Thermal Degradation of Poly(ethylene Terephthalate): A Kinetic Analysis of Thermogravimetric Data*

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Synopsis

The thermal decomposition of poly(ethylene terephthalate) has been studied using a conventional dynamic thermogravimetric technique in a flowing air atmosphere at several heating rates between 0.1°C and 100°C/min. The dynamic thermogravimetric analysis curve and its derivative have been analyzed using a variety of analytical methods reported in the literature to obtain information on the kinetic parameters. The degradation was found to be a complex process composed of at least three overlapping stages for which kinetic values can be calculated. The best approaches to solving the kinetics of the decomposition were found to be the multiple heating rate techniques of Friedman and Ozawa. The Friedman technique gave apparent activation energies (kJ/mol) for the three main decomposition stages of 122.2 ± 12.9, 201.0 ± 8.5, and 141.9 ± 12.7, with a value of 85.5 ± 10.2 for the prestage at low conversion. The Ozawa method, meanwhile, gave values of 101.6 ± 2.6, 182.6 ± 7.4, 142.5 ± 3.8, and 158.4 ± 26.1 for the prestage.

INTRODUCTION

The derivation of kinetic data in the study of polymer decomposition using dynamic thermogravimetric analysis (TG) has received increasing attention in the last decade,[1] along with much criticism regarding its use in the determination of rate constants, activation energies, reaction orders, and Arrhenius preexponential A factors.[2-8] This situation has arisen because the actual values obtained in the majority of studies are dependent not only on such factors as atmosphere, sample mass, sample shape, flow rate, heating rate, etc., but also upon the mathematical treatment used to evaluate the data. These mathematical and kinetic models used to calculate kinetic parameters have been the subject of several reviews,[9-11] and will not be described in detail in this paper. Instead, data derived from the dynamic thermogravimetric analysis of poly(ethylene terephthalate) (PET) fabric in air will be analyzed using a variety of these techniques, and the results compared. Some of the data presented in a previous publication[12] has been redetermined or reexamined in this present study.

EXPERIMENTAL

Material

The material evaluated in this study was a fabric woven from 100% spun Dacron Type 54 polyester yarn [(127 g/m²) obtained from Testfabrics Inc., Middlesex, N.J. (Style 767)]. The fabric was stored prior to evaluation in a condi-

TABLE I
Elemental Analysis of Residual Ash[a] from PET

| | Composition | |
Element	% w/w of the ash
Ti	major component
Sb	6
P	3
Mn	3
Ca	1
Na	1
Fe	0.3
Cu	0.3
Sn	0.2
Al	0.2
Pb	0.1
Mg	0.1
Si	0.06
B	0.03
Au	0.01
Cr	0.01
Ag	0.01

[a] % ash = 0.4.

tioning room at 65% relative humidity and 20°C. In view of the reported importance of catalyst residues on the thermal stability of PET,[13,14] the material was subjected to trace elemental analysis and the results obtained are presented in Table I. These results were obtained by ashing the sample at 600°C for 1 h, and then the ash was analyzed by dc-arc spectroscopy. It should be pointed out that this data is only semiquantitative, but should be within a factor of 3 of the actual value.

Apparatus

The thermogravimetric analysis was performed with a DuPont 951 instrument coupled to a 1090 Thermal Analyzer. Rectangular fabric samples (20 ± 3 mg) were stacked on top of each other in an open platinum sample pan, and the experiments conducted in air at a flow rate of 50 mL/min. The chromel–alumel sample thermocouple used to monitor the sample temperature was positioned within 2 mm of the sample pan approximately in line with the bottom of the attaching ring. This thermocouple was calibrated at room temperature and also at 353°C under all the programed-temperature conditions by the use of an ICTA certified reference material GM-761 (nickel) available from the U.S. National Bureau of Standards.[15] Appropriate temperature corrections were made for each heating rate from a comparison of the machine calculated derivative peak T_2 with the recommended nickel Currie point temperature T_2 value of 353°C. Nominal heating rates of 0.1°C, 0.3°C, 1°C, 2°C, 5°C, 10°C, 20°C, 30°C, 50°C, and 100°C/min were employed and continuous records of sample temperature, sample weight, and its first derivative were taken. In all the experiments a proportional band heater setting of 9 was employed except for the studies performed at heating rates of 20–100°C/min when a setting of 16 was used. Al-
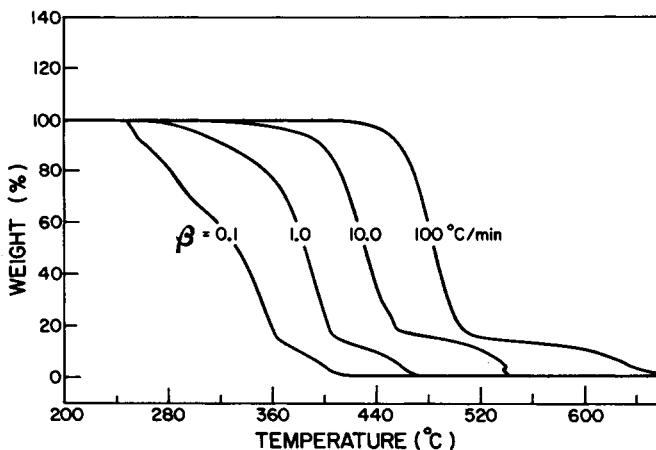
Fig. 1. Typical TG curves for PET samples heated in air at various heating rates.

though throughout this study machine selected heating rates are reported and used in the calculations, the actual heating rates were determined from the appropriate plots. With the exception of the 100°C/min heating rate, it was generally found that the discrepancy between the measured and machine-selected values were not significantly different and had a negligible effect on the calculated kinetic parameters.

RESULTS

Representative thermograms obtained for the polyester are given in Figure 1 for the nominal heating rates of 0.1°C, 1°C, 10°C, and 100°C/min. It will be noted that at the low heating rates the degradation can be perceived to be taking place in at least four distinct stages, while at the higher heating rates only two stages are clearly distinguishable. The degradation of PET can therefore be seen to be a complex process capable of providing more information at the lower heating rates than at the higher ones. However, the prime purpose of the present investigation is to obtain information relevant to our studies concerning combustion and flame retardancy, and this comes from measurements made at the higher heating rates.

The data obtained in this study have been analyzed using a variety of techniques in order to gain insight into the various chemical and physical processes taking place when PET is subjected to various heating conditions. Although the kinetic data will be expressed using such conventional notations as activation energies, orders of reaction, and preexponential factors, this is done mainly for the sake of convenience. In the methods employed, the following abbreviations have been used: E = apparent activation energy (kJ/mol); A = preexponential factor (min^{-1}); n = apparent order of reaction; R = gas constant (8.3136 J/mol·K); T = temperature in degrees absolute; t = time; α = degree of conversion; β = heating rate (°C/min); k = rate constant. All kinetic studies utilize the basic rate equation
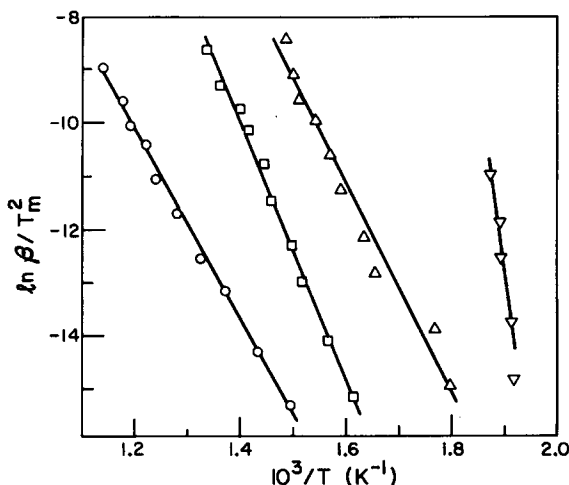
$$d\alpha/dt = kf(\alpha) \tag{1}$$

Fig. 2. Application of Kissinger's method to experimental data: (∇) prestage; ($\triangle$) stage 1; ($\square$) stage 2; ($\bigcirc$) stage 3.

which expresses the rate of conversion $d\alpha/dt$ at a constant temperature (T) as some function of the concentration of reactants $f(\alpha)$ and the rate constant k.

In the case of polymer degradation, it is usual to assume that the rate of conversion is proportional to the concentration of material which has yet to react; therefore,

$$f(\alpha) = (1 - \alpha)^n \qquad (2)$$

This function has received the greatest use in polymer degradation kinetics where a solid material is decomposing to give gaseous reaction products.

Meanwhile, the temperature dependence of the rate constant is given by the Arrhenius expression:

$$k = A \exp(-E/RT) \qquad (3)$$

The combination of the above three equations gives the following relationship:

$$d\alpha/dt = A(1 - \alpha)^n \exp(-E/RT) \qquad (4)$$

which forms the basis of subsequent analytical procedures used to derive kinetic parameters from TG data. In keeping with normal statistical practice, the data presented has been assigned error limits based on 95% confidence limits.

Kissinger Method[16]

This technique involves obtaining the temperature values (T_m) at the maxima of the first derivative weight loss curves. Since the maximum rate occurs when $d(d\alpha/dt)/dt$ is zero, differentiation of (4) with respect to t and setting the resulting expression to zero gives

$$\frac{E\beta}{RT_m^2} = An(1 - \alpha)_m^{n-1} \exp\left(\frac{-E}{RT_m}\right) \qquad (5)$$

TABLE II
Calculated First-Order Activation Energies by Kissinger's Method[16]

Region	Fractional weight loss α^a	Activation energy E (kJ/mol)	Correlation coefficient r
Prestage	0.00–0.09	577.7 ± 72.4	0.985
Stage 1	0.09–0.36	162.9 ± 10.0	0.985
Stage 2	0.36–0.92	202.1 ± 6.7	0.996
Stage 3	0.92–1.00	147.3 ± 3.5	0.998

^{a} Values determined from the 0.1°C/min data.

Kissinger then assumes that the product $n(1-\alpha)_m^{n-1}$ is independent of β and very nearly equal to unity for a first-order reaction such that the following expression can be derived:

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = \frac{-E}{R} \tag{6}$$

which allows the activation energy to be determined from a plot of $\ln(\beta/T_m^2)$ against $1/T_m$. These plots are shown in Figure 2, while the actual values obtained for each stage of the decomposition are given in Table II.

Freeman–Carroll Method[17]

This technique, which has been widely used for the analysis of nonisothermal data, involves taking the basic equation (4) in the logarithmic form and utilizing the rates of weight loss at different temperatures in the following expression:

$$\Delta \ln(d\alpha/dt) = n\Delta \ln(1-\alpha) - (E/R)\Delta(1/T) \tag{7}$$

To evaluate the constants in eq. (7), $\Delta \ln(d\alpha/dt)$ is plotted against $\Delta \ln(1-\alpha)$ for constant $\Delta(1/T)$ values of 0.01. Only the major stage of decomposition (stage 2) was evaluated using this technique, with the results summarized in Table III.

TABLE III
Kinetic Values Determined Employing the Technique of Freeman and Carroll[17]

| Heating rate (°C/min)	Order of reaction n	Activation energy E (kJ/mol)	Fractional weight loss α	Correlation coefficient r
0.1	0.90 ± 0.11	160.2 ± 10.1	0.48–0.88	0.974
0.3	1.26 ± 0.21	200.2 ± 19.9	0.43–0.76	0.951
1.0	1.68 ± 0.13	262.7 ± 14.9	0.25–0.78	0.982
2.0	1.99 ± 0.19	296.2 ± 21.4	0.19–0.76	0.974
5.0	1.70 ± 0.42	293.4 ± 48.3	0.17–0.74	0.873
10.0	1.83 ± 0.13	272.9 ± 11.1	0.06–0.74	0.981
20.0	2.43 ± 0.50	343.5 ± 62.0	0.13–0.76	0.894
30.0	2.62 ± 0.22	365.9 ± 29.1	0.14–0.78	0.979
50.0	2.04 ± 0.35	411.5 ± 50.4	0.10–0.76	0.935
100.0	1.63 ± 0.24	351.2 ± 37.6	0.06–0.77	0.941
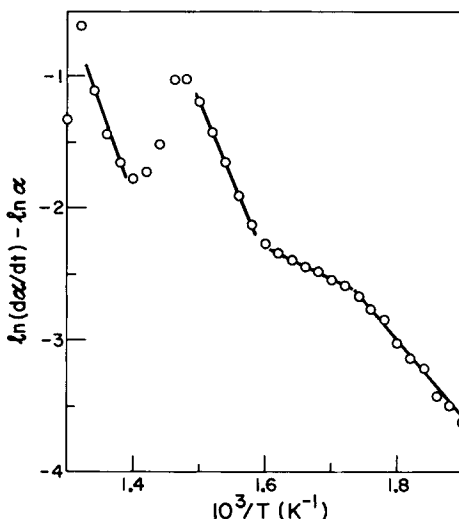
Fig. 3. Application of Chatterjee's method to the experimental data obtained at the 2°C/min heating rate.

Although this method has been shown[18] to be less subjective to changes in n allowing E values to be determined as a function of α, our findings were that the values generated were subject to large errors and did not compare favorably with the values generated using alternative techniques. In addition, discontinuities were frequently observed in the treatment of the data, a finding also observed by Chatterjee and Conrad[19] in their study of the thermal degradation of cellulose. They therefore proposed the following alternative approach to handling the data.

Chatterjee–Conrad Method[19]

According to Chatterjee and Conrad,[19] if $\ln(d\alpha/dt) - \ln\alpha$ is plotted against $1/T$, it is possible to obtain the activation energies for the individual stages of the decomposition from the slopes of the appropriate segments of the plots. Applying the same technique to our data, we were able to once again identify the different stages of the decomposition process. Figure 3 represents a typical plot obtained using this approach, while calculated activation energies are summarized in Table IV.

Friedman Method[20]

This method is probably the most general of the derivative techniques and is based on the intercomparison of the rates of weight loss $d\alpha/dt$ for a given fractional weight loss α determined using different linear heating rates β.

This method utilizes the following logarithmic differential equation derived from eq. (4):

$$\ln(d\alpha/dt) = \ln[\beta(d\alpha/dT)] = \ln A + n\ln(1 - \alpha) - E/RT \qquad (8)$$

Using this equation, it is possible to obtain values for E over a wide range of

TABLE IV
Calculated First-Order Activation Energies (kJ/mol) for Individual Stages in Degradation of
PET According to the Chatterjee–Conrad[19] Method

Heating rate (°C/min)	Prestage[a]	Stage 1[a]	Stage 2[a]	Stage 3[a]
0.1	134.4 ± 4.4 (0.002–0.083)	53.5 ± 1.9 (0.11–0.24)	147.0 ± 5.2 (0.38–0.78)	200.6 ± 31.2 (0.88–0.98)
0.3	132.5 ± 12.0 (0.003–0.030)	64.6 ± 3.0 (0.06–0.16)	177.5 ± 3.0 (0.34–0.60)	246.3 ± 18.8 (0.89–0.98)
1.0	147.4 ± 4.7 (0.005–0.029)	48.8 ± 2.1 (0.05–0.17)	206.0 ± 5.7 (0.20–0.57)	285.1 ± 13.7 (0.89–0.98)
2.0	110.5 ± 6.5 (0.005–0.024)	47.0 ± 2.2 (0.03–0.09)	223.9 ± 4.5 (0.13–0.45)	262.5 ± 29.7 (0.87–0.91)
5.0		72.2 ± 4.4 (0.01–0.05)	221.7 ± 5.9 (0.08–0.66)	261.7 ± 25.9 (0.86–0.91)
10.0		109.6 ± 3.3 (0.005–0.032)	231.8 ± 2.5 (0.06–0.44)	292.2 ± 45.4 (0.86–0.92)
20.0		141.9 ± 4.2 (0.007–0.027)	250.6 ± 5.8 (0.04–0.37)	251.2 ± 36.6 (0.84–0.89)
30.0		158.3 ± 2.7 (0.007–0.030)	241.2 ± 7.5 (0.05–0.40)	279.7 ± 26.3 (0.86–0.92)
50.0		163.4 ± 5.8 (0.003–0.009)	294.9 ± 5.2 (0.02–0.60)	237.4 ± 16.7 (0.84–0.91)
100.0		169.3 ± 6.9 (0.002–0.006)	301.4 ± 3.5 (0.01–0.47)	249.4 ± 1.9 (0.86–0.90)

[a] Values in parentheses correspond to the fractional weight loss values (α) for which the activation energies correspond.

conversions by plotting $\ln(d\alpha/dt)$ against $1/T$ for a constant α value. These results are tabulated in Table V. In addition, the values of n and $\log A$ can be determined from a plot of E/RT_0 against $\ln(1 - \alpha)$, where $1/T_0$ is the reciprocal of the temperature at which $\ln(d\alpha/dt) = 0$. The global kinetic parameters obtained by this technique using a weighted-mean calculation have been summarized in Table VI.

Horowitz–Metzger Method[21]

So far only differential methods, to determine the value of kinetic parameters, have been considered in which the relationship between $d\alpha/dt$ and T is utilized. In integral methods, however, the kinetic parameters are determined from the standard TG trace.

If the standard equation (4) is taken and a standard rate of heating $\beta = dT/dt$ is employed, it can be shown that

$$\frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT \tag{9}$$

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

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \tag{10}$$

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TABLE V
Dependence of Activation Energy upon Fractional Weight Loss According to Friedman's[20]
Calculations

Fractional weight loss α	Activation energy E (kJ/mol)	Correlation coefficient r
0.01	69.6 ± 10.0	0.927
0.02	79.0 ± 9.1	0.951
0.03	89.2 ± 9.0	0.961
0.04	94.4 ± 10.0	0.958
0.05	98.5 ± 10.5	0.957
0.10	118.8 ± 11.4	0.965
0.15	129.9 ± 12.3	0.966
0.20	140.9 ± 12.4	0.970
0.35	181.5 ± 9.0	0.990
0.50	203.8 ± 4.5	0.998
0.65	210.8 ± 8.5	0.994
0.75	199.2 ± 10.0	0.990
0.80	196.7 ± 16.0	0.975
0.85	115.5 ± 24.3	0.859
0.90	148.3 ± 4.8	0.996
0.95	140.9 ± 10.9	0.977
0.98	120.6 ± 12.8	0.958
0.99	97.5 ± 21.8	0.861

The differences between the various techniques employing integral methods lie in their approach to solving the above integral equation. In the case of the Horowitz–Metzger method[21] approximations are made regarding the exponential integral to derive the following equation for pseudo-first-order kinetics:

$$\ln(1 - \alpha) = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right) dT \qquad (11)$$

In order to integrate the right-hand side of this expression, they then defined a temperature T_s as the temperature at which $1/(1 - \alpha) = 1/\exp = 0.368$ and $\theta = T - T_s$. Assuming first-order kinetics and using a series of approximations and simplifications, they were then able to show that eq. (11) becomes

$$\ln(1 - \alpha) = -\exp(-E\theta/RT_s^2) \qquad \text{and eventually}$$
$$\ln \ln[1/(1 - \alpha)] = E\theta/RT_s^2 \qquad (12)$$

Thus a plot of $\ln \ln[1/(1 - \alpha)]$ against θ allows the activation energy to be de-

TABLE VI
Kinetic Values Determined Employing the Friedman Method[20]

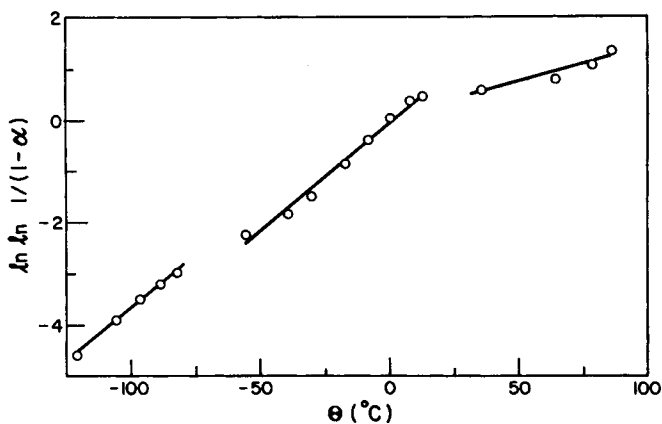| Region	Fractional weight loss α	Activation Energy E (kJ/mol)	Reaction order n	log A (min⁻¹)
Prestage	0.01–0.05	85.5 ± 10.2	1.3 ± 0.4	32.7 ± 7.8
Stage 1	0.10–0.20	129.2 ± 12.9	1.6 ± 0.1	7.9 ± 0.2
Stage 2	0.35–0.80	201.0 ± 8.5	2.0 ± 0.2	13.1 ± 0.3
Stage 3	0.85–0.99	141.9 ± 12.7	1.3 ± 0.3	8.6 ± 0.2

Fig. 4. Application of Horowitz and Metzger's method to the experimental data obtained at the 2°C/min heating rate.

termined. Figure 4 shows a typical plot which enabled the different stages of decomposition to be identified, for one heating rate condition. Similar plots were obtained employing all the heating rates examined, and the results are summarized in Table VII.

Coats–Redfern Method[22]

The integral approximation taken with this technique is to consider eq. (10) when it can be shown that

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{1-(1-\alpha)^{1-n}}{1-n} \qquad \text{for } n \neq 1 \qquad (13)$$

and

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = -\ln(1-\alpha) \qquad \text{for } n = 1 \qquad (14)$$

TABLE VII
Calculated First-Order Activation Energies (kJ/mol) for Individual Stages in Degradation of PET According to the Horowitz–Metzger Method[21]

Heating rate (°C/min)	Stage 1 ($\alpha = 0.01$–0.05)	Stage 2 ($\alpha = 0.1$–0.8)	Stage 3 ($\alpha = 0.9$–0.99)
0.1	1107.6 ± 158.3	78.9 ± 3.5	67.7 ± 9.5
0.3	183.7 ± 2.8	83.5 ± 3.6	63.3 ± 9.4
1.0	199.3 ± 8.9	128.6 ± 5.5	76.3 ± 10.8
2.0	163.1 ± 7.2	160.9 ± 6.8	50.4 ± 13.9
5.0	131.4 ± 4.6	199.7 ± 5.1	59.1 ± 18.2
10.0	137.4 ± 1.6	207.4 ± 8.3	55.1 ± 18.2
20.0	142.9 ± 4.7	206.3 ± 15.9	51.5 ± 10.3
30.0	169.1 ± 7.6	220.4 ± 13.5	83.2 ± 18.3
50.0	226.6 ± 10.8	275.1 ± 14.9	53.9 ± 7.7
100.0	311.9 ± 6.7	285.5 ± 13.8	56.2 ± 4.9

TABLE VIII
Calculated Activation Energies (kJ/mol) for Individual Stages in Degradation of PET According to the Coats–Redfern Method[22]

Heating rate (°C/min)	Prestage[a] (using $n = 1$)	Stage 1[a] (using $n = 1$)	Stage 2[a] (using $n = 3/2$)	Stage 3[a] (using $n = 1$)
0.1	88.3 ± 2.8 (0.08–0.24)	40.4 ± 1.7 (0.29–0.51)	138.8 ± 3.6 (0.59–0.85)	31.6 ± 1.1 (0.85–0.93)
0.3	122.8 ± 2.4 (0.03–0.10)	42.4 ± 2.9 (0.20–0.34)	121.6 ± 5.2 (0.34–0.70)	28.3 ± 3.7 (0.81–0.91)
1.	136.4 ± 1.9 (0.005–0.04)	74.6 ± 2.0 (0.05–0.25)	186.9 ± 6.4 (0.32–0.72)	20.2 ± 1.6 (0.83–0.91)
2.	122.9 ± 1.5 (0.003–0.024)	74.8 ± 1.3 (0.04–0.17)	198.9 ± 6.8 (0.22–0.62)	12.0 ± 1.0 (0.82–0.88)
5.		86.7 ± 0.8 (0.006–0.100)	218.1 ± 4.8 (0.14–0.66)	8.7 ± 0.7 (0.82–0.88)
10.		98.1 ± 1.4 (0.01–0.08)	228.7 ± 3.6 (0.11–0.61)	4.9 ± 1.4 (0.82–0.88)
20.		79.1 ± 5.2 (0.01–0.03)	241.6 ± 5.9 (0.08–0.71)	4.7 ± 2.5 (0.83–0.89)
30		83.1 ± 5.4 (0.005–0.021)	258.5 ± 3.7 (0.08–0.58)	1.5 ± 1.1 (0.84–0.86)
50		81.8 ± 6.5 (0.003–0.013)	311.7 ± 7.9 (0.05–0.60)	−3.3 ± 1.1 (0.84–0.87)
100		141.1 ± 5.8 (0.002–0.006)	306.4 ± 5.4 (0.02–0.69)	−2.7 ± 1.0 (0.85–0.89)

[a] Values in parentheses correspond to the fractional weight loss region (α) for which the activation energies correspond.

while

$$\frac{A}{\beta} \int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right) dT = \frac{ART^2}{\beta E}\left(1 - \frac{2RT}{E}\right) \exp\left(\frac{-E}{RT}\right) \tag{15}$$

After taking logarithms the following two equations can be obtained:

$$\log\left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)}\right] = \log\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right) \frac{-E}{2.303RT} \quad \text{for } n \neq 1 \tag{16}$$

and

$$\log\left[\frac{-\log(1 - \alpha)}{T^2}\right] = \log\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right) \frac{-E}{2.303RT} \quad \text{for } n = 1 \tag{17}$$

Thus plots of

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

and

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

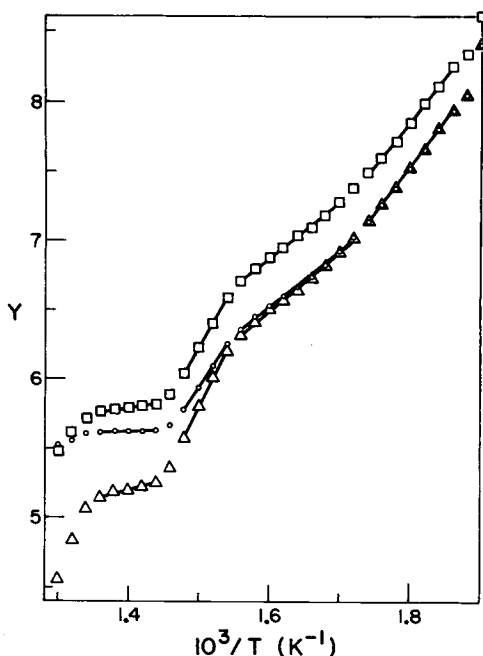result in straight lines with slopes equal to $-E/2.303R$ for the correctly chosen values of n.

Fig. 5. Application of Coats–Redfern method to the data obtained at a heating rate of 2°C/min for various values of n (order of reaction): (O) $\frac{1}{2}$; ($\square$) 1; ($\triangle$) $\frac{3}{2}$.

This technique has been applied to our data and the best fit values for each heating rate and stage of the decomposition of PET determined employing reaction order values n of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$ and 2. The best overall fit values were obtained using a value for $n = 1$ with the exception of the main stage of the decomposition (stage 2), for which the best fit of the data was obtained using a value of $n = \frac{3}{2}$. The calculated activation energies using this technique with these values of n are summarized in Table VIII while Figure 5 illustrates the types of plots obtained using a heating rate of 2°C/min.

Ozawa Method[23]

This method, which is essentially the same as that of Flynn and Wall[24] represents a relatively simple method of determining activation energies directly from weight loss vs. temperature data obtained at several heating rates. Essentially the technique assumes that A, $(1 - \alpha)^n$, and E are independent of T while A and E are independent of α, wherein the variables given in eq. (10) may be separated and integrated to give in logarithmic form:

$$\log F(\alpha) = \log (AE/R) - \log \beta + \log p(E/RT) \tag{18}$$

Using Doyle's[25] approximation for the integral which allows for $E/RT > 20$, then $\log p(E/RT)$ may be expressed as

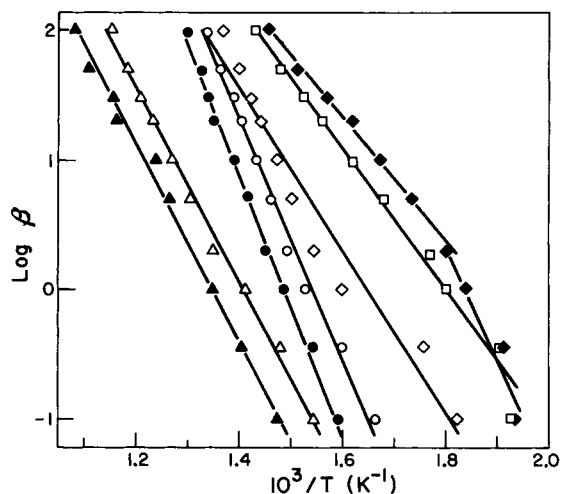$$\log p(E/RT) \simeq -2.315 - 0.4567E/RT \tag{19}$$

Fig. 6. Ozawa plots at the following fractional weight losses: (◆) 0.01; (□) 0.02; (◇) 0.2; (○) 0.50; (●) 0.80; (△) 0.90; (▲) 0.99.

Equation (18) now becomes

$$\log F(\alpha) = \log(AE/R) - \log \beta - 2.315 - 0.4567E/RT \qquad (20)$$

The apparent activation energy E can therefore be obtained from a plot of log β against $1/T$ for a fixed degree of conversion since the slope of such a line is given

TABLE IX
Activation Energies Determined from Isoconversional Plots According to Ozawa's Method[23]

Fractional weight loss α	Activation energy E (kJ/mol)	log A (min^{-1})	Correlation coefficient r
0.01[a]	158.4 ± 26.1	14.7 ± 2.8	0.974
0.01[a]	88.3 ± 3.4	8.1 ± 0.3	0.997
0.02	101.8 ± 3.6	9.3 ± 0.4	0.995
0.03	100.0 ± 3.0	9.2 ± 0.3	0.996
0.04	100.3 ± 2.8	9.2 ± 0.2	0.997
0.05	100.5 ± 3.2	9.3 ± 0.5	0.996
0.10	104.4 ± 5.6	9.7 ± 0.5	0.989
0.15	109.9 ± 7.3	10.2 ± 0.6	0.983
0.20	115.6 ± 8.4	10.7 ± 0.7	0.979
0.35	139.0 ± 9.2	12.6 ± 0.8	0.983
0.50	171.1 ± 5.8	15.0 ± 0.5	0.995
0.65	186.0 ± 8.8	16.2 ± 0.7	0.991
0.75	187.3 ± 4.6	16.2 ± 0.4	0.998
0.80	184.7 ± 5.2	16.0 ± 0.4	0.997
0.85	156.5 ± 11.1	13.6 ± 0.9	0.980
0.90	137.8 ± 3.2	11.8 ± 0.3	0.998
0.95	144.7 ± 2.3	12.2 ± 0.2	0.999
0.98	145.2 ± 3.6	12.2 ± 0.3	0.998
0.99	138.4 ± 4.7	11.7 ± 0.4	0.996

[a] Two values; see Figure 6.

TABLE X
Apparent Activation Energies Determined Using Ozawa's Method[23]

Region	Fractional weight loss α	Global activation energy E (kJ/mol)	Global log A (min^{-1})
Prestage	0.01	158.4 ± 26.1	14.7 ± 2.8
Stage 1	0.02–0.20	101.6 ± 2.6	9.4 ± 0.3
Crossover	0.35	139.0 ± 9.2	12.6 ± 0.9
Stage 2	0.50–0.80	182.6 ± 7.4	15.9 ± 0.5
Crossover	0.85	156.5 ± 11.1	13.6 ± 1.1
Stage 3	0.90–0.99	142.5 ± 3.8	12.0 ± 0.2

by $-0.4567E/R$. In addition, a value of log A can be found from the intercept on the log β axis.

Several of the isoconversional plots are shown in Figure 6, while the calculated apparent activation energies and log A values are given in Table IX. Close examination of these data clearly reveals the presence of three distinct stages in the thermal degradation of PET, which are summarized in Table X. These values were calculated using a weighed mean procedure. In the case of the data obtained at the lowest conversion (i.e., $\alpha = 0.01$) there was a noticeable demarcation in the plot between the low and high heating rate data. By analyzing these two zones, it was therefore possible to extract values for the prestage which are given in Table X.

DISCUSSION

For comparative purposes the results from the analytical manipulations of the experimental data are summarized in Table XI. Clearly, there are tre-

TABLE XI
Summary of Apparent Activation Energies for Various Stages in Thermal Decomposition of PET

Method	Prestage	Stage 1	Stage 2	Stage 3
Kissinger	577.7 ± 72.4	162.9 ± 10.0	202.1 ± 6.7	147.3 ± 3.5
Freeman–Carroll				
at 1°C/min			262.7 ± 14.9	
at 10°C/min			272.9 ± 11.1	
at 100°C/min			351.2 ± 37.6	
Chatterjee–Conrad				
at 1°C/min	147.4 ± 4.7	48.8 ± 2.1	206.0 ± 5.7	285.1 ± 13.7
at 10°C/min		109.6 ± 3.3	231.8 ± 2.5	292.2 ± 45.4
at 100°C/min		169.3 ± 6.9	301.4 ± 3.5	249.4 ± 1.9
Friedman	85.5 ± 10.2	129.2 ± 12.9	201.0 ± 8.5	141.9 ± 12.7
Horowitz–Metzger				
at 1°C/min		199.3 ± 8.9	128.6 ± 5.5	76.3 ± 10.8
at 10°C/min		137.4 ± 1.6	207.4 ± 8.3	55.1 ± 18.2
at 100°C/min		311.9 ± 6.7	285.5 ± 13.8	56.2 ± 4.9
Coats–Redfern				
at 1°C/min	136.4 ± 1.9	74.6 ± 2.0	186.9 ± 6.4	209.2 ± 1.6
at 10°C/min		98.1 ± 1.4	228.7 ± 3.6	4.9 ± 1.4
at 100°C/min		141.1 ± 5.8	306.4 ± 5.4	−2.7 ± 1.0
Ozawa	158.4 ± 26.1	101.6 ± 2.6	182.6 ± 7.4	142.5 ± 3.8

mendous variations in the calculated apparent activation energies depending upon the mathematical approach taken in the analysis and the actual heating rate, and/or degree of conversion values used in these calculations. These observations clearly indicate the problems and pitfalls in the selection and utilization of different analytical methods to solve complex multistage thermal degradations such as occur in the decomposition of PET. For example, it is possible for several degradation mechanisms to be responsible for the thermal degradation: thermal oxidation, pyrolysis, and thermal hydrolysis. Meanwhile, the random chain scission of PET has been shown to be characterized by a maximum in the rate of weight loss at a fractional weight loss of 0.26.[26]

Because of the wide variations in the calculated activation energies obtained with the single heating rate experiments, it was felt that the best methods for analyzing the data were those that involved the utilization of data collected at several different heating rates such as Ozawa's, Friedman's, and Kissinger's methods. The use of a multiple heating rate technique was also felt to represent more realistically the variety of heating rates obtainable during the pyrolysis and combustion reactions occurring when a polymeric material burns. While Ozawa's and Friedman's calculations are applicable to all points on the TG curves, Kissinger's method uses only one point, i.e. the point of maximum rate, and is therefore regarded in some respect as having limited applicability. However, examination of Table XI reveals that the technique, despite this apparent inadequacy, is capable of giving values in close agreement with those of Ozawa and Friedman, provided the data from the prestage are neglected, with simpler mathematical calculations. However, the fact that Kissinger's method utilizes the condition that $f(1 - \alpha) = (1 - \alpha)^n$ should not be overlooked, since it is possible to obtain a systematic deviation in eq. (6) dependent upon n. Meanwhile, Friedman's method, like Ozawa's procedure, makes no assumptions about $f(1 - \alpha)$, and therefore both are capable of providing reasonably reliable data from temperature-programed TG.

The literature contains several references to both the pyrolytic and thermooxidative degradation of poly(ethylene terephthalate). Papers which give values for the apparent activation energies for these decomposition processes are summarized in Table XII. The studies of Straus and Wall,[27] Goodings,[28] and Zimmermann[14,29] relate to the low temperatures encountered in processing PET rather than those expected to be encountered in the burning process. It would therefore be expected that results obtained under isothermal conditions at the relatively low reaction temperatures of about 300°C would not correlate well with those obtained under isothermal conditions at higher temperatures of about 500°C. However, Granzow et al.[30] obtained a value for the apparent activation energy of 155 kJ/mol in close agreement with Straus and Wall's[27] value despite the large temperature differences between the two studies. The complexity of the thermal degradation of PET observed in our studies has been observed as well by Birladeanu et al.,[31] who also used a dynamic technique. In that study they observed a dependence of the apparent activation energy on the heating rate, the degree of conversion, and the molecular weight of the sample. The multisteps in the thermal decomposition as reported in this paper are not new in that Matusevich and Kumachev[32] were able to establish the existence of three stages in the decomposition with the aid of an evolved gas analysis technique while Hedges et al.[33] and Baer[34] have proposed a four-stage process

TABLE XII
Reported Activation Energies for Thermal Degradation of Poly(ethylene Terephthalate)

Authors	Reference	E (kJ/mol)	Remarks	Technique
Straus and Wall	27	159	Temp 350–370°C	Isothermal under vacuum
Goodings	28	94–287	Dependent upon conditions and species being analyzed	Isothermal under N_2 283–306°C
Zimmermann and Schaff	29	86–93 in air	Values dependent upon impurities and catalyst residues	Isothermal in air 270–301°C
		183–188 in N_2		Isothermal in N_2 301–363°C
Zimmermann and Kim	14	122–170 in open N_2 system 153–187 in closed N_2 system	Dependent upon catalysis residues	Isothermal 280–300°C
Granzow et al.	30	155 in argon 126 in O_2	Temp 402–510°C	Isothermal technique
Birladeanu et al.	31	72–249 in air 227–272 in N_2	Dependent upon mol wt heating rate and conversion	TG, at heating rates of 2–10°C/min in air and 2.4–18.5°C/min in N_2
Matusevich and Kumachev	32	154, 234, 205 in vacuum 150, 33, 243 in O_2	Three stages identified	Gas evolution analysis
Hedges et al.	33	160, 171, 199, 292	Four stages of decomposition	Hot wire pyrolysis in air
Baer	34	135, 121, 176, 210	Four stages of decomposition	Hot wire pyrolysis in air
Bechev et al.	35	184	Destructive process	TG in air at 6°C/min
Bechev et al.	36	333	Destructive process	TG in air at 6°C/min
Prokopchuk et al.	37	238 in argon 201 in air	Combined thermal and mechanical degradation	DTA technique

for the rapid decomposition under conditions more representative of those encountered in the burning process.

In conclusion, it would appear that either the differential method of Friedman or the integral method of Ozawa provide satisfactory mathematical approaches to obtaining kinetic parameters for the thermal degradation of poly(ethylene terephthalate). Using either of these techniques, it is possible to identify the three main stages in the thermal decomposition of PET as well as a prestage, and derive values for the kinetic parameters. Taking the mean values from the two techniques suggests that realistic values for the apparent activation energies and log A for the three main stages in air would be 111.9, 191.8, and 142.2 kJ/mol and 8.7, 14.5, and 10.3 respectively, with an apparent activation energy of 121.9 kJ/mol for the prestage.

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