REPROCESSED POLYLACTIDE: STUDIES OF THERMO-OXIDATIVE DECOMPOSITION

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Abstract:

The combustion process of virgin and reprocessed polylactide (PLA) was simulated by multi-rate linear non-isothermal thermogravimetric experiments under O_2.A complete methodology that accounted on the thermal stability and emission of gases was thoroughly developed. A new model, Thermal Decomposition Behavior*,* and novel parameters, the Zero-Decomposition Temperatures, were used to test the thermal stability of the materials under any linear heating rate. The release of gases was monitored by Evolved Gas Analysis with in-line FT-IR analysis. In addition, a kinetic analysis methodology that accounted for variable activation parameters showed that the decomposition process could be driven by the formation of bubbles in the melt. It was found that the combustion technologies for virgin PLA could be transferred for the energetic valorizationof its recyclates. Combustion was pointed out as appropriate for the energetic valorization of PLA submitted to more than three successive reprocessing cycles.

List of abbreviations

α: degree of conversion

A:Pre-exponential factor

AIC: Advanced Isoconversional Method

β: TGA heating rate

DTG: First-derivative thermogravimetric curve

 Ea: Activation energy

Ea_α: Apparent Ea at a fixed α

EGA: Evolved Gas Analysis

$f(\alpha)$: kinetic function

FT-IR: Fourier-Transform InfraRed Spectroscopy

FWO: Flynn-Wall-Ozawa

KAS: Kissinger-Akashira-Sunose

MP: Master-Plots

n: order in kinetic functions $f(\alpha)$

n_β: n averaged from experiments at different β

n': n averaged from n_β

n'': n averaged from the n obtained analytically - Eq. (4) -

p: power

RPLA-i: reprocessed polylactide

TDB: Thermal Decomposition Behavior

TG: Thermogravimetric curve

TGA: Thermogravimetric analysis

VPLA: Virgin polylactide

ZDT: Zero-Decomposition Temperature

1. Introduction

The research in the packaging industry within a framework of sustainable development is focused on the use of bio-based materials which accomplish the benefit of coming from renewable resources, and being biodegradable once discarded, within a rational time. In this sense, polylactide (PLA) is an aliphatic polyester that can be obtained from agricultural resources, and reintroduced into the carbon cycle after being used.The increasing know-how in the technology of production of PLA (Gupta and Kumar, 2007) enhances its performance as suitable candidate for replacing commodities at the packaging sector.

Despite the potential of PLA for being treated by biological valorization in composting facilities,the foreseeable high amount of plastic waste invites to diversify and combine the available technologies of valorization. Among current procedures, material valorization by mechanical recycling is widely established (Vilaplana and Karlsson, 2008). It mainly consists in recovery, washing, drying, shredding and processing by means of extrusion or injection.The inherent thermo-mechanical degradation may modify the polymeric structure (Badia et al, 2009) and consequently affect the thermal, rheological and mechanical properties (Strömberg and Karlsson, 2009) (Badia et al, 2012a) thus reducing the performance rates of recycled goods.

A viable solution to manage bio-based recycled plastics waste, when no better performance can be guaranteed, could be the application of thermally-induced valorization technologies, such as pyrolysis and combustion (Al-Salem et al, 2009).

 The application of these thermal operations must be carefully handled by technologists during the design of energetic valorization facilities, taking into account

the knowledge of the thermal stability and the detection of emitted gases. As well, the characterization of the decomposition kinetics should be considered.

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

The majority of current studies on the combustion behavior of PLA are reported from the point of view of the flame retardancy (Bourbigot and Fontaine, 2010), but not approached from the point of view of the management of their wastes. The aim of this work was thus to assess the behavior of mechanically-recycled polylactide submitted to a combustion process,with the purpose of assuring the performance of energetic valorization processes as a contribution for further plastic waste management solutions.

2. Experimental procedure

2.1. Reprocessing simulation and sample preparation

Polylactide (PLA) 2002D is 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 ºC 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 with an Arburg420 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 190ºC; moulds set at 15 ºC;cooling time residence ~ 40 s and total residence time ~60s). Samples were

dried before each processing cycle. After injection, a fraction of the samples were kept as test specimens and the rest was ground by means of a cutting mill Retsch SM2000 (UK), which provide pellets of size d< 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 ºC at different heating rates (β = 2, 5, 7, 10, 12, 15 ºC·min^{-1}), under constant flow of 50 mL·min^{-1} of oxygen. Experiments were repeated at least three times, and the averages were considered as representative values. The assessment was performed with the help of the software STAR^e 9.10 from Mettler-Toledo.

Results are plotted in terms of {average, dev$_{max}$, dev$_{min}$}, where dev$_{max}$ = max (data)-average (data), and dev$_{min}$ = average (data) -min (data). Tabulated errors were obtained by dividing the standard deviation by the average of data.

2.3. Evolved Gas Analysis.

Evolved Gas Analysis (EGA) was applied to fumes released by combustion by means of coupled 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 ºC, by means of a heating rate of 1 ºC·min^{-1}.Samples weighing ~ 40 mg were heated in an alumina holder with capacity for 900 μL. The flow rate of the oxygen 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 ºC 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 FT-IR spectra were analyzed with the help of software OMNIC 7.0.2D-IR correlation spectroscopy was performed by means of the software 2Dshige (Morita, 2005).

3. Results and discussion

The potential of the use multi-rate thermogravimetric analyses, coupled to FT-IR, to approach the behavior of PLA and its subsequent recyclates under a thermo-oxidative decomposition process is discussed in detail in this section. The assessment comprises (i) the description of the decomposition profiles; (ii) the use of a novel model to functionalize the thermal stability at different heating rates; (iii) the application of a thorough kinetic strategy pursued for ascertaining the kinetics of decomposition accounting for variable activation parameters; and (iv) the detection of gases evolved during the decomposition.

3.1. Description of the thermo-oxidative decomposition profiles

Fig 1a shows the thermogravimetric curve at the heating rate $\beta = 5$ ºC·min^{-1} of virgin and fifth reprocessed PLAs. The rest of reprocessed materials showed intermediate profiles. As expected, higher β led to shift the thermograms towards higher temperatures, but the graphs have not been shown for the sake of clarity.The thermo-oxidative decomposition took place through a two-stage profile. The first mass-loss took place from 250 ºC to 370 ºC, consuming nearly 96-98 % of the material, which can be addressed to the decomposition of the backbone. Immediately afterwards, the second step appeared from 370 ºC to 400 ºC, eliminating 4-2 % of the polymer, without

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presence of char, as can be seen in the inset of **Fig 1a**. As expected, lower temperatures than those used in inert conditions (Badia et al, 2012c) were necessary under an oxidizing environment. For further calculations, the second step under O_2 was considered negligible if compared with the main decomposition and therefore the study was focused on the first mass-loss region.

A complete description of the thermo-oxidative decomposition of PLA recyclates is given in terms of thermal stability, decomposition kinetics, and detection of evolved gases, as a first approach to be used in combustion facilities.
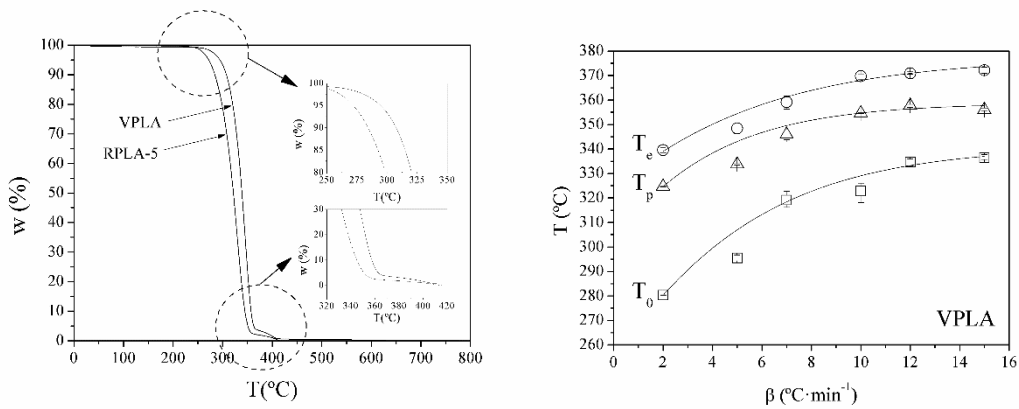

Figure 1. (a) Mass-loss profiles of virgin PLA and PLA reprocessed five times. Inset: detail of onset and endset of decomposition. (b) Application of the TDB model to fit the evolution of the characteristic thermogravimetric temperatures (0: onset, p: peak, e: endset), for the case of virgin PLA.

3.2. On the use of the TDB model to describe the thermal stability of PLA under any linear heating rate

With the aim of assessing the thermal stabilityof PLA and its further recyclates, the corresponding decomposition onset T_0 and endset T_e temperatures were obtained by a tangential intercept method onto the thermogravimetric curves for the whole process.

Likewise, the temperature at the maximum decomposition rate, i.e. the peak temperature T_p of the differential thermogravimetric curve was also considered for all applied heating rates β. To help enhance the analysis of the influence of the β on the characteristic decomposition temperatures and functionalize the thermal stability of PLA under combustion processes, the so-called Thermal Decomposition Behavior *TDB* model given in Eq. (1) was proposed. An example of its validity [1] is shown in **Fig. 1b** for the case of VPLA.

$$TDB(\beta) = a \cdot \left(1 + b \cdot e^{-k \cdot \beta}\right)^{-1} \text{ (1)}$$

In order to evaluate the differences in thermal stability under combustion conditions due to reprocessing, instead of choosing the experimental temperatures obtained at a specific β, the so-called onset Zero-Decomposition Temperature ZDT_0 was used, since this parameter is related to the trigger of the decomposition, and was obtained by extrapolating the *TDB* fitting of T_0 to infinitely low β (Badia et al, 2012c). **Table 1** shows the results of the proposed procedure. A sharp increase in ZDT_0 of ~ 30 ºC was registered from virgin PLA up to the second recyclate, dropping ~ 50 ºC when passed the third recyclate. A previous study by means of Differential Scanning Calorimetry (Badia et al, 2012b) showed that the influence of reprocessing on PLA structure formed shorter chains up to the third recyclate. Thus the apparition of new sites liable to O_2 in the PLA structure may promote faster decomposition at lower temperatures at high reprocessing cycles, which may need lower temperatures to start their decompositions.

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[1]See results of fitting in the supplementary material

Table 1 Results of fitting T0=f(β) to Eq. (1), along with the onset Zero-Decomposition Temperature obtained by extrapolating Eq (1) to β→0.

			TDB fitting values for T_0					
		a		b		k		
Material		value	e	value	e	value	e	R^2	$ZDT_0(^oC)$
VPLA		340,9	1,45 %	0,34	0,53 %	0,22	2,76 %	0,997	254.4
RPLA-1		345,4	0,63 %	0,35	0,34 %	0,19	0,10 %	0,993	255.8
RPLA-2	T_0	362,5	2,89 %	0,26	0,35 %	0,09	3,17 %	0,998	287.7
RPLA-3		337,3	0,08 %	0,45	1,02 %	0,49	0,99 %	0,998	232.6
RPLA-4		340,1	0,92 %	0,36	1,38 %	0,31	2,36 %	0,929	250.1
RPLA-5		339,2	1,12 %	0,40	2,03 %	0,26	2,07 %	0,965	242.3

3.3. Studies on the kinetics of thermo-oxidative decomposition

The intrinsic kinetics of solid-state decompositions, are usually described by a simplified reaction pathway in terms of three parameters: apparent activation energy *Ea*, pre-exponential factor *A* and kinetic function *f (α)* with reaction order *n*, conforming the so-called kinetic triplet. In this section, the results of the application of a detailed strategy are shown, according to the following steps: (i)the application of isoconversional methods to assess the evolution of the apparent activation energy, along with the proposal of a novel model to mathematically describe this evolution; (ii) the evaluation of the kinetic model, in terms of variable apparent activation energy and reaction order; (iii) the assessment of the variation of the pre-exponential factor, in order

to complete the kinetic triplet. As a result, instead of a kinetic triplet comprised by three constant parameters, this methodology provides the variation of the kinetic triplet along the decomposition process. Finally, the differences between the decomposition of virgin PLA and its recyclates are discussed.

3.3.1. Evolution of the apparent activation energy

A significant variation in activation energy (Ea_α) along the conversion range α ($\alpha = (m_0-m_t)/(m_0-m_\infty)$), where m was the mass and subscripts 0, t and ∞ stand for initial, actual and final, respectively), was found, as shown in **Figure 2**. This variation was detected by the application of three suitable integral isoconversional methods, namely linear Flynn-Wall-Ozawa (*FWO*) (Flynn and Wall, 1966) (Ozawa, 1970), linear Kissinger-Akahira-Sunose (*KAS*) (Kissinger, 1957) (Akahira and Sunose, 1971), and non-linear Advanced Isoconversional Method (*AIC*) (Vyazovkin, 1997). As can be seen in **Fig 2a**, the three methods offered similar Ea_α values for the assessment of virgin PLA, showing a good coincidence along the decomposition reaction, as also obtained for the rest of reprocessed materials. **Fig2b** and **2c** show the evolution of the Ea_α averaged from the application of the three isoconversional methods at each α, while **Table 2** gathers the averaged Ea values obtained by each method averaged along the whole α range. The Ea_α behaved increasing from values ~ 40 -60 kJ·mol^{-1} at low conversions α to values ~ 150 -170 kJ·mol^{-1} at the end of the decomposition. It should be pointed out that the large obtained deviation values (ϵ 18-40 %) did not permit to apply a simplified kinetic triplet (Badia et al, 2012c) that is, with constant activation parameters, and therefore the variation of Ea, A and n in $f(\alpha)$ was considered.
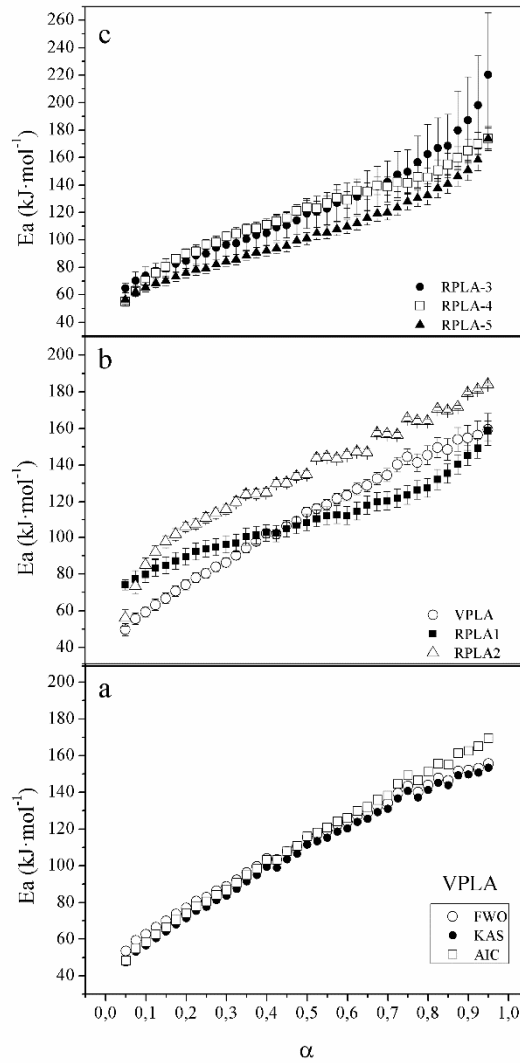
Figure 2.(a) Apparent Ea obtained for VPLA by means of FWO, KAS and AIC methods; (b) Average isoconversional activation energy of VPLA, RPLA-1 and RPLA-2; (c) Evolution of average isoconversional activation energy for RPLA-3, RPLA-4 and RPLA-5.

Table 2.Average activation energy along the thermo-oxidative decomposition process, as obtained by different isoconversional methods.

	Activation energy averaged from the α range					
	FWO		KAS		AIC	
Material	Ea (kJ·mol^{-1})	ε (%)	Ea (kJ·mol^{-1})	ε (%)	Ea (kJ·mol^{-1})	ε (%)
VPLA	101	30.7	96	31.2	112	25.0
RPLA-1	106	19.8	102	21.5	97	23.7
RPLA-2	127	30.6	123	33.3	120	31.0
RPLA-3	114	29.8	116	28.4	103	27.3
RPLA-4	121	21.8	119	19.6	114	18.5
RPLA-5	97	27.8	92	30.4	89	39.3

The physical meaning underlying the evolution of the apparent activation energy has been a matter of profuse debate (Galwey, 2003) (Vyazovkin, 2003). It seems reliable to understand that the increase of Ea_α is consistent with the decomposition of the residual material which is becoming more refractory as temperature increases (Vyazovkin et al, 2011). In any case, the mathematical characterization of its evolution may help control its kinetics. In order to define the evolution of Ea_α throughout the thermo-oxidative decomposition process, a powered equation was chosen, based on the *Freundlich* model (Freundlich, 1928) for growing behaviors, according to Eq. (2):

$$Ea(\alpha) = Ea_o^* + \sum_i b_i \cdot \alpha^{p_i} \quad (2)$$

,where *i* was the number of slopes in the curve, Ea^*_0 a fictive activation energy at $\alpha = 0$, *b* a fitting parameter and *p* a power that accounted for the shape of the curve; whether

$p< 1$, the increase is decelerative, and if $p> 1$, the increase is accelerative. **Table 3** shows the powers resulted from the fitting of Eq. (2) to the Ea_α evolution of all materials. Generally, two slopes could be considered, as described by Ea_α in Figs 2b and 2c, and thus i=1,2 in Eq. (2). As can be seen, virgin PLA only showed a decelerative curve, while the recyclates started with a decelerative trend and presented a change in tendency at advanced conversions, rapidly increasing its Ea_α in an accelerative fashion. Accordingly, it can be also observed how the smaller p_1 the faster initial increases and vice versa, as clearly happened from VPLA to RPLA-2; on the other hand, the smaller p_2 the brusquer changes in tendency to faster Ea_α increases along the reaction, as shown for RPLA-3 to 5. The functionalizing of Ea_α will be useful for further analysis in which the variation of the activation energy is considered.

Table 3. Results of fitting of Ea and lnA to Eq. (2)

| | ACTIVATION ENERGY / Ea | | | | | PRE-EXPONENTIAL FACTOR / lnA | | | | |
| | P1 | | P2 | | R^2 (%) | P1 | | P2 | | R^2 (%) |
Material	value	ε (%)	value	ε (%)		value	ε (%)	value	ε (%)	
VPLA	0.791	2.61	---	---	99.82	0.746	2.82	---	---	99.64
RPLA-1	0.591	6.39	9.352	7.81	99.85	0.672	7.99	9.467	8.30	99.80
RPLA-2	0.413	2.46	11.783	2.89	99.06	0.399	7.22	10.63	4.11	99.64
RPLA-3	0.746	6.55	5.737	8.40	99.82	0.712	7.86	5.732	8.51	99.79
RPLA-4	0.357	8.40	8.294	3.96	99.81	0.342	7.08	10.47	4.23	99.68
RPLA-5	0.807	6.93	7.545	6.10	99.79	0.775	7.65	7.377	6.52	99.69

3.3.2. How to obtain the kinetic model with varying Ea?

The next step in order to complete the kinetic triplet was to achieve the mathematical model of the decomposition that should best describe the combustion process along the valorization process. Thus, the kinetic function $f(\alpha)$ was approachedby the use of reduced differential Master-Plots MPf_e (Gotor et al, 2000). Eq. (3) was thus used for determining which family of theoretical curves MPf_t, namely, nucleation and growth (A_n), n-order reaction (F_n), reaction-controlled (R_n) and diffusion-controlled (D_n) -see description elsewhere (Khawan and Flanagan, 2006)- was more suitable to describe the experimental behavior of virgin and reprocessed PLAs facing combustion.

$$\Phi(f,\alpha) = \sum_{\beta}(\sum_{\alpha=0}^{1}[MPf_t(\alpha) - MPf_e(\alpha)]^2); \Delta\alpha = 0.025; \forall f \quad (3)$$

The minimization of Φ in Eq. (3) was achieved by the model A_n, with n ranging from 2 to 4 depending on the heating rate β of the analysis, as shown in **Table 4**. **Fig 3** shows the abacus of the theoretical differential master plots in comparison with those experimental for VPLA and RPLA-1, as an example of the accuracy of this methodology to predict the model of decomposition.

(3)

Table 4.nβ :Values of n of the Anmodel found for the thermo-oxidative decomposition of PLA and its recyclates at different β; n' : average of nβ ; n'' : values obtained from the minimization method, using Eq (4).

	nβ						n'	n''	
	β (°C·min⁻¹)								
Material	2	5	7	10	12	15		average	℮ (%)
VPLA	2.0	2.5	2.5	2.5	3.0	3.0	2.58	2.65	6.2
RPLA-1	2.0	2.0	2.5	2.5	3.0	3.0	2.50	2.41	6.9
RPLA-2	2.0	2.0	2.5	2.5	2.5	3.0	2.41	2.26	6.5
RPLA-3	2.0	2.5	2.5	2.5	3.0	4.0	2.76	2.76	5.3
RPLA-4	3.0	3.0	3.0	4.0	3.5	4.0	3.40	3.49	6.8
RPLA-5	2.5	2.5	3.0	4.0	4.0	4.0	3.33	3.38	6.4
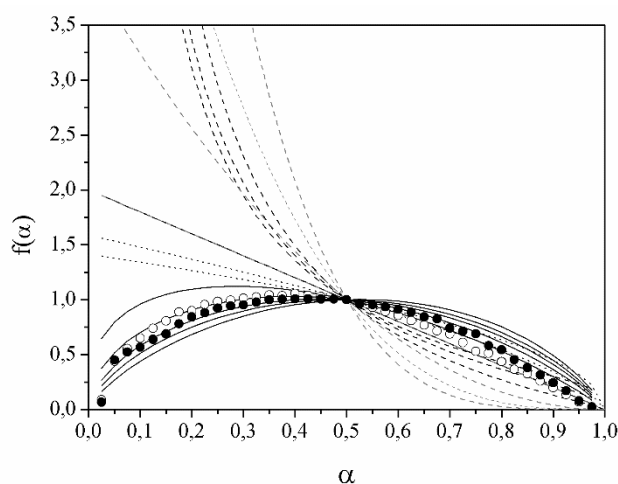
Figure 3.Master plots based on the differential form of the general kinetic law compared to experimental data obtained for thermo-oxidative decomposition of VPLA (hollow circles) and RPLA-1 (full circle). Kinetic models: An (nucleation and growth, solid black lines), Fn (n-order reactions, solid grey lines), Rn (reaction-controlled, pointed lines), Dn (diffusion-controlled, dashed lines)

The next step consisted in determining the value of n for each conversion degree α, which was achieved by the minimization of ξ in Eq. (4), being i the counter of the h experiments carried out at different heating rates β . This equation compared the Ea_α obtained by the isoconversional methods to the Ea given by the Coats-Redfern (Coats and Redfern, 1964) method in Eq. (5), using the mathematical expression of the kinetic model A_n, and took into account the *Perez-Maqueda et al* criterion (Pérez-Maqueda et al, 2002); that is, the independence of the activation parameters on β.Since the analysis was performed at particular α values, considering all results obtained at all β, the analysis could be considered also isoconversional.

$$\xi(n,\alpha) = \sum_i^h \left| (-R) \cdot \frac{d}{dT}\left(\frac{ln\left(\beta_i \cdot T^{-2}(-\ln(1-\alpha))^{\frac{1}{n}} \right)}{T^{-1}} \right) - Ea_\alpha \right| \quad (4)$$

Fig 4 shows the evolution of n along the α range, which could be assumed to be almost constant within a confidence margin lower than 7%, as shown by n'' in **Table 3**.Therefore, the suitability of the model A_n was strengthened. In addition, the possibility of using n' (average of n_β, those are, the n individually obtained for each material at each heating rate β) was remarked, since closer values to those given by the analytical procedure (n'') were obtained, thus permitting to continue the calculations with less time-consuming computations.
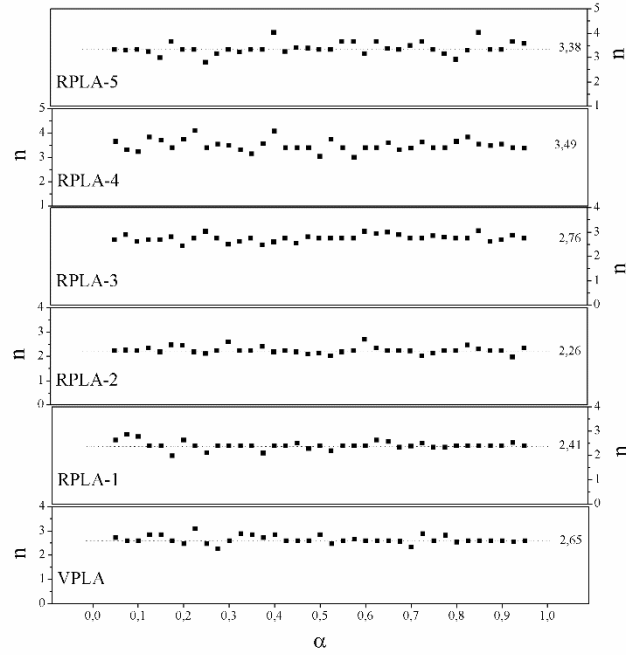
Figure 4. Evolution of n in the A_n model of thermo-oxidative decomposition of virgin PLA and its successive recyclates. The number is the average of data (n'' in Table 3)

3.3.3 Closing the kinetic triplet: pre-exponential factor

Finally, the evolution of the pre-exponential factor along the α decomposition range (lnA_α) was also isoconversionally obtained from the intercept at the origin in Eq. (5), considering the data at all heating rates β.

$$\left[ln\frac{\beta\cdot(-\ln(1-\alpha))^{\frac{1}{n}}\big|\alpha}{T^2} \right]_y = ln\frac{A_\alpha\cdot R}{Ea_\alpha} + \frac{Ea_\alpha}{R}\cdot\left[\frac{1}{T}\right]_x \quad (5)$$

Fig5a shows the evolution of lnA_α for VPLA and RPLA-2 as example. The rest are not presented to prevent overlapping curves. It can be seen how lnA_α was strongly connected to the behavior of Ea_α, since both presented similar profiles along the α range. Therefore, one may suggest that the application of Eq. (2) might also be suitable for fitting the experimental data and thus provide a mathematical description of lnA_α evolution. The accuracy of the fitting can be seen at **Fig 5a** and assessed at **Table 2**. The powers p_1 and p_2 were of the same order than those obtained for Ea_α, thus permitting the

use of the powers previously obtained for Ea_α as initialization values in the iteration process of the fitting of lnA_α.
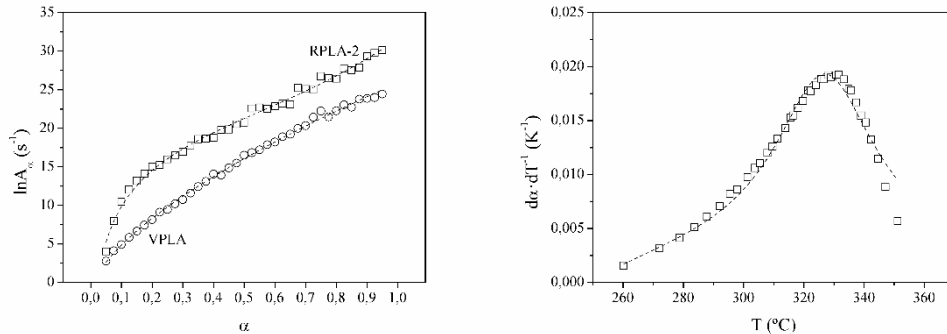

Figure 5. (a)lnA evolution given for VPLA and RPLA-2 as an example of the goodness of fitting of Eq. (2) to explain its behavior along the α range. Hollow symbols: obtained lnAα values; dashed lines: computed fittings.(b) Comparison of experimental DTG curves (symbols) to computed kinetic functions (dashed lines) obtained from the kinetic methodology.

Finally, the kinetic triplet was completed and the mathematical description of the combustion process of PLA and its recyclates was resolved. **Fig 5b** shows for virgin PLA the comparison between the experimental points of the differential thermogravimetric curve in terms of conversion degree, and the mathematical description obtained by the kinetic analysis for variable activation parameters. Similar results were found for the rest of recyclates. The proposed methodology thus stands out as a suitable and effective tool to model the kinetic behavior of virgin and reprocessed PLA under thermally-induced energetic valorizations.

3.3.4. Effects of reprocessing on the decomposition kinetics of PLA.

Results concluded that virgin PLA and its recyclates followed an A_n kinetic model (growth of previously formed nuclei) during their combustion. This kind of kinetic

model is scarcely reported in studies dealingwith thermal decomposition processes of polymers -see discussion elsewhere (Badia et al, 2010)-. However, the model A_n indicates the presence of active zones more chemically liable to thermo-oxidative decomposition, which activate the formation and growth of gas bubbles in the polymer melt.

With regards to the evolution of the apparent activation energy,, as expected, the Ea_α needed to trigger the decomposition under oxidative conditions was lower than under inert conditions, i.e. pyrolysis(Badia et al, 2012c), since the reactions were enhanced by oxidation processes which led to the formation of radical species such as carboxylic-ended species that accelerated the decomposition (Bikiaris and Karayannidis, 1999) (Liu et al, 2006). Concerning the differences in Ea_α among virgin material and recyclates facing the thermo-oxidative decomposition, it was assessed in terms of the apparent activation energy at the initial stages of combustion. For instance, selecting the Ea_α at a conversion rate of 0.2 (that is, $Ea_{0.2}$), a similar profile than that shown by the onset Zero-decomposition Temperature ZDT_0 at the studies of thermal stability was found. An increase up to the second recyclate was registered, which was not followed by the successive reprocessed materials, which kept their $Ea_{0.2}$ at lower values. Thus the apparition of reaction sites liable to O_2 in the PLA structure promoted the decomposition with less demanded energy from the third reprocessing cycle on, also pointing out the feasibility of combustion to valorize highly reprocessed polylactide.

3.4. Evolved Gases Analysis by in-line FT/IR

Finally, to exploit the potential of TGA to simulate the thermo-oxidative decomposition of PLA under combustion conditions, the emission of gases was monitored by in-line FT-IR analysis. Main detected evolved species were: carbon

dioxide [2349 cm^{-1} υ_{as}(O=C=O)]; carbon monoxide [2174/2116 cm^{-1} υ(C≡O)]; acetaldehyde [2968 cm^{-1} υ(CH$_3$), 2740 cm^{-1} υ(CHO), 1762 cm^{-1} υ(C=O), 1414/1371 cm^{-1} δ(CH$_3$) and 1127 cm^{-1} υ(C-O)]; acetic acid [3586 cm^{-1} υ(H-O), 1778 cm^{-1} υ(C=O)] which may be formed by oxidation of acetaldehyde; short-chain acids and their dimers and trimers [3589 cm^{-1} υ(OH), 2952 cm^{-1} υ(CH$_2$), 2816 cm^{-1} υ(CH), 1778 cm^{-1} υ(C=O), and 1164/1107 cm^{-1} υ(C-O)] (Vogel and Siesler, 2008); and traces of lactide [3008 cm^{-1} υ(CH), 2952 cm^{-1} υ_{as}(CH$_3$), 2893 cm^{-1} υ_s(CH$_3$), 1796 cm^{-1} υ(C=O), 1365 cm^{-1} δ(CH$_3$), 1248/1108 cm^{-1} υ(C-O-C) and 932 cm^{-1} corresponding to the ring skeletal vibration] and water [3900-3400 cm^{-1} υ(H-O), 1800-1300 cm^{-1} δ(H-O)]. The gases were similar to those obtained during the pyrolysis (Badia et al, 2012c). As main differences, carbon mono- and di- oxides evolved with bigger intensity, due to the combustion processes were enhanced; the bands of acetaldehyde decreased, and those related to acetic acid slightly increased, due to the oxidation effect of O$_2$; as well, lactide still appeared, but its bands were overlapped along with those corresponding to short-chain acids and their dimers and trimers and thus a finer identification was complicated. The application of 2D-correlation spectra (Noda, 1990) gave an asynchronous spectrum where positive cross-peaks at (2378, 1796) and (2316, 1796) and a negative cross-peak at (2116, 1796), which exposed that CO$_2$ was evolved before the main decomposition products with υ(C=O) vibrations, while CO was released afterwards.

After mechanical reprocessing, the chemical nature of polylactide was essentially the same (Badia et al, 2011b), though shorter chains can be obtained (Badia et al, 2012b), and thus no differences were found at the IR spectra of the evolved gases of reprocessed PLAs. The necessary facilities for detecting the emission of evolved gases from the combustion of reprocessed PLAs could thus be the same than those

needed for virgin PLA, which may reduce costs of investing and implementation in new technologies.

5. Conclusions

Multi-rate linear-non-isothermal thermogravimetric (TGA) experiments under oxidative (O_2) conditions, coupled to FT-IR analysis for gas detection, were suitable to simulate the thermal behavior of virgin and multiple-injected PLA facingcombustion.A kinetic methodology was applied accounting for the evolution of the activation parameters along the decomposition. A powered equation was used to explain the variations of activation energy and pre-exponential factor along the decomposition process.A nucleation and growth model which gave importance to the formation of gas bubbles in the polymer melt was valid for all materials. Reprocessed PLA did not modify the profile of evolved gases.

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