



Thermal Degradation Kinetic of Polylactic Acid in Multiple Extrusions¹

Cinética de degradación térmica de políácido láctico en múltiples extrusiones²

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Abstract

Results of a thermal degradation kinetic study of polylactic acid (PLA), raw and reprocessed by extrusion are shown. The reprocessed samples were obtained after each one of five successive extrusions. The samples were tested for glass transition temperature, melt flow index, higher heating value, and dynamic thermogravimetry. Kinetic triplet was determined from the dynamic thermogravimetry data by Flynn-Wall-Ozawa (FWO), Friedman, Gyulai, Kissinger-Akahira-Sunose (KAS), Kissinger, Differential and Integral Arrhenius, Briodo, Chang, Coats-Redfern, Flynn Wall, Horowitz-Metzger, MacCallum-Tanner, Madhusudanan, and Dynamic methods. It was found that activation energy (E) increases with the reprocessing, and that frequency factor (A) increases with the heating rate. It indicates that PLA experiences thermal degradation when is processed by continuous extrusion. It was also found that the average kinetic triplet obtained by isoconversional methods is $E=147,14$ kJ/mol, $\ln(A)=26,94$ (with A in min^{-1}), and reaction order $n=0,86$, and the triplet averaged from non-isoconversional methods is $E=225,30$ kJ/mol, $\ln(A)=45,07$, and $n=0,91$.

Keywords

Thermal degradation; kinetic triplet; multiple extrusions; PLA

Resumen

Este artículo presenta los resultados del estudio cinético de la degradación térmica del políácido láctico (PLA, por sus iniciales en inglés), sin procesar y reprocesado por extrusión. Las muestras reprocesadas se obtuvieron después de cada uno de los cinco ciclos de extrusión y se analizaron para obtener la temperatura de transición vítrea, el índice de fluidez, el poder calorífico superior y la termogravimetría dinámica. Se determinó el triplete cinético usando los datos de termogravimetría dinámica por medio de los métodos Flynn-Wall-Ozawa (FWO), Friedman, Gyulai, Kissinger-Akahira-Sunose (KAS), Kissinger, Arrhenius Differential e Integral, Briodo, Chang, Coats-Redfern, Flynn-Wall, Horowitz-Metzger, MacCallum-Tanner, Madhusudanan y dinámico. Se encontró que la energía de activación (E) disminuye con el reprocesamiento y que el factor de frecuencia (A) aumenta con la velocidad de calentamiento. Esto indica que el PLA experimenta degradación térmica al ser sometido a procesos continuos de extrusión. También con métodos isoconversionales se obtuvo un triplete cinético promedio de $E=147,14$ kJ/mol, $\ln(A)=26,94$ (con A en min^{-1}), y orden de reacción $n=0,86$; el triplete promedio obtenido con métodos no isoconversionales es $E=225,30$ kJ/mol, $\ln(A)=45,07$, y $n=0,91$.

Palabras clave

Degradación térmica; triplete cinético; múltiples extrusiones; PLA

1. Introduction

Due to the need for recycling during the life cycle of materials reprocessing results very interesting in the production of plastic, it minimizes waste and allows reaping economic benefits by reducing the consumption of raw materials [1]. Reprocessing is defined as the operation that returns material already processed to the production line substituting part of the raw material [2]. During each reprocessing the polymer experiences i) thermal and mechanical degradation, ii) physical chemical changes, and iii) a loss of mechanical properties that make the polymer brittle and reduces its life span [3].

The degradation processes of polymers occur not only during their production, processing, and reprocessing; but also during their final life stage: the waste disposal [4]. Reprocess-induced degradation is mechanical and thermal, it breaks the polymer's main chain, which reduces the molecular weight and the viscosity, and increases the melt flow index [5]. Reprocessing also changes other properties such as glass transition temperature (T_g), crystallinity percentage, and flow index (FI). But the nature of the change is completely variable for different types of polymer and process [2], [6].

Besides T_g and FI measurements the effect of reprocessing can be quantified with the higher heating value (Q) and thermogravimetric analysis (TGA). The latter is one of the most applied thermal analysis techniques in the study of solid materials' thermal degradation [7]. In this analysis the weight loss is measured as a function of temperature (TG curve or gravimetric thermogram). The derivative of the TG curve is named differential thermogravimetric thermogram, or DTG curve [8]. The DTG curve is used to obtain the temperature at the maximum weight loss rate (peak temperature, T_m) [9], and the TG/DTG data are employed to establish the degradation kinetics by means of isoconversional and non-isoconversional methods. [10], [11].

The purpose of this work is to study the effect of five cycles of extrusion processing on the properties and thermal degradation kinetics of polylactic acid (PLA). To this end T_g , FI , and Q were measured and TG/DTG curves were

obtained at four heating rates (B). The reprocessing-induced degradation was quantified, and the kinetic triplet was determined from the TG/DTG data using 10 non-isoconversional and 5 isoconversional methods.

2. Materials and methods

2.1. Raw polymer properties and extrusion

Extrusion-grade polylactic acid (PLA) was supplied by Nature Works – USA. This polymer had a flow index of 14,2 g/10min (210°C/2,16kg), with glass transition, fusion, and crystallization temperatures of 63°C, 165°C, and 120°C respectively. The PLA was subject to five reprocessing cycles. Each one included the same operations: an initial drying, extrusion, cooling, size reduction, and a second drying. The size obtained was 2mm (diameter) by 3mm (height), approximately. The drying was held in an oven at 90°C for one hour. The extruder was a single-screw EXTRUDEX ED-N 45-30D, with a 45mm screw diameter, and a length/diameter ratio $L/D=30$. It was operated with a polymer exit dosifier restriction of 10 (minimum is 0, and maximum is 56), a 30 rpm rotating speed, and a 180/190/200/205/210/210/210/210 temperature profile for the extruder's eight heating zones.

2.2. Extruded polymer characterization

Samples of raw and extruded polymer were characterized with T_g , FI , Q , and thermogravimetric curves. The glass transition temperature was measured following the ASTM D3418-08 standard in a Netzsch DSC 200-PC differential scanning calorimeter. The samples, with a $10,0 \pm 1,0$ mg mass were subject to this controlled heating / cooling program: heating from 20°C to 160°C, constant (160°C) temperature for 5 minutes, followed by cooling from 160°C to 20°C. Flow index was measured in a Dynisco D4003 melt flow indexer. For PLA the FI is measured with the mass that flows through a capillary tube in a 10 min lapse, at 210°C, and an equipment mass of 2,16kg (ASTM D1238 standard). The calorific value was measured in a LECO AC 350 calorimeter following the standard ASTM D5865 using 1g samples. Thermogravimetric (TGA) analysis was carried out in a TA Instruments TGA SDT Q600 analyzer. Samples with mass between 10mg and 15mg were heated from room temperature to 600°C at four heating rates, $B = 5, 10, 20,$ and 40°C/min in inert atmosphere with a nitrogen flow of 50mL/min.

2.3. Quantification of reprocessing degradation

The extent of degradation induced by the polymer processing was quantified using the Processing Degradation Index, *PDI*, [12]:

$$PDI = abs \left[\frac{(IF_0 + IF_1 + \dots + IF_n) - (n+1)IF_0}{(n+1)IF_0} \right] \quad (1)$$

where *abs* means absolute value, *n* is the number of reprocessing cycles, and FI_i is the flow index in the reprocessing *i* (for raw polymer $i=0$). Degradation is proportional to *PDI*; an ideal, non-degraded polymer has $PDI = 0$, while $PDI \gg 1$ indicates a very high degradation.

2.4. Kinetic triplet determination

Activation energy (*E*), frequency factor (*A*), and reaction order (*n*) values were calculated with the isoconversional and non-isoconversional methods described in Table 1. The non-isoconversional methods are differential (with an assumed $n = 1$), Arrhenius integral ($n = 1$), Briodo ($n = 1$), Chang, Coats-Redfern, Flynn-Wall, Horowitz-Metzger ($n = 1$), MacCallum-Tanner, Madhusudanan, and dynamic method. The isoconversional methods are Flynn-Wall-Ozawa ($n = 1$), Friedman, Gyulai-Greenhow ($n = 1$), Kissinger-Akahira-Sunose ($n = 1$) and Kissinger ($n = 1$). Temperature and conversion (*a*) data were fitted to the isoconversional and non-isoconversional models using functions written for the software Scilab-5.4.0.

Table 1. Methods applied to obtain the kinetic triplet

Method	Equation	Source
Flynn-Wall-Ozawa - FWO	$Ln(B) = \log \left(\frac{AE}{RF(\alpha)} \right) - 5,3305 - \frac{1,052E}{RT}$	Park et al., 2000 [13]
Friedman	$ln \left(\frac{da}{dt} \right) = ln \left[A(1-\alpha)^n \right] - \frac{E}{RT}$	Kim and Oh, 2005 [14]
Gyulai-Greenhow	$ln B = ln \left(\frac{A}{F(\alpha)} \right) + 8,1614 - 0,915784 ln E - \frac{621,302E^{0,95823}}{T}$	Mallakpour and Taghavi, 2009 [15]

Method	Equation	Source
Kissinger-Akahira-Sunose - KAS	$\ln\left(\frac{B}{T^2}\right) = \ln\left(\frac{AR}{EF(\alpha)}\right) - \frac{E}{RT}$	Aboulkas et al., 2010 [16]
Kissinger	$\ln\left(\frac{B}{T^2}\right) = \ln\frac{AR}{E} - \frac{E}{RT_m}$	Kim and Oh, 2005 [14]
Arrhenius Differential	$\ln\left(\frac{1}{1-\alpha} \frac{da}{dT}\right) = \ln\frac{A}{B} - \frac{E}{RT}$	Wan et al., 2005 [17]
Arrhenius Integral	$\ln[-\ln(1-\alpha)] = \ln\left[\frac{ART^2}{BE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$	Wan et al., 2005 [17]
Briodo	$\ln\left[\ln\left(\frac{1}{1-\alpha}\right)\right] = -\frac{E}{RT} + \ln\left(\frac{ART_m^2}{BE}\right)$	Kim and Oh, 2005 [14]
Chang	$\ln\left[\frac{\frac{da}{dt}}{(1-\alpha^n)}\right] = \ln(A) - \frac{E}{R} * \left(\frac{1}{T}\right)$	Wan et al., 2005 [17]
Coats-Redfern	$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{BE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} n = 1$ $\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{BE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} n \neq 1$	Mallakpour and Taghavi, 2009 [15]
Flynn-Wall	$\frac{E}{nRT_m^2(1-\alpha_m)^{n-1}} = \frac{A}{B} \exp\left(-\frac{E}{RT_m}\right)$	Wan et al., 2005 [17]
Horowitz-Metzger	$\ln[-\ln(1-\alpha)] = \frac{E\theta}{RT_m^2} n = 1$ $\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln\frac{ART_m^2}{BE} - \frac{E}{RT_m} + \frac{E\theta}{RT_m^2} n \neq 1$	Kim and Oh, 2005 [14]
MacCallum-Tanner	$\ln F(\alpha) = \ln\left(\frac{AE}{RB}\right) - 1,1124E^{0,4351} - \left(\frac{449+217E}{0.434}\right)\left(\frac{1}{T}\right)$	Mallakpour and Taghavi, 2009 [15]
Madhusudanan	$\ln\left(\frac{F(\alpha)}{T^{1,921503}}\right) = -\ln\left(\frac{AE}{BR}\right) + 3,772049679 - 1,921503 \ln(E) - 1,000953 \frac{E}{R} \left(\frac{1}{T}\right)$	Wan et al., 2005 [17]
Method Dynamic	$\ln(B) = \ln(n) + (n-1)\ln(1-\alpha_m) + \ln(A) + \frac{3}{2}\ln(T_m) - \frac{E}{RT_m} - \ln\left(\frac{E}{RT_m} + \frac{1}{2}\right)$	Kim and Oh, 2005 [14]

Source: authors' own representation

3. Results

3.1. Extruded polymer characterization

Raw and processed polymer T_g , FI , and Q values are shown in Table 2. It can be noticed that T_g varies only slightly with the number of extrusions (Ext. 1 – Ext. 5), and hence it can be assumed that reprocessing does not alter such parameter. Although Q reduced with each extrusion this effect is small and the reduction for all reprocessed samples is below 0,5%. On the contrary, FI increases with each reprocessing, which suggests that polymer's molecular structure was degraded. This result also explains the reduction of Q with reprocessing.

Table 2. Physical properties of raw and extruded PLA

Polymer	Glass transition temperature, T_g , °C	Flow index g/10 min	Higher heating value, kJ/kg
Raw	63	14,20	18562
Ext. 1	62	17,10	18560
Ext. 2	63	18,50	18555
Ext. 3	63	21,50	18534
Ext. 4	64	22,90	18527
Ext. 5	64	24,70	18502

Source: authors' own representation

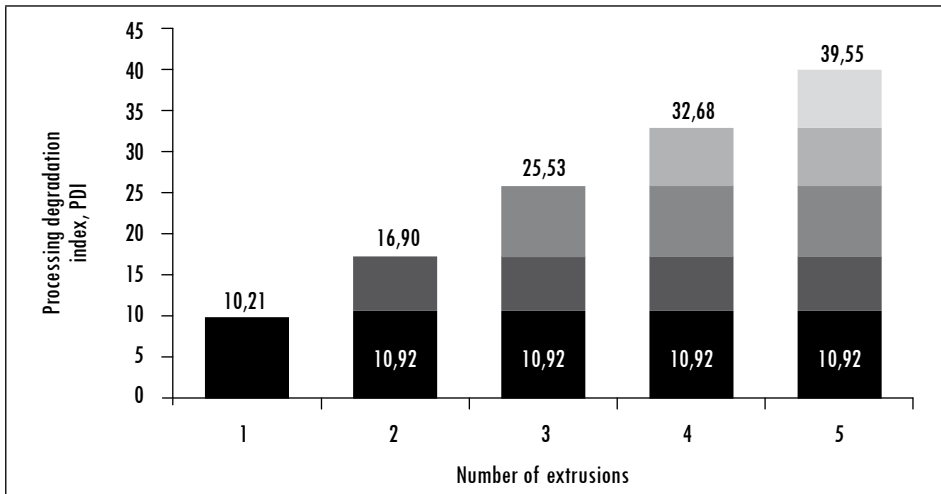
3.2. Processing degradation index

In Figure 1 each gray tone represents the degradation experienced by PLA in each reprocess in terms of the PDI . The first reprocessing produces most degradation, and as expected the effect is accumulative with the number of reprocesses. There is a linear relationship between the number of reprocess (P) and PDI : $PDI=2,636+7.446P$, with determination coefficient $R^2 = 0,998$. This is in agreement with thermal degradation results obtained from TG curves, see Figure 3.

3.3. Thermogravimetric analysis

The TG and DTG analyses were done at four heating rates (B) for each extrusion. TG and DTG curves for extrusion 5 with all B s are shown in Figure 2. The curves for $B=10^\circ\text{C}/\text{min}$ for all five extrusions are in Figure 3. These results are representative of the other extrusions and heating rates.

Figure 1. Processing (extrusion) degradation index



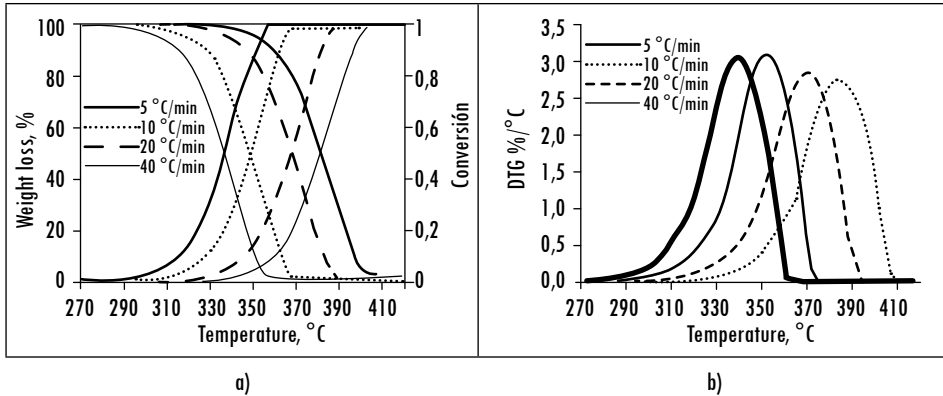
Source: authors' own representation

The TG a curves displace to the right when B increases (Figure 2a), it implies that the same a will be reached at a higher temperature. Therefore the increase in B causes a delay in material's degradation, which reflects in the shift to the right in the a curves. The same behavior appeared with all samples, in agreement with results reported for commercial rubber [18]. This effect has been attributed to the change in the mechanism of reaction when B is increased [13]. Similar results were obtained for DTG, when B increases the curves shift to the right and the peaks appear at higher temperature (Figure 2b). This can also be attributed to the reduction of reaction time, the final temperature of the thermogravimetric analysis is reached in a shorter time [18].

Figure 3 shows TG and DTG curves obtained with a $10^{\circ}\text{C}/\text{min}$ heating rate for the unprocessed sample and the five reprocesses. The thick black solid line represents the polymer unprocessed data, the first reprocessing is the dotted line, the second is the thin dashed line, the third continuous thin line, the thick fourth and fifth dashed line is the gray line reprocessing. It is observed that the thermal degradation profile and the a curve exhibit a subtle shift to the left, it suggests that: i) polymer degradation affects very little the PLA thermal properties, ii) there is a small variation in the degradation mechanisms. It can be also noticed that reprocessed samples reach the same a value with a lower temperature, which confirms that the polymer degrades with reprocessing. Figure 3b shows that DTG curves have a single peak, indicating a single stage

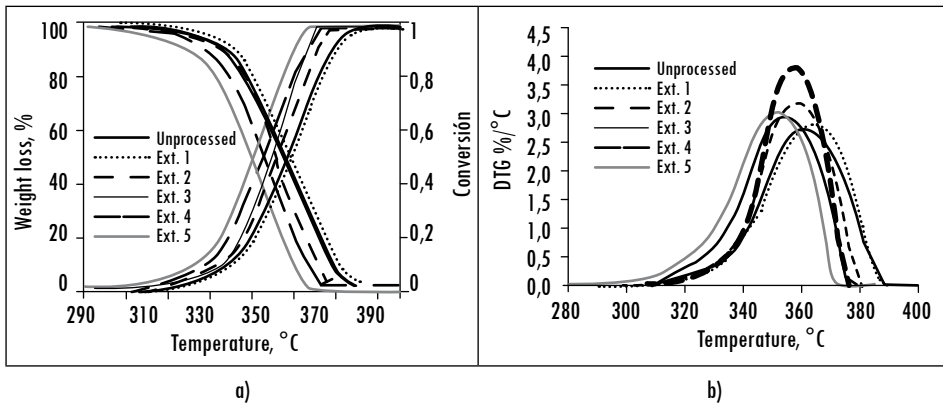
thermal degradation process in the reprocessed samples [16]. A similar behavior appears at different B_s (Figure 2b).

Figure 2. TG (a) and DTG (b) curves for extrusion 5 at different heating rates



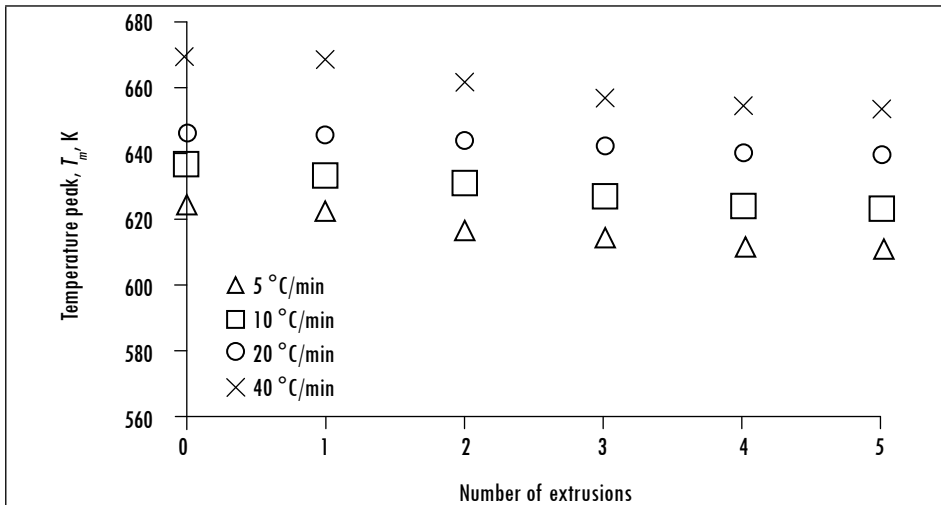
Source: authors' own representation

Figure 3. TG (a) and DTG (b) curves at 10 °C/min for different numbers of extrusions



Source: authors' own representation

The variation of T_m with the number of reprocesses, for each B , is shown in Figure 4. T_m increases with B at each extrusion, but it decreases with the number of extrusions for a given B . Therefore, considering T_m as an indicator it is concluded that PLA suffers a small degree of thermal degradation with reprocessing.

Figure 4. T_m variation with the number of extrusions at different heating rates

Source: authors' own representation

3.4. Thermal degradation kinetics – kinetic triplet

Results from non-isocovertional methods assuming first order reactions are shown in Table 3 for the four heating rates (B). It can be observed in the kinetic triplet values that both A and E increase with B . The parameter A is a probability measure for polymer molecules collisions that lead to a degradation reaction [19]. According to the Table in most samples such probability, i.e. A , increases with B , an expected result because the kinetic energy of the molecules increases in a shorter time and therefore a higher number of them will have enough energy to reach the transition state and react. It is worth to mention that the Horowitz-Metzger method gives the lowest E values for any B and number of reprocesses, while Briodo and Arrhenius integral methods give the same E values, alongside with very close A values.

For the other non-isoconversional methods (MacCallum-Tanner, Madhusudan, Coats-Redfern, Flynn-Wall, Chang, and dynamic), which are not shown in this document, $n \neq 1$ reaction orders were found, with values between 0,56 and 1,10, and a 0,86 average (it is calculated with results from all five extrusions and four heating rates). It was also found that n is approximately the same for MacCallum-Tanner, Madhusudan, Coats-Redfern, and dynamic methods. Average n for Flynn-Wall method was 0,69, and 1,07 for Chang method, which gives the highest n values, close to 1. The average values are calculated as the arithmetic average of all the data obtained in 5 extrusions and 4 B s. It was also

found that, with a fixed heating rate there is not a definite relationship between n and the number of reprocesses, and that n tends to increase with B [13].

Table 3. Kinetic triplet results for non-isoconversional methods with $n = 1$

Extrusion	B (°C/min)	Briodo		Arrhenius differential		Arrhenius integral		Horowitz - Metzger
		E (kJ/mol)	Ln A (min ⁻¹)	E (kJ/mol)	Ln A (min ⁻¹)	E (kJ/mol)	Ln A (min ⁻¹)	E (kJ/mol)
0 (raw)	5	212,67	40,90	244,57	46,12	212,67	40,73	74,84
	10	284,31	54,49	265,50	49,68	284,31	54,31	100,86
	20	217,73	41,36	241,21	44,75	217,73	41,18	83,39
	40	264,53	49,48	298,81	54,77	264,53	49,34	102,66
1	5	203,01	39,00	158,07	28,38	203,01	38,84	72,93
	10	244,25	46,64	273,05	50,85	244,25	46,40	88,99
	20	247,67	47,14	260,56	48,39	247,67	46,96	92,19
	40	296,82	55,65	283,47	52,10	296,82	55,52	110,77
2	5	252,80	49,45	277,13	52,96	252,80	49,30	85,01
	10	239,62	46,19	267,99	50,61	239,62	46,05	86,47
	20	257,36	49,04	266,28	49,63	257,36	48,89	94,94
	40	292,53	55,56	271,04	50,50	292,53	55,47	107,34
3	5	222,52	43,51	255,56	49,01	222,52	43,33	74,59
	10	250,64	48,69	278,43	52,82	250,64	48,52	88,07
	20	280,49	54,07	270,11	50,99	280,49	53,93	99,46
	40	281,42	53,28	298,87	55,43	281,42	53,15	104,77
4	5	246,08	48,48	268,71	51,74	246,08	48,33	80,53
	10	278,78	54,02	291,54	55,36	278,78	53,89	96,60
	20	289,43	55,64	311,34	58,64	289,43	55,50	103,57
	40	297,68	56,60	329,75	61,39	297,68	56,47	109,22
5	5	233,81	46,04	261,18	50,29	233,81	45,88	78,27
	10	259,65	50,82	259,25	49,51	259,65	50,63	89,62
	20	260,14	50,10	318,48	60,06	260,14	49,96	93,49
	40	294,26	55,99	276,63	51,55	294,26	55,82	107,93

Source: authors' own representation

The averaged $\ln A$ obtained with dynamical method was 37,91 (with A in min^{-1}), the Chang method gave the highest values (55,57), Flynn-Wall gave the

lowest (29,43), while MacCallum-Tanner (44,92), Madhusudanan (43,82), and Coats-Redfern, (43,75) gave similar values. The highest E values were obtained with the Chang method, a 294,72 kJ/mol average, followed by MacCallum-Tanner (240,13 kJ/mol), Madhusudanan (229,43 kJ/mol), Coast-Redfern (228,74 kJ/mol), dynamic (219,74 kJ/mol), and Flynn-Wall methods (158,13 kJ/mol).

Kinetic triplet results for isoconversional Kissinger, KAS, FWO, Gyulai, and Friedman methods are included in Table 4. The values are averages from the four B_s and conversions 0,05, 0,1, 0,2, 0,3, 0,4, 0,5, 0,6, 0,7, 0,8, 0,9 and 0,95 in each reprocess. Parameter n was 1, except for Friedman method, which gave n s that vary slightly with reprocess, between 0,23 and 0,39. It is also observed in this Table that E and the frequency factor decrease with the number of reprocesses.

Table 4. Kinetic triplet results for some isoconversional methods

Sample	Kissinger		KAS		FWO		Gyulai		Friedman		
	E (kJ/mol)	$\ln A$ (min ⁻¹)	E (kJ/mol)	$\ln A$ (min ⁻¹)	E (kJ/mol)	$\ln A$ (min ⁻¹)	E (kJ/mol)	$\ln A$ (min ⁻¹)	E (kJ/mol)	$\ln A$ (min ⁻¹)	n
Ext. 0	149,69	27,50	148,26	26,60	151,06	27,48	149,58	27,06	140,58	25,17	0,23
Ext. 1	144,73	26,51	150,13	27,23	152,88	27,77	151,45	27,47	156,82	28,43	0,39
Ext. 2	165,46	30,86	153,75	28,24	156,39	28,80	155,06	28,46	145,49	26,49	0,27
Ext. 3	137,82	25,50	141,84	25,97	145,00	26,69	143,29	26,20	144,33	26,41	0,35
Ext. 4	146,92	27,35	142,92	26,15	145,83	26,85	144,16	26,37	151,12	27,71	0,25
Ext. 5	145,24	27,14	138,21	25,34	141,32	26,10	139,51	25,56	135,52	24,82	0,29

Source: authors' own representation

The analysis of A , E , n results is challenging because all methods give different values, as can be observed in tables 3 and 4. But all these methods are data fit models and their goodness of fit was measured defining a square error with the differences between left-hand and right-hand sides (y_i^l, y_i^r) of the equations in Table 1, divided by the smallest value. The residuals average was calculated as

$$IS_r = -\log \left[\frac{1}{N} \sum_{i=1}^N \left(\frac{y^l - y^r}{\min(y^l, y^r)} \right)_i^2 \right] \quad (2)$$

where N is the number of experimental points, and higher IS_r values indicate a better fit. Results for isoconversional methods are presented in Table 5, the Kissinger method produced the best fit.

Table 5. Residuals average (IS_r) for isoconversional methods

Proc.	Kissinger	KAS	FWO	Gyulai	Friedman
0	2,741	2,250	0,350	0,299	-0,976
1	3,315	2,221	0,728	0,751	-1,081
2	2,981	2,083	0,013	-0,024	-0,977
3	3,602	2,077	-3,016	0,360	-1,373
4	3,884	2,042	-3,021	-0,405	-1,730
5	3,474	1,989	-2,994	0,034	-1,125

Source: authors' own representation

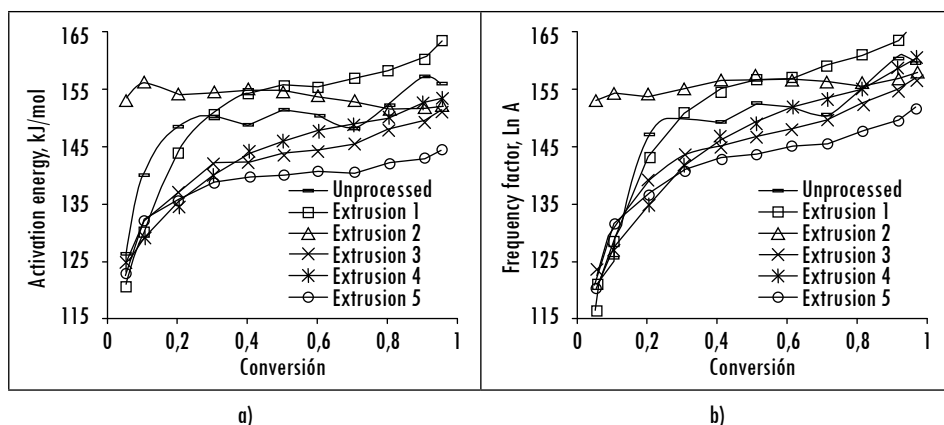
The variation of E , A (calculated with KAS method) with a is shown in Figure 5. The activation energy E increases with a , except for the second reprocess, in which E remained almost constant. This behavior indicates that degradation is delayed because the material becomes more refractory, and more stable, when it decomposes due to the temperature increase [19], [20].

It is also observed that E increases in the 20-150 kJ/mol range for $0,05 \leq a \leq 0,30$, and remains almost constant between $a = 0,35$ and $a = 0,95$. These values are in agreement with previously reported PLA thermal degradation results obtained by different methods [21]. Despite the initial increase the change of E was not significant, which suggest that polymer's decomposition occurs in a single stage [16]. In Figure 5b it is shown that in most extrusion reprocesses $\ln A$ increases from $a = 0,05$ to $a = 0,2$, and then it remains almost constant with values between 25,5 and 29,0. These behaviors of E and $\ln A$ were also observed in the results from FWO and Gyulai methods (Table 4).

The variation of E (obtained from isoconversional and non-isoconversional methods) with the number of reprocesses is shown in Figure 6 for a heating rate of $10^\circ\text{C}/\text{min}$. The tendencies observed in this Figure are the same for the other B_s . Regarding the isoconversional methods (Figure 6a) KAS, FWO, and Gyulai results have the same tendency, while results from Kissinger method show two maxima in reprocesses 2 and 4. The variation of E calculated with KAS, FWO, and Gyulai methods is similar to reprocessing results reported for other polymers [6]. Briodo, Arrhenius integral, Madhusudanan, and Coats-Redfern methods show the same results in Figure 6b. It can also be seen that Chang

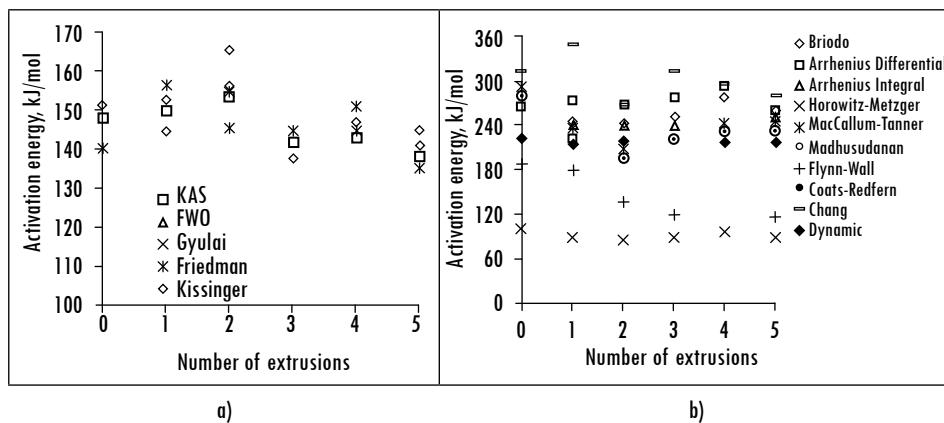
method gives the highest E values and Horowitz-Metzger the lowest, and that the method with the highest E variation is Flynn-Wall.

Figure 5. Variation of E and A (from KAS method) with α for each extrusion reprocess



Source: authors' own representation

Figure 6. Variation of E , calculated with isoconversional (a) and non-isoconversional (b) methods, with the number of extrusions for $B = 10^\circ\text{C}/\text{min}$

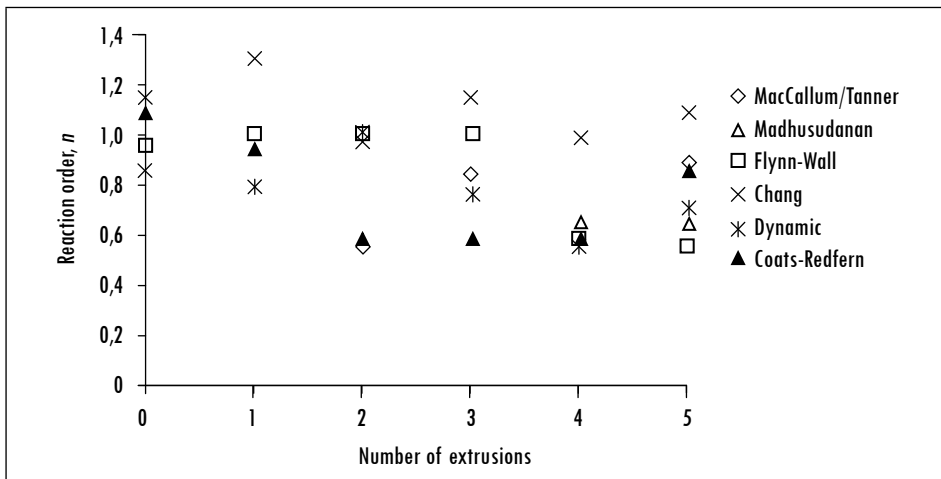


Source: authors' own representation

The variation of n with the number of reprocesses, calculated with $n \neq 1$ non-isoconversional methods is shown in Figure 7 for $B = 10^\circ\text{C}/\text{min}$. In the results from MacCallum-Tanner, Madhusudanan, and Coats-Redfern methods

n varies in the same way, giving similar values for each extrusion. With Flynn-Wall method n is approximately 1 up to the third reprocess, after that it falls to a value close to 0,6. The Chang method gives the highest n values, while Coats-Redfern gives the lowest ones.

Figure 7. Reaction order ($n \neq 1$) from non-isoconversional methods for $B = 10^\circ\text{C}/\text{min}$



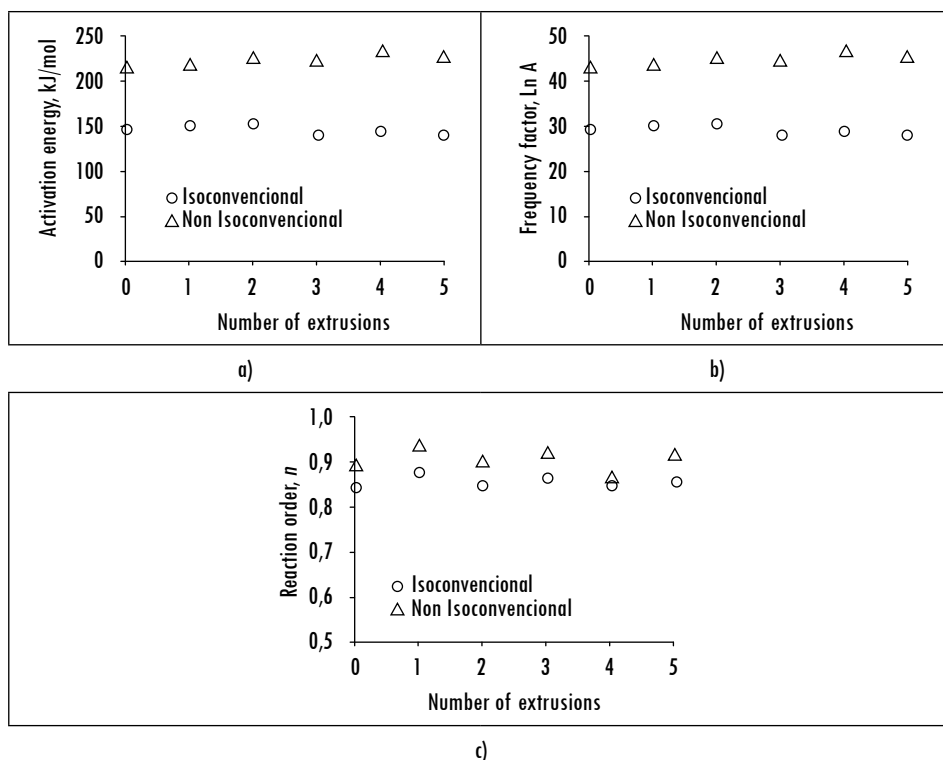
Source: authors' own representation

Averaged values of E , A , n are shown for each extrusion in Figure 8. Isoconversional results were obtained in the same way described for Table 4; but non-isoconversional results from all B s were averaged first for each extrusion and the resulting values were then averaged for each method. In this Figure it can be seen that E , A , n values from isoconversional methods are lower than the respective values from non-isoconversional methods. This behavior indicates that kinetic triplet, mainly E , is influenced by a ; in fact, when the effect of a on is taken in account E reduces 25%.

Figure 8a shows that E increases with the number of reprocesses when it is calculated with isoconversional methods, but it decreases when calculated from non-isoconversional methods. It indicates that isoconversional methods adequately represent the thermal degradation behavior of PLA, in successive thermal treatments it suffers bond rupture and its degradation requires less energy [22]. The parameter A increases with the number of extrusions (Figure 8b), and it is more evident for results from non-isoconversional methods. On the other hand n decreases slightly with the number of reprocesses (Figure 8c), which

indicates that degradation produces smaller molecules, reducing the number of bonds to be broken.

Figure 8. Variation of kinetic triplet (a) E , (b) A , and (c) n with the number of reprocesses



Source: authors' own representation

The kinetic triplet averages from raw and extruded polymer samples are $E = 147,14$ kJ/mol and $225,30$ kJ/mol, $A = 26,94$ and $45,07$ min⁻¹, and, $n = 0,86$ and $0,91$ from isoconvencional and non-isoconvencional methods, respectively.

Conclusions

Extrusion reprocessing of polylactic acid barely alters its glass transition temperature and heating value. But its melt flow index changes noticeably, and processing degradation index results indicate that most of the effect comes from the first reprocess.

Thermogravimetry results suggest that PLA decomposition occurs in a single stage, with a reaction order 1. The Kissinger method gave the most appropriate

description of the thermal decomposition kinetics, with activation energies between 137,82 and 165,46 kJ/mol, and preexponential factor ($\ln A$) values between 25,50 and 30,86, with A in min^{-1} .

It was found that the averaged kinetic triplet of PLA extruded in five processes, from isoconversional and non-isoconversional methods has E values between 147.14 and 225,30 kJ/mol, A values between 26,94 and 45,07 min^{-1} , and n values between 0,86 and 0,91, respectively.

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