Kinetic Analysis of Thermal Decomposition of Polymer Using a Dynamic Model

Jin Woo Park, Sea Cheon Oh*, Hae Pyeong Lee, Hee Taik Kim[†] and Kyong Ok Yoo

Department of Chemical Engineering, Hanyang University, 17 Haengdang-dong,
Sungdong-gu, Seoul 133-791, Korea
*Department of Environmental Engineering, Chonan National Technical College,
275 Budae-dong, Chonan, Chungnam 330-717, Korea
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Abstract−The objective of this work was to develop a kinetic analysis method by using a dynamic model that accounts for the thermal decomposition behavior of polymers with the variation of the conversion. The proposed method was applied to predict the thermal decomposition of polyethylene. The kinetic analysis was studied by conventional thermogravimetric technique with various heating rates in nitrogen atmosphere. To verify the appropriateness of the proposed method, the results from this work were compared with those of various analytical methods and the literature. The TG data were also compared with the values calculated by using the kinetic parameters from the dynamic method. It was found that the dynamic method gave a reliable value of kinetic parameters, and the activation energy and the reaction order of thermal decomposition of high-density polyethylene were larger than those of low-density and linear low-density polyethylene.

Key words: Thermal Decomposition, Kinetic Analysis, Dynamic Method, Polyethylene

INTRODUCTION

Thermogravimetric analysis (TGA) cannot be used to elucidate clearly the mechanism of thermal decomposition of polymer. Nevertheless, the derivation of kinetic data in the study of polymer decomposition using TGA has received increasing attention in the last decade [Jimenez et al., 1993; Salin et al., 1993; Albano and Freitas, 1998], because it gives reliable information on the activation energy, the overall reaction order and the preexponential factor.

Recently, much effort has been devoted to developing a new mathematical method for kinetic analysis using TGA [Kim, 1991; Nam and Seferis, 1992; Chen et al., 1997]. However, most of it involves some degree of approximations and simplications. In general, the approaches calculate a set of kinetic constants for each heating rate and sometimes set the reaction order to unity. Moreover, the kinetic analysis methods using TGA mostly cannot yield information on the thermal decomposition behavior of polymers at a desired time. Denq et al. [1997] developed a parallel competitive reaction model based on the assumption that the rate constant at any weight loss fraction is approximately equal to the rate constant of its neighboring weight loss fraction, which accounts for the type of bond scission and the state of a scission of the polymeric chain at any time. Oh et al. [1999] proposed the numerical method to solve the thermal decomposition rate equation based on the kinetic model of Denq et al.

In this work, the method of kinetic analysis using a dynamic model that accounts for the continuous thermal decomposition behavior of polymer at any time was proposed. The proposed method was applied to predict the thermal decomposition of high-den-

sity polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). In addition, various analytical methods reported in the literature [Coats and Redfern, 1964; Friedman, 1964; Ozawa, 1965; Cooney et al., 1983; Kim, 1995; Oh et al., 1999] were used in the comparative work for the kinetic analysis results obtained from this work. To verify the appropriateness of the proposed method, the results from this work were compared with those of the literature [Jellinek, 1950; Urzendowski and Guenther, 1971; Mucha, 1976; Wu et al., 1993; Westerhout et al., 1997]. The TG data were also compared with the values calculated by using the kinetic parameters from the dynamic method.

EXPERIMENTAL

The kinetics of thermal decomposition of polyethylene for non-isothermal conditions have been investigated thermogravimetrically. The thermogravimetric analysis was performed with a Shimadzu TG model TGA-50. The HDPE (TR480-BL), LDPE (LD01A), and LLDPE (LL04) from commercial grade (from Daelim Co., Ltd., Korea), whose densities are 0.954, 0.922, and 0.923 g/cm^2 and melt indexes (M.I.) 0.1, 0.3, and 1.0 g/10 cm, respectively, were studied at various heating rates between 10±0.1 and 50±0.5 K/min. The initial mass of the sample was 24.0±1 mg. The thermobalance measured mass to 0.001 mg, with an accuracy of ±1%. The experiments were carried out in a nitrogen atmosphere with a flow rate of 25 ml/min and a purge time of 20 min.

KINETIC ANALYSIS

1. Development of Dynamic Method
1-1. Kinetic Model
In the kinetics of thermal decomposition of polymer using TGA,

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[†]To whom correspondence should be addressed.
E-mail: khtaik@email.hanyang.ac.kr

it is usual to assume that the rate of decomposition $d\alpha/dt$ is proportional to the concentration of material which has to react. Therefore, by power law model it can be expressed as

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \qquad (1)$$

where K, n and α are the rate constant (1/min), the overall reaction order and the weight loss fraction, respectively. The temperature dependence of the rate constant K may be described by the Arrhenius expression as follows:

$$K = A \exp(-E/RT) \qquad (2)$$

Combining Eqs. (1) and (2), the overall decomposition rate of polymer is given by Eq. (3).

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

where A, E, T and R are the preexponential factor (1/min), the apparent activation energy (J/mol), the reaction temperature (K), and the gas constant (8.314 J/mol · K), respectively. However, A is not strictly constant but depends, based on collision theory [Turn, 1994], on $T^{0.5}$. Therefore, if the basic Eq. (3) is taken and a heating rate $\beta = dT/dt$ (K/min) is employed, it can be shown that

$$\frac{d\alpha}{dt} = \frac{A_0}{\beta}T^{1/2}\exp(-E/RT)(1-\alpha)^n \qquad (4)$$

If the temperature rises with a constant heating rate β, and the kinetic parameter at any weight loss fraction is approximately equal to that of its neighboring weight loss fraction, then by differentiation of Eq. (4),

$$\frac{d^2\alpha}{dT^2} = \frac{1}{\beta}\left(\frac{d\alpha}{dt}\right)\left[n(1-\alpha)^{-1}\left(-\frac{d\alpha}{dT}\right) + \frac{E}{RT^2} + \frac{1}{2}T^{-1}\right] \qquad (5)$$

Eqs. (4) and (5) give the following expressions for n and E.

$$n = \frac{\left[\beta\left(\frac{d^2\alpha}{dT^2}\right)\left(\frac{d\alpha}{dt}\right) - \frac{E}{RT^2} - \frac{1}{2}T^{-1}\right](1-\alpha)}{\left(-\frac{d\alpha}{dT}\right)} \qquad (6)$$

$$E = -RT \ln\left[\frac{\left(\frac{d\alpha}{dt}\right)}{A_0 T^{1/2}(1-\alpha)^n}\right] \qquad (7)$$

If the factor A_0 is determined, the n and E values at any weight loss fraction can be obtained from Eqs. (6) and (7) by numerical method. The average reaction order and activation energy can be calculated from Eqs. (8) and (9) as follows:

$$n_{ave} = \frac{\sum_{i=1}^{N} n_i(\alpha_i - \alpha_{i-1})}{\alpha_f} \qquad (8)$$

$$E_{ave} = \frac{\sum_{i=1}^{N} E_i(\alpha_i - \alpha_{i-1})}{\alpha_f} \qquad (9)$$

where α_f is the final weight loss fraction and N denotes the

total number of TG data.

1-2. Determination of Factor A_0

The maximum decomposition rate occurs at a temperature T_m defined by setting $d^2\alpha/dT^2$ to zero. Therefore, Eq. (5) at maximum rate gives

$$\frac{A_0}{\beta}T_m^{1/2}\exp(-E/RT_m)n(1-\alpha_m)^{n-1} = \frac{E}{RT_m^2} + \frac{1}{2}T_m^{-1} \qquad (10)$$

where α_m is the weight loss fraction at the temperature T_m. Using Murray and White's expression [1955], integration of Eq. (4) results in

$$\frac{1}{n-1}\left[\frac{1}{(1-\alpha)^{n-1}} - 1\right] \cong \frac{A_0 R}{\beta E}T^{5/2}\left[1 - \frac{5RT}{2E}\right]\exp\left(-\frac{E}{RT}\right) \qquad (11)$$

If Eq. (10) is combined with Eq. (11), the following result is obtained [Kissinger, 1957]:

$$n(1-\alpha_m)^{n-1} = n - (n-1)\left(1 + \frac{RT_m}{2E}\right) \approx 1 \qquad (12)$$

Eq. (12) does not contain the heating rate β except as T_m varies with heating rate. The product $n(1-\alpha_m)^{n-1}$ is not only independent of β, but is nearly equal to unity. By substituting this value in Eq. (10) and taking the logarithm, one obtains

$$\ln \beta = \ln A_0 + \frac{3}{2}\ln T_m - \ln\left(\frac{E}{RT_m} + \frac{1}{2}\right) - \frac{E}{RT_m} \qquad (13)$$

In Eq. (13), $\ln(E/RT_m + 1/2)$ is very small as compared with $\ln A_0 + 3/2\ln T_m$. Thus, a plot of $\ln \beta$ against $1/T_m$ will give a straight line with slope $-E/R$ from which the activation energy E at maximum rate can be calculated, and $\ln A_0$ can be calculated from T_m and the intercept of the Y axis.

2. Differential Methods

2-1. Freeman-Carroll Method [Cooney et al., 1983]

This technique involves taking the basic Eq. (3) in the logarithmic form and utilizing the rates of weight loss at different temperature as follows:

$$\Delta \ln\left(\frac{d\alpha}{dt}\right) = n\Delta \ln(1-\alpha) - \left(\frac{E}{R}\right)\Delta\left(\frac{1}{T}\right) \qquad (14)$$

In this work, in order to remove the discontinuities in the treatment of data, from Eq. (14) we have

$$\frac{\Delta \ln(d\alpha/dt)}{\Delta(1/T)} = \frac{n\Delta \ln(1-\alpha)}{\Delta(1/T)} - \frac{E}{R} \qquad (15)$$

To evaluate the constants in Eq. (15), $\dfrac{\Delta \ln(d\alpha/dt)}{\Delta(1/T)}$ is plotted against $\dfrac{\Delta \ln(1-\alpha)}{\Delta(1/T)}$.

2-2. Flynn-Wall Method [Kim, 1995]

From Eq. (3), it can be shown that

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-E/RT)(1-\alpha)^n \qquad (16)$$

Since the maximum rate occurs when $d^2\alpha/dT^2=0$, differentiation of Eq. (16) with respect to T and setting the resulting expression to zero gives

$$\frac{E}{nRT_m^2(1-\alpha_m)^{n-1}} = \frac{A}{\beta}\exp\left(-\frac{E}{RT_m}\right) \tag{17}$$

where H_m is the peak height of DTG curve at peak temperature. Substituting Eq. (17) into Eq. (16) yields the expression for the reaction order as follows:

$$n = \frac{E(1-\alpha_m)}{RT_m^2 H_m} \tag{18}$$

Also, the activation energy can be calculated from two peak temperatures at different heating rates as in the following:

$$
\begin{aligned}
E &= R\left(\frac{T_{m1}T_{m2}}{T_{m1}-T_{m2}}\right)\ln\left\{\left(\frac{\beta_1}{\beta_2}\right)\left(\frac{1-\alpha_{m2}}{1-\alpha_{m1}}\right)^{n-1}\left(\frac{T_{m2}}{T_{m1}}\right)^2\right\} \\
&\approx R\left(\frac{T_{m1}T_{m2}}{T_{m1}-T_{m2}}\right)\ln\left\{\left(\frac{\beta_1}{\beta_2}\right)\left(\frac{T_{m2}}{T_{m1}}\right)^2\right\}
\end{aligned}
\tag{19}
$$

where subscripts 1 and 2 refer to different heating rates. Therefore, the activation energy and the reaction order can be obtained from Eq. (18) and (19).

2-3. Friedman Method [Friedman, 1964]

This method utilizes the following logarithmic differential equation derived from Eq. (3).

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\{A(1-\alpha)^n\} - \frac{E}{RT} \tag{20}$$

For fixed α, the first term on the right-hand side of Eq. (20) is constant. Thus, 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 $1/T$. Rearrangement of the first term on the right-hand side of Eq. (20) gives

$$\ln\{A(1-\alpha)^n\} = \ln A + n\ln(1-\alpha) \tag{21}$$

The next step is to obtain the value of $\ln\{A(1-\alpha)^n\}$ for various heating rates at a given α and plot this value against $\ln(1-\alpha)$ to hopefully yield a straight line with slope n and intercept lnA.

3. Integral Method

3-1. Coats-Redfern Method [Coats and Redfern, 1964]

After taking the integral approximation and logarithm of Eq. (16), the following equations can be obtained:

$$\ln\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \ln\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right) + \frac{-E}{RT}, \quad \text{for } n\neq1 \tag{22}$$

and

$$\ln\left\{\frac{-\ln(1-\alpha)}{T^2}\right\} = \ln\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right) + \frac{-E}{RT}, \quad \text{for } n=1 \tag{23}$$

Thus plot of

$$Y = -\ln\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} \text{vs.} \frac{1}{T}, \quad \text{for } n\neq1 \tag{24}$$

$$Y = -\ln\left\{\frac{-\ln(1-\alpha)}{T^2}\right\} \text{vs.} \frac{1}{T}, \quad \text{for } n=1 \tag{25}$$

results in straight lines with slopes equal to $-E/R$ for the correctly chosen values of n.

3-2. Ozawa Method [Ozawa, 1965]

The integrated expression of Eq. (16) is obtained as

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_{T_0}^T \exp\left(\frac{-E}{RT}\right)dT \tag{26}$$

The variables given in Eq. (26) may be separated and integrated to give in logarithm form as the following:

$$\log F(\alpha) = \log\left(\frac{AE}{R}\right) - \log\beta + \log p\left(\frac{E}{RT}\right) \tag{27}$$

Using Doyle's approximation for the integral which allows for $E/RT>20$, then $\log p(E/RT)$ may be expressed as

$$\log p(E/RT) = -2.315 - 0.4567E/RT \tag{28}$$

Eq. (27) now becomes

$$\log F(\alpha) \approx \log\left(\frac{AE}{R}\right) - \log\beta - 2.315 - 0.4567\left(\frac{E}{RT}\right) \tag{29}$$

The apparent activation energy E can therefore be obtained from a plot of $\log\beta$ against $1/T$, for fixed α the slope of such a line is given by $-0.4567E/R$.

4. Parallel Competitive Reaction Model [Oh et al., 1999]

The thermal decomposition rate equation that accounts for each of three reaction orders can be written as

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = K_0 + K_1(1-\alpha) + K_2(1-\alpha)^2 \tag{30}$$

where K_0, K_1 and K_2 are the summations of rate constants (1/min) that represent the zero-order, first-order, and second-order reactions, respectively. Oh et al. [1999] used the optimization technique to estimate these rate constants. The optimization problem can be formulated by the form

$$\text{Minimize } f(\mathbf{K}) = (\alpha_e - \alpha_c(\mathbf{K}))^2 \tag{31a}$$

$$\text{Subject to } K_i \geq 0; i=0, 1, 2 \tag{31b}$$

where $\mathbf{K}$ denotes the rate constant vector which consists of K_0, K_1 and K_2. In Eq. (31a) α_e is the weight loss fraction obtained by thermogravimetric analysis and α_c is the weight loss fraction calculated by the 4th Runge-Kutta integration method from Eq. (30) and $\mathbf{K}$. The average reaction order and rate constant can be obtained from Eqs. (32) and (33) as the following:

$$n_{ave} = \frac{\sum_{i=1}^N\left(\sum_{n=0}^2 nP_n\right)(\alpha_i - \alpha_{i-1})}{\alpha_f} \tag{32}$$

$$K_{ave} = \frac{\beta\left(\frac{d\alpha}{dT}\right)}{(1-\alpha)^{n_{ave}}} \tag{33}$$

In Eq. (32) P_0, P_1 and P_2 are the relative contributions to the entire thermal decomposition rate for the zero-order, first-order and second-order reactions, respectively, and calculated by Eq. (34) as the following:

$$P_n = \frac{K_n(1-\alpha)^n}{\sum_{n=0}^2 K_n(1-\alpha)^n} \tag{34}$$

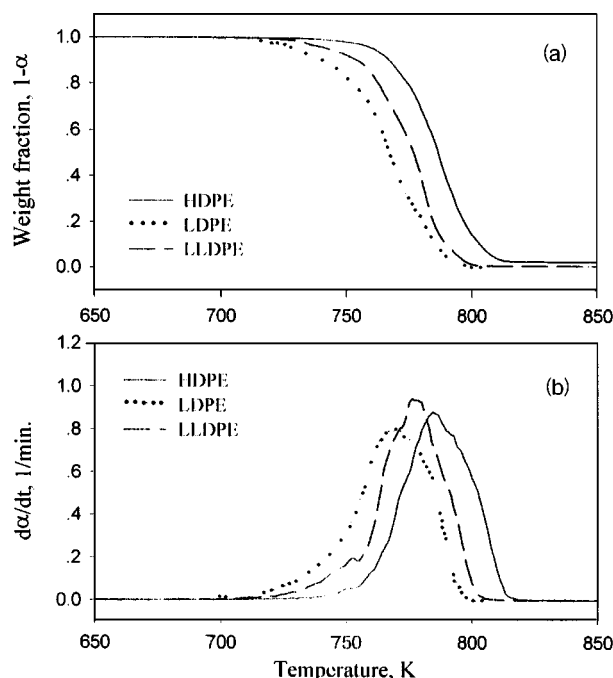The activation energy can be calculated by using the Arrhenius

Fig. 1. Typical TG (a) and DTG (b) curves for the polyethylene samples in N_2 atmosphere at heating rate of 30 K/min.

equation from K_{ave} and absolute temperature.

RESULTS AND DISCUSSION

Fig. 1 shows the typical TG and DTG curves of HDPE, LDPE and LLDPE in nitrogen atmosphere at a heating rate of 30 K/min. It is seen from this figure that the thermal decomposition of LDPE took place most rapidly, and the reaction shifted to a low temperature with the extent of branching, as HDPE chains are not branched at all and LDPE, LLDPE chains have some branches. And each of the TG curves are smooth with one inflection point during
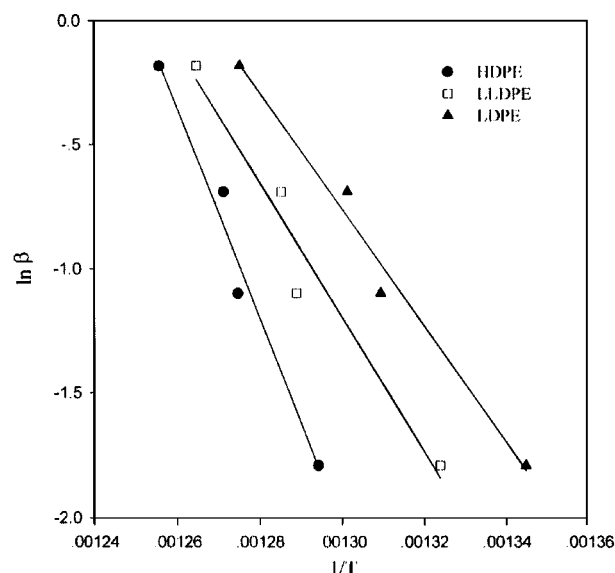

Fig. 2. Plot of 1/T vs. ln β for the determination of factor, A_0.

Table 1. Determination of factor A_0 in Eq. (4)

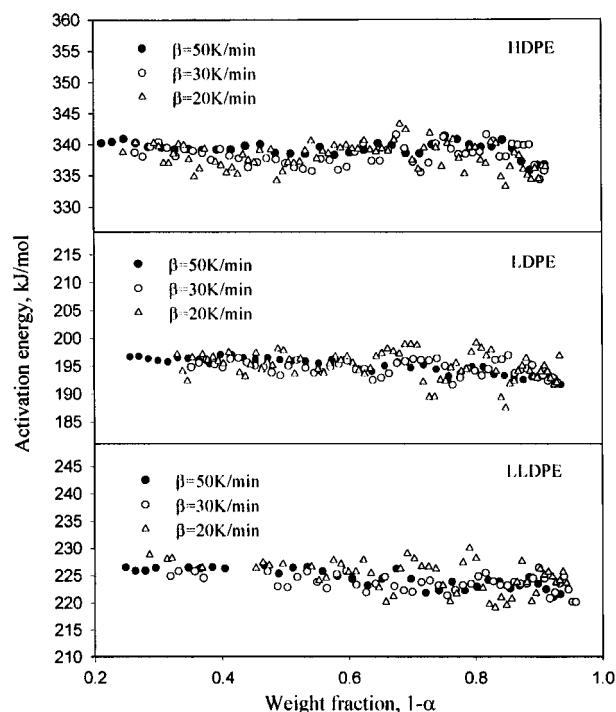| Material	Factor, A_0		
	β : 20 K/min	β : 30 K/min	β : 50 K/min
HDPE	3.1×10^{19}	3.2×10^{19}	3.1×10^{19}
LDPE	1.4×10^{10}	1.4×10^{10}	1.3×10^{10}
LLDPE	1.1×10^{12}	1.1×10^{12}	1.1×10^{12}

Fig. 3. Activation energy upon weight loss fraction for the thermal decomposition of polyethylene.

reaction. There is just one peak in the DTG curve for each polyethylene, so that only one kind of reaction occurs in pure nitrogen [Chen et al., 1997]. Fig. 2 shows the plot of $1/T_m$ against ln β to calculate the factor A_0 in Eq. (13). The plots on this figure result in straight line with slopes equal to $-E/R$, thus the activation energy E at maximum decomposition rate can be easily obtained. The factor A_0 can be calculated from T_m and the intercept of the Y axis. The results are summarized in Table 1. The activation energies upon weight loss fraction obtained from this work are shown in Fig. 3. In this work, Eqs. (6) and (7) could not give reasonable results for thermal decomposition at a heating rate of 10 K/min because TG data were biased by noise where the thermal decomposition rate was slow. As can be seen, the activation energies for the thermal decomposition of polyethylene were little affected by heating rates. Also, the dynamic method gave apparent activation energies of 333-343 kJ/mol, 188-199 kJ/mol and 219-230 kJ/mol for HDPE, LDPE and LLDPE, respectively. Fig. 4 shows the decomposition reaction order upon weight loss fraction. As shown in this figure, the overall reaction order was also little affected by heating rates. The average activation energy and reaction order calculated from Eqs. (8) and (9) are summarized in Table 2. Murty et al. [1998] reported that the difference of thermal decomposition for HDPE, LDPE and LLDPE could be due
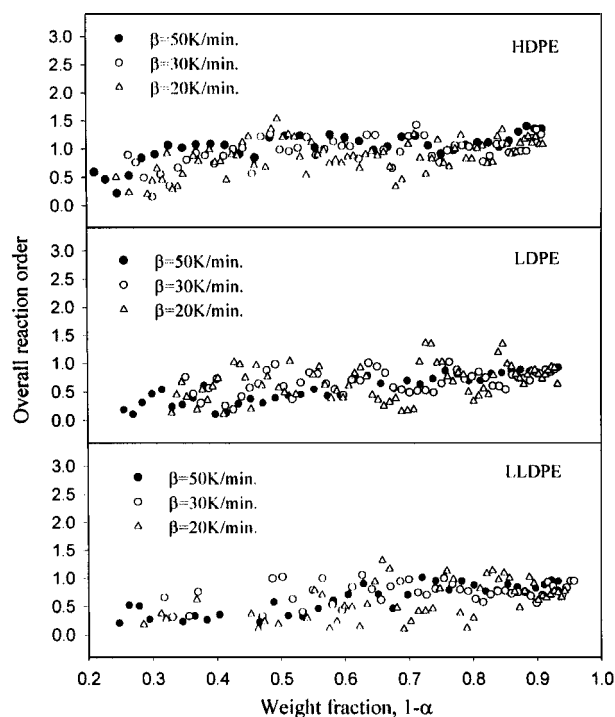
Fig. 4. Overall reaction order upon weight loss fraction for the thermal decomposition of polyethylene.

Table 2. Kinetic parameters determined by dynamic method

Material	Heating rate, β (K/min)	Average reaction order, n	Average activation energy, E (kJ/mol)
HDPE	20	0.98 (0.28)	338
	30	0.93 (0.24)	338
	50	0.96 (0.30)	338
LDPE	20	0.64 (0.24)	196
	30	0.54 (0.19)	196
	50	0.45 (0.30)	196
LLDPE	20	0.67 (0.26)	227
	30	0.60 (0.19)	225
	50	0.47 (0.33)	225

The values in the parentheses are the standard deviations.

to the differences in their branching. Table 2 indicates that branching has a clear influence on the kinetic parameters. The activation energy increases in the following order: HDPE>LLDPE>LDPE. Also the reaction order of HDPE is the largest, which implies that the reaction order increases with the extent of branching. According to Denq et al. [1997], the thermal decomposition by zero-order reaction indicates the weight loss by monomer scission from the polymer chain end and small molecule scission from a side chain. The thermal decomposition by first-order indicates the weight loss by the random scission of a main chain, and thermal decomposition by the second-order reaction indicates the weight loss related to the intermolecular transfer and scission. Thus, we think that the reaction order of the thermal decomposition of LDPE and LLDPE having some branches is lower than HDPE. Fig. 5 shows the TG data and the values calculated by using 4th Runge-Kutta numerical integration to verify the performance of the proposed
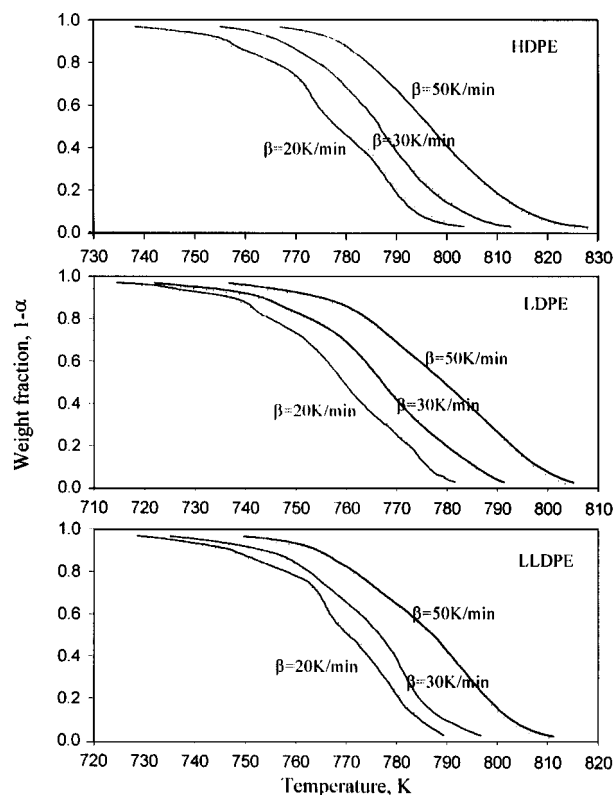

Fig. 5. Comparison of TG data (solid line) and calculated values (dotted line) from the numerical integration for the thermal decomposition of polyethylene.

method. Computations performed were based on the kinetic parametes of Table 2. It is seen that the computed values agree very well with the TG data.

For the purpose of comparison, the kinetic analysis results from the analytical methods reported in the literature are summarized in Table 3. Flynn-Wall method gave apparent activation energies of 243-277 kJ/mol, 186-210 kJ/mol and 189-275 kJ/mol, and the overall reaction orders of 0.03-0.12, 0.04-0.16 and 0.03-0.13 for HDPE, LDPE and LLDPE at the maximum thermal degradation rate, respectively. However, this method uses only one point, i.e., the point of maximum rate, and is therefore regarded in some respect as having limited applicability. The Friedman method gave the overall reaction orders of 3.82, 2.14 and 2.45 for HDPE, LDPE and LLDPE, while the activation energy upon fractional weight loss is shown in Fig. 6. From Fig. 6, it was found that the tendency of activation energy for each polyethylene was similar to the results from dynamic method, that is, the activation energy increases with the extent of branching. The Coats-Redfern method gave the apparent activation energies of 123-229 kJ/mol, 124-302 kJ/mol and 140-295 kJ/mol for HDPE, LDPE and LLDPE at various heating rates. This technique has been applied to TG data and the best fit values for each heating rate determined employing reaction order n of 0, 0.5, 1.0, 1.5 and 2.0. The best overall fit values were obtained by using n=1.0. Fig. 7 shows the activation energy upon fractional weight loss by the Ozawa method. From this figure, the activation energies of 201-258 kJ/mol, 125-203 kJ/mol and 144-218 kJ/mol for HDPE, LDPE and LLDPE were obtained. It was also found from this figure that the activation

Table 3. Kinetic parameters using the various analytical methods

Method	Reaction order, n			Activation energy, E (kJ/mol)		
	HDPE	LDPE	LLDPE	HDPE	LDPE	LLDPE
Differential method						
Freeman-Carroll						
at 10 K/min	0.67	0.81	0.70	321	296	321
at 20 K/min	0.91	0.97	0.79	421	413	446
at 30 K/min	1.32	1.16	1.01	486	412	473
at 50 K/min	1.70	1.15	1.03	561	388	376
Flynn-Wall						
at 10 K/min	0.12	0.16	0.13	252	186	189
at 20 K/min	0.07	0.09	0.07	277	210	275
at 30 K/min	0.05	0.06	0.06	273	209	271
at 50 K/min	0.03	0.04	0.03	243	191	225
Friedman	3.82	2.14	2.45	164-288	168-234	173-250
Integral method						
Coats-Redfern						
at 10 K/min				123	124	140
at 20 K/min				162	228	197
at 30 K/min	1.0	1.0	1.0	221	247	224
at 50 K/min				229	302	295
Ozawa	-	-	-	210-258	125-203	144-218
Parallel competitive reaction method						
Oh						
at 10 K/min	0.66	0.86	0.80	274	305	347
at 20 K/min	1.21	0.54	0.56	348	271	343
at 30 K/min	1.32	0.41	0.83	389	227	338
at 50 K/min	1.63	0.42	0.52	404	226	311
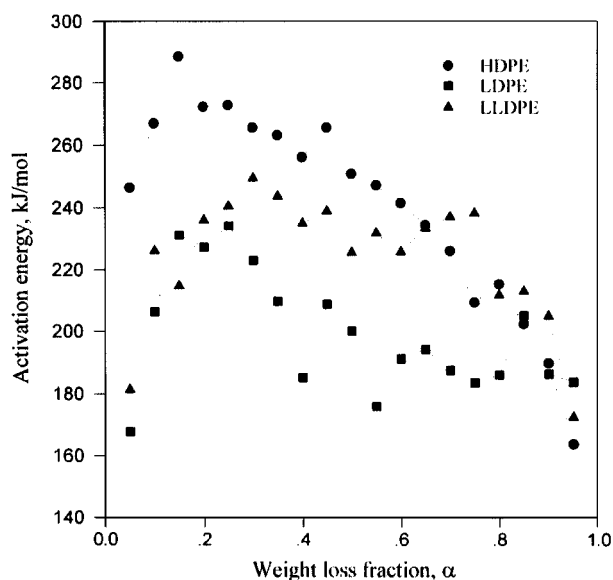
Fig. 6. Activation energy upon fractional weight loss according to Friedman's method.
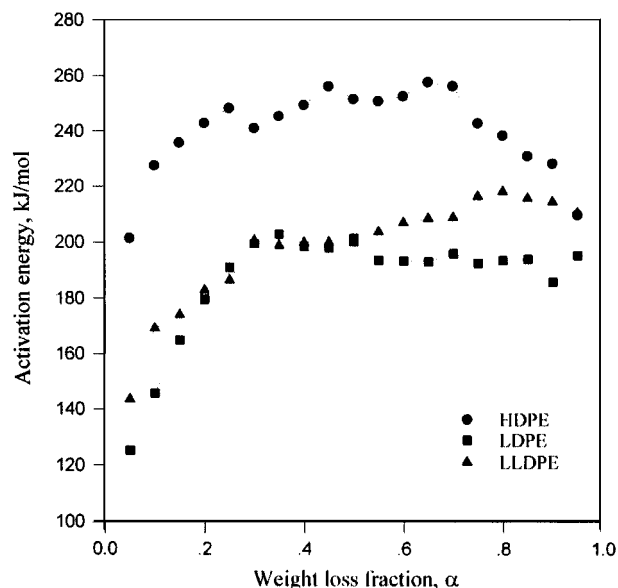
Fig. 7. Activation energy upon fractional weight loss according to Ozawa's method.

energy of the thermal decomposition of HDPE was larger than that of LDPE and LLDPE.

As shown in Table 3, there are tremendous variations depend-

ing upon the mathematical approach taken in the analysis. These observations clearly indicate the problems in the selection and uti-

Table 4. Kinetic parameters for the thermal degradation of polyethylene reported in the literature

Reference	Reaction order, n		Activation energy, E (kJ/mol)	
	HDPE	LDPE	HDPE	LDPE
Mucha [1976]	0.0-1.0	0.0-1.0	330-247[a,b]	163-230[a,b]
Urzendowski and	1.0	1.0	304[c]	290[c]
Guenther [1971]	1.0	1.0	320[b]	303[b]
Wu et al. [1993]	0.74	0.63	234[b]	206[b]
Westerhout et al. [1997]	1.0	10	220[b]	241[b,d]
	-	1.0	-	201[b,d]
Jellinek [1950]	-	0.0	-	192-276[a]

[a]Activation energy decreases with increasing molecular weight of sample.
[b]Measured in a nitrogen environment.
[c]Measured in a vacuum environment.
[d]Different initial molecular weight distributions.

lization of different analytical methods to solve the thermal decomposition of polymer. And because of the wide variations with various heating rates in a single heating rate technique, it was felt that the best methods for analyzing the data were the methods using data collected at various heating rates such as the Friedman and Ozawa methods. However, though the single heating rate experiment has been used in the suggested dynamic method, the kinetic analysis results from this method were little affected by heating rates.

Finally, to verify the appropriateness of the results obtained from this work, the kinetic parameters reported in the literature are summarized in Table 4, which shows that the proposed method gave reliable kinetic parameters for thermal decomposition of polyethylene.

CONCLUSIONS

A kinetic analysis method using a dynamic model which accounts for the thermal decomposition of polymer at any time was developed in this work. From the kinetic parameters reported in the literature, it was found that the proposed method gave reliable kinetic parameters for thermal decomposition of polyethylene. And from the comparison of the TG data and the values calculated using the kinetic parameters obtained by the dynamic method, it was seen that the computed values agree very well with the TG data. The kinetic analysis using the various analytical methods showed the tremendous variations depending upon the mathematical approach taken in the analysis. Because of the wide variations in the kinetic parameters obtained with the single heating rate experiments, the use of a multiple heating rate technique was felt to represent more realistically the thermal decomposition of polymer. By using our method, we calculated the apparent activation energies of the thermal decomposition of HDPE, LDPE and LLDPE to be 333-343 kJ/mol, 188-199 kJ/mol and 219-230 kJ/mol, while the reaction order of HDPE was the largest. It was also found that branching has a clear influence on the kinetic parameters.

NOMENCLATURE

A	:	pre-exponential factor [min^{-1}]
A_0	:	proportional factor [min^{-1}K$^{-0.5}$]
E	:	apparent activation energy [kJ/mol]
E_{ave}	:	average activation energy [kJ/mol]
H_m	:	the peak height of DTG curve at peak temperature
K	:	rate constant [min^{-1}]
K_i	:	the summation of rate constants of ith-order reaction [min^{-1}]
K	:	the rate constant vector which consists of K_0, K_1 and K_2
N	:	the total number of TG data
n	:	apparent reaction order
n_{ave}	:	average reaction order
P	:	the relative contribution to the entire thermal decomposition rate
R	:	gas constant [8.3136 J/mol · K]
T	:	absolute temperature [K]
T_0	:	temperature at α=0 [K]
T_{m1}, T_{m2}	:	temperature at the maximum decomposition rate for different heating rates [K]
t	:	time [min]

Greek Letters

α	:	degree of conversion
α_c	:	the weight loss fraction calculated by numerical method
α_e	:	the weight loss fraction obtained by thermogravimetric analysis
α_f	:	the final weight loss fraction
α_m	:	the weight loss fraction at T_m
β	:	heating rate [K/min]

Subscripts

0	:	value at the zero-order reaction
1	:	value at the first-order reaction
2	:	value at the second-order reaction
m	:	value at the maximum decomposition rate

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