Kinetics of Thermal Degradation of Thermotropic Poly(*p*-oxybenzoate-*co*-ethylene-2,6-naphthalate) by Single Heating Rate Methods

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ABSTRACT: The kinetics of thermal degradation of thermotropic liquid crystalline poly(*p*-oxybenzoate-*co*-ethylene-2,6-naphthalate) (PHB/PEN) with the monomer ratio of 60 : 40 and PEN in nitrogen was studied by dynamic thermogravimetry (TG). The kinetic parameters, including the activation energy E_a, the reaction order n, and the frequency factor $\ln(Z)$ of the degradation reaction for PHB/PEN (60 : 40) and PEN were analyzed by the single heating rate methods of Friedman and Chang. The effects of the heating rate and the calculating method on the thermostable and degradation kinetic parameters are systematically discussed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3915–3920, 2004

Key words: poly(*p*-oxybenzoate-*co*-ethylene 2,6-naphthalate); liquid crystalline polyester; thermal degradation; thermogravimetry; kinetics; thermostability

INTRODUCTION

Poly(oxybenzoate-*co*-ethylene terephthalate) (PHB/PET) copolymer, is a well-known and commercially available liquid crystalline polymer, which has been studied extensively over the past years.[1–4] Poly(ethylene-2,6-naphthalate) (PEN) is a slow-crystallizing polymer.[5–7] The naphthalene moiety in PEN provides more stiffness than PET to the linear polymer backbone, leading to improved thermal resistance; excellent mechanical properties, such as tensile properties and dimensional stability; and outstanding gas barrier characteristics. PHB/PEN copolymer might have more applications and letter properties than PHB/PET copolymer. Hitherto, no attention has been given to its thermal degradation behavior.

Thermal stability of a polymeric material is one of the most important properties for both processing and application. Thermogravimetry (TG) is a technique widely used to characterize thermal degradation of polymer materials. In this article, TG and differential thermogravimetry (DTG) measurements of PHB/PEN polymer are reported; the thermal degradation temperature and the kinetics of PHB/PEN copolymer with the monomer mole ratio, PHB/PEN (60 : 40), and PEN were studied by two kinds of calculating methods through nonisothermal TG thermograms. The dependencies of the degradation temperature and kinetic parameters on the heating rate and calculating method are discussed in detail.

EXPERIMENTAL

PHB/PEN polymer with the structural formula shown in Scheme 1 was synthesized following the procedure described elsewhere.[8,9] The intrinsic viscosity of the PHB/PEN polymer was measured at 0.5% concentration in phenol/1,1,2,2-tetrachloroethane (1 : 1, w/w) at 25°C.

The TG and DTG thermograms were obtained by using a Perkin–Elmer 7 series analyzer under a dynamic nitrogen atmosphere flowing at 50 ml/min, varying heating rate from 5 to 45 K/min, while the sample weights were kept at 1.0 ± 0.1 mg.

There are several methods (proposed by Friedman,[10] Freeman and Carroll,[11] Chang,[12] Flynn and Wall,[13] Chaterjee and Conrad,[14] Horowitz and Metzger,[15] Kissinger,[16] Coats and Redfern,[17] Van Krevelen,[18] Reich,[19] and Ozawa[20]) for calculating kinetic parameters that depend not only on the experimental conditions but also on the mathematical treatment of the data. We will use the Friedman and Chang methods to evaluate the activation energy E_α the reaction order n, and the frequency factor Z based on a single heating rate measurement without making any assumptions. Detailed descriptions of the two methods are not given because the methods for evaluating the kinetic parameters from TG/DTG traces are easily available from the literature.[10,12] The equations employed in the methods are listed below.

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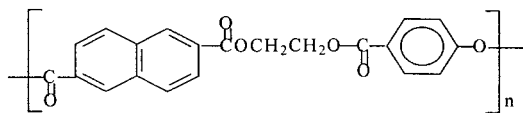
PEN/PHB

Scheme 1

Friedman method[10]

$$\ln (Z) = \ln (d\,\alpha/dt) - n\,\ln(1 - \alpha) + E_a/(RT) \quad (1)$$

where α is the weight loss of the polymer undergoing degradation at time t; R is the gas constant (8.3136J $mol^{-1}\,K^{-1}$), and T is the absolute temperature (K); Z, n, E_a are the frequency factor, the order, and the activation energy of the thermal degradation reaction, respectively. The plot of $\ln(d\,\alpha/dt)$ versus $1/T$ should be linear with $-E_a/R$ as the slope. Additionally, the $E_a/(n\,R)$ value could be determined from the slope of the linear plot of $\ln(1 - \alpha)$ versus $1/T$.

Chang method[12]

Equation (1) can be rewritten in the following form:

$$\ln\,[(d\,\alpha/dt)/(1 - \alpha)^n] = \ln(Z) - E_a/(R\,T) \quad (2)$$

A plot of $\ln[(d\,\alpha/dt)/(1 - \alpha)^n]$ against $1/T$ will yield a straight line if the degradation order n is selected correctly. The slope and intercept of this line will provide the $-E_a/R$ and $\ln(Z)$ value, respectively.

RESULTS AND DISCUSSION

The TG and DTG curves of PHB/PEN (60 : 40) and PEN in nitrogen at heating rates of 10,15,20,30,35,45

and 5,10,15,20,30,35 K/min are shown, respectively, in Figures 1 and 2.

The DTG curves of PHB/PEN (60 : 40) and PEN indicate that only one weight-loss stage occurs during degradation. PHB/PET copolymer with monomer mole ratio 60 : 40 shows two weight-loss stages in nitrogen at low heating rates (1 and 2 K/min). Generally, in the case of random copolymer, stepwise degradation of individual A and B homopolymer segments may merge into one-step degradation. The maximum degradation temperature of the random copolymer mediates between the maximum degradation temperatures of the two corresponding homopolymers. For stepwise degradation of individual A and B segments in block copolymer, however, the maximum degradation temperatures get close to each other.[4]

The degradation behavior of the PHB/PEN polymer under nitrogen is quite different from that of the respective PHB or PEN homopolymers. The TG results obtained and discussed so far could be taken as proof of the presence of a random sequence distribution in the polymer backbone because no distinct peaks representative of thermal degradation of individual PHB and PEN homopolymers are observed during the thermal degradation of the PHB/PEN polymer. In the case of random copolymer, generally stepwise degradation of individual PHB and PEN homopolymer segments merge into single steps located in between the maximum degradation temperatures of the corresponding homopolymers.

Kinetics of nonisothermal degradation analyzed by single heating rate methods

All of the methods can determine the kinetic parameters for the thermal degradation of PHB/PEN (60 : 40) and PEN by using only one heating rate. Figures 3
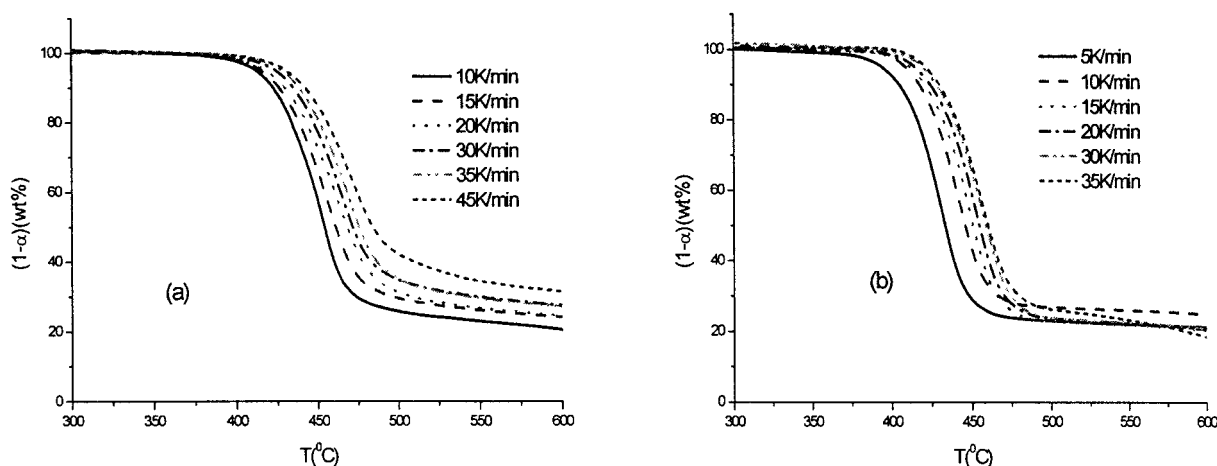

Figure 1 Dynamic TG curves at six heating rates in nitrogen: (a) PHB/PEN (60 : 40); (b) PEN.
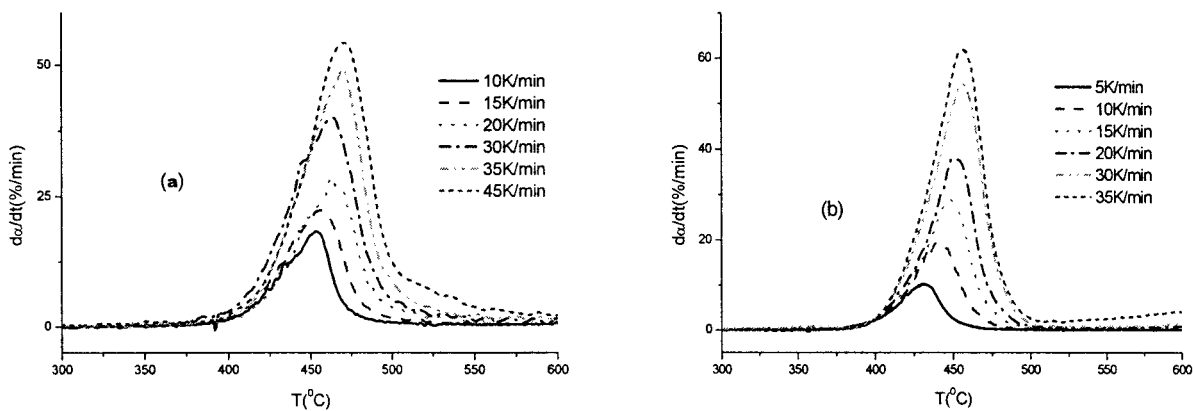
Figure 2 Dynamic DTG curves at six heating rates in nitrogen: (a) PHB/PEN (60 : 40); (b) PEN.

and 4 show the relationship given by eq. (1) of the Friedman method.

Figure 5 shows the relationship proposed by Chang where the degradation orders are assumed to be 1.2–1.7 for PHB/PEN (60 : 40) and 0.7–1.6 for PEN. Because the lines of $\ln[(d\ \alpha/dt)/(1-\alpha)^n]$ versus $1/T$

overlapped each other, the Waterfall Graph (in Microcal Origin version 5.0, Microcal Software, Inc., Northampton, MA) was used to obtain a distinct view. Each dataset is displayed as a line data plot, which is offset by a specified amount in both the X and Y directions. For the Chang method, the absolute X and
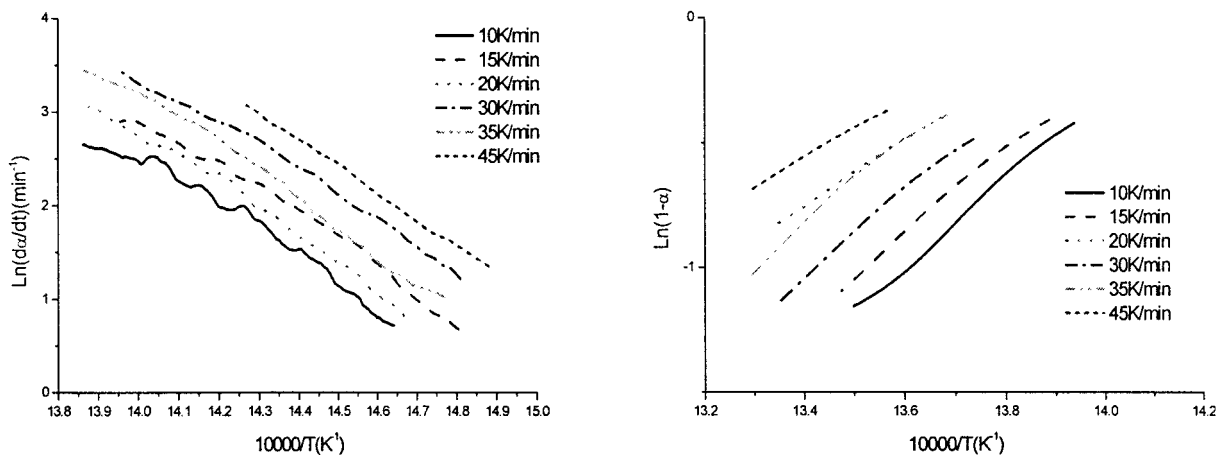

Figure 3 Friedman plots of $\ln(d\ \alpha/dt)$ or $\ln(1-\alpha)$ versus $1/T$ for PHB/PEN (60 : 40) in nitrogen at six heating rates.
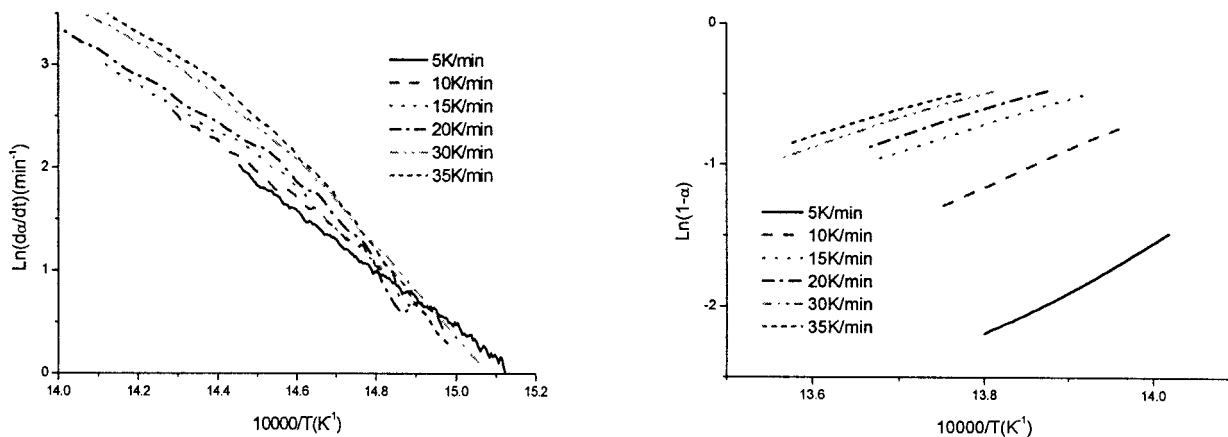

Figure 4 Friedman plots of $\ln(d\ \alpha/dt)$ or $\ln(1-\alpha)$ versus $1/T$ for PEN in nitrogen at six heating rates.
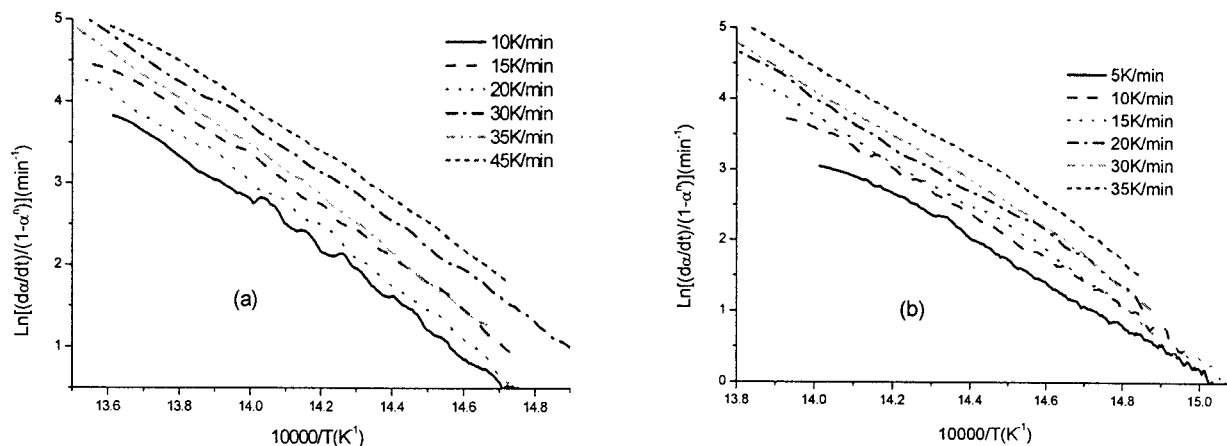
Figure 5 Chang plots of $\ln[(d\,\alpha/dt)/(1-\alpha)^n]$ versus $1/T$ for the thermal degradation in nitrogen at six heating rates: (a) PHB/PEN (60 : 40); (b) PEN.

Y values do not affect the calculation of thermal degradation kinetic parameters, so the offset X- and Y-axes are omitted here.

Figure 6 shows the relationship between the maximum weight loss rate $(d\,\alpha/dt)_m$ and heating rate for PHB/PEN (60 : 40) and PEN.

The kinetic parameters calculated by the two single heating rate methods for the PHB/PEN (60 : 40) are summarized in Table I. The data for the PEN are listed in Table II.

The effect of heating rate

From Table I, it can be concluded that the kinetic parameters of PHB/PEN (60 : 40) change with the heating rate. Most of E_a, $\ln(Z)$, T_d, and T_{dm} values increase significantly with heating rate, whereas the n values stay roughly the same as the heating rate changes from 10 to 45 K/min. That is to say, when the
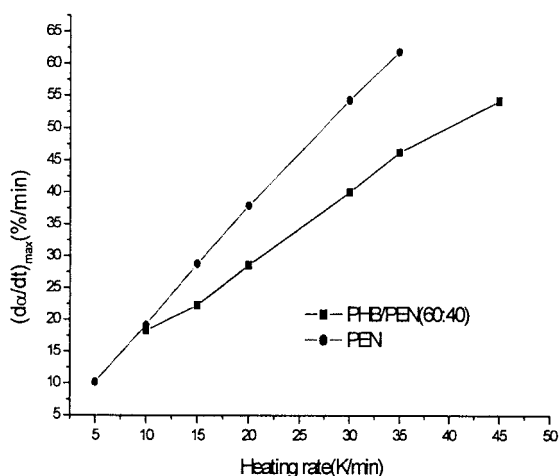
heating rate is high enough, the effect of the concentration of degradation products from PHB/PEN (60 : 40) on thermal degradation reaction will remain roughly unchanged. From Table II it can be seen that the variation of the E_a, $\ln(Z)$, T_d, and T_{dm} for PEN with heating rate is similar to that of PHB/PEN (60 : 40). The reaction order n varies little with the heating rates adopted in this article.

Additionally, Figure 6 shows $(d\,\alpha/dt)_m$ values increase linearly with heating rate for PHB/PEN (60 : 40) and PEN.

Generally, the variation of these kinetic parameters reveals the change of thermal degradation mechanism (i.e., transformation from the diffusion-controlled kinetics into the decomposition-controlled kinetics, or vice versa).[21] At lower heating rates, the diffusion of the degradation products apparently does not affect the kinetics of the degradation process, so kinetic parameter values were found to be lower. Alternatively, at a higher heating rate, the decomposition of the polymer is probably faster than the diffusion of the degradation products through the polymer melt; therefore, the kinetics of the degradation process are under diffusion control of degradation products. Consequently, higher kinetic parameters were observed with increasing heating rate.[4]

Additionally, there are some differences in the kinetic data calculated by using the different methods, as shown in Tables I and II. The Friedman method gave lower E_a values but higher n values of the two methods. As shown in Figure 5, the Chang method actually tends to form straight lines in the widest temperature range, which means a smaller error in the calculation of the kinetic parameters by this method. However, the temperature range used for the determination of the kinetic parameters by the Friedman method is wide enough to obtain reliable results.

Figure 6 Effect of heating rate on the maximum decomposition rate.

TABLE I
Kinetic Parameters of Thermal Degradation of PHB/PEN (60 : 40) Under Nitrogen Calculated
by Two Single Heating Rate Methods

Heating rate (K/min)	T_d/T_{dm} (°C)	Friedman			Chang			Average[a]		
		E_a (KJ/mol)	n	ln(Z) (min^{-1})	E_a (KJ/mol)	n	ln(Z) (min^{-1})	E_a (KJ/mol)	n	ln(Z) (min^{-1})
10	420.47/452.87	216	1.4	39.2	236	1.2	42.8	226	1.3	41.0
15	423.07/456.14	223	1.6	40.7	238	1.6	43.4	231	1.6	42.1
20	425.85/463.12	234	1.5	41.9	227	1.7	41.2	231	1.6	41.6
30	427.19/464.45	218	1.5	40.0	244	1.7	44.8	231	1.6	42.4
35	431.21/469.74	240	1.7	43.8	247	1.7	45.1	244	1.7	44.5
45	432.65/470.41	237	1.5	42.5	226	1.7	41.5	232	1.6	42.0
Average[b]	426.74/462.79	228	1.5	41.4	236	1.6	43.1	232	1.6	42.3

[a] Calculated with different analyzed methods.
[b] Calculated with the heating rate ranging from 10 to 45 K/min.

Thermal stability

No matter which method was used above, the fundamental equation is the same:

$$d\,\alpha/dt = Z(1-\alpha)^n \exp\left[-E_a/(R\,T)\right] \quad (3)$$

Because the value of $(1-\alpha)$ is always less or equal to 1, $d\,\alpha/dt$ decreases with increasing n, and the zero order ($n = 0$) characterizes the most rapid degradation reaction.[4] From eq. (3), it can be concluded that higher n and E_a values or a lower Z value results in a lower $d\,\alpha/dt$ value, which means higher thermal stability.

As shown in Tables I and II, the average n, T_d, and T_{dm} values calculated from the heating rate for PHB/PEN (60 : 40) are larger than those for PEN, whereas $(d\,\alpha/dt)_m$ and ln(Z) values at different heating rates for PHB/PEN (60 : 40) are lower than those for PEN. This may be attributed to the difference between PHB/PEN (60 : 40) and PEN in molecular structures. It has been mentioned that the higher the n value, the slower the degradation. More aromatic carbon atoms (or less hydrogen atom) will decrease the thermal degradation rate and increase thermal stability. PHB/PEN (60 : 40) possesses a higher n value and lower degradation rate than PEN because of the existence of PHB units. On the contrary, the average E_a value calculated from the heating rate is lower than that for PEN. This could be attributed to the effect of molecular weight. In the melt polycondensation process, PEN degrades first and then copolymerizes with p-acetoxybenzoic acid. Because of the poor copolymerization ability, long blocks of PHB units formed, which may increase the melt viscosity greatly and may make further polycondensation become impossible in the melt state. So, PHB/PEN (60 : 40) studied here, which was obtained through melt polycondensation, has lower molecular weight than PEN. It is evident that the lower the molecular weight, the more the end groups. End groups can initiate thermal degradation.[4] As a result, lower molecular weight leads to a lower E_a value. Therefore, a higher E_a value would be obtained if the molecular weight of PHB/PEN (60 : 40) could be increased through solid-state polymerization.

CONCLUSIONS

On the basis of TG and DTG results obtained at a single heating rate, some important kinetic parameters

TABLE II
Kinetic Parameters of Thermal Degradation of PEN under Nitrogen Calculated by Two Single Heating Rate Methods

Heating rate (K/min)	T_d/T_{dm} (°C)	Friedman			Chang			Average[a]		
		E_a (KJ/mol)	n	ln(Z) (min^{-1})	E_a (KJ/mol)	n	ln(Z) (min^{-1})	E_a (KJ/mol)	n	ln(Z) (min^{-1})
5	401.85/429.68	235	0.9	42.7	253	0.7	46.2	244	0.8	44.5
10	405.87/438.66	235	1.1	42.4	254	1.0	46.3	245	1.1	44.4
15	418.64/448.58	243	1.5	44.3	270	1.4	49.2	257	1.5	46.8
20	420.45/449.74	251	1.6	46.0	270	1.5	49.3	261	1.6	47.7
30	421.63/456.10	268	1.6	48.8	272	1.6	49.9	270	1.6	49.4
35	423.90/456.69	263	1.7	48.1	272	1.6	50.0	268	1.7	49.1
Average[b]	415.39/446.58	249	1.4	45.4	265	1.3	48.5	257	1.4	47.0

[a] Calculated with different analyzed methods.
[b] Calculated with the heating rate ranging from 5 to 35 K/min.

of thermal degradation for the thermotropic liquid crystalline PHB/PEN (60 : 40), such as the activation energy, the degradation order, and the frequency factor, have been calculated by the Friedman and Chang methods. The kinetic parameters exhibit a dependence on molecular weight, heating rate, and method of calculation. The degradation seems to be a random scission process of the ester linkages.

Compared with PEN, PHB/PEN (60 : 40) has higher T_d, T_{dm}, and n, but lower $(d\,\alpha/dt)_m$, E_a, and $\ln(Z)$. All these parameters except for E_a indicate that PHB/PEN (60 : 40) is more heat stable than PEN. The T_d, T_{dm}, and $(d\,\alpha/dt)_m$ values, as well as E_a and $\ln(Z)$ values derived from single heating rate methods, increase significantly with heating rates.

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