A METHODOLOGY TO ASSESS THE ENERGETIC VALORIZATION OF BIO-BASED POLYMERS FROM THE PACKAGING INDUSTRY: PYROLYSIS OF REPROCESSED POLYLACTIDE

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Keywords: pyrolysis, polylactide (PLA), reprocessing, thermal decomposition kinetics, evolved gas analysis (EGA)

Abstract:

The energetic valorization process of bio-based polymers is addressed in this study, taking polylactide (PLA) as model. The pyrolysis of virgin and multiple-injected PLA was simulated by means of multi-rate linear-non-isothermal thermogravimetric experiments. A complete methodology, involving control of gases, thermal stability and thermal decomposition kinetics was proposed. The release of gases was monitored by Evolved Gas Analysis of the fumes of pyrolysis, by in-line FT-IR, with the aid of 2D-correlation IR characterization. A novel model to establish the thermal stability of PLAs under any linear heating profile was proposed. A kinetic strategy was methodically applied to assess the thermal decomposition in terms of activation energy and kinetic model. It was found that the pyrolysis technologies for virgin PLA could be straightforwardly transferred for the valorization of its recyclates.
List of abbreviations

2D-IR: Two-dimensional InfraRed Spectroscopy,

3D-FTIR: Three-dimensional plot from EGA,

$\alpha$: degree of conversion

A: Pre-exponential factor

$A_\beta$: A at a defined $\beta$

AIC: Advanced Isoconversional Method

$\beta$: TGA heating rate

DTG: First-derivative thermogravimetric curve

Ea: Activation energy

$Ea_\alpha$: Apparent Ea at a fixed $\alpha$

$Ea_{av}$: average of Ea along the $\alpha$ range

$Ea_{iso}$: Average of Ea for the three isoconversional methods

EGA: Evolved Gas Analysis

FT-IR: Fourier-Transform InfraRed Spectroscopy

FWO: Flynn-Wall-Ozawa

KAS: Kissinger-Akahira-Sunose


MP: Master-Plots

MP_e: Experimental MP

MP_r: Differential form of MP

MP_{e\#}: Differential/Integral form of MP

MP_{\#}: Integral form of M-P

MP_t: Theoretical MP

PMc: Perez-Maqueda et al criterion

RPLA-i: reprocessed polylactide

TDB: Thermal Decomposition Behavior

TG: Thermogravimetric curve

TGA: Thermogravimetric analysis

VPLA: virgin polylactide

ZDT: Zero-Decomposition Temperatures
1. Introduction

The packaging industry is a highly important economic sector that involves big quantities of plastic materials. The current research is focused on bio-based polymers which accomplish the double benefit of coming from renewable resources, and being biodegradable once discarded, within a rational time. Polylactide (PLA) was used in this study as polymer model due to its good processability, mechanical properties, thermal stability and low environmental impact (Gupta and Kumar, 2007), which enhance its performance as suitable candidate for replacing commodities at the packaging sector. However, adding another material into the market chain will imply a new source of polymeric waste, which will have to be managed. Despite its potential of compostability, it would be advisable to explore the possibilities of extending its use during service life, recovering it and obtaining an added value from its discard. Among all recovery methods, material valorization by mechanical recycling is widely established (Vilaplana and Karlsson, 2008; Badia et al, 2011a), but the performance of recyclates may arrive to a threshold (Strömbergard Karlsson, 2009; Badia et al, 2009, 2012), when no suitable properties can be guaranteed. Then, a viable solution to manage recycled plastics waste is the application of thermally-induced recovery technologies, such as pyrolysis, gasification or combustion (Al-Salem et al, 2009). The application of these thermo-chemical operations must be carefully tackled by technologists when designing energetic valorization facilities, taking into account three basic pillars. Firstly, healthy and environmental issues must be addressed, and thus the management of emitted gases should be guaranteed. Previous lab-scale experiments such as Evolved Gas Analysis (EGA) permits testing the hazard of the released fumes, as well as helps identify the order of emitted compounds, which is related to the thermal decomposition mechanism. Secondly, the stability of the material under a specific heating profile
should be known, in order to delimit the temperature ranges where the efficiency of the thermal process is improved. Finally, the thermal performance in terms of decomposition kinetics should be handled, with the aim of understanding the behavior of the polymer under the thermo-chemical process, and thus selecting the proper operational parameters for the correct performance of the valorization.

Thermogravimetric analysis (TGA) is a widely used technique to assess the thermal stability and reaction kinetics of biomass (Barneto et al, 2010) and bio-based polymers (Carrasco et al, 2010). As well, detection techniques such as Fourier Transform – InfraRed Spectroscopy (FT-IR) can be hyphenated to TGA for the gas identification (Materazzi and Vecchio, 2010).

The pyrolysis process of PLA is addressed in this study. Current related studies report the impact of zeolites (Yuzay et al, 2010), hydrolytic fillers (Liu et al, 2010) or burial in soil (Badia et al, 2010) on PLA decomposition kinetics during pyrolysis. Concerning the assessment of the pyrolysis of mechanically reprocessed PLA, the literature describes the influence of several extrusion cycles on the thermal stability (Zenkiewicz et al, 2009) and the effect of one stage of extrusion, injection and annealing on the thermal decomposition kinetics (Carrasco et al, 2010), but no studies have been found reporting the pyrolytic process of multi-injected PLA.

Thus, the aim of this work was to define a suitable methodology to assess the pyrolysis on mechanically reprocessed PLA in terms of (i) emitted gases, (ii) thermal stability, and (iii) thermal decomposition kinetics, as a contribution to further plastic waste management solutions.
2. Materials and methods

2.1. Reprocessing simulation and sample preparation

Polylactide (PLA) 2002D was a thermo-forming grade PLA obtained from Natureworks LLC (Minnetonka, MN) in the form of pellets. Prior to processing, virgin PLA (VPLA) pellets were dried during 2 h at 80 °C in a dehumidifier Conair Micro-D FCO 1500/3 (UK), in order to remove as much humidity as possible from PLA flakes. Afterwards, samples were processed by means of injection molding by means of an Arburg 420 C 1000-350 (Germany) injector, single-screw model (diameter Φ=35 mm, length/Φ=23). Successive processing steps were applied under the same conditions (temperature gradient set from hopper to die: 160, 170, 190, 200 and 190°C; moulds set at 15 °C; cooling time residence ~ 40 s and total residence time ~60 s). Samples were dried before each processing cycle. After injection, a fraction of the samples was kept as test specimen and the rest was ground by means of a cutting mill Retsch SM2000 (UK), which provided pellets of size lower than 20 mm to be fed back into the recirculation process. Up to five processing cycles were applied to obtain the different testing specimens of reprocessed PLA (RPLA-i, with i: 1-5).

2.2. Thermogravimetric experiments

Multi-rate linear non-isothermal thermogravimetric experiments were carried out in a Mettler-Toledo TGA/SDTA 851 (Columbus, OH). Samples weighing ~ 5 mg were heated in an alumina holder with capacity for 70 μL. Experiments were performed from 25 to 750 °C at different heating rates (β = 2, 5, 7, 10, 12, 15 °C·min⁻¹), under constant flow of 50 mL·min⁻¹ of Argon to ensure inert conditions. Experiments were repeated at least three times, and the averages were considered as representative values.
Characterization was assessed with the aid of the software STAR® 9.10 from Mettler-Toledo.

2.3. Evolved Gas Analysis.

Evolved Gas Analysis (EGA) was applied to the fumes released by pyrolysis by means of coupling Fourier-Transform Infrared Analysis to the TGA (TGA/FT-IR). In this case, the TGA analysis was focused on a temperature range in which the main decomposition range of PLA occurred, from 180 to 500 °C, by means of a heating rate of 1 °C·min⁻¹. Samples weighing ~40 mg were heated in an alumina holder with capacity for 900 μL. The flow rate of the carrier gas was set to 25 mL·min⁻¹, according to technical specifications. FT-IR gas-phase spectra were collected by a previously calibrated Thermo Nicolet 5700 FT-IR Spectrometer (MA, USA), from 4000 to 600 cm⁻¹ of wavenumber, at a resolution of 4 cm⁻¹. Both transfer line and gas cell were kept at 250 °C to prevent gas condensation. 16 co-added spectra were recorded every 30 s to assure accuracy of the temperature scanning. The Gram-Schmidt plots as well as its corresponding 3D and 2D FT-IR spectra at different constant temperatures were analyzed with the help of software OMNIC 7.0. In addition, 2D-correlation spectroscopy was performed by means of the software 2Dshige (Morita, 2005).
3. Results and discussion

The thermal decomposition of virgin PLA took place through a single-step process between 250 °C and 370 °C, consuming nearly 98-99 % of mass when the polymeric chains broke down to evolve to the gaseous phase, as shown elsewhere (Badia et al., 2010). The formation of char was thus negligible, which pointed out the suitability of PLA wastes to be used in pyrolysis facilities due to the high efficiency of conversion. The thermogravimetric curves of PLA recyclates showed a similar mass-loss profile. A thorough analysis of their suitability in terms of evolved gases, thermal stability and decomposition kinetics is given hereafter in order to consider if the same operating conditions for VPLA could be assimilated for RPLA-i.

3.1. Evolved Gases Analysis

The FT-IR analysis of the evolved gases from the thermal decomposition of PLA showed that the main detected species were lactide, acetaldehyde, carbon monoxide and, in traces, carbon dioxide, water, and acetic acid. The vibration and wavenumbers of the corresponding functional groups are gathered in Table 1. It is known that the thermolysis of PLA occurs through a predominant pathway in which intramolecular hydroxyl end-initiated transesterifications of PLA mainly give rise to the formation of cyclic oligomers of lactic acid and lactide. Simultaneously, β-elimination, recombination of cyclic oligomers with linear polyesters through insertion reactions, hydrolytic reactions, or other radical degradation reactions give rise to compounds such as may occur, giving rise to the release of the aforementioned gaseous species (Mc Neill and Leiper, 1985; Kopinke and Mackenzie, 1997). Accordingly, different mechanisms might take place in the formation of each compound: acetaldehyde might have been formed by
homolytic reactions, along with CO, whereas lactide might have been formed by transesterification and/or by chain homolysis of PLA.

**Table 1.** IR absorption bands of evolved gases from thermal decomposition of PLA

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Vibrations *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>3475</td>
<td>$2 \times \nu$ (C=O)</td>
</tr>
<tr>
<td></td>
<td>2968</td>
<td>$\nu$ (CH$_3$)</td>
</tr>
<tr>
<td></td>
<td>2740</td>
<td>$\nu$ (CHO)</td>
</tr>
<tr>
<td></td>
<td>1762</td>
<td>$\nu$ (C=O)</td>
</tr>
<tr>
<td></td>
<td>1414+1371</td>
<td>$\delta$ (CH$_3$)</td>
</tr>
<tr>
<td></td>
<td>1127</td>
<td>$\nu$ (C-O)</td>
</tr>
<tr>
<td>Lactide</td>
<td>3008</td>
<td>$\nu$ (CH$_3$)</td>
</tr>
<tr>
<td></td>
<td>2952</td>
<td>$\nu_{as}$ (CH$_3$)</td>
</tr>
<tr>
<td></td>
<td>2893</td>
<td>$\nu_s$ (CH$_3$)</td>
</tr>
<tr>
<td></td>
<td>1795</td>
<td>$\nu$ (C=O)</td>
</tr>
<tr>
<td></td>
<td>1365</td>
<td>$\delta$ (CH$_3$)</td>
</tr>
<tr>
<td></td>
<td>1248+1108</td>
<td>$\nu$ (C-O-C)</td>
</tr>
<tr>
<td>Short-chain acids</td>
<td>3589</td>
<td>$\nu$ (H-O)</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>their dimers and trimers</th>
<th>2952</th>
<th>( \nu ) (CH(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2816</td>
<td>( \nu ) (CH)</td>
</tr>
<tr>
<td></td>
<td>1778</td>
<td>( \nu ) (C=O)</td>
</tr>
<tr>
<td></td>
<td>1164 + 1107</td>
<td>( \nu ) (C-O)</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>2349</td>
<td>( \nu_{\text{as}} ) (O=C=O)</td>
</tr>
<tr>
<td>CO</td>
<td>2174 + 2116</td>
<td>( \nu ) (C≡O)</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>3900-3400 + 1800-1300</td>
<td>( \nu ) (H-O) + ( \delta ) (H-O)</td>
</tr>
</tbody>
</table>

* Notation on vibrations
\( \nu \): stretching / \( \delta \): in-plane bending / s: symmetric / as: asymmetric

In order to offer deeper information, 2D-correlation spectroscopy (hereafter 2D-IR) was applied. Basically, in 2D-IR, a spectrum is obtained as a function of two independent IR wavenumbers \( \nu_1 \) and \( \nu_2 \), due to the application of an external perturbation, such as temperature. These measurements provide information that cannot be drawn from conventional one-dimensional IR spectra (Noda, 1990). The synchronous spectra \( \varphi(\nu_1,\nu_2) \) reflect the correlation of simultaneously variation of spectral intensity, whereas on the other hand the asynchronous spectra \( \psi(\nu_1,\nu_2) \) reflect the non-comparability of spectral intensity variations, being both signals out-of-phase. The discussion of both types of graphs is given in terms of auto and cross peaks. The auto-peaks \( (\nu_1,\nu_1) \), \( (\nu_2,\nu_2) \) in synchronous spectra rely on a diagonal line and their intensities reflect the influence of the external perturbation on the molecular groups of wavenumbers \( \nu_1 \) and \( \nu_2 \). The
asynchronous spectrum has not auto-peaks by definition. The cross-peaks ($\nu_1,\nu_2$),
($\nu_2,\nu_1$) are located off-diagonal, and represent the synchronicity of groups
corresponding to wavenumbers $\nu_1$ and $\nu_2$, highlighting the strong cooperation or
interaction between their different molecular groups. A positive cross-peak thus
describes the increase or decrease of the intensities of both $\nu_1$ and $\nu_2$, while a negative
cross-peak indicates an increase in the intensity of $\nu_1$ during a decrease of $\nu_2$, or vice versa. The cross-peaks in this case represent the sequential changes of the spectral
intensities $\nu_1$ and $\nu_2$ due to the asynchrony of the variations in their intensities. This
characteristic is also very useful for distinguishing between overlapped bands that arise from different spectral variations.

The rules for determination of the sequence of spectral intensity changes are determined
according to the sign of the peaks at the synchronous spectrum, which can be positive
($\varphi(\nu_1,\nu_2)>0$), or negative ($\varphi(\nu_1,\nu_2)<0$).

If the sign in the synchronous spectrum is positive ($\varphi(\nu_1,\nu_2)>0$), a positive cross-peak in
the asynchronous spectrum ($\psi(\nu_1,\nu_2)>0$) states that the change in intensity of $\nu_1$ occurs
before the change in $\nu_2$, whereas a negative cross-peak in the asynchronous spectrum
($\psi(\nu_1,\nu_2)<0$) states that the change in intensity of $\nu_2$ occurs before the change in $\nu_1$.
If the sign in the synchronous spectrum is negative ($\varphi(\nu_1,\nu_2)<0$), the abovementioned rules are reversed.
Figure 1 shows the synchronous and asynchronous spectra at different infrared regions, for the study of the thermal decomposition of VPLA. Note that negative cross-peaks are grey-shadowed. In the 2400-1600 cm\(^{-1}\) region, the synchronous spectrum shows (Fig 1a) a wide positive auto-peak corresponding to the \(\nu(C=O)\) region, which reflects the strong influence of the temperature on this spectral vibration. In the 1600-800 cm\(^{-1}\) region (Fig 1c), two positive auto-peaks (1371, 1371), (1127, 1127) for acetaldehyde and a positive auto-peak (1248, 1248) for lactide were detected. The asynchronous spectra (Fig 1b, d, e) completed the information, taking into account positive and negative cross-peaks. Lactide evolved before acetaldehyde, as can be guessed from the positive cross-peaks at (1248, 1127)-Fig 1d and (1795, 1762)-Fig 1e, and negative cross-peaks at (1414, 1248)-Fig 1d and (1376, 1248)-Fig 1d. Carbon dioxide traces evolved before acetaldehyde and lactide, as drawn from positive cross-peaks at (2349, 1795)-Fig 1b, and (2349, 1762)-Fig 1b. Carbon monoxide evolved before lactide, as shown by the negative cross-peak at (2116, 1795)-Fig 1b. Summing up, the emission profile followed the sequence: CO, CO\(_2\), lactide, acetaldehyde, due to different mechanisms, as introduced above.
**Figure 1.** 2D correlation spectra of VPLA under inert conditions at different wavenumber ranges. Negative cross-points are grey-shadowed.

After reprocessing, the gas emission profile gave similar IR spectra. Since the chemical nature of polylactide was essentially the same (Badia et al, 2011b) when it comes to the evolved gases, no differences were likely to be found. The necessary facilities for controlling the emission of evolved gases from reprocessed PLAs could thus be the same than those needed for VPLA, which may reduce costs of investing and implementation in new technologies.
3.2. Studies on the thermal stability

In order to assess the thermal stability of PLA and its further recyclates, the corresponding decomposition onset $T_0$ and endset $T_e$ temperatures were initially obtained by a tangential intercept method onto the thermogravimetric curves $TG$ for the whole process. Likewise, the temperature at the maximum decomposition rate, i.e. the peak temperature $T_p$ of the differential thermogravimetric curve $DTG$, which is related to the inflection temperature of the $TG$ curve, was also considered. Technologists may be interested in finding the relationship between the influence of the heating rate $\beta$ and the characteristic decomposition temperatures ($T_0, T_e, T_p$) to model the thermal stability behavior of bio-based plastics in thermo-chemical processes. Despite other authors have proposed linear relationships to describe the evolution of the thermogravimetric characteristic temperatures with $\beta$ (Liu et al, 2003), Figure 2a clearly shows for VPLA that, when considering lower $\beta$, the linear assumption may not be operative. Therefore, other models must be used in order to functionalize this evolution under any $\beta$. The exponential relationship shown in Eq. (1), named thermal decomposition behavior (TDB), where $a$, $b$ and $k$ are parameters of the fitting, was proposed and successfully applied for this purpose$^1$.

\[
TDB(\beta') = a \cdot (1 + b \cdot \exp (-k \cdot \beta'))^{-1}
\]

In order to evaluate the influence of multiple reprocessing on PLA’s thermal stability in terms of its characteristic temperatures, instead of choosing the experimental temperatures ($T_0$, $T_e$, or $T_p$) obtained at one specific $\beta$, which can be locally affected by both experimental errors and misleading calculation assumptions (i.e., the tangent slope is strongly dependent on the points chosen for drawing), the so-called Zero-

$^1$See results of fitting in the supplementary material.
Decomposition Temperatures \( ZDT \), those are, the values obtained when the heating rate tends to zero \( (TDB(\beta \rightarrow 0)) \) were proposed, due to the fitting of \( TDB \) smoothens the possible variations in local temperatures. **Figure 2b** shows the evolution of the Zero-Decomposition Temperatures along the reprocessing cycles, for onset \( (ZDT_0) \), peak \( (ZDT_p) \) and endset \( (ZDT_e) \). As well, the evolution of \( \Delta ZDT \) \( (ZDT_e - ZDT_0) \) is also depicted.

**Figure 2.** Thermal stability results. (a) Fittings applied to the evolution of the characteristic TGA temperatures for VPLA (dashed line: linear regression; solid line: regression applied according to \( TDB \)). (b) Evolution of Zero-Decomposition Temperatures along the reprocessing cycles.
$ZDT_0$ showed a $\sim 10$ °C increase up to the third recyclate, whereas $ZDT_p$ and $ZDT_e$ showed a small decrease. Afterwards, all $ZDT$s followed the same steady trend, slightly decreasing the $\Delta ZDT$, as a consequence of the diminution of thermal stability. These results are in agreement to the conclusions given in a previous study (Badia et al, 2011b) in which a significant increase of methoxyl-terminated linear species was found, specially up to the third recyclate, accompanied by a decrease of initially predominant cyclic species, as well as a diminution of hydroxyl/carboxyl terminated linear species. Despite the chemical nature of polylactide did not essentially change, these variations in the oligomeric distribution affected to the heterogeneity of the material, weakening its polymeric structure. Thus the increase of $ZDT_0$ may be assigned to the disappearance of cyclic structures, which possess latent ring tension and need less temperature to depolymerize than the new methoxyl-terminated linear species. When operating the pyrolysis of reprocessed PLA, higher initial decomposition temperatures should then be used.

The changes in thermal stability of virgin and reprocessed PLA were governed by modifications in their thermal decomposition behavior. Subsequent analysis was therefore needed to establish a suitable methodology to model their pyrolysis for full-scale energetic valorization facilities.

3.3. Assessment of the thermal decomposition kinetics

The thermo-chemical transformation of solid raw materials to diverse gaseous products is highly dependent on the kinetic rates of the pyrolytic reactions, and thus accurate kinetic models are needed to design the pyrolysis process in the best conditions. Macroscopic solid-state kinetics is complex, since it might give information about multiple steps taking place simultaneously. In the attempt to develop a model for plastic
thermal behavior in full-scale systems, the main purpose is to describe the thermal
decomposition in terms of an intrinsic kinetics, without taking into account the rigorous
chemistry of decomposition, thus describing the process by means of a simplified
reaction pathway, representative of a complex network of reactions. Literature indicates
that different researchers use different kinetic models and diverse kinetic methodologies
to perform their studies. This fact often provokes confusion concerning which model is
more suitable and therefore should be used to best represent the system under study.
With the aim of shedding light on this matter, a detailed methodology is presented in
this work.

3.3.1. Description of the kinetic triplet

The intrinsic kinetics of solid-state decompositions are usually described by
three parameters: activation energy ($E_a$), pre-exponential factor ($A / \ln A$) and kinetic
function ($f(\alpha)$), conforming the so-called kinetic triplet. These kinetic functions
mathematically express different physical kinetic models. The relationship between the
theoretical decomposition mechanisms and their mathematical models can be found in
literature (Khawan and Flanagan, 2006). These reaction models may adopt various
expressions, based on nucleation and nuclei growth, phase boundary reactions, diffusion
or order reactions\(^2\). The kinetic analysis of non-isothermal processes is generally
performed by using a single step kinetic equation:

$$\frac{d\alpha}{dt} = \beta \cdot \frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot k(T) = A \cdot f(\alpha) \cdot e^{-\frac{E_a}{RT}} \quad (2)$$

, where $t$ is the time (s), $T$ is the temperature (K), $\alpha$ is the conversion degree and $R$ is the
ideal gas constant (8.31 J·mol\(^{-1}\)·K\(^{-1}\)). For thermogravimetric experiments, $\alpha = (m_0$-

\(^2\)See the expressions of the different kinetic models in the supplementary material
\( m(t) / (m_0 - m_\infty) \), where \( m \) stands for mass (g), and subscripts \( 0, \infty \) and \( t \) respond to initial, final and actual mass values. The integration of Eq. (2), after rearranging, leads to:

\[
g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A \cdot E_\alpha}{k R} \cdot \int_0^\infty \frac{e^{-x}}{x^2} \cdot p(x) \quad , \quad x = \frac{E_\alpha}{R T} (3)
\]

where \( g(\alpha) \) is the inverse integral kinetic function. Under linear heating rate program, Eq. (3) has not an exact analytical solution to the temperature integral \( p(x) \) and therefore a vast number of publications have performed approximated equations to approach the best values within the lowest error margin (Pérez-Maqueda et al, 2005). In this work, the Senum-Yang approximation shown at Eq. (4) truncated at its fifth term was used, since it gives deviations lower than \( 10^{-8} \% \) from the exact value of the temperature integral for \( x > 10 \) (Pérez-Maqueda and Criado, 2000), which permits its application in solid-state decomposition reactions, where \( x \) is usually higher.

\[
p(x) = \frac{e^{-x}}{x^2} \cdot \sum_n^{n} \frac{n \cdot (1-n)}{x + 2 \cdot (n+1)} (4)
\]

### 3.3.2 Assessment of the activation energy

The first step in the study of decomposition kinetics is the assessment of the evolution of the apparent activation energy (\( E_{a\alpha} \)). It should be noted that solid-state kinetics adopted the theory for reaction kinetics in homogeneous systems (i.e., gases and liquids), and it is generally assumed that the \( E_{a\alpha} \) and the pre-exponential factor (\( A \)) remain constant. However, it has been proved that these kinetic parameters may vary with the progress of the decomposition. This variation can be detected by isoconversional methods, which use data from different multi-linear non-isothermal experiments and do not take modelistic assumptions for the analysis, main source of
error of simpler model-fitting methods. The most broadly used isoconversional methods are those integral linear methods developed by Flynn-Wall-Ozawa (FWO) (Flynn and Wall, 1966; Ozawa, 1970) (supported on Doyle’s integral approximation (Doyle, 1965) and Kissinger-Akahira-Sunose (KAS) (Kissinger, 1957; Akahira and Sunose, 1971), which are represented at Eqs.(5) and(6), respectively. These methods give rise to linear functions from which slopes the $Ea_\alpha$ at a fixed decomposition degree $\alpha$ are obtained.

\[
\log (\beta) = \log \left( \frac{A_\alpha \cdot Ea_\alpha}{R \cdot g(\alpha)} \right) - 2.315 - \frac{0.457 \cdot Ea_\alpha}{R} \cdot \left[ \frac{1}{T_\alpha} \right]_x \tag{5}
\]

\[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{A_\alpha \cdot R}{Ea_\alpha \cdot g(\alpha)} \right) - \frac{Ea_\alpha}{R} \cdot \left[ \frac{1}{T_\alpha} \right]_x \tag{6}
\]

The results were compared to those obtained by the non-linear Advanced Isoconversional method (AIC) (Vyazovkin, 1997), in order to test the consistency of the results. This method, which accounts for variable $\beta$ and systematic errors in the $Ea_\alpha$, is given at Eq. (7)

\[
\Omega = \left[ \sum_{i=1}^{h} \sum_{j=1}^{h} \frac{f(Ea_\alpha, T(t))}{f(Ea_\alpha, T(t))} \right]_i^j, \quad f(Ea_\alpha, T(t)) = \int_{t_{\alpha}}^{t_{\alpha+\Delta\alpha}} e^{-\frac{Ea_\alpha}{R \cdot T(t)}} \cdot dt \tag{7}
\]

, where $i$ and $j$ are counters through the $h$ experiments performed at $\beta, T(t)=T_0+\beta \cdot t$, where $T_0$ is the initial temperature, and $\Delta\alpha = (m^{-1})$, with $m=40$, the number of $\alpha$ segments chosen for integration. The integral $I(Ea_\alpha, T(t))$ was numerically evaluated by the Simpson 1/3 method. The $Ea_\alpha$ was the value that minimized $\Omega$ at Eq. (7) for a particular $\alpha$. This method required the tool Solver of MS Excel software, by applying the Newton method with progressive derivatives, setting an accuracy of $10^{-6}$ and a tolerance of $10^{-4}$. Kinetic analyses were carried out in the conversion degree $\alpha$ range from 0.1 to 0.8 since the main reaction took place in this region. In order to check the
suitability of using a constant value for the activation energy, the averages of those obtained by FWO, KAS and AIC methods are gathered at Table 2. The average values (\(E_{aav}\)) lay within coincident values among all methods, with low dispersion values. Therefore, it was assumed that the average isoconversional energy (\(E_{a\text{iso}}=\text{average of } E_{aav}\), given in Table 3) may be used as constant, i.e. \(E_{a\alpha}\sim E_{a\text{iso}}\), throughout the decomposition process for the following calculations.

**Table 2.** \(E_a\) averages (\(E_{aav}\)) of the thermal decompositions obtained by the isoconversional methods (FWO: Flynn–Wall–Ozawa, KAS: Kissinger–Akahira–Sunose, AIC: Advanced Iso-Conversional).

<table>
<thead>
<tr>
<th>ISOCONVERSIONAL METHODS</th>
<th>FWO</th>
<th>KAS</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
<td>(E_{aav}) (kJ·mol(^{-1}))</td>
<td>e (%)</td>
<td>(E_{aav}) (kJ·mol(^{-1}))</td>
</tr>
<tr>
<td>VPLA</td>
<td>153</td>
<td>6.3</td>
<td>151</td>
</tr>
<tr>
<td>RPLA-1</td>
<td>208</td>
<td>1.2</td>
<td>208</td>
</tr>
<tr>
<td>RPLA-2</td>
<td>202</td>
<td>2.9</td>
<td>202</td>
</tr>
<tr>
<td>RPLA-3</td>
<td>219</td>
<td>6.1</td>
<td>220</td>
</tr>
<tr>
<td>RPLA-4</td>
<td>205</td>
<td>4.7</td>
<td>207</td>
</tr>
<tr>
<td>RPLA-5</td>
<td>216</td>
<td>1.1</td>
<td>216</td>
</tr>
</tbody>
</table>
The $E_{a_{iso}}$ of virgin PLA gave out a value of 152 kJ·mol$^{-1}$, which was comparable to the values reported in different studies for PLA grades in the same order of molecular weight (Li et al, 2009; Zhou and Xanthos, 2009). After the first reprocessing step, a sharp 26.5% increase was registered up to 207 kJ·mol$^{-1}$, keeping this order of value within a 5% margin along the successive recyclates. In accordance to the results found for the thermal stability, this change can be related to the presence of more linear methoxyl-terminated species in the oligomeric distribution of PLA recyclates, to a detriment of mainly predominant cyclic species in virgin PLA (Badia et al, 2011b), which may vary the principal thermal decomposition mechanisms.

<table>
<thead>
<tr>
<th>Material</th>
<th>Function</th>
<th>$n$</th>
<th>$E_{a_{iso}}$ (kJ·mol$^{-1}$)</th>
<th>$e$ (%)</th>
<th>$\ln A$ (s$^{-1}$)</th>
<th>$e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPLA</td>
<td></td>
<td>1.611</td>
<td>153</td>
<td>6.1</td>
<td>24.4</td>
<td>5.2</td>
</tr>
<tr>
<td>RPLA-1</td>
<td>$A_n$</td>
<td>1.354</td>
<td>207</td>
<td>2.5</td>
<td>34.7</td>
<td>2.7</td>
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<tr>
<td>RPLA-2</td>
<td></td>
<td>1.510</td>
<td>201</td>
<td>4.3</td>
<td>32.6</td>
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<tr>
<td>RPLA-3</td>
<td></td>
<td>1.231</td>
<td>217</td>
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<td>40.1</td>
<td>6.1</td>
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<tr>
<td>RPLA-4</td>
<td></td>
<td>1.529</td>
<td>204</td>
<td>6.0</td>
<td>33.7</td>
<td>5.6</td>
</tr>
<tr>
<td>RPLA-5</td>
<td></td>
<td>1.346</td>
<td>212</td>
<td>3.9</td>
<td>35.7</td>
<td>4.1</td>
</tr>
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</table>
3.3.3. The use of Master-curves for determining the kinetic model

To achieve the mathematical decomposition model will help design the proper pyrolysis systems, regardless the specific decomposition pathway. Thus, the kinetic function $f(\alpha)$ was approached for virgin and reprocessed PLA by the use of reduced Master-Plots ($MP$) which are reference theoretical curves dependent on the kinetic model, but generally independent of the kinetic parameters of the process. The comparison of the experimental with the theoretical master curves, i.e. $MP_e=MP_t$, allows for the selection of the appropriate kinetic model of the process under investigation or, at least, reducing the span of suitable kinetic models (Gotor et al, 2000). There exist three main types of $MP_t$, those based on the differential form ($MP_f$) of the generalized kinetic equation, Eq.(2); those based on the integral form ($MP_g$), according to Eq. (3); and the most common one that combines both differential and integral forms ($MP_{fg}$), that are usually reduced at $\alpha=0.5$ for better visualization. The mathematical description of each curve can be found elsewhere (Gotor et al, 2000). They are described after the introduction of the so-called generalized time $\theta$, which denotes the reaction time taken at a particular conversion degree $\alpha$ at infinite temperature, defined as:

$$\theta = \int_0^\tau e^{-\frac{E_a}{R \cdot T}} \cdot dt$$  (8)

, which differentiation in combination with Eq. (2), one obtains:

$$\frac{d\alpha}{d\theta} = A \cdot f(\alpha) = \frac{d\alpha}{dt} \cdot e^{\frac{E_a}{R \cdot T}}$$  (9)

Therefore, assuming $A$ and $E_a$ constant, due to interdependence of kinetic parameters, and using a reference point at $\alpha=0.5$, the theoretical $MP_f$ and $MP_g$ and the expression for
their corresponding reduced form of the experimental data can be drawn from the following expressions:

\[ \frac{\alpha}{\Delta \alpha} = \frac{f(\alpha)}{f(0.5)} = MP^t = MP_e = \frac{\alpha}{\alpha_0} e^{\alpha_0 t} \] (10)

\[ \frac{\theta}{\theta_0} = \frac{g(\alpha)}{g(0.5)} = MP^t = MP_e = \frac{p(\alpha)}{p(0,5)} \] (11)

The advantage of using \( MP^t \) and \( MP^g \) is that the former clearly disperse among different \( f(\alpha) \) in the range \( \alpha < 0.5 \) while the latter disperse for \( \alpha > 0.5 \) and therefore permits a straightforward identification. Contrarily, the use of the common \( MP^{fg} \) tends to produce confusion due to the coincidence of different kinetic models under the same line. In order to select the best kinetic model, the condition of minimization of \( \Phi \) in Eq. (12) was applied, taking into account experiments performed at all heating rates:

\[ \Phi(f_t, g_t, \alpha) = \sum_{\alpha=0.5}^{1.0} \left[ \sum_{i=1}^{3} [MP^t_f(\alpha) - MP^e_f(\alpha)]^2 + \sum_{i=1}^{3} [MP^t_g(\alpha) - MP^e_g(\alpha)]^2 \right]; \Delta \alpha = 0.025; \forall f_t, g_t \] (12)

Figure 3 shows as an example the comparison of the experimental master curves of RPLA-2 at \( \beta = 5 \, ^{\circ}C \cdot min^{-1} \) with the differential (Fig 3a) and integral (Fig 3b) abaci. Similar plots were obtained for the rest of characterized materials. Results conclude that virgin PLA and its recyclates followed an \( A_n \) kinetic model, ascribed to a model of growth of previously formed nuclei, with \( n \) close to 1.5. This kind of kinetic model is quite common in crystallization processes, though scarcely reported in studies dealing with thermal decomposition processes of polymers, as discussed elsewhere (Badia et al, 2010), where the controversy of the relationship between themathematical models and the physical mechanisms was
addressed. The model $A_n$ indicates the presence of active zones more chemically liable to thermal decomposition, which activate the formation and growth of gas bubbles in the polymer melt.

**Figure 3.** Master plots based on the differential (a) and integral (b) forms of the general kinetic law compared to experimental data obtained for thermal decomposition of RPLA-2 (hollow circles). (Black solid lines: Nucleation; Grey solid lines: n-order; Dashed grey lines: diffusion, Pointed black lines: reaction).

### 3.3.4. Determination of the pre-exponential factor

In order to complete the kinetic triplet and thus obtain a full mathematical description of the kinetics of pyrolysis, the pre-exponential factor $A$ had to be found, along with the $n$ of the kinetic model. Taking into account that a suitable kinetic triplet should fulfill the Perez-Maqueda et al criterion (Pérez-Maqueda et al, 2002); that is, the independence of the activation parameters $E_a$, $A$ on the heating rate $\beta$, the minimization of $\xi$ in Eq. (13) provided the best $n$ for the model, and thereafter endowed with the most accurate $A$, by averaging the $A_\beta$ obtained from the intercept at $y=0$ of Coats-Redfern (Coats and Redfern 1964) equation (Eq. (14)) at each experiment with different heating rates $\beta$:
Table 3 shows the results obtained by this methodology completing the kinetic triplet of the thermal decomposition of virgin and reprocessed PLA. Figure 4 shows the fulfillment of the Perez-Maqueda criterion by virgin and all subsequent reprocessed materials as a proof of the goodness of the fitting procedure. It is important to notice that technologist may use the same experimental settings for the pyrolysis of PLA to the rest of its recyclates, by only smoothly adjusting 3 parameters, since the thermal behavior of the materials was essentially the same after recycling.
Figure 4. Application of Perez-Maqueda et al. criterion to virgin PLA and subsequent recyclates. Symbols correspond to experiments at different heating rates (°C·min⁻¹): □-2, ■-5, △-7, ▲-10, ○-12, ●-15.
5. Conclusions

A complete methodology in terms of gas control, thermal stability and decomposition kinetics, was thoroughly applied.

The gas control facilities could be transferable to reprocessed PLA.

A new model ($TDB$) and novel parameters ($ZDT$) to test the thermal stability of the materials was useful.

An increase in the trigger of the thermal decomposition as well as in the average activation energy indicated was found up to the third recycle.

Similar experimental settings for the pyrolysis of virgin PLA could be applied for the valorization of reprocessed PLA with minimum corrections in the initial decomposition stages.
Acknowledgements

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References


ANNEX. OPEN-ACCESS POLICIES