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A kinetic analysis of the thermal-oxidative decomposition of expandable polystyrene

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Abstract–The kinetics of the thermal-oxidative decomposition of expandable polystyrene (EPS) was studied by a conventional thermogravimetric technique in various concentrations of oxygen from 0 to 21%. A kinetic model that accounts for the effects of oxygen concentration was proposed to describe the thermal-oxidative decomposition of EPS. The thermogravimetric analysis curve and its derivative have been analyzed by using differential and integral methods with modification of the Friedman and Coats-Redfern methods. The activation energy, the pre-exponential factor, and the reaction order for unreacted material and oxygen concentration have been determined. When oxygen was present, the activation energy was reduced significantly.

Key words: Kinetic Analysis, Thermal-Oxidative Decomposition, Expandable Polystyrene

INTRODUCTION

Thermogravimetric analysis (TGA) cannot be used to elucidate the clear mechanism of thermal decomposition of polymer. Nevertheless, the derivation of kinetic data in the study of polymer decomposition has received increasing attention in the last decade [Nam and Seferis, 1992; Jimenez et al., 1993; Lin et al., 1996; Oh et al., 1999; Park at al., 2000], along with much criticism regarding its use in the determination of activation energies, reaction orders, and pre-exponential factors.

It is known that complicated processes occur when polymers are subjected to heating or burning conditions. There is no intention in this work to describe the fundamental mechanisms of EPS decomposition. Rather, this work focuses on the measurement of apparent kinetic parameters useful for the engineering design of large chemical reactor. Thermogravimetric analysis is a relatively fast and exact method for the determination of kinetics of thermal decomposition. Conversion of data from weight loss curves given by the instrument into kinetic parameters, activation energy, reaction order, and pre-exponential factor is based on the utilization of classical laws of kinetics [Cooney et al., 1983; Salin and Seferis, 1993; Wu et al., 1993]. The rate of chemical reaction, $d\alpha/dt$, can be expressed as a function of the degree of conversion, α, using the general formulation:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{1}$$

where k is rate constant and $f(\alpha)$ is some function of the degree of conversion. In thermogravimetry, α can be expressed using initial (W_0), instantaneous (W) mass of the sample by:

$$\alpha = \frac{W_0 - W}{W_0} \tag{2}$$

However, Eq. (1) cannot account the effect of oxygen concentration for thermal-oxidative decomposition characteristics of polymeric materials. Therefore, in this work, a kinetic model that accounts for the effects of oxygen concentration was proposed to describe the thermal decomposition of expandable polystyrene (EPS). The thermogravimetric analysis curve and its derivative have been analyzed by using differential and integral methods with modification of the Friedman and Coats-Redfern method [Coats and Redfern, 1964; Friedman, 1964].

EXPERIMENTAL

EPS was obtained from LG Chemical Ltd., Korea and used without further treatment. The thermogravimetric analysis was performed with a Shimadzu TG model TGA-50. The experiments were carried out for various heating rates (10-50 °C/min.) in the presence of oxygen from 0% to 21% in nitrogen. The initial mass of the sample was 18-19 mg. The temperature of the instrument was controlled by a type-K chromel-alumel thermocouple wire placed 1-2 mm below the platinum crucible. Variation of the sample mass with reaction temperature was detected by a photoelectric element and weight-measuring circuits in the thermobalance. The signals were then transmitted to a personal computer through an analog-to-digital converter for subsequent data storage, analysis, and plotting.

KINETIC ANALYSIS

In general, the overall rate equation of conversion α for thermal

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decomposition is expressed in Arrhenius form as follows:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)(1-\alpha)^n \quad (3)$$

where A, E, T and R are the pre-exponential factor (1/min), the activation energy (J/mol), the temperature of reaction (K), and the gas constant (8.314 J/mol·K), respectively, and n denotes the overall reaction order with respect to unreacted material. However, though Eq. (3) gives a reliable estimation of kinetic parameters for thermal decomposition of a polymer, it cannot account for the effects of the concentration of oxygen. The kinetic model that accounts for the effects of oxygen concentration can be written as follows:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)(1-\alpha)^n(O_2)^m \quad (4)$$

where O_2 is the oxygen concentration in nitrogen, and m denotes the overall reaction order with respect to oxygen concentration. In this work, the differential and integral methods were employed to determine the kinetic parameters E, n, m and A from the TG data.

1. Differential Method

This method is based on the intercomparison of the rates of weight loss $d\alpha/dt$ for a given degree of conversion α determined by using different linear heating rates β. After taking logarithms of Eq. (4) we can obtain

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + n\ln(1-\alpha) + \ln[A\cdot(O_2)^m] \quad (5)$$

Using this equation it is possible to obtain values for E over a wide range of conversion from slope $-E/R$ by plotting $\ln(d\alpha/dt)$ against 1/T, because the second and third term on the right-hand side of Eq. (5) are constant for fixed O_2 and α.

In addition, the values of n and $\ln[A\cdot(O_2)^m]$ can be determined from a plot of E/RT_0 against $\ln(1-\alpha_0)$, where T_0 and α_0 are the temperature and the degree of conversion at the correctly chosen constant values of $\ln(d\alpha/dt)$. When oxygen is absent, m=0 and A is readily obtained. The next step is to obtain the value of lnA and m for various concentrations of oxygen. Rearrangement of $\ln[A\cdot(O_2)^m]$ gives the following:

$$\ln[A\cdot(O_2)^m] = \ln A + m\ln(O_2) \quad (6)$$

If oxygen is present, such that $m\neq 0$, then a plot of $\ln[A\cdot(O_2)^m]$ versus $\ln(O_2)$ yields a straight line of slope m and intercept lnA. This completes the evaluation of all the kinetic parameters.

2. Integral Method

In the differential technique, the relationship between $d\alpha/dt$ and T is utilized. However, in the integral method, the kinetic parameters are determined from the standard thermogravimetric analysis trace. If Eq. (4) is taken and a standard rate of heating $\beta = dT/dt$ is employed, it can be shown that

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}(O_2)^m\exp\left(\frac{-E}{RT}\right)dT \quad (7)$$

which on integrating and introducing the initial condition of $\alpha=0$ at $T=T_0$ the following expression is obtained:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}(O_2)^m\int_{T_0}^{T}\exp\left(\frac{-E}{RT}\right)dT \quad (8)$$

The integral approximation [Coat and Redfern, 1964] taken with this technique is to consider Eq. (8) when it can be shown that

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{1-(1-\alpha)^{1-n}}{1-n} \qquad \text{for } n\neq 1 \quad (9)$$

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = -\ln(1-\alpha) \qquad \text{for } n=1 \quad (10)$$

while

$$\frac{A}{\beta}(O_2)^m\int_{T_0}^{T}\exp\left(\frac{-E}{RT}\right)dT = \frac{ART^2}{\beta E}(O_2)^m\left(1-\frac{2RT}{E}\right)\exp\left(\frac{-E}{RT}\right) \quad (11)$$

After taking logarithms, the following two equations can be obtained:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}(O_2)^m\left(1-\frac{2RT}{E}\right)\right] + \frac{-E}{RT} \qquad \text{for } n\neq 1 \quad (12)$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}(O_2)^m\left(1-\frac{2RT}{E}\right)\right] + \frac{-E}{RT} \qquad \text{for } n=1 \quad (13)$$

Thus, plots of

$$Y = -\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \text{ vs. } \frac{1}{T} \qquad \text{for } n\neq 1 \quad (14)$$

and

$$Y = \ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] \text{ vs. } \frac{1}{T} \qquad \text{for } n=1 \quad (15)$$

result in straight lines with slope equal to $-E/R$ for fixed O_2, β and the correctly chosen values of n. Rearrangement of the first term on the right-hand side of Eqs. (12) and (13) gives

$$\ln\left[\frac{AR}{\beta E}(O_2)^m\left(1-\frac{2RT}{E}\right)\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] + m\ln(O_2) \quad (16)$$

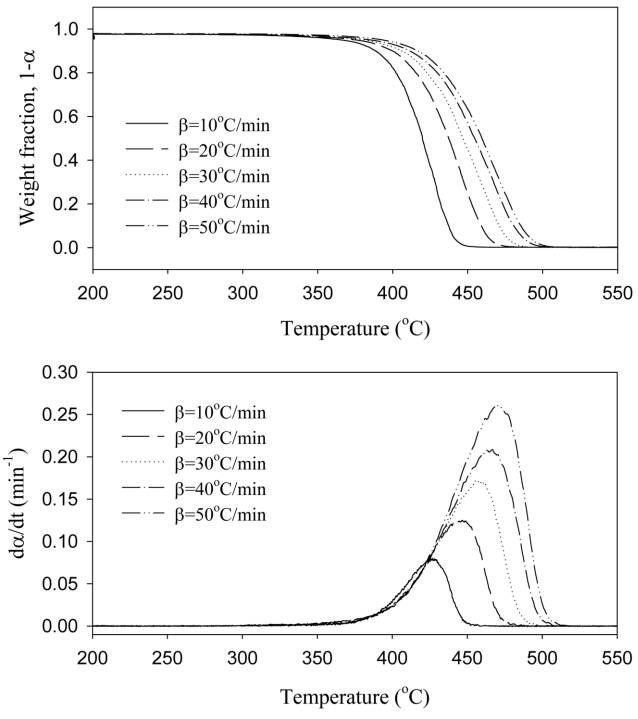

Fig. 1. TG and DTG curves of EPS for various heating rates in pure nitrogen.

The value of $\ln[AR/\beta E(O_2)^m(1-2RT/E)]$ can be obtained from the intercept of the plot of Eqs. (14) and (15). For various concentrations of oxygen at given β, the plot of this value against $\ln(O_2)$ yields a straight line with slope m. And A can be easily obtained from the intercept of this plot because $(1-2RT/E)\approx 1$.

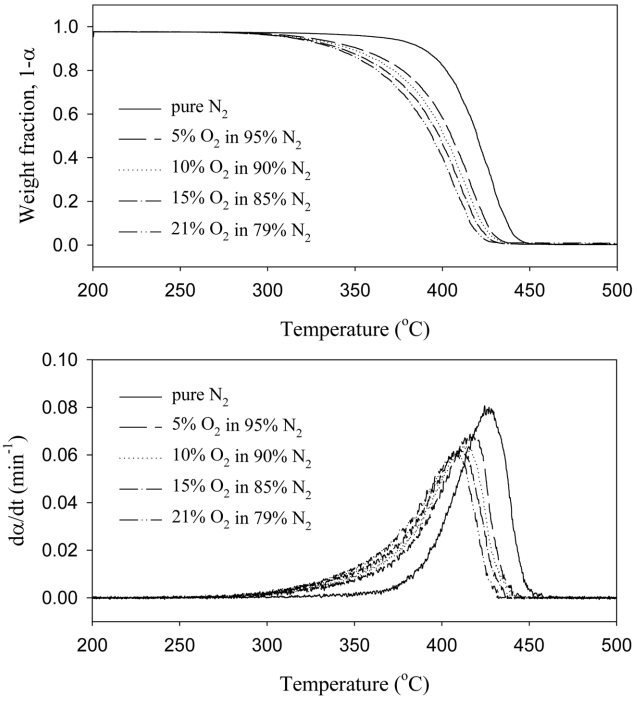

Fig. 2. TG and DTG curves of EPS for various concentrations of oxygen at a heating rate of 10 °C/min.

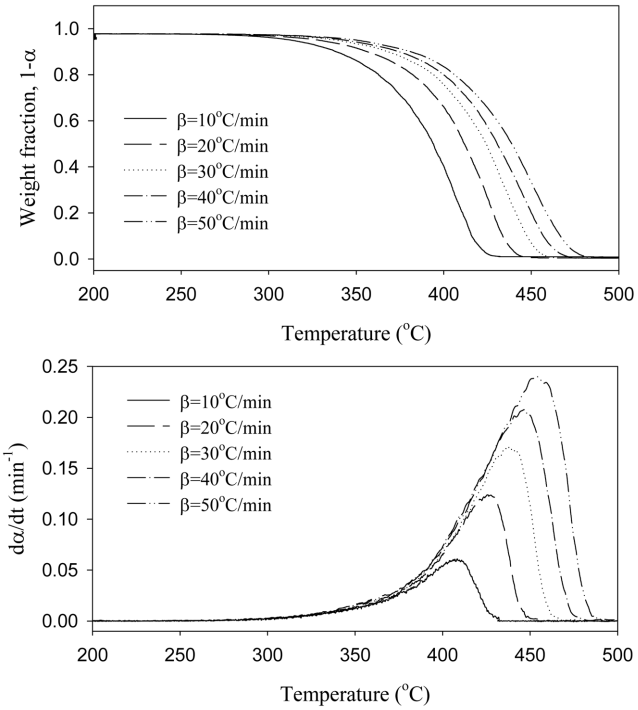

Fig. 3. TG and DTG curves EPS for various heating rates in 21% O_2.

RESULTS AND DISCUSSION

It is known that when polymers are subjected to heating or burning conditions, complicated processes occur, such as random-chain scission, end-chain scission, chain stripping, cross-linking, and coke formation. There is no intention in this work to describe the fundamental chemical mechanisms of EPS decomposition or to analyze its product yields. Rather, this paper focuses on the measurement of apparent kinetic parameters useful for thermal-oxidative decom-

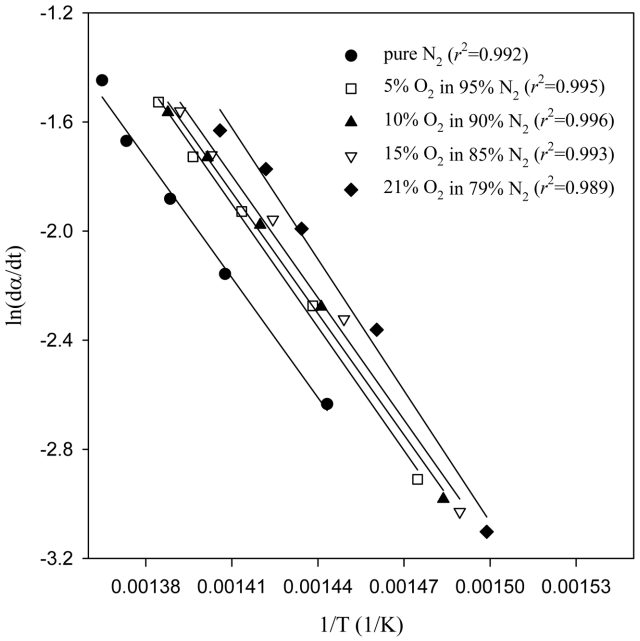

Fig. 4. Application of differential method to obtain the activation energy for α=0.5.

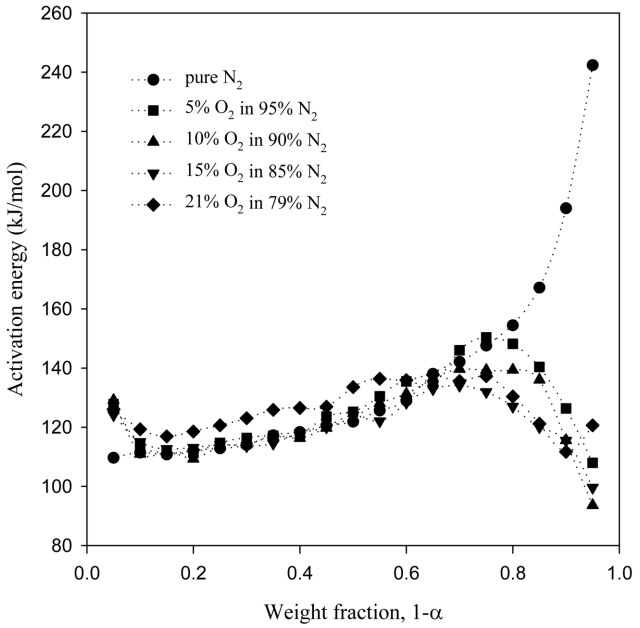

Fig. 5. Activation energy over a range of conversion determined by differential method.

position of EPS. Fig. 1 shows the variations of the TG curves and their first derivative (DTG curves) with respect to temperature for various heating rates in pure nitrogen. It is seen from Fig. 1 that each TG curve is smooth with one inflection point during reaction. There is just one peak in the DTG curve for each heating rate, so that only one kind of reaction occurs in pure nitrogen. The reaction shifts to a high temperature and the height of the DTG peak increases with the heating rate. Typical TG and DTG curves for various concentration of oxygen for a heating rate of 10 °C/min are illustrated in Fig. 2. From this figure, though oxygen present, it is also found that one kind of reaction occurs because there is just one peak in the DTG curve for each concentration. The reaction shifts to a lower temperature and the height of the DTG peak decreases with the concentration of oxygen. As the oxygen concentration is increased, the reaction becomes more sluggish. Fig. 3 shows the TG and DTG curves of EPS for various heating rates in 21% O_2. From this figure, it is shown that the reaction shifts to a high temperature and the height of the DTG peak increases with the heating rate like those of pure nitrogen.

Fig. 4 shows the typical plots of ln(dα/dt) against 1/T of the dif-

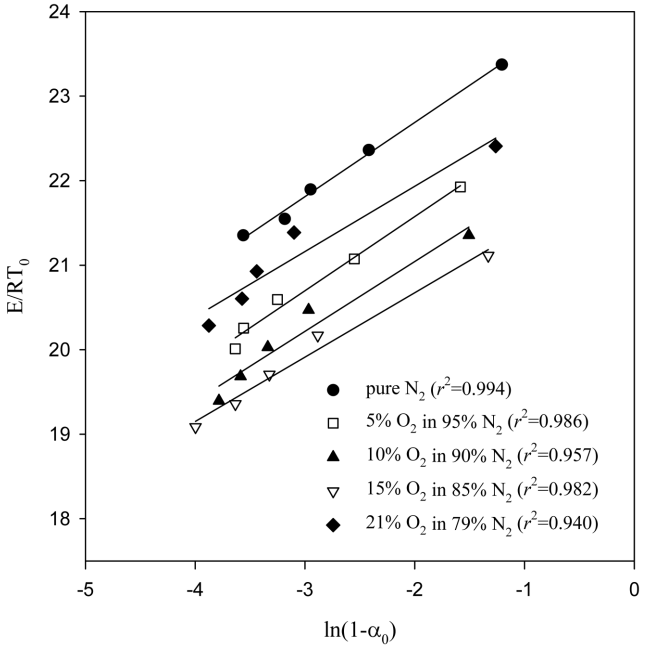

Fig. 6. Plot of E/TR_0 against $\ln(1-\alpha_0)$ of differential method to obtain the reaction order n.

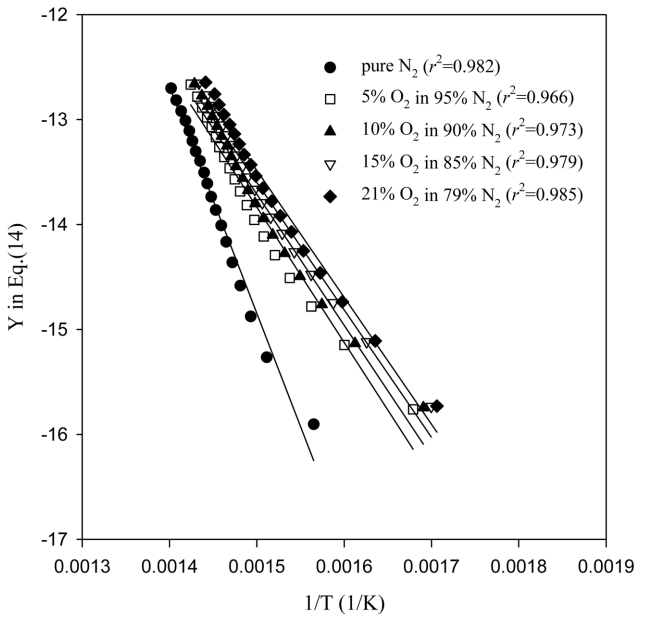

Fig. 8. Application of integral method to obtain the activation energy at a heating rate of 10 °C/min of n=0.5.

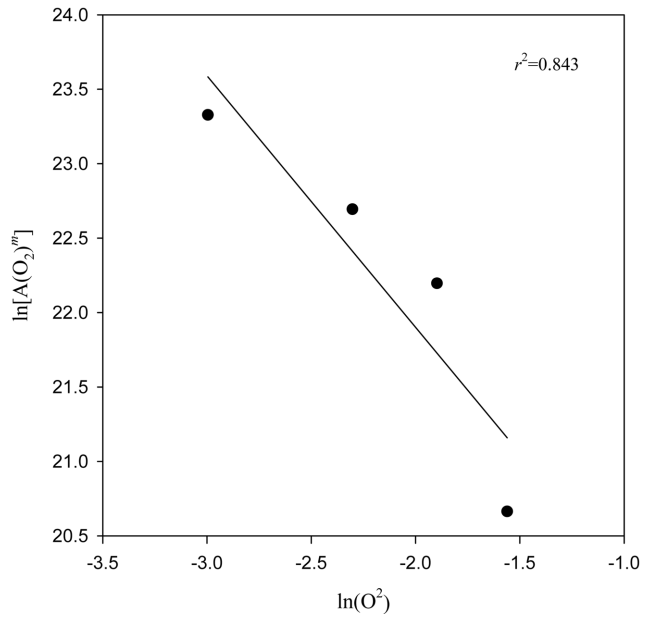

Fig. 7. Plot of $\ln[A(O_2)^m]$ against $\ln(O_2)$ of differential method to obtain the reaction order m.

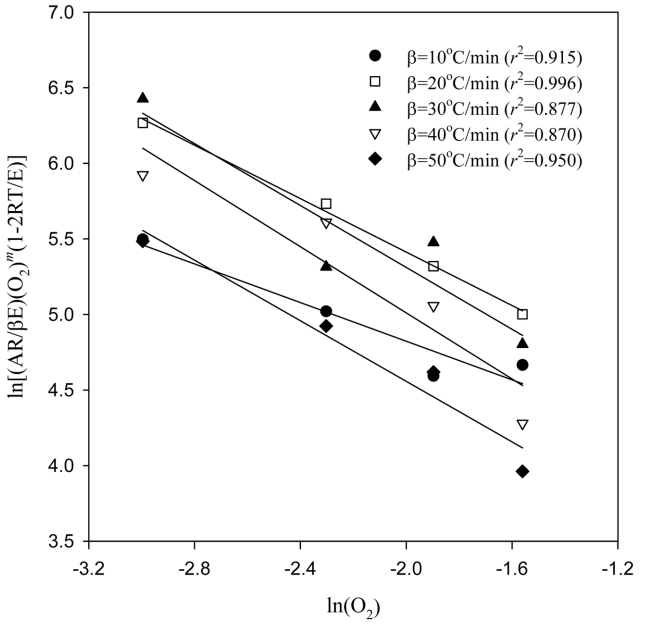

Fig. 9. Application of integral method to obtain the reaction order m for various heating rates.

ferential method to obtain the activation energy for α=0.5. In Fig. 4, r^2 denotes the correlation coefficient for linear regression analysis. The activation energies of the thermal-oxidative decomposition of EPS can be easily obtained from the slope −E/R of the straight lines of Fig. 4, and these values over a wide range of conversion for each concentration of oxygen are shown in Fig. 5. Fig. 6 shows the plots of E/TR_o against $\ln(1-a_0)$ to obtain the value of the reaction order n with respect to unreacted material. Cooney et al. [1983] used the temperature and the degree of conversion at which $\ln(d\alpha/dt)=0$, i.e. $d\alpha/dt=1$, for T_0 and α_0. However, in this work it is seen from Figs. 1, 2 and 3 that the decomposition rate, $d\alpha/dt$ of 1 cannot be obtained. Therefore, the temperature and the degree of conversion at the adequately chosen constant values of $\ln(d\alpha/dt)$ were used in this work. The reaction order n can be obtained from the slope of each plot. When oxygen is absent, m=0 and lnA is readily obtained from the intercept of Y-axis minus $\ln(d\alpha/dt)$. Fig. 6 gives the reaction order n of 0.88 and the pre-exponential factor of 3.23×10^9 in pure nitrogen, respectively. The plot of $\ln[A\cdot(O_2)^m]$ against $\ln(O_2)$ to obtain the value of the reaction order m with respect to oxygen concentration and the pre-exponential factor A is shown in Fig. 7. From Fig. 7, we can obtain the reaction order m of −1.69 and the pre-exponential factor of 1.11×10^8, respectively.

Fig. 8 shows the application of the integral method to the experimental data obtained at a heating rate of 10 °C/min. This method has been applied to TG data and the best fit values for each heating rate determined employing reaction order values n of 0, 0.5, 1.0, 1.5 and 2.0. The best-fit values were obtained by using 0.5 for pure nitrogen and the presence of oxygen. The application of the integral method to obtain the reaction order with respect to oxygen concentration is shown in Fig. 9. From Fig. 9, the reaction orders m of

Table 1. Kinetic parameters of the thermal-oxidative decomposition of EPS

Method	Carrier gas	Reaction order n	Reaction order m	Activation energy E (KJ/mol)	Pre-exponential factor A (1/min)
Differential	pure N_2	0.88	-	136.26	3.23×10^9
method	5% O_2 in 95% N_2	0.88	−1.69	126.25	1.11×10^8
	10% O_2 in 90% N_2	0.82	−1.69	122.33	1.11×10^8
	15% O_2 in 85% N_2	0.76	−1.69	120.02	1.11×10^8
	21% O_2 in 79% N_2	0.77	−1.69	126.52	1.11×10^8
Integral	pure N_2				
method	10 °C/min	0.5	-	179.11	2.35×10^{14}
	20 °C/min	0.5	-	156.13	1.91×10^{12}
	30 °C/min	0.5	-	146.23	2.38×10^{11}
	40 °C/min	0.5	-	139.98	6.33×10^{10}
	50 °C/min	0.5	-	145.96	1.54×10^{11}
	5% O_2 in 95% N_2				
	10 °C/min	0.5	−0.64	107.15	1.26×10^8
	20 °C/min	0.5	−0.88	114.91	1.55×10^8
	30 °C/min	0.5	−1.02	118.01	1.12×10^8
	40 °C/min	0.5	−1.09	116.66	7.40×10^7
	50 °C/min	0.5	−1.00	115.13	5.75×10^7
	10% O_2 in 90% N_2				
	10 °C/min	0.5	−0.64	103.83	1.22×10^8
	20 °C/min	0.5	−0.88	111.32	1.50×10^8
	30 °C/min	0.5	−1.02	110.81	1.06×10^8
	40 °C/min	0.5	−1.09	114.24	7.24×10^7
	50 °C/min	0.5	−1.00	111.41	5.57×10^7
	15% O_2 in 85% N_2				
	10 °C/min	0.5	−0.64	100.84	1.19×10^8
	20 °C/min	0.5	−0.88	108.27	1.46×10^8
	30 °C/min	0.5	−1.02	111.36	1.06×10^8
	40 °C/min	0.5	−1.09	110.71	7.02×10^7
	50 °C/min	0.5	−1.00	109.14	5.45×10^7
	21% O_2 in 79% N_2				
	10 °C/min	0.5	−0.64	100.60	1.18×10^8
	20 °C/min	0.5	−0.88	105.56	1.42×10^8
	30 °C/min	0.5	−1.02	106.50	1.01×10^8
	40 °C/min	0.5	−1.09	104.72	6.64×10^7
	50 °C/min	0.5	−1.00	104.17	5.21×10^7

−0.64, −0.88, −1.02, −1.09, and −1.00 for each heating rate are obtained.

For comparison, the results from the differential and integral methods are summarized in Table 1. In the differential method, the overall reaction orders n of 0.88, 0.88, 0.82, 0.76 and 0.77 for each concentration of oxygen are obtained. And the reaction order n slightly decreases with increasing oxygen concentration. It is also found that the activation energy decreases with increasing oxygen concentration. In the integral method, the activation energy also decreases for each heating rate as the concentration of oxygen increases. However, as shown in Table 1, there is tremendous variation in the kinetic parameters obtained from the integral method depending upon heating rates. This observation clearly indicates the problems in the selection of kinetic values to solve the thermal-oxidative decomposition of EPS. Because of these variations with various heating rates in the calculated kinetic values, it is felt that the differential method using data collected at various heating rates is better for kinetic analysis of the thermal-oxidative decomposition of EPS than the integral method using the single heating rate experiments.

CONCLUSIONS

In this work, a kinetic model that accounts for the effects of oxygen concentration was proposed to describe the thermal-oxidation decomposition of EPS. Thermogravimetric analysis curves and derivatives were analyzed by using the differential and integral methods. The activation energy, the pre-exponential factor, and the reaction orders for unreacted material and oxygen concentration were determined. There is tremendous variation in the kinetic parameters obtained from the integral method depending upon heating rates. This observation clearly indicates the problems in the selection of kinetic values to solve the thermal-oxidative decomposition of EPS. Thus, it is felt that the differential method using data collected at various heating rates is better for kinetic analysis of the thermal decomposition of EPS than the integral method using single heating rate experiments. And when oxygen was present, the activation energy was reduced significantly.

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