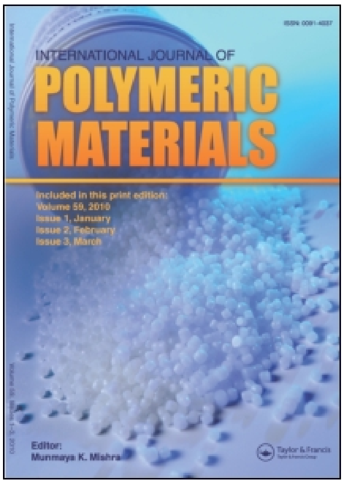

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Thermal Degradation of Poly(Trimethylene Terephthalate) and Acrylonitrile Butadiene Styrene Blends: Kinetic Analysis of Thermogravimetric Data

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Thermal Degradation of Poly(Trimethylene Terephthalate) and Acrylonitrile Butadiene Styrene Blends: Kinetic Analysis of Thermogravimetric Data

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The thermal degradation of virgin poly(trimethylene terephthalate) (PTT), acrylonitrile butadiene styrene (ABS), and three different novel blends PTT20/ABS80, ABS80, PTT50/ABS50 and PTT80/ABS20, wt/wt%, was studied using a non isothermal thermogravimetric technique. Kinetic parameters such as activation energies, reaction orders, and pre-exponential factors are calculated using integral and differential methods reported in the literature. Advantages and disadvantages of these methods are discussed in order to characterize PTT, ABS and their blends.

Keywords: acrylonitrile butadiene styrene, degradation behavior, polymer blends, poly(trimethylene terephthalate)

INTRODUCTION

PTT is an important polyester material. Molecular weight and crystallinity studies of PTT have been reported [1]. The durability of ABS blends is important in many applications and depends on the composition, processing and operating conditions. Tiganis et al. [2] reports that the most critical degradation process in ABS is the thermo-oxidative degradation of the butadiene styrene block.

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Performance of ABS is dependent on adequate levels and distributions of stabilizers for specific temperature applications. In polymer science, thermal methods of analysis have found important applications, one among them is the determination of kinetic parameters. For this purpose thermogravimetric analysis (TGA) is a technique widely used because of its simplicity and the information obtained from a simple thermogram [3–10]. There are, however, many proposed methods to calculate kinetic parameters, and these reported values depend not only on experimental conditions but also on the mathematical treatment of data. In this article the suitability of a few kinetic models to interpret the TGA data of virgin PTT, ABS and their blends is reported.

EXPERIMENTAL

PTT used was a semi-crystalline polymer (RTP 4700). The specific gravity of the resin was 1.33 and the weight average molecular weight was approximately 138,000. The ABS (RTP600) used had a specific gravity of 1.06. PTT and ABS were dried in an oven at 100°C for 8 h. COLLIN E 20 T single screw extruder supplied by COLLIN, Germany, was used in blending PTT and ABS at the three chosen compositions. The barrel temperatures for extruding PTT20/ABS80, PTT50/ABS50 and PTT80/ABS20 were 200, 210, 205 and 198°C. The screw speed was set around 400 rpm for all three compositions. The extruded strands were cooled in a water bath and simultaneously pelletized. All blends were extruded twice to ensure blend homogeneity. The blends were then kept in a moisture-free environment.

Simultaneous Differential Scanning Technique (SDT) 2690, supplied by TA Instruments, Inc. was used in obtaining the TGA data for the virgin and blended materials. The temperature calibration was performed using calcium oxalate (as the sample) and gold (as the reference) and heating up to 1150°C at a heating rate of 20°C/min. The weight calibration was performed using standard ceramic calibration weights and heating up to 1450°C at a rate of 20°C/min. For a typical TGA run alumina cups are placed in an external furnace at 1000°C for 6 h for cleaning. Two clean empty cups are then placed on the sample and reference beams inside the TGA machine, the furnace is closed and the weight is tarred. A nitrogen flow of 25 ml/min was maintained to keep an inert atmosphere inside the furnace. 7–8 mg of the sample were placed in the sample cup and heated to 900°C at a predecided heating rate. The data of weight loss versus temperature were simultaneously recorded.

RESULTS AND DISCUSSION

The thermal degradation values at different conversions for PTT, ABS, PTT20/ABS80, PPT50/ABS50 and PTT80/ABS20 are indicated in Table 1. It is observed that at lower conversions the degradation occurs at low temperature. A general observation noted is that as the heating rate increases, the degradation temperature increases. The maximum temperature of degradation is found for 70% conversion. Another observation noted is that at the same heating rate, PTT degrades faster than ABS. As the percentage of ABS decreases in the blends, the degradation temperature is found to decrease.

The basic equation used to describe decomposition reactions is

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

TABLE 1 Thermal Degradation Characteristics for Virgin PTT, Virgin ABS and Their Blends

System	Heating rate °C/min	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	$T_{70\%}$ (°C)
Virgin PTT	5	367.54	382.57	391.45
	10	380.71	396.04	405.26
	15	389.09	404.26	413.20
	20	393.94	409.29	418.49
	40	408.99	424.06	432.80
Virgin ABS	5	386.16	401.80	411.20
	10	400.62	417.88	428.85
	15	406.56	423.84	433.96
	20	414.18	431.74	442.84
	40	428.02	447.01	458.82
PTT20/ABS80	5	372.08	389.47	400.53
	10	386.19	403.48	414.49
	15	394.26	411.29	422.95
	20	399.86	417.35	428.90
	40	414.22	431.21	443.05
PTT50/ABS50	5	369.10	384.24	393.99
	10	384.46	402.35	413.68
	15	391.67	405.78	415.27
	20	396.11	410.35	419.67
	40	413.48	427.04	435.77
PTT80/ABS20	5	366.71	382.10	391.34
	10	381.02	396.23	405.44
	15	389.17	403.98	413.00
	20	395.46	410.62	419.65
	40	412.26	427.32	435.50

The rate constant $k(T)$ is a function of temperature, whereas $f(\alpha)$ is a function of conversion, α, which may be defined as

$$\alpha = \frac{M_0 - M_t}{M_0 - M_f} \tag{2}$$

where M_0 is the initial sample weight, M_t is the sample weight at time t and M_f is the final sample weight. Usually k is assumed to follow Arrhenius relationship

$$k = A \exp\left(\frac{-E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor, R is the universal gas constant, T is the temperature and E is the activation energy.

Several models have been proposed to solve the integration of the rate equation. The models selected in this study are Broido [11], Horowitz–Metzger [12], Friedman [13], and Kissinger [14].

Broido's Model

This model assumes a first order decomposition reaction and is given as follows:

$$\ln(-\ln(1-\alpha)) = \frac{-E}{RT} \tag{4}$$

where T is the temperature, α is the conversion at temperature T, R is the gas constant and E is the activation energy. E can be determined from the plot of $\ln(-\ln(l-\alpha))$ versus $1/T$. The results obtained using this method are tabulated in Table 2.

Horowitz–Metzger's Model

Assuming a first order reaction, this model is given as:

$$\ln\left[\ln\left(\frac{1}{1-\alpha}\right)\right] = \frac{E(T - T_{\max})}{RT_{\max}^2} \tag{5}$$

where T is the temperature, $T_{\max}$ is the temperature at which the first derivative of TGA data is maximum, α is the conversion at temperature T, R is the gas constant and E is the activation energy. Plotting $\ln[\ln(1/(1-\alpha))]$ versus $T - T_{\max}$ allows for determining E from the slope. The results are tabulated in Table 2.

TABLE 2 Activation Energy of Virgin PTT, Virgin ABS and Their Blends Calculated from Broido's and Horowitz–Metzger's Models

		Broido		Horowitz–Metzger	
System	Heating rate °C/min	E (kJ/mol)	R^2	E (kJ/mol)	R^2
Virgin PTT	5	274.5	0.999	288.0	0.997
	10	81.8	0.992	270.6	0.996
	15	59.2	0.993	315.1	0.999
	20	45.7	0.992	245.7	0.992
	40	25.7	0.992	294.9	0.997
Virgin ABS	5	199.2	0.992	215.8	0.990
	10	153.9	0.997	211.0	0.990
	15	98.9	0.991	230.6	0.997
	20	185.3	0.994	217.6	0.996
	40	208.2	0.999	240.3	0.999
PTT20/ABS80	5	220.5	0.994	240.5	0.995
	10	252.1	0.996	275.8	0.997
	15	270.3	0.999	273.2	0.992
	20	280.1	0.999	303.4	0.999
	40	297.0	0.998	320.3	0.998
PTT50/ABS50	5	263.7	0.996	270.3	0.994
	10	229.2	0.997	251.1	0.998
	15	259.3	0.994	279.1	0.996
	20	276.6	0.997	295.6	0.998
	40	304.5	0.995	330.3	0.997
PTT80/ABS20	5	240.0	0.996	240.7	0.994
	10	256.1	0.998	281.4	0.999
	15	277.2	0.999	302.1	0.9995
	20	299.5	0.999	305.4	0.994
	40	320.0	0.999	327.0	0.993

Friedman's Model

The model is given as

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln(1-\alpha) - \frac{E}{RT} \tag{6}$$

where T is temperature, α is the conversion at temperature T, $d\alpha/dt$ is the derivative of conversion with respect to time, R is the gas constant, n is the order of degradation reaction, A is the pre-exponential factor and E is the activation energy. This model determines the activation energy at a certain weight loss α by plotting $\ln(d\alpha/dt)$ versus $1/T$ using different heating rates. Using Equation 6, it is possible to obtain values for E over a wide range of conversions by plotting $\ln(d\alpha/dt)$

TABLE 3 Activation Energy of Virgin PTT, Virgin ABS and Their Blends Calculated Using Friedman Model

Fractional weight loss (%)	Friedman				
	Virgin PTT E (kJ/mol)	Virgin ABS E (kJ/mol)	PTT20/ABS80 E (kJ/mol)	PTT50/ABS50 E (kJ/mol)	PTT80/ABS20 E (kJ/mol)
$\alpha = 0.8$	221.4	178.6	203.5	211.2	210.4
$\alpha = 0.7$	204.2	165.8	190.0	192.7	196.0
$\alpha = 0.6$	199.8	161.7	184.7	199.7	189.0
$\alpha = 0.5$	195.1	161.5	181.6	185.3	180.2
$\alpha = 0.4$	190.8	164.3	192.5	170.5	170.5
$\alpha = 0.3$	185.3	171.0	186.2	176.4	168.1
$\alpha = 0.2$	181.3	179.1	177.0	179.5	168.7
$\alpha = 0.1$	176.4	173.0	186.0	170.0	170.6
Average	194.3	169.4	187.8	185.7	181.7

against $1/T$ at a constant value of α. The activation energy values obtained by this technique are shown in Table 3.

Kissinger Model

Kissinger model is given as

$$\ln\left(\frac{r}{T_{\max}^2}\right) = \ln\left[n(1-\alpha_{\max})^{n-1}A\frac{R}{E}\right] - \frac{E}{RT_{\max}} \tag{7}$$

where $T_{\max}$ is the temperature at which first derivative of TGA data is maximum, $\alpha_{\max}$ is the weight loss at $T_{\max}$, r is the heating rate in K/min, R is the gas constant, n is the degradation reaction order, A is the pre-exponential factor and E is the activation energy. A plot of $\ln(r/T_{\max}^2)$ versus $1/T_{\max}$ would give a slope of $-E/R$. n is determined according to Equation 8 and accordingly A is obtained from the intercept.

$$n = 1.88\left[\frac{(d^2\alpha/dt^2)_L}{(d^2\alpha/dt^2)_R}\right] \tag{8}$$

In Equation 8 $(d^2\alpha/dt^2)_L$is the maximum of the second derivative of TGA data while $(d^2\alpha/dt^2)_R$ is the minimum of that curve.

The kinetic parameters obtained using Equation 7 are shown in Table 4.

Representative thermograms for PTT, PTT20/ABS80 and PTT80/ABS20 in N_2 atmosphere are indicated in Figures 1–3. The heating rates used are 5, 10, 15, 20 and 40°C/min. Figure 1 indicates

TABLE 4 Kinetic Constants of Virgin PTT, Virgin ABS and Their Blends Calculated using Kissinger Model

		Kissinger				
System	Heating rate °C/min	LnA (min^{-1})	R^2	n	E (kJ/mol)	R^2
Virgin PTT	5 10 15 20 40	32.4	0.998	1.72	186.3	0.998
Virgin ABS	5 10 15 20 40	23.7	0.999	2.36	179.5	0.999
PTT20/ABS80	5 10 15 20 40	31.0	0.986	2.21	214.9	0.986
PTT50/ABS50	5 10 15 20 40	22.1	0.988	2.37	143.7	0.988
PTT80/ABS20	5 10 15 20 40	19.4	0.995	1.49	151.5	0.995

that more than 90% PTT has degraded in a single stage at all five different heating rates. A similar observation is noted for ABS and the blends. The temperature range of decomposition is found to increase with increasing heating rate for all the systems studied.

Tables 2–4 clearly indicate that there are large variations in the calculated apparent activation energies depending on the mathematical approach taken in the analysis and the heating rate and/or degree of conversion values used in these calculations. These observations clearly indicate the problems and pitfalls when selecting and utilizing different analytical methods to solve complex multistage thermal degradations occurring in PTT, ABS and PTT/ABS blends. One situation in which applying different models could be complicated is when several degradation mechanisms occur during the thermal degradation.

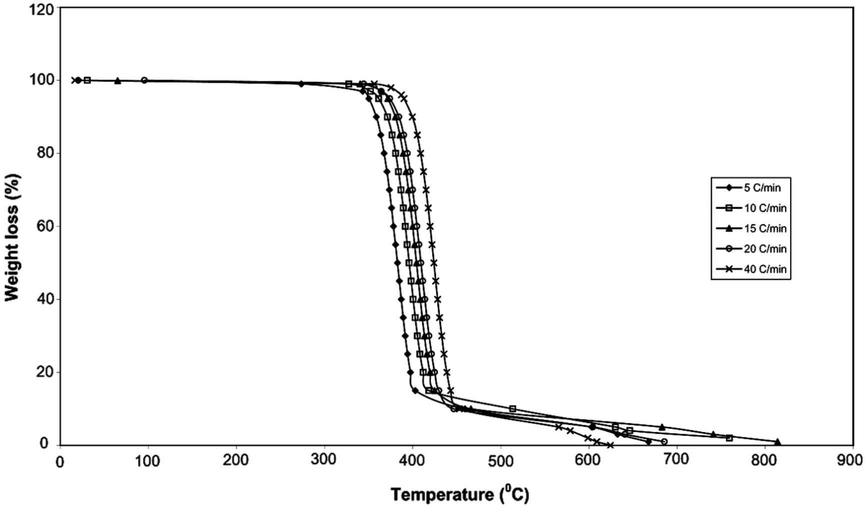

FIGURE 1 TGA curves for PTT heated in N_2 atmosphere.

Figures 4 and 5 show the application of Broido and Horowitz–Metzger models to the degradation of PTT50/ABS50 and PTT80/ABS20. Comparison of the activation energy values obtained using Broido model with that of Horowitz-Metzger models shows discrepancies for PTT data. The low values of activation energy obtained by Broido for

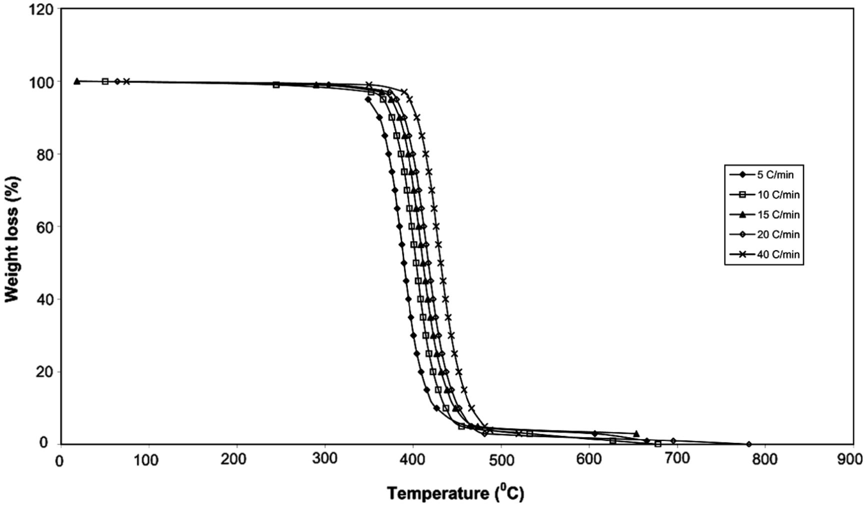

FIGURE 2 TGA curves for PTT20/ABS80 heated in N_2 atmosphere.

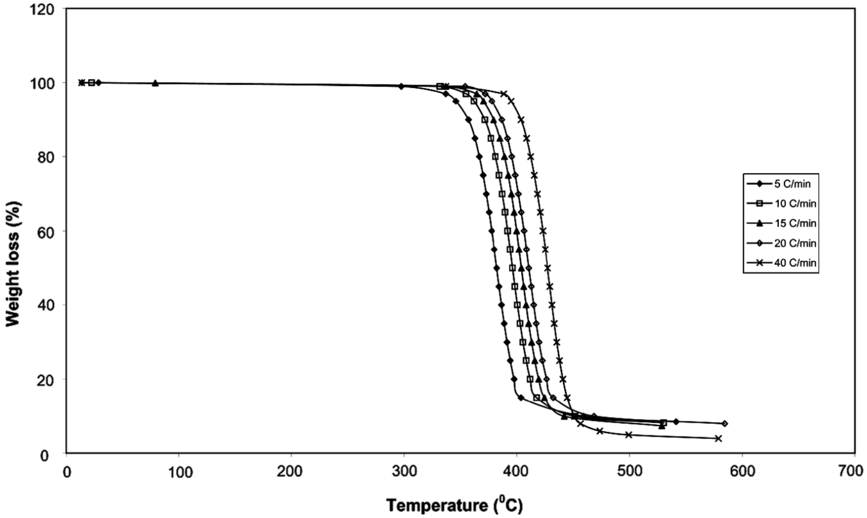

FIGURE 3 TGA curves for PTT80/ABS20 heated in N_2 atmosphere.

PTT seem to be doubtful. Higher activation energy values are obtained using the Horowitz-Metzger model when compared to those of Kissinger and Friedman. The Horowitz-Metzger model depends on the value of

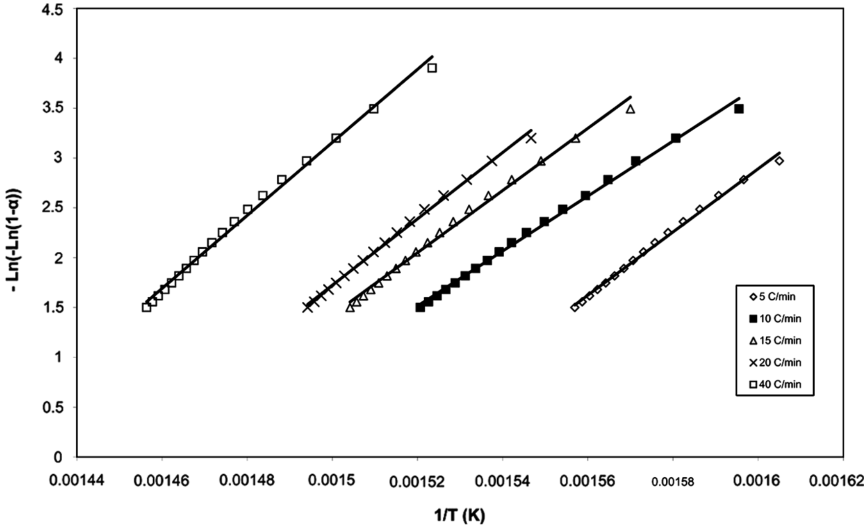

FIGURE 4 Application of Broido's model to the nonisothermal degradation of PTT50/ABS50.

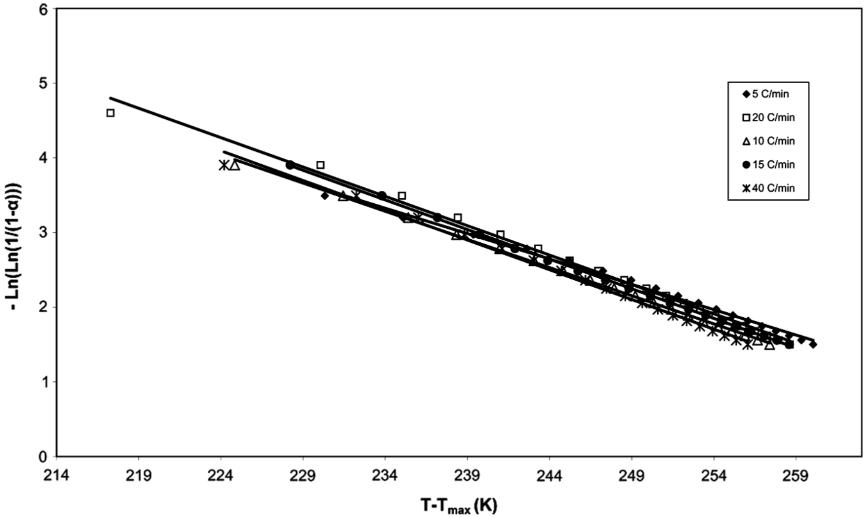

FIGURE 5 Application of the Horowitz–Metzger model to the nonisothermal degradation of PTT80/ABS20.

$T_{\max}$. Variations due to a single point ($T_{\max}$) can lead to changes in the activation energy values.

The use of multiple heating rates also helps to obtain realistic kinetic degradation parameters for the degradation reactions when a polymeric material burns. An example of this is the Kissinger model. Figure 6 is a typical illustration of the plot of $\ln(r/{T_{\max}}^2)$ versus $1/T$. While the Friedman model is applicable to the complete TGA curve, the Kissinger model is utilized for obtaining degradation parameters until 20% conversion. The order of reaction obtained by Kissinger varies between 1.49 and 2.37. The ln A for the blends seem to decrease as the ABS content decreases. The higher ln A value of ABS, compared to PTT, indicates a higher degradation rate, based on the concept of frequency factor. The activation energy given by Kissinger ranges from 143.7 to 214.9 kJ/mol. A drawback of the Kissinger model is that it is based on one point, i.e. the temperature $T_{\max}$, and is thus regarded to have limited applicability. Another drawback of the Kissinger model is that it relies on the value of n, which is obtained using an approximate equation. However, despite the drawbacks, the Kissinger model gives values of activation energy in a range closer to that of the average values given by Friedman.

The Friedman model, on the other hand, does not make any assumptions about $f(\alpha)$ and is therefore capable of providing

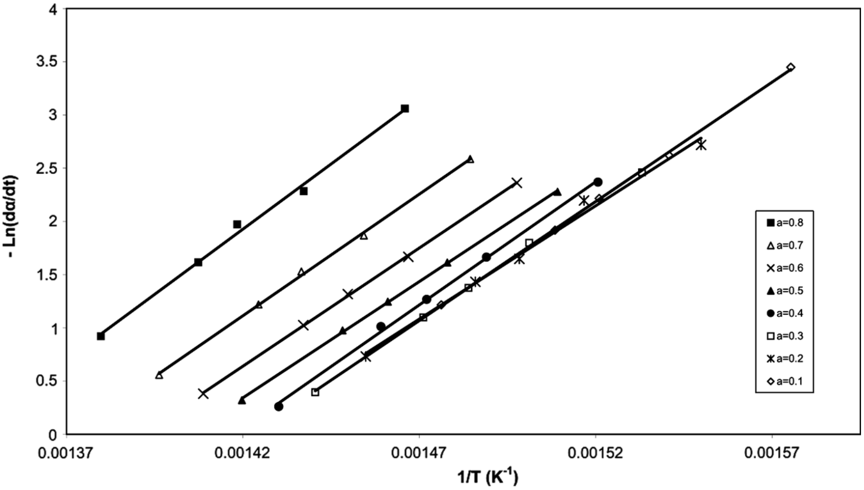

FIGURE 6 Application of the Kissinger model to the nonisothermal degradation of PTT20/ABS80.

reasonably reliable data from temperature-programmed TG. The experimental data fulfill the precision of the Friedman model [13], as shown in Figure 7. Wang et al. [15] have reported an activation energy of 161 kJ/mol for PTT with a $\overline{M}_n$ of 1.3×10^4 g/mol. Because

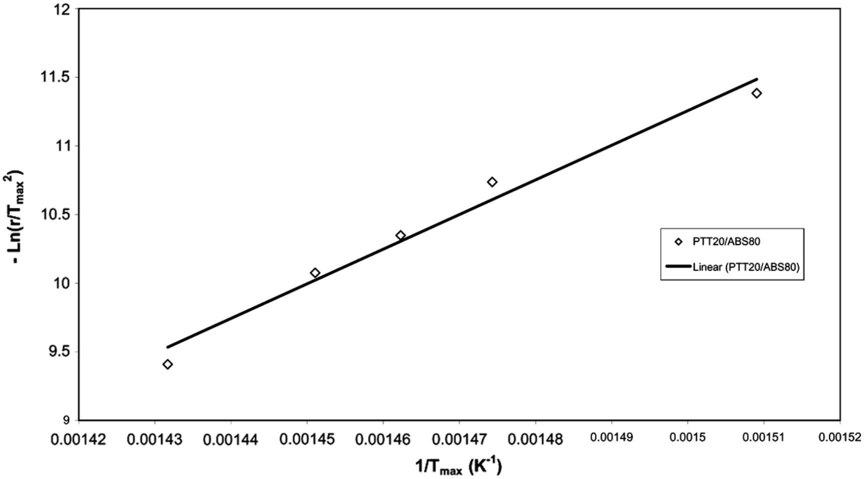

FIGURE 7 Application of the Friedman model to the nonisothermal degradation of PTT20/ABS80.

of the wide variations in the calculated activation energies obtained from Broido and Horowitz-Metzger, we feel that the best method is the one which utilized different conversion steps, namely the Friedman method.

The literature does not contain references to the degradation kinetics of PTT/ABS blends. Thus the degradation data given in Table 3 could be of immense value for knowing the processing range of PTT/ABS blends.

Isothermal studies on degradation of PET were carried out by Cooney et al. [3] and Goodings and Zimmermann [16] at temperatures below 350°C. It is also obvious that degradation kinetic parameters obtained at 350°C will not be equal to those obtained at 500°C. Since the processing temperature of PTT or ABS or PTT/ABS blends will not exceed 400°C, the maximum conversion reached at 400°C will be around 10%. According to the Friedman model, for 10 percent conversion the activation energy obtained is between 170–186 kJ/mol for virgin polymers and their blends.

CONCLUSION

The activation energy values obtained using the Broido method for virgin PTT and virgin ABS do not compare with any of the other methods. These values therefore might be unreliable. The Horowitz–Metzger values are found to be higher than those obtained using Kissinger and Friedman. Since the Horowitz–Metzger model is T_{max} dependent, the activation energy values obtained using this model are also questionable. The decreasing $\ln A$ values for the blends obtained using the Kissinger method indicate that as the PTT content in the blend increases, the volatilization rate decreases. It seems that the differential method of Friedman provides a satisfactory mathematical approach to obtain kinetic parameters for the thermal degradation of PTT/ABS blends. The average activation energies for virgin PTT, ABS, PTT20/ABS80, PTT50/ABS50 and PTT80/ABS20 calculated using Friedman are 194, 169, 188, 186 and 182 kJ/mol, respectively.

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