Accepted Manuscript

Thermal, thermo-oxidative and thermomechanical degradation of PLA: A comparative study based on rheological, chemical and thermal properties

A.A. Cuadri, J.E. Martín-Alfonso

PII: S0141-3910(18)30054-5
DOI: 10.1016/j.polymdegradstab.2018.02.011
Reference: PDST 8465

To appear in: Polymer Degradation and Stability

Received Date: 23 October 2017
Revised Date: 11 January 2018
Accepted Date: 13 February 2018

Please cite this article as: Cuadri AA, Martín-Alfonso JE, Thermal, thermo-oxidative and thermomechanical degradation of PLA: A comparative study based on rheological, chemical and thermal properties, Polymer Degradation and Stability (2018), doi: 10.1016/j.polymdegradstab.2018.02.011.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Thermal, thermo-oxidative and thermomechanical degradation of PLA: a comparative study based on rheological, chemical and thermal properties

A.A. Cuadri *, J.E. Martín-Alfonso

Departamento de Ingeniería Química, Centro de Investigación en Tecnología de Productos y Procesos Químicos (Pro²TecS), Campus de ‘El Carmen’, Universidad de Huelva, 21071, Huelva (Spain).

* Author to whom correspondence should be addressed:

A.A. Cuadri
E-mail: antonio.cuadri@diq.uhu.es
Phone: +34 959 21 98 82
Fax: +34 959 21 93 85

- 1 -
ABSTRACT

This research studies the effect of thermal, thermo-oxidative and thermomechanical degradation conditions on the melt rheological, chemical and thermal properties of PLA at temperatures around its normal processing temperature. Thermal and thermo-oxidative degradations were conducted on a rheometer by using nitrogen or air as gas, respectively, and the thermomechanical degradation was performed on a mixer equipped with two counter-rotating rollers. Dynamic oscillatory rheology, TGA, DSC and FTIR were performed on PLA samples subjected to different degradation conditions: temperature (180, 200 or 220 °C), time (15, 30 or 60 min), atmosphere (air or atmosphere) and the application of mechanical stress or not. Thus, rheological results indicate the synergic effect that temperature, mechanical stress and time exerts on the extent of chain scission phenomena, which was also corroborated by FTIR results; however, the individual contribution of mechanical stress diminishes gradually with the degradation time, being more pronounced for higher degradation temperature. In addition, degree of crystallinity ($\chi_c$) turned out not to be a suitable parameter for comparing degraded samples, since all of them became amorphous after degradation. Instead, glass transition ($T_g$) and cold crystallization ($T_{cc}$) temperatures as well as the cold crystallization enthalpy ($\Delta H_{cc}$) reveal that the chain scission phenomena makes degraded samples easier to crystallize. Finally, TGA results point out a worsening of the PLA thermal stability, with lower values of the characteristic temperatures ($T_{5\%}$ and $T_{\text{max}}$) for degraded samples.

Keywords: Poly(lactic acid), thermal degradation, thermo-oxidative degradation, thermomechanical degradation, dynamic oscillatory rheology.
1. INTRODUCTION

Poly(lactic acid) (PLA) is an emerging polymer from renewable sources having good thermoplastic behaviour, good processability and fulfilling biodegradable requirements. These properties make it a promising candidate to replace petroleum-based polymers like polyolefins in different industrial applications (e.g., packaging, films for agro-industry, fibers, etc.) [1-5]. In addition, PLA can be found under several forms depending on the enantiomeric ratio of the lactic acid group, namely PLLA (poly-L-lactic acid), PDLA (poly-D-lactic acid) and the common one, PDLLA (poly-DL-lactic acid), each PLA having specific properties [4].

Likewise many aliphatic polyesters, PLA is reported to degrade during processing due to the action of external driving force (e.g., temperature, oxygen, mechanical stress, etc.) [2]. Thus, depending on their combination, different polymer degradation can occur: thermal degradation (i.e., polymer degradation only due to the effect of temperature), thermo-oxidative degradation (i.e., degradation arises as a result of elevated temperatures and the presence of oxygen) and thermomechanical degradation (i.e., when also mechanical stress is involved) [6,7]. Regarding PLA, its thermo-oxidative degradation at the normal processing temperature (around 200 °C) follows a random chain scissions mechanism determining a significant level of molecular degradation and leading to the formation of degradation products (e.g., linear hydroxyl, ester and carbonyl groups, etc.) [1,8]. This is all reflected in a dramatic change of the molecular structure, typically evolve towards a decrease in the molecular weight, which are undesired, not only because the material’s melt viscosity and elasticity decrease, but also the processing equipment can be damaged due to the volatile lactide formation [2,5,7,9].

On these grounds, some authors [4,5,10] reported studies about both thermo-oxidative
and thermomechanical degradation of PLA and PLA-based composites, but at temperatures below PLA’s melting point. However, since the main production processes of PLA are based on melt processing, especially extrusion and injection moulding which require high temperature and mechanical stress, it is crucial to understand the structural, thermal and rheological changes that can occur during their processability [3]. Interestingly, no studies were found in the scientific literature studying the effect that temperature, time, mechanical stress and atmosphere exert on melt rheological response, chemical and thermal properties of virgin PLA at temperatures around its processing temperatures (~ 200 ºC).

In order to detect and quantify the changes in chemical structure of polymer macromolecules, dynamic oscillatory rheology of melted polymers, especially under low frequency, was found to be one of the most efficient techniques for detecting microstructural transformations due to chain scission and long chain branching/crosslinking, because different polymer chains could behave diagnostic viscoelastic response in long time regime due to the difference of relaxation rate [11-14]. In addition to that, dynamic oscillatory rheological measurements are conducted in the linear viscoelasticity (LVE) region, so its strain is too small to damage the structure of a polymer, in contrast with the large strains applied for the steady shear measurements [11,15].

Therefore, the objective of this contribution is to investigate the effect that thermal, thermo-oxidative and thermomechanical degradation conditions (which are the results of combining different atmosphere, degradation time/temperature and mechanical stress) exert on the melt rheological response, chemical and thermal properties of virgin PLA at temperature around its normal processing temperature (200 ºC). To that end, thermal and thermo-oxidative degradations were conducted on a rheometer under
nitrogen or air atmosphere, respectively, and the thermomechanical degradation was performed on a mixer equipped with two counter-rotating rollers. Melt rheological behaviour was studied by means of dynamic oscillatory measurements, and the chemical and thermal changes due to the degradations were evaluated by thermogravimetric analysis, differential scanning calorimetry and Fourier transform infrared spectroscopy.

2. MATERIAL AND METHODS

2.1. Material and sample preparation

The poly(DL-lactide) (PDLLA) used in this study was kindly supplied by NatureWorks (USA). The selected grade 2002D had a D content of 4.25 %, \( M_w = 2.09 \times 10^5 \) g mol\(^{-1}\), \( M_n = 1.01 \times 10^4 \) g mol\(^{-1}\) and \( M_w/M_n = 2.07 \).

Prior to use, PLA pellets were dried in an oven for 2 h at 100 °C for preventing hydrolysis of PLA since this polymer is very hygroscopic. Before its thermal or thermo-oxidative degradations, PLA disks about 1.5 mm in thickness and 25 mm in diameter were prepared by compression-moulding in a hot press. To that end, firstly, as-received PLA pellets were subjected to 50 bar of pressure for 5 min, at 175 °C. Subsequently, the disks were allowed to cool down to room temperature. These conditions (50 bar, 175 °C, 5 min) were selected to diminish to the maximum a possible polymer degradation during the compression-moulding, since the objective of this stage was only to obtain disk-shaped specimens.

2.2. Thermal/thermo-oxidative degradation and rheological characterization

Rheological measurements were carried out in a controlled-stress rheometer Physica MCR-301 (Anton Paar, Austria), using rough plate-and-plate geometry (25 mm diameter; 1 mm gap), and equipped with a CTD450 convection oven, which provides a gas flow of 1 L/min. Before starting with the rheological measurements (stress or
frequency sweep test), the thermal or thermo-oxidative degradation of PLA was conducted on the rheometer itself, by using nitrogen or air, respectively, as gas. The procedure can be summarized as follows: a) a PLA disk was placed on the lower plate at the degradation temperature (180, 200 or 220 °C); b) after 30 s, which was used to ensure that the sample is in melt state, the gap was adjusted to 1 mm and the remaining melted PLA was trimmed with the help of a metallic spatula. Afterwards, the convection oven was closed; c) the sample was degraded at the previously selected degradation temperature for 0, 15, 30 or 60 min under nitrogen or air atmosphere; d) a stress sweep tests, at 1 rad/s, was performed to determine the LVE region; e) a fresh PLA disk was again subjected to the same degradation conditions (i.e., the steps a), b) and c) were repeated) and a frequency sweep test, from 100 to 0.1 rad/s, under a stress value within the LVE region, was performed. It is important to highlight that both stress and frequency sweep tests were always conducted under nitrogen atmosphere for avoiding further degradation during the testing time.

On the other hand, after completing the step b) (i.e., just before starting PLA degradation), a time sweep test (within the LVE region) was performed for 60 min at each degradation temperature (180, 200 or 220 °C) and under nitrogen or air atmosphere. This enables us to monitor the evolution of the linear viscoelastic functions with the degradation time for samples degraded under different atmospheres. Consequently, for time sweep tests, the testing time corresponds to the degradation time.

2.3. Thermomechanical degradation

The thermomechanical degradation was carried out in a Rheomix 3000p mixer from Thermo Haake (Germany), equipped with two counter-rotating rollers. The rotor speed was 50 rpm and the set temperature, similar to the thermal/thermo-oxidative
degradation, was 180, 200 or 220 °C. After 15, 30 or 60 min of mixing the sample was
removed and stored at room temperature until its characterization. A portion was used
for its rheological characterization with the controlled-stress rheometer Physica MCR-
301. In this case, after completing the stages a) and b) above-commented, the stress and
frequency sweep tests were conducted at the same degradation temperature applied in
the mixer (and also under nitrogen atmosphere).

### 2.4. Thermal and chemical characterization

In addition to rheological characterization, thermogravimetric (TGA) analysis,
differential scanning calorimetric (DSC) tests and a chemical characterization by
Fourier transform infrared spectroscopy (FTIR) were carried out on dried PLA and its
corresponding degraded samples. These samples were directly taken from the rheometer
when the frequency sweep test is finished (for the thermal or thermo-oxidative
degradation) or from the mixer (for the thermomechanical degradation).

TGA analysis were conducted in a TA Q-50 (TA Instrument, USA). Temperature
sweeps (10 °C/min; between 30 and 600 °C) were carried out on 5–10 mg samples
placed on a Pt pan and under nitrogen gas flow of 100 mL/min. The temperature
corresponding to a 5 wt. % weight loss (T_{5\%}) and the temperature at which
decomposition rate is maximum (T_{max}) were obtained from TGA curves.

DSC tests were performed with a TA Q-100 (TA Instruments, USA) using 5–10 mg
samples sealed in hermetic aluminium pans. All tests were performed with a nitrogen
gas flow rate of 50 mL/min. The samples were subjected to two heating steps, from 0 to
200 °C, and an intermediate cooling step, all them at the same rate of 10 °C/min. The
objective of the first heating step was to eliminate the heat history of the sample.
Therefore, the glass transition (T_{g}), cold crystallization (T_{cc}) and melting (T_{m})
temperatures, and the cold crystallization (∆H_{cc}) and melting (∆H_{m}) enthalpies, were
recorded from the second heating sequence. FTIR spectra were recorded in a Jasco FT/IR 4200 spectrometer (Jasco Analytical Instrument, Japan), in a wavenumber range of 400-4000 cm\(^{-1}\), at 4 cm\(^{-1}\) resolution in the absorbance mode. FTIR analysis was carried out on films of dried PLA and its corresponding degraded samples. Surface IR analyses of the films were conducted using ATR accessory fitted with a diamond crystal. For film preparation, 4 mg of each sample was dissolved in 4 mL of dichloromethane, the solution was transferred to a Petri dish and, after solvent evaporation, a thin film was obtained [16].

In order to ensure accurate results, at least three replicates were conducted for every sample/test. Figures present the average values and the data were presented as mean ± standard deviation (SD).

3. RESULTS AND DISCUSSION

3.1. Melt rheological properties

Figure 1 displays the evolution of the storage (\(G'\)) and loss (\(G''\)) modulus with the degradation time for samples subjected to different degradation temperatures (180, 200 and 220 °C) under nitrogen (thermal degradation) or air (thermo-oxidative degradation) atmosphere. As can be observed, all degraded PLA samples, regardless of the degradation temperature and atmosphere, show a predominant viscous behaviour, with \(G''\) values higher than \(G'\) over the entire degradation time. Interestingly, significant differences can be deduced by comparing the results obtained after degradation under nitrogen or air atmosphere. On the one hand, for each degradation temperature, the values of both moduli for the thermal degradation samples (i.e., samples degraded under nitrogen atmosphere) remain constant with the time. These results confirm that 30 s is enough waiting time before starting the rheological tests, since no decrease of both moduli are noticed and, consequently, the sample is completely melted after this waiting
time. In addition to that, under nitrogen atmosphere, an increase in the degradation temperature is reflected in lower $G'$ and $G''$ values. This fact points out that a degradation temperature increase brings an acceleration in chain scission phenomena [12,17-19]. On the other hand, under air atmosphere (i.e., thermo-oxidative degradation), degraded PLA samples show similar qualitative response for each degradation temperature. When increasing the degradation time, both moduli undergo a drop, which is more remarkable for the first 15 min, and then they tend to level off. These facts can be more easily observed for those samples degraded at higher temperatures, in particular for that degraded at 220 ºC (Figure 1C). Furthermore, two consequences can be deduced from the thermo-oxidative degradation: a) when increasing degradation time, the difference between both moduli is kept almost constant, which implies that the predominant viscous behaviour is maintained, and b) the isothermal frequency sweep tests should be conducted under nitrogen atmosphere, in order to prevent PLA degradation during its testing time (ca. 14 min).

It is well known that the dynamic oscillatory measurements are very sensitive to the topological structure changes of melted polymers as a consequence of alterations in its molecular weight, distribution (polydispersity) and level of long chain branching [12,17,18,20,21]. After studying the evolution of linear viscoelastic functions with the degradation time for thermal and thermo-oxidative degradation (i.e., degradation under nitrogen or air atmosphere), the interest is now focused on making a comparative study about the changes on melt rheological properties for all the degradation procedure here proposed. This involves comparing PLA samples after being degraded in the rheometer under nitrogen (thermal degradation) or air (thermo-oxidative degradation) atmosphere, together with those from the mixer (thermomechanical degradation). To that end,
frequency sweep tests were conducted on these samples at the same time/temperature degradation. As an illustrative example, the evolution of both viscoelastic moduli and complex viscosity (|η*|) with frequency are displayed in Figure 2A and 2B, respectively, after subjecting PLA sample to different degradation times (from 0 to 60 min) at 180 ºC under air atmosphere. From Figure 2A, it is deduced that degraded samples show similar mechanical spectra, which are characterized by a predominant viscous behaviour (G''>G'), typical of the terminal zone reported for polymer [22]. In addition, as expected from Figure 1A, when increasing degradation time, both moduli decreases, especially after 15 min of degradation. Regarding the |η*| in Figure 2B, all samples present a Newtonian region at low frequencies, which is characterized by a constant viscosity (η₀), followed by a shear-shinning drop beyond a threshold (or “critical”) value of frequency. All degraded samples here studied (after thermal, thermo-oxidative or thermomechanical degradation) present similar mechanical spectrum, which is the typical response for linear PLA [23-26]. Some researchers [12,17,18,20,21] have reported the significance of the |η*| vs. ω curve for understanding possible changes in the length and level of entanglement of polymer chains. They stated that: a) an increase in |η*| at low/intermediate frequencies is related to a drop in the chain mobility which may result from chain branching, and b) a decrease in η₀ values indicates that chain scission may have occurred. On these grounds, the increase in |η*| observed for the thermo-oxidative degradation of HDPE was ascribed to an increase in the long chain branching/crosslinking phenomena [19]. However, as for PLA, it can be deduced from Figure 2B that an increase of degradation time favours the chain scission phenomena and an earlier decrease of η₀. In this sense,
the \( \eta_0 \) values from Figure 2B can be used to estimate their corresponding weight-average molecular weights (\( M_w \)) by the following equation [27]:

\[
\eta_0 = 5.50 \cdot 10^{-15} M_w^{3.4} \quad (1)
\]

Thus, for the PLA samples subjected to thermo-oxidative included in Figure 2B, the \( M_w \) values decreased from \( 1.33 \cdot 10^5 \), \( 1.03 \cdot 10^5 \), \( 9.40 \cdot 10^4 \) to \( 8.58 \cdot 10^4 \) after 0, 15, 30 and 60 min of degradation time, respectively. Similarly, a decrease in \( \eta_0 \) values after subjecting PLA samples to thermo-mechanical degradation shall be accompanied by lower \( M_w \) values, again due to the chain scission phenomena.

In addition to that, the linear viscoelasticity functions (\( G' \) and \( G'' \)) from Figure 2A can be used to obtain the relaxation behaviour, which provides valuable information about possible changes in PLA structures due to branching or chain scission phenomena [28]. A discrete relaxation spectrum may be described by many Maxwell elements combined in series, the generalized Maxwell model. Thus, both moduli for a generalized Maxwell model are given for the following relationships [22,29]:

\[
G'(\omega) = \sum_{i=1}^{N} G_i \left( \frac{\omega \lambda_i}{1 + (\omega \lambda_i)^2} \right) \quad (2)
\]

\[
G''(\omega) = \sum_{i=1}^{N} G_i \frac{\omega \lambda_i}{1 + (\omega \lambda_i)^2} \quad (3)
\]

where \( G_i \) and \( \lambda_i \) are the relaxation strength and relaxation time, respectively, and the sets of \( G_i \) and \( \lambda_i \) represent the discrete Maxwell relaxation time spectrum. In this paper, the discrete relaxation spectrum (\( G_i \) vs. \( \lambda_i \)) was calculated by means of a linear regression procedure using algorithms developed in MathCad v14 Pro software. It was corroborated that for the experimental frequency range used in Figure 2 (from 0.1 to 100 rad/s) four Maxwell elements are sufficient for recalculated the values of \( G' \) and \( G'' \) with high levels of significance. Figure 3 shows the discrete relaxation spectrum for
the samples included in Figure 2B (i.e., those samples subjected to thermo-oxidative
degradation and different degradation times), which are similar to those reported by
Wang et al. [28] for a similar frequency range. The presence of long, heavy and
branched PLA chains restricts their mobility which is reflected in an increase in the
relaxation time. However, in our case, as the chain scission phenomena increases with
the degradation time, the resulting short PLA chains lead to lower relaxation times [30].
Finally, the discrete relaxation spectrum gathered in Figure 3 can be also combined for
determining $\eta_0$ values as follows [29]:

$$\eta_0 = \sum_{i=1}^{N} G_i \lambda_i$$  \hspace{1cm} (4)

Interestingly, $\eta_0$ values of values 1609, 654, 483 and 364 Pa·s were calculated using the
equation (5) which are in good agreement with those displayed in Figure 2B, indicating
that the procedure to obtain the discrete relaxation spectra were appropriate.

Taking account that all degraded samples present a $|\eta^*|$ vs. $\omega$ curve similar to that
displayed in Figure 2B, the estimation of a relative modification index (R.M.I.) from the
values of $\eta_0$ may be considered as a useful parameter to quantify the chain scission
achieved after PLA degradation. Thus, a R.M.I. for each degradation temperature (180,
200 and 220 ºC) has been defined as follows:

$$\text{R.M.I.} = \frac{\eta_{0,1=0}}{\eta_{0,t}}$$  \hspace{1cm} (5)

where $\eta_{0,1=0}$ and $\eta_{0,t}$ are the complex viscosity value at 0.1 rad/s for a sample subjected
to a degradation time of 0 min (i.e., just after 30 s of waiting time before testing) and
after a time “t” of 15, 30 or 60 min of degradation, both at the same degradation
temperature. The values of $\eta_{0,1=0}$ are 1429, 451 and 134 Pa·s for degradation
temperatures of 180, 200 and 220 ºC, respectively.
Hence, this parameter allows us to quantify the drop in melt viscosity due to the chain scission for the different degradation conditions applied, as well as the individual contribution of temperature or stress. Thus, for the same degradation temperature, higher R.M.I. values would indicate that the chain scission mechanism has taken place in a greater extent. Figure 4 displays the evolution of the R.M.I. with the degradation time after thermal, thermo-oxidative and thermomechanical degradation at the three degradation temperatures considered in this work. Firstly, as no change in G’ and G’’ with the time are noticed for the degradation under nitrogen atmosphere (Figure 1), R.M.I. takes a value of 1 for each temperature. As for thermo-oxidative degradations (i.e., those conducted under air atmosphere) significant conclusions may be deduced: a) on the one hand, for each temperature, when the degradation time increases, so does its corresponding R.M.I. values and, b) on the other hand, for a fixed degradation time, higher R.M.I. values are obtained as degradation temperature rises, mainly for those degraded at 220 ºC. Regarding the thermomechanical degradations, their R.M.I. values displayed in Figure 4 are the contribution of the effect of both temperature and stress applied in the mixer. Therefore, if the R.M.I. values of the thermo-oxidative degradation (which are only due to the temperature) are subtracted from those obtained from thermomechanical degradation, it can be stated that the individual contribution of mechanical stress diminishes gradually with the degradation time, being more pronounced for higher degradation temperature.

In any case, these results confirm the synergic effect that temperature, mechanical stress and time exerts on the chain scission, which are consequence of the PLA degradation mechanism. McNeill and Leiper [31] reported their findings after PLA degradation under inert atmosphere without being subjected to any mechanical stress. Thus, PLA thermal degradation occur predominantly by random chain scissions through non-
radical reactions along the polymer backbone. Depending of the point in the backbone at which this reaction occurs, the final product could be a lactide molecule, an oligomeric ring with more than two repeat units or acetaldehyde plus carbon monoxide. Therefore, all these reactions lead to a reduction of molecular weight, which is reflected in lower melt viscosity values. In addition, the presence of oxygen under the PLA thermo-oxidative degradation induces a chain scission mechanism of alkoxyl radicals (alkyl- and acyl-oxygen), thus leading the formation of new free radicals that can cause chain scission [1,8,16] and the formation of oxidation product degradations (mainly ester and carbonyl groups). Finally, the high level of stress applied in the mixer produces a decrease in the carbon-oxygen bonding energy and alkyl and acyl-oxygen homolysis on the backbone of PLA and, consequently, this fact again favours the chain scission which is noticed in higher values of R.M.I. [1,4,8,10,16]. The McNeill and Leiper work supports that radical reaction just occurs at temperature above 270 °C. However, although the temperature degradation used in the present work was lower than that, it has been demonstrated that such reactions might occur due to the high level of stress and the oxygen presence inside the mixer [5,16].

3.2. Chemical and thermal properties
Once the melt rheological properties of PLA samples subjected to different degradation conditions has been studied, the objective now is to deepen their effects on the chemical structure and thermal properties. To that end, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetric (DSC) and thermogravimetric (TGA) analysis were conducted on degraded PLA at 200 °C (since this temperature represents a potential temperature in the perspective of extrusion process). Assessment of the chemical structure changes of degraded PLA samples provoked by the degradation conditions applied were investigated by infrared analysis. Figure 5
displays the ATR-FTIR spectra in the range of 2000 to 600 cm$^{-1}$ for virgin PLA as well as selected degraded samples after two degradation times (15 min or 60 min) and subjected to thermo-oxidative degradation (referred to as “PLA,15min,TO” and “PLA,60min,TO”) or thermomechanical degradation (“PLA,15min,TM” and “PLA,60min,TM”). The spectrum for degraded sample after thermal degradation for 15 min (“PLA,15min,T”) is coincident with that after 60 min of degradation and, consequently, it is not included for the sake of comparison.

It is well known that the random chain scission reaction associated with the formation of anhydrides, carbonyl and/or carboxyl groups, is the predominant degradation pathway for PLA during its photo-oxidation (with UV light irradiation) and thermo-oxidative/thermomechanical degradation. As a consequence, the most noticeable changes appear at 1085 and 1183 cm$^{-1}$ due to the asymmetric vibration of the ester group, and at 1750 cm$^{-1}$ attributed to the carbonyl stretching [4,5,10,16,32,33]. In addition, all degraded PLA samples (including those obtained under nitrogen atmosphere) present changes in their spectra in the 750 to 650 cm$^{-1}$ which is assigned to changes in crystallinity [34].

Aiming to obtain comparable results without the experimental influence, absorbance values of these characteristic peaks (at 1750, 1183 and 1083 cm$^{-1}$) were normalized using the absorbance value at 1455 cm$^{-1}$ assigned to the asymmetric bending of CH$_3$ group and known to be a suitable as internal standard for PLA [4,5,10,16]. Thus, the absorbance ratios displayed in the Figure 6 provide valuable information about the chemical changes due to the different degradation conditions applied. As can be deduced, no significant changes are noticed on those samples subjected to thermal degradation, which points out that nitrogen is required to prevent the PLA chain scission phenomena with the degradation time. However, after expose to thermo-
oxidative or thermomechanical degradation conditions, the absorbance ratio clearly increases with the degradation time rises, especially for the formation the new carbonyl compounds (at 1750 cm\(^{-1}\)). These results are in agreement with the R.M.I. displayed in Figure 4, indicating, again, the synergic effect that degradation time and stress exerts on the extent of the PLA chain scission at 200 °C.

DSC analysis was carried out in an attempt to find out possible changes of PLA thermal events induced by the degradation conditions applied. Figure 7 shows the DSC thermograms derived from the second heating scan of virgin PLA and selected degraded samples, and in Table 1, the corresponding glass transition (\(T_g\)), cold crystallization (\(T_{cc}\)) and melting (\(T_m\)) temperatures, and crystallization (\(\Delta H_{cc}\)) and melting (\(\Delta H_m\)) enthalpies are summarized. In addition, degree of crystallinity (\(\chi_c\)) in each sample was calculated as follows:

\[
\chi_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m}^{100\%}} \times 100
\]

where \(\Delta H_{m}^{100\%}\) is the theoretical melting enthalpy for PLA with 100 % of crystallinity.

According to the literature [35], a theoretical enthalpy of 93.1 J/g was used for the melting enthalpy of PLA with 100 % of crystallinity.

It can be observed that virgin PLA only presents a thermal event at around 59 °C which corresponds to the glass transition of its amorphous fraction. Thus, only the first heating ramp (data no shown) shows, at about 148 °C, the melting peak of the PLA crystalline fraction. The absence of the melting peak for the second heating ramp indicates that recrystallization upon cooling from the melt does not occur at the cooling rate of 10 °C/min applied (too fast for the PLA polymer chains to reorganize into crystalline regions). Taking the melting enthalpy from the first heating ramp, virgin PLA displays a percentage of crystallinity of 34.3 %. Interestingly, all degraded samples present,
besides the glass transition and melting peak above-commented, a new cold crystallization peak which extents in different temperature range depending on the degradation procedure (i.e., thermal, thermo-oxidative or thermomechanical) applied. As reported Signori et al. [2], when PLA is degraded at 200 °C and under nitrogen atmosphere the cold crystallization is also noticed. Even though no significant differences on $T_g$ values are noticed between thermo-oxidative and thermomechanical degraded samples, all these systems display a significant decrease in $T_g$ value compared to virgin PLA, which can be attributed without any doubt to the chain scission process occurring during their degradation [4,10]; however, thermal degraded samples (under nitrogen atmosphere) present a similar value, since chain scission phenomena is not relevant.

If attention is paid on the crystallinity degree ($\chi_c$), all degraded samples are amorphous (crystallinity degree is about zero), since the absolute values of the cold crystallization and melting enthalpy are almost the same due to the slow crystallization kinetics of PLA and the relatively fast cooling rate applied (10 °C/min). Therefore, $\chi_c$ is not a suitable parameter for studying the effect of degradation conditions.

On the other hand, it is possible to observe that thermograms of degraded samples after thermo-oxidative degradation (PLA, 15min, TO and PLA, 60min, TO), and more pronounced for that subjected to thermomechanical degradation at the longest time (PLA, 60min, TM), show a double melting peak attributed to the melting crystalline phases formed during the second heating ramp, since no crystallization is negligible during the cooling cycle. It is well known [10, 36-38] that PLA exhibits double melting behaviour associated to with the stable pseudo-orthorhombic structure melting at the higher temperature ($\alpha$-form) and the orthorhombic ($\beta$-form) that melts at a lower temperatures. In addition, both characteristic melting temperatures for the
thermomechanical degraded samples are higher than those after thermo-oxidative degradation, since the chain scission mechanism involves the presence of lower molecular weight polymeric chains. Moreover, it is interesting to note that the cold crystallization event occurred during the second scan becomes well pronounced for thermomechanical degraded samples after 60 min of degradation (PLA,60min,TM). Thus, the increase in $\Delta H_{cc}$ values together with the decrease $T_{cc}$ for these samples reveal that a reduction of PLA molar mass due to the chain scission phenomena makes the systems easier to crystallize [10].

Considering that one of the main disadvantages of PLA is its thermal stability, Figure 8 shows the weight loss (Figure 8A) and its derivative, DTG, (Figure 8B) for virgin PLA and the degraded samples previously considered. TGA curves for samples degraded under nitrogen atmosphere are quite similar to those obtained for virgin PLA and they are not included for purpose of clarity. The characteristic temperatures $T_{5\%}$ (temperature for the 5 wt.% of weight loss, which can be considered as the onset degradation temperature) and $T_{\text{max}}$ (temperature of maximum weight loss rate) are summarized in Table 2 for an easier comparison of the data. As can be deduced, the characteristic temperatures ($T_{5\%}$ and $T_{\text{max}}$) are shifted to lower values with increasing degradation time from 15 to 60 min, with the lowest values for the thermomechanical degraded sample (PLA,60min,TM). Compared to virgin PLA, the thermo-oxidative degradation at 200 ºC produces a reduction in $T_{5\%}$ of ca. 5 and 14 ºC for 15 or 60 min of degradation; however, they reach a value of 27 and 36 ºC for the thermomechanical degraded samples. In addition, a rather slight decrease of $T_{\text{max}}$ are observed, with a maximum value of 14 ºC. Therefore, the chain scission, which is the mechanism responsible for the thermo-oxidative and thermomechanical degradation, produces the formation of low-thermal stability compounds which are eliminated at moderate or low temperature.
[19]. Furthermore, oxidation products containing ester or carbonyl group formed during these degradations (see Figure 6) which are able to accelerate the thermal instability of PLA [5,16,39], producing a larger decrease in $T_{5\%}$ values and, consequently, a worsening of the PLA thermal stability.

4. CONCLUDING REMARKS

In the current study, the influence of thermal, thermo-oxidative and thermomechanical degradation conditions on dynamic oscillatory rheology, chemical structure and thermal properties of PLA has been evaluated. To that end, thermomechanical degradation was conducted on a mixer equipped with two counter-rotating rollers, while both thermal and thermo-oxidative degradation was performed on a rheometer, by using nitrogen or air, respectively, as gas.

Dynamic oscillatory measurements in melt state indicated that an increase in the temperature or time degradation, together with the application of the mechanical stress, produces a larger extent of the chain scission phenomena (which was also corroborated by FTIR results), since there are not rheological evidences of the formation of long chain branching/crosslinking. All degraded samples present similar mechanical spectrum, which are characterized by a predominant viscous behaviour ($G''>G'$), typical of the terminal zone reported for polymer. In addition, the complex viscosity at low frequency ($\eta_0$) enables to quantify the individual contribution of temperature/time degradation and mechanical stress on the PLA chain scission after degradation; interestingly, the contribution of mechanical stress diminishes gradually with the degradation time, being more pronounced for higher degradation temperature. Even though an increase in degradation temperature brings an acceleration in chain scission phenomena, nitrogen is required to prevent PLA degradation with the degradation time.
With regards to the DSC findings, the comparative study between degraded samples is not possible through the crystallinity degree ($\chi_c$), since all of them became amorphous; however, the decrease in the glass transition ($T_g$) is clearly ascribed to the chain scission phenomena, and the changes in the cold crystallization ($\Delta H_{cc}$) enthalpy and its corresponding cold crystallization ($T_{cc}$) temperature reveal that the chain scission makes degraded samples easier to crystallize.

Finally, the thermo-oxidative and thermomechanical degradation here applied produces a worsening of the PLA thermal stability, with lower values of the characteristic temperatures ($T_{5\%}$ and $T_{max}$).

5. ACKNOWLEDGEMENTS

The authors thank the Departamento de Ingeniería Química of Universidad de Huelva (Centro de Investigación en Tecnología de Productos y Procesos Químicos, Pro²TecS) for providing full access to laboratory equipment.

6. REFERENCES


Oxidative degradation of polylactide (PLA) and its effects on physical and mechanical properties. Eur Polym J 2014;50:109-16.


[14] Hussein IA. Rheological investigation of the influence of molecular structure on


morphology, segmental dynamics, thermal and mechanical performance. Polym Degrad.

Stab 2012;97(4):670-78.


[37] Mohapatra AK, Mohanty S, Nayak SL. Poly(lactic acid) and layered silicate nanocomposites prepared by melt mixing: Thermomechanical and morphological properties Polym Compos 2012;33(12):2095-104.


Table 1. Thermal properties evaluated from the second heating scan of virgin PLA and selected degraded samples ("T", "TO" and "TM" corresponds to thermal, thermo-oxidative and thermomechanical degradation, respectively).

<table>
<thead>
<tr>
<th></th>
<th>Tg (ºC)</th>
<th>Tcc(ºC)</th>
<th>Tm or Tm1/Tm2 (ºC)</th>
<th>ΔHm (J/g)</th>
<th>ΔHcc (J/g)</th>
<th>χc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PLA</td>
<td>58.9 ± 0.5</td>
<td>--</td>
<td>a148.2 ± 0.3</td>
<td>a31.9 ± 1.3</td>
<td>--</td>
<td>a34.3 ± 1.5</td>
</tr>
<tr>
<td>PLA,15min,T</td>
<td>59.1 ± 0.5</td>
<td>135.1 ± 0.5</td>
<td>148.7 ± 0.3</td>
<td>1.9 ± 0.5</td>
<td>1.6 ± 0.5</td>
<td>b Amorphous</td>
</tr>
<tr>
<td>PLA,60min,T</td>
<td>59.3 ± 0.5</td>
<td>135.5 ± 0.5</td>
<td>148.9 ± 0.3</td>
<td>1.8 ± 0.6</td>
<td>1.7 ± 0.5</td>
<td>b Amorphous</td>
</tr>
<tr>
<td>PLA,15min,TO</td>
<td>49.7 ± 0.5</td>
<td>124.5 ± 0.6</td>
<td>144.5/150.2 ± 0.4</td>
<td>5.5 ± 1.0</td>
<td>5.2 ± 1.1</td>
<td>b Amorphous</td>
</tr>
<tr>
<td>PLA,60min,TO</td>
<td>50.6 ± 0.5</td>
<td>124.8 ± 0.6</td>
<td>144.7/150.4 ± 0.4</td>
<td>5.9 ± 1.0</td>
<td>5.4 ± 1.2</td>
<td>b Amorphous</td>
</tr>
<tr>
<td>PLA,15min,TM</td>
<td>51.2 ± 0.6</td>
<td>120.8 ± 0.6</td>
<td>147.2/153.0 ± 0.4</td>
<td>17.1 ± 1.2</td>
<td>16.6 ± 1.4</td>
<td>b Amorphous</td>
</tr>
<tr>
<td>PLA,60min,TM</td>
<td>52.0 ± 0.6</td>
<td>122.1 ± 0.6</td>
<td>147.3/153.5 ± 0.4</td>
<td>21.4 ± 1.2</td>
<td>21.2 ± 1.5</td>
<td>b Amorphous</td>
</tr>
</tbody>
</table>

a Evaluated form the first heating scan.
b Amorphous; calculated crystallinity degree is about zero, i.e., less than 1 %.
Table 2. Thermal degradation characteristic temperatures of virgin PLA and selected degraded samples ("T", "TO" and "TM" corresponds to thermal, thermo-oxidative and thermomechanical degradation, respectively).

<table>
<thead>
<tr>
<th></th>
<th>T₅% (ºC)</th>
<th>T_max (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PLA</td>
<td>322.4 ± 1.0</td>
<td>367.1 ± 1.0</td>
</tr>
<tr>
<td>PLA,15min,T</td>
<td>322.0 ± 1.0</td>
<td>366.7 ± 1.0</td>
</tr>
<tr>
<td>PLA,60min,T</td>
<td>321.7 ± 1.0</td>
<td>366.6 ± 1.3</td>
</tr>
<tr>
<td>PLA,15min,TO</td>
<td>317.9 ± 1.1</td>
<td>361.1 ± 1.2</td>
</tr>
<tr>
<td>PLA,60min,TO</td>
<td>308.8 ± 1.1</td>
<td>357.2 ± 1.2</td>
</tr>
<tr>
<td>PLA,15min,TM</td>
<td>295.7 ± 1.2</td>
<td>357.4 ± 1.2</td>
</tr>
<tr>
<td>PLA,60min,TM</td>
<td>286.1 ± 1.2</td>
<td>353.1 ± 1.2</td>
</tr>
</tbody>
</table>
Figure captions

Figure 1. Evolution of the storage (G’) and loss (G’’) modulus with the degradation time for samples subjected to different degradation conditions.

Figure 2. Evolution of (A) the storage (G’) and loss (G’’) modulus, and (B) complex viscosity with frequency for degraded samples under air atmosphere at 180 °C, as a function of degradation time.

Figure 3. Discrete relaxation spectra for degraded samples under air atmosphere at 180 °C, as a function of degradation time.

Figure 4. Evolution of relative modification index (R.M.I) with the degradation time for samples subjected to different degradation conditions.

Figure 5. ATR-FTIR spectra for virgin PLA and selected degraded samples subjected to different degradation conditions (“T”, “TO” and “TM” corresponds to thermal, thermo-oxidative and thermomechanical degradation, respectively).

Figure 6. Absorbance ratio for the peak at 1085, 1183 and 1750 cm\(^{-1}\) for virgin PLA and selected degraded samples subjected to different degradation conditions (“T”, “TO” and “TM” corresponds to thermal, thermo-oxidative and thermomechanical degradation, respectively).

Figure 7. DSC curves corresponding to the second heating cycle for the virgin PLA and selected degraded samples subjected to different degradation conditions (“T”, “TO” and “TM” corresponds to thermal, thermo-oxidative and thermomechanical degradation, respectively).

Figure 8. (A) Weight loss and (B) its derivative curves for the virgin PLA and selected degraded samples subjected to different degradation conditions (“T”, “TO” and “TM”
corresponds to thermal, thermo-oxidative and thermomechanical degradation, respectively).
A) 180 °C

B) 200 °C

C) 220 °C

G', G''

Atmosphere: Air

Atmosphere: N₂

Degradation time (min)
Degradation temperature: 180 °C; Atmosphere: air

Graph A: Graphs showing $G'$ and $G''$ vs. $\omega$ for different $t_{\text{degradation}}$ (min).

Graph B: Graph showing $|\eta^*|$ vs. $\omega$.
Degradation temperature: 180 °C; Atmosphere: air

\[ G' \] (Pa)

\[ \lambda' \] (s)

- 0
- 15
- 30
- 60

\[ t_{\text{degradation}} \] (min)
Degradation temperature: 200 °C

Absorbance (u.a.)

Wavenumber (cm\(^{-1}\))

PLA
PLA,60min,T
PLA,15min,TO
PLA,60min,TO
PLA,15min,TM
PLA,60min,TM
Degradation temperature: 200 °C

Absorbance ratio

1085 cm⁻¹  1183 cm⁻¹  1750 cm⁻¹
Degradation temperature: 200 °C

Heat Flow (W/g)

T (°C)

- PLA
- PLA, 60min, T
- PLA, 15min, TO
- PLA, 60min, TO
- PLA, 15min, TM
- PLA, 60min, TM
Degradation temperature: 200 °C

A

B
Thermal, thermo-oxidative and thermomechanical degradation of PLA: a comparative study based on rheological, chemical and thermal properties

A.A. Cuadri *, J.E. Martín-Alfonso

**Highlights**

- Synergic effect of temperature, mechanical stress and time on PLA chain scission.
- The individual contribution of mechanical stress diminishes with degradation time.
- Degree of crystallinity is not a suitable parameter for comparing degraded samples.
- All degraded samples became amorphous after degradation without nitrogen atmosphere.