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Instituto de Investigación en Tecnología de Materiales.

Universidad Politécnica de Valencia,

Camino de Vera s/n 46071 Valencia, Spain

*To whom correspondence should be addressed.

Corresponding author. Fax: +34963879817

E-mail address: aribes@ter.upv.es

THERMAL ANALYSIS APPLIED TO THE CHARACTERIZATION OF DEGRADATION IN SOIL OF POLYLACTIDE: I. CALORIMETRIC AND VISCOELASTIC ANALYSES

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

Abstract

An accelerated soil burial test has been performed on a commercial polylactide (PLA) for simulating non-controlled disposal. Degradation in soil promotes physical and chemical changes in polylactide properties, which can be characterized by Thermal Analysis techniques. Physical changes occurred in polylactide due to the degradation in soil were evaluated by correlating their calorimetric and viscoelastic properties. It is highly remarkable that each calorimetric scan offer specific and enlightening information. Degradation in soil affects the polylactide chains reorganization. A multimodal melting behaviour is observed for buried PLA, since degradation in soil also promotes the segregation of the crystalline phase, enlarging the lamellar thickness distribution of the population with bigger average size. Morphological changes lead to an increase in the free volume of the polylactide chains in the amorphous phase that highly affected the bulk properties. Thermal Analysis techniques provide reliable indicators of the degradation stage of polylactide induced by degradation in soil, as corroborated by molecular weight analysis.

Keywords: polylactide (PLA), degradation in soil, differential scanning calorimetry (DSC), dynamical-mechanical-thermal analysis (DMTA), free-volume, lamellar thickness distribution.

1. Introduction

Polylactide (PLA) is an aliphatic, biodegradable, and compostable polyester which can be easily processed with standard equipment to yield articles that can be used in many applications such as in industrial packaging, in the building area, in medical, agriculture and textile field, etc [1,2,3]. Initially, polylactide products were produced for biomedical purposes and thus their hydrolysis processes captured the whole research attention [4-5]. Studies performed in neutral media such as phosphate-buffered solution, in vivo solution and water, have been extensively analyzed in order to determine the hydrolytic degradation mechanism [6,7,8,9,10]. Nowadays PLA stands out as a reliable alternative to commodities in packaging applications. This solution will therefore imply an increase of a new source of plastic waste. Hence, to correctly manage the PLA disposal, its biodegradability performance has been studied in several environmental conditions, such as composting, microbiological cultures, biological degradation and disposal in soil [11,12,13,14].

Extensive work has been performed by several researchers for understanding the degradation in soil of polymers. Former PLA biodegradation studies stated that hydrolytic reactions seem to act in the initial stage of the overall PLA biodegradation, proceeding by chain-end scission in the PLA matrix, which eases the successive biotic assimilation [11,15,16,17]. A biotic environment implies chain scissions and the physical and chemical properties of the polymer can be severely modified. Thus, the common characterization is mainly carried out by means of the measurement of the molecular weight or the weight loss changes. Ho et al. found that about 20% of a PLA film was mineralised to CO_2 after 182 days in a laboratory respirometer charged with soil at 28ºC [18]. Calmon et al. found that PLA films had weight losses varying from 0 to 100% after burial in soil for 24 months depending on PLA type and location [19]; in

contrast Urayama et al. only found a decrease of a 20% in molecular weight of PLA (100% L) plates after 20 months in soil [14]. In addition, it has been suggested that traditional techniques as the measurement of the weight loss changes for studying polymer biodegradation have some limitations especially after 3 months, because of the adhesion of soil and fungi to the polymer, which can mask real results and thus induce misleading information [14,20,21]. Fast, cost-effective and reliable characterization procedures for testing the biodegradation effects on polymers should be developed and implemented. Thermal Analysis techniques have been successfully applied in our research group to monitor and control the degradation effects on the macroscopic properties of polymers submitted to different degradative environments since they offer a huge amount of parameters that can act as indicators of the extent of degradation [22,23,24,25,26]. Figure 1 summarizes the Thermal Analysis techniques proposed for the study of the extent of degradation on PLA: Thermogravimetry (TGA), Differential Scanning Calorimetry (DSC) and Dynamic-Mechanical-Thermal Analysis (DMTA), as well as the principal parameters selected for the study. The first paper is focused on the DSC and DMTA study and the second one on the TGA.

		THERMAL ANALYSIS			
		Technique	**Experiment**	**Direct observation**	**Further data analysis**
ANALYSIS OF CHEMICAL AND PHYSICAL PROPERTIES	**1 st Paper**	**Differential Scanning Calorimetry (DSC)**	Heating/ Cooling/ Heating	→ Glass transition temperature → Crystallization temperatures and enthalpies → Melting temperatures and enthalpies → Crystallinity degree	→ Structural relaxation / physical ageing → Lamellar thickness distribution → Multi-modal melting behaviour characterisation
		Dynamical-Mechanical Thermal Analysis (DMTA)	Multi-frequency	→ Storage and Loss Moduli → Loss tangent	→ Activation energies of relaxations → Free-volume ratio (thermal expansion coefficient)
	2nd Paper	**Thermogravimetry (TGA)**	Non-isothermal analysis Multi-heating rates	→ Decomposition temperatures (thermal stability) → Percentage of mass loss and residue	→ Safety decomposition temperatures → Activation energies evolution → Kinetic models

Figure 1: Summary of parameters used to assess the extent of degradation in soil on polylactide.

The aim of this work is to simulate the degradation in the environmental conditions that PLA is subjected during non-controlled disposal. In this set of papers, physical changes occurred to polylactide properties throughout the degradation in soil process are analysed by Thermal Analysis, making efforts on establishing new insights in studying the degradation in soil process on polymers. The study is complemented with the analysis of the evolution of the average molecular weight in number and weight by Gel Permeation Chromatography, aiming to test the reliability and consistency of the techniques proposed in the assessment of degradation in soil effects on PLA.

2. Experimental section

2.1. Material and sample preparation

A commercial polylactide (PLA), obtained from renewable resources by ring opening polymerization supplied by Natureworks (Minnetonka, USA) was used in this study. This PLA is a commercial resin with 3.8% meso-lactide and with a number-average molecular weight of 102.230 g/mol, as measured by Gel Permeation Chromatography.

PLA pellets were previously dried with demoisturized air at 80ºC during 4 hours. Rectangular plates were prepared by melt compression in a Collin PCS-GA Type Press 800 (GA, USA) at an initial temperature of the hot plates of 195ºC and final temperature of 60ºC. Five pressure steps were performed as follows starting with an 5 minutes at 6 bar, 8 minutes at 75 bar, 8 minutes at 155 bar, 4 minutes at 215 bar, and 11 minutes at 45 bar. Specimens of 145 x 10 x 2 mm were cut from the melt-pressed plates for the degradation in soil tests. Since this work approaches the degradation in soil of non-controlled landfilling of consumer goods, which are obtained by means of, at least, one processing step, “non-buried PLA” has been considered the reference material of the study.

2.2. Accelerated soil burial test

PLA plates were subjected to a controlled degradation in soil test under controlled conditions (temperature, water content and pH), following the ISO 846-1997 International Norm, method D [27]. Samples were buried in biologically active soil and kept in a Heraeus B12 (Hanau, Germany) culture oven at 28 ºC. The soil used in these tests was a red soil extract taken from a culture field in Alginet (Valencia). Microbial activity of soil was monitored with cotton along the extension of the experiment. The soil was maintained at approximately pH 7 and a relative humidity of 0.87 g water/g wet soil. To ensure the oxygenation of the soil, a protocol of periodical air oxygen supply was followed. Test specimens were extracted at 30, 150, 300 and 450 days, cleaned and kept in a desiccator during 4 days in order to ensure water desorption before being analyzed.

2.3. Analytic procedures

Samples were thermally characterized by means of Differential Scanning Calorimetry (Mettler Toledo DSC822, Columbus, OH, USA). The calibration of the DSC was previously checked by In and Zn standards. Three calorimetric scans were performed to each sample at a heating/cooling rate of 10ºC/min. Samples of around 4 mg were introduced in a pierced aluminium crucible, with capacity for 40 μL. The first heating scan, in which the thermal history influence is presented, was performed from 0 to 200ºC; the cooling scan went from 200ºC to 0º and the second heating scan from 0 to 200ºC. All experiments were performed under N_2 dry gas as protective gas (50 ml/min) to avoid the water condensation in the equipment and purged with N_2 (200 ml/min) in the furnace.

The mechanical and viscoelastic properties were assessed by means of a Rheometric Scientifics Dynamic-Mechanical-Thermal Analyser Mark IV (USA). The

deformation force was set at 0.01 N. The displacement was checked before all the experiments. Experiments were performed by using dual cantilever clamping in bending mode. Specimens of 40 x 10 x 2 mm were heated from 35 to 150ºC in iso-step mode every 2ºC in the frequency (*f)* range from 0.1 to 39 Hz measuring 5 points per decade.

In order to correlate the results obtained by Thermal Analysis with the molecular weight changes, the number and weight average molecular weights ($\overline{M}_n$ and $\overline{M}_w$ respectively) of the samples were evaluated in tetrahydrofuran (THF) at 25ºC by a GPC Agilent 1100 Series, using a PL Gel 5 μm 104 Å column, of 300 x 7.5 mm, from Polymer Laboratories.

3. Results and discussion

The extent of biodegradation of polylactide (PLA) has been deeply characterized by means of Differential Scanning Calorimetry (DSC) and Dynamical-Mechanical-Thermal Analysis (DMTA) experiments. A parallel DSC/DMTA results interpretation along the study will thus provide specific indicators to monitor the extent of degradation, by understanding the role of both amorphous and crystalline fractions of PLA. Furthermore, these results have been associated with the average molecular weight evolution in order to validate the suitability of Thermal Analysis techniques for monitoring degradation in soil on PLA.

Figures 2a and 2b show the calorimetric thermogram and the mechanical relaxation spectrum of non-buried PLA, respectively. In the Figure 2a, the three calorimetric (heating, cooling, and second heating) scans are plotted. From the first heating scan, the degradation in soil effect on PLA was assessed, since it represents the current status of the buried polymer. The following transitions are observed along the increasing temperature-axis: glass transition (between 40ºC-75ºC), cold crystallization (between 90ºC-140ºC) and melting process (between 140ºC-160ºC). From each

calorimetric transition, sensitive indicators were studied to evaluate degradation. The cooling DSC scan only shows the glass transition and the second DSC heating scan shows the glass transition, overlapped with the structural relaxation enthalpy. In the second heating scan, PLA has different thermal history than the shown at the first scan; because the amorphous phase does not crystallize after cooling the material at 10ºC/min.

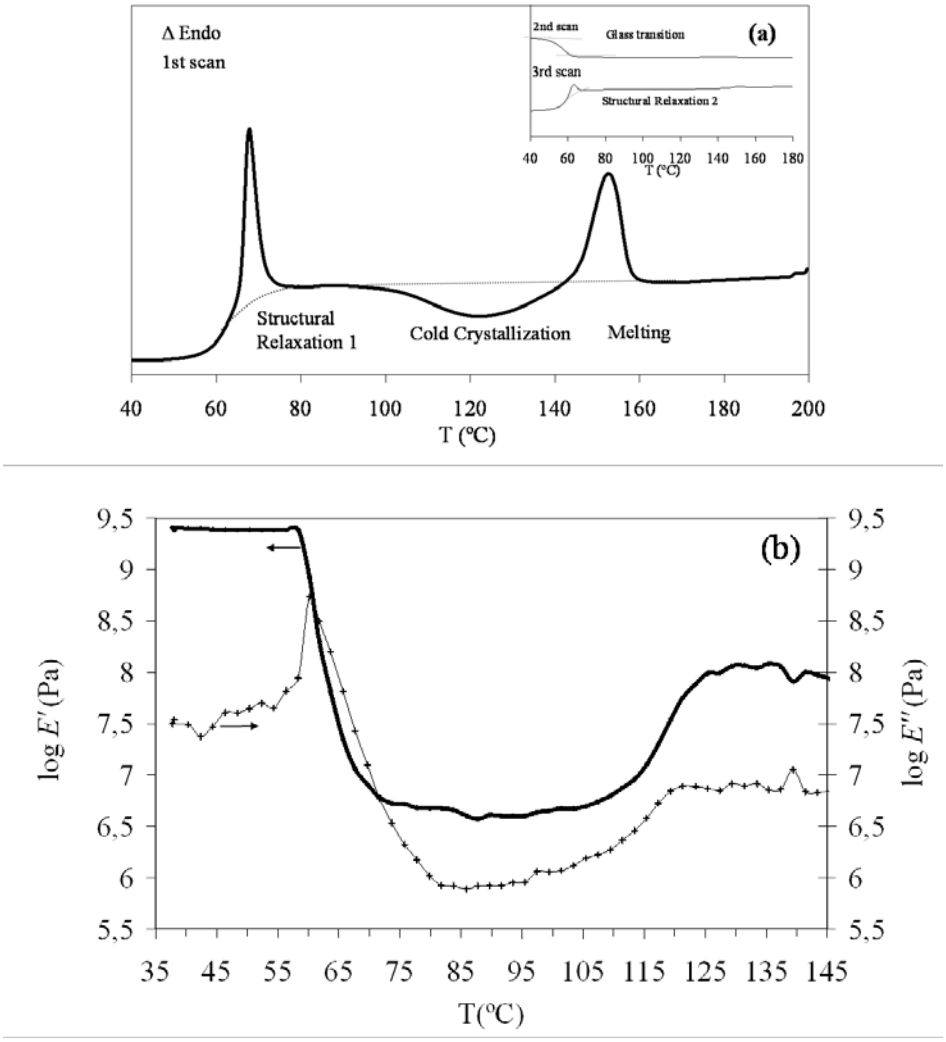

Figure 2: Calorimetric and viscoelastic behavior of non-buried polylactide (a) calorimetric thermogram and (b) log (*E'*) and log (*E''*) versus temperature.

In the Figure 2b the storage (*E'*) and loss (*E''*) moduli versus temperature at the commonly used frequency of 1 Hz are plotted. Similar curves are obtained for all the other frequencies between 0.1 and 39 Hz, but are not displayed for the sake of clarity.

The mechanical relaxation spectra show different relaxation zones which can be assigned to the calorimetric transitions along the increasing temperature-axis: glass/rubber transition (55-75ºC), rubbery plateau (75-90ºC), rubber/crystallization transition (90-140ºC), and melting/flowing (from 140ºC on).

Figure 3 shows the effect of degradation in soil on the first DSC heating scan. The degradation in soil modifies the storage and loss modulus spectra as can be seen at Figures 4a and 4b, respectively. Taking into account that the first calorimetric thermogram (first DSC scan) and the mechanical relaxation spectrum (DMTA scan) are directly related; the discussion of the results is focused in the three important transitions observed in the calorimetric thermogram and the corresponding mechanical relaxation spectrum.

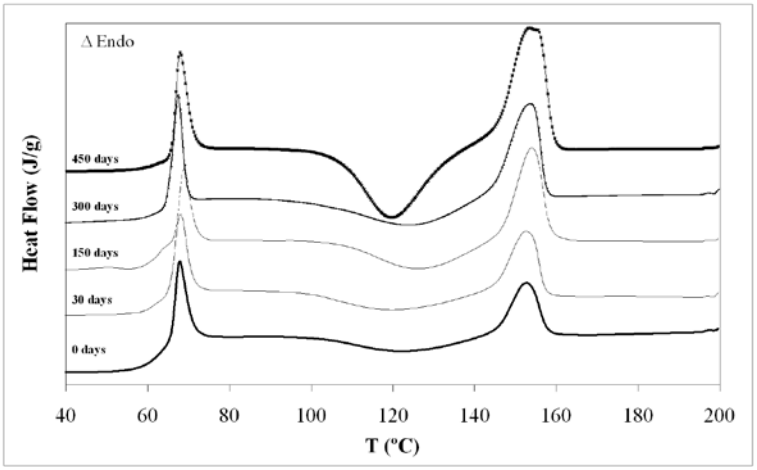

Figure 3: Comparative first scan of the calorimetric thermograms at different degradation times.

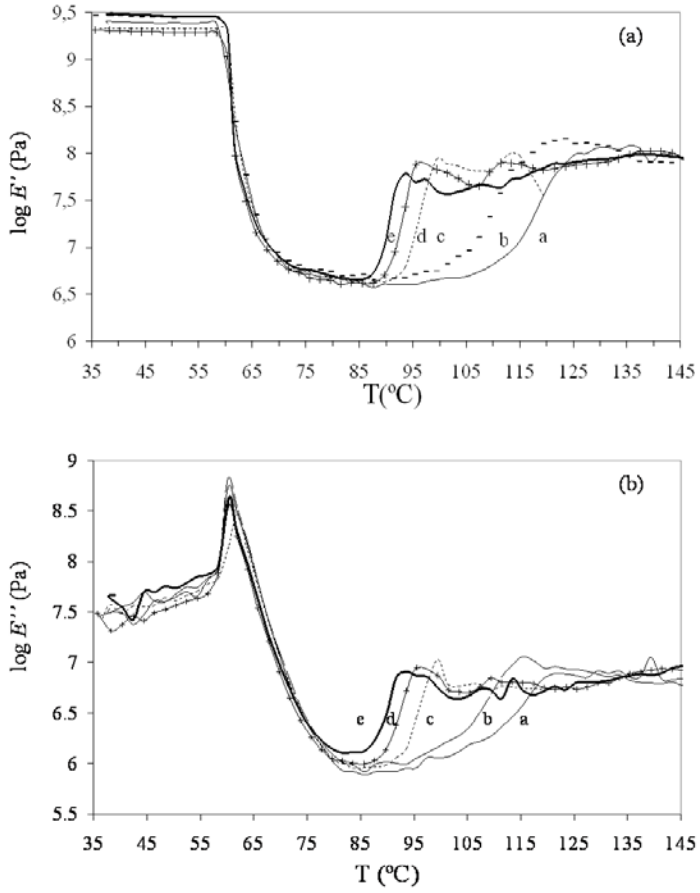

Figure 4: (a) Effect of degradation in soil on log *E'* vs. temperature. (b) Effect of degradation in soil of polylactide on log *E''* vs. temperature.(a. 0 days; b. 30 days; c. 150 days; d 300 days; e. 450 days).

3.1. Glass transition assessment

The study of the glass transition region from the calorimetric and the mechanical techniques enables analyzing the effect of degradation on the amorphous molecular chains. At the first calorimetric scan (Figure 2) an endothermic phenomenon, the structural relaxation, overlapped to the glass transition relaxation, is observed at 61ºC. In order to assess this phenomenon, the relative structural relaxation enthalpy (ΔH_R) is proposed as indicator. The enthalpies were calculated by the specific area (J/g) of the consequent endotherm using a spline baseline. The relative structural relaxation enthalpy (ΔH_R) is obtained by the subtraction of the structural relaxation enthalpy of

the first scan (ΔH_{R1}) to the one related obtained in the second heating scan (ΔH_{R3}). It is provided in relative terms with regards to the non-buried sample (sample"o") to study the "*i*" times of degradation in soil $\Delta H_{Ri} = (\Delta H_{R1i} - \Delta H_{R3i}) / (\Delta H_{R1o} - \Delta H_{R3o})$.Table 1 shows the changes of ΔH_R. It can be seen that when the soil burial test advances, there is an increasing tendency of this indicator reaching a 70% increase at 450 days.

The glass transition temperature (T_g) is obtained from the second heating DSC scan in which this is the only phenomenon shown, due to the applied cooling rate does not allow crystallization. The T_g is calculated as the temperature at the inflection point of the phenomenon, and for non-buried PLA it is located around 56ºC.

Table 1: Calorimetric and viscoelastic parameters relaxation related to the glass transition.

	DSC			DMTA
Time in soil (days)	T_g **(ºC)**	ΔH_{R1} **(J/g)**- ΔH_{R3} **(J/g)**	ΔH_R **(J/g)**	T_{max} **(ºC)**
0	56.5±1.0	4.3±0.1	1.0+0.02	60.9±0.5
30	56.1±0.8	4.7±0.1	1.1+0.02	60.9±0.3
150	56.7±1.0	5.2±0.2	1.2+0.04	62.0±0.7
300	55.7±0.7	6.0±0.3	1.4+0.07	60.7±0.2
450	55.9±0.6	7.3±0.3	1.7+0.04	60.8±0.7

The glass-rubber relaxation of PLA appears in DMTA as a drop of the storage modulus (*E'*) to very low values. The peak temperature (T_{max}) taken from the maximum of the loss modulus (*E''*) related to the glass transition gives a value of approx. 60 ºC at the frequency of 1 Hz. As was expected, the temperature related to the glass-rubber relaxation is higher than the calorimetric glass transition temperature. The values of T_g and T_{max} obtained for PLA submitted to degradation in soil are shown at Table 1. These

parameters do not offer significant changes with burial, because are sensitive to large-scale morphological changes. With the aim of assessing the morphological rearrangements of PLA amorphous chains, a closer inspection has been carried out.

The calculation of the Arrhenius maps has thus been performed (Figure 5) in order to predict the influence of the degradation in soil on the viscoelastic performance of PLA. As expected, the relationship of ln *(f)* and $T_{\max}^{-1}$ can be fitted to the Vogel-Fulcher-Tamman-Hesse (VFTH) equation [28]:

$$\ln f = A - m_v \cdot \frac{1}{T_{\max} - T_\infty} \qquad (1)$$

where f represent the selected frequencies in Hz, $T_{\max}$ in K, is the temperature obtained at the maximum value of *E''*, $m_v = B/\alpha_f$ the slope of the equation, being α_f the thermal expansion coefficient and $B \cong 1$, T_∞ is the temperature at which the free volume would be zero and *A* is a pre-exponential factor. The thermal expansion coefficient trend during the degradation in soil for all samples is shown in Figure 6. The thermal expansion coefficient presents an increasing tendency when degradation time becomes longer. The increase is more noticeable from 300 days on**.**

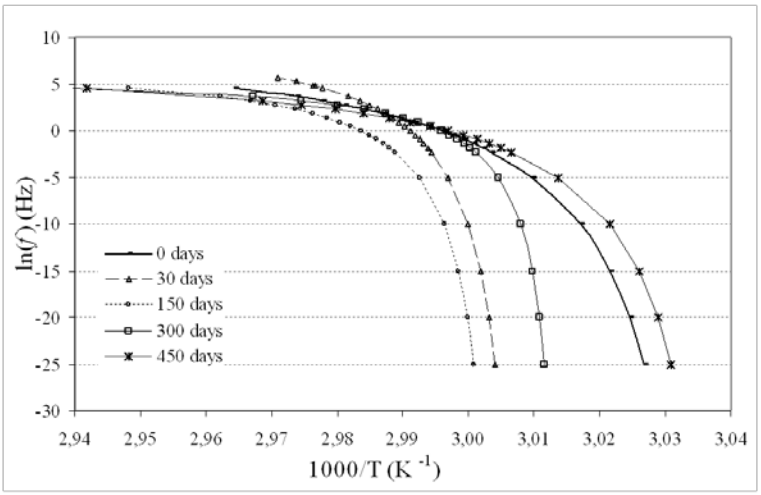

Figure 5: Arrhenius Maps obtained from multi-frequency DMTA analysis

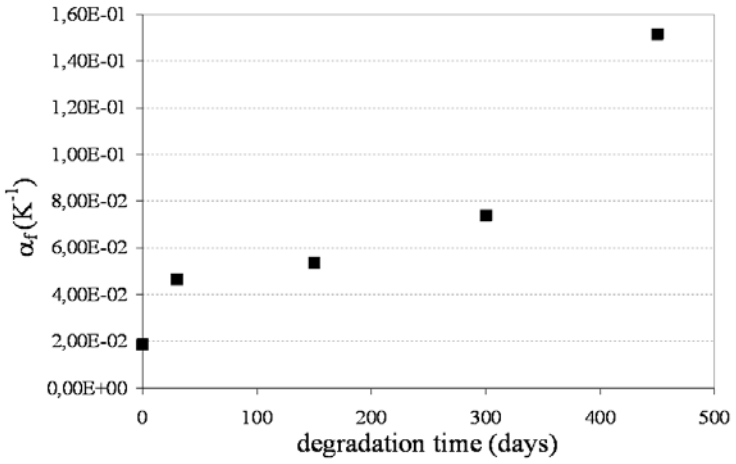

Figure 6: Thermal expansion coefficient vs. degradation time

Therefore, the free volume existing among the amorphous chains is higher as the extent of degradation rises up**.** This may be a direct consequence of chain cleavages in the amorphous phase, caused by degradation in soil agents (water and microorganisms) on the PLA matrix. Specifically in the presence of water it has been found to proceed through two alternative mechanisms: surface or heterogeneous, and bulky or homogeneous erosion [29].The free volume of the studied PLA arises with degradation in soil strengthening the suggestion of the higher compression as degradation in soil advances.

3.2. Cold-crystallization evaluation

When the glass transition relaxation is overcome other phenomenon very significant presented by PLA is the cold crystallization. In the first heating DSC scan, the cold crystallization is observed in an onset (T_{0n}) around 85ºC, since the chains which were constrained have the condition to freely crystallize and at around 123ºC the exothermic peak (T_c) is situated. Mechanical relaxation spectrum shows that the storage modulus increases again after the glass transition, at a determined temperature named onset crystallization temperature (T_O), around 85ºC, which is in good agreement with

the DSC results. The endset temperature (T_e) of the crystallization phenomenon is taken as the temperature reached when the increase in both viscoelastic modulus achieve a second plateau, being for the non-buried sample around 125ºC. This increase in the storage modulus indicates an increase of the rigidity of the material. The slow heating rate enhances the crystallization process during the DMTA measurement and the development of spherulites as other authors have confirmed using Thermal Optical Analysis and X-Ray Diffraction methods [30].

Significant changes due to the degradation in soil are observed by both techniques. The principal parameters evaluated for the analysis of the cold crystallization are listed in Table 2. Degradation in soil principally modifies the magnitude of the cold crystallization exotherm (ΔH_C), especially from 300 days of burying in soil. The increase of this parameter indicates the presence of more polymeric chains involved in the crystallization process as the degradation time is higher, thus strengthening the hypothesis of morphological changes previously drawn from the glass transition assessment.

Table 2: Calorimetric and viscoelastic parameters related to the cold crystallization.

Cold Crystallization					
	DSC		**DMTA**		
Time in soil (days)	T_{0n} **(ºC)**	T_c **(ºC)**	$log_E E'$ **(Pa)**	T_O **(ºC)**	T_e **(ºC)**
0	84.9±1.5	123.0±1.0	7.9±0.2	85.5±1.0	125.3±1.0
30	84.3±1.0	119.0±1.3	7.8±0.3	85.1±1.0	125.4±1.4
150	86.6±1.8	125.2±1.6	7.9±0.2	85.0±0.8	99.5±1.0
300	84.3±1.6	123.2±1.1	7.8±0.3	85.1±0.9	95.6±0.6
450	89.9±1.3	119.7±1.2	7.7±0.1	85.0±0.7	93.6±1.2

Changes are also observed in the mechanical spectra; the rubbery plateau is narrower as samples are more degraded, since the crystallization ends at lower temperatures. These results may suggest that the degradation in soil of the amorphous phase regions is forming shorter chains that easyly rearrange in spherulites, since the mobility is enhanced by the availability of more free volume.

3.3. Melting characterization

The study of the PLA melting process allows the determination of new parameters that will reinforce the knowledge of the degradation in soil effects on PLA morphology and thermal properties. The melting process of non-buried PLA has been analysed by the deconvolution of the melting endotherms that represent two different crystalline distributions. The lowest melting temperature peak, corresponding to the population with lower size (peak 1) is located at 151ºC and the highest, corresponding to crystalline conformations with larger size (peak 2), appears at 155ºC, (T_{m1}) and (T_{m2}) respectively. Figure 7 represents the evolution of both melting (ΔH_m) and cold-crystallization (ΔH_c) enthalpies along the degradation test. It is obtained that the melting enthalpy slightly differs from the immediately previous cold-crystallization enthalpy regardless the time of the experiment, confirming that PLA is initially amorphous. Higher degradation time leads to equally increase both enthalpies: as can be seen, the initially melting enthalpy was around 7 J/g and at 300 days it reached 18 J/g but it is up to this time when the increase is more significant, achieving at 450 days, 30 J/g.

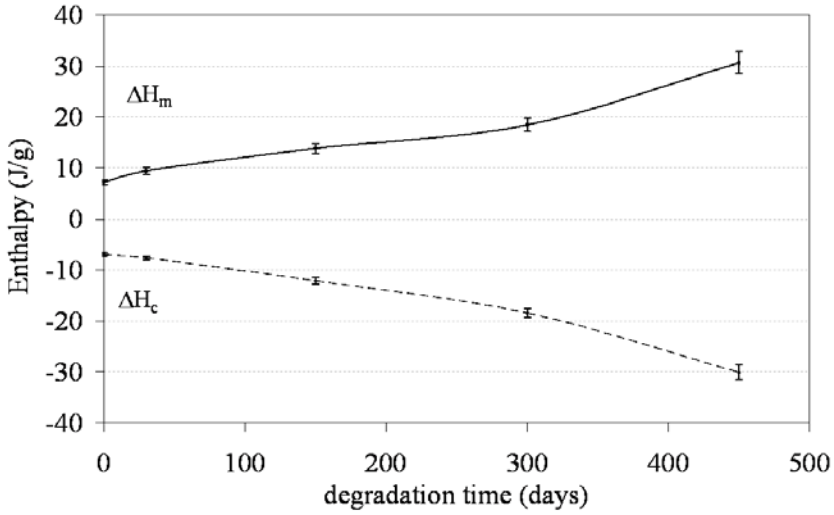

Figure 7: Crystallization and melting enthalpies vs. degradation time

Nonetheless, it has been considered interesting to perform an accurate study of the morphology of the cold crystallites obtained. Hence, from the obtained results of the melting process during the first scan, the lamellar thickness distribution "l_c" (in Åmströngs (1 $Å = 10^{-10}$ m) of the newly grown crystallites was calculated by means of Thompson equation.

$$l_c = \frac{2 \cdot \sigma_e}{\Delta h_m^{\infty} \cdot \left(1 - \frac{T}{T_m^o}\right)} \quad (2)$$

where: T = observed melting temperature (K), T_m^o = equilibrium melting temperature (K), σ_e = free surface energy of the basal plane $(J \cdot m^{-2})$ and Δh_m^{∞} = melting enthalpy per volume unit for a crystalline phase $(J \cdot m^{-3})$. For PLA the values used for calculating the lamellar thickness are, T_m^0 = 480 K, $\sigma_e = 60.89 \cdot 10^{-3}$ $J \cdot m^{-2}$, and $\Delta h_m^{\infty} = 111.083 \cdot 10^8$ $J \cdot m^{-3}$ [31]. According to the Thompson equation, Eder assumes that at a given temperature for a sample of molten polymer, the rate of heat consumption is proportional to the fraction of lamellar which thickness is l_c [32]. For the non-buried material, l_c relays between 75 and 115 Å, the plot has been done subtracting the baseline of the endotherm

and normalized to the maximum value of the enthalpy. The influence of degradation in soil on the lamellar thickness of the crystallites is shown at Figure 8. The plots slightly shift to higher l_c values with longer degradation in soil, showing the continuous formation of crystalline zones with higher lamellar size. The lamellar thickness distribution is splitting into two different shoulders. A multimodal endothermic behavior, attributed to a segregation of the initial crystalline distribution into two main populations can be observed. A deconvolution procedure was applied to the melting thermograms in order to individually characterize the behavior of each population and their contribution to the overall effect using a partial areas study [33]. The following expression was employed as deconvolution.

$$l_c(T) = \sum_i A_i \cdot \exp\left(\frac{-(T - T_i)^2}{\frac{w_i^2}{\ln(16)}} \right) \quad (3)$$

where T_i represents the average value of the temperatures range considered; A_i is the maximum intensity of the curve; w_i acts as a dispersion parameter. Deconvoluted peak temperatures, as well as the lamellar thickness at the maximum of both populations are gathered at Table 3. As can be seen, T_{m1} remains almost constant and T_{m2} slightly increases with degradation. The areas of the individual curves have been analyzed and the relative values (listed at Table 3) indicate that degradation in soil promotes the growing of the lamellar distribution with lower crystalline sizes. These results indicate that as a consequence of the degradation, the heterogeneity of this material increase. As mechanical results, DSC technique has shown the crystallization process as an important indicator of the samples degradation.

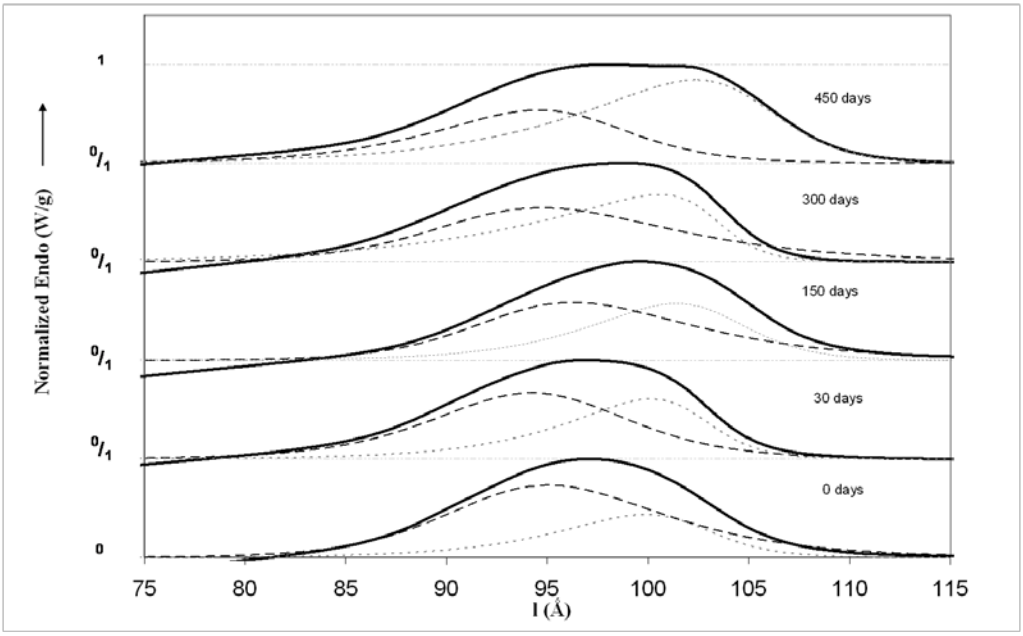

Figure 8: Influence of degradation in soil on the lamellar thickness distribution of polylactide. ( ) overall endotherm, (—) 1st deconvoluted lamellar thickness distribution with lower crystalline sizes and (---) 2nd deconvoluted lamellar thickness distribution with higher crystalline sizes.

Table 3: Calorimetric parameters related to the melting transition.

Melting						
	DSC					
Time in soil (days)	T_{m1} **(°C)**	T_{m2} **(°C)**	l_{max1} **(Å)**	***Area₁***	l_{max2} **(Å)**	***Area₂***
0	151.6±2.0	154.9±2.0	101.3±1.4	4.5 (39%)	93.7±1.2	7.0 (61%)
30	151.7±1.8	155.1±1.4	101.6±1.2	6.8 (44%)	94.5±0.8	8.5 (56%)
150	151.8±1.6	155.6±1.7	102.7±1.1	8.6 (51%)	94.4±1.0	8.6 (49%)
300	151.4±1.2	154.9±2.0	102.6±0.8	10.8 (55%)	92.8±1.2	8.7 (46%)
450	151.8±1.3	156.9±1.3	104.5±0.9	11.6 (63%)	95.9±0.8	6.8 (37%)

Summing up, the increase of the relative structural relaxation enthalpy and the thermal expansion coefficient manifest the chain cleavages induced by degradation in soil of PLA. Elevate free volume of the molecular chains that form the amorphous phase allows a major mobility of the free chains. The apparition of shorter chains is

monitored by the continuous increase in the cold-crystallization enthalpy, especially after 300 days of burying. The raise of crystallization is confirmed by the increase of the relative area of the melting endotherm related to the coldly-formed crystalline population with higher lamellar thickness.

Results provided by Thermal Analysis have been correlated with the obtained by directly measuring the molecular weight. Figure 9 shows the behaviour of average molecular weight in number and weight **(** $\overline{M}_n$ and $\overline{M}_w$ **,** respectively) as a function of the days in soil. A slight increase in the molecular weight after 30 days due to the rearrangements that PLA underwent in contact with water and soil [34] is shown. The molecular weight continuously decreases from 30 days on and it specially drops after 300 days, reaching a 50% decrease of the molecular weigh of PLA at 450 days.

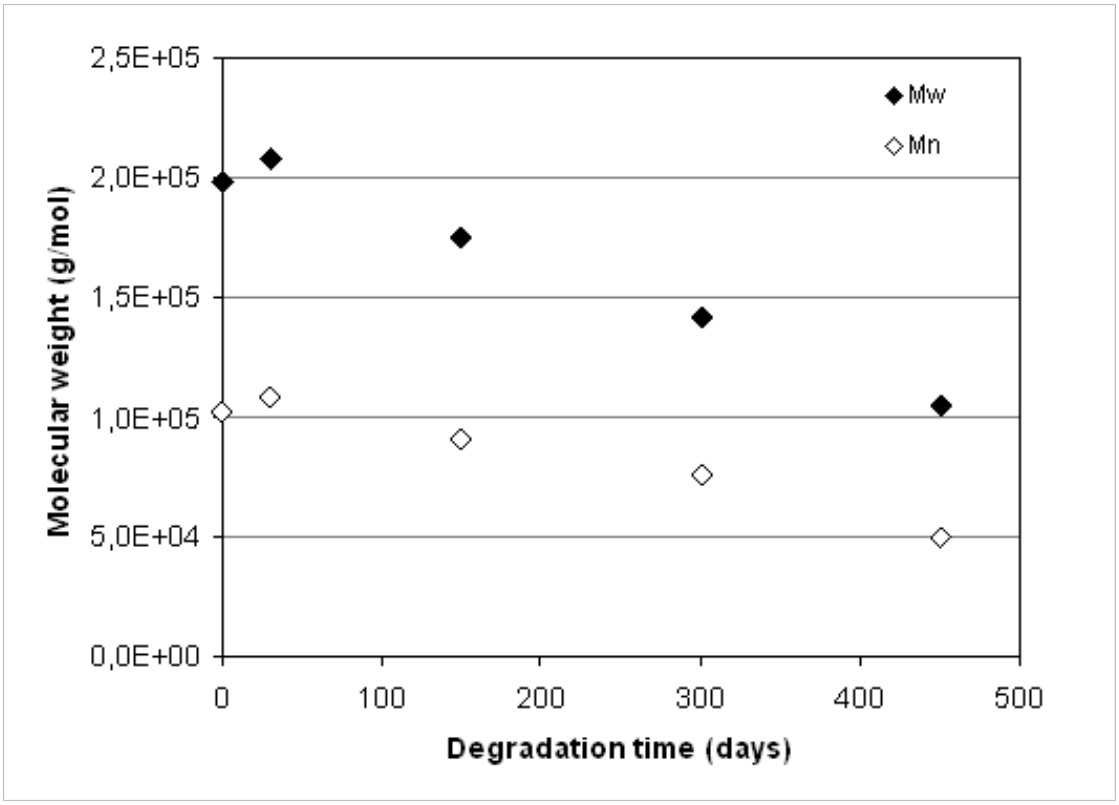

Figure 9: $\overline{M}_n$ and $\overline{M}_w$ evolution calculated by GPC.

The correlation of Thermal Analysis assessment with the molecular weight characterization has been therefore shown to be complementary and interesting, since the stage of degradation can be effectively examined by both types of analysis. DSC and DMTA techniques are very sensitive to molecular rearrangements happening before large-scale degradation processes, and therefore capable of explaining the morphological changes induced during degradation in soil, even when no significant changes in molecular weight have occurred. Likewise, Thermal Analysis techniques have effectively monitored the effects of burial when the molecular weight experiences a remarkable decrease, thus confirming the suitability of these techniques for understanding the influence of degradation in soil on polylactide.

5. Conclusions

Polylactide was buried in active soil in order to simulate its disposal stage following an international standard, and the changes in their physical properties were assessed by Differential Scanning Calorimetry and Dynamical- Mechanical Thermal Analysis.

Along the degradation in soil process, indicators such as the relative structural relaxation enthalpy and the thermal expansion coefficient have given an idea about the free volume generated within the amorphous matrix. Onset, endset and peak cold crystallization temperatures and enthalpies showed the apparition of a new crystalline phase, due to the liability of shorter chains to recombine after cleavages induced by degradation in soil. The melting temperatures and the lamelar thickness distribution shown that, especially after 300 days of burial, the crystalline fraction experiences a change from a unimodal towards a multimodal melting behaviour, coinciding with the macroscopic molecular weight decrease. These facts stress the relation between the heterogeneity acquired by PLA after chain scissions and the notable loss of properties due to a remarkable molecular weight reduction.

The combination of both Thermal Analysis and Molecular Weight Characterization stands out as a very interesting option for characterizing not only the macroscopic changes on PLA structure induced by degradation in soil, but also for establishing new insights on the morphological rearrangements involved during the whole process.

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