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APPLICATION OF CONSTANT REACTION RATE TG TO THE DETERMINATION OF KINETIC PARAMETERS BY Hi-Res TG

X. E. Cai[1*], *H. Shen*[2], *C. H. Zhang*[2], *Y. X. Wang*[3] *and Z. Kong*[3]

[1]Department of Chemistry, Fudan University, Shanghai 200433
[2]Shanghai Import and Export CIB of the P. R. China, Shanghai 200092
[3]Shanghai Customs Laboratory, Shanghai 200120, P. R. China

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Abstract

A simple operation mode to determine the apparent activation energy E_a is introduced. E_a can be determined with a double-curve method by using a constant reaction rate (CRR) approach of Hi-Res TG. The most appropriate mechanism function $f(\alpha)$ and frequency factor A are determined by a single-curve method when the activation energies provided by the two methods are in good agreement with each other. The deacetylation of EVA copolymer has been used for illustration. Advantages of the CRR are discussed.

Keywords: activation energy, constant reaction rate TG, CRTA, EVA, thermal degradation

Introduction

Ortega [1] reviewed the successes and failures of TG, and regarded constant or controlled transformation rate thermal analysis (CRTA) as the opposite of TG. More than one-fourth century ago, Rouquerol [2, 3] and Paulik [4] had the idea of quasi-static condition to increase the resolution of thermal analysis. CRTA was developed from the vacuum TG by Rouquerol [5]. The applications and theoretical analyses of CRTA have been discussed [1, 5]. Associated with rate-jump method and the shape analysis of α *vs. T* curve, CRTA has shown to be a useful and efficient measure to make a kinetic analysis of TG. A number of inorganic compounds and minerals have been investigated by Rouquerol, Ortega, Criado and their coworkers [6–9]. By using a specially designed control system, the reaction rate was controlled by the pressure of evolved gas in a vacuum condition. The pressure of evolved gas was set in the order of 10^{-2} to 10^{-5} mbar [10]. The rate-jump method was operated automatically to bring the rate of reaction to swing between two preset values. One of the temperatures at the two reaction rates was measured directly, and another was obtained by extrapolation.

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[*] Author for correspondence: e-mail: caixiane_fudan@yahoo.com or xcai@zoo.uvm.edu

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In principle, either the pressure of the evolved gas or the mass of sample can be taken as the physical property to control the reaction rate. The advantage of mass-controlled mode will be discussed in the Conclusions.

In the present work, mass-controlled operation mode of TG showed to be much easier to get the kinetic result. Hi-Res TG, TG 2950 produced by TA Instruments for example, which aimed to deliver superior resolution, might be a suitable thermogravimeter. It was found in our work that the ‘constant reaction rate’ (CRR), one of the four operation modes of TG 2950, offered the possibility to do CRTA. The problem here is the rate setting can only be set in 8 preset values but not be the value at will. In order to calculate the activation energy, two simple runs in different reaction rates should be done.

A polymer has been chosen as the sample since there exists no vacuum gauge and there is no worry about the contamination of evolved organic gas.

Experimental

Thermogravimeters

TG measurements were carried out by employing Hi-Res TG, TG 2950, and conventional TG, TG 2050 thermogravimeters. Temperature calibration was accomplished by using indium and aluminum, while mass calibration was done with a standard mass. Nitrogen was used as the purge gas at a flow rate of 50 ml min^{-1}. The sample size was 10–25 mg.

The operation mode of CRR and ‘dynamic rate’ (DR) are two of the functions of the Hi-Res TG, TG 2950. There are 8 settings respectively. The reaction rate of CRR decreases from the preset settings ‘–1’ to ‘–8’ step by step. DR was used as a Hi-Res mode to the analytical purpose in this paper too.

Materials

For the illustration of the decomposition of a copolymer, the first stage of thermal degradation of EVA was used. Two samples were taken from Borealis Polymer OY, Finland, and DuPont Co., USA. They were identified by using FT-IR. The contents of acetic acid in the copolymer samples were determined [11] with both high-resolution and conventional thermogravimeters. The respective results were (20.38±0.18) and (30.62±0.10)%. The contents of vinyl acetate in these two samples thereby calculated [11] were 29.1 and 43.8%, respectively. These were consistent with the results determined chemically [12]. Therefore, these two samples were designated EVA-29 and EVA-43 in this paper.

Results and discussion

CRRTG curves

Figure 1 showed a typical result of the CRRTG measurement. 11.98 mg of the sample EVA-29 was heated to 200°C at a rate of 20°C min^{-1}, and followed by a dual-parameter program to 500°C. Either the setting of 'Res' or the heating ramp was satisfied. In this run the resolution was set on '–5' and the heating ramp was 5°C $\min^{-1}$ from 200 to 500°C.

In contrast with the conventional TG, curve '*T*' in Fig. 1 showed an increasing trend. When the mass loss rate was lower than the resolution setting, the temperature increased rapidly. This could be noticed before the decomposition started, and at the end of the first stage of degradation as well. It also happened when the sample was almost depleted.

Curve '*W*' in Fig. 1 showed that the mass loss could not be detected until about 250°C, and then it remained almost constant at a rate of about 0.1% per min. There was a tiny deviation, which was hardly found, at around 20.38%, when the deacetylation completed and the chain scission started. When a very low CRR is set, the reaction rate can be kept almost unchanged. The $W\%\sim t$ curve of resolution setting on '–6' or '–7' showed a perfect straight line. No any deviation could be observed even though at mass loss of 20.38% where the reaction mechanism changed and temperature increased sharply.

Table 1 The results obtained by double-curve and single-curve methods

Sample	'Res' setting	$(\mathrm{d}W/\mathrm{d}t)$/% $\min^{-1}$ (Average, found)	Double-curve method		Single-curve method (F1)		
			$\ln(\mathrm{d}\alpha/\mathrm{d}t)$	E_a/ kJ mol^{-1}	E_a/ kJ mol^{-1}	$\ln A$/ $\min^{-1}$	*r*
EVA-43	'–4'	0.3125	–4.58	168.6±4.9	149.4	27.37	0.9994
	'–5'	0.1026	–5.70		148.5	27.03	0.9993
EVA-29	'–6'	0.04104	–6.21	166.5±9.1	177.2	32.18	0.976
	'–7'	0.01290	–7.37		159.1	28.12	0.96

Curve '$\mathrm{d}W/\mathrm{d}t$' revealed the fact that the reaction rate fluctuated to some extent. The reaction rates were listed in Table 1. When the heating ramp was set too low, the operation would run in conventional mode. However, if the heating rate were too high, more serious noise of the curve '*T*' and '$\mathrm{d}W/\mathrm{d}t$' would occur as a result.

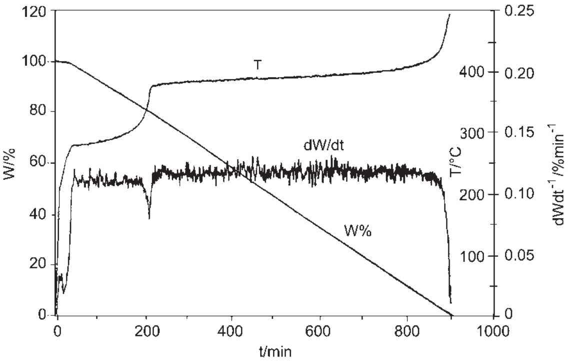

Fig. 1 TG curves of EVA-29 measured by using CRR mode of Hi-Res TG

Estimation of E_a by double curve method

If two parallel experiments are done at different CRR, two curves of $W\%{\sim}t$ with slopes $(\mathrm{d}W\%/\mathrm{d}t)_\mathrm{i}$ and $(\mathrm{d}W\%/\mathrm{d}t)_\mathrm{j}$ can be obtained. The slopes can easily be converted to the reaction rate $(\mathrm{d}\alpha/\mathrm{d}t)_\mathrm{i}$ and $(\mathrm{d}\alpha/\mathrm{d}t)_\mathrm{j}$ as long as the total mass loss W_1 of the first stage reaction is known. When a value of $W\%$ is chosen the corresponding T_i and T_j at an iso-conversion can be obtained from the two curves of $W\%{\sim}T$. As a matter of fact, the exact T values at a given $W\%$ are easily read from the TG files. Assuming that the E_a and ln$A$ in the two runs are the same at a given conversion fraction α, then E_a can be calculated by the well-known formula:

$$E_\mathrm{a}=R\frac{T_\mathrm{i}T_\mathrm{j}}{T_\mathrm{i}-T_\mathrm{j}}\ln\left[\frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\mathrm{i}}{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\mathrm{j}}\right] \tag{1}$$

Certainly, $\mathrm{d}W/\mathrm{d}t$ can also be used here instead of $\mathrm{d}\alpha/\mathrm{d}t$. However, W_1 is necessary if the mechanism function and ln$A$ are to be determined as discussed in Eq. (2). In this case, W_1 can be estimated from the critical point of two stages as shown at the curve of $\mathrm{d}W/\mathrm{d}t$ in Fig. 1 or determined with DR approach of a high-resolution TG in advance as done in this work.

For illustration, the settings of CRR resolution '–4' and '–5', and '–6' and '–7' were matched into two pairs and used for EVA-43 and EVA-29, respectively. In principle, any given α can be applied to calculate the activation energy, which varies a bit along with α increases. In order to minimize the experimental error and to compare with the single-curve method, a number of α were chosen. The mean values were shown in Table 1.

Determination of E_a, lnA and the mechanism function by single-curve method

A series of $W\%$ and T were read from the file of CRRTG curve, then they can be fit by using Sharp's method [13, 14]:

$$\ln f(\alpha)=\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)-\ln A+\frac{E_\mathrm{a}}{RT} \tag{2}$$

Fourteen kinetic models commonly used in solid-state reaction were applied as the probable mechanism functions. Among them, function F1 $[f(\alpha)=(1-\alpha)]$ gave both highest correlation factor r and the closest E_a value to that got from double-curve method. The closest E_a and highest r were conductive to the discrimination of the most appropriate mechanism function from the others and to the evaluation of ln$A$. The results were also shown in Table 1 and consistent with those reported [15, 16]. It should be pointed out that the heater control system of the CRR approach makes the temperature changeable to maintain a constant rate of mass loss, the fluctuating temperature could result in poor correlation factor of $\ln f(\alpha)$ *vs*. T^{-1} as shown in Table 1. Such temperature noise could be improved when the heating ramp was set lower.

It can be found from Eq. (2) that the mechanism functions with the general form of $m(1-\alpha)^n$ give the same correlation factors. Their slopes can be related to the slope of F1 with multiplying by n. Thus, do the E_a values. Their intercepts are related by both n and m.

Conclusions

1. CRTA is a concept in broad senses, either pressure of the evolved gas or the mass of sample can be taken as the physical property to control the reaction rate. CRR mode is only a special case of the CRTA. In fact, they can also be called as sample control thermal analysis (SCTA) [17, 18]. In addition to the excellent analytical result, CRR mode can also be applied to kinetic analysis of TG, and controlled preparation as well.
2. Since no vacuum gauge exists in the Hi-Res TG, there is no worry about the contamination of the evolved organic gas. Therefore, the deacetylation of EVA can be chosen in this work. The result just proves the feasibility, simplicity and reliability of the CRR operation mode to kinetic analysis.
3. Some advantages of the operation mode CRR can be summarized as follows:
   - The operation is just like a conventional TG;
   - Experiment can be done in normal atmospheres as done in conventional TG;
   - Reaction rate can be kept almost constant even in multi-step decomposition;
   - No contamination exist, polymer materials can be applied to.

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