Kinetic Analysis of High-Resolution TGA Variable Heating Rate Data

I. M. SALIN and J. C. SEFERIS*

Polymeric Composites Laboratory, Department of Chemical Engineering, University of Washington, Seattle, Washington 98195

SYNOPSIS

Isothermal and constant heating rate thermogravimetric analysis (TGA) experiments have been performed for examining decomposition of polymers and composites. In practice, low heating rates are necessary to obtain good resolution under nonisothermal conditions thus increasing the time required for experiments. A novel TGA mode, high-resolution TGA (Hi-Res™ TGA), provides a means to remarkably increase the resolution while often decreasing the time required for experiments. In this variable heating rate mode of Hi-Res™ TGA, the heating rate is continuously and dynamically varied to maximize resolution. Thus, traditional methods cannot be directly utilized to determine kinetic parameters. Accordingly, in this work, variable heating rate experiments were run on ethylene–vinylacetate (EVA) copolymer, poly (ether ether ketone) (PEEK), and carbon-fiber-reinforced bismaleimide (BMI), whose kinetics have been quantitatively described with traditional isothermal and nonisothermal experiments. Comparison of the different techniques led to the development of a simplified method by which the activation energy, preexponential factor, and reaction order can be extracted from variable heating rate TGA experiments. The technique, based on the principle that maximum weight loss rate is observed at minimum heating rate, gave kinetic results that were in excellent agreement with values that have been determined by traditional isothermal and dynamic experiments. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Traditionally, both isothermal and constant heating rate thermogravimetric analyses (TGA) have been used to obtain kinetic information from decomposition of polymers and their composites. Constant heating rate experiments are often faster to run than a series of isothermal experiments. However, obtaining good resolution usually requires low heating rates, thus increasing the time scale of the experiments. With complex systems such as polymers and their fiber-reinforced composites, good resolution is essential in obtaining reliable results and kinetic parameters that can be used to compare the stability of different systems and assess their lifetime.

A novel TGA mode, High-Resolution TGA (Hi-Res™ TGA), introduced by TA-Instruments,[1] provides a means to remarkably increase the resolution

while often decreasing the time required for experiments. Hi-Res TGA has two novel nonisothermal modes of operation: variable heating rate mode and constant reaction rate mode. In the variable heating rate mode, heating rate is dynamically and continuously varied to maximize resolution. In the constant reaction rate mode, reaction rate is attempted to be kept at a specified constant value by changing the heating rate. However, even though resolution of the data is increased, methods for extracting kinetic information from variable heating rate experiments have not been developed. Accordingly, this work established a methodology to extract kinetic parameters from variable heating rate data.

BACKGROUND

In the variable heating rate mode of high-resolution thermogravimetry, the heating rate is continuously and dynamically varied to maximize resolution, i.e., the ability to separate closely occurring events.[1]

Thus, if the reaction rate increases, the heating rate decreases, or vice versa. Parameters that affect the heating rate and are controllable by the operator are resolution, sensitivity, and initial heating rate, q_{init}. A mathematical function uses these three parameters to relate the observed reaction rate $d\alpha/dt$ (%/min) to heating rate q (°C/min).[2] Thus, the observed heating rate can be expressed as

$$q = f\left(q_{init}, \frac{d\alpha}{dt}, \text{resolution, sensitivity}\right) \quad (1)$$

Equation (1) specifies the algorithm by which the heating rate is controlled. The variable heating rate mode provides a choice of resolutions ranging from 0 to 8. If the resolution is 0, heating rate is constant; when the resolution is increased, the instrument will react to smaller changes in the weight loss rate. Sensitivity controls the magnitude of response relative to changes in reaction rate. Since the heating rate is reduced if the reaction rate increases, the heating rate should be minimum when reaction rate is maximum.

To fully utilize the capabilities of variable heating rate TGA, a method to obtain kinetic information from the data is needed. With the possible exception of Kissinger's method, none of the constant heating rate methods is applicable to variable heating rate data.[3]

The basic equation used to describe decomposition reactions and as a foundation for deriving Kissinger's method is[3]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

The rate constant $k(T)$ is a function of temperature only, whereas $f(\alpha)$ is some function of conversion, α, which may be defined as

$$\alpha = \frac{M_0 - M_t}{M_0 - M_f} \quad (3)$$

where M_t is the sample weight at any time t, and M_0 and M_f are the initial and final sample weights, respectively. Usually k is assumed to follow an Arrhenius-type expression, and $f(\alpha)$ is expressed as $(1 - \alpha)^n$ assuming nth-order kinetics, giving

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right)(1 - \alpha)^n \quad (4)$$

Kissinger's method is derived by taking the time derivative of eq. (4), and noting that at maximum degradation rate, $d/dt(d\alpha/dt) = 0$. This allows for calculation of the activation energy E_a and preexponential factor A at maximum rate of degradation. When the heating rate is constant, time and temperature derivatives of weight loss rate are linearly related. As a result, data can be plotted as a function of time or temperature, and then analyzed using Kissinger's method.

In principle, this method could be extended to variable heating rate data, since constant heating rate is not a necessary assumption in eq. (4) or in the derivation of Kissinger's method. However, data should be analyzed as a function of time since the time and temperature derivatives are no longer linearly related when heating rate is not constant. In addition, the sample spends longer time at certain temperature when maximum degradation rate is approached. Therefore, the maximum in weight loss derivative with respect to time becomes broad and does not have a clear maximum.

For nonisothermal conditions, eq. (4) can be written as

$$\frac{d\alpha}{dT} = \frac{A}{q} \exp\left(\frac{-E_a}{RT}\right)(1 - \alpha)^n \quad (5)$$

The temperature derivative of eq. (5) will involve the derivative of the heating rate q, which is not constant in variable heating rate experiments. However, according to the Hi-Res™ TGA operation principles, heating rate should have its minimum at the maximum weight loss rate. Therefore, when $d/dT(d\alpha/dT) = 0$, also $dq/dT = 0$. Consequently, at maximum rate of degradation, temperature derivative of eq. (5) can be written as

$$\frac{d}{dT}\left(\frac{d\alpha}{dT}\right) = \frac{A}{q} \exp\left(\frac{-E_a}{RT}\right)n(1 - \alpha)^{n-1}\left(-\frac{d\alpha}{dT}\right)$$

$$+ \frac{A}{q}(1 - \alpha)^n \exp\left(\frac{-E_a}{RT}\right)\frac{E_a}{RT^2} \quad (6)$$

Equation (6) can be simplified using eq. (5) for $d\alpha/dT$, viz.

$$A \exp\left(\frac{-E_a}{RT}\right)n(1 - \alpha)^{n-1} = \frac{E_a q}{RT^2} \quad (7)$$

Taking logarithms of both sides of (7) and rearranging,

$$\ln \frac{q}{T^2} = \frac{-E_a}{R} \frac{1}{T} + \ln\left[\frac{AR}{E_a} n(1-\alpha)^{n-1}\right] \quad (8)$$

Even though derived from different principles, eq. (8) is identical to that introduced by Kissinger.[3] Kinetic parameters can be obtained from eq. (8) by plotting $\ln(q/T^2)$ as a function of $1/T$ at the maximum weight loss rate. For variable heating rate experiments, both temperature and heating rate at maximum weight loss rate (minimum heating rate) must be determined from the data. Activation energy E_a can then be obtained from the slope and preexponential factor A from the intercept assuming that n is known. If $n = 1$, A becomes independent of conversion, α, at maximum degradation rate.

In principle, heating rate q can be written as a function of initial heating rate, weight loss rate with respect to time, resolution, and sensitivity as shown in eq. (1). This equation specifies the operating principle of the High-Res TGA, i.e., the algorithm by which the heating rate is controlled. If this algorithm is available, it can be substituted for q in the preceding equations, and new expressions can be derived in which resolution and sensitivity are the input parameters rather than the heating rate itself.

The reaction order n can be determined from isothermal experiments[4] or by assuming a value using other criteria.[5] However, isothermal experiments are time consuming, so a method for obtaining reaction order from the variable heating rate data would be preferable. Accordingly, a possible scheme for determining n from the dynamic data was developed.

From eq. (8), the intercept of a plot of $\ln(q/T^2)$ as a function of $1/T$ at the maximum weight loss rate is

$$I = \ln\left[\frac{AR}{E_a} n(1-\alpha)^{n-1}\right] \quad (9)$$

Solving for A and substituting it into (5) gives an expression for n, viz.

$$n = \left(\frac{d\alpha}{dT}\right)^{-1} \frac{E_a B}{qR} (1-\alpha)\exp\left(\frac{-E_a}{RT}\right) \quad (10)$$

where $B = \exp(I)$. The reaction order, n, can be easily obtained from (10) by using E_a and the intercept value determined from eq. (8). In addition

to q and T at the maximum weight loss rate, also $d\alpha/dT$ and α at this point must be determined from the experimental data. Since a different set of values for q, T, α, and $d\alpha/dT$ will be obtained with different initial heating rates, resolutions, and sensitivities, the method for obtaining reaction order using eqs. (9) and (10) will be valid if similar results are obtained using these different sets of values. In principle though, only one experiment is required to get A and n once the activation energy has been determined. Naturally, several experiments are needed to get E_a and the intercept value. In summary it should be emphasized that eq. (10) is quite general and applicable to constant heating rate data as well as variable heating rate data.

EXPERIMENTAL

Two fully characterized model systems were used in this work to assess the feasibility of the method: Ethylene–vinylacetate (EVA) copolymer and neat poly(ether ether ketone) (PEEK). These materials were chosen since kinetic parameters obtained from a variety of traditional thermogravimetric methods have been reported for them in the literature.[5-9] In addition, an IM7-carbon-fiber-reinforced bismaleimide (BMI) system was used to demonstrate the advantages of high-resolution thermogravimetry for analysing complex composite systems.[10]

Experiments were performed on a TA-Instruments Hi-Res™ TGA 2950 interfaced to TA-Instruments 2000 controller. Sample size in all experiments was 13–15 mg, and purge gas flow rate was fixed at 100 cm³/min air or nitrogen. EVA and PEEK samples were used as pellets, and BMI composite samples were cut from a laminate and subsequently dried in an oven for several hours to evaporate moisture. The laminate was cured and post-cured according to the manufacturer's recommendations.

In principle, heating rate and temperature at maximum degradation rate can be affected by varying the initial heating rate, resolution, or sensitivity. A series of experiments using EVA in nitrogen were run to find the best way to conduct variable heating rate experiments. In all these experiments, sensitivity was fixed at its default value, 1. First, initial heating rate was fixed at 30 and 45°C/min, and resolution was varied. Then, resolution was fixed at 2 and 3, and initial heating rate was varied. Equations (8) through (10) were then applied to the data in order to extract kinetic parameters. In addition,

constant heating rate experiments were run at 1, 3, 10, and 20°C/min to provide a control set of values for kinetic parameters that could be compared to existing literature values. Kinetic parameters were determined from constant heating rate data using the procedure described previously for variable heating rate data.

A series of variable heating rate experiments were also run on PEEK in nitrogen and BMI composite in air. In these experiments, initial heating rate was fixed at 30°C/min, and resolution was varied. Selected constant heating rate experiments were also run on the BMI composite to compare the resolution of constant and variable heating rate experiments.

RESULTS AND DISCUSSION

Figure 1 shows a typical Hi-Res TGA curve of EVA as a function of time. In addition to weight loss, heating rate and the time derivative of weight loss are also shown. It should be obvious that data analysis becomes very subjective since derivative and

heating rate peaks are relatively broad. Figure 2 shows weight loss, heating rate, and temperature derivative of weight loss presented as functions of temperature. Clearly, data analysis as a function of temperature is likely to give more reproducible results than analysis of data as a function of time.

A typical Hi-Res TGA curve for PEEK in nitrogen is shown in Figure 3 as a function of temperature. The transition is very sharp and degradation onset is relatively easy to determine. Because of the excellent resolution and sharp transitions observed in variable heating rate experiments, Hi-Res TGA may prove an excellent tool for comparing different material stabilities.

The advantages of high-resolution thermogravimetry are fully demonstrated when applied to complex systems such as carbon-fiber-reinforced BMI. Figure 4 shows a comparison of the temperature derivatives of weight loss for a variable heating rate experiment performed at resolution 5 and initial heating rate 30°C/min and several constant heating rate experiments (0.5, 5, and 10°C/min) for this system. Clearly, the resolution of variable heating
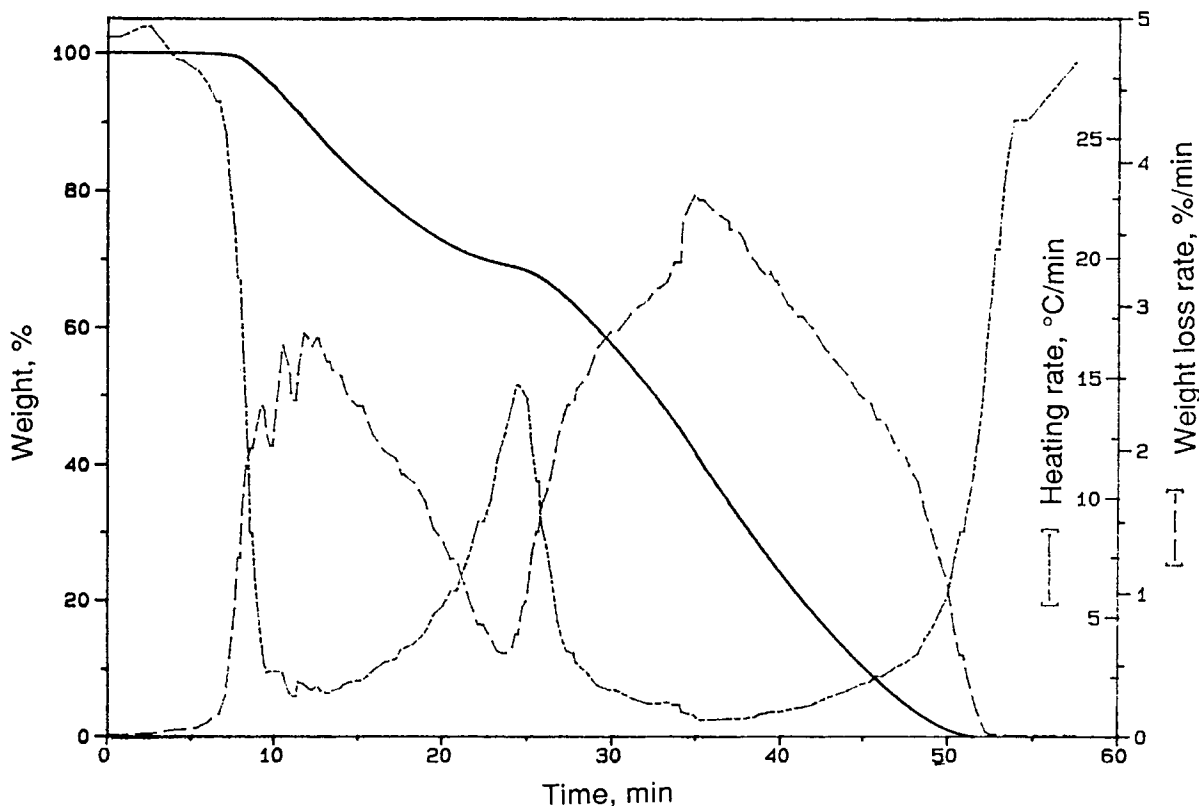

Figure 1   Weight loss, heating rate, and time derivative of weight loss plotted as a function of time for EVA in nitrogen. Initial heating rate 30°C/min, resolution 4.
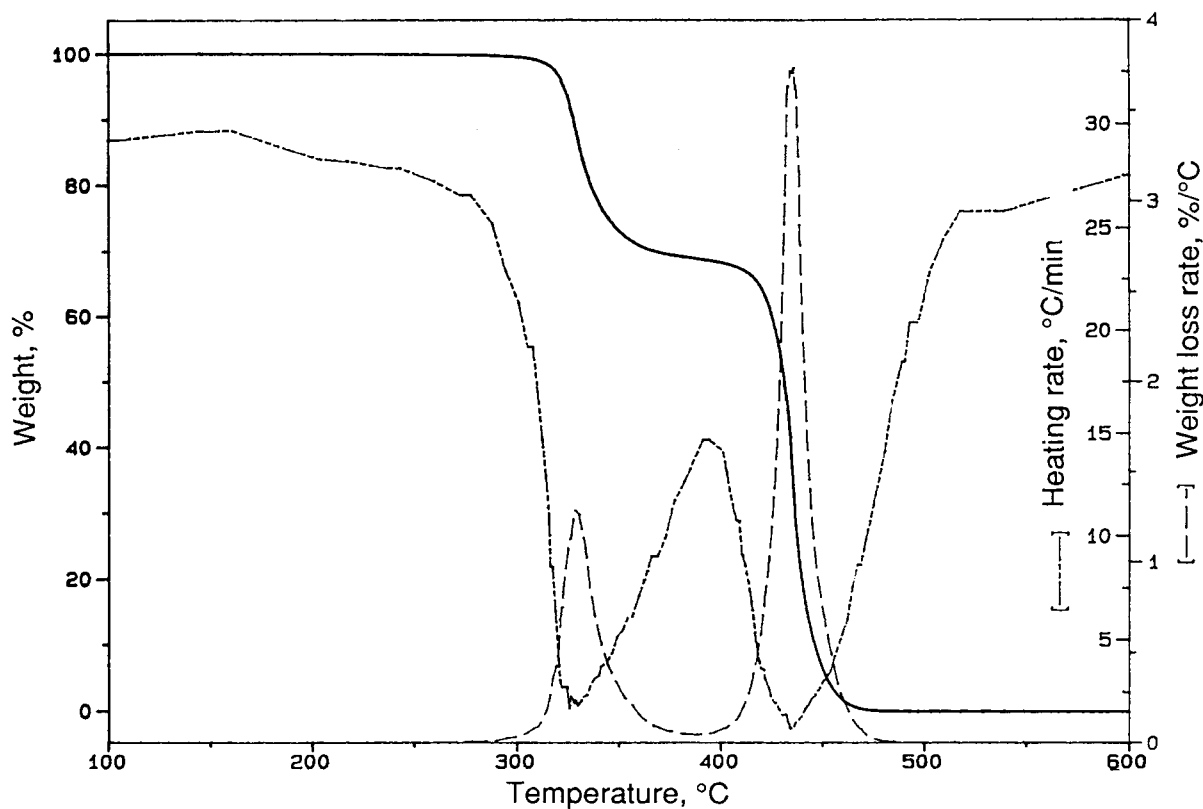
Figure 2   Weight loss, heating rate, and temperature derivative of weight loss plotted as a function of temperature for EVA in nitrogen. Initial heating rate 30°C/min, resolution 4.
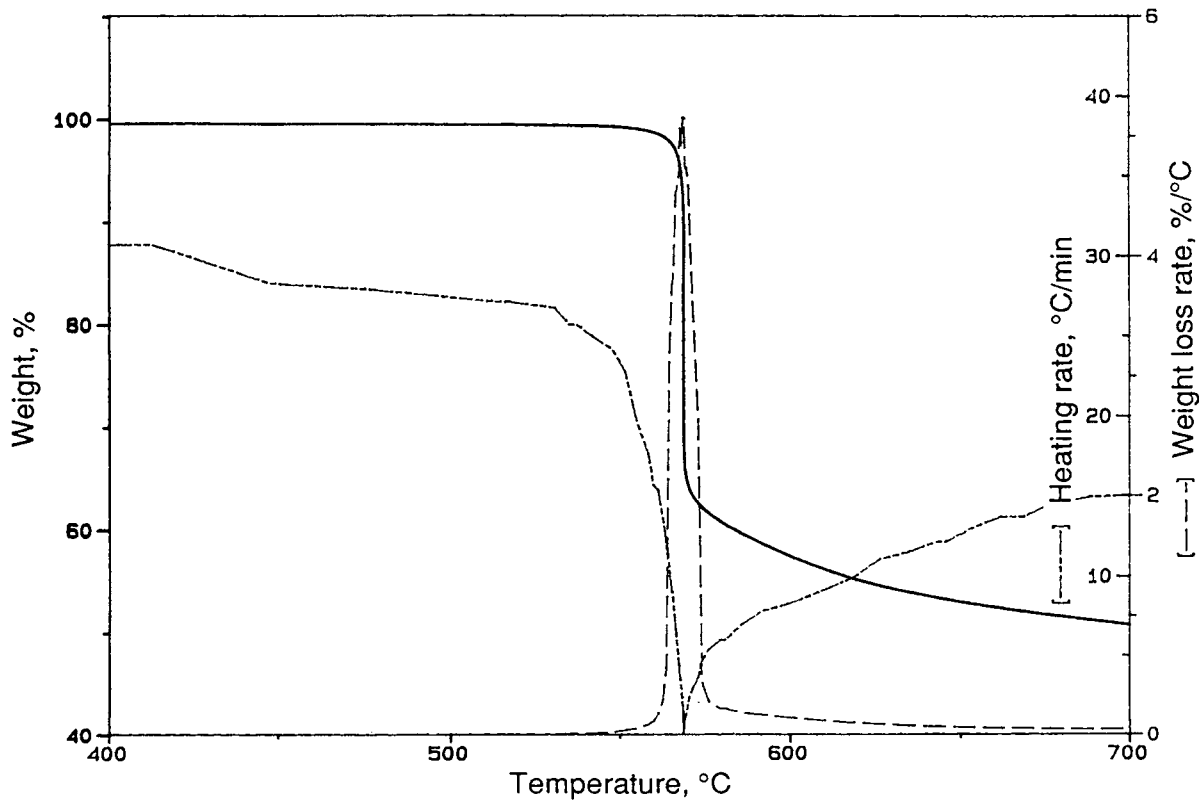
Figure 3   Weight loss, heating rate, and temperature derivative of weight loss for PEEK in nitrogen. Initial heating rate 30°C/min, resolution 4.
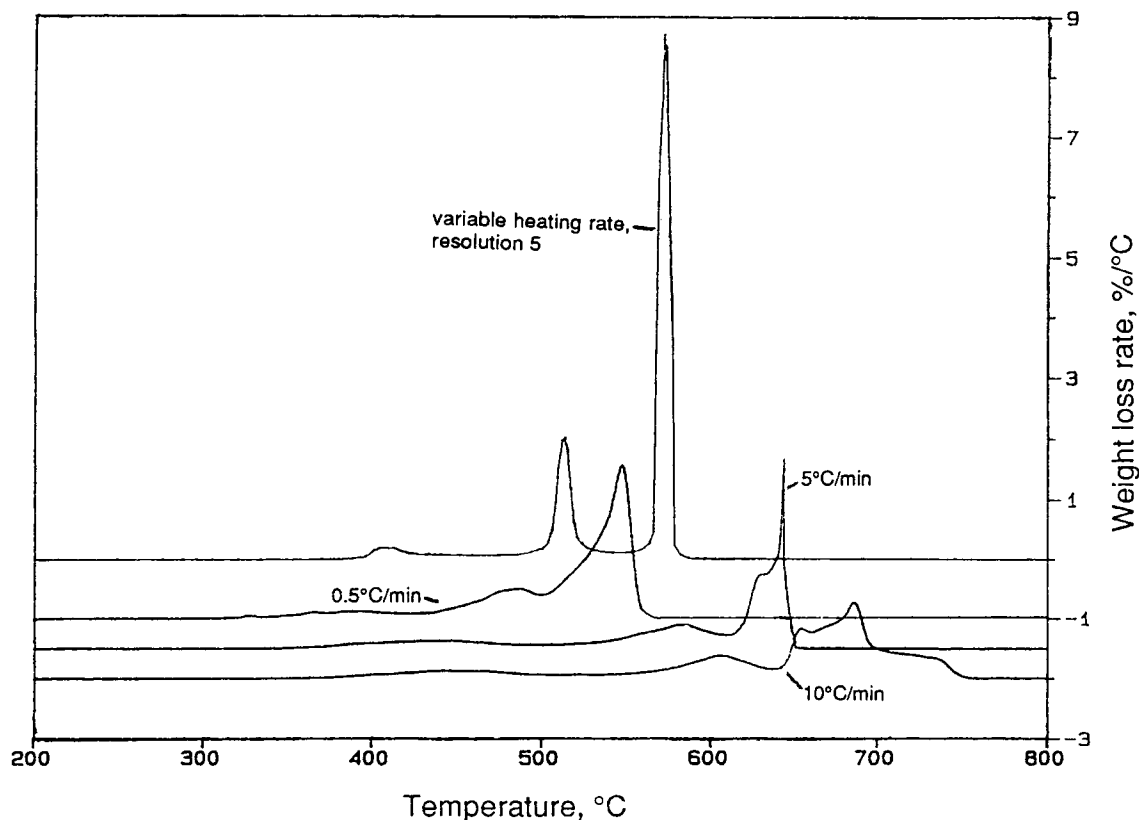
Figure 4 Comparison of temperature derivatives of weight loss at variable and several constant heating rates for BMI composite in air.

rate experiments is superior to that of constant heating rate experiments. Even a constant heating rate as low as 0.5°C/min does not give a resolution comparable to variable heating rate data. Furthermore, the variable heating rate experiment was performed in 100 min whereas the constant heating rate experiment at 0.5°C/min took more than 1500 min.

Kinetic Analysis of Variable Heating Rate Data

In order to calculate activation energies, temperature and heating rate at maximum degradation rate must be determined from experimental data. If the peak position varies only slightly upon changing operating parameters (initial heating rate or resolution), results might be seriously affected by even minor errors in determining the peak values. Similarly, maximum reaction rate and minimum heating rate may not always coincide: A high heating rate when approaching transition or very fast reaction may cause the temperature to overshoot. Consequently, assessing the effect of experimental conditions on these two factors is important.

Tables I and II show the values of heating rate and temperature at maximum degradation rate for both degradation steps of EVA in nitrogen. Table I shows the data at fixed initial heating rate whereas Table II shows the data at fixed resolution. When initial heating rate was fixed and resolution was varied from 2 to 6, temperature and heating rate values spanned a wide range of values. When resolution was fixed at 2, the same phenomena was observed. However, at resolution as low as 2, minimum heating rate and maximum degradation rate did not occur at the same temperature. A difference of up to 7.5°C was observed in peak temperatures when resolution was 2 and the initial heating rate high (30–45°C/min). Thus, the resolution needed to be increased to bring the temperature at maximum reaction rate and minimum heating rate closer to each other. However, when the resolution was increased to 3, peak temperatures and heating rates were only slightly affected by changing the initial heating rate. Therefore, peak temperature and heating rate were strongly affected by resolution whereas initial heating rate had less of an effect. As a result, fixing the

Table I   EVA Decomposition in Nitrogen at Fixed Initial Heating Rate

Operating Parameters		First Step		Second Step	
Initial Heating Rate	Resolution	Heating Rate (°C/min)	Temperature (°C)	Heating Rate (°C/min)	Temperature (°C)
30°C/min	2	15.31	362.62	7.33	467.90
	3	6.16	346.86	2.43	251.18
	4	1.95	328.30	0.72	434.31
	6	0.20	289.14	0.08	401.88
45°C/min	2	19.63	366.77	9.35	469.18
	3	6.77	348.66	2.97	451.31
	5	0.42	308.88	0.32	416.57
	6	0.19	290.40	0.07	402.14

initial heating rate and varying the resolution was found to be the best approach for generating data for kinetic analysis. Consequently, changing the resolution in variable heating rate experiments can be visualized as being equivalent to changing the heating rate in constant heating rate experiments.

Based on the observation above, data generated at the initial heating rate of 30°C/min was chosen for further analysis. Activation energies were obtained for both stages of EVA decomposition from Eq. (8) by plotting $\ln(q/T^2)$ versus $1/T$ using values reported in Table I. This plot is shown in Figure 5. Activation energies were obtained as 165.0 kJ/mol for the first step and 270.0 kJ/mol for the second step. For comparison, activation energies were also determined at initial heating rate of 45°C/min as 177.0 and 284.3 kJ/mol for the first and second steps, respectively. Activation energies were obtained as 160.8 and 259.7 kJ/mol from constant heating rate experiments. Values from both variable

and constant heating rate experiments were in good agreement with each other and with literature values obtained by a variety of methods[5]: 163.0–186.1 kJ/mol for the first step and 248.2–269.6 kJ/mol for the second step.

According to Nam and Seferis,[5] decomposition of EVA in nitrogen consists of two independent first-order reactions. To analyze these two reactions, conversion must be normalized with respect to weight factors determined from the data. In general, each weight factor w_i can be determined from the weight loss data as

$$w_i = \frac{M_i}{M_0} \tag{11}$$

where M_0 is the total weight of the sample, and M_i is the amount that degrades in the ith reaction. Here, the sum of weight factors must equal 1. In the analysis of variable as well as constant heating rate data,

Table II   EVA Decomposition in Nitrogen at Fixed Resolution

Operating Parameters		First Step		Second Step	
Resolution	Initial Heating Rate (°C/min)	Heating Rate (°C/min)	Temperature (°C)	Heating Rate (°C/min)	Temperature (°C)
2	10	6.99	342.36	4.90	454.86
	15	9.73	351.49	5.96	459.18
	25	13.09	356.59	7.31	464.28
	30	15.31	362.62	7.96	466.46
	45	19.63	366.77	9.35	469.18
3	10	4.28	333.40	2.16	442.77
	15	4.94	336.88	2.31	444.58
	30	5.59	348.54	2.43	451.18
	45	6.77	348.66	2.97	451.31

Table III   Kinetic Parameters for EVA Decomposition from Variable and Constant Heating Rate Experiments

	First Step			Second Step		
	n	$\log A$	$\log A$ (1st order)	n	$\log A$	$\log A$ (1st order)
Resolution (q_{init} = 30°C/min)						
3	0.88	13.42		0.61	18.95	
4	0.94	13.41	13.40	0.70	18.93	18.86
6	0.95	13.41		0.65	18.94	
Constant heating rate, °C/min						
1	1.24	13.22		0.87	18.20	
3	1.15	13.22	13.23	0.87	18.20	18.14
10	1.15	13.23		0.78	18.25	
20	1.08	13.22		0.67	18.32	

activation energy is independent of normalization whereas A and n are not.

To examine the validity of our approach, reaction order and preexponential factor were determined from individual variable and constant heating rate experiments separately. q, T, α, and $d\alpha/dT$ at maximum degradation rate as well as weight factors were determined from each individual experiment. Ideally, n and A should be independent of which individual run was used to obtain parameters for eq. (10). Naturally, all runs will affect the intercept and activation energy value used in determination of n and A.

Since the two degradation steps of EVA can be assumed independent,[5] α and $d\alpha/dT$ were normalized with respect to weight factors, viz.

$$\alpha_{1,N} = \frac{\alpha_1}{w_1} \tag{12}$$

$$\alpha_{2,N} = \frac{\alpha_2 - w_1}{w_2} \tag{13}$$

where the subscript N refers to normalized values.

Equation (10) was used to calculate values for n, and preexponential factors were then obtained from eq. (9). Results from both variable and constant heating rate experiments at different resolutions and heating rates are shown in Table III. Even though there was variation within the reaction order values obtained from individual experiments, they were all close to 1, thus validating a first-order kinetics assumption. Furthermore, reaction orders and especially preexponential factors obtained from individual runs were close to each other confirming

the applicability of this method to EVA decomposition. However, it is recommended that n and A be calculated from more than one experiment as done here, and that the values then be compared to each other.

In Table III, $\log A$ is calculated both using n's obtained from experiments and assuming first-order kinetics to facilitate comparison to literature values. When $n = 1$, A becomes independent of the conversion at which maximum weight loss rate is observed, so the same value for A is obtained at all resolutions/heating rates. The literature values for logarithm of first-order preexponential factor are 14.12 and 18.48,[5] which are close to the values obtained here from both constant and variable heating rate experiments.

Overall, high-resolution thermogravimetry gave excellent results for EVA copolymer. Values obtained for activation energies, preexponential factors, and reaction order compared favorably to both constant heating rate experiments and literature values.

Activation energies were also determined for PEEK in nitrogen. Heating rate and temperature at the maximum degradation rate were determined from variable heating rate data generated at q_{init} = 30°C/min and resolutions ranging from 3 to 6. The plot of $\ln(q/T^2)$ as a function of $1/T$ is shown in Figure 6. Activation energy was obtained from the slope as 281.4 kJ/mol. Reported literature values are 241.2 kJ/mol,[6] 227.9–280 kJ/mol,[7] 231.8,[8] and 198.4–219.7 kJ/mol.[9] Apparent reaction order and preexponential factor could be obtained from the PEEK weight loss data as for EVA. However, the decomposition of PEEK in nitrogen reportedly does
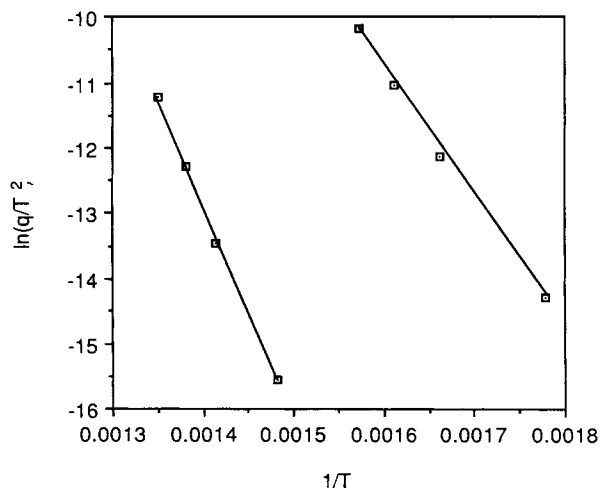
not follow simple nth-order kinetics,[6,9] and therefore, constants based on nth-order kinetics would have little practical meaning.
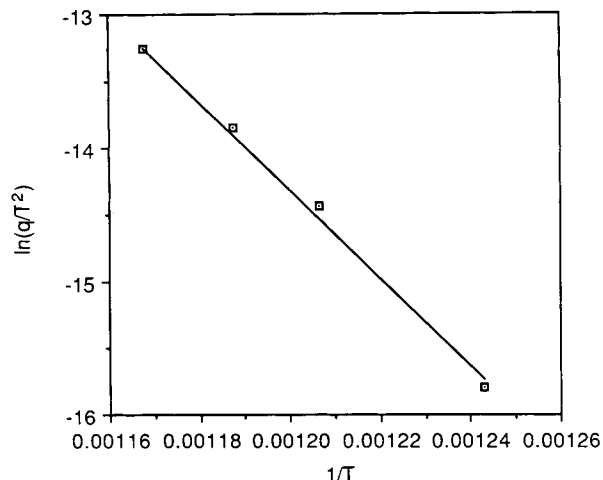
CONCLUSIONS

High-resolution thermogravimetry (Hi-Res TGA) was applied to EVA copolymer and PEEK in nitrogen, and carbon-fiber-reinforced BMI in air. In variable heating rate mode of Hi-Res TGA, heating rate is continuously and dynamically varied depending on the weight loss rate and operation parameters, which are chosen by the operator. These parameters are initial heating rate, resolution, and sensitivity. In this work, sensitivity was kept constant in all experiments.

For all the materials examined, use of variable heating rate resulted in sharper transitions and clearer onset of degradation than traditional constant heating rate experiments. Also, the time required for experiments giving reasonable resolution was often remarkably reduced compared to constant heating rate experiments.

A simplified method to extract kinetic information from variable heating rate data was introduced and evaluated using EVA copolymer as a fully characterized model system. The technique is based on the fact that the maximum weight loss rate is observed at the minimum heating rate. In order to obtain kinetic parameters, temperature and heating

Figure 6 Plot of $\ln(q/T^2)$ as a function $1/T$ for decomposition of PEEK in nitrogen. Note activation energy as the slope of the straight line.

rate at maximum weight loss rate must be varied. In principle, this can be done by either varying the resolution or initial heating rate. Fixing the initial heating rate and varying the resolution was experimentally found to be the best approach. Activation energy, preexponential factor, and reaction order were determined for the two stages of EVA decomposition in nitrogen from both variable and constant heating rate experiments. Since EVA decomposition in nitrogen consists of two independent steps, conversion was normalized with respect to weight factors determined from the data. Results (activation energy, preexponential factor, and reaction order) from variable and constant heating rate experiments were in excellent agreement with each other and with existing literature values.

Activation energy was also determined for PEEK resin in nitrogen. n and A were not determined since PEEK decomposition in nitrogen does not follow nth-order kinetics.

Overall, high-resolution TGA may offer a new, improved way to analyze complex thermogravimetric data without loss of analytical capabilities.

Figure 5 Plot of $\ln(q/T^2)$ as a function of $1/T$ for the two stages of EVA decomposition in nitrogen. Note activation energy as the slope of the straight lines.

REFERENCES

1. S. R. Sauerbrunn, C. J. Lundgren, and B. S. Grove, *Proc. 20th NATAS Conf.*, 299, (1991).
2. TGA 2950 Manual, Appendix D, TA-Instruments Inc., New Castle, Delaware (1991).
3. H. E. Kissinger, *Analyt. Chem.*, **29**, 1702 (1956).
4. C. H. Bamford and C. F. H. Tipper, Eds., *Comprehensive Chemical Kinetics*, Vol. 22, *Reactions in Solid State*, Elsevier, New York, 1980.
5. J. D. Nam and J. C. Seferis, *J. Polym. Sci. Polym. Phys. Ed.*, **29**, 601 (1991).
6. J. D. Nam and J. C. Seferis, *J. Polym. Sci. Polym. Phys. Ed.*, **30**, 455 (1992).
7. J. D. Nam, Polymer Matrix Degradation: Characterization and Manufacturing Process for High Temperature Composites, Ph.D. Dissertation, Department of Chemical Engineering, University of Washington (1991).
8. W. D. Moddeman, W. C. Bowling, E. E. Tibbits, and R. B. Whitaker, *Polym. Eng. Sci.*, **26**, 1469 (1991).
9. M. Day, J. D. Cooney, and D. M. Wiles, *Polym. Eng. Sci.*, **29**, 19 (1989).
10. I. M. Salin and J. C. Seferis, *Polymer Preprints*, **33**, No. 1, 372 (1992).