Macromol. Symp. **2008**, 272, 93–99

DOI: 10.1002/masy.200851213

A Thermogravimetric Approach to Study the Influence of a Biodegradation in Soil Test to a Poly(lactic acid)

*J. D. Badía, R. Moriana, L. Santonja-Blasco, A. Ribes-Greus**

Summary: An amorphous grade Poly (lactic acid) (PLA) was selected for an accelerated burial in soil test during 450 days. Thermogravimetric analyses were carried out to study the effects of degradation in soil on the thermal stability and the thermal decomposition kinetics. A single stage decomposition process is observed for all degradation times. It is shown that the thermal stability of PLA is slightly affected by degradation in soil. Concerning the study of the thermal decomposition kinetics, Criado master curves were plotted from experimental data to focus the study of the thermodegradation kinetic model.The kinetic methods proposed by Broido and Chang were used to calculate the apparent activation energies (Ea) of the degradation mechanism. These results were compared to the Ea values obtained by the method developed by Coats and Redfern in order to prove the applicability of the former methods to the kinetic study. As expected, non-linear tendency is found out for Ea variation along the degradation times, which can be explained as an evolution by stages.

Keywords: activation energy; biodegradation in soil; kinetics (polim.); poly(lactic acid); thermogravimetry analysis (TGA)

Introduction

Poly(lactic acid) (PLA) is a well-known green polymer, since it can be obtained from renewable resources and can be compostable when its service life has finished. Last decades it is been widely employed because of its biomedical and pharmaceutical applications.[1] Its good mechanical and gas barrier qualities also confer on the polymer the capability to compete with other commodities such as PE, PS or PET at the packaging sector.[2] Although this application is not well established yet, the increasing interest in PLA will raise the consumption ratios and therefore the disposal problems. The knowledge of the degradation mechanisms concerning the disposal stage of PLA must be hence assessed, in order to assure the complete material loop of the biodegradable material.

Some studies have revealed that degradation in soil tests are suitable to analyze the degradation phenomena in bio-based polymers.[3–5] Thermal analysis techniques represent a powerful tool to control and monitor the degradation evolution in polymers.[6–8] In this work, thermogravimetric experiments have been performed in order to characterize the effects of a degradation in soil test on the thermal stability and the thermal decomposition kinetics of an amorphous PLA.

Theoretical Background

In an heterogeneous reaction $A(s) \rightarrow B(s) + C(g)$, the decomposition rate for

---

Instituto de Tecnología de Materiales. Escuela Técnica
Superior de Ingeniería del Diseño. Universidad
Politécnica de Valencia. Camino de Vera, s/n,
46022, Valencia (Spain)
E-mail: aribes@ter.upv.es

Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY InterScience®

A(s) can be defined as follows:

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

where α is the conversion degree of A(s) at time t (further defined for thermogravimetric analyses); $f(\alpha)$ is a temperature-independent function of conversion (kinetic model); and $k(T)$ is a temperature-dependent function assumed as an Arrhenius equation:

$$k(T) = A\cdot\exp\left(\frac{-Ea}{R\cdot T}\right) \tag{2}$$

where A is the frequency factor (also called pre-exponential factor); R is the ideal gases constant (8.31 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$); T is the temperature; and Ea is the activation energy of the equation. Substituting the Arrhenius equation into Equation (1), we obtain:

$$\frac{d\alpha}{dt} = A\cdot\exp\left(\frac{-Ea}{R\cdot T}\right)\cdot f(\alpha) \tag{3}$$

If the temperature of a sample varies as a function of a controlled and constant value of heating rate β ($\beta = dT/dt$), the decomposition rate can be expressed as a function of the temperature:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\cdot\exp\left(\frac{-Ea}{R\cdot T}\right)\cdot f(\alpha) \tag{4}$$

Separating variables, rearranging and integrating Equation (4), we obtain:

$$g(\alpha) = \int_{\alpha_0}^{\alpha_f}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\cdot\int_{T_0}^{T_f}\exp\left(\frac{-Ea}{R\cdot T}\right)\cdot dT \tag{5}$$

For thermogravimetric experiments, the conversion degree is defined as:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \tag{6}$$

where m is the mass of the sample at time t; and 0 and f represent the initial and final times, respectively.

In this article, several fitting methods have been employed, which are described as follows. By representing the lefth-hand of Equation (7), Equation (8) and Equation (9) versus 1/T, the Ea can be obtained from the slope of the different plots.

Chang Method[9]

Assuming $f(\alpha) = (1-\alpha)^n$, being n the reaction order into Equation (3), rearranging and taking logarithms, Chang proposed the following differential model:

$$\ln\left(\frac{\frac{d\alpha}{dt}}{(1-\alpha)^n}\right) = \ln A - \frac{Ea}{R\cdot T} \tag{7}$$

Broido Method[10]

This method is valid for n = 1 and employs the following model:

$$\ln\left(\ln\left(\frac{1}{1-\alpha}\right)\right) = \frac{-Ea}{R\cdot T} + \ln\left(\frac{R\cdot C}{Ea\cdot\beta}\cdot T_m^2\right) \tag{8}$$

where C is an integration constant and T_m the temperature of the maximum reaction velocity.

Coats-Redfern Method[11]

This model applies an asymptotic approximation to solve Equation (5) at different conversion values. If $(2RT/Ea) \to 0$ is true for the Doyle approximation,[12] and taking natural logarithms, the model adopts the following form:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{A\cdot R}{\beta\cdot Ea}\right) - \frac{Ea}{R\cdot T} \tag{9}$$

Criado Method[13]

By combining Equation (3) and (9) without logarithms, Criado described the obtaining of reduced master curves of the type:

$$\frac{z(\alpha)}{z(0.5)} = \frac{f(\alpha)\cdot g(\alpha)}{f(0.5)\cdot g(0.5)} = \left(\frac{T}{T_{0.5}}\right)^2\cdot\frac{\left({}^{d\alpha}/_{dt}\right)}{\left({}^{d\alpha}/_{dt}\right)_{0.5}} \tag{10}$$

where 0.5 refers to the conversion degree of 0.5. The left-hand of the Equation (10) is the reduced theoretical curve, which is

Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

characteristic of each reaction mechanism, whereas the right-hand is associated with the reduced decomposition rate and can be obtained from the experimental data. A comparison of both sides of Equation (10) indicates the kinetic model which best describes the experimental decomposition process.

Experimental Part

PLA with a 3.8% of meso-lactide content samples (supplied by Natureworks.DDL, Minnetonka, U.S.A) were submitted to accelerate soil burial test in a culture oven Heraeus 12 at 28 ± 0.5°C during 450 days following the DIN 53739 standard.[14] Specimens extracted at 0, 30, 150, 300 and 450 days were analyzed by thermogravimetry. Measures were carried out in a Mettler-Toledo TGA/SDTA 851, from 25 to 750 °C at a heating rate of 20 °C/min, under Ar atmosphere.

Results and Discussion

Thermal Stability

Figure 1 (a,b) illustrates the thermogravimetric curves and derivative thermogravimetric curves (in advanced called TG and

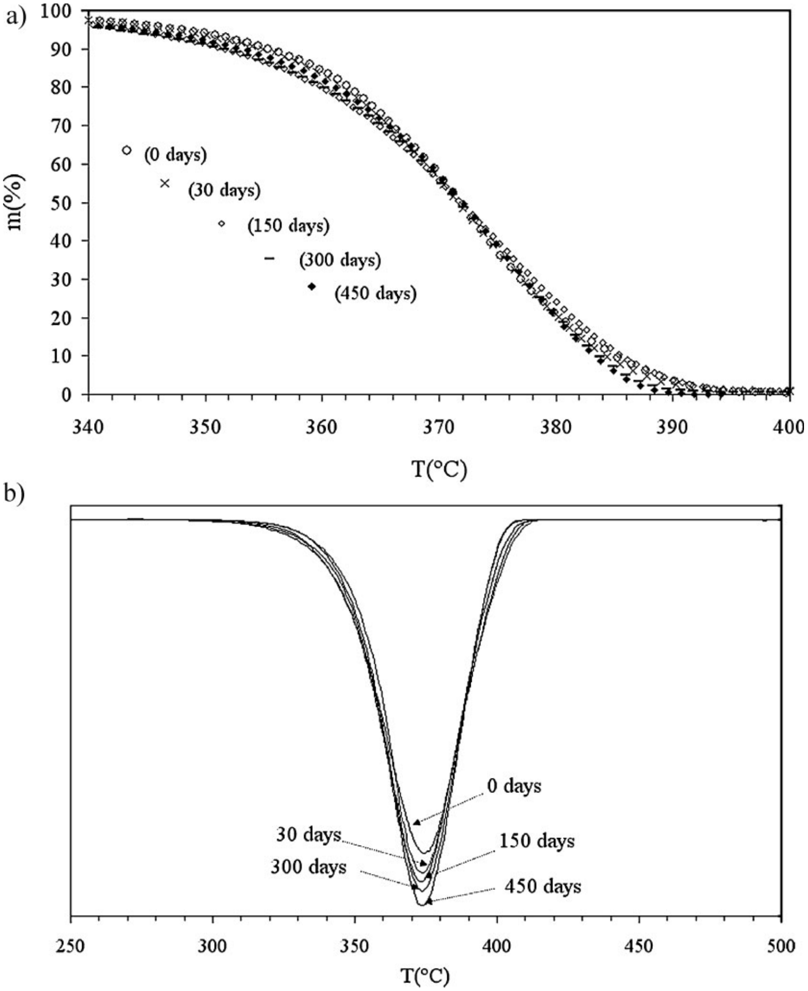

Figure 1.
TG (a) and DTG (b) curves of PLA thermal degradation.

Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

DTG, respectively), of the thermal decomposition of PLA for all the degradation in soil times. The DTG curves show only one maximum, which is related to a single-stage decomposition process, regardless of the degradation time studied. The DTG temperature peak (T_{peak}), the degradation onset (T_{onset}) and endset (T_{endset}), as well as the temperature range between T_{onset} and T_{endset} (ΔT_{deg}), were selected as characterization parameters. Results are listed at Table 1.

There are not remarkable changes in the T_{peak} as the exposure in soil time becomes longer, whereas the T_{onset} evolution presents a slight overall decrease. Regarding the T_{endset} tendency, an approx. 8 °C decrease is seen, with leads to sharpen the degradation temperatures interval. It might be explained as an effect of biodegradation in soil, which produces chain scission processes to the polymer that seems to slightly decrease the thermal resistance of PLA, according to literature.[15] However, no conclusions should be given out yet, since little changes at the degradation temperatures are seen after 450 days.

Thermal Decomposition Kinetics

According to the literature, several molecular as well as radical reactions are involved in PLA decomposition, mainly considering non-radical intra or intermolecular exchange reactions involving –OH groups, as well as cis-elimination or radical and non-radical concerted reactions.[15] The characterization of the thermal decomposition mechanism is hence complicated, due to the relative action of all the competitive reactions above mentioned.

Nonetheless, it is generally possible to mathematically study the overall decomposition process kinetics from the TG-DTG data of polymers [16]. In that sense, several methods which can be applied to a single TG run have been chosen (Criado, Broido, Chang and Coats-Redfern) as a first approach of the problem. The apparent activation energy (Ea) of the thermal decomposition mechanisms is the monitoring parameter selected to assess the effects of degradation in soil. Since the conversion degree related to the maximum decomposition rate (which corresponds to the DTG peak temperature, T_{peak}) is 0.6, all kinetic measurements have been performed in the interval $\alpha \varepsilon (0.01–0.6)$.

Criado master curves were plotted from experimental data to focus the study of the thermodegradation kinetics. Figure 2 shows the comparison between the experimental curves of the original and the last tested samples (0 and 450 days) with the theoretical master curves. It is seen that curves lie between the theoretical curves for $f(\alpha) = (1–\alpha)^n$ with reaction order n between 1 and 1.5, behavior proved for all times of exposure in soil studied.

In order to evaluate the differences between employing $n = 1$ or $n = 1.5$ to describe the thermodegradation mechanism at each degradation time studied, the kinetic methods developed by Broido (for $n = 1$) and Chang (for $n = 1$ and $n = 1.5$) to obtain the Ea of the thermodegradation process were applied. The results were compared to the Ea values obtained by the kinetic method worked out by Coats and Redfern, which is considered as reference by many authors.[16–18] Table 2 lists the Ea values obtained by all methods and reaction

Table 1.
Thermal stability parameter of PLA submitted to soil burial test.

Burial in soil time (days)	T_{onset} (°C)	T_{endset} (°C)	T_{peak} (°C)	ΔT_{deg} (°C)
0	360,4	415,0	373,6	54,5
30	358,0	412,9	373,2	54,8
150	356,4	411,0	374,5	54,6
300	356,4	407,8	373,8	51,4
450	358,9	407,8	373,6	48,4

Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

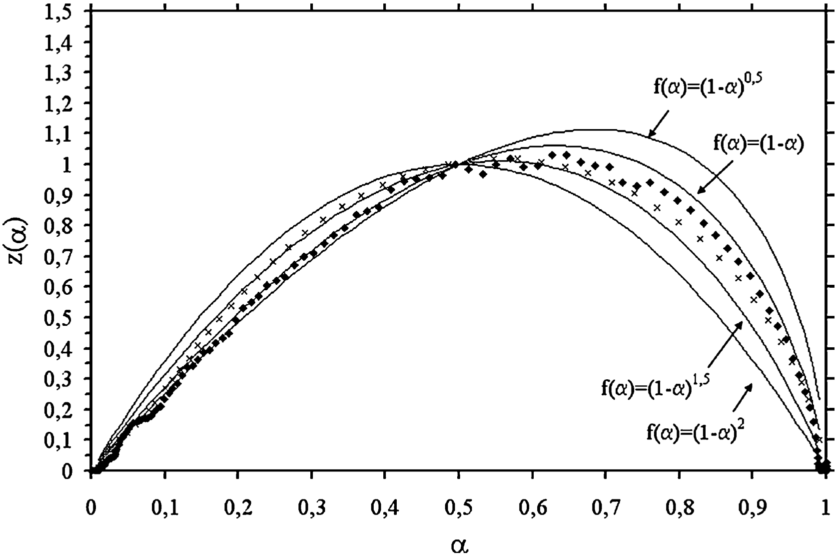

Figure 2.
Comparison of the experimental data of virgin (X) and 450 days (◆) buried PLA with the theoretical master curves.

orders for PLA at all times of exposure in soil studied. The behaviour of the Ea evolution plotted by each methodology is shown at Figure 3.

Regarding the Ea values, they should be defined between the Ea boundary values obtained by the Coats-Redfern method for $n=1$ and $n=1.5$. The differences observed in Ea values from each kinetic method might be attributed to the different mathematical approaches employed at each one.[16] Although neither Chang method nor Broido one provide Ea values in that region, the later shows exactly the same Ea tendency as the evolution described by the Ea calculated by Coats-Redfern method. It could be hence solved that to approach the reaction order to $n=1$ and to use Broido method is useful, due to the qualitative interpretation of the influence of degradation in soil on the Ea of the thermal decomposition kinetics of PLA does not change.

Concerning the Ea evolution behaviour, no linear trend was established for the Ea variation along the degradation in soil time. As it is been proved to other polymers submitted to soil burial test,[3] the Ea evolution evidences a behaviour by stages, with an underlying overall 20% decrease.

Table 2.
Activation energies obtained by the Broido, Chang and Coats-Redfern methods for PLA at all exposure in soil times analyzed.

Burial in soil time (days)	$n=1$			$n=1.5$	
	Ea (Broido) (kJ/mol)	Ea (Chang) (kJ/mol)	Ea (Coats-Redfern) (kJ/mol)	Ea (Chang) (kJ/mol)	Ea (Coats-Redfern) (kJ/mol)
0	387	315	324	318	344
30	379	352	317	332	337
150	313	236	262	239	278
300	311	275	266	284	281
450	336	241	279	244	295

Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

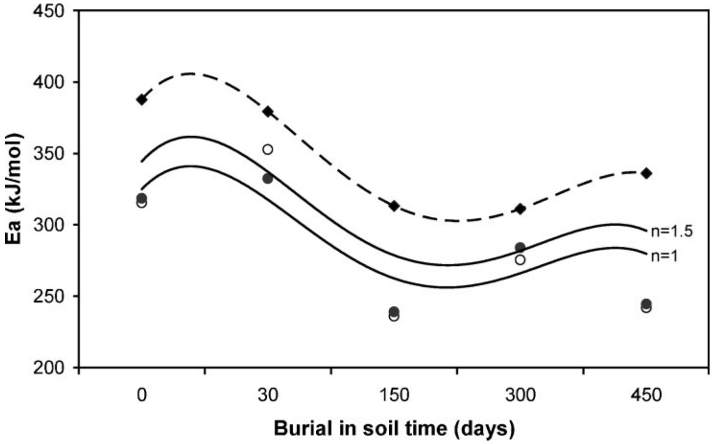

Figure 3.
Ea evolution shown by the different kinetic methodologies (Coats-Redfern: –; Broido: -◆-; Chang with $n = 1$: ○, and with $n = 1.5$: ●).

Conclusion

The thermodegradation mechanism is governed by a single-stage decomposition process regardless of the burial in soil time studied, which can be modelled by a kinetic function $f(\alpha) = (1-\alpha)^n$ with n between 1 and 1.5.

The Ea evolution can be qualitatively explained by using the Coats-Redfern and Broido methods, which describe the same behaviour. As expected, non-linear tendency is found out for Ea variation along the exposure in soil time, which may be understood as an evolution by stages, which overall decreases.

The thermal resistance of PLA has not been too affected by degradation in soil after 450 days of experiment, due to its thermal properties have not significantly changed.

Acknowledgements: The authors would like to acknowledge the Ministerio de Educación y Ciencia (Spanish Government) and the European Regional Development Fund for the economical support through the Project CTM2004-04977/TECNO and for the concession of the pre-doctoral grants through the programmes FPI and FPU.

[1] H. Tsuji, Polylactides, Biopolymers. in: *Polyesteres III. Applications and Commercial Products*, Y. S. Doi, A., Eds., Wiley-VCH, Weinheim **2002**, p. 129–177.

[2] N. H. Naitove, *Plast. Tech.* **1998**, *44*, 13.

[3] L. Santonja-Blasco, et al. Thermal characterization of polyethylene blends with a biodegradable masterbach subjected to thermo-oxidative treatment and subsequent soil burial test. *Journal of Applied Polymer Science*, **2007**, Pendent of publication.

[4] L. Contat-Rodrigo, A. Ribes-Greus, Thermal and Viscoelastic Properties of some commercial Starch products. *Journal of Applied Polymer Science* **2003**, *88*, 1242–1251.

[5] L. Contat-Rodrigo, A. Ribes-Greus, Biodegradation Studies of LDPE Filled with Biodegradable Additives: Morphological Changes. I. *Journal of Applied Polymer Science* **2002**, *83*, 1683–1691.

[6] F. Vilaplana, A. Ribes-Greus, S. Karlsson, Degradation of recycled high-impact polystyrene. Simulation by reprocessing and thermo-oxidation. *Polymer Degradation and Stability* **2006**, *91*(9), 2163–2170.

[7] F. Vilaplana, A. Ribes-Greus, S. Karlsson, Analytical strategies for the quality assessment of recycled high-impact polystyrene: A combination of thermal analysis, vibrational spectroscopy, and chromatography. *Analytical Chimica Acta*, Available online 27 April **2007**, In Press, Corrected Proof.

[8] L. Contat-Rodrigo, A. Ribes-Greus, C. T. Imrie, Thermal Analysis of High-Density Polyethylene and Low-Density Polyethylene with Enhanced Biodegradability. *Journal of Applied Polymer Science* **2002**, *86*, 764–772.

[9] W. L. Chang, *J. of Apply. Polym. Sci.* **1994**, *53*, 1759.

[10] A. Broido, A simple, sensitive graphical method of treating thermogravimetric analysis data. *Journal of Polymer Science Part A-2: Polymer Physics* **1969**, *7*(10), 1761–1773.

[11] A. Coats, A. Redfern, *Nature* **1964**, *68*(201), 4914.

[12] C. D. Doyle, *Nature* **1965**, *207*, 290.

[13] J. M. Criado, Kinetic Analysis of DTG data from master curves. *Thermochimica Acta* **1978**, *24*, 186–189.

Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

[14] DIN 53739. Testing of Plastics. Influence of fungi and bacteria. Visual Evaluation. Change in Mass and Physical Properties. **1984**.

[15] F. D. Kopinke,, et al. Thermal decomposition of biodegradable polyesters–II. Poly(lactic acid). *Polymer Degradation and Stability* **1996**, *53*(3), 329–342.

[16] M. Brown, *Introduction to Thermal Analysis. Second Edition. Techniques and Applicattions*, Kluwer Academic Publishers, Secaucus, NJ, USA **2001**.

[17] X. C. Ramis, A. Salla, J. M. Morancho, A. Vallés, L. Contat, A. Ribes, Thermal Degradation of Polypropylene/ starch-based materials with enhanced biodegradability. *Polymer Degradation & Stability* **2004**, *86*, 483–491.

[18] B. Z. Liu, X. Wang, F. Wang, Thermal Degradation Kinetics of Poly(propylene carbonate) Obtained from the Copolymerization of Carbon Dioxide and Propylene Oxide. *J. of Apply. Polym. Sci.* **2003**, *90*, 947–953.

Copyright © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim