

Thermal Oxidative Degradation Kinetics and Thermal Properties of Poly(ethylene terephthalate) Modified with Poly(lactic acid)

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ABSTRACT: The thermal oxidative degradation kinetics of poly(ethylene terephthalate) (PET) copolymers modified with poly(lactic acid) (PLA) were investigated with thermogravimetric analyzer (TGA). The thermal properties of the modified products were also determined by differential scanning calorimeter (DSC) technique. Waste PET (P100) obtained from postconsumer water bottles was modified with a low-molecular-weight PLA. The PET/PLA weight ratio was 90/10 (P90) and 50/50 (P50) in the modified samples. The thermal oxidative degradation kinetics of the modified samples was compared with those of PET (P100). The segmented block and/or random copolymer structure of the modified samples formed by a transesterification reaction between the PLA and PET units in solution and the length of the aliphatic and

aromatic blocks were found to have a great effect on the degradation behavior. On the basis of the results of the degradation kinetics determined by Kissinger method, the degradation rate of the samples decreased in the order of P50 > P90 > P100, depending on the amount of PLA in the copolymer structure. However, the degradation activation energies (E_A) of the samples decreased in the order of P100 > P90 > P50. It was concluded that the degradation rate and mechanism were affected significantly by the incorporation of PLA into the copolymer structure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2747–2755, 2008

Key words: degradation; TGA; DSC; biodegradable; polyesters

INTRODUCTION

The degradation of polymers has been at the center of a large number of research studies into the management of plastic wastes for many years. Studies on degradation kinetics of polymers are important to modeling the degradation processes. While polymer degradations are more commonly studied in inert atmospheres, degradation in an oxygen environment is equally important. Thermal oxidative degradation of polymers can provide practical, important information on how polymeric materials behave under more realistic atmospheric conditions.¹ Most common and rapid method is thermogravimetric analysis (TGA), which is the measurement of the weight change of a material as a function of temperature and time to study the degradation kinetics of polymers under controlled atmosphere.¹

Poly(ethylene terephthalate) (PET) is the most widely used thermoplastic polyester in many fields in the plastic industry, such as fibers, packaging films, food and beverage bottles, containers for pharmaceutical and household products, and cosmetics, because of its superior thermal and mechanical properties, nontoxic nature, low permeability, and chemical resistance.²

As the amount of PET in waste plastic feedstock has increased, recycling has become more crucial from an ecological point of view. Nowadays, ecological and economic considerations have led to research studies focusing on the chemical recycling of waste PET. One of the recent solutions is to prepare biodegradable PET materials by chemical modification reactions, reactive blending, or copolymerization.

PET shows interesting thermal characteristics and there are various studies about thermal degradation of PET, PET blends, and copolymers.^{3–17} On the other hand, the thermal degradations of polyesters^{18–22} and the degradation of polyolefins have been studied intensively under a variety of conditions.^{23–25}

Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic, high-strength, high-modulus, and biodegradable polyester. This polyester undergoes thermal

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degradation at temperatures above 200°C by hydrolysis, lactide reformation, oxidative main chain scission, and interior intra molecular transesterification reactions.²⁶ And it is easily processed on standard plastics processing equipment to yield molded parts, film, or fibers.^{26–28} Recently, it has become the most common and promising green polymer in various applications because of its biodegradability.

In this study, the thermal oxidative degradation kinetics of biodegradable PET copolymers prepared by the modification of waste PET with low-molecular-weight PLA were investigated with TGA. To the best of our knowledge, PET-co-PLA copolymers were prepared in various weight ratios of PET/PLA by the chemical modification of waste PET in a solution phase for the first time.^{29,30} Degradation behaviors of the PET-co-PLA copolymers were tested with different heating rates and the degradation temperatures of the modified samples were compared. The activation energy of the degradation process was also calculated with the Kissinger method. In addition, the influence of segment length and composition of PET-co-PLA copolymer on the degradation behavior were also discussed.

Kinetic method

The kinetics of polymer degradation is usually described by the basic kinetic equation³¹

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

where α represents the conversion (extent of reaction; $\alpha = 0-1$), t is the time, $k(T)$ is the rate constant, and $f(\alpha)$ is the reaction model, which describes the dependence of the reaction rate on the extent of reaction.¹ Temperature dependence of $k(T)$ could be described by the Arrhenius equation

$$\frac{d\alpha}{dt} = Ae^{-E_A/RT}f(\alpha) \quad (2)$$

where E_A is the activation energy of the process, A is the pre-exponential factor, R is the universal gas constant, and $f(\alpha)$ depends on the decomposition mechanism.³² The simplest and most frequently used model for $f(\alpha)$ is

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

where n is the order of reaction.

The rate of conversion, $d\alpha/dt$, at constant rate of temperature change, $\beta = dT/dt$, can be expressed by

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \quad (4)$$

The combination of eqs. (2), (3), and (4) gives following relationship:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = (1 - \alpha)^n Ae^{-E_A/RT} \quad (5)$$

Kissinger method

The activation energy of the degradation process could be determined by the Kissinger method³³ without a precise knowledge of the reaction mechanism,⁷ using the following equation:

$$\ln \left(\frac{\beta}{T_m^2} \right) = \ln \frac{AR}{E_A} + \ln [n(1 - \alpha)^{n-1}] - \frac{E_A}{RT} \quad (6)$$

where β is the heating rate and T_m is the temperature corresponding to the inflection point of the thermal oxidative degradation curves which corresponds to the maximum reaction rate.⁷ The Kissinger equation is used to acquire the activation energy E_A , which can be calculated from the plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ and fitting to a strength line with slope of E_A/R .

EXPERIMENTAL

Materials

Modified PET products employed in this study were prepared in solution and experimental details of the preparation reactions, chemical characterization of the modified samples by FTIR and DSC and hydrolytic stability results were reported in previous article.³⁰ Biodegradation studies and hydrolytic stabilities of the samples prepared in a very wide composition range and reaction conditions were investigated.²⁹ The hydrolytic stabilities of PET-co-PLA copolymers were evaluated indirectly on the basis of weight loss after keeping them for various periods of time in phosphate buffer solutions of pH 7.2 at 60°C. The weight losses of the copolymers were between 10.60% and 46.15%, after 28 days. The biodegradation studies of samples were realized using PET-co-PLA copolymer as the sole carbon source for the growth of *Pseudomonas aeruginosa* (ASTM G22-76: Standard Practice for Determining Resistance of Plastics to Bacteria). The weight losses of the copolymers were between 5.90% and 17.90%, after 7 days. Bacterial growth was also observed with SEM in PET-PLA copolymer sample plates.²⁹ A positive bacterial growth and a weight loss of average 11.9% for PET-co-PLA copolymer samples were evident to show that the PET-PLA copolymer is biodegradable. Detailed results of the biodegradation studies and hydrolytic stabilities of the samples were also

TABLE I
Modification Reaction Conditions of PET and PLA

Sample	PET/PLA ratio (wt %) (in the feed)		Reaction temp. (°C)	Reaction time (h)
P1	P90	90/10	140	24
P2		90/10	170	24
P3	P50	50/50	170	8
P4		50/50	170	24

reported in previous studies.^{29,30} In addition, the nonisothermal crystallization kinetics of these products was investigated with DSC and crystal morphology of the samples was observed with SEM in previous article.³⁴

Modification reactions of PET with PLA were carried out in *o*-nitrophenol as solvent at 140 and 170°C for 8 and 24 h in the presence of dibutyl tin oxide as catalyst. The weight ratios of PET/PLA were 50/50, and 90/10. Viscosity average molecular weight (M_v) of the waste PET obtained from water bottles and number average molecular weight (M_n) of the oligomeric PLA synthesized in the laboratory were 3.7×10^4 and 2600 g mol^{-1} , respectively.^{30,35} Samples used in this study are denoted as P1, P2, P3, and P4. The PET/PLA weight ratio was 90/10 in the P1 and P2 samples, while 50/50 in the P3 and P4 samples. P100 is 2-0.85 mesh waste PET flakes obtained by grinding of postconsumer water bottles. All modified samples are also grinded as flakes in similar size. Sample compositions of modified PET products were shown in Table I.

Thermal analysis

DSC runs were carried out with a Setaram DSC-131, differential scanning calorimeter (Caluire, France). Before the DSC runs, all samples were dried well at 40°C in a vacuum oven at the pressure of 100 mbar overnight. The temperature and heat flow calibration of the instrument were achieved with high-purity indium, zinc, and copper metals. The samples weighing about 25 mg in an aluminum crucible were heated from room temperature to 280°C at a heating rate of 5°C min^{-1} in inert atmosphere.

Thermal oxidative degradation experiments were carried out in Shimadzu TA-60WS, Thermogravimetric Analyzer (Kyoto, Japan). Experiments were conducted in dynamic condition at different heating rates of 5, 10, 15 and $20^\circ\text{C min}^{-1}$. Constant heating rates were used between room temperature and 600°C. TGA was calibrated according to ASTM E1582 by using the certified Curie Point Standards kit for the each heating rate employed. Air flow rate was maintained at $40\text{--}50 \text{ mL min}^{-1}$ according to the specification of the equipment. Sample weights were

approximately 16–18 mg in all runs. The experiments were repeated for three times at heating rate of $10^\circ\text{C min}^{-1}$ to confirm the repeatability of the experiments and authenticity of the generated data. Activation energies of thermal oxidative degradation process were determined by using the Kissinger equation.

RESULTS AND DISCUSSION

DSC study

Thermal behaviors of the modified products obtained by the reaction between PET and PLA were determined by DSC technique. DSC analysis results of modified samples are given in Figure 1 together with that of original waste PET. The DSC thermogram of waste PET was obtained from the 2-0.85 mesh sample, which was also used for the modification reactions. The comparison of the thermograms showed that the melting points (T_m) of samples were not changed noticeably, while the shape of the peaks became sharper. The thermogram of the PLA shows the maximum at 148°C, which represents the melting of PLA.^{26,30}

The modification of PET by the reaction with PLA resulted in a product having a lower melting point compared to that of waste PET. The modification reaction carried out at 140°C by using 10% PLA with respect to total polymer resulted in the product (P1) having a melting point of 258°C for the reaction times of 24 h. The thermograms of the samples prepared at 170°C showed that the incorporation of PLA succeeded noticeably (Fig. 1). The melting point of the modified product P2 was 235°C, which confirms that the reaction occurred at a higher degree compared to the reaction at 140°C. The melting points of the samples P3 and P4 were determined as 245 and 212°C, respectively. The melting point of the modified product decreased with increasing reaction times from 8 to 24 h, which also shows the progress in the reaction. A double peak was observed for the sample P2, which may be due to the partial degradation reaction of PET chains or the second type of product having higher amount of LA units. Increasing the PLA weight ratio from 10 to 50% in the reaction mixture yields products having a lower melting

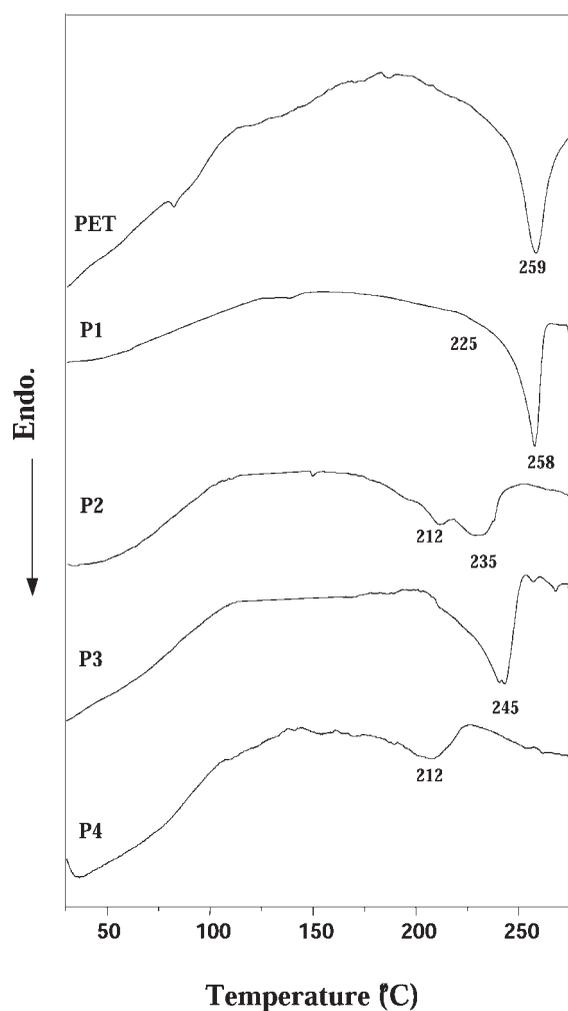


Figure 1 The DSC curves of original waste PET and modified samples.

point when the reaction temperature was 170°C. On the other hand, increasing the reaction temperature from 140 to 170°C decreased the melting point of the samples. Besides this decrease of the melting point of the samples, a single peak observed for the sample P4 shows that the incorporation of PLA was at a higher amount compared with, especially, the sample of P2. This may also indicate that the double peak for P2 (Fig. 1) resulted from the higher amount of LA units not from the degradation reaction, as mentioned earlier.

TGA study

For kinetic study of PET copolymers, thermal degradation runs of samples were recorded in TGA. Only one TGA thermogram can be enough to describe kinetic behavior of the system by various models, but kinetic analysis requires a set of TGA thermograms.¹ In this study, degradation runs of the modified samples were recorded at four different (5, 10, 15, and

20°C min⁻¹) heating rates. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for the all samples were shown in Figures 2 and 3, respectively. As predicted TGA curves were shifted to higher temperature as heating rate increased from 5 to 20°C min⁻¹ for all samples, because when the heating rate is increased a shorter time is required to reach a given temperature. This heating rate dependence is also indicated in the DTG thermograms. That is, the peak of the DTG thermogram shifted towards higher temperatures as the heating rate increased. The DTG peak maximum temperatures shown in Table II indicate the temperature of the maximum rate of degradation (T_{max}).

As it is seen in Figure 2, PET has two main weight loss steps. The first weight loss step of waste PET occurred between about 340 and 450°C was due to the degradation of PET chains into smaller fragments by an initial scissoring of the chain end.¹⁵ The second weight loss step also occurred between about 450 and 550°C due to the thermo-oxidative degradation of the small fragments into volatile products.^{16,17} As clearly shown in Figure 3, incorporation of PLA to the polymer backbone decreases the degradation temperature of PET significantly. PET almost degrades in a two step and this degradation behavior is different that in case of PET-co-PLA copolymer. Furthermore, the initial step of degradation of PET starts at higher temperature for all heating rates than those of PET-co-PLA copolymer.

As it seen from TGA curves in Figure 3, while P1 and P2 exhibit two decomposition steps, P3 and P4 exhibit exactly three weight-loss steps. These differences are also seen clearly at DTG curves. It is seen that in Table II, maximum peak temperatures of modified products decreases as the amount of PLA in the polymer structure increased.

PET, P1, and P2 have maxima in first degradation step at 402, 396, and 392°C respectively, when the heating rate of 5°C min⁻¹. We have suggested that this shifting corresponds to the change of PET backbone by the incorporation of PLA. In case of P3 three degradation steps that have maxima at 186, 378, and 445°C were seen (Fig. 3). We have concluded that the peak at 186°C attributed the degradation of PLA segments that incorporated in the polymer structure and the shifted peaks (at 378 and 445°C) according the PET degradation peak, indicates the changed main polymer backbone. As similar P4 have also three degradation steps at 174, 376, and 440°C, which can be attributed the degradation of PLA segments and changed main polymer backbone, respectively (Fig. 3).

PLA units enter in the PET backbone by transesterification reactions between the PET and PLA units. However, the incorporation of PLA units affects the degradation behavior of PET; we have

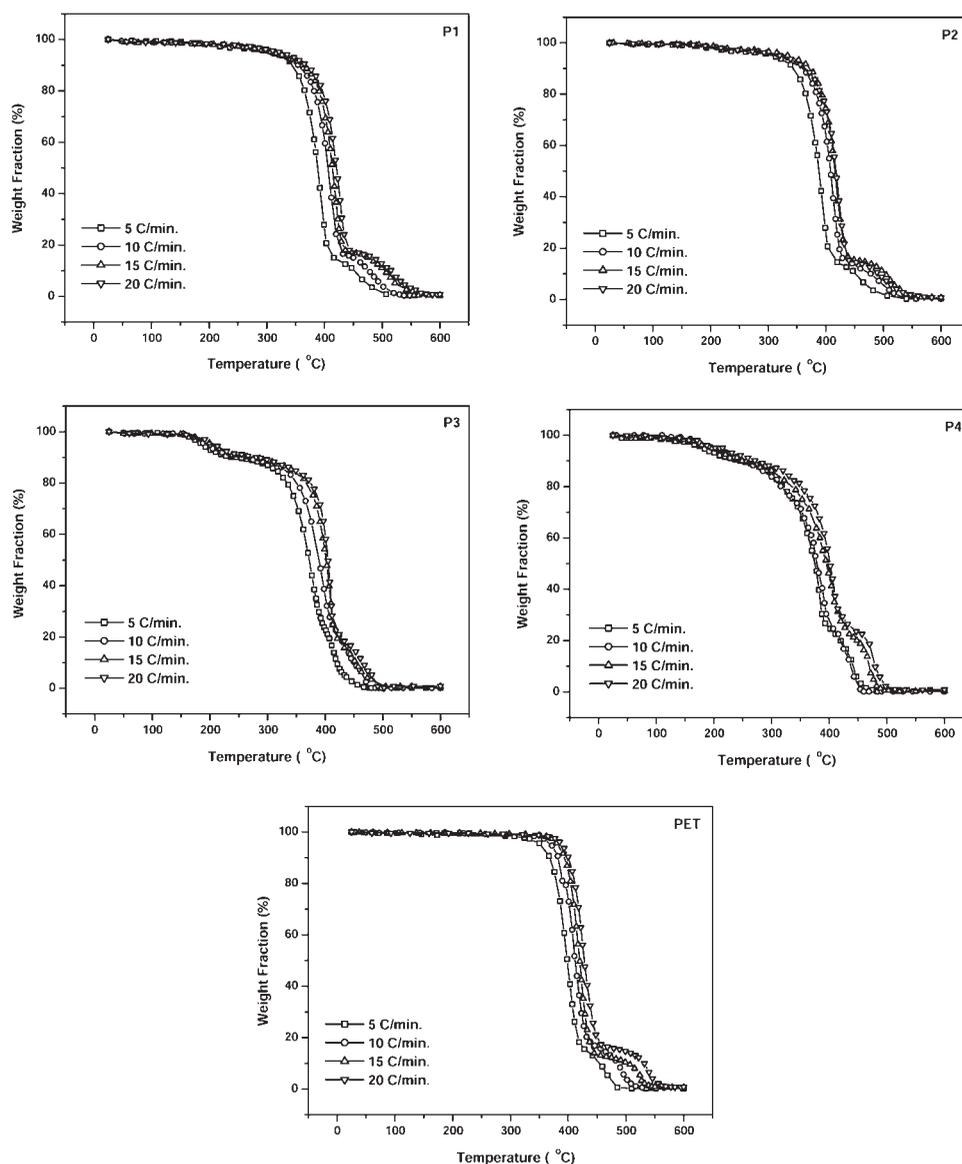


Figure 2 The TGA curves of original waste PET and modified samples.

deduced that PLA units enter the PET backbone as a result of the formation of a block or random copolymer by transesterification reactions between the PET and PLA units. The structure of the segmented block copolymer is schematized in Scheme 1. According to the TGA curves of modified samples, we can say that while P1 and P2 were random type copolymers, P3 and P4 seemed more like block copolymers with short PLA segments.

This structure has also been characterized with an FTIR study of the modified samples; absorption bands have been observed at 1750 cm^{-1} , which indicates the O—CO and C=O bonds, and at 1456 cm^{-1} , which indicates CH_3 groups of the PLA units, which have been reported previously.³⁰

The extent of transesterification affects the segment length and final composition. The maximum

degradation peak temperatures of the modified product decreased with increasing reaction times from 8 to 24 h, which also shows the progress in the reaction. So, the reaction conditions and feeding compositions were compared for the investigating of the thermal oxidative behavior of modified products. Different feeding compositions in the same reaction temperature and time, affected excessively the thermal oxidative behavior of the modified product. For example; the comparison of P2 and P4, the first step degradation peak was observed at 392°C for P2 and 376°C for P4 when the heating rate of 5°C min^{-1} (Table II). That is, increasing the feed amount of PLA from 10 to 50% caused decreasing the degradation peak maxima from 392 to 376°C (Fig. 3). Since PLA degrades at lower temperatures than the PET, it is expected that the modified struc-

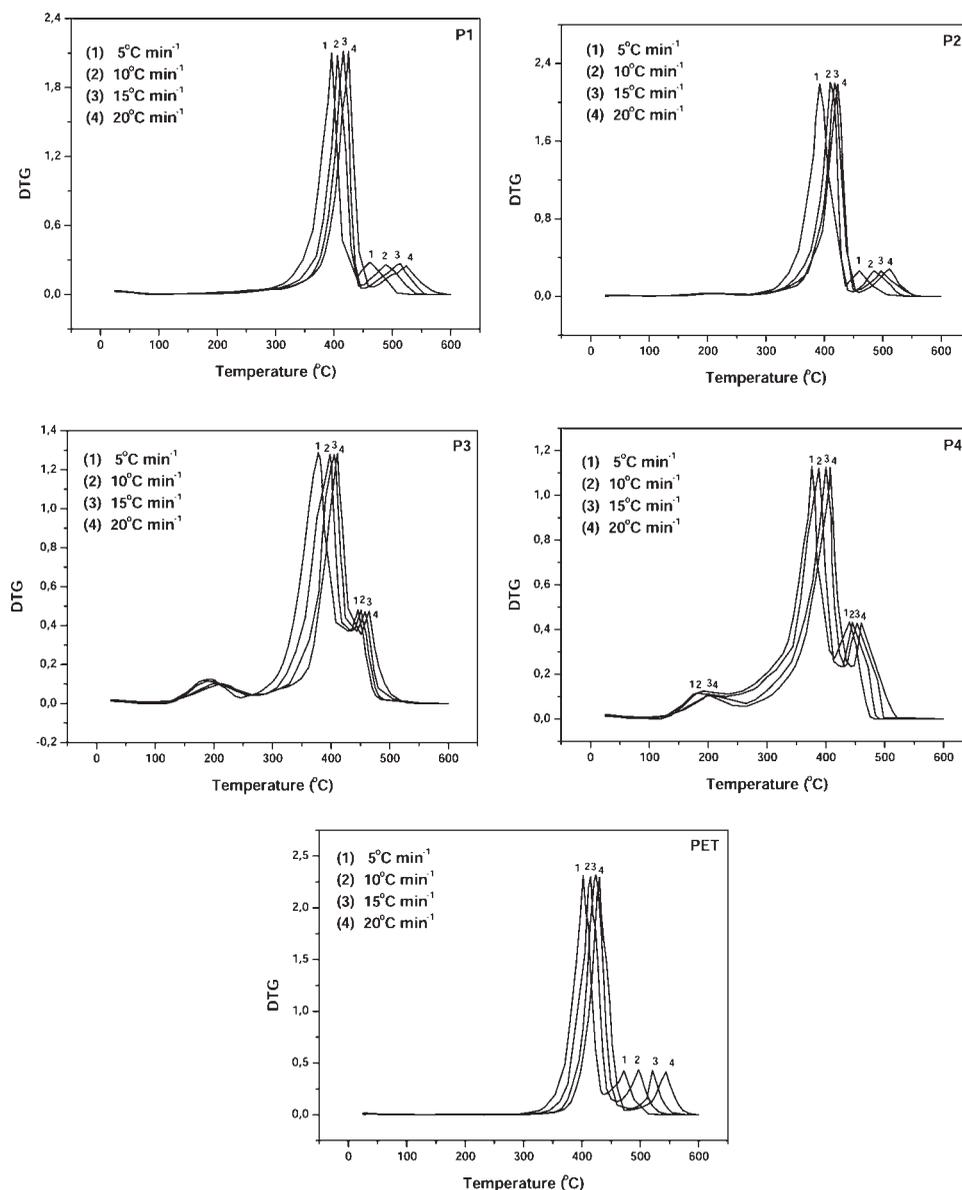


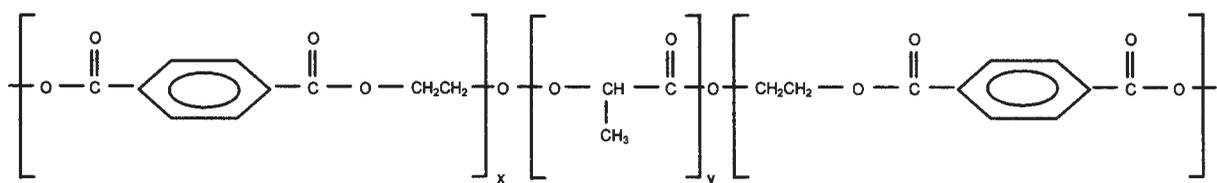
Figure 3 The DTG curves of original waste PET and modified samples.

ture should degrade at lower temperatures according to PET. These results clearly demonstrated that thermal oxidative degradation rates of these copolyesters substantially increased with the incorporation of PLA units into the more rigid poly ethyl-

ene terephthalate backbone. In case of same feeding compositions, increasing the reaction temperature from 140 to 170°C for the same reaction time (P1 and P2) and increasing the reaction time from 8 to 24 h for the same temperature (P3 and P4)

TABLE II
DTG Peak Temperatures (T_{max}) of Original Waste PET and Modified Samples

Heating rate ($^{\circ}\text{C min}^{-1}$)	PET		P1		P2		P3			P4		
	1st Step	2nd Step	3th step	1st Step	2nd Step	3th step						
5	402	472	396	461	392	460	378	445	186	376	440	174
10	415	497	406	489	410	485	398	451	188	388	445	180
15	424	531	416	514	418	497	405	458	199	400	453	198
20	430	544	425	524	423	512	411	465	212	407	460	204



Scheme 1 Structure of the PET-PLA copolymer.

decreased the maximum degradation peak temperatures for all heating rates.

The temperature values required for reaching to certain weight losses (25, 50, and 75%) were obtained from TGA curves are listed in Table III. According to these values, P1 and P2 have better thermal oxidative stability than the P3 and P4 because of the high PET ratio in the structure.

The DSC and TGA results showed that when the amount of PLA incorporated into PET structure increased, melting points and the degree of crystallinity of the samples decreased. Because of these changes, the copolymer became more thermally unstable. In general, the chemical modification of PET by the incorporation of secondary units (copolymerization, reactive blending, etc.) changes the crystallization behavior as well as its other physical and thermal properties.³⁶ Some studies have also shown that an ionic end group such as ionomers can change the chain mobility.^{37,38} We have concluded that when the amount of PLA increases in the sample composition, the number of PLA units in the PET-co-PLA structure or length of the PLA segments along the copolymer structure also increases. On the other hand, PLA units can be called soft segments in the copolymer structure.³⁴ These PLA blocks must have higher mobility than PET blocks at the degradation temperatures because of the relatively low T_m value of PLA. Therefore these segments vibrate and degrade more readily. We have speculated that such a decrease in the degradation temperatures originates from the higher mobility of soft PLA segments and the degree of crystallinity.

In addition, the nonisothermal crystallization kinetics of these products was also investigated in previous article in detail.³⁴ Several authors have studied the crystallization kinetics of PET copolymers, using different comonomers with various properties, and reported similar behaviors for the crystallization of PET copolymers.^{39–44} Our results in the previous article indicated similar trends for the crystallization behavior of PET-co-PLA copolymers and these results were very consistent with the reported studies on the crystallization behavior of PET copolymers.

Activation energies of the samples determined by the Kissinger method were given in Table IV. Equation (6) was used to obtain the activation energy which can be calculated from the plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ and fitting to a strength line. Kissinger plots for all samples thermal oxidative degradation are shown in Figure 4. The activation energies of the thermal oxidative degradation of waste PET and PLA were calculated to be 193 and 125 kJ mol^{-1} , respectively. As it seen in Table IV, activation energy values (E_A) of all samples are lower than the values of waste PET. That is, the degradation rates of modified products are higher than that of waste PET. However, the comparison of activation energy values of modified products shows that, since the reaction temperature is increased from 140 to 170°C for same feeding composition and reaction time (P1 and P2), the E_A values of modified products decreased. As the reaction time increased from 8 to 24 h for same feeding compositions and reaction temperature (P3 and P4) the E_A values of modified

TABLE III
The Temperatures Required for Reaching to Certain Weight Losses (%)

Sample	T (°C) ^a									Final degrad. temp (°C)	Residue (%)
	10%	20%	30%	40%	50%	60%	70%	80%	90%		
PET	382	394	403	408	412	418	423	433	486	528	0.59
P1	360	384	396	403	408	413	418	423	478	520	0.33
P2	353	381	393	400	406	411	416	426	476	518	0.25
P3	250	350	370	380	390	397	406	425	450	471	0.15
P4	249	316	353	371	379	389	398	424	446	452	0.12

^a The temperature where various weight loss has occurred.

TABLE IV
Activation Energies of Original Waste PET and Modified Samples Determined by Kissinger Method

Sample	Activation energy E_A (kJ mol ⁻¹)	Correlation coefficient r^2
PET	193	0.9898
PLA	125	0.9943
P1	186	0.9771
P2	160	0.9978
P3	150	0.9628
P4	147	0.9508

products were not changed remarkably. In addition, increasing the PLA weight ratio from 10 to 50% in the feed amount for the same reaction time and temperature (P2 and P4) caused decreasing the E_A values of samples.

We have offered that incorporation of PLA units into the polymer structure affects the degradation behavior of PET. Consequently, we can say that, the E_A values of these copolyesters were decreased with the incorporation of PLA units into the PET backbone. In the other words, increasing the feed amount of biodegradable PLA in the preparation of the modified product increases thermal oxidative degradation rate of these copolyesters.

CONCLUSIONS

We have studied the thermal behavior, thermal degradation, and kinetics of PET copolymers prepared through modification reactions of waste PET with low-molecular-weight and biodegradable PLA. These PET-PLA copolymers were synthesized by the chemical modification of waste PET in a solution phase for the first time. The degradation activation energies (E_A) of the samples were determined by the Kissinger method. The E_A values calculated by the Kissinger equation decreased in the order of P100 >

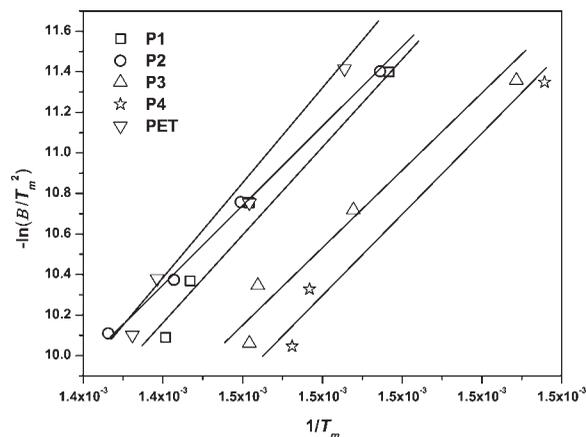


Figure 4 Kissinger plots of original waste PET and modified samples.

P90 > P50. The incorporation of PLA units into the copolymer structure as a result of transesterification reactions between PLA and PET blocks was found to increase the degradation rate of segmented block or random type copolymers. PLA incorporation into the more rigid PET backbone resulted biodegradable PET-PLA copolymers having a higher degradation rate than that of PET. On the basis of the TGA and DSC studies of the samples it can be said that, the degradation rate of the samples decreased in the order of P50 > P90 > P100, depending on the amount of PLA in the copolymer structure.

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