced the temperature sine wave forcing function [1, 2] to thermal analysis in the form known as Modulated DSC®. In MDSC®, a linear temperature ramp is modulated with a sinusoidal temperature oscillation producing a corresponding oscillatory heat flow (i.e., rate of heat transfer) proportional to physical properties of the test specimen. Deconvolution of the oscillatory temperature and heat flow lead to the separation of the overall heat flow into heat capacity and kinetic components, called reversing and nonreversing heat flow. The overall heat flow (dQ/dt) may be described as the sum of a heat capacity (heating rate dependent) term and a kinetic (time and temperature dependent) term.

$$dQ/dt = C_p dT/dt + f(t,T) \tag{1}$$

The modulated temperature concept may be applied to other thermal analytical techniques such as thermogravimetry. By analogy, the corresponding oscillatory temperature equation for thermogravimetry is given by :

$$dw/dt = C dT/dt + f(t,T) \tag{2}$$

where the rate of mass loss (dw/dt) is analogous to the rate of heat flow in DSC. In the TG case, however, the first term, proportional to the rate of heating, is zero and Eq. (2) reduces to the common kinetic expression where the rate of mass loss is directly proportional to the kinetic term.

For the study of chemical reactions, the kinetic term in Eqs (1) and (2) [i.e., $f(t,T)$] is often modeled using two equations. The first of these, the rate equation, describes the relationship between the rate of reaction and amount of material. The second, the Arrhenius equation, describes the temperature dependence. These two equations are commonly combined into a single form:

$$\mathrm{d}\alpha/\mathrm{d}t = Z[f(\alpha)]\exp(-E/RT) \tag{3}$$

where:	α	reaction fraction
	$\mathrm{d}\alpha/\mathrm{d}t$	rate of reaction
	Z	pre-exponential factor
	$f(\alpha)$	kinetic expression
	exp	exponent of the natural logarithm base e
	E	activation energy
	R	gas constant, and
	T	absolute temperature.

For an experiment in which the temperature is modulated by a sine wave, this equation may be evaluated as the ratio for adjacent peaks, and valleys, of the periodic rate of reaction [3].

$$\frac{\mathrm{d}\alpha_\mathrm{p}/\mathrm{d}t}{\mathrm{d}\alpha_\mathrm{v}/\mathrm{d}t} = \frac{Zf(\alpha_\mathrm{p})\exp(-E/RT_\mathrm{p})}{Zf(\alpha_\mathrm{v})\exp(-E/RT_\mathrm{v})} \tag{4}$$

If the reacted fraction changes little between adjacent half cycles, then the value for $f(\alpha_\mathrm{p})$ approaches that of $f(\alpha_\mathrm{v})$ and their ratio approaches unity. Solving for E yields:

$$E = \frac{RT_\mathrm{p}T_\mathrm{v}\ln(\mathrm{d}\alpha_\mathrm{p}/\mathrm{d}\alpha_\mathrm{v})}{T_\mathrm{p} - T_\mathrm{v}} \tag{5}$$

In any modulated experiment, the oscillatory temperature forcing function is defined by an average temperature (T), the temperature amplitude (A) and its period (or frequency). The values for T_p and T_v in Eq. (5) may be replaced with ($T+A$) and ($T-A$), respectively, while $T_\mathrm{p}-T_\mathrm{v}$ is equal to $2A$. The equation may further be simplified with the introduction of a new parameter L which is set equal to the difference between the maximum and minimum value for the $\ln\mathrm{d}\alpha$ envelope; $L=\ln\mathrm{d}\alpha_\mathrm{p}-\ln\mathrm{d}\alpha_\mathrm{v}=\ln(\mathrm{d}\alpha_\mathrm{p}/\mathrm{d}\alpha_\mathrm{v})$. Equation (5) thus reduces to:

$$E = \frac{R(T^2 - A^2)L}{2A} \tag{6}$$

This relation, anticipated by Flynn as early as 1969 [4], is applicable to any periodic forcing function (e.g., square wave, sawtooth, sine wave) whose period is sufficiently long to ensure equilibrium between the rate of mass loss and the oscillatory temperature forcing function. The use of the smoothly varying temperature sine wave, however, has many advantages over other periodic functions. For example, the sine wave permits the use of real time deconvolution techniques, such as discrete Fourier transformation (DFT), to obtain average values and amplitudes on a continuous basis. In MTG, DFT is used to provide the average and amplitude values for temperature, mass, rate of mass loss and logarithm of the rate of mass loss required in Eq. (6). Moreover, the use of real time DFT provides the ability to use the average rate of mass loss in controlled rate experiments. Furthermore, activation energy may be calculated and reported on a continuous basis permitting a wide variety of useful plotting options.

Equation 6 may be said to be 'model free' as it does not depend on knowledge of the kinetic function for its calculation. The assumption of a suitable kinetic model, however, permits other kinetic parameters, such as pre-exponential factor to be obtained. Many decomposition and volatilization reactions may be described using first order kinetics where the value for pre-exponential factor (Z) may be determined using $\ln Z=\ln[\mathrm{d}\alpha/(1-\alpha)]+E/RT$.

Experimental

MTG is performed using a TA Instruments, Inc. Model TGA 2950 equipped with Windows® NT Thermal Solutions software. The TG is equipped with the standard (Hi-Res™) furnace to provide close coupling between the test specimen, furnace and temperature sensor required for rapid temperature modulation. Typical experimental conditions include an amplitude of ±5°C, a period of 200 s and an underlying heating rate of 2°C min^{-1}. A typical MTG mass loss profile for polytetrafluoroethylene (PTFE) is shown in Fig. 1.

The continuous activation energy curve resulting from the linear heating rate experimental shown in Fig. l, is shown in Fig. 2. When there is no mass loss, the value for activation energy is set to zero. Once the onset of mass loss is observed (near 425°C), calculation of the kinetic parameters is initiated. Because it takes several cycles to produce reliable data, the first few data points are unrealistically high. The calculated values become constant once a few cycles are achieved. At the end of the mass loss region, the kinetic parameter once again goes to unrealistically high values as the sine waves become distorted by the lack of reacting material.

The simplest MTG experiment is a quasi-isothermal one in which the test temperature is raised rapidly to a predetermined temperature where its average temperature is held constant as the kinetic parameters are recorded. A quasi-isothermal experiment for polytetrafluoroethylene (PTFE) is shown in Fig. 3. Qualitatively, following a short equilibration time, the rate of mass loss curve shows an exponential decay both in average rate of mass loss and in oscillation amplitude. This behavior is characteristic of an *n*th order reaction.

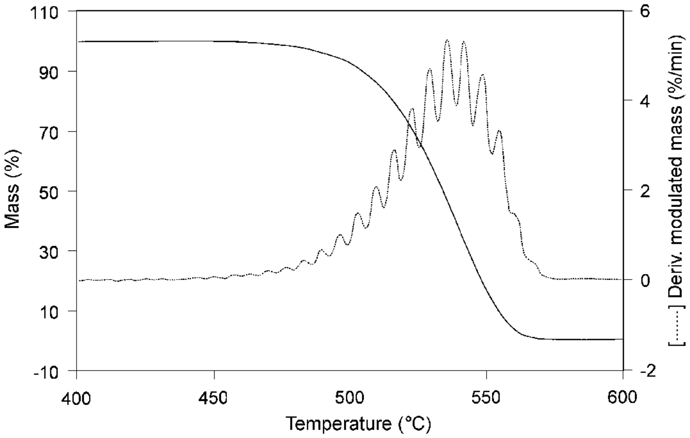

Fig. 1 Modulated temperature profile for polytetrafluoroethylene

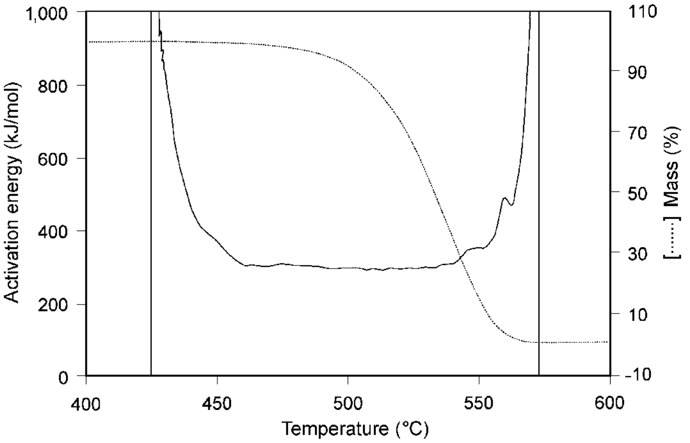

Fig. 2 Activation energy for polytetrafluoroethylene

By contrast, Fig. 4 shows the same type of quasi-isothermal experiment for polystyrene (PS), the activation energy of which is known to change with extent of reaction [5]. Here the rate of mass loss and amplitude increase during the initial isothermal period, peak and then decay away as the reactant is consumed. This curve shape is a characteristic of autocatalyzed reactions.

Quasi-isothermal experiments are usually quite long since the rate of reaction is small and decreases with increased conversion. Often the experiment is terminated before 100% conversion is reached in order to reduce experimental time.

Use of a linear temperature programming is one tool for decreasing experimental time. Even here, however, experiments may be lengthy due to the low

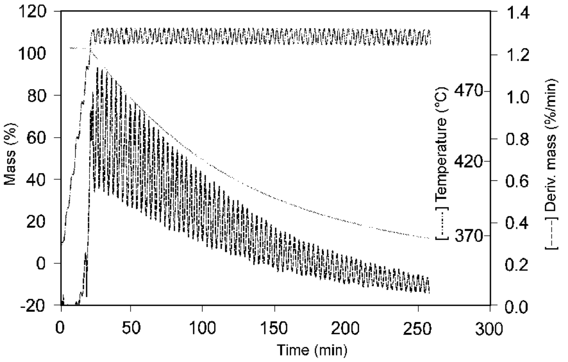

Fig. 3 Quasi-isothermal profile for polytetrafluoroethylene

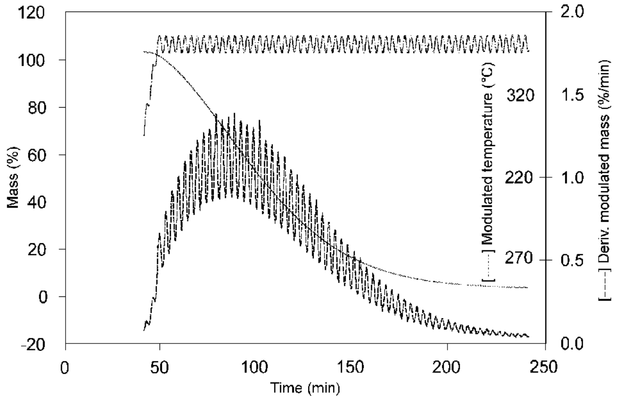

Fig. 4 Quasi-isothermal profile for polystyrene

heating rates required particularly if the total decomposition involves more than one mass loss.

Increased efficiency may be obtained by heating rapidly between the mass loss regions. Control of the experimental temperature by controlled rate thermogravimetry (CRTG) is one way to accomplish this. CRTG was first described by Rouquerol [6]. Its modern embodiment is commercially known as high resolution (Hi-Res™) thermogravimetry [7, 8]. Dynamic rate TG continuously and smoothly varies the heating rate in response to the sample's measured rate of mass loss. In temperature ranges where the mass is stable, the sample is heated rapidly. At the onset of a mass loss, the heating rate slows in response to the increasing rate of mass loss. As the reaction reaches completion, the heating rate increases (in response to the decreasing rate of mass loss) until the next mass loss is seen. This approach materially reduces the experiment time. Dynamic rate controlled rate thermogravimetry, using the DFT generated average rate of mass loss, is the preferred embodiment for use with MTG to reduce experimental time.

On a philosophical note then, MTG may be thought of as a marriage of MDSC and Hi-Res TG technologies.

Results

To compare the activation energy and pre-exponential results obtained by MTG with other approaches, a series of polymer, organic and inorganic materials were examined by MTG and the commonly used multi-heating rate Flynn and Wall method [9] embodied in ASTM standard E1641 [10]. The comparative results are shown in Table 1. The ASTM method requires the identification of a specific conversion level for the calculation of kinetic parameters. The MTG values were taken at the same conversion as that used for the E1641 approach. In general, the results of the two types of determinations agree well. In a few cases, such as that for EVA, the results are dissimilar. Such cases of disagreement seem to involve autocatalytic reactions.

Table 1 MTG kinetics comparison

Material	E/kJ mol^{-1}		ln$Z$ min^{-1}	
	ASTM[1] E1641	MTG[2]	ASTM1 E1641	MTG[2]
Poly(ethylene)	190	190	12.9	12.8
Poly(tetrafluoroethylene)	316	341	19.1	21.1
Poly(styrene)	173	182	13.0	14.0
Poly(ethylene vinyl acetate)				
first loss	183	167	14.5	13.2
second loss	289	174	20.4	11.5
Dicumyl peroxide	104	101	12.0	11.8
1,4 Diphenylbutadiene	81	99	8.1	10.4
Calcium oxalate monohydrate	117	121	13.8	13.5
Calcium oxalate	207	194	14.0	12.2
Calcium carbonate	210	188	10.5	8.7

[1] repeatability RSD=5.0%
[2] repeatability RSD=1.7%

The precision of activation energy measurement by MTG may be estimated from replicated determination of EVA. A relative standard deviation of <2% was obtained for both the side chain and backbone decomposition’s. By comparison the relative standard deviation for E1641 is reported to be under 5% [10].

Because MTG calculates kinetic parameters in real time within the TG itself, post analysis data treatment via Universal Analysis software permits the reporting of kinetic parameters in a wide variety of ways. One of the tools used to explore the nature of a particular reaction is how activation energy changes as a function of conversion. Conversion is related to mass percent (conversion is amount reacted, while mass percent is amount remaining). A plot of activation energy as a function of mass loss, such as those in Fig. 5, provides a visual tool for comparison of reactions. In this presentation, the reaction begins at low conversion on the right side and moves to high conversion on the left.

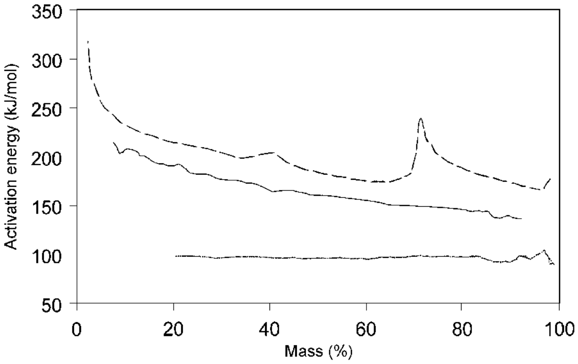

Fig. 5 Effect of conversion on activation energy. —— poly (60% ethylene vinyl acetate); — polystyrene; - - - 1,4-diphenylbutadine

Activation energy as a function of conversion for 60% ethylene vinyl acetate (EVA), polystyrene (PS) and for 1,4-diphenylbutadiyne (DPBD) is shown in Fig. 5. DPBD and PS have single mass losses and their activation energy *vs.* mass remaining curves are smooth. EVA, on the other hand, has a two step decomposition. The peak in the activation energy profile near 70% mass is the transition between mass loss regions. Moreover, the curve for DPBD is smooth and flat indicating a single decomposition mechanism. Those for EVA and PS show a changing value for activation energy with conversion. The decomposition for EVA and for PS are thought to be autocatalytic rather than first order reactions, leading to the changing value for E [5].

Discussion

Ruggedness testing of any new method requires the systematic variation of one or more experimental parameters to observe the effects. Experimental parameters tested for MTG, include modulation amplitude, period, form of the underlying temperature program (i.e., linear heating, quasi-isothermal operation or variable heating rate conditions) and the value of the underlying heating rate.

The modulation amplitude in the TG 2950 can be varied from 0 to ±10°C. The selection of a proper temperature modulation amplitude depends on the measurement to be made. Small amplitudes provide resolution between mass loss regions. High amplitudes provide increased reliability of results (as the amplitude value is in the denominator of the activation energy equation). Larger amplitudes are rarely needed but may be used if the temperature range over which the mass loss takes place is large. Such samples often have a low activation energy value (e.g., <100 kJ mol^{-1}). Smaller amplitudes may be required for samples with narrow mass loss temperature range. Such samples often have a high activation energy value (e.g., >200 kJ mol^{-1}). Amplitude values less than ±2°C should be avoided, however, as they may lead to poor precision in the derived kinetic values. Flynn and Dickens balanced these two effects in their factor jump method with the choice of an amplitude of ±4–5°C [5] and these values also serve well for MTG.

TG cooling capacity affects the ability of the instrument to achieve a selected modulation amplitude. Higher amplitudes and shorter periods may be used for transitions at temperatures greater than 400°C where cooling capacity is the highest. Smaller amplitudes and longer periods may be required for transitions at temperatures less than 150°C, where cooling capacity is weak. A possible concern when using large amplitudes, especially at low temperatures, is that some amplitude settings cannot be achieved at some periods. In particular, shorter periods required smaller amplitudes settings than do longer periods. This a natural result of the temperature-time constant for the TG.

The use of high conductivity helium as a purge gas aids performance at lower temperatures. For this reason, helium is the purge gas of choice in the study of dehydration reactions below 120°C.

The oscillation period can be varied from 100 to 1000 s (10 to 1 mHz). In general, the period should be as short as possible to reduce experimental time, consistent with quantitative heat transfer to the test specimen. Good design calls for the period to be at least ten times the apparatus time constant. A period of 200 s easily satisfies this condition, even at temperatures below 100°C.

Heating rate selection in MTG has the same effect on experimental results as in traditional TG. Faster heating rates reduce experiment time and increase TG sensitivity while generally sacrificing resolution. Slower heating rates lengthen experiment time and increase resolution at the expense of sensitivity. In MTG experiments, however, there is an even more important effect of the heating rate. It contributes to the number of modulation cycles that occur during a transition. In order to get acceptable results, a minimum number of cycles is required. A useful tool to determine the appropriate heating rate is to observe the full width at half height of the mass loss rate signal for a scouting experiment at 10°C min^{-1} such as that shown for EVA in Fig. 6. A maximum heating rate (β) should be selected to provide a minimum of 5 cycles within this full width temperature range ($T_{1/2}$):

$$\beta = T \cdot 60\ \text{s/min}/(PN) \tag{7}$$

where *P* is the period and *N* the number of cycles. For example, the narrowest peak in Fig. 6 is about 36°C wide. For a period of 200 s the maximum heating rate is about 2.2°C min^{-1}. In practice, MTGA™ can be performed at any underlying heating rate, however, rates of 2°C min^{-1} and less are recommended for most work. Lower heating rates are used to improve precision of the kinetic parameters but, of course, do so at the expense of experimental time.

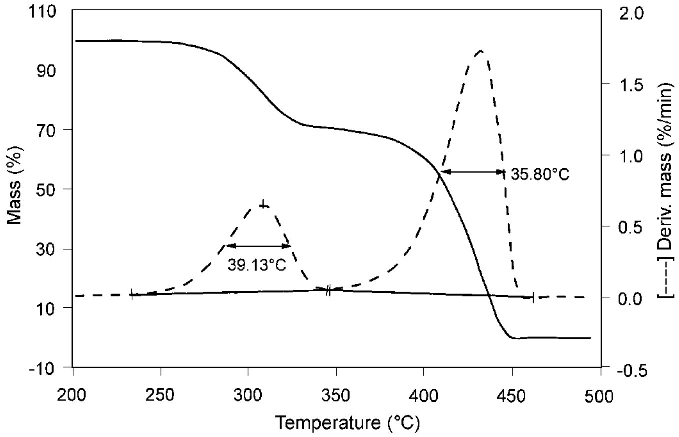

Fig. 6 Determination of full width temperature at half height.

The variable heating rate of dynamic rate TG is controlled by the resolution index parameter. The effect of maximum heating rate and resolution index were examined using the two step decomposition of EVA using the limiting condition of a minimum of ten cycles across each mass loss region. The values in Table 2 represent the maximum heating rate and minimum resolution index which met these conditions.

Table 2 Heating rates and resolution indexes suitable for use in MTG

Maximum heating rate/ °C min^{-1}	Resolution index	Approximate experiment time/ min
5	6	130
10	7	200
15	8	260

These results show that resolution index has a greater effect on experimental time than does heating rate as a resolution index of 6 and heating rate of 5°C min^{-1} results in a shorter experiment than does a resolution index of 8 and heating rate of 15°C min^{-1}.

Summary

A new technique, called modulated thermogravimetry, is introduced which makes use of an oscillatory temperature program to obtain decomposition kinetic information in a single experiment. The approach provides continuous measurement of kinetic parameters during the whole of the decomposition process, permitting the important kinetic parameters of activation energy and pre-exponential factor to be continuously plotted as a function of conversion, temperature and time. In addition, the use of controlled rate TG provides for the average temperature to be increased during the experiment so that multiple decomposition steps of a material may be observed in the same experiment.

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