

Application of Different Methods for the Thermogravimetric Analysis of Polyethylene Samples

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Received 14 April 2010; accepted 2 October 2010

DOI 10.1002/app.33538

Published online 14 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The kinetics of thermal degradation of standard and commercial polyethylene (PE) samples is investigated, by employing different methods like Flynn-Wall-Ozawa, Coats-Redfern, Kissinger, and Augis-Bennett. The order of reaction obtained was 0.741 and 1.124 for standard and commercial samples, respectively. The activation energy obtained in this way was 279.6–311.0 kJ/mol and 300.5–374.1 kJ/mol for standard and commercial samples, respectively, depending upon the method used. The activation energy obtained by different methods decreases in the order Flynn-Wall-Ozawa > Augis and Bennett > Kissinger > Coats and Red-

fern. It is observed that most of the methods deviated from the experimental results, in low (0.1–0.3) degree of conversion region but worked well in the middle (0.5–0.7) degree of conversion region. It has also been noticed that both the order and activation energy were slightly dependent over the heating rate and degree of conversion. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3511–3518, 2011

Key words: activation energy; Augis-Bennett's method; Coats-Redfern method; Flynn-Wall-Ozawa method; Kissinger method; order of reaction; polyethylene

INTRODUCTION

Because of wide applications of polyethylene its annual production is tremendously increased. However, due to its nonbiodegradability it has created various problems.¹ Some of the solutions to these problems are recycling or reutilization of it as a fuel. However, the process of recycling is very complex and needs a detailed study to find out optimum conditions at which it can be converted to reusable material. Therefore, a lot of work is going on to understand the thermal degradation of polyethylene and for the purpose a number of methods has been introduced.^{2–7} Among these the important methods are Flynn-Wall-Ozawa, Coats and Redfern, Kissinger and Augis and Bennett.^{8–11} It is normally claimed that all the proposed methods work well but in reality each method has certain short comings. Therefore, the aim of our work is to apply these methods to two different polyethylene samples. The selected samples are PE standard which is not yet processed whereas the other is PE commercial which was already processed are available in the market as shopping bags. The order of degradation and activation energy has been obtained using different methods and employing thermal analysis technique. The results obtained are compared

and discussed in the light of accuracy of the methods and effect of polymer processing.

Kinetic modeling

Polymer degradation is known to be a very complex phenomenon, comprising of several elementary reactions, which are difficult to analyze separately and whose quantitative contribution to the global degradation process is virtually impossible to assess. This is the reason that several equations (models) have been developed to investigate the kinetics and mechanism of degradation of polymers^{12–14} and some of these are applied and discussed over here.

The reaction rate in TGA studies can be defined as the variation in degree of conversion with time or temperature; where the degree of conversion (α) is calculated in terms of mass loss according to eq. (1).

$$\alpha = \frac{w_0 - w_t}{w_0 - w_\infty} = \frac{\Delta w}{\Delta w_0} \quad (1)$$

Here W_0 , W_t , and W_∞ are the mass at the initiation of the degradation process, mass at temperature t and the final mass at a temperature at which the mass loss remains almost unchanged, respectively. The conversion rate for a kinetic process can be typically indicated as the product of two contributions; one is the temperature, which affects the kinetic constant and the other is the concentration of reactive species. Therefore, the most general kinetic model for the degradation process is defined by eq. (2).

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$$\frac{d\alpha}{dt} = Kf(\alpha) \quad (2)$$

The function K can be usually described according to Arrhenius-type equation, given as:

$$K = Ae^{-E_a/RT} \quad (3)$$

The term A is the pre-exponential factor (1/s), E_a is the apparent activation energy (kJ/mol), R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K). $f(\alpha)$ is generally a very complex function and therefore, difficult to solve the differential eq. (2). Therefore, it is necessary to introduce some simplifications for the determination of the kinetic parameters. $f(\alpha)$ can be considered as a function of a parameter which is dependent over the concentration or mass of reactant or product and varies with time. However, in this case one can measure the reduction in the mass of the reactant/polymer, in term of degree of conversion (α) with time. Further to it the order of degradation process is unknown it is safe and a general practice to use " n " as order of reaction, which can be determined experimentally and can have value right from zero to ∞ . Therefore to meet the requirement of definition of α and to have a plausible solution of the equation, $f(\alpha)$ is taken as:^{15,16}

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

Where n is the order of reaction. Combining eqs. (2-4), it gives:

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}(1 - \alpha)^n \quad (5)$$

For a constant heating rate, β (K/min), defined as

$$\beta = \frac{dT}{dt} \quad (6)$$

The following equation is obtained:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT}(1 - \alpha)^n \quad (7)$$

Equation (7) is the fundamental relation to determine kinetic parameters based over TG data. Integration of eq. (7) under the conditions that temperature has the values from T_o (an initial temperature) to T_p , (peak temperature) and degree of conversion α_o , (corresponding to T_o) to α_p (corresponding to T_p) yield

$$\int_{\alpha_o}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_o}^{T_p} \exp\left(-\frac{E_a}{RT}\right) dT \quad (8)$$

Where $f(\alpha)$ is the integral function of conversion. Suggesting $\alpha = E_a/RT$ and

$$\frac{A}{\beta} \int_{T_o}^{T_p} \exp\left(-\frac{E_a}{RT}\right) dT = \frac{AE_a}{\beta R} f(\alpha) \quad (9)$$

Using Doyle's approximation,¹⁷ if $20 \leq \alpha \leq 60$ then

$$\log f(\alpha) \approx 2.315 - 0.4567\alpha \quad (10)$$

and

$$\log \beta = \log \frac{E_a}{f(\alpha)R} - 2.315 - \frac{0.4567E_a}{RT} \quad (11)$$

Equation (11) is known as Flynn-Wall-Ozawa equation. Here, A and R is constant and for a particular conversion, $f(\alpha)$ can be taken as constant. Hence, the value of E can be computed from the slope of $\log \beta$ versus $1/T$ plots, obtained at various heating rates without the knowledge of order of reaction for a particular degree of conversion.^{8,18-21}

Coats and Redfern method

Coats and Redfern method⁹ is an integral type, it assumes different order of reaction that compares the linearity in each case to select the correct one.²² The proposed equation is produced below;

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{AR}{\beta E_a} \left[1 - \frac{2RT}{\beta E_a} \right] - \frac{E_a}{2.303RT} \text{ for } n \neq 1 \quad (12)$$

$$\log \left[\frac{-\log(1 - \alpha)}{T^2} \right] = \log \frac{AR}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] - \frac{E_a}{2.303RT} \text{ for } n = 1 \quad (13)$$

The meanings of all the symbols have already been stated. Plotting left hand side of these equations versus $1/T$, the slope will be equal to $-E_a/2.303R$ and hence E_a and A values can be obtained. It is to be noted that in this the value of $2RT/E_a$ is considered as very small ($\ll 1$) hence taken as constant and neglected.

Kissinger method

Kissinger's method¹⁰ has been used by the scientists to determine the activation energy of solid state reactions. According to Kissinger's method, the activation energy can be determined without having precise knowledge of the reaction mechanism, using the following equation:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{ \ln\frac{AR}{E_a} + \ln[n(1 - \alpha_{\max})^{n-1}] \right\} - \frac{E_a}{RT_{\max}} \quad (14)$$

and plotting $\ln(\beta/T_{\max}^2)$ versus $1/T_{\max}$. Here, T_{\max} is the temperature corresponding to the peak temperature of the derivative thermogravimetric curves and corresponding to maximum reaction rate and α_{\max} being the maximum conversion. The other symbols carry the same meaning.

Augis and Bennett's method

According to the method suggested by Augis and Bennett,¹¹

$$\ln\left[\frac{\beta}{T_p - T_0}\right] = \frac{E}{RT_p} + \ln A \quad (15)$$

T_p and T_0 are the peak temperatures and onset temperature of the differential thermogram peak, respectively. The activation energy, E_a , can be obtained from the slope of the plots $\ln[\beta/(T_p - T_0)]$ versus $1/T_p$.

EXPERIMENTAL

Materials

Low density polyethylene has been investigated in this report. One of the samples was purchased from Fluka, Switzerland, named as standard. Its molecular mass was 80,000 g/mol and used as such. The other was purchased, locally in the form of shopping bags from Lahore, Pakistan. The name of the brand of shoppers was Yaadgar and named as commercial. The Kerosene oil, used for dissolving the polyethylene bags was also purchased locally and distilled twice before using.

FTIR measurement

The FTIR spectroscopic measurements of both the samples were made over Tensor 27, FTIR spectrophotometer supplied by Bruker, Germany.

Preparation of sample for TGA/DTA

1. Sample obtained from Fluka was in granules form and used as such.
2. Commercially available Polyethylene shopping bags were cut into small pieces with the help of stainless scissor. These pieces were dissolved in double distilled kerosene oil at the concentration of 0.012 g/mL and refluxed for 10 min at 160 to 180°C. The polymer was then converted to jelly like material. It was then filtered and dried at

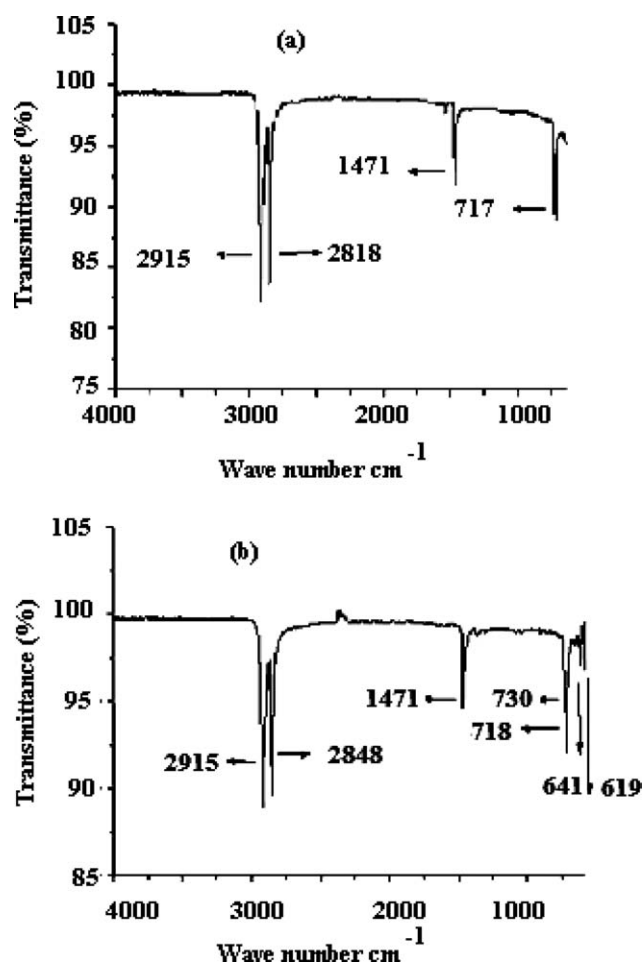


Figure 1 IR spectra of (a) standard and (b) commercial polyethylene samples.

room temperature up to a constant mass. It was then ground and the material which was passed through a sieve of 100 mesh (size less than 250 μm) that was used for investigation.

TGA/DTA measurement

Thermogravimetric analyses were performed using Diamond Thermogravimetric/Differential Thermal analyzer, Perkin-Elmer, USA; using aluminum sample pans for all investigation. The experiments were performed at different heating (5; 10; 15; 20°C/min) rates, loading 3.5–4 mg of sample; whereas, the temperature was varied from 30 to 600°C. All the analysis was performed thrice and the mean values of the parameters were used for further calculations. All the tests were carried out under nitrogen atmosphere, with flow rate of 100 mL/min.

RESULTS AND DISCUSSION

FTIR spectra, obtained for both the samples of polyethylene, are displayed in Figure 1. The

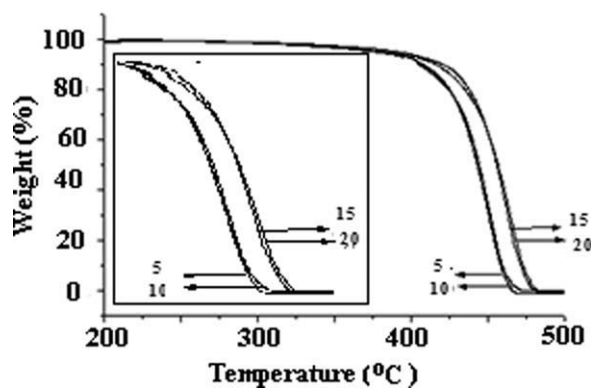


Figure 2 Thermograms of standard polyethylene sample at heating rate of 5, 10, 15, and 20°C/min. The insertion is the same data plotted for degradation period only to high light the difference in degradation temperature with the variation in heating rate.

characteristic peaks observed in both the spectra were 2915.0, 2818.0, 1471.4, and 717.4 cm^{-1} which were superimposable over the one available in the library of the instrument and thus concluded that both the investigated samples were polyethylene. Although, in case of commercial PE samples, some additional peaks at wave number cm^{-1} 729.6, 641.5, and 618.8 were observed, but their percent transmittance was less than 0.5, attributed to the presence of additives, may have been added during the processing of the sample, PE.

Thermograms of standard and commercial polyethylene samples are shown in Figures 2 and 3, respectively. It can be noted from the figures that the thermograms were shifted towards the higher temperature with the increase in heating rate; which may be due to the fact that it required less time to reach to a specific temperature, in other words lagging behind of sample temperature than the furnace temperature.¹⁶ It was noted that the mass of standard sample remained almost constant up to 300°C, showing thermal stability of the sample up to this temperature, that may be due

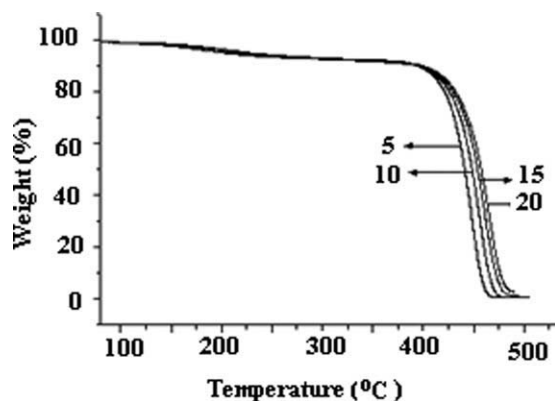


Figure 3 Thermogram of commercial polyethylene sample at heating rate of 5, 10, 15, and 20°C/min

TABLE I
Activation Energy in kJ/mol of Polyethylene Standard and Commercial Samples Determined by Flynn-Wall-Ozawa Method

Degree of conversion	Activation energy for standard sample	Activation energy for commercial sample
0.1	254.9	438.9
0.2	303.1	357.9
0.3	344.4	425.8
0.4	351.5	412.5
0.5	317.1	381.6
0.6	281.1	391.9
0.7	308.9	325.1
0.8	335.2	305.8
0.9	303.1	327.3
Mean	311.0	374.1
Standard Deviation	± 28.9	± 45.0

to compactness of polymer chains and having high degree of crystallinity.²³ By the increase in sample temperature the degradation took place with almost constant rate up to about 375.1°C and the reduction in mass up to about 5.7%. This loss in mass was attributed to the presence of some low molecular mass molecules which degraded or evaporated at the mentioned temperature range. As the sample temperature became higher than 375.1°C, the rate of degradation was significantly increased till the reduction in mass was 92.4%. In case of commercial sample, the decrease in mass at lower (<186°C) temperature was up to 9%, which was quite high as compared to standard one. It was concluded that this decrease was due to volatilization of plasticizers and/or elastomers and solvent (kerosene oil), which may be present in the sample. The high rate of degradation, took place at 381.5°C, which was higher than standard one, concluding that the commercial sample was more stable than the standard one. The over all mass loss was up to 89.31%, showing the presence of some thermodynamically stable material. We have also correlated the energy change in lower temperature to mass loss and concluded that the small molecules of polymer present in the sample were responsible for the change in mass of the samples.

Activation energy of the standard and commercial polyethylene samples was obtained using all the above reviewed methods. The values obtained are discussed and compared in the following section and tabulated in Tables I-III.

Flynn-Wall-Ozawa method

The degree of conversion, α , was calculated using eq. (1) and activation energy was obtained by plotting $\text{Log}(\beta)$ versus $1/T$ (eq. (11)), for standard as well as commercial polyethylene (Figs. 4 and 5). It was interesting to note that the data of commercial samples gave better fit as compared with standard one. The

TABLE II
Activation Energy of Standard and Commercial Polyethylene Samples Determined by Coats-Redfern Method

β °C/min	Ea (kJ/mol)	
	PE (standard) $n = 0.741$	PE (commercial) $n = 1.124$
5	294.1	320.91
10	268.3	297.93
15	280.7	290.8
20	275.3	292.4
Mean	279.6	300.5
Standard deviation	± 9.5	± 12.1

overall activation energy was found to be degree of conversion dependent for both the samples (Table I), as observed by others,^{15,24–26} however, it showed a decreasing trend with the increase in α for commercial samples. The plausible explanation for such trend was that the commercial polymer has the fillers and plasticizer, which stabilizes the polymer at low conversion; with the increase in degree of conversion, as the added material were exhausted (at high α), the degradation rate increased and the activation energy went down. This interpretation was further supported by the average activation energy which was low (311.0 ± 28.9 kJ/mol) for standard and high (374.1 ± 45.0 kJ/mol) for commercial samples; concluding that the commercial sample was more stable than the standard one due to additives.

Coats and Redfern method

To apply Coats and Redfern method, the data was plotted according to eqs. (12) and (13), considering the order of reaction as 0, 0.5, 0.741, 1, 1.5, 2 for standard and 0, 0.5, 1, 1.124, 1.5, 2 for commercial samples, respectively. The data fitted much better if $n = 0.741$ and 1.124 for standard and commercial samples, respectively. The activation energy obtained from the slope of plots, shown in Figures 6 and 7 and taking the value of n as 0.741 and 1.124 were 279.6 ± 9.5 kJ/mol and 300.5 ± 12.1 kJ/mol for standard and commercial samples respectively,

TABLE III
Activation Energy Determined by Kissinger's and Augis-Bennett's Method

Samples	Activation energy (kJ/mol)			
	Kissinger's method	Standard deviation	Augis and Bennett's method	Standard deviation
PE (standard)	294.2	0.1	307.8	0.40
PE (commercial)	304.8	0.12	308.5	0.31

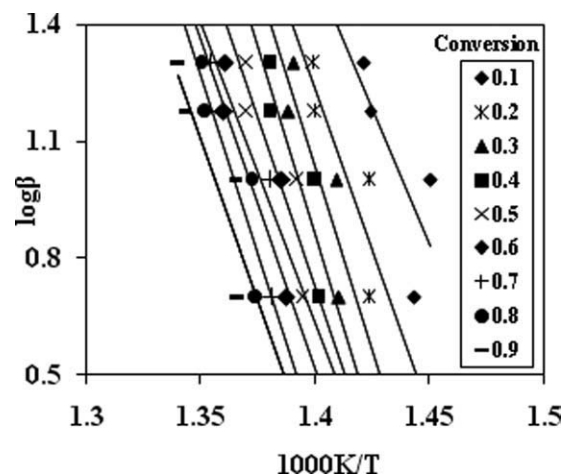


Figure 4 Heating rate as a function of temperature for different degree of conversion of standard polyethylene sample.

which was less than the average value obtained by Flynn-Wall-Ozawa method.

Kissinger method

The activation energy was obtained by plotting $\ln(\beta/T_{\max}^2)$ versus $1000/T_{\max}$. The degree of data fitness was better for commercial as compared to standard sample (Fig. 8). The activation energy obtained in this way was 294.2 and 304.8 kJ/mol for standard and commercial samples, respectively. These values were in-between the one obtained by Flynn-Wall-Ozawa and Coats methods.

Augis and Bennett's method

The data was plotted in the form that $\ln[\beta/(T_p - T_0)]$ versus $1/T_p$ and the activation energy from slope of

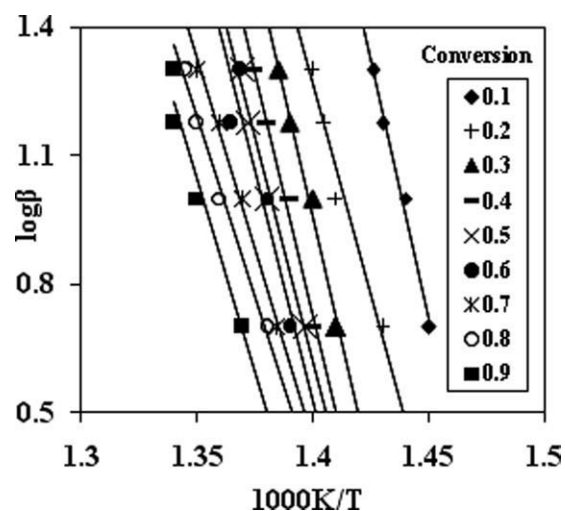


Figure 5 Heating rate as a function of temperature for different degree of conversion for commercial polyethylene sample.

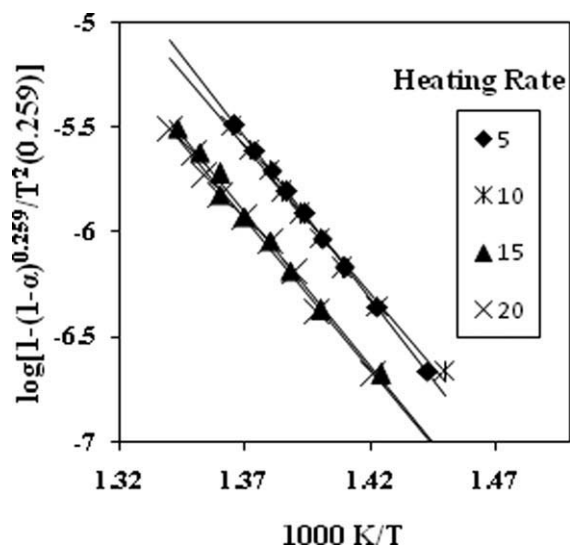


Figure 6 Coats-Redfern plots of standard polyethylene sample for $n = 0.741$.

the plots. The degree of fitness of data to equation was better for commercial as compared with standard sample (Fig. 9). The value of activation energy obtained by this method was 307.8 and 308.5 kJ/mol for standard and commercial, respectively.

It was noted that the activation energy for the degradation of commercial sample, obtained through all the methods was higher than the standard one and the reason seemed to be the addition of stabilizers and/or plasticizers to the commercial sample. It was further noted that the activation energy obtained through different methods decreases in the order Flynn-Wall-Ozawa » Augis and Bennett » Kissinger » Coats and Redfern as shown in Figure 10. The plausible explanation can be that different methods make different suppositions which may not be true for every sample and at all degree of conversion, hence give different results. For example, Flynn-Wall-Ozawa takes into account the degree of

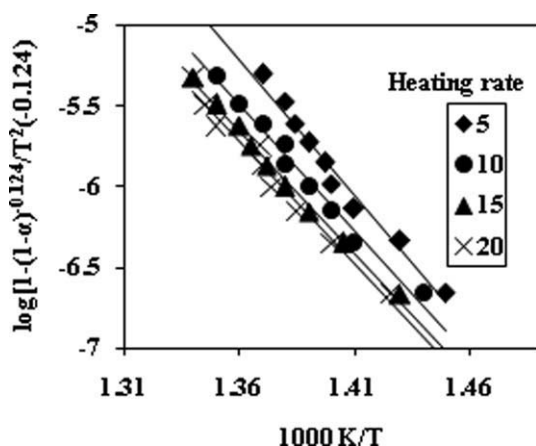


Figure 7 Coats and Redfern plots of commercial polyethylene for $n = 1.124$.

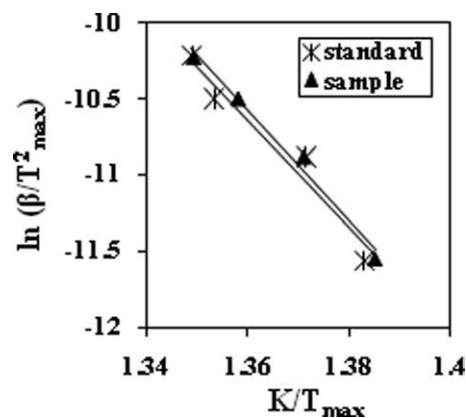


Figure 8 Kissinger plots of standard and commercial polyethylene samples.

conversion and provides quite high value at the initial conversions (degradation), which may be due to fact that the polymer at lower degradation temperature is still in semisolid (or even in melted) form and hence still have quite high molecular interactions and energy is needed to overcome the forces.²¹ With the increase in temperature, the polymer is converted to molecular state and the energy provided will be utilized only for the degradation purpose and hence the apparent activation energy goes down, which is according to observations. In case of commercial samples, the average activation energy decreases with the degree of conversion as obtained through Flynn-Wall-Ozawa method. This trend is attributed to the presence of some small molecules as additives etc, as stated earlier, which melt at low temperature and their apparent activation energy will be low. In case of Coats and Redfern, the heating rate is considered for the purpose and the activation energy decreases with the increase in heating rate. Further to it, the Coats and Redfern method assumes the order of reaction, whereas rest of the

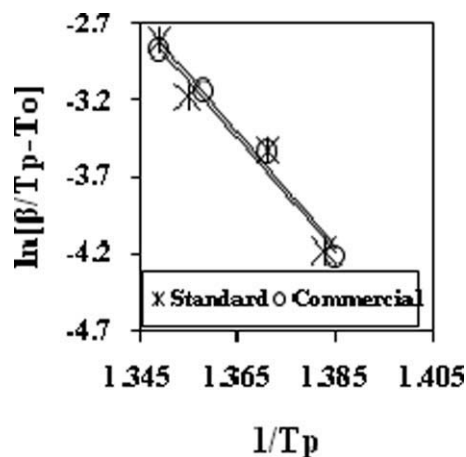


Figure 9 Augis and Bennett's plots of standard and commercial polyethylene samples.

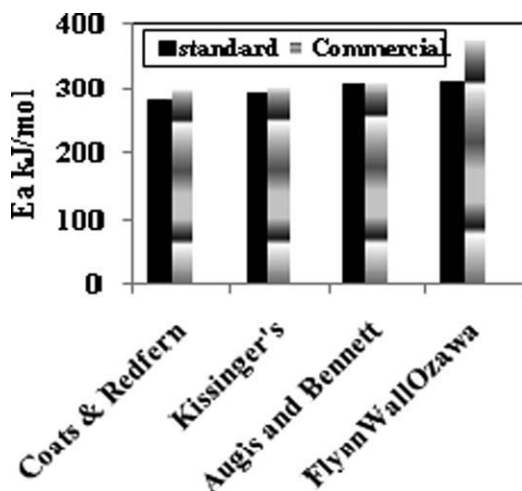


Figure 10 Activation energy of standard and commercial polyethylene samples determined by different kinetic methods.

methods don't need this information for the determination of activation energy.

Activation energy determined by Flynn-Wall-Ozawa method was different for different degree of conversion which is attributed to parallel reactions occurring under the conditions.²⁷ E_a determined by Flynn-Wall-Ozawa method for α equal to 0.6–0.9 for standard and 0.7–0.9 for commercial was comparable with the E_a obtained through other methods.

Determination of kinetic mechanism

The following equation [eq. (16)] was obtained by taking logarithm of eq. (7), used in Flynn-Wall-Ozawa method, and the order of reaction was obtained by plotting left side of equation versus $\ln(1-\alpha)$ and the slope was considered as the order of reaction.²⁰

$$\ln \left[\frac{\frac{\beta dx}{dT}}{\text{Exp} - \left(\frac{E_a}{RT} \right)} \right] = \ln A + n \ln(1 - \alpha) \quad (16)$$

It was noted that the equation deviates from the data in case of lower degree of conversion so the data for 0.1 degree of conversion was ignored to get better fitting (Fig. 11). The reason behind such deviations could be the same as in case of activation energy. It was observed that the values of n slightly increased with the increase in heating rate and the average came out as 0.741 and 1.124 for standard and commercial polymer samples, respectively, (Table IV). The Activation energy obtained through Coats and Redfern model, considering $n = 0.741$ for standard sample is 279.6 kJ/mol which is close to the one obtained through Flynn-Wall-Ozawa (311.0), Kissinger (294.2), and Augis and Bennett (307.8)

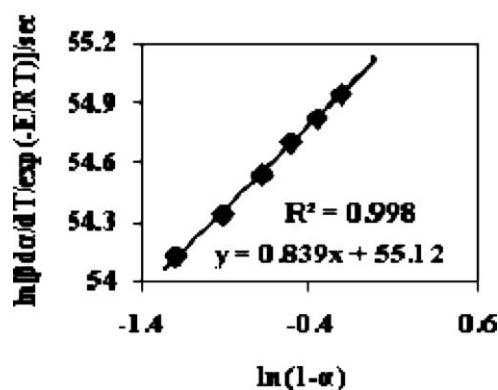


Figure 11 Friedman calculation of reaction order and the pre-exponential factor using experimental data of standard polyethylene sample at a heating rate of 20°C/min.

method. The activation energy determined through Coats and Redfern method considering $n = 1.124$ for commercial sample is 300.5 kJ/mol which is in agreement with the one obtained through Flynn-Wall-Ozawa (374.1) method Kissinger (304.8) and Augis and Bennett (308.5) methods. It was therefore, concluded that the order of reaction which best fits is 0.741 for standard and 1.124 for commercial samples. However, the literature reveal that the reaction order can be (0.5–0.74) fractional or even up to 1.5.^{28–30} Similarly, some of the scientists concluded that it depends upon heating rate, whereas others declared it as independent.²⁷ The results obtained also conclude that the kinetic parameters calculated, using different methods were different and attributed to application of different approach to analyze the thermogravimetric data.³¹ However, our observation concludes that the activation energy is both degree of conversion and heating rate dependent and same is the case for order of reaction though the difference is not so significant.

CONCLUSIONS

It has been observed in case of both samples (standard and commercial) of polyethylene that with the

TABLE IV
Order of Reaction and Other Constants of Polyethylene Samples as Obtained by Friedman's Method

β °C/min	Polyethylene (standard)			Polyethylene (commercial)		
	n	$A10^{-23}/s$	R^2	n	$A10^{-28}/s$	R^2
5	0.794	8.01	0.998	1.046	3.85	0.998
10	0.656	13.07	0.959	1.093	4.13	0.996
15	0.675	7.93	0.982	1.135	4.17	0.993
20	0.839	8.68	0.998	1.222	2.97	0.973
Mean	0.741	9.42		1.124	3.78	
Standard deviation	0.089	2.452		0.048	0.558	

increase in heating rate the degradation rate and peak temperature at DTG increases while total degradation time decreases and process of degradation starts at earlier time. Activation energy determined by different methods is in the following order Flynn-Wall-Ozawa » Augis and Bennett » Kissinger » Coats and Redfern. It has also been investigated that the activation energy of commercial polyethylene is always greater than of standard sample of polyethylene. Order of reaction determined by Friedman's method is 0.741 for standard and 1.124 for commercial. Furthermore heating rate has a little effect over the reaction order and both the parameters are in the range available in the literature.

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