J Therm Anal Calorim (2013) 112:1171–1177
DOI 10.1007/s10973-012-2535-8

Kinetic study of the thermal and thermo-oxidative degradations of polylactide-modified films for food packaging

I. Blanco · V. Siracusa

Received: 23 March 2012 / Accepted: 4 June 2012 / Published online: 23 September 2012

Abstract In this study, the thermal degradations of some commercial polylactide (PLA) films, pure and subjected to various superficial treatments, were investigated in both inert (flowing nitrogen) and oxidative (static air) atmospheres. Degradations were carried out in a thermobalance, in the scanning mode, at various heating rates, and the obtained thermogravimetric curves were discussed and interpreted. Experiments, performed in the temperature range of 35–700 °C, showed similar behavior in both the atmospheres used. The initial decomposition temperature (T_{i}) and the apparent activation energy (E_{a}) of degradation of the differently treated PLA films were determined and compared with each other and with those of untreated PLA. The E_{a} of degradation was obtained by Kissinger's method, and the values were found increased linearly as a function of crystallinity percentage (*%c*) as well as the T_{i} values. The glass transition temperature (T_{g}) was also determined by differential scanning calorimetry. All the investigated parameters showed dependence on different treatments made to the films. The results obtained for the degradations of PLA films were compared with each other, and a classification of thermal stability in the studied environments were made.

Keywords Polylactide · Activation energy of degradation · Initial decomposition temperature · Thermogravimetric analysis

I. Blanco (✉) · V. Siracusa
Department of Industrial Engineering, University of Catania,
V.le A. Doria, 6, 95125 Catania, Italy
e-mail: iblanco@dmfci.unict.it

Introduction

Polylactide (PLA), is a biobased, biocompatible, and biodegradable thermoplastic polyester produced by condensation polymerization of lactic acid (LA; 2-hydroxy propionic acid), which is extracted from fully renewable resources such as corn, sugar beet, or rice. PLA has been widely studied for use in medical applications because of its bioresorbable and biocompatible properties in the human body [1–13]. Economic studies show that PLA is an economically feasible material for use as a packaging polymer [14–16]. Medical studies have shown that the level of LA that migrates to food from packaging containers is much lower than the amount of LA used in common food ingredients [17]; therefore, polymers derived from LA may be good candidates for packaging applications [6, 9, 18, 19]. The biodegradability of PLA, known as an environmental-friendly material, by various enzymes has been studied by many authors [20–28]. In particular, it was reported that the enzymatic degradation preferentially occurs in the amorphous region of PLA and that degradation rate increases with decreasing crystallinity [24].

Thermal properties of PLA have been widely studied [29–37], and it is well known that the typical PLA glass transition temperature (T_{g}) ranges from 50 to 80 °C, while the melting temperature (T_{onset}) ranges from 130 to 180 °C [6, 34, 38], giving useful information about article service temperature range and processing (foaming and extrusion) temperature range [34]. To the best of our knowledge, no study about the kinetics of degradation of PLA has ever been reported.

In view of the fact that degradation rate should increase with decreasing crystallinity, it seems interesting to carry out a comparative kinetic study of PLA to establish if and how much external factors like $\mathrm{SiO_x}$ coatings or anti ultraviolet (UV) coatings could influence the kinetics of thermal degradation. To this purpose, in this study, we investigated four different PLA films identified as follows:

Natural PLA film	**1**
PLA with SiO_x coatings	**2**
PLA with anti UV coatings	**3**
PLA varnished	**4**

The characteristic parameters associated with the thermal stability [39–41] of these commercial PLA films were compared with each other and with those of natural PLA, to verify if any difference occurs in respect of the natural PLA and if and how much it is affected by crystallinity degree (*%c*). Thermal and thermo-oxidative degradations were studied by thermogravimetric (TG) and differential thermogravimetric (DTG) analyses, while T_g values were determined by differential scanning calorimetry (DSC).

Experimental

Materials

Four PLA films, used for commercial packaging, were studied as received without any special preliminary treatments. The specific surface treatments are protected under industrial secrets, and so it is not possible to give a detailed description of the treatment methods used. All the compounds are made of a PLA film on a polymer substrate: one was a natural PLA film, while the other three were subjected by the supplier to superficial treatments with coatings (SiO_x coatings for the sample **2**, anti UV coatings for the sample **3**, and varnish for the sample **4**) to change their barrier properties.

DSC measurements

A Mettler DSC 20 differential scanning calorimeter, coupled with a Mettler TC 10A processor as control and evaluation unit, was employed to evaluate T_g values of the analyzed samples. Both the heat flow and the temperature of the calorimeter were calibrated according to the procedure suggested by Mettler and prescribed in the printed operating instructions of equipment [42]. The calibrations were repeated every 2 weeks. Samples of $\sim 6.0 \times 10^{-3}$ g were cut off from foils in the form of small disks of 5 mm in diameter and held in sealed aluminium crucibles. In order to avoid contamination of the film, special care was taken during handling. The samples were heated, under flowing nitrogen (0.02 L/min) and in a static air atmosphere, in the temperature from 35 to 250 °C at a heating rate of 10 °C min^{-1}. The experiments were performed in triplicate, and the considered values were averaged from those of three runs, the maximum difference between the average and the experimental values being within ±1 °C.

TG analysis

Thermal degradations were carried out in a Mettler TA 3000 thermobalance, coupled with the same Mettler TC 10A processor as that was used for DSC measurements. The temperature of furnace was calibrated according to the procedure reported in the user's manual of equipment [42] and considered in the literature to be the most precise [43], based on the change of the magnetic properties of the three metal samples (Isatherm, Nickel, and Trafoperm) at their Curie points (142.5, 357.0, and 749.0 °C, respectively). The temperature calibration was repeated every 2 weeks.

Degradations were carried out under flowing nitrogen (0.02 L/min) and in a static air atmosphere, in dynamic heating conditions, in the temperature range from 35 to 700 °C, at various selected heating rates ($\Phi = 2, 5, 7.5, 10, 12.5, 15, 17.5$, and 20 °C min^{-1}). Samples of $\sim 6.0 \times 10^{-3}$ g were used for degradations, and their masses as a function of temperature were stored in the list of data of the appropriate built-in program of processor. The samples were cut off from foils in the form of small disks of 5 mm in diameter and held in alumina open crucibles. The experimental data at various temperatures were elaborated by the TC 10A processor at the end of each experiment, and the corresponding TG and DTG curves were immediately printed. The same data were then transferred to a PC, and used to plot the percentage of the undegraded polymer $(1 - D)$ % as a function of temperature, where $D = (W_0 - W)/W_0$, and W_0 and W were the masses of the sample at the starting point and during scanning.

Results and discussion

The aim of this study was the comparison among the thermal stabilities of pure PLA (sample **1**) and those of the differently modified PLA (samples **2**, **3,** and **4**), to verify if and how much the thermal properties of polymer changed as a function of different treatments performed on the PLA films for their marketing.

The initial decomposition temperature (T_i) is often considered to be the only parameter to evaluate the thermal stability of polymers, but, in our opinion, it is not strictly correct. The T_i value of a polymer must be considered a measure of its resistance to thermal degradation [44–46], but in order to evaluate its thermal stability, it is necessary

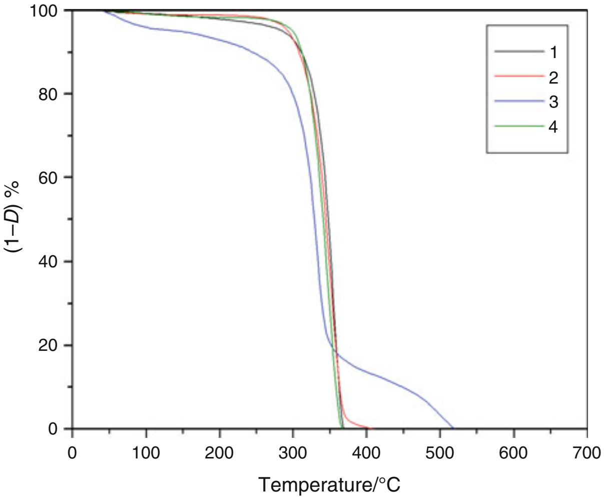

Fig. 1 TG curves under nitrogen flow of pure PLA and differently modified PLA films

to take into account also the degradation rate, in particular, if we compare compounds with T_i which are quite close to each other. In this case, the polymer with higher activation energy of degradation might be considered more thermally stable [47].

Two parameters were thus here determined for each compound: the T_i values, obtained by the degradation TG curves as the intersection between the starting mass line and the maximum gradient tangent to the curve; and the degradation apparent activation energy (E_a), which is correlated with the kinetics of process.

The degradations of various films were first carried out in flowing nitrogen, at various heating rates, in the range of 2–20 °C min^{-1}. All the studied compounds degraded, in every case, up to complete mass loss in temperature intervals ranging approximately from ~370 to 520 °C. As the experimental conditions, and the scanning rate in particular, largely affect both the shape and the position of TG curves, the T_i values of each sample at different scanning rates were different from each other, although the values of various samples at the same heating rate showed the same trend in every case. For the sake of simplicity, only the T_i values at a single scanning rate, namely, at 10 °C min^{-1}, were considered. This heating rate was selected because it is a medium rate among those we employed for degradation experiments as well as, the one we used for T_g determinations. The degradation TG curves in nitrogen of pure PLA and various PLA-modified films, at 10 °C min^{-1}, are plotted in Fig. 1, while the corresponding T_i values are listed in Table 1.

Analogous degradation experiments were then carried out in a static air atmosphere. Also in oxidative environment, all the studied compounds degraded up to complete mass loss and within the same temperature intervals (~370–520 °C) than under nitrogen. The T_i values obtained at 10 °C min^{-1} are reported in Table 1, and the corresponding TG curves are presented in Fig. 2.

The DTG curves in nitrogen and in air for the various compounds are reported in Figs. 3 and 4, while the T_m values of all studied compounds in both atmospheres are listed in Tables 2 and 3.

The sets of data from Tables 2 and 3 were thus used to determine the degradation E_a values of PLA films through the classical Kissinger's method [48], based on the following linear equation:

$$\ln\left(\Phi/T_m^2\right) = \ln\left(nRAW_m^{n-1}/E_a\right) - E_a/RT_m \qquad (1)$$

where Φ is the heating rate, T_m is the temperature at maximum rate of weight loss, n is the apparent reaction order, R is the universal gas constant, A is the pre-exponential factor and W_m is the weight of the sample at the maximum rate of mass loss. Thus, the E_a value could be obtained through the linear dependence of ln (Φ/T_m^2) on $1/T_m$ at various heating rates. We used as T_m values the temperatures of DTG peaks.

From the least square treatment of the data in Tables 2 and 3, performed according to the Eq. (1), single linear ln (Φ/T_m^2) versus $1/T_m$ relationships were obtained for all the samples in both studied environments. The corresponding regression

Table 1 Crystallinity degree (%*c*)[a], glass transition temperatures (T_g), initial decomposition temperatures (T_i), and apparent activation energies of degradation (E_a) for the various PLA films in static air atmosphere and in flowing nitrogen

Sample	%*c*[a]	Air static atmosphere			Nitrogen flow		
		T_g/K[b]	T_i/K[b]	E_a/kJ mol^{-1}	T_g/K[b]	T_i/K[b]	E_a/kJ mol^{-1}
1	22.6	332.8	607.9	193 (±7)	333.3	606.0	203 (±10)
2	17.9	332.5	603.8	181 (±8)	332.8	600.3	191 (±5)
3	7.6	n.d.	580.1	162 (±4)	n.d.	580.8	172 (±6)
4	19.7	332.2	606.7	185 (±8)	331.8	605.9	196 (±7)

[a] From ref. [49]

[b] Determined at 10 °C min^{-1}

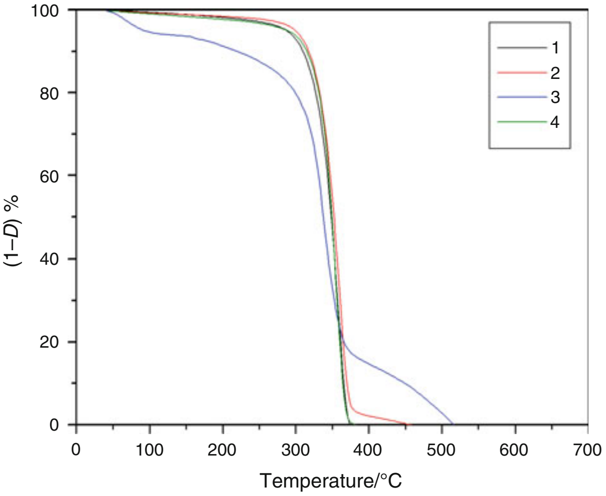

Fig. 2 TG curves in static air atmosphere of pure PLA and differently modified PLA films

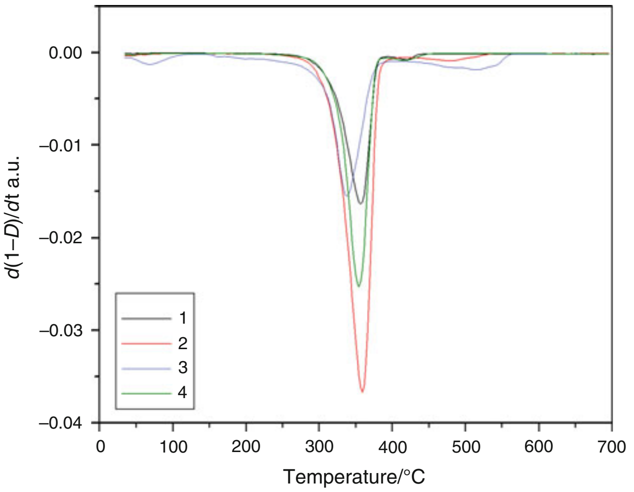

Fig. 4 DTG curves in static air atmosphere of pure PLA and differently modified PLA films

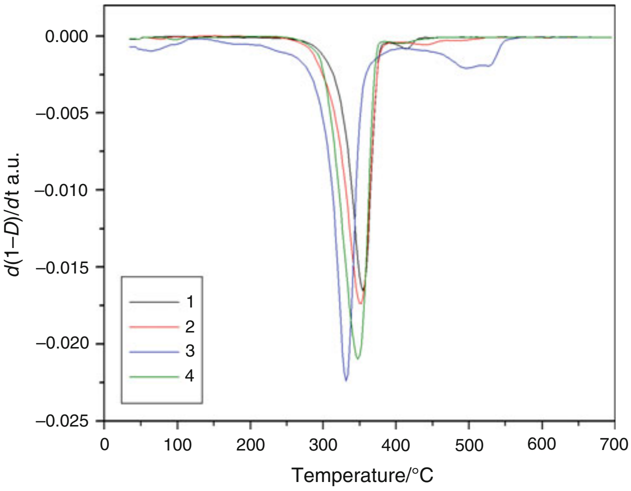

Fig. 3 DTG curves under nitrogen flow of pure PLA and differently modified PLA films

Table 2 Temperatures at maximum rate of mass loss (T_m) for the degradation stage of the PLA films in flowing nitrogen, at the various heating rates used (Φ)

Φ/°C min^{-1}	**1** T_m/K	**2** T_m/K	**3** T_m/K	**4** T_m/K
2	602.8	597.7	582.6	598.0
5	615.6	612.0	594.9	612.1
7.5	619.1	616.5	601.3	620.3
10	623.1	622.8	606.7	623.5
12.5	629.0	626.7	611.2	626.7
15	631.1	629.5	615.4	628.7
17.5	635.6	631.7	617.7	630.7
20	636.5	632.6	618.8	633.1

coefficients and the calculated E_a values are reported in Tables 4 and 5 for nitrogen and air, respectively.

Finally, the T_g values of the considered compounds were determined calorimetrically. The T_g values obtained are reported in Table 1 together with T_i, degradation E_a values, and crystallinity percentage (%c).

A preliminary observation on the results obtained: even though all the samples degraded in all cases up to complete mass loss, the TG curves in flowing nitrogen exhibited a difference as evidenced, for example, from those reported in Fig. 1. The samples **1** and **4** degraded completely in a single step, while PLA with SiO_x and anti UV coatings, samples 2 and 3, respectively, showed first a very sharp degradation stage, followed by a second one with low degradation rate in the last section of the TG curves. This second stage was more evident for the sample **3** and less evident for the sample **2**, and this can be attributed to a decrease in the crystallinity of the coated samples in respect of pure PLA (sample **1**) and varnished PLA (sample **2**), respectively [49].

The degradation TG curves of the studied compounds in oxidative atmosphere exhibited the same behavior observed in inert environment, suggesting that the presence of oxygen does not influence the degradation mechanism.

Some considerations are possible on the basis of the data reported in Table 1:

– the heat resistances of the coated PLA films (samples **2** and **3**) were worse than those of the pure and varnished PLA compounds, respectively. In particular, the sample from the anti UV coated PLA film appears to be less heat resistant, as indicated by the considerably high decrement of T_i values (∼20–26 °C under nitrogen and ∼23–28 °C in static air atmosphere);

Table 3 Temperatures at maximum rate of weight loss (T_m) for the degradation stage of the PLA films in static air atmosphere, at the various heating rates used (Φ)

Φ/°C min^{-1}	**1** T_m/K	**2** T_m/K	**3** T_m/K	**4** T_m/K
2	602.8	598.1	579.5	603.3
5	618.0	613.8	594.1	613.3
7.5	626.0	621.8	601.4	622.8
10	628.8	627.3	608.0	628.1
12.5	633.8	629.5	611.5	631.4
15	634.7	631.7	614.5	634.0
17.5	636.8	633.9	616.6	637.8
20	638.9	635.2	618.1	638.9

Table 4 Regression coefficients and apparent activation energies of degradation (E_a) derived from Kissinger's equation for the various PLA films in flowing nitrogen

Sample	a[a]	$b \times 10^{-3}$/K[b]	r[c]	E_a/kJ mol^{-1}
1	28.4 (±2.0)	24.4 (±1.2)	0.9922	203 (±10)
2	26.3 (±1.0)	23.0 (±0.6)	0.9978	191 (±5)
3	23.6 (±1.1)	20.7 (±0.7)	0.9967	172 (±6)
4	27.4 (±1.3)	23.6 (±0.8)	0.9963	196 (±7)

[a] $a = \ln\left(nRAW_m^{n-1}/E_a\right)$

[b] $b = E_a/\mathrm{R}$

[c] Product moment correlation coefficient

Table 5 Regression coefficients and apparent activation energies of degradation (E_a) derived from Kissinger's equation for the various PLA films in static air atmosphere

Sample	a[a]	$b \times 10^{-3}$/K[b]	r[c]	E_a/kJ mol^{-1}
1	26.3 (±1.5)	23.2 (±0.9)	0.9949	193 (±7)
2	24.3 (±1.6)	21.8 (±1.0)	0.9941	181 (±8)
3	21.6 (±0.8)	19.5 (±0.5)	0.9982	162 (±4)
4	25.0 (±1.6)	22.3 (±1.0)	0.9937	185 (±8)

[a] $a = \ln\left(nRAW_m^{n-1}/E_a\right)$

[b] $b = E_a/\mathrm{R}$

[c] Product moment correlation coefficient

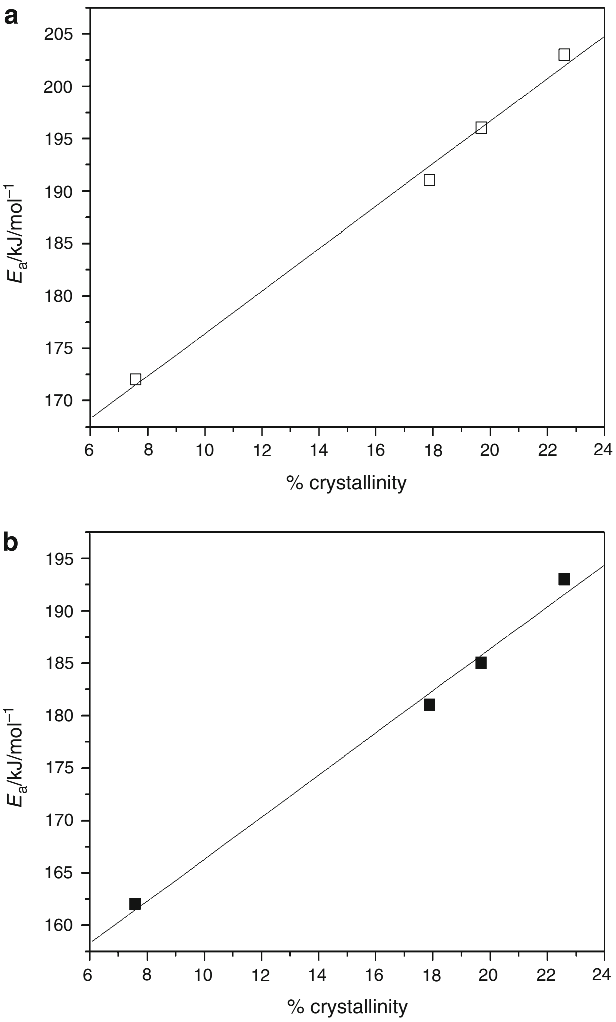

Fig. 5 Apparent activation energy of degradation (E_a) as a function of crystallinity percentage (%c) in **a** flowing nitrogen, and **b** in static air atmosphere

- the degradation activation energies of pure PLA film, in both the studied environments, were higher than those of the modified samples, thus meaning lower degradation rate and then better thermal stability from the kinetic viewpoint. This finding, together with the results obtained for the T_i values, indicated a higher overall thermal stability of unmodified PLA film in respect of the samples **2**, **3**, and **4** and allowed us to make a thermal stability classification on the basis of the different treatments on samples. According to this classification, the sample **3** appears to be less thermally stable, while the samples **2** and **4** have slightly lower thermal stabilities than that of the sample **1**;
- the enhancements observed in both T_i and degradation E_a values observed for the samples **1**, **2**, and **4** in relation to those of the sample **3** were dependent on the crystallinity percentage as can be noted from Figs. 5 and 6 in which are shown the linear increases of activation energy of degradation (Fig 5a, b) and T_i (Fig 6a, b) as a function of %c, in both the above mentioned conditions of the atmosphere;
- in contrast to the T_i and degradation E_a values, the various treatments on PLA films appear not to affect T_g values that were the same for the studied samples, in both the flowing nitrogen and a static air atmosphere (Table 1), except the sample **3** for which it was not possible to determine T_g owing to an endothermic event that overlaps the glass transition, probably due to a secondary molecular reordering in the amorphous phase of this PLA film [49].

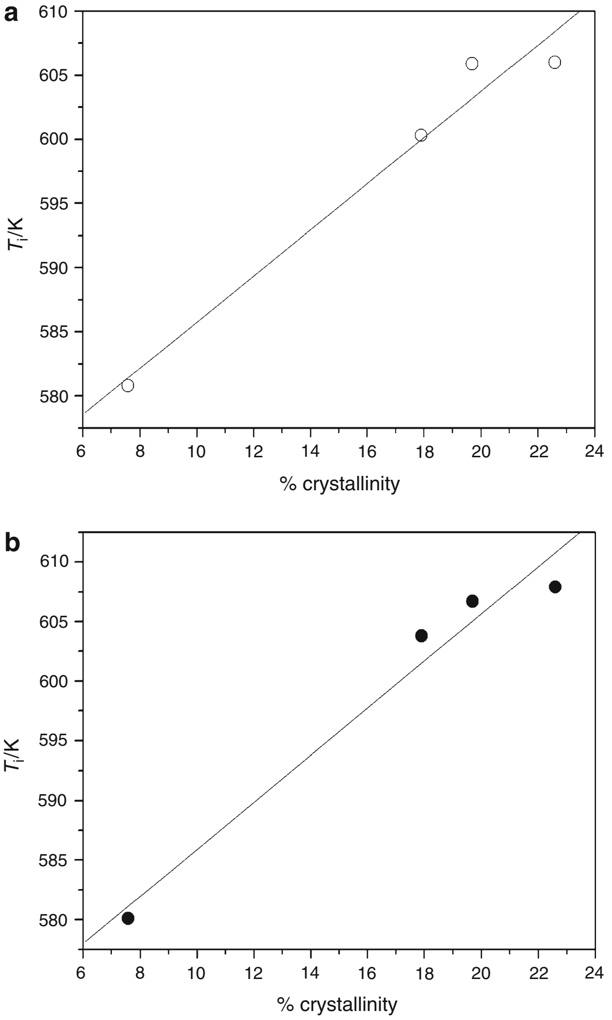

Fig. 6 Initial decomposition temperature (T_i) as a function of crystallinity percentage ($\%c$) in **a** flowing nitrogen, and **b** in static air atmosphere

Conclusions

The results obtained indicate a lesser thermal stability for the anti UV coated PLA films in comparison with the other, pure and differently modified, PLA films, not only for the lower starting point of decomposition, but also from the point of view of the degradation kinetics. This lesser thermal stability can be attributed to a decrease in density and crystallinity caused by exposure to UV [50]. The high values of T_i and E_a of degradation for the pure PLA are encouraging and allow us to implement our plan to use this polymer in the design of PLA-based nanocomposites.

References

1. Cha Y, Pitt CG. The biodegradability of polyester blends. Biomaterials. 1990;11(2):108–12.
2. Coombes AGA, Meikle MC. Resorbable synthetic polymers s replacements for bone graft. Clin Mater. 1994;17(1):35–67.
3. Zhang L, Xiong C, Deng X. Biodegradable polyester blends for biomedical application. J Appl Polym Sci. 1995;56(1):103–12.
4. Ikada Y. Polymeric biomaterials research. Adv Eng Mater. 1999;1(1):67–8.
5. Duek EAR, Zavaglia CAC, Belangero WD. In vitro study of poly(lactic acid) pin degradation. Polymer. 1999;40(23):6465–73.
6. Ikada Y, Tsuji H. Biodegradable polyesters for medical and ecological applications. Macromol Rapid Commun. 2000;21(3): 117–32.
7. Vert M. Lactide polymerization faced with therapeutic application requirements. Macromol Symp. 2000;153(1):333–42.
8. Bleach NC, Tanner KE, Kellomaki M, Tormala P. Effect of filler type on the mechanical properties of self-reinforced polylactide–calcium phosphate composites. J Mater Sci. 2001;12(10–12): 911–5.
9. Dorgan JR, Lehermeier HJ, Palade LI, Cicero J. Polylactides: properties and prospects of an environmentally benign plastic from renewable resources. Macromol Symp. 2001;175(1):55–66.
10. Lehermeier HJ, Dorgan JR, Way D. Gas permeation properties of poly(lactic acid). J Membr Sci. 2001;190(2):243–51.
11. Mochizuki M. Properties and application of aliphatic polyester products. In: Doi Y, Steinbuchel A, editors. Biopolymers. Polyesters III. Applications and commercial products. 1st ed. Weinheim: Wiley-VCH Verlag GmbH; 2002, p. 1–23.
12. Tsuji H. Polylactides. In: Doi Y, Steinbuchel A, editors. Biopolymers. Polyesters III. Applications and commercial products. 1st ed. Weinheim: Wiley-VCH Verlag GmbH; 2002, p. 129–77.
13. Ouchi T, Ohya Y. Design of lactide copolymers as biomaterials. J Polym Sci. 2004;42(3):453–62.
14. Dattaa R, Tsaia SP, Bonsignorea P, Moona SH, Frank JR. Technological and economic potential of poly(lactic acid) and lactic acid derivatives. FEMS Microbiol Rev. 1995;16(2):221–31.
15. Bogaert JC, Coszach P. Poly(lactic acids): a potential solution to plastic waste dilemma. Macromol Symp. 2000;153(1):287–303.
16. Sawyer DJ. Bioprocessing—no longer a field of dreams. Macromol Symp. 2003;201(1):271–82.
17. Conn RE, Kolstad JJ, Borzelleca JF, Dixler DS, Filer LJ, LaDu BN Jr, Pariza MW. Safety assessment of polylactide (PLA) for use as a food-contact polymer. Food Chem Toxicol. 1995;33(4): 273–83.
18. Gruber PR, O'Brien M. Polylactides. Nature works TM PLA. In: Doi Y, Steinbuchel A, editors. Biopolymers. Polyesters III. Applications and commercial products. 1st ed. Weinheim: Wiley-VCH Verlag GmbH; 2002, p. 235–50.
19. Kawahima N, Ogawa S, Obuchi S, Matsuo M, Yagi T. Polylactic acid LACEA. In: Doi Y, Steinbuchel A, editors. Biopolymers. Polyesters III. Applications and commercial products. 1st ed. Weinheim: Wiley-VCH Verlag GmbH; 2002, p. 251–74.
20. Williams DF. The effects of enzymes on polylactic acid. Eng Med. 1981;10:5–7.
21. Ashley SL, McGinity JW. Enzyme-mediated drug release from poly(D, L-lactide) matrices. Congr Int Technol Pharm. 1989;5:195–204.
22. Fukuzaki H, Yoshida M, Asano M, Kumakura M. Synthesis of copoly(DL-lactic acid) with relatively low molecular weight and in vitro degradation. Eur Polym J. 1989;25(10):1019–26.
23. Lim HA, Raku T, Tokiwa Y. A new method for the evaluation of biodegradable plastic using coated cellulose paper. Macromol Biosci. 2004;4(9):875–81.
24. Reeve MS, McCarthy SP, Downey MJ, Gross RA. Polylactide stereochemistry: effect on enzymatic degradability. Macromolecules. 1994;27(3):825–31.
25. Cai H, Dave V, Gross RA, McCarthy SP. Effects of physical aging, crystallinity, and orientation on the enzymatic degradation of poly(lactic acid). J Polym Sci Pol Phys. 1996;34(16):2701–8.

26. Li S, Tenon M, Garreau H, Braud C, Vert M. Enzymatic degradation of stereocopolymers derived from L-, DL-and meso-lactides. Polym Degrad Stab. 2000;67(1):85–90.
27. Li S, Girard A, Garreau H, Vert M. Enzymatic degradation of polylactide stereocopolymers with predominant D-lactyl contents. Polym Degrad Stab. 2001;71(1):61–7.
28. Arvanitoyannis I, Nakayama A, Kawasaki N, Yamamoto N. Novel star-shaped polylactide with glycerol using stannous octoate or tetraphenyl tin as catalyst: 1. Synthesis, characterization and study of their biodegradability. Polymer. 1995;36(15): 2947–56.
29. Jamshidi K, Hyon SH, Ikada Y. Thermal characterization of polylactides. Polymer. 1988;29:2229–34.
30. Garlotta D. A literature review of poly(lactic acid). J Polym Environ. 2001;9(2):63–84.
31. Ljungberg N, Wesslen B. The effects of plasticizers on the dynamic mechanical and thermal properties of poly(lactic acid). J Appl Polym Sci. 2002;86:1227–34.
32. Vink ETH, Rábago KR, Glassner DA, Gruber PR. Applications of life cycle assessment to NatureWorks^{TM} polylactide (PLA) production. Polym Degr Stab. 2003;80(3):403–19.
33. Auras RA, Harte B, Selke S, Hernandez R. Mechanical, physical, and barrier properties of poly(lactide) films. J Plast Film Sheet. 2003;19(2):123–35.
34. Auras R, Harte B, Selke S. An overview of polylactides as packaging materials. Macromol Biosci. 2004;4:835–64.
35. Auras R, Singh S, Singh J. Performance evaluation of PLA against existing PET and PS containers. J Test Eval. 2006;34: 530–6.
36. Ahmed J, Zhang JX, Song Z, Varshney SK. Thermal properties of polylactides. Effect of molecular mass and nature of lactide isomer. J Therm Anal Calorim. 2009;95(3):957–64.
37. Manich AM, Carilla J, Miguel RAL, Lucas JM, Franco FGF, Montero LA, Cayuela D. Thermal transitions of polylactide false-twist textured multifilaments determined by DSC and TMA. J Therm Anal Calorim. 2010;99:723–31.
38. Witzke DR. Ph.D. Thesis, Michigan State University, East Lansing; 1997, p. 389.
39. Abate L, Blanco I, Pollicino A, Recca A. Determination of degradation apparent activation energy values of polymers: regression of kinetic parameters derived from TG data. J Therm Anal Calorim. 2002;70:63–73.
40. Blanco I, Abate L, Bottino FA, Bottino P, Chiacchio MA. Thermal degradation of differently substituted cyclopentyl polyhedral oligomeric silsesquioxane (CP-POSS) nanoparticles. J Therm Anal Calorim. 2012;107(3):1083–91.
41. Blanco I, Abate L, Antonelli ML. The regression of isothermal thermogravimetric data to evaluate degradation E_a values of polymers: a comparison with literature methods and an evaluation of lifetime prediction reliability. Polym Degrad Stab. 2011;96:1947–54.
42. User's manual TA 3000 system. Greifensee: Mettler Instrument, AG; 1984.
43. Csaba N. Handbook of thermal analysis and calorimetry. In: Gallagher Patrick K, Brown Michael E, editors. Principles and practice, vol. 1. Amsterdam: Elsevier; 1998.
44. Blanco I, Abate L, Bottino FA, Bottino P. Hepta isobutyl polyhedral oligomeric silsesquioxanes (hib-POSS): a thermal degradation study. J Therm Anal Calorim. 2012;108:807–15.
45. Abate L, Asarisi V, Blanco I, Cicala G, Recca G. The influence of sulfonation degree on the thermal behaviour of sulfonated poly(arylene ethersulfone)s. Polym Degrad Stab. 2010;95:1568–74.
46. Blanco I, Oliveri L, Cicala G, Recca A. Effects of novel reactive toughening agent on thermal stability of epoxy resin. J Therm Anal Calorim. 2012;108:685–93.
47. Abate L, Blanco I, Cicala G, Mamo A, Recca G, Scamporrino A. The influence of chain rigidity on the thermal properties of some novel random copolyethersulfones. Polym Degrad Stab. 2010;95: 798–802.
48. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29(11):1702–6.
49. Siracusa V, Blanco I, Romani S, Tylewicz U, Roccoli P, Dalla Rosa M. Correlation between thermal, mechanical and barrier properties of poly(lactic acid) (PLA) modified films used on food packaging application. J Appl Polym Sci. 2012;125:E390–E401.
50. Hoekstra HD, Spoormaker JL, Breen J, Audouin L, Verdu J. UV-exposure of stabilized and non-stabilized HDPE films: physico-chemical characterization. Polym Degr Stab. 1995;49(2):251–62.