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Detail kinetic analysis of the thermal decomposition of PLA with oxidized multi-walled carbon nanotubes

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ABSTRACT

Nanocomposites of poly(L-lactic acid) (PLA) with oxidized multi-walled carbon nanotubes (MWCNTs-COOH) were prepared by solved evaporation method containing 2.5 wt% MWCNTs-COOH. From the thermogravimetric curves it can be seen that PLA/MWCNTs-COOH nanocomposite present a relatively better thermostability than PLA. The activation energy was calculated with the isoconvertional Ozawa–Flynn–Wall and Friedman's methods. For all the mass conversions, PLA has lower values than the nanocomposite. From the variation of the activation energy (E) with increasing degree of mass conversion, especially for the PLA, it was concluded that the decomposition of all the samples is taking place with a complex reaction mechanism with the participation of at least two different mechanisms. The best fitting of experimental data with theoretical models for PLA and PLA–2.5 wt% MWCNTs-COOH give nth-order for the first mechanism and nth-order with autocatalysis (Fn–Cn) for the second mechanism with different activation energies.

1. Introduction

Biodegradable polymers have been extensively studied and used over the past two decades in both fundamental research and chemical industry. Among the numerous polyesters studied so far, poly(L-lactic acid) (PLA), has proven to be the most attractive and useful biodegradable polymer [1]. PLA is a biodegradable, biocompatible and compostable polyester derived from renewable resources such as corn, potato, cane molasses and beet sugar. It is one of the most promising environmentally friendly thermoplastics [2].

Several studies have focused on the thermal degradation and thermal stability of PLA [3]. The calculated values of the activation energy present a great dispersion while a first-order reaction model has been used in few works for the determination of the activation energy. Also, there are a few works in which it was proposed that the degradation process is followed by more complex kinetics [4].

There are only few works in the literature in which the influence of MWCNTs on the thermal degradation of PLA is studied. Kuan et al. [5] and Moon et al. [6] who studied PLLA/MWCNTs nanocomposites resulted that the decomposition temperature of the nanocomposites is higher than that of PLLA. Kim et al. [7,8] also studied thermal degradation of PLLA-MWCNT and PLLA-graft-MWCNT and the composites investigated showed higher onset degradation temperature along with a higher amount of residue at the completion of degradation than neat PLLA.

The reaction mechanism of the polymer decomposition is a very complex radical chain mechanism, including initiation, propagation and termination reactions. As known, two main types of reaction models are generally applied on the thermal degradation of polymers: the nth-order model, with only one parameter – the reaction order, and the first-order model. Other models have also been used occasionally, but they are complex models containing several fitting parameters [9–13]. Kim et al. [7,8] determined also the activation energy and the calculated values were: 131.5 and 125.1 kJ/mol for PLLA, 143.7 and 150.7 kJ/mol for PLLA/MWCNT and 151.2 and 160.1 kJ/mol for PLLA/PLLA-g-MWCNT, using Kissinger and Ozawa's methods respectively. Till now, the mechanisms of the decomposition of PLLA/MWCNTs have not been studied yet, especially in comparison with the mechanisms of PLA. The purpose of this work is the determination of the appropriate kinetic models for the detailed study of the decomposition mechanisms of the PLA–MWCNTs-COOH nanocomposite in comparison to the neat PLA.

2. Experimental

2.1. Materials

Commercially reinforcement ligament consisted from amorphous poly(L-lactic acid) (PLA) supplied under the trade name Resorbaid® from Cousin Biotech (France). Multi-walled carbon

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nanotubes (MWCNTs) used in this work were synthesized by the chemical vapor deposition (CVD) process and were supplied by Nanothinx (Patra, Greece). Their diameter was between 9 and 20 nm, their length >5 μm and were used in oxidized form (MWCNTs-COOH). Samples (1 g) of the nanotubes were suspended in 40 ml of a mixture of concentrated nitric acid and sulfuric acid (1:3 in volume ratio) and refluxed for 15 min. After washing with deionized water until the supernatant attained a pH around 7, the samples were dried under vacuum at 100 °C [14]. Dichloromethane anhydrous ($\geq$99.8%) and tetrahydrofuran anhydrous ($\geq$99.8%) were obtained from Aldrich Chemical Co.

2.2. Preparation of PLA/MWCNTs nanocomposites

PLA ligament were dissolved in a mixture of dichloromethane/tetrahydrofuran 50/50 w/w at room temperature while at the same mixture were dispersed MWCNTs-COOH under sonication for 1 h. The PLA solution and MWCNTs-COOH dispersion were mixed under stirring for 1 h and sonicated for additionally 1 h. The mixture remained at room temperature for 24 h for solvent evaporation and dried under vacuum at 110 °C for 24 h. The prepared films were placed in a desiccator to prevent any moisture absorption. According to this procedure nanocomposites containing 2.5 wt% MWCNTs-COOH were prepared.

2.3. Thermogravimetric analysis

Thermogravimetric analysis was carried out with a SETARAM SETSYS TG-DTA 16/18 instrument. Samples (6.0 ± 0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. PLA nanocomposites were heated from ambient temperature to 450 °C in a 50 ml/min flow of N$_2$ at heating rates of 5, 10, 15 and 20 °C/min. Continuous recordings of sample temperature, sample weight and heat flow were taken.

3. Results and discussion

3.1. Thermal stability

In general, addition of filler can improve the thermal stability of the filled polymer composite systems to some extent in which the filler plays an important role. Previous studies [7,15] have reported that the polymer/MWCNTs composites present higher thermal stability than that of the neat polymer matrix.

The thermogravimetric (TG) curves of PLA and PLA/2.5 wt% MWCNTs-COOH nanocomposite with heating rate 10 °C/min are shown in Fig. 1. The PLA/2.5 wt% MWCNTs-COOH nanocomposite begins to decompose at a higher temperature and completes the decomposition at about the same temperature with the PLA. This is an indication that the addition of MWCNTs-COOH causes a substantial thermal enhancement of PLA, at least at the initial stages of decomposition. This improvement is mainly attributed to good matrix–nanotube interaction, good thermal conductivity of the nanotubes and also due to their barrier effect. The nanocomposite begins to decompose at higher temperatures, although the addition of MWCNTs-COOH seems to have little effect on the temperature that the maximum decomposition rate takes place. Wu et al. [15] referring to the presence of all the three studied PLA/MWCNTs, concluded that they almost cannot improve the thermal stability effectively enough at the initial stage of degradation and that the temperature corresponding to a weight loss of 5 wt% only shows a slight increase in contrast to that of the neat PLA. Moreover, the increase of decomposition level and the presence of carboxylic and purified MWCNTs retard the depolymerisation of PLA, showing remarkable increase in the temperature corresponding to maximum rate of decomposition. However, Kim et al. [7] showed that the addition of MWCNTs increases the temperatures corresponding to a weight loss of 5 wt% and/or to the onset of decomposition by about 10–20 °C or even more. For this reason, a detailed decomposition kinetic analysis in necessary, in order to evaluate the real effect of MWCNTs-COOH on thermal degradation of PLA.

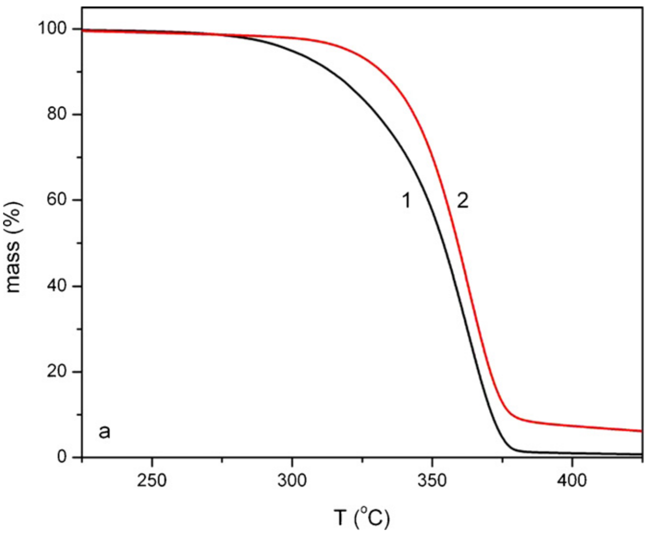

Fig. 1. TG curves of PLA (1) and PLA/2.5 wt% MWCNTs-COOH and (2) nanocomposite for heating rate β = 10 °C/min.

3.2. Thermal degradation kinetics

For the study of the degradation mechanisms of PLA and PLA/2.5 wt% MWCNTs-COOH nanocomposite it is important that the kinetic parameters (activation energy E and pre-exponential factor A) and the conversion function $f(\alpha)$ are evaluated. The relationship between kinetic parameters and conversion (α) can be found using the mass curves recorded in TG dynamic thermograms. The thermogravimetric (TG) curves of PLA–2.5 wt% MWCNTs-COOH at different heating rates, 5, 10, 15 and 20 °C/min are shown in Fig. 2.

For the determination of the conversion function, $f(\alpha)$, and the activation energy, E, various methods have been worked out. These methods can, in general, be categorized as: (i) isoconversional and

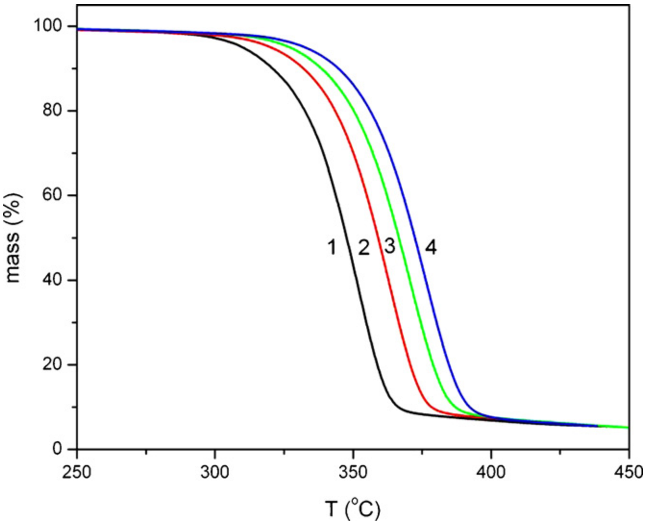

Fig. 2. TG curves of PLA/2.5 wt% MWCNTs-COOH nanocomposite for different heating rates. (1) β = 5 °C/min, (2) β = 10 °C/min, (3) β = 15 °C/min and (4) β = 20 °C/min.

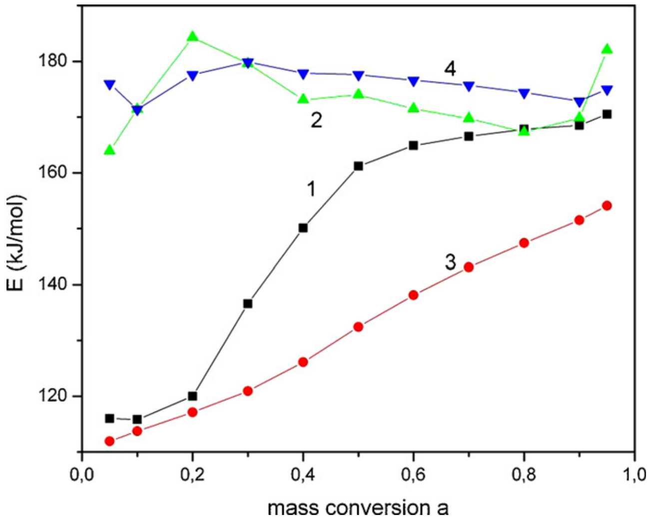

Fig. 3. Activation energy E, as calculated with OFW and Friedman methods, versus degree of conversion α. (1) PLA – Friedman, (2) PLA/2.5 wt% MWCNTs-COOH – Friedman, (3) PLA–OFW and (4) PLA/2.5 wt% MWCNTs-COOH – OFW.

(ii) model fitting methods. The isoconversional method is in fact, a "model free" method which assumes that the conversion function $f(\alpha)$ does not change with the variation of the heating rate for all values of the degree of conversion (α). It involves the measuring of the temperatures corresponding to fixed values of α by experiments at different heating rates β [16]. The isoconversional methods are considered to give accurate values of the activation energy [17].

Model fitting methods of kinetic analysis depend on the reaction model and also assume the Arrhenius temperature dependence of the rate constant $k(T)$. They do not achieve a clean separation between the temperature dependent $k(T)$ and the reaction model $f(\alpha)$. Moreover, the temperature sensitivity of the reaction rate depends on the extent of conversion. As a result, these methods are considered to be approximate. One of these methods is the multivariate non-linear regression method [18,19].

For the determination of the activation energy, we choose to use two different methods, comparatively, since every method comes with its own error. Firstly, the isoconversional Ozawa, Flynn and Wall (OFW) method [20–22] was used. The OFW method is based on the following equation:

$$\ln \beta = -1.0516 \frac{E}{RT} + \text{const}$$

where β is the heating rate, E is the activation energy, R is the gas constant and T is the temperature. Secondly, Friedman's method [23] was used, which is based on the following equation:

$$\ln \left(\beta \frac{d\alpha}{dT} \right) = \ln A + \ln f(\alpha) - \frac{E}{RT}$$

where α is the degree of conversion, $f(\alpha)$ is the conversion function (reaction model) and A being the pre-exponential factor.

Table 1
Three different kinetic models and their conversion functions $f(\alpha)$.

Kinetic model	Symbol	$f(\alpha)$
nth-order	Fn	$(1-a)^n$
Expanded Prout–Tompkins	Bn	$(1-\alpha)^n\alpha^m$
nth-order with autocatalysis	Cn	$(1-a)^{n(1+K_{cat}X)}$

The calculated values of the activation energy for different values of mass conversion α are shown in Fig. 3. The difference in the E value calculated by the two methods can be explained by a systematic error due to improper integration. The method of Friedman employs instantaneous rate values and is therefore very sensitive to experimental noise. In OFW method, the equation used is derived assuming constant activation energy, introducing systematic error in the estimation of E in the case that E varies with α. This error can be estimated by comparison with the Friedman results [24]. It is followed from Fig. 3 for PLA, that the dependence of E on α, as calculated with Friedman's method and can be separated in three distinct regions, the first for values of α up to 0.2, in which E is almost stable, the second ($0.2 < \alpha < 0.5$) in which E presents a monotonous increase and the third ($0.5 < \alpha < 0.95$) in which E can be considered as having a constant average value as in the first region. The different regions are not obvious in the dependence of E from α as calculated with the OFW method since it presents a monotonous increase. This dependence of E on α is an indication of a complex reaction with the participation of at least two different mechanisms. From Fig. 3 for PLA/2.5 wt% MWCNTs-COOH the dependence of E from α is not as complicated as it is for PLA. It shows only one region with a relatively constant value of E. Furthermore, comparing the activation energies of PLA and its nanocomposite it is clear that for all conversions PLA has lower values than the nanocomposite. The differences are even higher at lower conversions, which are corresponded to the initial decomposition stages. The values of E for PLA/2.5 wt% MWCNTs-COOH are greater than in the work of Kim et al. [7] who studied PLA/2 wt% MWCNTs. The calculated values of E for PLA and its nanocomposite are showing the same trend as in this work. Furthermore, from the activation energies it is clear that MWCNTs-COOH causes a thermal stabilization effect to PLA decomposition. From Fig. 3 it seems that the nanocomposite decomposes with different activation energies and if possible with different mechanisms than neat PLA.

The determination of the reaction model mechanism using multiple heating rates is based at the "model fitting method". Initially it is considered that the degradation of the samples can be described only by a single mechanism, without presuming the exact mechanism. If the result of the fitting cannot be considered as accepted, then we must proceed to fit the experimental data with a combination of two mechanisms. The multivariate non-linear regression method is used [18,19] for the determination of the kinetic triplet. The calculated values of E and A after the fitting for three kinetic models (Table 1), for which the quality of the mathematical fitting depending on the regression coefficient R is at an accepted level, are presented at Table 2.

In the studied samples, the best kinetic model is the nth-order with autocatalysis (Cn) according to the values of the regression coefficient R. The values of the activation energy for all these models are in the same area of values that have been calculated with the isoconversional methods. In Fig. 4 the plots of the fitting with the best fitting model Cn for PLA/2.5 wt% MWCNTs-COOH samples are presented.

The quality of the fitting with the Cn model is good for both studied samples. At the PLA samples small divergences appear mainly in the plots with the lower heating rates at a first region and at the end of the degradation. At the PLA/2.5 wt% MWCNTs-COOH samples, the divergences are only at the end of the degradation and

Table 2
Calculated values of E, A of three kinetic models and its regression coefficient R. Conversion range $0 < \alpha < 1$.

	PLA			PLA/MWCNTs-COOH 2.5 wt%		
	Cn	Bna	Fn	Cn	Bna	Fn
$\log(A)$	8.9	8.9	8.9	12.1	12.5	12.9
E	134.9	135.2	135.3	175.2	176.6	183.7
n	0.42	0.36	0.38	1.12	0.76	0.54
$\log(K_{cat})$	−1.0	2.8E−5[a]		0.44	0.16[a]	
R	0.99957	0.99957	0.99957	0.99975	0.99962	0.99950

[a] m.

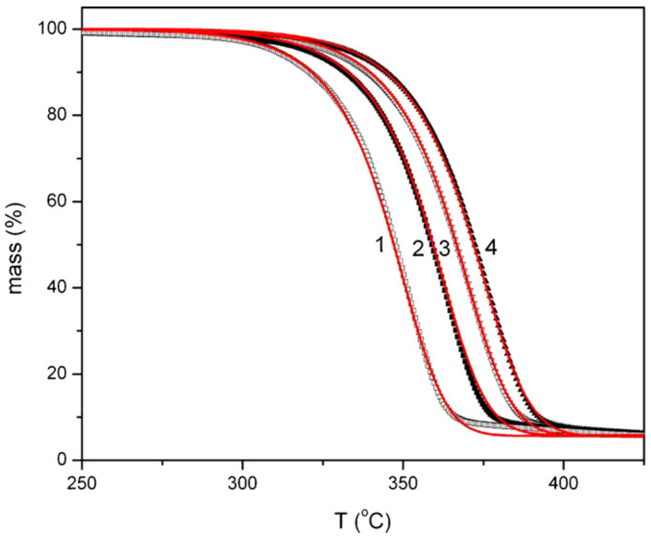

Fig. 4. TG curves and fitting curves with Cn mechanism of PLA/2.5 wt% MWCNTs-COOH for different heating rates. (1) $\beta = 5\,^{\circ}\mathrm{C/min}$, (2) $\beta = 10\,^{\circ}\mathrm{C/min}$, (3) $\beta = 15\,^{\circ}\mathrm{C/min}$ and (4) $\beta = 20\,^{\circ}\mathrm{C/min}$.

Table 3
Activation energy, pre-exponential factor, reaction order and the regression coefficients after fitting with two reaction mechanisms.

	PLA		PLA/2.5 wt% MWCNTs-COOH	
First mechanism	Cn	Fn	Cn	Fn
log(A)	7.6	7.7	12.4	12.4
E	116.2	117.3	175.4	175.3
n	0.47	0.39	0.61	0.61
log(K_{cat})	−0.7		−11.6	
Second mechanism	Cn	Cn	Cn	Cn
log(A)	10.8	10.8	13.7	13.7
E	161.6	161.3	179.0	179.0
n	1.03	1.03	2.74	2.74
log(K_{cat})	0.7	0.8	0.24	0.24
R	0.99992	0.99992	0.99988	0.99988

the total quality of the fit is better than the fit of the PLA samples. The regression coefficients show that the differences between the three models are negligible for the PLA and they are very small for the PLA/2.5 wt% MWCNTs-COOH samples. In order to make a comparison, since in the literature the nth-reaction model is usually used, the fitting with this model for PLA/2.5 wt% MWCNTs-COOH is presented in Fig. 5. The main difference of the fittings with the Fn and Cn models is at the final stages of the decomposition. For these polymers, mainly for PLA, we can say that the Fn reaction model, the simplest one, can give acceptable results. Since the differences among the regression coefficient values are rather small, especially for PLA samples, it is very difficult for everyone to choose the real kinetic model from the presented models. This difficulty seems to be greater if we take into account that the reaction mechanisms of the polymers are very complex. For this reason, the choice of the appropriate kinetic model, considering one-step reaction, only denotes a possible mathematical form for the conversion function [25]. Knowing that the thermal degradation of the polymers is a very complex reaction, in order to enhance further the quality of the fitting, we must consider more than one reaction mechanisms using the conclusions from the dependence of the activation energy of the partial mass loss. In the identification process by two different mechanisms, at least six unknown factors are being involved. So, the mathematical problem of the identification is a very complex one and it has several possible solutions. For this reason, at this stage of identification, it is important to limit the scope of the search among all possible combinations of the widely used models. So the models that were used and their combinations were only those, which have given us satisfactory results from the identification through a single mechanism such as the reaction models Fn, Cn and Bna.

In this stage of identification, for the best possible results we left the parameters (E, A and n) of the second mechanism to be recalculated and the results are presented in Table 3. The results of the best fitting are presented in Fig. 6 for PLA/2.5 wt% MWCNTs-COOH samples and the fitting to the experimental data is very good for the whole area of mass loss. At Table 3 the results of the best two combinations of models, nth-order and nth-order with autocatalysis (Fn–Cn) as well as nth-order with autocatalysis in both mechanisms (Cn–Cn), are presented. Since the calculated value of the log(K_{cat}) for the PLA/2.5 wt% MWCNTs-COOH has a very large negative value, and therefore the parameter K_{cat} (portion of autocatalysis) is almost zero, the Cn kinetic model coincides with the

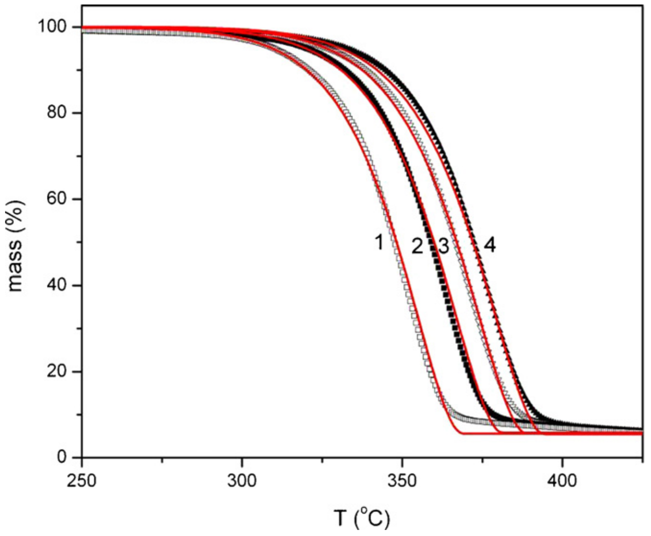

Fig. 5. TG curves and fitting curves with Fn mechanism of PLA/2.5 wt% MWCNTs-COOH for different heating rates. (1) $\beta = 5\,^{\circ}\mathrm{C/min}$, (2) $\beta = 10\,^{\circ}\mathrm{C/min}$, (3) $\beta = 15\,^{\circ}\mathrm{C/min}$ and (4) $\beta = 20\,^{\circ}\mathrm{C/min}$.

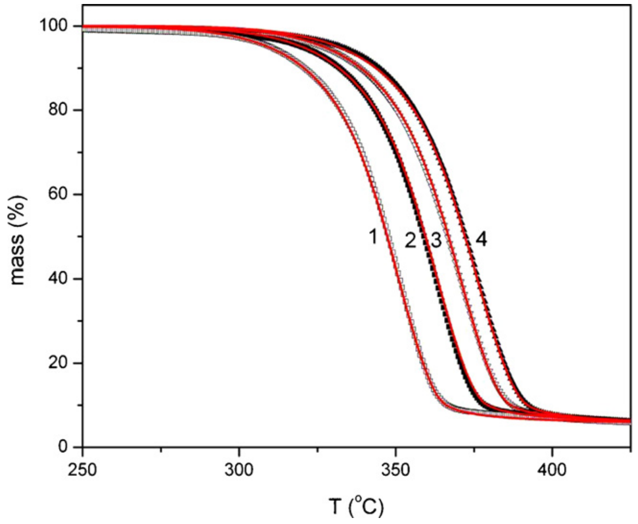

Fig. 6. TG curves and fitting curves with Fn–Cn mechanisms of PLA/2.5 wt% MWCNTs-COOH for different heating rates. (1) $\beta = 5\,^{\circ}\mathrm{C/min}$, (2) $\beta = 10\,^{\circ}\mathrm{C/min}$, (3) $\beta = 15\,^{\circ}\mathrm{C/min}$ and (4) $\beta = 20\,^{\circ}\mathrm{C/min}$.

Fn model for the first part of mass loss. The values of the activation energy for both mechanisms are in the area of the calculated values using the isoconversional methods. At the PLA samples, the mass area in which the first reaction mechanism takes place is 40% of mass loss and that is in very good agreement with the results of the dependence of the activation energy of the mass conversion α as it has been calculated with the Friedman's method. From this point of view it is obvious why it is better to use more than one method for the calculation of the activation energy. On the other hand, the dependence of the activation energy of the mass conversion α for the PLA/2.5 wt% MWCNTs-COOH samples does not show the existence of two different mechanisms, since the value of E is almost stable for the whole area of mass conversion, yet, best fitting results are predicted using two reaction mechanisms. From the fitting results seems that the values of the activation energy are almost the same for the two mechanisms and only the values of the reaction order n are quite different. The calculated values for the activation energy present the same trend as the ones shown in Fig. 3. For these samples the mass area in which the first reaction mechanism takes place is 65% of mass loss.

Comparing the results of the two mechanisms for the studied materials, we can say that although for the better kinetic description of the degradation, we use the same combination of mechanisms for PLA and its nanocomposite there are interesting differences. For the kinetic description the followings are important: the reaction model, $f(\alpha)$, the activation energy (E), the pre-exponential factor (A) and depending on the reaction model the reaction order (n). The studied samples have the same combination of the reaction models but quite different values for the activation energy and the reaction order. Also, it is important that the values of E for the first and the second mechanism are almost the same for the PLA/MWCNTs nanocomposite, while for PLA they are quite different.

4. Conclusions

From the thermogravimetric curves it can be seen that PLA/MWCNTs-COOH nanocomposite present a relatively better thermostability than PLA. The activation energy was calculated with the isoconvertional Ozawa–Flynn–Wall and Friedman's methods. For PLA, as calculated with Friedman's method the dependence of E on α can be separated in three distinct regions, the first in which E is almost stable, while in the second it presents a monotonous increase and in the third it can be considered as having a constant average value, as in the first region. For PLA/2.5 wt% MWCNTs-COOH, the dependence of E from α shows only one region with relatively constant value of E. For all the mass conversions, PLA has lower values than the nanocomposite. From the variation of E with increasing degree of mass conversion, especially for the PLA, it was concluded that the decomposition of all the samples is taking place with a complex reaction mechanism with the participation of at least two different mechanisms. The best fitting of experimental data with theoretical models for PLA and PLA–2.5 wt% MWCNTs-COOH give nth-order for the first mechanism and nth-order with autocatalysis (Fn–Cn) for the second mechanism with different activation energies. The studied samples have the same combination of the reaction models but quite different values for the activation energy and the reaction order. The values of E for the first and the second mechanism are almost the same for the PLA/MWCNTs nanocomposite, while for PLA they are quite different.

References

[1] J.-H. Chang, Y.U. An, D. Cho, E.P. Giannelis, Poly(lactic acid) nanocomposites; comparison of their properties with montmorillonite and synthetic mica (II), Polymer 44 (2003) 3715.

[2] C. Bastioli, Biodegradable materials, in: A.L. Brody, K.S. Marsh (Eds.), Wiley Encyclopedia of Packaging Technology, 2nd ed., Wiley, New York, 1997, p. 77.

[3] H. Zou, C. Yi, L. Wang, H. Liu, W. Xu, Thermal degradation of poly(lactic acid) measured by thermogravimetry coupled to Fourier transform infrared spectroscopy, J. Therm. Anal. Calorim. 97 (2009) 929–935, references therein.

[4] Q. Zhou, M. Xanthos, Nanosize and microsize clay effects on the kinetics of the thermal degradation of polylactides, Polym. Degrad. Stab. 94 (2009) 327–338.

[5] C.-F. Kuan, C.-H. Chen, H.-C. Kuan, K.-C. Lin, C.-L. Chiang, H.-C. Peng, Multi-walled carbon nanotube reinforced poly(L-lactic acid) nanocomposites enhanced by water-crosslinking reaction, J. Phys. Chem. Solids 69 (2008) 1399–1402.

[6] S.-I. Moon, F. Jin, C.-j. Lee, S. Tsutsumi, S.-H. Hyon, Novel carbon nanotube/poly(L-lactic acid) nanocomposites; their modulus, thermal stability, and electrical conductivity, Macromol. Symp. 224 (2005) 287–295.

[7] H.-S. Kim, B.H. Park, J.-S. Yoon, H.-J. Jin, Thermal and electrical properties of poly(L-lactide)-graft-multiwalled carbon nanotube composites, Eur. Polym. J. 43 (2007) 1729.

[8] H.-S. Kim, Y.S. Chae, H.I. Kwon, J.-S. Yoon, Thermal degradation behaviour of multi-walled carbon nanotube-reinforced poly(L-lactide) nanocomposites, Polym. Int. 58 (2009) 826–831.

[9] K. Chrissafis, G. Antoniadis, K.M. Paraskevopoulos, A. Vassiliou, D.N. Bikiaris, Comparative study of the effect of different nanoparticles on the mechanical properties and thermal degradation mechanism of in situ prepared poly(ε-caprolactone) nanocomposites, Compos. Sci. Technol. 67 (2007) 2165.

[10] K. Chrissafis, K.M. Paraskevopoulos, D.N. Bikiaris, Effect of molecular weight on thermal degradation mechanism of the biodegradable polyester, poly(ethylene succinate), Thermochim. Acta 440 (2006) 166.

[11] D.N. Bikiaris, K. Chrissafis, K.M. Paraskevopoulos, K.S. Triantafyllidis, E.V. Antonakou, Investigation of thermal degradation mechanism of an aliphatic polyester using pyrolysis-gas chromatography–mass spectrometry and a kinetic study of the effect of the amount of polymerisation catalyst, Polym. Degrad. Stab. 92 (2007) 525.

[12] S. Papadimitriou, D.N. Bikiaris, K. Chrissafis, K.M. Paraskevopoulos, S. Mourtas, Synthesis, characterization and thermal degradation mechanism of fast biodegradable PPSu/PCL copolymers, J. Polym. Sci. A: Polym. Chem. 45 (2007) 5076.

[13] K. Chrissafis, K.M. Paraskevopoulos, S.Y. Stavrev, A. Docoslis, A. Vassiliou, D.N. Bikiaris, Characterization and thermal degradation mechanism of isotactic polypropylene/carbon black nanocomposites, Thermochim. Acta 465 (2007) 6.

[14] D. Bikiaris, A. Vassiliou, K. Chrissafis, K.M. Paraskevopoulos, A. Jannakoudakis, A. Docoslis, Effect of acid treated multi-walled carbon nanotubes on the mechanical, permeability, thermal properties and thermo-oxidative stability of isotactic polypropylene, Polym. Degrad. Stab. 93 (2008) 952–967.

[15] D. Wu, L. Wu, M. Zhang, Y. Zhao, Viscoelasticity and thermal stability of polylactide composites with various functionalised carbon nanotubes, Polym. Degrad. Stab. 93 (2008) 1577–1584.

[16] S. Vyazovkin, Model-free kinetics. Staying free of multiplying entities without necessity, J. Therm. Anal. Calorim. 83 (2007) 45.

[17] A. Pratap, T. Lilly Shanker Rao, K.N. Lad, D. Heena, Dhurandhar, Isoconversional vs. model fitting methods. A case study of crystallization kinetics of a Fe-based metallic glass, J. Therm. Anal. Calorim. 89 (2007) 399.

[18] E. Kaisersberger, J. Opfermann, Kinetic evaluation of exothermal reactions measured by DSC, Thermochim. Acta 187 (1991) 151.

[19] J. Opfermann, Kinetic analysis using multivatiate non-linear regression i. Basic concepts, J. Therm. Anal. Calorim. 60 (2000) 641.

[20] T. Ozawa, A new method of analyzing thermogravimetric data, Bull. Chem. Soc. Jpn. 38 (1965) 1881.

[21] J.H. Flynn, L.A. Wall, General treatment of the thermogravimetry of polymers, J. Res. Natl. Bur. Stand. Phys. Chem. A 70 (1966) 487.

[22] J.H. Flynn, L.A. Wall, A quick, direct method for the determination of activation energy from thermogravimetric data, Polym. Lett. 4 (1966) 323.

[23] H.L. Friedman, Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic, J. Polym. Sci. C 6 (1964) 183.

[24] S. Vyazovkin, Modification of the integral isoconversional method to account for variation in the activation energy, J. Comput. Chem. 22 (2001) 178.

[25] P. Simon, The single step approximation. Attributes, strong and weak sides, J. Therm. Anal. Calorim. 88 (2007) 709.