

EFFECT OF VARIOUS STABILIZERS ON THE THERMO-OXIDATIVE DEGRADATION OF (POLY ETHYLENE TEREPHTHALATE) (PET)

Flaviu Călin Ciolacu Ladașiu

Institute of Life Sciences, "Vasile Goldiș" Western University of Arad

ABSTRACT: The effect of various stabilizers on the thermo-oxidative stability of PET was investigated using isothermal and dynamic thermogravimetric analysis (TGA) in the presence of oxygen. From the kinetic analysis of the thermo-oxidative process it was found that the material decomposes via an autocatalytic mechanism. Addition of stabilizers leads to a delay of degradation as suggested by the higher activation energies and pre-exponential factors obtained from the polymer samples containing stabilizers.

Keywords: PET, thermal analysis, stabilizers, thermo-oxidative degradation

INTRODUCTION:

The effect of various stabilizers on the thermo-oxidative stability of poly (ethylene terephthalate) (PET) can be precisely determined using isothermal and dynamic thermogravimetric analysis (TGA).

TGA is an important tool to study the decomposition characteristics of polymeric materials. The mechanism of degradation and kinetic parameters such as activation energy and reaction order can also be obtained. This provides information about the process and the influence of stabilizers on the thermal stability of the material.

The kinetics of thermal and thermo-oxidative degradation of PET has been previously investigated by several authors both in inert and oxygen atmosphere using mainly TGA dynamic heating method. The influence of various stabilizers on PET degradation stability has also been studied. Wu and coworkers studied the thermo-oxidative degradation of phosphorus containing flame retardant in PET. Le et al. investigated the stabilization of thermal degradation and discoloration of PET in the presence of hindered phenol and phosphate type stabilizers. These investigations provided information about the mechanism and kinetics of thermal and thermo-oxidative degradation of PET and the influence of various stabilizers on such degradations. However, fewer studies have been dedicated to understand the kinetics of the process using isothermal methods.

In this work, the effect of low and higher molecular weight reactive stabilizers (containing epoxy groups) on the thermo-oxidative stability of PET is investigated using isothermal and non isothermal kinetic methods. The mechanism and kinetic parameters of the degradation process are evaluated.

The stabilizing effect of the reactive stabilizers are compared with a commercially available stabilizer (Irganox B561) and a nanostructured chemical (trisilanol isobutyl POSS).

MATERIALS AND METHODS:

Experimental Materials

PET (soft drink bottle grade) samples prepared (by compression molding) with reactive stabilizers (containing epoxy reactive groups) were used in this the degradation is an n^{th} order reaction, then $f(\alpha)$ can be expressed as:

work. The amount of stabilizer used for each sample was 0.2 wt%.

The reactive stabilizers are designated as EIF126 (higher molecular weight) and EPP (low molecular weight) depending on their core chemical structure, the commercial one as B561 and the nanostructured chemical as T-POSS throughout the paper.

Thermal Analysis

All TGA investigations were performed using a Thermo-gravimetric Analyzer, TA Instruments (Model 2950).

Both non-isothermal and isothermal TGA analysis of PET samples with stabilizers were performed on 10 mg samples under high purity oxygen atmosphere at a flow rate of 50mL/min. The non-isothermal degradation of PET, and PET with stabilizers was performed by heating the samples from room temperature to 50°C at different heating rates (2, 5 and 8 deg/min). In the isothermal experiment, the samples were heated from ambient temperature at a heating rate of 20°C/min to 280, 290 and 300°C and maintained at these temperatures for 5 hours, to observe the degradation process as a function of time.

The experiments were repeated twice to verify consistency of the data obtained. The instrument was calibrated for each heating rate using the "Curie" point of nickel as reference.

The linear and nonlinear regressions analyses were performed using SigmaPlot® (Systat Software Inc, California, USA) software.

RESULTS AND DISCUSSION:

Theory

The most general kinetic model for a single step degradation process is described by the following equation

$$r = da/dt = k(T)f(\alpha) \quad (1)$$

where: $f(\alpha)$ is the reaction model, α is the degree of conversion, $k(T)$ is the temperature dependent rate constant, T is the temperature, t is the time and r is the rate of degradation. The function $k(T)$ may be described as an Arrhenius-type equation:

$$k(T) = A \exp(-E/RT) \quad (2)$$

where: E is the activation energy, A is the pre-exponential factor; R is the universal gas constant. If

$$f(\alpha) = (1-\alpha)^n = W^n \quad (3)$$

where 'n' is the order of reaction and 'W' is the weight fraction remaining

A slightly higher complexity is introduced by using the autocatalytic model where $f(\alpha)$ can be written as:

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

In Eq. 4 'n' and 'm' are the reaction orders. By substituting Eq. 4 in Eq. 1 we obtain:

$$da/dt = k(T)(1-\alpha)^n \alpha^m \quad (5)$$

This equation describes reactions that begin with the acceleration (autocatalysis) of the degradation rate until reaching a maximum, where an n^{th} order-like reaction becomes dominant until reaction completion.

Non isothermal Method

The non isothermal method was used to investigate the effect of the heating rate on the degradation process of PET and PET with stabilizers (0.2 wt% stabilizer).

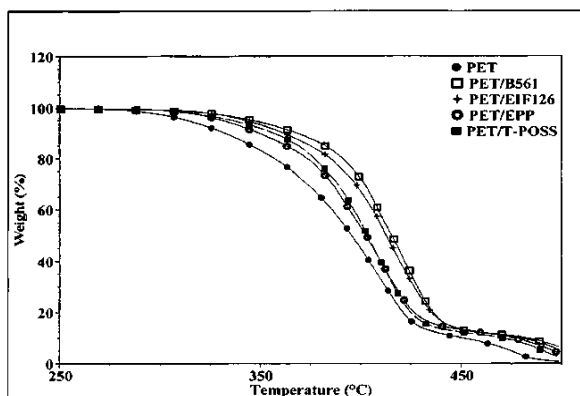


Fig. 1 Non isothermal TGA weight loss curves of PET and PET with different stabilizers at a heating rate of 5°C/min

Figure 1 shows a typical non isothermal TGA weight loss curves of PET and PET with different stabilizers at a heating rate of 5°C/min. To evaluate the thermal stability of the samples, a weight loss temperature of 6% was used as standard. It can be observed that the TGA curves of PET with stabilizers are shifted to higher temperatures. Consequently, the onset decomposition temperature also increases by at least 20°C as shown in Table 1.

Such observation clearly indicates an improved thermo-oxidative stability of the material and similar trend was observed for all heating rates used.

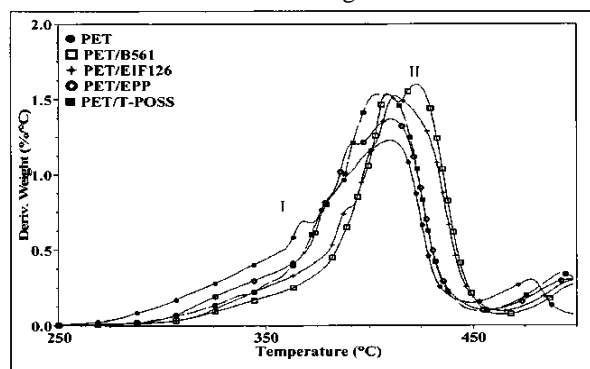


Fig. 2 Non isothermal weight loss rate curves of PET and PET with different stabilizers at a heating rate of 5°C/min

Figure 2 shows the derivative TGA weight loss curves of PET and PET with stabilizers at a heating rate of 5°C/min. At least three decomposition steps can be observed, the peak temperature of the first decomposition step being presented in Table 1. The presence of multiple decomposition steps of PET in air was previously noted by many other investigations indicating the complexity of such degradation process.

Table 1.

TGA data of PET and PET with stabilizers (0.2 wt %) at a heating rate of 5°C/min

Sample	Onset Temperature (°C)	Peak maximum (first decomposition step) (°C)	Maximum Decomposition Temperature (°C)
PET	281	303	410
PET/B561	309	361	414
PET/EIF26	309	359	412
PET/EPP	300	356	410
PET/T-POSS	300	357	404

From Table 1 it can be observed that the peak temperature of the first step is increased by more than 50°C due to the presence of stabilizers. This suggests that the degradation process of PET is retarded, the polymer being stable over a higher temperature range. The maximum decomposition temperature (Table 1) is similar for all the samples.

The evaluation of the kinetic parameters for thermo-oxidative degradation using different heating rates was performed using the Flynn-Wall method:

$$\Delta \ln \beta = -1.052(E_a/R)\Delta(1/T) \quad (6)$$

where: ' β ' is the heating rate, ' E_a ' is the activation energy, ' R ' is the universal gas constant and ' T ' is the temperature (°K). The activation energy for different conversion values can be calculated from a plot of ' $\ln \beta$ ' versus ' $1/T$ '. Figure 3 shows the Flynn-Wall plots of PET at different conversions. A good fit of the model used with the experimental data was observed ($r^2 > 0.96$). This indicates that this model can be applied to describe the degradation of PET in a non isothermal degradation process.

A reasonable good fitting was complicated the degradation mechanism.

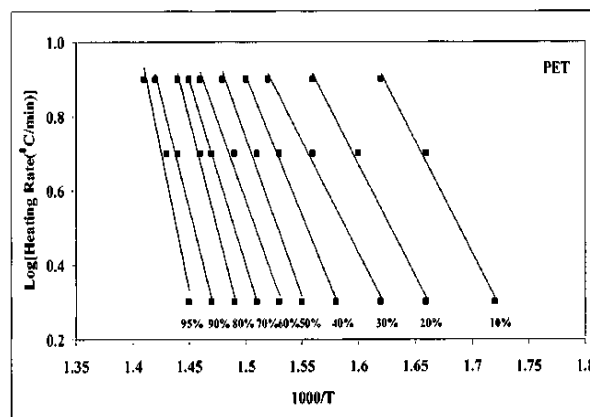


Fig. 3 Flynn-Wall plots of PET at different conversions

Table 2.

Kinetic parameters at different conversion values of PET and PET with stabilizers

Conversion (%)	PET		PET/B561		PET/T-POSS		PET/EIF126		PET/EPP	
	Ea (KJ/mol)	LogA (1/min)	Ea (KJ/mol)	LogA (1/min)	Ea (KJ/mol)	LogA (1/min)	Ea (KJ/mol)	LogA (1/min)	Ea (KJ/mol)	LogA (1/min)
10	101.3	7.05	112.1	7.37	97.4	6.30	102.8	6.75	149.8	11.01
20	97.0	6.65	132.6	9.08	117.9	8.06	103.5	6.83	145.7	10.53
30	103.1	7.14	146.5	10.23	140.4	9.93	121.9	8.37	173.6	12.75
40	122.8	8.77	169.0	12.06	152.0	10.86	129.7	9.02	190.5	14.07
50	134.4	9.70	186.6	13.46	155.2	11.11	141.5	9.99	213.6	15.86
60	150.0	10.94	203.1	14.75	159.1	11.42	156.8	11.21	241.1	17.98
70	162.7	11.84	216.9	15.80	164.7	11.86	172.2	12.41	268.8	20.08
80	178.2	13.14	229.8	16.78	172.9	12.51	187.1	13.56	295.3	22.05
90	202.5	15.02	248.8	18.20	188.7	13.74	201.3	14.64	326.6	24.33
95	267.6	19.97	282.8	20.71	221.2	16.17	218.6	15.93	393.9	29.20

The activation energies of PET samples obtained from Fig. 3 at different conversion levels are presented in Table 2. From Table 2 it can be seen that the activation energy increases with the increase of the conversion level, indicating that the degradation process mechanism changes with the increase in temperature. Similar observations were also made by other authors (Gupta *et al.* 2004), suggesting that PET degradation in oxygen atmosphere takes place in at least two or more distinct steps, as noted from Figure 2. The activation energies obtained for the unstabilized polymer generally agree with those obtained by various authors (Kim *et al.*, 1992). The highest activation energy at all conversion levels was obtained for PET/EPP system (Table 2).

Isothermal Method

The isothermal degradation was carried out to consider the effect of temperature and time on the kinetics of the degradation process of PET and PET with stabilizers. Figures 4 and 5 show the typical TGA weight loss and the derivative of weight loss curves for PET and PET with the different stabilizers at 290°C over 30 minutes. From Figures 4 and 5 it can be observed that the presence of the stabilizers influences both the weight loss and weight loss rate of PET.

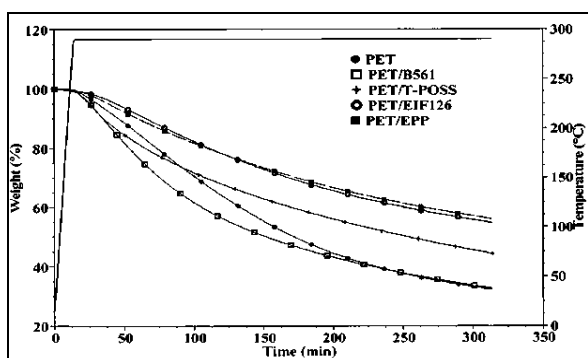


Fig. 4 Isothermal weight loss curves for PET and PET with different stabilizers at 290°C

Depending on the chemical composition of the stabilizer, either an increase or decrease in the percentage of weight loss can be observed (Fig. 4). The unstabilized PET experienced the highest weight loss (68%) of all samples within the experimental time frame. Compared with the unstabilized polymer, the

lowest weight loss is observed for PET/EPP and PET/EIF126 samples (44% and 45%) respectively, suggesting better thermo-oxidative stability of the material. For PET/B561 sample, the weight loss was slightly lower (6%) than that of PET although initially the weight loss occurred faster than for the virgin polymer. Similar observation was made for the PET sample containing T-POSS, the weight loss value being lower (56%) than for both PET and PET/B561.

Comparable trend is observed from Figure 5 showing the weight loss rate of PET and PET with stabilizers. Again, it can be noted that PET/B561 and PET/T-POSS samples exhibit higher weight loss rates compared to PET and PET/EP and PET/EIF126 samples have the lowest weight loss rates of all samples. In order to describe the effect of temperature and time on thermal degradation of the polymer in the presence of stabilizers, two different degradation mechanisms were considered. The isothermal degradation can also provide detailed information about the mechanism and kinetics of PET thermo-oxidative degradation.

n^{th} Order Degradation Mechanism

From Figure 5 it can be clearly seen that the maximum rate of degradation does not occur at zero time but in more than 20 minutes (depending on the stabilizer used) after the isothermal temperature is reached. This indicates that the PET samples do not degrade via n^{th} order degradation process. In a n^{th} order process, substituting Eq. 3 into Eq. 1 and taking the natural logarithm on both sides we obtain:

$$\ln(-dW/dt) = n \ln W + \ln k \quad (7)$$

If the degradation of PET is described by a n^{th} order degradation mechanism, then by plotting ' $\ln(-dW/dt)$ ' against ' $\ln W$ ', a straight line should be obtained with the slope of ' n ', and intercept equal to ' $\ln k$ '.

From Figure 6 it can be clearly observed that the plots of ' $\ln(-dW/dt)$ ' against ' $\ln W$ ' are not straight over the whole regime confirming that the PET samples do not degrade via a n^{th} order process if the heating is conducted in oxygen atmosphere. Therefore, the activation energy was not calculated using the n^{th} order degradation mechanism due to poor fitting of the mathematic model ($r^2 < 0.5$). Similar trend was also obtained for the experimental samples in other isothermal temperatures employed.

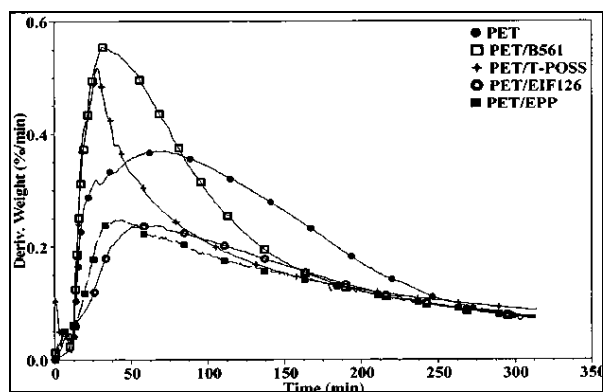


Fig. 5 Isothermal rate of weight loss curves for virgin PET and PET with different stabilizers at 290°C

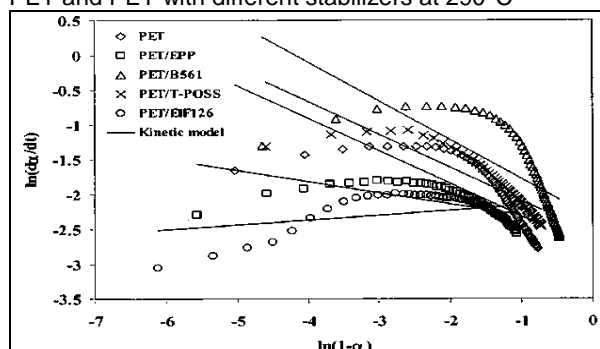


Fig. 6 Double log plot of degradation rate against fractional weight remaining for PET and PET with various stabilizers at 280°C

Autocatalytic Mechanism

As previously observed, the thermo-oxidative degradation of PET could not be satisfactorily described by the n^{th} order degradation model due to the complexity of such degradation. Therefore, the autocatalytic reaction mechanism described by Equation 5 was considered to model the thermo-oxidation of the polymer. Figure 7 shows the weight loss rate of PET and PET with stabilizers at 280°C with non-linear regression lines based on Equation 5 using ' $k(T)$ ', ' n ' and ' m ' as fitting parameters. A good fit ($r^2 > 0.95$) between the mathematic model and the experimental data was observed for all the samples used in this study.

These results clearly show that PET degradation may be realistically modeled via an autocatalytic mechanism in oxygen atmosphere.

By plotting ' $\ln k(T)$ ' against ' $-100/RT$ ' (Figure 8), the activation energy for all PET samples was calculated, (all plots showing a good fit, $r^2 > 0.96$).

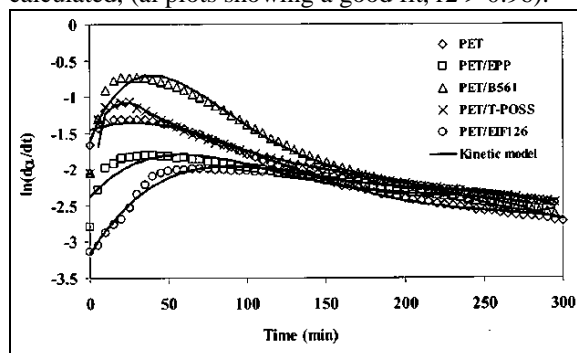


Fig. 7 Weight loss rate of PET and PET with stabilizers at 280°C

The kinetic parameters obtained using the autocatalytic model are presented in Table 3. It can be observed that the ' n ' and ' m ' values for a particular sample are largely similar and do not show significant temperature dependence.

This suggests that the mechanism of degradation does not change with temperature and that the mechanism of degradation is similar for all the samples studied.

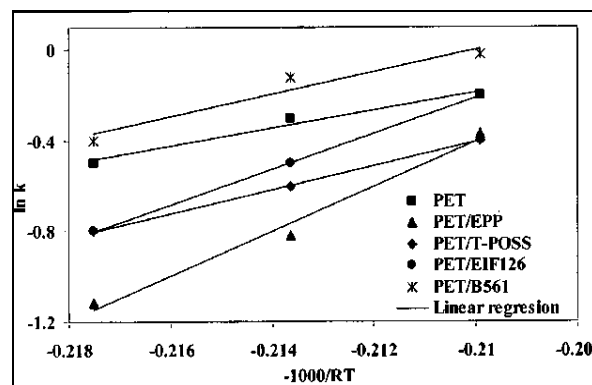


Fig. 8 Arrhenius plot of PET and PET with stabilizers using ' $\ln(k)$ ' value calculated from Equation 5.

Further examination of kinetic data shows that the addition of stabilizers increases the activation energy of the stabilized PET. PET/EPP sample has the highest E_a value (98.7 KJ/mol) (Table 3). The higher activation energies imply an increased thermal stability of the material due to retardation of the degradation process.

Table 3.

Kinetic parameters obtained using Equation (5) for thermo-oxidative degradation of PET and PET with stabilizers (isothermal test).

Sample	n (280 °C)	m (280 °C)	N (290 °C)	M (290 °C)	n (300 °C)	m (300 °C)	E_a (KJ/mol)	$\ln A$
PET	0.2	3.6	0.2	2.8	0.2	3.2	39.6	8.1
PET/EPP	0.2	3.0	0.2	3.0	0.2	3.6	98.7	20.3
PET/B561	0.3	2.9	0.2	2.8	0.2	2.2	49.9	10.8
PET/T-POSS	0.1	2.9	0.2	2.7	0.2	2.1	52.7	10.7
PET/EI126	0.4	3.3	0.3	3.4	0.3	3.2	79.3	16.5

As has been observed from Figure 4, for PET/B561 and PET/T-POSS samples the weight loss occurred initially faster compared with PET and PET with other stabilizers. However, the activation energies of both systems are higher than that of virgin PET (Table 3). This suggests that some stabilization of the material is achieved.

Compared with the non-isothermal method, in this case lower activation energies were obtained for PET and PET with stabilizers (Table 3) however, the same trend was observed in both cases. The observed differences in the activation energy values are

attributed to the particularities of each method used and to the polymer properties.

In addition, in both isothermal and non isothermal methods, differences between the activation energies of PET samples with various stabilizers can be observed. Such differences can be attributed to the different structures of the stabilizers used, mode of interaction with PET and stabilizing efficiency. The higher values of E_a , in both cases were observed for PET/EPP sample implying best stabilizing effect.

To further investigate the efficiency of the stabilizers, a lifetime estimation was carried out when the samples experienced a 10% weight loss (10% conversion level).

By using the kinetic data obtained from the non isothermal run, the lifetime of the samples was calculated for temperatures between 40°C and 300°C using the following equation proposed by Toop:

$$\ln t_f = Ea/RT_f \ln [(Ea/\beta R) * P(X_f)] \quad (8) \text{ where:}$$

' E_a ' is the activation energy ' t_f ' is the estimated time to failure (min), ' T_f ' is the failure temperature (°K), ' R ' is the gas constant, ' β ' is the heating rate, ' $P(X_f)$ ' is a function depending on ' E_a ' at the failure temperature ' T_f '.

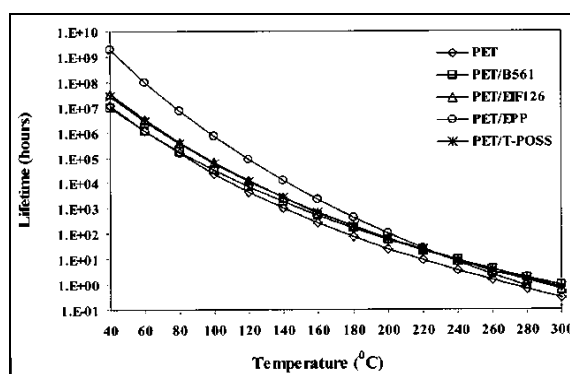


Fig. 9 Variation of lifetime with temperature for PET and PET with stabilizers.

Figure 9 shows the temperature dependence of calculated lifetime of PET and PET with stabilizers. It can be observed that the lifetime falls with temperature for all samples. However, the polymer samples containing various stabilizers have higher lifetime values and the rate of fall is lower compared to virgin PET. Again, it should be noted that PET/EPP system has the highest lifetime value. This is ascribed to the higher activation energy and higher pre-exponential factor values (Gupta *et al.*, 2004) observed for PET with stabilizers at 10% conversion, especially for PET/EPP system (Table 2). By having higher lifetime value means that the polymer is less likely to have premature failure during its intended application and use.

CONCLUSIONS:

THE mechanism of thermo-oxidative degradation of PET and the effect of various stabilizers on the thermo-oxidative stability of PET were investigated

using isothermal and non-isothermal TGA kinetic analysis. The results from this study confirmed that the polymer samples decompose via an autocatalytic mechanism in presence of oxygen.

However, the degradation is delayed by the addition of stabilizers which is suggested by the higher values of the activation energies and pre-exponential factors obtained for PET with stabilizers. Between the stabilizers used, EPP (low molecular weight) was found to have the best stabilizing effect on PET reflected in higher activation energy and lifetime value.

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