

Investigation of Thermal Degradation Kinetics of Polylactide-Perlite Composites

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Abstract

In this study, the thermal degradation behavior and kinetics of biodegradable and biocompatible polylactide were investigated by preparing composites with low-cost perlite at various ratios under an inert atmosphere. Polylactide (PLA) was characterized with FTIR, ¹H-NMR, ¹³C-NMR, GPC and TGA after being synthesized with ring-opening polymerization in the presence of tin octoate. The number average molecular weight (M_n) of the synthesized polymer was determined to be 20,091 g/mol. PLA/perlite composites were prepared with the method of solvent casting, by mixing the synthesized PLA in ratios of 10%, 20% and 40% with perlite. The structure of the composites was characterized by FTIR, while their thermal properties were analyzed using TGA. The PLA/perlite (60/40) composite exhibited an increase in degradation temperature of approximately 35 °C compared to pure PLA. The thermal degradation kinetics of the polymeric and composite material was investigated at different heating rates (5-10-15 and 20 °C/min) with thermogravimetric analysis using the Flynn-Wall-Ozawa, Tang and Kissinger methods. The thermal degradation activation energies were determined as 114.59 kJ/mol, 112.06 kJ/mol and 124.12 kJ/mol respectively. These results highlight the potential of PLA/perlite composites as cost-effective and thermally stable alternatives for sustainable material applications.

Keywords: Polylactide, perlite, biodegradable polymers composite, thermal degradation kinetics

Polilaktit-Perlit Kompozitlerinin Termal Bozunma Kinetiğinin İncelenmesi

Öz

Bu çalışmada; biyobozunur ve biyoyumlu olan polilaktitin, düşük maliyetli perlit ile farklı oranlarda kompozitleri hazırlanarak inert atmosferde termal bozunma davranışı ve kinetiği incelendi. Polilaktit, (PLA), kalay oktoat varlığında halka açılma polimerizasyonu ile sentezlenerek; FTIR, ¹H-NMR, ¹³C-NMR, GPC ve TGA ile karakterize edildi. Polimerin sayı ortalama moleküler ağırlığı (M_n) 20091 g/mol olarak bulundu. Sentezlenen PLA, %10, %20 ve %40 oranlarında perlit ile karıştırılarak çözgen uçurma yöntemiyle PLA/perlit kompozitleri hazırlandı. Kompozitlerin yapısı FTIR ile karakterize edilirken termal özellikleri TGA ile incelendi. PLA/perlit (60/40) kompoziti, saf PLA'ya kıyasla yaklaşık 35 °C daha yüksek bir bozunma sıcaklığı göstermiştir. Polimer ve kompozit malzemenin termal bozunma kinetiği farklı ısıtma hızlarında (5-10-15 ve 20 °C/dk) termogravimetrik analiz ile Flynn-Wall-Ozawa, Tang ve Kissinger metotları ile incelendi. Termal bozunma aktivasyon enerjileri sırasıyla 114,59 kJ/mol, 112,06 kJ/mol ve 124,12 kJ/mol olarak bulundu. Bu sonuçlar, PLA/perlit kompozitlerinin sürdürülebilir malzeme uygulamaları için ekonomik ve termal olarak kararlı alternatifler olma potansiyelini vurgulamaktadır.

Anahtar Kelimeler: Polilaktit, perlit, biyobozunur polimer kompoziti, termal bozunma kinetiği

1. Introduction

In the modern era, the demand for bio-based polymers has increased significantly with the impact of adopting the cyclical economic model, environmental issues and rising energy prices [1, 2]. These polymers offer environment-friendly solutions which may serve as a substitute for the oil-based alternatives and they have a widespread area of usage in numerous industries such as textile, food, cosmetics, construction and medicine [3]. Especially polylactide (PLA) comes to the forefront among the bio-based polymers thanks to its availability of being extracted from reliable sources, its biocompatible structure and its biodegradable thermoplastic features [4]. Previous studies indicate that PLA has a broad spectrum of usage, including medicine carriage systems, packaging materials, fibers and other applications. These studies also indicate that each newly examined property contributes to environmental protection goals [5]. However, there are still studies required for improving some features of PLA such as mechanical endurance, thermal stability, gas barrier feature, solvent resistance and flame retardant performance [6].

In order to increase the performance of polymers, either chemical or physical methods can be applied. The chemical methods comprise the modification of the polymer structure with functional groups and these methods may provide significant enhancements in the performance of the polymer. However, these kinds of modifications are strongly dependent on the synthesis step and they might require complex procedures [7, 8]. On the other hand, in physical methods, the addition of inorganic particulates to the polymer by using various techniques may improve the stability and other functional features of the materials [9]. In this context, the composite materials obtained by adding the natural backfill materials to the biodegradable polymers are remarkable in terms of their application fields, thanks to their environment-friendly and cost-friendly nature. The performance of polymer composites containing minerals are affected by numerous characteristic factors such as the size, shape and addition amount of the particulates [10-14.]. Perlite, which is a natural clay, is used in many fields such as insulation products, paints, cement and plaster coatings, pharmaceuticals, dental materials, cleaning agents, soil and water filtration applications. Also, it has been utilized as an alternative inorganic filling agent in polymeric composite studies [15-21]. In one of their studies Tian and Tagaya prepared PLA/perlite and PLA/montmorillonite (MMT) composites with the methods of melt extrusion and solvent casting, and investigated the effects of organic/inorganic ratio and types of inorganic compounds on the characterization of the materials [6]. Together with the mathematical models applied, the analysis of the thermal degradation kinetics of a material may provide detailed information about the kinetic parameters and mechanisms related to the process, and it may enable the development of applications regarding the relevant product [22, 23]. Thermogravimetric analysis (TGA) is a widely used and reliable technique for investigating thermal degradation kinetics [24, 25]. While there are isothermal or non-isothermal techniques which can be used in the calculation of the activation energy, the methods without isoconversional models, especially the Flynn-Wall-Ozawa (FWO) method has become one of the most recognized and preferred methods, since it provides high accuracy and reliability in the thermal degradation analysis of solid materials. This method is being used frequently by many researchers [25-28].

Poly lactide has a more sensitive thermal characteristic above the melting heat, especially during the process. This situation can cause a limitation on the number of application fields for PLA and various challenges encountered during the production process. Therefore, the new studies that are carried out for the purpose of extending the application fields of PLA and decreasing the production costs of it by increasing the thermal stability of PLA are quite remarkable. So far there is no record of a study in the literature which addresses the thermal degradation kinetics of PLA/perlite composites. Therefore, among various inorganic fillers, perlite was chosen due to its natural abundance, low cost, lightweight structure, and its potential to improve thermal properties without significantly affecting the biodegradability of PLA. In this paper, polylactide was synthesized and characterized by FTIR, ^1H -NMR, GPC and TGA analysis. Polymer composites were prepared at different PLA/perlite ratios by solvent casting method. Then the optimum polymer/perlite ratio was determined according to the increase in thermal character. The thermal degradation kinetics studies of PLA/Perlite composite were investigated employing Flynn-Wall-Ozawa, Tang and Kissinger process.

2. Material and Methods

2.1 Materials

All reactions and manipulations were carried out using conventional schlenk tube techniques. The L-lactide (98%) with m.p. 93 °C was obtained from Alfa Aesar. It was purified by recrystallization three times from dry ethyl acetate, dried under vacuum and kept under argon. It was stored at 4 °C. Tin 2-ethylhexanoate (95%) was purchased from Sigma-Aldrich, and was used without further purification. Commercial grade dichloromethane, chloroform and toluene (Sigma-Aldrich) were used without any purification. Perlite was obtained from Genper Expanded Perlite Industry Business Co. (Turkey). Before use, it was dried in a vacuum oven and ground then the particles passed through a 63-micron sieve were used.

2.2 Characterization techniques

FTIR spectra were taken with a PerkinElmer Spectrum Two FT-IR Spectrometer with ATR attachment. ^1H -NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in CDCl_3 containing TMS as an internal standard, using a Varian AS-400 spectrometer. Chemical shifts are reported in ppm. J values were given in Hz. Thermal analysis of polymer and composites were carried out using PerkinElmer Pyris 1 TG/DTA in the temperature range of 25-600 °C at the different rate (5-10-15-20 °C/min) under nitrogen flow (100mL/min). Molecular weight (M_n and M_w) of synthesized polymers were determined by gel permeation chromatography (GPC) on a Hewlett-Packard (HP) HPLC system with a differential refractometer detector. THF served as the eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities were reported versus monodisperse polystyrene standard.

2.3 Polymerization of L-lactide (LLA)

Purified L-lactide was added in a schlenk tube. It was dried for half an hour under high vacuum (5 mmHg) at room temperature. Then, the tin (II) ethylhexanoate was added into schlenk

keeping with the monomer to initiator ratio at 100. Polymerizations were carried out under 130 °C and 8 h under in inert atmosphere [31]. At the end of the reaction time, the schlenk was immersed quickly in liquid nitrogen to stop the polymerization. The obtained products were dissolved in dichloromethane and precipitated in large amount of methanol. The precipitated polymers were dried at room temperature in vacuum oven for 24 hours. The polymers were characterized by using FTIR, ^1H NMR, ^{13}C NMR, GPC and TG methods.

2.4 Preparation of PLA/perlite composites

Polymer composites were prepared using solvent casting method, with a polymer/additive ratio of as 90/10, 80/20, 60/40 (w/w). Firstly, the predetermined amount of PLA was solved in chloroform for about an hour. Then, the determined amount of perlite additive was added to the polymer solution. Then, the mixture was stirred for about 24 hours in a closed beaker with the aid of a magnetic stirrer, and then the solvent was evaporated for one day at room temperature. The product was dried in a vacuum oven at 45 °C for 24 hours.

2.5 Thermal degradation kinetic methods

Dynamic thermogravimetric methods are widely employed in the investigation of polymer degradation processes and play an important role in elucidating the underlying mechanisms [32-34].

The rate of solid-state, non-isothermal decomposition reactions is commonly expressed using an Arrhenius-type equation, which correlates the decomposition rate with the activation energy and temperature through an exponential function, as presented in Equation (1). This equation is the fundamental expressions of analytical methods to calculate kinetic parameters on the basis of TG data.

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (1)$$

where A is the pre-exponential factor (min^{-1}), assumed to be independent of temperature, E is the activation energy (kJ/mol), T is the absolute temperature (K), and R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

By rearranging Equation 1 and integrating both sides of the equation, the following equation (2) is obtained:

$$g(\alpha) = \left(\frac{A}{\beta}\right) \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT = \left(\frac{AE}{\beta R}\right) p(u) \quad (2)$$

$$p(u) = \int_{\infty}^u -\left(\frac{e^{-u}}{u^2}\right) du \quad \text{and} \quad u = \frac{E}{RT}$$

There are several methods based on the basic rate equation to understand the thermal degradation kinetics process from TGA and DTG data. In this study, the thermal degradation activation energy (E) value of the PLA/perlite composite was calculated using the Flynn-Wall-Ozawa, Kissinger and Tang integral methods, which are integral isoconversion methods.

2.5.1 Flynn-Wall-Ozawa Process

This method, which is isoconversional, is used to determine the activation energy, which is a function of the degree of conversion, without knowing the reaction mechanism. The temperatures corresponding to the constant values obtained from the thermograms taken at different heating rates are measured and the calculation is made using the equation (1) [35, 36] below:

$$\log \beta = \log \left[\frac{AE}{g(\alpha)R} \right] - 2.315 - \frac{0.457E}{RT} \quad (1)$$

The logarithmic expression can also be written by converting it to the natural logarithm:

$$\ln \beta = \ln \frac{AE}{g(\alpha)R} - 5.331 - 1.052 \left(\frac{E}{RT} \right)$$

where T is the absolute temperature, β is the heating rate, E is the activation energy, A is the pre-exponential factor (min^{-1}), α is the conversion degree and R is the universal gas constant (8.314 J/K mol). Plotting $\ln(\beta)$ against $1/T$ should give straight lines and its slope is directly proportional to the activation energy ($-E/R$).

2.5.2 Kissinger process

The Kissinger method, which is another non-isothermal kinetic method independent of the reaction mechanism, was used to calculate the activation energy. The activation energy for the Kissinger method can be determined by the following equation (2) [37]:

$$\ln \left(\frac{\beta}{T_{max}^2} \right) = \left\{ \ln \frac{AR}{E} + \ln [n(1 - \alpha_{max})^{n-1}] \right\} - \frac{E}{RT_{max}} \quad (2)$$

Here, β represents the heating rate; T_{max} is the temperature at the maximum degradation point in the DTG thermogram; α_{max} denotes the maximum conversion rate; and n is the reaction order. The activation energy (E_a) is calculated from the slope of the plot of $\ln(\beta/T_{max}^2)$ versus $1/T$.

2.5.3 Tang Method

Tang proposed a modified form of Equation (2) to enhance the accuracy of the integral temperature approach. This approach, known as the Tang method, can be expressed as follows [38]:

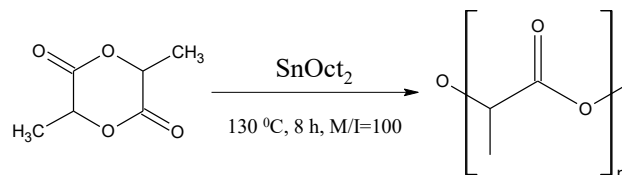
$$\ln \left(\frac{\beta}{T^{1.894661}} \right) = \ln \left(\frac{AE}{Rg(\alpha)} \right) + 3.635041 - 1.894661 \ln E - \frac{1.001450E}{RT} \quad (3)$$

A graph is plotted between $\ln(\beta/T^{1.894661})$ and $1/T$, and the activation energy (E) is determined from the slope of the graph as $(-1.001450E/R)$.

3. Results and Discussion

3.1 Characterization of the PLA and PLA/perlite composite

Poly(lactide) was synthesized by coordination-insertion ring opening polymerization reaction of L-lactide with tin(II) 2-ethylhexanoate in bulk medium at 130 °C, 8 h and monomer/initiator ratio was 100. The general polymerization reaction scheme was given in Scheme 1.



Scheme 1. The general polymerization scheme for PLA initiated by SnOct₂

The FTIR spectrum of PLA can be seen at Figure 3.1. The peaks at 2998 cm⁻¹ and 2950 cm⁻¹ are belong to the C–H stretching vibration in polymer. The characteristic band at 1752 cm⁻¹ corresponds to the C=O bond stretching. The absorption peaks at 1183 cm⁻¹ and 1081 cm⁻¹ are associated with the C–C and C–O–C stretching vibrations, respectively. In the ¹H-NMR (400 MHz, CDCl₃) spectrum, the peaks at δ 1.57 ppm (d, 3H, *J* = 6.8 Hz) and 5.17 ppm (q, 1H, *J* = 6.8-7.2-14.0 Hz) correspond to the –CH₃ and CH–groups, respectively (Figure 3.1-b). The ¹³C NMR spectrum of the polymer is also shown in Figure 3.1(c). ¹³C-NMR (100 MHz, CDCl₃) signals at 169.55 ppm, 68.98 ppm and 16.61 ppm assigned to the OCOCH–, –COCHCH₃ and –CHCH₃– groups, respectively. The number average molecular weight (M_n) of synthesized polymer was found as 20,091 g/mol (PDI=2.13) by GPC. The thermal character of the polymer was investigated by thermogravimetric analysis (TGA), and the thermogram recorded at a heating rate of 10 °C/min under a nitrogen atmosphere is presented at Figure 3.1(d). The degradation of PLA occurs in a single step, with the degradation temperature range and the maximum degradation temperature determined to be 170–275 °C and approximately 250 °C, respectively. The 4% residue observed at 600 °C is likely due to the metal compound used in the initiator.

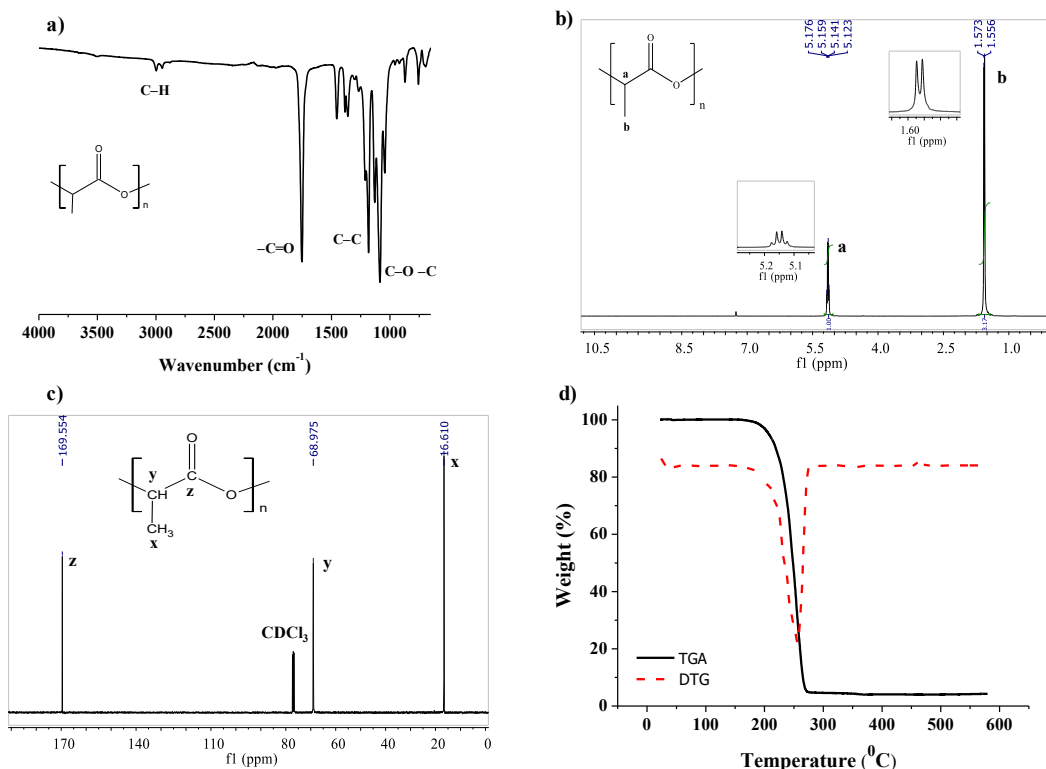


Figure 3.1 FTIR (a), ^1H -NMR (b) and ^{13}C -NMR (c) spectrum, TGA and DTG curve (d) of polylactide.

In the FTIR spectrum of perlite (Figure 3.2), a characteristic broad Si–O–M (M=Si or Al) band was observed at 1015 cm^{-1} . The peak at 788 cm^{-1} was assigned to the symmetric stretching vibration of the Si–O bond [39, 40]. The TGA analysis of perlite, performed under a nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$, is shown in Figure 3.2 (b). It was determined that the degradation of perlite occurred slowly, and the remaining weight was 96% at $600\text{ }^{\circ}\text{C}$.

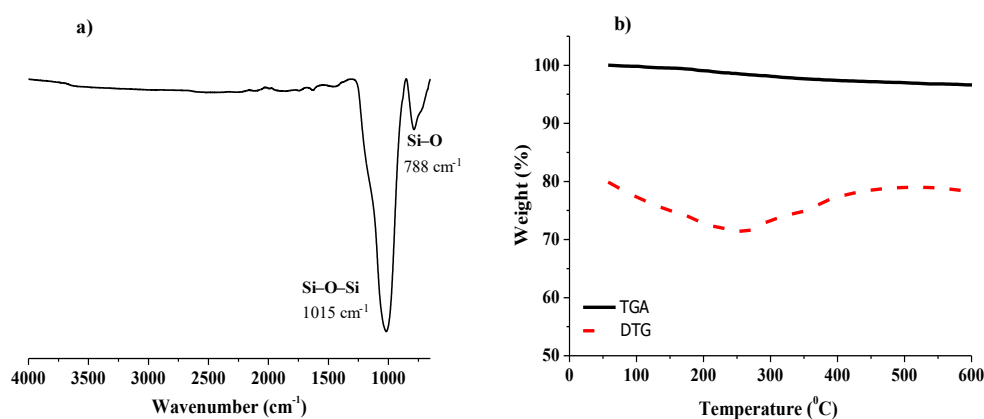


Figure 3.2 FTIR spectrum (a) and TG and DTG curve (b) of perlite.

The FTIR spectra of Perlite/PLA composites with 10%, 20%, and 40% perlite content are presented comparatively in Figure 3.3(a). The characteristic C–H and C=O stretching vibration peaks of the polymer are observed at approximately 2900 cm^{-1} and 1750 cm^{-1} , respectively. The broad band between 1100 cm^{-1} and 950 cm^{-1} arises from the overlap of the C–O–C bond present in the polymer structure and the Si–O–Si bond in perlite. This observation confirms the successful formation of the composite.

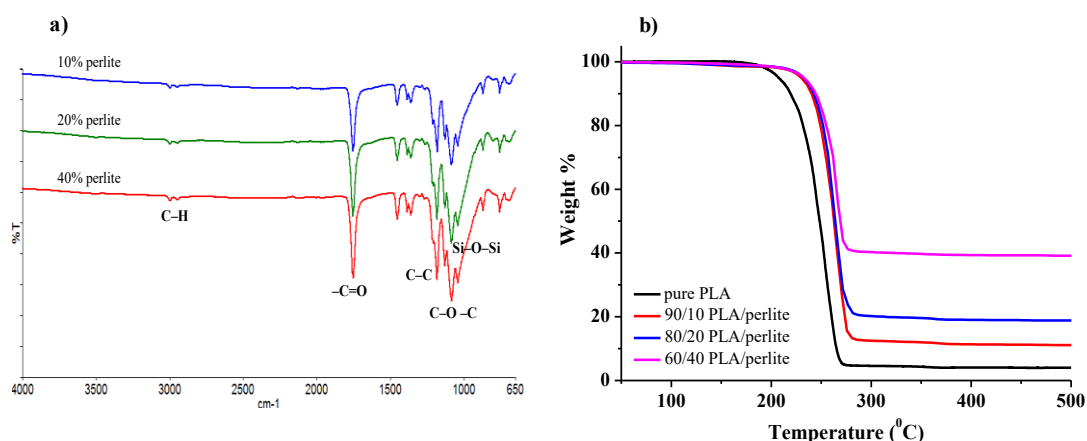


Figure 3.3 FTIR spectra (a) and TGA thermograms (b) of pure PLA and PLA/Perlite composites prepared in different ratios.

The thermogravimetric analysis results related to pure PLA and PLA composites with varying perlite ratios are given at Figure 3.3 (b), obtained under a nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. Degradation takes place in single step for both pure polymer and for the composites that have been prepared. The different mass amounts of composites left over from the degradation are proportionate with the perlite they contain. And this situation indicates that the additive is homogeneously spread into the polymer. It was determined from the thermograph that the pure PLA starts degrading at $\sim 205\text{ }^{\circ}\text{C}$ and the perlite/PLA composites in ratios of 10%, 20% and 40% degrade at $\sim 233\text{ }^{\circ}\text{C}$, $237\text{ }^{\circ}\text{C}$ and $239\text{ }^{\circ}\text{C}$ respectively. It is considered that the onset degradation temperature of perlite/PLA composite being $35\text{ }^{\circ}\text{C}$ higher compared to pure polymer shall yield a significant outcome in terms of increasing thermal stability and decreasing the costs for the application fields. Besides, since there are not significant differences between the degradation temperatures of the perlite/PLA composites in ratios of 10%, 20% and 40% according the analysis results, and since it will be more advantageous in application fields in terms of costs, the ratio of 40%, which comprises the highest level of additive, is preferred in the studies of thermal degradation kinetics.

3.2 Thermal Degradation Kinetics of PLA and PLA/Perlite Composite

In order to investigate the thermal degradation kinetics of pure PLA and PLA/perlite (60/40), using the thermogravimetric analysis method (TGA), the thermographs of the samples were obtained in a nitrogen atmosphere from 25 °C to 600 °C, with heating rates of 5, 10, 15 and 20 °C/min. The TGA and DTG curves obtained at different heating rates for polymer and composite are given at Figure 3.4. After examining the thermographs, it was clarified that the change in the heating rates does not create any difference in the thermal degradation characteristic of polymer and composite. However, it was observed that the onset degradation temperatures of both PLA and PLA/perlite composite increases and that the apex of DTG curves ascend to higher temperature levels with increasing heating rates (β). This increase can be attributed to the reduced time for heat transfer at higher heating rates, as the sample reaches the target temperature more rapidly, which may result in incomplete thermal equilibrium. Therefore, it can be noted that heating rate has a significant effect on the thermal degradation kinetics of the sample [29].

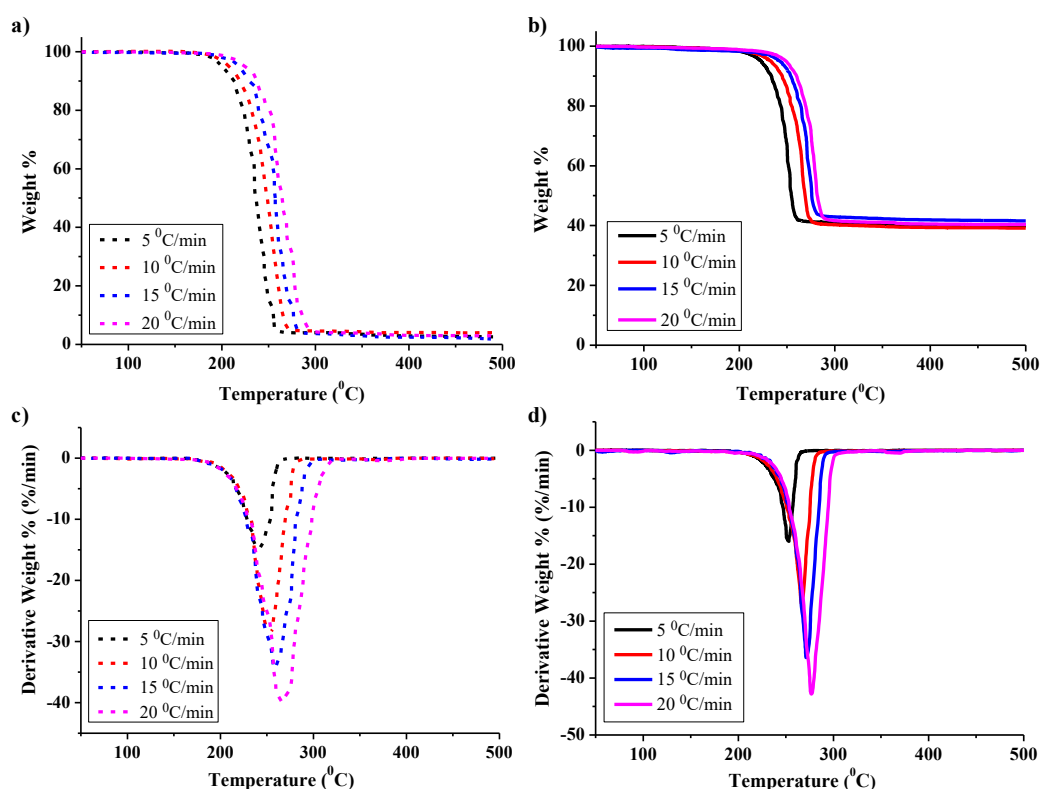


Figure 3.4 TGA and DTG curves of PLA (a and c) and PLA/Perlite (60/40) composite (b and d) at different heating rates.

Firstly, iso-conversional Flynn–Wall–Ozawa (FWO) method was applied for calculating the thermal degradation activation energies (E) of PLA and PLA/perlite. The TGA characteristic heat values obtained for 0.05 and 0.10 conversion values at different heating rates (β) are given at Table 3.1. Graphs were drawn between $\log \beta$ values corresponding to the $1/T$ value which is calculated at different conversion values pertaining to different heating rates (β), and they are given at Figure 3.5 (a and b) for polymer and composite. It is apparent that PLA and its composite have a similar inclination at different heating rates. However, the values of the slopes and overall form of the curves indicate that these two materials have different thermal stabilities. This situation proves that adding perlite to the PLA matrix affects the degradation behavior of the polymer. The conversion values for PLA are (α) 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75 and 0.80; And the transformation values for PLA/perlite are (α) 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50 and 0.55.

Table 3.1 Characteristic temperatures of the thermal degradation of PLA and PLA/Perlite (60/40) composite

β (°C/min)	T_i (°C)		T_{max} (°C)		$T_d (\alpha=0.05)$ (°C)		$T_d (\alpha=0.10)$ (°C)	
	PLA	PLA/perlite	PLA	PLA/perlite	PLA	PLA/perlite	PLA	PLA/perlite
5	193.4	215.6	240.7	252.3	200.8	223.0	213.5	233.5
10	202.6	225.7	252.6	266.3	213.0	233.2	225.0	244.9
15	213.5	237.6	258.1	271.7	217.8	242.7	229.2	253.9
20	218.5	242.6	267.5	277.0	224.1	248.7	237.2	260.1

T_i : Initial temperature of the TG; **T_{max} :** Peak temperature of the DTG; **T_d :** Degradation temperature for a specific degradation percentage

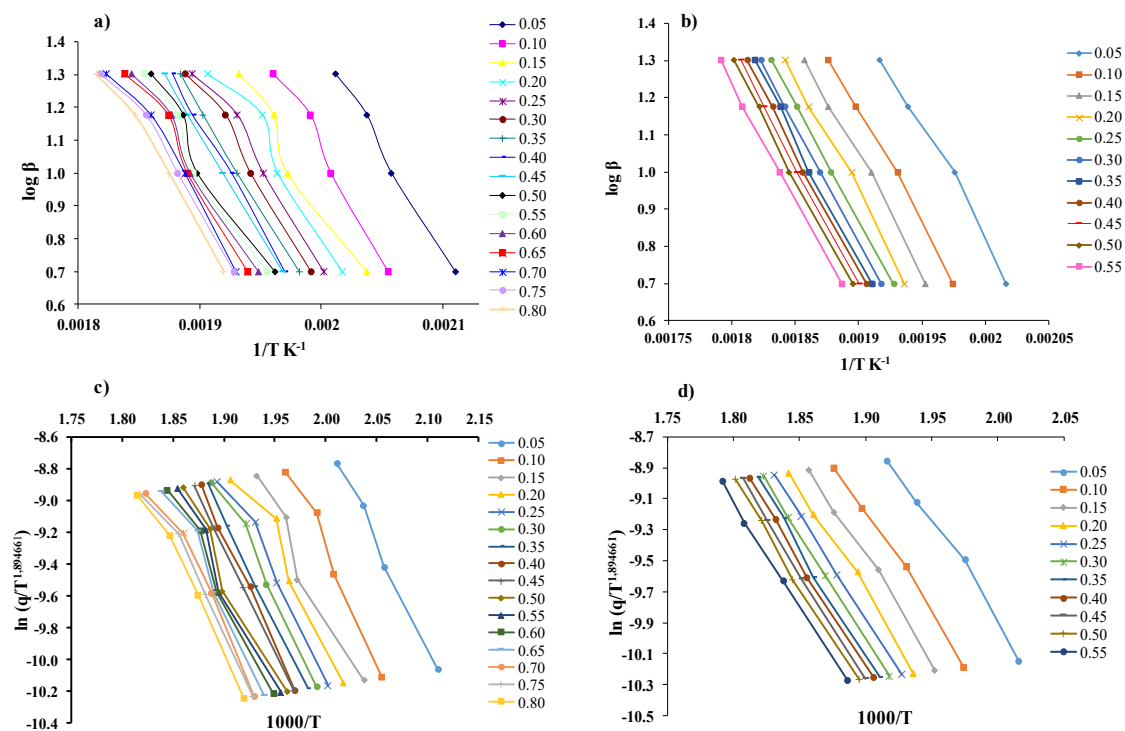


Figure 3.5 Curves of PLA and PLA/Perlite (60/40) composite at different conversion values, respectively for the Flynn-Wall-Ozawa (a and b) and Tang (c and d) methods.

Based on the FWO method, using Equation 1, the inclination values ($-0.457E/R$) were calculated from the graphs drawn between $\log \beta$ - $1/T$ corresponding to different conversion values, and the activation energy (E) was determined specifically for each conversion value.

$$\log \beta = \log \left[\frac{AE}{g(\alpha)_R} \right] - 2.315 - \frac{0.457E}{RT} \quad (1)$$

Based on the activation energy values obtained from the inclination values corresponding to different conversion values, the average activation energies of PLA and PLA/perlite composite were determined as 108.39 kJ/mol and 114.59 kJ/mol respectively (Table 3.2). For PLA, the value which is closest to the average activation energy value (108.39 kJ/mol) was obtained at conversion value 30%, and for PLA/Perlite composite, this value was obtained at conversion value 20%. The higher thermal degradation activation energy of PLA/perlite composite compared to pure PLA indicates that the additive is effective towards the slow-paced progression of the process of polymer's degradation mechanism.

The Tang method, which is one of the isoconversional methods, demonstrates a similar approach to Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods when calculating the activation energy in kinetic analysis, however, it differs drastically from them when it comes to mathematical expressions. By using Equation 3, the activation energy (E_a) and logarithmic prefactor ($\ln A$) values were also calculated using Tang model. The Figure 3.5 (c and d) shows respectively for PLA and PLA/perlite composite the graphs of $1000/T$

corresponding to $\ln [q/T^{1.894661}]$ at 5-10 °C/min heating rates within the total conversion range of 5-80%. Based on the data obtained from these graphs, the activation energy value (E_a) obtained for PLA ranges between 97.78 and 116.36 kJ/mol depending on the conversion values, while this value ranges between 105.74 and 116.72 kJ/mol for PLA/perlite composite (Table 3.2). The average activation energy values for PLA and PLA/perlite composite were calculated as 105.75 kJ/mol and 112.06 kJ/mol respectively, based on Tang method. In general, the results obtained with Tang method are coherent with the results obtained with FWO method and they indicate that the perlite additive increases the activation energy.

Table 3.2 Activation energies calculated using the Flynn-Wall-Ozawa and Tang methods at different conversion values.

α (%)	Flynn-Wall-Ozawa method				Tang method			
	E_a (kJ/mol)		R^2		E_a (kJ/mol)		R^2	
	PLA	PLA/perlite	PLA	PLA/perlite	PLA	PLA/perlite	PLA	PLA/perlite
0.05	112.55	108.24	0.9931	0.9897	110.64	105.74	0.9921	0.9881
0.10	118.19	110.69	0.9821	0.9962	116.36	108.14	0.9796	0.9956
0.15	104.66	113.18	0.9673	0.9960	102.07	110.67	0.9624	0.9954
0.20	101.24	114.52	0.9502	0.9952	98.37	112.01	0.9421	0.9945
0.25	103.21	113.88	0.9786	0.9997	100.38	111.30	0.9749	0.9997
0.30	108.36	114.74	0.9843	0.9998	105.76	112.17	0.9817	0.9998
0.35	110.71	119.09	0.9992	0.9970	108.20	116.72	0.9991	0.9966
0.40	116.85	117.06	0.9976	0.9981	114.61	114.56	0.9972	0.9979
0.45	111.63	117.70	0.9997	0.9993	109.11	115.20	0.9997	0.9992
0.50	107.51	117.58	0.9688	0.9978	104.75	115.05	0.9639	0.9975
0.55	109.11	113.85	0.9738	0.9988	106.41	111.09	0.9698	0.9987
0.60	107.60		0.9802		104.78		0.9770	
0.65	111.80		0.9728		109.16		0.9685	
0.70	103.68		0.9737		100.56		0.9690	
0.75	101.04		0.9773		97.78		0.9731	
0.80	106.10		0.9868		103.07		0.9844	
Average:	108.39	114.59			105.75	112.06		

The activation energy values of PLA and PLA/perlite composites were also calculated using the Kissinger method, which is another kinetic method independent from the reaction mechanism. The relevant equation on which the method is based, is given below at (Equation 2).

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \left\{ \ln \frac{AR}{E} + \ln[n(1 - \alpha_{max})^{n-1}] \right\} - \frac{E}{RT_{max}} \quad (2)$$

The temperature levels at which ($T_{\max}$) the degradation occurs in the fastest form at different heating speeds (β) were determined from the DTG curves of the samples of pure polymer and composite, and they are presented at Table 3.3 and Table 3.4. A graph was drawn between $\ln(\beta/T_{\max}^2)$ values obtained at different heating rates and $1000/T_{\max}$ using Equation 2, and the activation energy values were calculated using the slope values ($m = -E/R$) obtained from this graph. The graphs generated for PLA and PLA/perlite composite are shown at Figure 3.6 (a and b, respectively). The activation energies calculated with this method were determined as 101.06 kJ/mol for PLA and 124.12 kJ/mol for PLA/perlite composite.

Table 3.3 Maximum degradation temperatures ($T_{\max}$) of PLA at different heating rates

β (°C/min)	$T_{\max}$ (°C)	$T_{\max}$ (K)	$T_{\max}^2$	$\ln(\beta/T_{\max}^2)$	$1000/T_{\max}$
5	240.70	513.70	263888	-10.87	1.95
10	253.56	526.56	277265	-10.23	1.90
15	261.10	534.10	285263	-9.85	1.87
20	270.58	543.58	295479	-9.60	1.84

Table 3.4 Maximum degradation temperatures ($T_{\max}$) of PLA/Perlite (60/40) composite at different heating rates

β (°C/min)	$T_{\max}$ (°C)	$T_{\max}$ (K)	$T_{\max}^2$	$\ln(\beta/T_{\max}^2)$	$1000/T_{\max}$
5	251.86	524.86	275478	-10.92	1.91
10	266.27	539.27	290812	-10.28	1.85
15	271.31	544.31	296273	-9.89	1.84
20	276.98	549.98	302478	-9.62	1.82

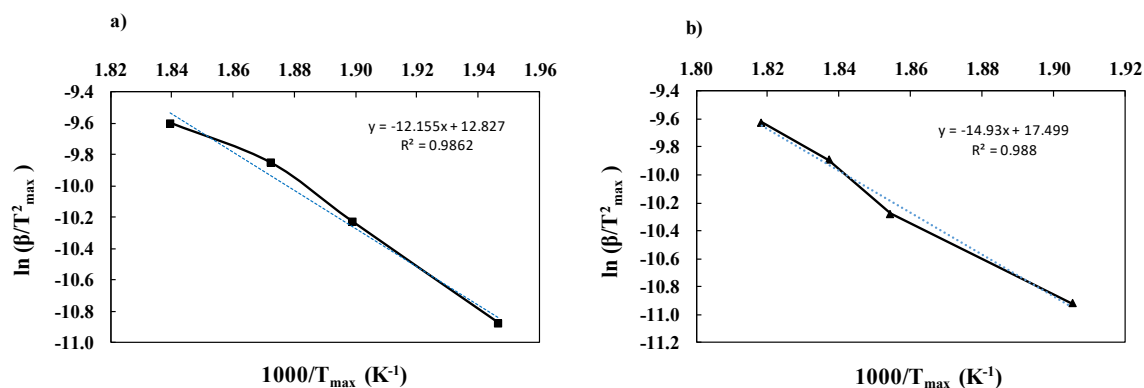


Figure 3.6 Kissinger curves of PLA (a) and PLA/Perlite (60/40) composite (b) plotted between $\ln(\beta/T_{\max}^2)$ and $1000/T_{\max}$

4. Conclusion

For the purpose of increasing the basic thermal stability of the biodegradable and biocompatible Polylactide, PLA/perlite composites with the perlite additive in different ratios (10%, 20%, 40%) were prepared by using the method of solvent casting. It was determined that a 40% addition of perlite increases the degradation temperature of neat PLA by 35 °C. However, TGA thermograms showed that increasing the perlite content did not significantly alter the overall thermal stability of the polymer. Using the Flynn-Wall-Ozawa, Tang and Kissinger methods, the thermal degradation activation energies for PLA were calculated as 108.39 kJ/mol, 105.75 and 101.06 kJ/mol respectively, and for PLA/perlite composite (60/40) they were calculated as 114.59 kJ/mol, 112.06 and 124.12 kJ/mol respectively. The determination of a higher value of degradation activation energy for PLA/perlite compared to pure PLA after calculation with the applied methods, indicates that perlite has a complicating effect on the process of the degradative reaction of polymer. In other words, it has been revealed that the perlite, which is used as an additive, causes the decrease of the PLA's rate constant (k). The observed increase in the thermal stability of PLA with the addition of perlite suggests that this composite material could serve as a promising alternative for applications such as packaging and biodegradable agricultural films. In future studies, the use of surface-modified perlite or hybrid filler systems may be explored to further enhance both the thermal and mechanical properties.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

Author Contributions

S.G. designed the study. S.G. and N.A.B. conducted the experiments. S.G. evaluated the analysis results and performed the calculations. S.G. wrote the manuscript. All authors have read and approved the published version of the manuscript.

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