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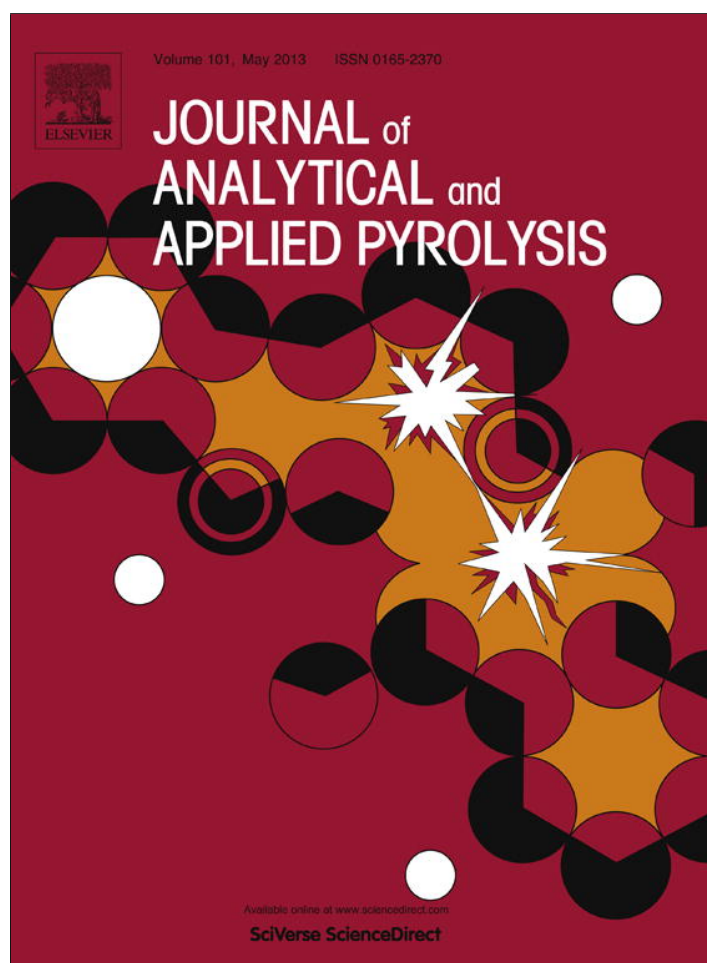


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Development of a novel pyrolysis-gas chromatography/mass spectrometry method for the analysis of poly(lactic acid) thermal degradation products

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ABSTRACT

Thermal degradation of PLA is a complex process since it comprises many simultaneous reactions. The use of analytical techniques, such as differential scanning calorimetry (DSC) and thermogravimetry (TGA), yields useful information but a more sensitive analytical technique would be necessary to identify and quantify the PLA degradation products. In this work the thermal degradation of PLA at high temperatures was studied by using a pyrolyzer coupled to a gas chromatograph with mass spectrometry detection (Py-GC/MS). Pyrolysis conditions (temperature and time) were optimized in order to obtain an adequate chromatographic separation of the compounds formed during heating. The best resolution of chromatographic peaks was obtained by pyrolyzing the material from room temperature to 600 °C during 0.5 s. These conditions allowed identifying and quantifying the major compounds produced during the PLA thermal degradation in inert atmosphere. The strategy followed to select these operation parameters was by using sequential pyrolysis based on the adaptation of mathematical models. By application of this strategy it was demonstrated that PLA is degraded at high temperatures by following a non-linear behaviour. The application of logistic and Boltzmann models leads to good fittings to the experimental results, despite the Boltzmann model provided the best approach to calculate the time at which 50% of PLA was degraded. In conclusion, the Boltzmann method can be applied as a tool for simulating the PLA thermal degradation.

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1. Introduction

Biopolymers are becoming more and more interesting for many industrial sectors, such as packaging, automotive and many others since they are obtained from renewable resources and they are intrinsically biodegradable. Several biopolymers have been investigated as alternatives to non-degradable commodities to produce materials with similar properties to those of the common polymers [1].

Among all commercial biopolymers, poly(lactic acid) (PLA) is one of the most attractive and mainly used in many applications, being biocompatible and biodegradable [2]. Currently, PLA is used in food packaging industry for short shelf life products [3,4]. Although the inherent biodegradable and compostable characteristics of PLA, the high growth on its production in the last years and application in the packaging market represents an upcoming new main source of polymer waste and new strategies for PLA

waste management should be proposed [5]. Therefore, the fact that biodegradable polymers, and particularly PLA, should be considered as waste suggests that pyrolysis may offer an alternative option for waste treatment of biomass and biopolymers [6]. In this sense, PLA has a high potential energy content making it suitable for thermal processes with energy recovery. It has been reported that PLA waste is suitable to be used in pyrolysis facilities due to the high conversion efficiency of the polymer [7]. Therefore, pyrolysis of PLA may offer an alternative to this polymer waste management, while being economically and environmentally attractive [2]. The application of thermo-chemical operations to PLA must be carefully tackled, taking into account healthy and environmental issues and guaranteeing the right management of emitted gases [7]. Although some research work has been published on the PLA pyrolysis [8], only semi-quantitative results of the PLA degradation products were reported [8–10].

The study of polymers thermal degradation is especially important because it is relevant for their processing, characterization, potential applications and thermal recycling [9] as well as to guarantee their complete life cycle. The obtained products during thermal degradation depend on the selected conditions. Furthermore, degradation mechanisms of a particular polymer are dependent on its structure and they can follow different paths

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by the complexity of the polymeric chains and their breaking under heat [11]. In this sense, PLA thermal stability is often evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). However these techniques lack on the identification of the thermal degradation products and pyrolysis coupled to gas chromatography/mass spectrometry (Py-GC/MS) is an alternative to identify these products in polymers and biodegradable polymers [12,13]. To the best of our knowledge, no methodologies for the quantification of PLA thermal degradation products by using Py-GC/MS have been already reported.

The main objective of this work was to develop a Py-GC/MS method for the simultaneous identification and quantification of PLA thermal degradation products by optimization Py-GC/MS experimental parameters: pyrolysis time and temperature. This methodology was successfully applied to PLA film samples by using sequential pyrolysis.

2. Materials and methods

2.1. Materials

Poly(lactic acid) (PLA 2002D, $M_n = 98,000$ Da, 4 wt% D-isomer) was supplied by NatureWorks (USA). Chloroform (99.8% purity) was obtained from Sigma Aldrich (Móstoles, Spain).

2.2. Films preparation

PLA was processed into films by compression moulding following the methodology developed by Martino et al. [14]. Since PLA is highly hygroscopic [15], pellets were previously dried in a vacuum oven (60 °C for 6 h) and then moulded at 170 °C in a hot press (Mini C 3850, Caver, Inc. USA) at atmospheric pressure for 5 min until melting and then it was submitted to the following pressure cycles, 3 MPa for 1 min, 5 MPa for 1 min, and 10 MPa for 3 min, with the aim to eliminate the trapped air bubbles [16]. Film samples were then quenched at room temperature at atmospheric pressure.

2.3. Samples and standards preparation

1.0 g of PLA in pellets (for standards) or PLA films previously prepared as described (for sample solutions) were dissolved in 30 mL of chloroform. 10 μ L of each solution were then put in the pyrolysis tube to get a complete solvent evaporation. Samples were prepared at the lowest quantity used for standard solutions (0.34 μ g).

2.4. Py-GC/MS analyses

Samples were pyrolyzed with the use of a Pyroprobe 1000 instrument (CDS Analytical, Oxford, PA, USA), which was coupled to a gas chromatograph (6890N, Agilent Technologies, Madrid, Spain) equipped with a 5973N mass selective detector (Agilent Technologies). The column used for the analysis was 30 m long HP-5 (0.25 mm thickness) using helium as carrier gas with a 50:1 split ratio. The GC oven was programmed at 40 °C for 2 min, followed by a stepped increase of 5 °C min⁻¹–200 °C, where it was held for 15 min, and then the temperature was increased by 20 °C min⁻¹–300 °C, where it was held for 5 min. The mass selective detector was programmed to detect masses between 30 and 650 amu. PLA samples were pyrolyzed at 600 °C for 0.5 s. Samples were repeatedly subjected to sequential pyrolysis under the same conditions up to 36 cycles were completed. The identification of PLA degraded products was confirmed by the characteristic fragmentation patterns observed in Py-GC/MS spectra or by comparison with literature mass spectra.

2.5. Validation

Linear relationships between the instrumental response and product concentrations were established by using least-squares regression (peak area vs. concentration, ranging from 0.34 to 1.36 μ g). Intra-day repeatability of peak-areas expressed as relative standard deviations (RSD) were calculated. The method reproducibility was evaluated by the variation coefficients of five measurements of the same standard at different days (inter-day precision). The sensitivity and limit of detection (LOD) were estimated as three times the standard deviation provided by the relationship between the signal-to-noise ratio and the slope of the corresponding calibration curve, determined as the curve sensitivity [17].

2.6. Data statistical analysis and fitted models

The relationship between the cumulative mass of each degraded PLA and the pyrolysis time was fitted to two non-linear regression models based on the empirical use of the Logistic and Boltzmann equations in OriginPro 8.0 software. Firstly data were adjusted to a sigmoidal fit using a logistic type equation (Eq. (1)):

$$m = \frac{(m_i - m_\infty)}{1 + (t/t_0)^p} + m_\infty \quad (1)$$

where m_i and m_∞ are the initial and final mass values at the initial and final asymptotes, p is the Hill slope coefficient [18], and t_0 is the time at which cumulative mass reaches the average value between m_i and m_∞ , known as the half-maximal degradation.

Secondly, the Boltzmann equation (Eq. (2)) was fitted to the data.

$$m = \frac{(m_i - m_\infty)}{1 + e^{-(t - t_0)/d_t}} + m_\infty \quad (2)$$

where d_t is a parameter that describes the shape of the curve between the upper and lower asymptotes [19].

3. Results and discussion

3.1. Optimization of pyrolysis conditions

The selection of experimental parameters is a critical issue for an accurate analysis of pyrolytic products. These parameters, in particular pyrolysis temperatures and times, are the key factors to achieve a good separation and further identification of compounds from degraded materials. Several pyrolysis conditions for PLA were proposed in previous works. Westphal et al. proposed pyrolysis of PLA for 2 s at 400 and 500 °C [20]. Kopinke and Mackenzie [21] proposed the study of PLA pyrolysis for 10 s at temperatures between 400 and 600 °C. Aoyagi et al. [9] also used 10 s but lower temperatures, i.e. 280 °C. In the present work different times and temperatures were evaluated. The starting pyrolysis time was 2 s and pyrolysis temperature was firstly selected at 400 °C, with further increases to 500 °C and 600 °C. Under these conditions, the high number of compounds involved in the PLA pyrolysis gave highly complex chromatograms. As expected, a higher number of reaction products was obtained when the pyrolysis temperature increased, resulting in poor separation of the degradation compounds. In order to improve the chromatographic resolution between the pyrolyzates, the influence of pyrolysis time was also evaluated maintaining the pyrolysis temperature at 600 °C. It is known that the use of short pyrolysis times can improve the chromatographic separation of the pyrolyzates. Therefore, a reduction in pyrolysis time was considered 1.5, 1 and 0.5 s were used in tests. The best resolution was reached when the selected time was 0.5 s since good chromatographic separation between peaks was achieved (Fig. 1). Under these conditions, seven

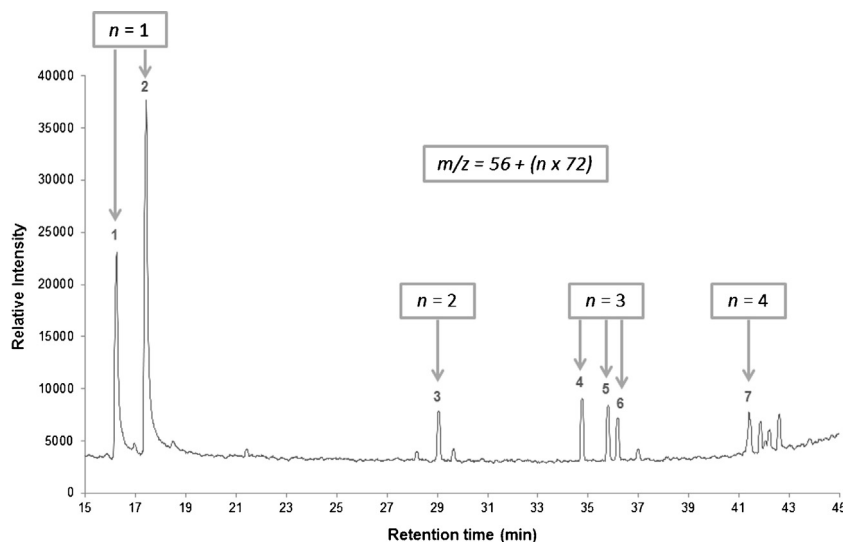


Fig. 1. Py-GC/MS chromatogram of PLA pyrolyzates for 0.5 s at 600 °C.

PLA pyrolyzated products were detected and identified by getting the mass spectra of each main chromatographic peak (Table 1). It was observed that the thermal degradation of PLA under these conditions showed a dominant series of signals with $m/z = 56 + (n \times 72)$ in which n assumed values of 1, 2, 3 and 4. Fig. 1 shows the presence of two peaks (1 and 2) with very similar mass spectra (Fig. 2), where their main fragments were those with $m/z = 32, 43, 45$ and 56. These two peaks were assigned to mesolactide and lactide, respectively [8,21,22]. The groups of peaks appearing periodically at retention times higher than 20 min were assigned to higher cyclic lactide oligomers [8,10,22]. Three trimer peaks were observed with very similar spectra. This is due to the fact that lactide oligomers are diastereomers derived from the asymmetric C atom [8,21] in the lactic acid monomer, suggesting that the dominant reactions during pyrolysis of PLA followed an intramolecular *trans* esterification [10,20].

3.2. Validation of the analytical method

The validation of this method was carried out by evaluating the main analytical parameters, in particular limit of detection (LOD), limit of quantification (LOQ), linearity, and repeatability for each compound (Table 2). Linear calibration curves for all these reaction products were evaluated at 6 calibration points in the range 0.34 μg –1.36 μg , using triplicates at each standard. Linear relationships between instrumental responses for each compound, in terms of PLA amount, were verified by the analysis of the variance of the regression curve. The linear correlation between each compound (axis x) and chromatographic peak areas (axis y) was given by the regression equation, $y = ax + b$ permitting the calculation of correlation coefficients (r^2). It could be observed in Table 2 that

Table 1
List of products formed during Py-GC-MS at 600 °C for 0.5 s.

Peak number	Retention time (min)	Compound	Ion EI (m/z) ^a
1	16.2	Mesolactide	32, 43, 45, 56
2	17.4	Lactide	32, 43, 45, 56
3	29.5	Dimer: $56 + (2 \times 72)$	32, 56, 100, 128 , 200
4	34.6	Trimer: $56 + (3 \times 72)$ ^a	32, 56, 100, 128, 200 , 272
5	35.6	Trimer: $56 + (3 \times 72)$ ^b	32, 56, 100, 128, 200 , 272
6	36.7	Trimer: $56 + (3 \times 72)$ ^c	32, 56, 100, 128, 200 , 272
7	42.4	Tetramer: $56 + (4 \times 72)$	32, 56, 100, 128, 200 , 272, 344

^a Main ion (base peak in bold) for electron ionization (EI).

nearly all compounds showed a linear correlation coefficient above 0.900 over the whole concentration range. This is a reasonably good result since it is a complex separation and no better results have been reported in literature. Only two exceptions were observed,

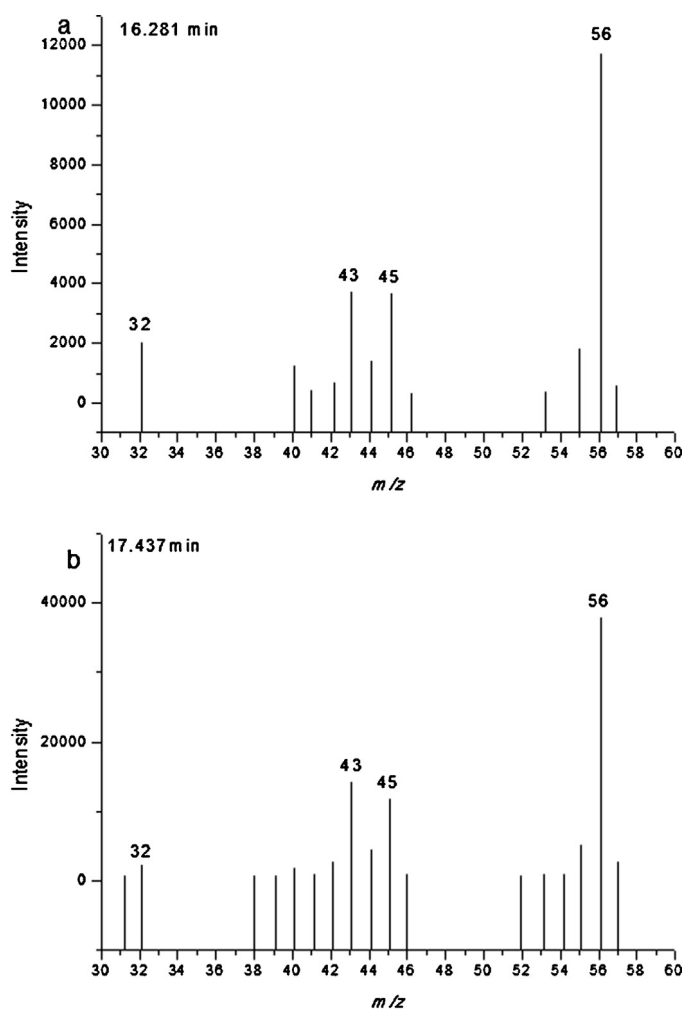


Fig. 2. Py-GC/MS spectra of peak 1 (a) and peak 2 (b).

Table 2

Validation parameters of the development analytical method.

Compound	r^2	LOD (μg) ^a	Repeatability RSD ($n=5$) ^b	Reproducibility RSD ($n=5$)
Mesolactide	0.921	0.15	4.18	3.89
Lactide	0.968	0.20	4.09	2.65
56+(2 × 72)	0.880	0.22	3.49	3.42
56+(3 × 72) ^a	0.841	0.27	2.83	4.23
56+(3 × 72) ^b	0.925	0.26	3.05	4.56
56+(3 × 72) ^c	0.947	0.10	3.56	4.32
56+(4 × 72)	0.985	0.23	4.68	4.48

^a Responses of each compound in terms of μg of PLA.^b Number of replicates.

for 56+(3 × 72)^a and 56+(2 × 72) oligomers that showed lower correlation coefficients (0.841 and 0.880 respectively).

Table 2 shows that the LOD of the developed method increased when the molar mass of PLA pyrolysis products decreased, and consequently the lowest detection limit when applying this analytical method was calculated for the lactide peak. The relationship between areas corresponding to mesolactide and lactide peaks was reported as a semi-quantitative indication of the pyrolysis mechanism of PLA [8,20]. In this work this mesolactide:lactide relationship was 1:7.7, remaining constant for all the calibration samples with a standard deviation 0.7, demonstrating the good reproducibility of the method. This parameter was also validated by the variation coefficients of five measurements of the same standard at different days (inter-day precision), while repeatability of the method was evaluated by the variation coefficient for the measurement of five identical samples during one working day

(intra-day precision). This parameter was evaluated and results are shown in Table 2 reflected by the relative standard deviation (%RSD). It was observed that all %RSD values were lower than 5%, indicating that the Py-GC/MS method proposed in this study can be carried out with a satisfactory level of precision for the determination of PLA pyrolysis products.

3.3. Application of the sequential pyrolysis to PLA films

This method was successfully applied to the quantification of PLA thermal degraded products in PLA films by using sequential pyrolysis, defined as the consecutive pyrolysis reactions applied to the same sample under identical experimental conditions, until no more products are detected [23]. In this procedure, sample sizes should be small enough to discard any diffusion effect. Thus, a first pyrolysis run was performed and the total product peaks were recorded. A second pyrolysis was then performed to the residue remaining from the first pyrolysis, and this sequence was repeated until no more products evolved [24]. Data obtained from sequential pyrolysis were further used to create a plot of cumulative areas as a function of time in a variety of polymers, such as polysulfones [23], poly(butyl acrylate) [25], polyamide-6 [26], poly(epichlorohydrin-co-ethylene oxide) [24], poly(methyl methacrylate) [25,27], and polystyrene [25,27], where the system is expected to show a first order behaviour with exponential growth. No studies on sequential pyrolysis of PLA have been previously reported.

The introduction of the m_∞ term in the equations used in this study ensures that the asymptotic value for the pyrolysis limit might be different from 100% [28]. But, in this work, samples

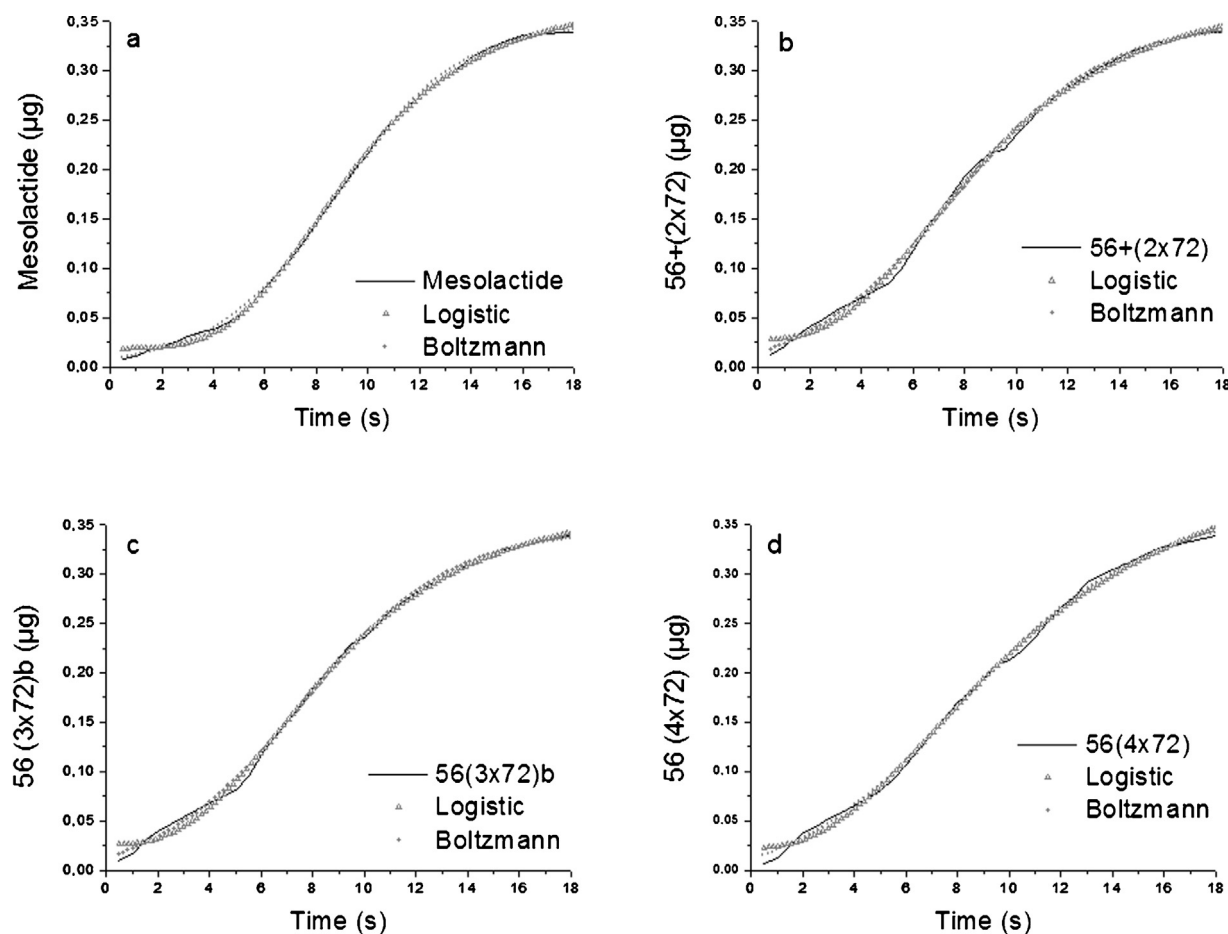


Fig. 3. Cumulative amount of PLA products (μg PLA) as a function of time, after consecutive pyrolysis for (a) mesolactide, (b) dimer, (c) trimer and (d) tetramer.

Table 3
Parameters estimated for PLA sequential pyrolysis by using the Logistic and Boltzmann models.

Compound	Parameter estimation		r^2			r^2
	Logistic (Eq. (1))			Boltzmann (Eq. (2))		
	m_{∞} (μg) ^a	t_0 (min)		m_{∞} (μg) ^a	t_0 (min)	
Mesolactide	0.378 ± 0.004	9.4 ± 0.1	0.999	0.348 ± 0.001	8.8 ± 0.1	0.999
Lactide	0.370 ± 0.006	8.2 ± 0.1	0.996	0.346 ± 0.002	7.5 ± 0.1	0.999
56 + (2 × 72)	0.391 ± 0.002	8.8 ± 0.2	0.997	0.346 ± 0.002	7.5 ± 0.1	0.998
56 + (3 × 72) <i>a</i>	0.412 ± 0.003	9.2 ± 0.3	0.997	0.355 ± 0.005	7.2 ± 0.2	0.998
56 + (3 × 72) <i>b</i>	0.386 ± 0.008	8.7 ± 0.2	0.998	0.346 ± 0.003	7.6 ± 0.1	0.998
56 + (3 × 72) <i>c</i>	0.385 ± 0.006	8.6 ± 0.1	0.998	0.348 ± 0.002	7.6 ± 0.1	0.999
56 + (4 × 72)	0.437 ± 0.002	10.4 ± 0.4	0.997	0.340 ± 0.005	8.2 ± 0.1	0.998

^a Responses of each compound in terms of μg of PLA.

were repeatedly subjected to sequential pyrolysis under the same pyrolysis conditions until no more products were detected. Consequently, the m_{∞} term could be attributed to the total amount of PLA degraded during pyrolysis. It was observed that PLA thermal degradation under the selected conditions did not show the expected exponential growth, as it was reported for other materials [23,26]. However, the thermal decomposition pattern of PLA showed a sigmoidal pyrolysis behaviour for all compounds. In this sense, Sanchez-Jimenez et al. reported a non-first order behaviour for another biodegradable polymer [29]. Sigmoidal curves were obtained during the study of the kinetics of cellulose pyrolysis by TGA. They showed that this sigmoidal model fits better to the experimental degradation curves for cellulose. They proposed a new kinetic model based on the assumption that random scission of the polymer chains occurs. A random scission mechanism implies the cleavage of the polymeric chains followed by the release of fragments once they become small enough to volatilize [30]. This explanation could be extended to PLA pyrolysis, since it should be expected that a random scission could lead to the formation of the lactide monomer as well as dimers, trimers and tetramers, as indicated in Table 1. Moreover, in the case of PLA, it has been reported that processed PLA showed lower thermal stability than unprocessed PLA due to a certain depolymerization reactions caused by PLA melting with the result of volatilization of the small molecules formed during melting [31].

A further analysis of these results makes necessary the use of empirical equations to permit the data treatment for each PLA thermal degradation product. Therefore, the cumulative mass of PLA degradation products was studied by using non-linear regression methods. The Logistic (Eq. (1)) and Boltzmann (Eq. (2)) methods were used to fit the cumulative experimental masses vs. the cumulative pyrolysis time for each product in order to correlate the observed sigmoidal behaviour (Fig. 3). The estimated regression parameters of the two non-linear models, m_{∞} and t_0 , were calculated from these curves and they are shown in Table 3. The correlation coefficients between theoretical and experimental data (r^2) were higher than 0.995 in all cases, indicating that only minor differences were observed between the two applied models in their fitting to experimental values. Therefore, the cumulative amount of these seven degradation products seems to be well described by both models. Logistic model provided slightly higher values of m_{∞} than Boltzmann for all PLA thermal degradation products. In the case of t_0 calculations, which represent the time at which 50% of each PLA product was degraded, results were significantly different when applying the Logistic (Eq. (1)) and the Boltzmann (Eq. (2)) approaches (see Table 3). We can conclude that although both models lead to good fitting to experimental results, the Boltzmann model provided the best approach to calculate the value for t_0 since the m_{∞} value proposed by Boltzmann model was closer to the initial mass (0.34 μg).

4. Conclusion

A Py-GC/MS method for the identification and quantification of PLA thermal degradation products has been developed and successfully applied to PLA films. The optimum pyrolysis conditions were set at 600 °C for 0.5 s and the analytical methodology was successfully validated. Seven different compounds produced during the PLA thermal degradation were identified and quantified in terms of PLA amount. It was observed that the pyrolyzed PLA gave a dominant series of signals with $m/z = 56 + (n \times 72)$. This work demonstrated that the use of short pyrolysis times and diluted film samples were key factors to achieve good chromatographic resolutions and to avoid diffusion effects, respectively. The validated methodology was applied to PLA films by using sequential pyrolysis to the same sample until no more products were detected. It was found that the thermal degradation of PLA revealed a sigmoidal behaviour and this could be an indication of the PLA complex degradation mechanism. The use of processed PLA in this study and the obtained results could lead to the conclusion that the hot-melt treatment to produce films could significantly change the polymer behaviour at high temperatures. However, further work should be carried out to assess such complex mechanism since it is known that a variety of experimental factors could be also responsible of such differences in PLA thermal degradation. The Logistic and Boltzmann models could describe well this behaviour since the complete sample was pyrolyzed before the end of the test. Therefore, sequential pyrolysis allowed assuming that the final mass (m_{∞}) should be equal to the initial amount. Although both models lead to good fittings to experimental results, it could be concluded that the Boltzmann model provided the best approach to calculate the value for t_0 at which 50% of each PLA compound was degraded. In conclusion, it could be expected that the Boltzmann model could be applied to PLA other formulations with different additives by using low amount of materials and short pyrolysis times.

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