

THE KINETICS OF THE OXIDATIVE DEGRADATION OF POLY(ARYL-ETHER-ETHER-KETONE) (PEEK) *

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ABSTRACT

The kinetic parameters of the thermal decomposition of poly(aryl-ether-ether-ketone) (PEEK) in air have been investigated using an isothermal weight-loss method. The results from these studies indicate that the decomposition process is a complex one which proceeds in several overlapping stages. Calculation of the kinetic parameters by a variety of models suggests that at the lower isothermal temperatures the initial weight-loss process occurs with an apparent activation energy of about 100 kJ mol^{-1} . At higher isothermal temperatures, however, the rates appear to be controlled by diffusion factors and higher apparent activation energies are noted of around 185 kJ mol^{-1} for the earlier weight-loss fractions and of about 220 kJ mol^{-1} for the later weight-loss data. The analyses presented demonstrate the difficulties which can arise in determining meaningful mechanistic information from standard weight-loss data even when isothermal heating conditions are employed.

INTRODUCTION

Chemical kinetics applied to thermal stability studies of polymers employing weight-loss data has been used extensively by researchers. In these studies the rate of weight loss is analysed using a kinetic model which provides the best fit of the experimental and predicted data. These evaluations not only provide the kinetic parameters for the decomposition process but also provide some insight into the mechanism of the weight-loss process. Unfortunately, from a practical point of view, thermogravimetry (TG) alone, although relatively simple experimentally, does not easily lead to an understanding of the decomposition mechanism of complex, concurrent and consecutive reaction processes. The problems encountered in the analysis of weight-loss data will be examined in this study using data obtained for the isothermal weight loss of poly(aryl-ether-ether-ketone) (PEEK) heated in air.

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Previous studies of the thermal degradation of PEEK in nitrogen [1,2] have shown the weight-loss process to be relatively simple and the data can be conveniently analysed by several kinetic models to provide parameters of 210 kJ mol^{-1} for the apparent activation energy (E_a) and 11.6 for the pre-exponential factor ($\log A$) [2]. The weight-loss kinetics in air [1], however, indicated competing reactions taking place simultaneously. Some of these reactions were obviously oxidative in nature and caused the polymer to have a reduced thermal stability and faster weight loss reflected in much lower E_a values of the order of 120 kJ mol^{-1} .

Considering the great interest in the use of PEEK as a matrix material in new high temperature thermoplastic composites [3], a greater understanding of its thermal behaviour in air is required. This study was therefore undertaken to provide this information by applying a more detailed application of several kinetic models to weight-loss data.

EXPERIMENTAL

The PEEK sample used in this study was commercial grade PEEK monofilament supplied by Albany International and prepared from I.C.I. resin.

The weight loss during isothermal heating was measured with a DuPont model 951 Thermobalance which was controlled by a 1090 Thermal Analyzer using the same conditions as reported previously [2] with the exception that dry air at a flow rate of 50 ml min^{-1} was used throughout this study.

RESULTS AND DISCUSSION

Some of the weight-loss curves of PEEK from isothermal heating between 375 and 509°C are shown in Fig. 1. In order to determine degradation rate constants from these weight-loss data, rates of weight loss as a function of fractional weight loss (α) for some of the low and high temperatures studied are shown in Figs. 2 and 3 respectively. These curves, especially those at high temperatures (Fig. 3), indicate that oxidative degradation of PEEK is indeed complex with several processes taking place.

In the case of the low temperature data (Fig. 2), after the weight-loss rate goes through a maximum it appears to establish a linear apparent first-order reaction stage between α values of about 0.2 and 0.6. Rate constants of the first-order weight-loss were calculated from the linear portions of the plots for the temperatures between 385 and 432°C . The Arrhenius plot of the rate constants then yielded an E_a value of $132.9 \pm 1.5 \text{ kJ mol}^{-1}$ and a $\log A$ value of $6.41 \pm 0.07 (\text{min}^{-1})$. Analysis of the rate plots for the higher temperatures (Fig. 3), however, reveals that after the initial rapid weight loss

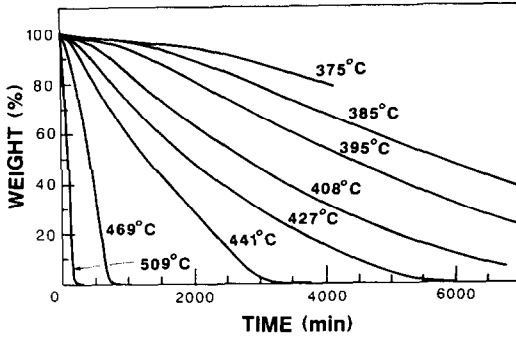


Fig. 1. Isothermal weight-loss curves for PEEK degraded in air at various temperatures.

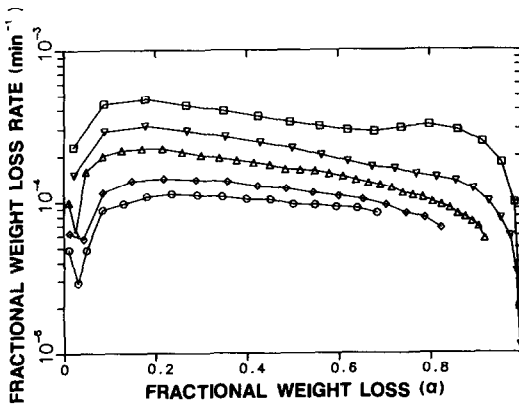


Fig. 2. Plots of weight-loss rates ($d\alpha/dt$) against fractional weight loss (α) at isothermal temperatures of 385°C (○); 395°C (◇); 404°C (Δ); 427°C (▽); and 440°C (□).

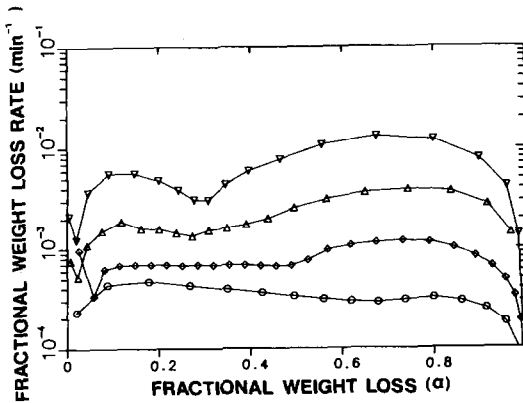


Fig. 3. Plots of weight-loss rates ($d\alpha/dt$) against fractional weight loss (α) at isothermal temperatures of 440°C (○); 460°C (◇); 480°C (Δ); and 509°C (▽).

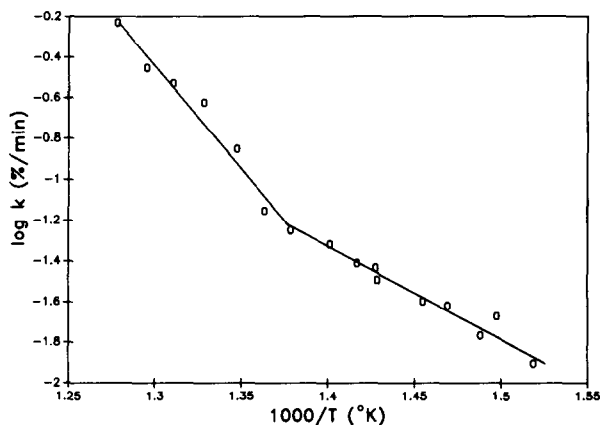


Fig. 4. Arrhenius plot for maximum weight-loss rate data for the first maxima ($\alpha \approx 0.2$).

there is no real linear first-order region before the rate commences to accelerate again to a second maximum value at about $\alpha = 0.7$. The analysis of a linear apparent first-order reaction stage at temperatures above 440°C is therefore impossible.

Several workers [4–6] have proposed the use of the maximum rate obtained from a series of isothermal runs as a method of determining the apparent activation energy of thermal decomposition. In these studies a plot of the log (rate maximum) against reciprocal temperature ($1/T$) is used to give E_a from the slope. The maximum rate data for the first maxima ($\alpha \approx 0.2$) are plotted in Fig. 4. From these data it is clear that the same slope does not apply to all of the points. An E_a value of $85.9 \pm 5.1 \text{ kJ mol}^{-1}$ is obtained from the low isothermal temperatures while high isothermal temperatures yield an E_a value of $192.4 \pm 14.9 \text{ kJ mol}^{-1}$.

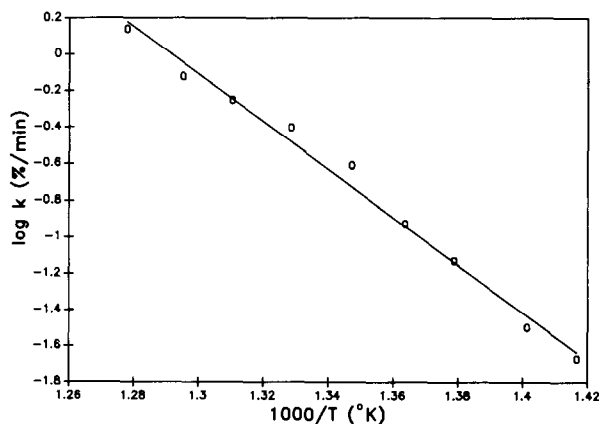


Fig. 5. Arrhenius plot for maximum weight-loss rate for the second maxima ($\alpha \approx 0.75$).

These values clearly reflect two different processes occurring at the high and low temperatures during this initial weight-loss process. The E_a value for the high temperature data in fact closely resembles the value obtained in nitrogen [2] suggesting that perhaps at higher temperatures oxygen diffusion is slow in comparison to the degradation process such that the E_a value resembles that obtained in a non-oxidative environment.

As well as analysing the first weight-loss maximum, the second maximum rate at $\alpha \approx 0.75$ was also investigated. Because this peak rate could only be detected at temperatures above 430°C , this applies only to the higher temperature experiments. The Arrhenius plot for this data is shown in Fig. 5, which gives an E_a value of $250.0 \pm 9.7 \text{ kJ mol}^{-1}$. Based upon these analyses, it would appear that indeed the isothermal weight loss of PEEK in air is a complex process with at least three different processes occurring, depending upon temperature and fractional weight loss.

Generally, for thermogravimetric experiments the rate of weight loss $d\alpha/dt$ is described by the equation

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where α is the degree of conversion, k the reaction rate constant and $f(\alpha)$ the function which describes the degree of conversion. When the nature of $f(\alpha)$ is unknown, the above expression may be combined with the Arrhenius equation

$$k = A \exp(-E/RT) \quad (2)$$

to obtain

$$\frac{d\alpha}{dt} = f(\alpha)A \exp(-E/RT) \quad (3)$$

By determining the rates $(d\alpha/dt)_i$ at fixed degrees of conversion α_i at different isothermal temperatures, it is therefore possible to determine the Arrhenius parameter from a plot of log rate against reciprocal temperatures

$$\ln(d\alpha/dt)_i = \ln A f(\alpha_i) - (E/R)(1/T_i) \quad (4)$$

The advantage of this method suggested by Flynn [7], is that it allows E_a to be determined without a knowledge of $f(\alpha)$. These plots for $\alpha = 0.05-0.20$ are shown in Fig. 6 while Fig. 7 shows the data for $\alpha = 0.2-0.8$. These results clearly indicate that the data do not follow the same Arrhenius equation over the whole temperature range. Instead, the slopes at the lower temperatures are less than those at higher temperatures, and while there is some variation with conversion, the differences are not as large as those obtained due to temperature variation. Once again, however, the temperature at which the slopes change appears to be 440°C , a value noticed in the previous methods of analysis. Changes in the slopes with conversion are demonstrated graphically in Fig. 8. In these plots, the E_a values have been

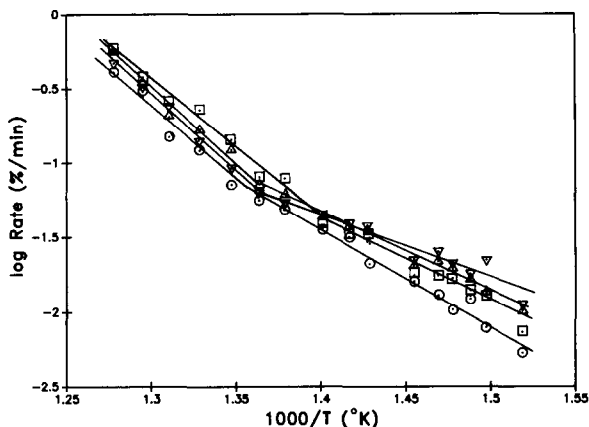


Fig. 6. Arrhenius plots of isoconversional data obtained for $\alpha = 0.05$ (○); 0.10 (□); 0.15 (Δ); and 0.2 (▽).

separately calculated for the low and high temperature data. As was noted with the previous analyses, there are large differences between the high and low temperature data. The experiments conducted at the low isothermal temperatures gave E_a values of about 130 kJ mol^{-1} for $\alpha = 0.05$ – 0.10 which then fell to values of around 95 kJ mol^{-1} from $\alpha = 0.15$ – 0.60 . The high temperature data, meanwhile, suggests that the E_a for the initial weight-loss range $\alpha = 0.05$ – 0.3 is around 185 kJ mol^{-1} climbing to a value of about 225 kJ mol^{-1} for the higher α values.

The methods of analysis employed so far in this study have ignored the form of $f(\alpha)$ although the low temperature data between $\alpha = 0.2$ and 0.6 were analysed according to first-order kinetics, i.e. $f(\alpha) = (1 - \alpha)$. However, it is clear from the current study that this simple form is not sufficient to

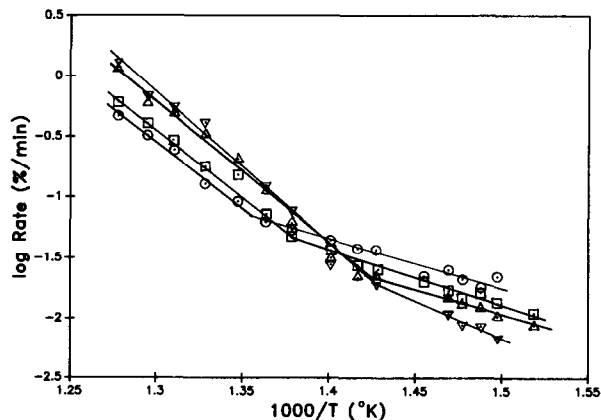


Fig. 7. Arrhenius plots of isoconversional data obtained for $\alpha = 0.2$ (○); 0.4 (□); 0.6 (Δ); and 0.8 (▽).

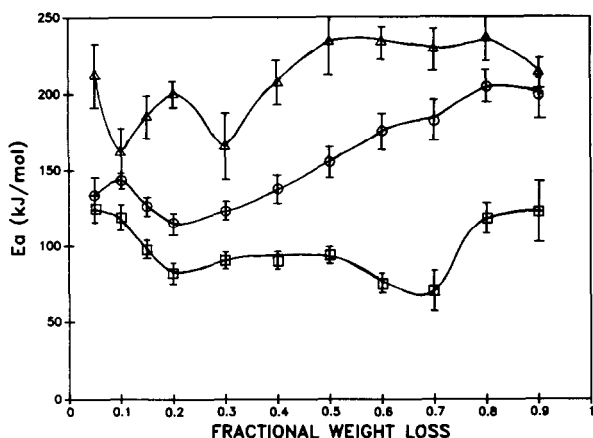


Fig. 8. Variation of activation energies E_a calculated by the isoconversional method; low temperature data (\square); high temperature data (Δ); all data (\circ).

explain the complex kinetics. It therefore becomes necessary to evaluate this function in the light of the weight-loss data. The approach that we have taken was to compare the shape of the α -reduced time plots with lines calculated for various integrated forms of the rate function $g(\alpha)$ documented in the literature [8–11]. These reduced time plots using $t_r = 1.00$ at $\alpha = 0.50$ are shown in Figs. 9 and 10 for the low temperature and high temperature data respectively. Also shown in these graphs are the mathematically determined lines calculated for several $g(\alpha)$ functions, namely

(1) The Avrami–Erofeev (A_n); $kt = [-\ln(1 - \alpha)]^{1/n}$ where $n = 1, 3/2, 2, 3$ and 4.

(2) The Geometric Model (R_n); $kt = 1 - (1 - \alpha)^{1/n}$ for $n = 1$ and 2.

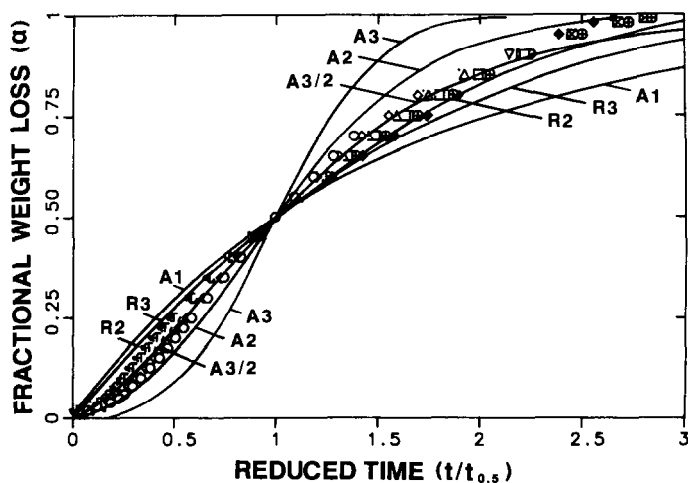


Fig. 9. Reduced time plots for the low isothermal temperature data, i.e.: 385 (\circ); 395 (\diamond); 399 (Δ); 404 (∇); 408 (\square); 414 (\boxtimes); 427 (\oplus); 427 (\boxtimes); and 433°C (\diamond).

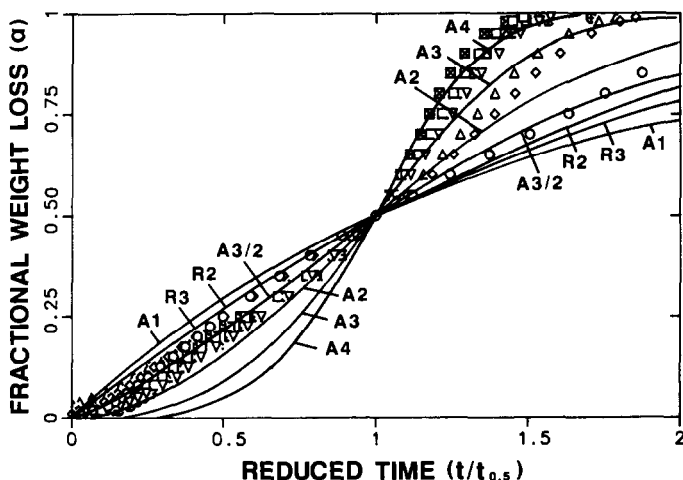


Fig. 10. Reduced time plots for the high isothermal temperature data, i.e.: 440 (○); 452 (◇); 460 (△); 469 (▽); 480 (□); 490 (◻); 499 (⊕); and 509°C (⊗).

For the low temperature data (Fig. 9), it would appear that the best fit is obtained with an Avrami-Erofeev equation with $n = 3/2$. When this value is employed to calculate the Arrhenius parameters, an E_a value of 101.8 ± 3.2 kJ mol⁻¹ is obtained. The kinetic significance of a fractional value for n once again suggests that the rate process is not simple. For the higher temperature data, an Avrami-Erofeev equation with $n = 3/2$ only fits the lower fractional weight-loss data. At higher fractional weight-loss values, the value of n required to fit the data increase with the isothermal temperature. The apparent activation energy calculated at these higher temperatures was found to be 177.1 ± 4.8 kJ mol⁻¹ (when n is assumed to be $3/2$). However it should be noted that the data in Fig. 10 clearly indicates that no simple mechanism is operating. Furthermore it is evident that several competing and consecutive reactions are occurring which are both temperature and conversion dependent.

CONCLUSION

From these isothermal weight-loss experiments in air it appears that the degradation of PEEK is a complex process involving many consecutive and competing reactions. Analysis of the data in terms of the Arrhenius activation energy enables some insight into the complexity of the decomposition reactions occurring. These values are summarized in Table 1. Based on these data, it may be tentatively suggested that the degradation of PEEK in air is dependent on both the rate of oxygen diffusion to the degrading polymer and the rate of volatilization of degraded fragments. At the lower isothermal temperatures, the degradation reactions are sufficiently slow that oxygen is able to diffuse to the reaction sites and cause oxidative processes to occur.

TABLE 1

Summary of the kinetic parameters determined for the isothermal degradation of PEEK in air

Method	Comments	E_a (kJ mol ⁻¹)	Log A (min ⁻¹)
Multiple heating rate method (previous study)	Slow heating rates $\alpha = 0.2$	107.1 ± 8.0	5.57 ± 0.61
	Fast heating rates $\alpha = 0.2$	235.0 ± 22.7	14.01 ± 1.47
First-order plot	$\alpha = 0.2-0.6$ Temperature 385-432 °C	132.9 ± 1.5	6.41 ± 0.07
Max. rate method	Low temperatures $\alpha \approx 0.2$	85.9 ± 5.1	2.96 ± 0.38
	High temperatures $\alpha \approx 0.2$	192.4 ± 14.9	10.63 ± 1.03
	$\alpha \approx 0.75$	250.0 ± 9.7	14.88 ± 0.68
Flynn method	Low temperatures $\alpha = 0.2$	115.4 ± 7.2	5.19 ± 0.53
	$\alpha = 0.8$	118.1 ± 10.6	5.09 ± 0.80
	High temperatures $\alpha = 0.2$	199.8 ± 8.8	11.03 ± 0.61
	$\alpha = 0.8$	236.5 ± 15.0	13.92 ± 1.05
Reduced time with Avrami-Erofeev $n = 3/2$	Low temperature	101.8 ± 3.2	4.22 ± 0.24
	High temperature	177.1 ± 4.8	9.66 ± 0.33

At the higher temperatures (greater than about 440 °C), the degradation processes are faster than the rate of oxygen diffusion to the reactive sites, and the partial pressure of oxygen available for the oxidative reactions is limiting. Consequently, the measured E_a values are correspondingly higher and are similar to those observed in nitrogen experiments.

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