

Research Article

Enthalpy-Entropy Compensation in Polyester Degradation Reactions

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In an earlier work the author had studied the degradation kinetics of polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT), and polybutylene terephthalate (PBT) under nonisothermal conditions in air and N_2 at heating rates of 5, 10, 15, and 20°C/min. In this paper the kinetic degradation parameters of PET, PTT, and PBT were estimated using the Coats-Redfern method for two different weight loss regions ranging from 2–8% (Zone I) and 8–40% (Zone II). A comparative analysis of the enthalpy-entropy compensation effect for these polyesters in air and N_2 is presented. A linear relationship was found to exist between entropy and enthalpy values. The following criteria were applied to establish an enthalpy-entropy compensation effect and to check the presence of an isokinetic temperature: (a) Exner's plot of $\log k_{3T_1}$ versus $\log k_{3T_2}$, and (b) Krug et al. linear regression of ΔH versus ΔG . By the use of the latter two methods, varying isokinetic temperatures were obtained. These temperatures were not in the range of the experimental work conducted, indicating that these systems do not display compensation phenomena.

1. Introduction

Kinetic studies carried out on similar compounds with a correctly chosen mechanism function $f(\alpha)$ (α is the weight fraction of material decomposed at temperature T and time t) exhibit a linear relationship between the logarithm of the preexponential factors and activation energies known as the compensation effect [1–5]. Several theories and explanations for such compensation behavior have been put forth [6–8].

In the case of thermal decomposition of solids, the existence of the compensation effect permits certain conclusions concerning the decomposition mechanism and thermal characteristics of the compounds under investigation. The changes of Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for the degradation reactions can be obtained by studying the kinetics of the thermal decomposition of solid compounds with nonisothermal heating using the thermogravimetric (TG) curves and a correct algebraic expression of the conversion function, $f(\alpha)$.

The reaction mechanism for polymer degradation is a very complex chain mechanism that includes initiation, propagation, and termination reactions. Normally, two types of reaction models, the first order $f(\alpha)_1 = (1 - \alpha)$ and the

second order $f(\alpha)_2 = (1 - \alpha)^2$, are used for the thermal degradation studies of polymers.

The author has previously reported [5] the kinetic parameters characterizing the degradation of PET, PTT, and PBT in air and N_2 using data from nonisothermal thermogravimetry and the calculation procedure of Coats and Redfern [5].

The aim of this work was to obtain the thermodynamic parameters, ΔS , ΔH , and ΔG , relating to the degradation of PET, PTT, and PBT and to determine whether the false compensation effect (presence of an isokinetic temperature) observed in the previous work can also be noticed when the thermodynamic parameters (enthalpy-entropy relationship) are used to check the compensation effect. Plots of ΔS and ΔH were used to confirm this result.

2. Theoretical Background

Mathematical analysis was performed on the TG data using the integral method of Coats and Redfern, [9] which has been used successfully for studies on the kinetics of decomposition of solid substances [10–14]. The activation energy (E) and

the preexponential factor (A) for the degradation of PET, PTT, and PBT have been previously calculated from the TG curves.

Degradation of polymers can be described with chemical reactions of different rate constants [15]. Because the molecular weight of a chain reduces continuously throughout a process the dependence of chain length becomes weak. Therefore the dependence of rate constant of degradation on molecular weight is normally observed at moderate values of molecular weight [16]. Breakdown of the chain molecules leads to an increase of the number of molecules and a decrease of the length, thus altering the dependence of the system free energy on the molecular length [16, 17].

Kinetics of a degradation process can be described by the theory of activated complexes [18, 19]. On assuming that the system equilibrium can be achieved faster at given composition of solution, than the ongoing degradation process the constant rate of reaction can be defined by free energies of formation of initial chain and activated complex by [20–22]:

$$k = \frac{xek_B T}{h} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{E}{RT}\right), \quad (1)$$

where k is the degradation rate constant, x is a transmission coefficient (unity for monomolecular reactions), k_B is the Boltzmann constant, h is the corresponding Planck's constant, $e = 2.7183$ is the Neper number, and ΔS is the change of entropy for the active complex formation [23]. Equation (1) is based on the basic Arrhenius equation:

$$k = Ae\left(\frac{-E}{RT}\right), \quad (2)$$

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

Taking into account the preexponential constant A , the following expression is obtained:

$$A = \frac{xek_B T}{h} \exp\left(\frac{\Delta S}{R}\right), \quad (3)$$

and ΔS can be calculated as follows:

$$\Delta S = R\left(\ln A - \frac{\ln xek_B T}{h}\right), \quad (4)$$

where A is the preexponential factor in the Arrhenius equation. Because

$$E = \Delta H + RT. \quad (5)$$

The change of the enthalpy ΔH and Gibbs free energy ΔG can be calculated using the following equation:

$$\Delta G = \Delta H - T\Delta S. \quad (6)$$

ΔS , ΔH , and ΔG were calculated at $T = T_p$ (T_p is the differential peak temperature. This temperature characterizes the highest rate of the process).

3. Experimental

3.1. Materials. PET, PTT, and PBT with number average molecular weight (M_n) = 20,000, 28,000, and 26,000 used here was a product of Century Enka. Ltd. (India).

3.2. Polymer Degradation. To determine the kinetic degradation parameters, all the polymers were subjected to TGA. The decomposition temperatures for PET, PTT, and PBT were measured using an SDT 2960 simultaneous DSC-TGA instrument supplied by TA Instruments Ltd. The TGA machine was calibrated using ASTM method, E 1582-93, "standard practice for calibration of temperature scale for thermogravimetry" (ASTM, 1993). The heating rates chosen were 5, 10, 15, and 20°C/min, and the temperature range scanned was 30 to 700°C. The weight loss of the polymers was determined by loading 7–8 mg into a platinum crucible and heating it at one of the rates chosen under a steady flow of air and nitrogen (20 mL/min). The output signals from the TA 2960 analyzer were fed to a computer interface, where the data was stored.

4. Results and Discussion

PET, PTT, and PBT were analyzed using a differential scanning calorimeter (DSC) to determine its melting point. The melting points were found to be 254, 240, and 227°C, respectively. Differential thermal analysis (DTA) of the thermograms for PET, PTT, and PBT revealed that the maximum weight loss temperature for degradation occurred at around 40% weight loss [5]. Initial weight loss till around 2 weight percent was not considered since it could be due to volatilization of low molecular weight compounds present in the polymers.

The thermograms for all the three polymers had two linear regions (2–8% (Zone 1) and 8–40% (Zone 2)) having correlation coefficient (r) above 0.99 was found for all the three polymers. Figure 1 indicates the linear region obtained for zone 1 (2–8%) which corresponds to the horizontal portion of the degradation curve, while Figure 2 indicates the linear region for zone 2 which corresponds to the vertical portion of the thermogram covering the range 8–40%. The maximum rate of weight loss temperature (T_p) (peak of differential thermal analysis (DTG) curve) was obtained from the thermogravimetric data using the manufacturer thermal analysis software.

The Coats Redfern (CR) integral method was used in the previous work [5] to estimate the degradation kinetic parameters $\ln A$ and E . The CR equation is given as follows:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \left(\frac{AR}{E\beta}\right) - \frac{E}{RT}, \quad (7)$$

where β is the heating rate and the other parameters are the same as those found in the equations above.

First order ($f(\alpha)_1 = (1 - \alpha)$) and a second order ($f(\alpha)_2 = (1 - \alpha)^2$) models, the integral forms of which are $g(\alpha)_1 = [-\ln(1 - \alpha)]$ and $g(\alpha)_2 = [(1 - \alpha)^{-1} - 1]$, [23] were fitted to the Coats-Redfern (7) to obtain the activation energy (E)

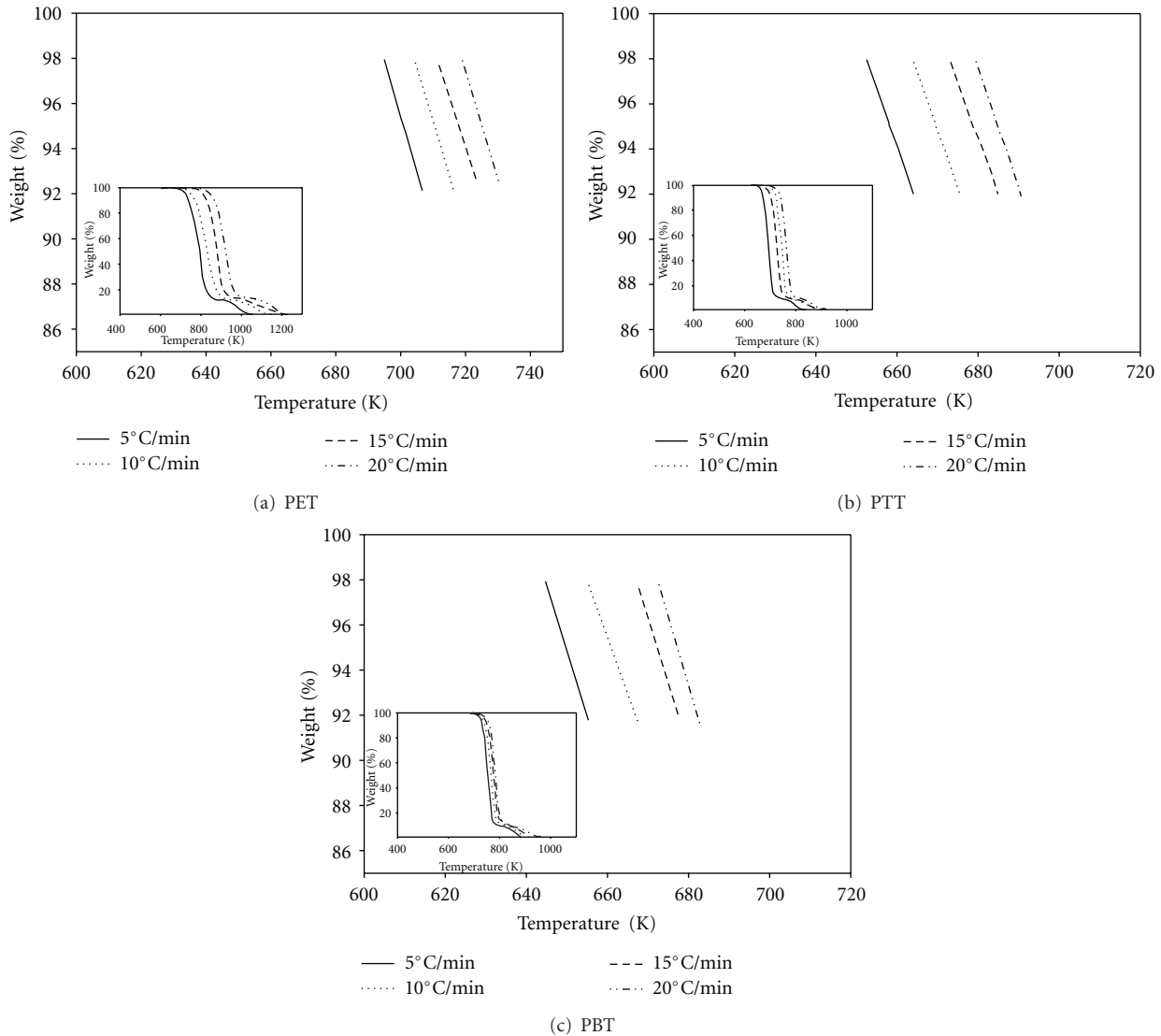


FIGURE 1: Plot of weight loss (2–8% conversion range) as a function of temperature for polyester degradation in air atmosphere (zone 1).

and the preexponential factor for degradation of these polyesters. The E and A for the two different $g(\alpha)$ functions were calculated at constant heating rates by fitting $\ln g(\alpha)/T^2$ versus $1/T$ plots. It was observed that when $g(\alpha)_1$ was used for the Arrhenius parameter estimation in the CR equation, correlation coefficient values greater than 0.99 was obtained (Figure 3). When $g(\alpha)_2$ was used in the CR equation, the plots obtained had a correlation coefficient less than 0.97. Figure 4 is a plot indicating the poor fit.

Figures 5 and 6 indicate that linear plots obtained between $\ln A$ and E using Arrhenius equation. It has correlation coefficients greater than 0.99 for all the polyesters degraded in air and N_2 . In some systems, [24, 25] it has been observed that the activation energy varies under different measuring conditions. It is also found that the variation in activation energy is accompanied by a change in A that is; a large activation energy is accompanied by a large preexponential factor and vice versa, a phenomena often referred to as compensation effect.

The frequency factor (A) given in (3) contains an entropy term ($\exp \Delta S/R$). The values of A will reflect in a specific way on the change of entropy for the formation of degradation products from the solid polymer. The enthalpy-entropy and free energy values computed using (3), (5), and (6) are reported in Table 1. It is noted that higher E has low entropy values. The ΔS values are also found to be negative. As anticipated, the graphical representation of the dependence between the values of ΔS and E for the polyesters studied shows a linear relationship for all the systems (Figures 7 and 8). Another obvious relationship found from these plots is the existence of a linear relationship between ΔS and E which implies a direct proportionality between these two quantities. The E values thus have an effect on the values of the change in entropy. As the value of E increases, the value of ΔS was also found to increase for all the polyesters. The relationships observed can be interpreted, first, as a proof that the activated complex (before forming gaseous products) had a less organized structure and the rearrangements taking place were

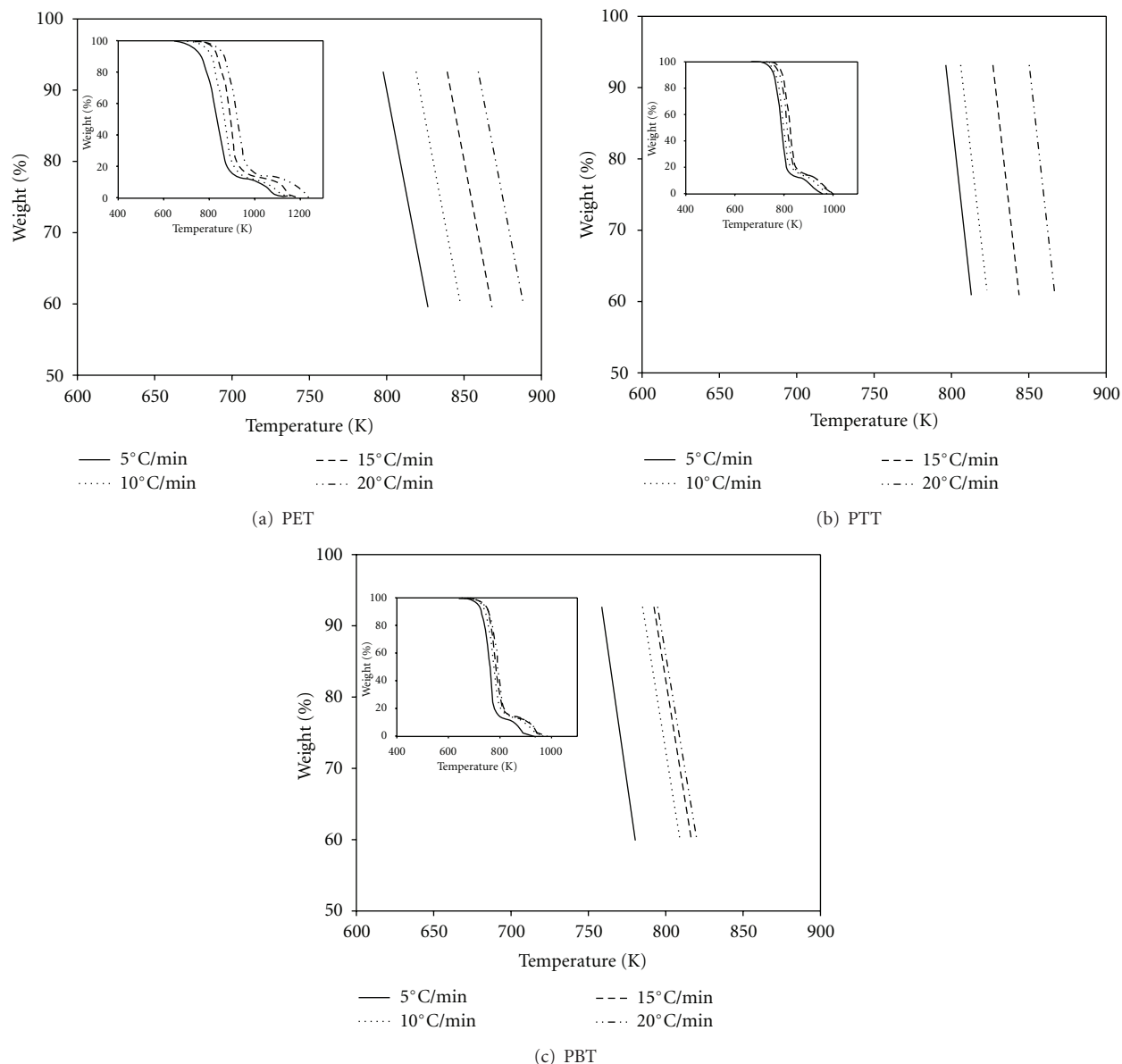


FIGURE 2: Plot of weight loss (8–40% conversion range) as a function of temperature for polyester degradation in N_2 atmosphere (zone 2).

accompanied by an increase in the entropy of the system. The degrees of freedom of the unstable activated complex formed before degradation into gaseous products were more than the degrees of freedom of the parent polyester. The slopes and the intercepts of the lines observed in Figures 7 and 8 were found to be not identical, possibly indicating that there could be different dissimilar chemical processes. Figures 7 and 8 show that the value of ΔS for PET was higher than that for PTT and PBT, possibly implying that the corresponding activated complexes for PET degradation have a lower degree of arrangement (higher entropy) than the initial state. According to the theory of the activated complex, [26] thermal degradation of PBT and PTT may be interpreted as a fast reaction, while thermal degradation of PET is a slow reaction. The correlation coefficient (r) values of the latter

plots were found to be greater than 0.99. In deducing the compensation effect from temperature dependent data, the temperature dependence of a suitable kinetic parameter, k , is analyzed by making Arrhenius plots of $\ln k$ versus $1/T$. The slope and intercept of the resulting plots are reprocessed in the light of the theory of formation of an active complex [20] to yield estimates of enthalpy and entropy. The values of enthalpy and entropy given in Table 1 tells us about the changes in the internal structure or organization during the degradation process. The majority of the researchers have concluded that thermodynamic compensation in any chemical reaction occurs because of the linear relationship of the enthalpy-entropy plot, which is supported by the high correlation coefficient [24]. Plotting enthalpy against entropy yields a “compensation plot,” typically a straight line when

TABLE 1: Kinetic characteristics of different polyesters.

		PBT-N ₂					PTT-N ₂					PET-N ₂							
		β	T_p	E	ΔS	ΔG	ΔH	β	T_p	E	ΔS	ΔG	ΔH	β	T_p	E	ΔS	ΔG	ΔH
Zone 1	5	648	270	-0.015	275	265	5	673	439	-0.022	448	433	5	695	483	-0.169	594	477	
	10	669	278	-0.011	280	273	10	693	450	-0.022	458	444	10	710	494	-0.148	593	488	
	15	674	295	-0.005	292	289	15	718	429	-0.025	441	423	15	717	480	-0.174	599	474	
	20	682	281	-0.010	283	276	20	726	429	-0.025	441	423	20	725	475	-0.182	601	469	
Zone 2	5	771	253	-0.016	258	246	5	799	310	-0.027	326	304	5	901	459	-0.031	480	452	
	10	793	273	-0.012	276	266	10	822	370	-0.022	381	363	10	972	470	-0.029	490	462	
	15	800	295	-0.008	294	288	15	834	379	-0.021	389	372	15	949	443	-0.036	470	435	
	20	807	266	-0.013	270	259	20	848	290	-0.031	309	283	20	973	430	-0.042	463	422	
		PBT-AIR					PTT-AIR					PET-AIR							
		β	T_p	E	ΔS	ΔG	ΔH	β	T_p	E	ΔS	ΔG	ΔH	β	T_p	E	ΔS	ΔG	ΔH
Zone 1	5	652	304	-0.031	318	298	5	657	328	-0.045	352	323	5	701	397	-0.168	509	391	
	10	663	390	-0.015	395	385	10	671	397	-0.033	413	391	10	706	463	-0.151	564	457	
	15	670	382	-0.017	388	376	15	679	411	-0.030	426	405	15	719	446	-0.157	552	440	
	20	676	407	-0.012	410	402	20	686	389	-0.037	408	383	20	725	402	-0.167	517	396	
Zone 2	5	767	184	-0.036	205	178	5	763	274	-0.040	298	268	5	901	309	-0.029	328	302	
	10	790	207	-0.021	216	200	10	787	300	-0.036	321	293	10	905	391	-0.019	401	383	
	15	805	196	-0.027	212	190	15	803	296	-0.036	318	289	15	928	432	-0.013	436	424	
	20	808	179	-0.042	205	172	20	823	280	-0.039	305	273	20	950	382	-0.021	393	374	

β : heating rate (°C/min), T_p : peak degradation temperature (°C), E : activation energy (kJ/mol), ΔS : change in entropy (kJ/mol), ΔG : change in free energy (kJ/mol), ΔH : change in enthalpy (kJ/mol).

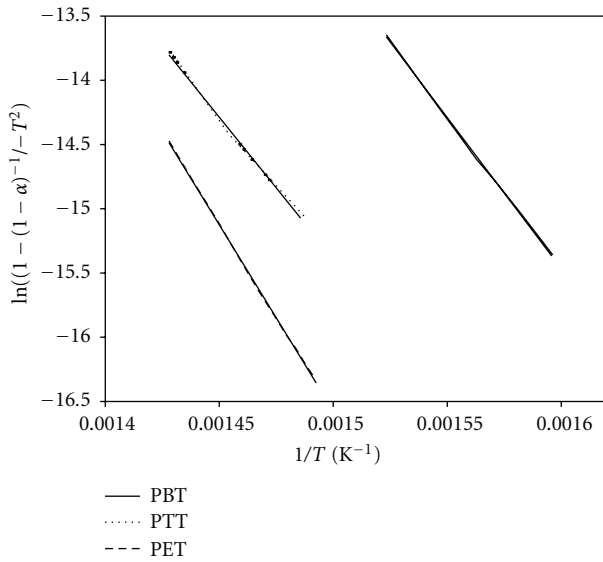


FIGURE 3: Plot of $\ln[1 - (1 - \alpha)^{-1}]/-T^2$ versus $1/T$ for different polyesters degraded in air atmosphere (zone 1).

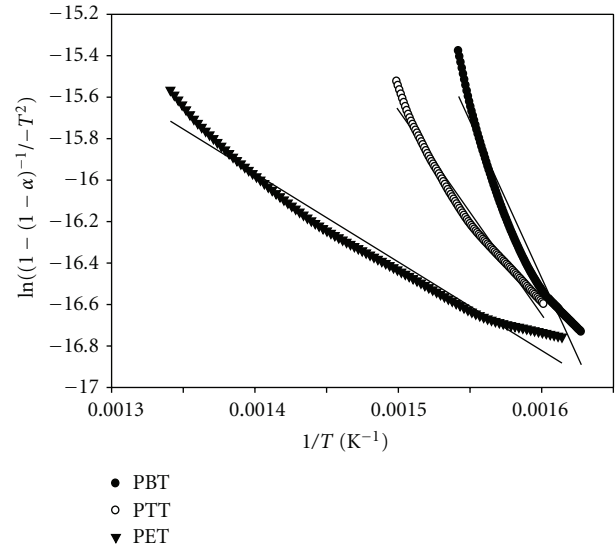


FIGURE 4: Plot of $\ln[1 - (1 - \alpha)^{-1}]/-T^2$ versus $1/T$ for different polyesters degraded in N₂ atmosphere (zone 1).

the compensation effect is noted in the system under investigation. The name “compensation effect” refers to the idea that variations in enthalpy that accompany variations in temperature where molecular level splitting of the polymer occurs during degradation are “compensated for” by variations in change in enthalpy. Figures 9 and 10 show variation of enthalpy as a function of entropy. As seen in Table 1 values of enthalpy and entropy is affected by varying heating rates.

Free energy values are also found to be varying. This type of behavior might be an indication that enthalpy-entropy compensation effect does not operate in such systems [27]. According to Exner [28], a criterion for the existence of a compensation effect is the linear relationship of kinetic constants at two temperatures:

$$\log k_{3T_1} = b \log k_{3T_2} + \text{const}, \quad (8)$$

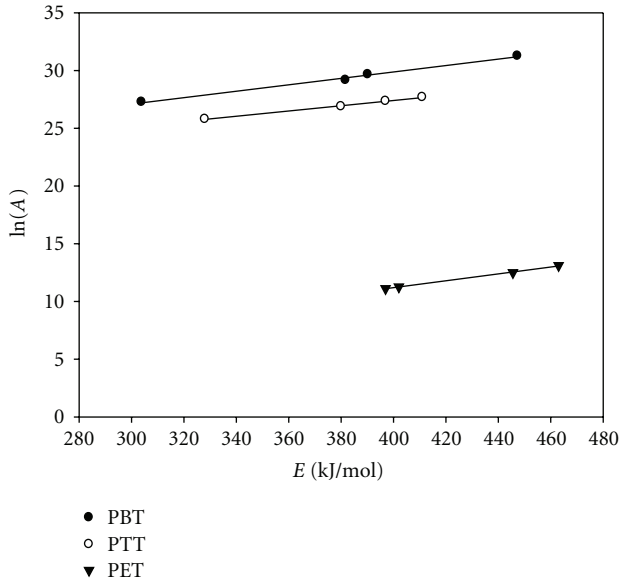


FIGURE 5: Plot indicating a linear relationship between $\ln A$ versus E for different polyesters degraded in air atmosphere (zone 1).

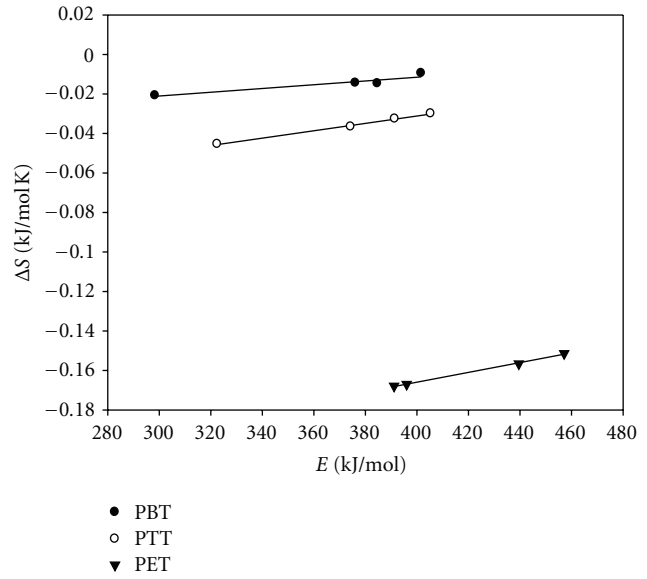


FIGURE 7: Plot indicating a linear relationship of ΔS versus E for different polyesters degraded in air atmosphere (zone 1).

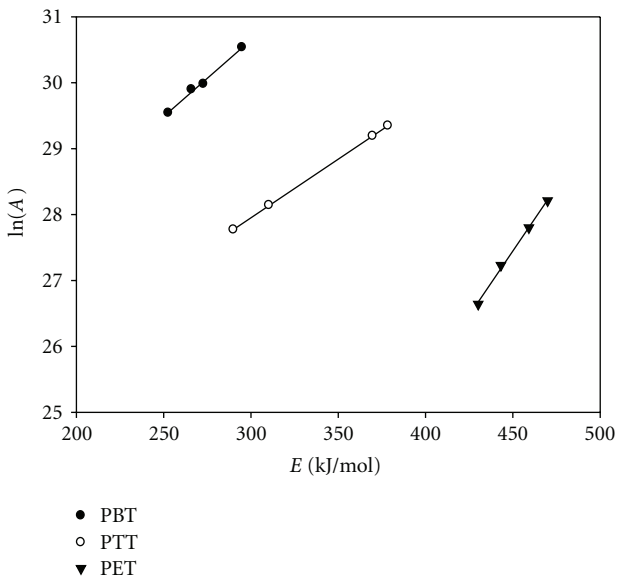


FIGURE 6: Plot indicating a linear relationship between $\ln A$ versus E for different polyesters degraded in N_2 atmosphere (zone 2).

where k_{3T_1} and $\log k_{3T_2}$ are kinetic constants at two different temperatures T_1 and T_2 .

The slope b is related to the isokinetic temperature (Φ) by the following equation:

$$\Phi = T_1 T_2 \frac{b-1}{bT_1 - T_2} \quad (T_1 > T_2). \quad (9)$$

The values of $\log k_{3T_1}$ and $\log k_{3T_2}$ were determined from the experiments. A plot of $\log k_{3660k}$ versus $\log k_{3680k}$ for PBT in N_2 atmosphere (zone 1) is indicated in Figure 11. The dependence of both the temperatures for this plot was found

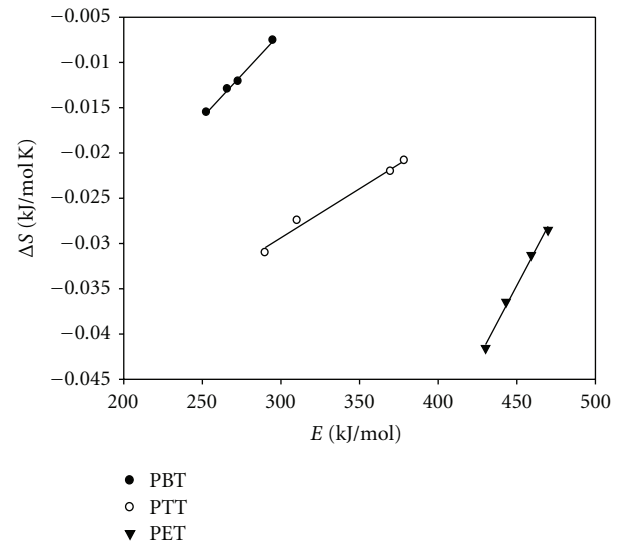


FIGURE 8: Plot indicating a linear relationship of ΔS versus E for different polyesters degraded in N_2 atmosphere (zone 2).

to be linear with an r value of 0.99 and slope (b) equal to 0.852 ± 0.156 . Estimations were also conducted for $\log k_{3620k}$ versus $\log k_{3630k}$ and b value was found to be 0.842 ± 0.2 with an r of 0.99. Even though a good r was obtained for both the plots, the isokinetic temperature for both the temperature ranges (660–680°K and 620–630°K) were obtained as $990^\circ\text{K} \pm 150^\circ\text{K}$ and $1010^\circ\text{K} \pm 210^\circ\text{K}$ which indicated that an isokinetic temperature obtained using (9) does not lie in the experimental range studied. The author in an earlier work [5] tried to employ the criterion used by Peterson and Kevan [29] to check the presence of compensation effect. In this work $\ln k$ versus $1/T$ was plotted to check the presence of compensation effect operating in these system. An isokinetic

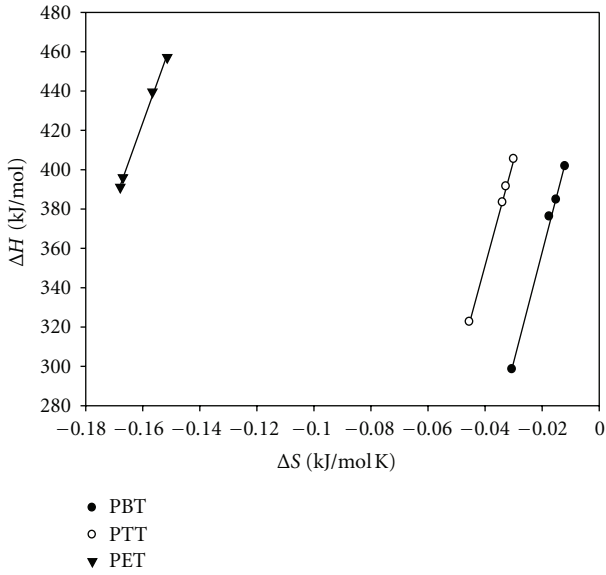


FIGURE 9: Plot of change in enthalpy as a function of change in entropy for the degradation of different polyesters in air atmosphere (zone 1).

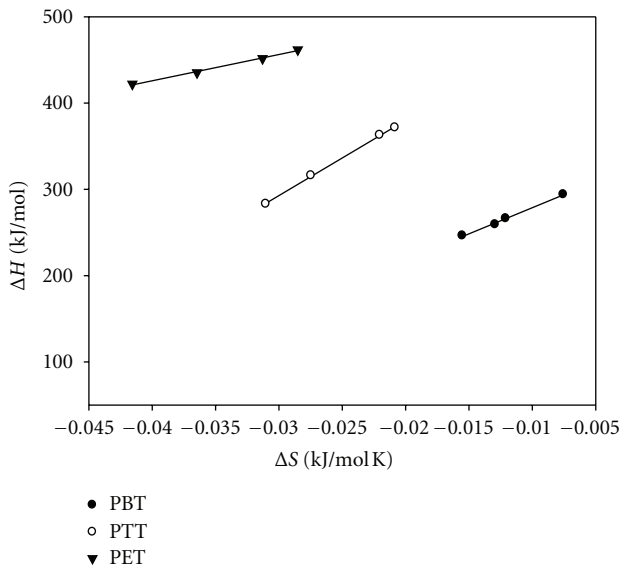


FIGURE 10: Plot of change in enthalpy as a function of change in entropy for the degradation of different polyesters in N₂ atmosphere (zone 2).

temperature (temperature at which all the lines concur to a single point) was not obtained in these plots proving the absence of compensation effect.

Another plot (Figure 12) was made to check the variation of ΔH as a function of ΔG [30]. A linear relationship with a slope γ was obtained. The slope γ is related to the isokinetic temperature (Φ) by the following equation:

$$\Phi = \frac{T_{hm}}{1 - (1/\gamma)}, \quad (10)$$

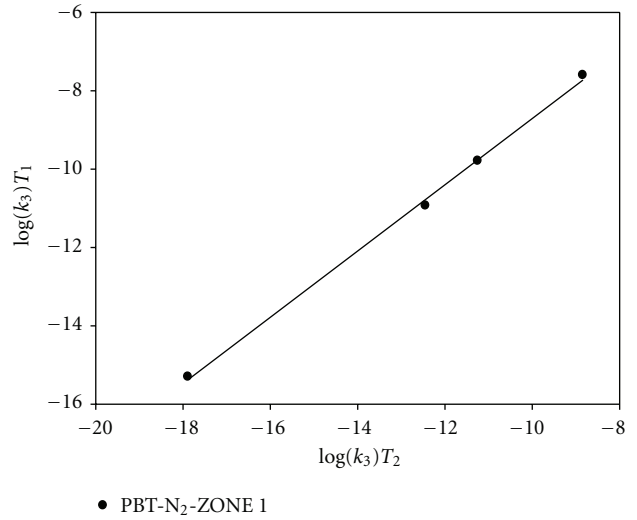


FIGURE 11: Plot of $\log k_{3660}$ versus $\log k_{3680}$ for PBT in N₂ atmosphere (zone 1).

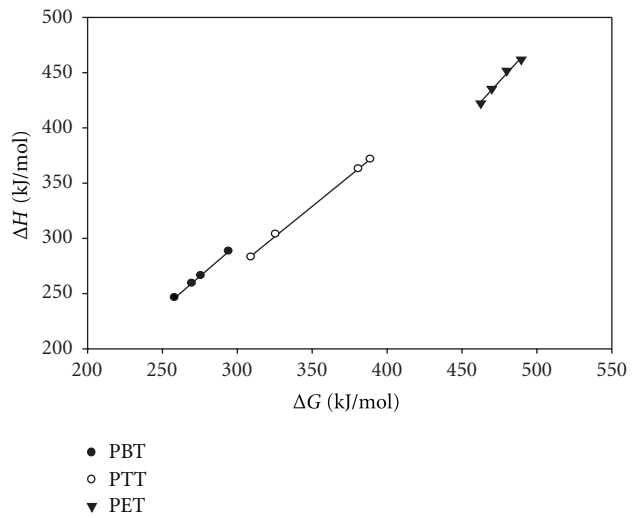


FIGURE 12: Plot of enthalpy change as a function of free energy change for different polyesters in N₂ atmosphere (zone 2).

where T_{hm} is the harmonic mean of experimental temperatures. The value of γ was obtained from the plot of enthalpy and free energy and the corresponding value of Φ were obtained from (10). In this case Φ was found to be $1089^\circ\text{K} \pm 120^\circ\text{K}$, which is not within the limits of the temperature range conducted in this study, thus proving that compensation effect does not exist in the degradation of PET, PBT, and PTT.

5. Conclusions

The Coats-Redfern equation was used to calculate the values of activation energy and the preexponential factor (A) for the nonisothermal degradation of PET, PTT, and PBT in N₂ and air atmospheres. A linear dependence was found by

plotting $\ln A$ and activation energy. A linear relationship was also found to exist between changes in entropy and enthalpy of activation for the degradation of these polyesters. These dependences are related to the assumption that the kinetic degradation mechanisms of these polyesters could be identical. The negative values of entropy show that the degradation activated complex is a more organized structure than the initial polymer structure. The slopes and the intercepts of the lines for the plot of entropy versus activation energy were found to be not identical, possibly indicating that there could be different dissimilar chemical processes occurring on degradation.

The positive values of free energy and enthalpy indicate that the polyester degradation process is a nonspontaneous reaction.

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