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End-life Prediction of Commercial PLA Used for Food Packaging through Short Term TGA Experiments: Real Chance or Low Reliability?

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Abstract A long-term (about nine months) isothermal degradation experiment of two different commercial polylactide (PLA) samples used for food packaging was carried out at a relatively low temperature (423 K). Thermooxidative degradations of the same polymers were carried out in a thermogravimetric (TG) analyser, at higher temperatures (453 K $\leq T \leq$ 523 K), under isothermal heating conditions. The obtained set of experimental TG data was used to determine the apparent activation energy (E_a) of degradation through two isothermal kinetic methods. The results from long-term experiment evidenced considerable mass loss for both PLA samples in the investigated period, but the experimental data were not in agreement with those from the short-term degradations at higher temperatures, thus suggesting a different degradation kinetics, and, then a low reliability of the lifetime predictions for polymers in service or degradation forecasts for the end of their life based on experiments at higher temperatures.

Keywords: Lifetime prediction; Degradation activation energy; Kinetics of polymer degradation; Thermogravimetry.

INTRODUCTION

Polymers, polymer matrix composites and nanocomposites, bio-polymers are increasingly being used in a wide range of applications where long-term service, often in hostile environments, is required. Independently of the nature and the use of polymer-based material, there is a growing demand for manufacturers to guarantee the life expectancy of the product. The problem is very heard in many polymer derivative applications and there is a great need to demonstrate that a product, selected for specific applications, is fit for service[1]. This is particularly important for polymeric materials and its composites as their mechanical and thermal properties, like strength, stiffness and resistance to thermal degradation are time/temperature dependent due to the hereditary nature (viscoelasticity) of polymers[2]. On the basis of the above considerations the practical use of polymeric materials requires the estimation of their correct performances, well known in literature as thermal lifetime[3–6]. Lifetime prediction is done on the basis of the identification of the critical reaction which limits the life of a material[7] and, since there is a strong need for accelerated lifetime characterization methodologies, it is evaluated from the measurement of the reaction kinetics at high temperatures. Kinetic analysis can have either a practical or theoretical purpose: the major practical purpose is the prediction of process rates and material lifetimes[8]. A possibility of obtaining of this information is the use of data supplied by thermal analysis methods. Particularly, thermogravimetric analysis (TGA) is a very rapid accurate technique which, given that the connection between TGA and long-term life testing can be established[9], should provide proper kinetic expressions and corresponding apparent activation energy (E_a) of degradation values that can be used to predict the thermal lifetime of polymeric materials. Therefore through extrapolation of the results obtained at higher temperatures,

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one can estimate fairly accurately the service life of a material. Before you engage in a laborious kinetic analysis of a complex process, like polymer degradation, which could be performed in some favourable cases by employing software packages available for commercial use[10–14], it is good to ask whether isothermal or constant heating rate experiments are better. Probably the correct answer is that both isothermal and non-isothermal methods have advantages and disadvantages. As reported by Vyazovkin *et al.* strictly isothermal experiments are not possible, because there is always a finite non-isothermal heat-up time[8] (usually a few minutes) and anyway these experiments are rather time consuming. By contrast the inherent experimental errors, the relative high number of adjustable kinetic parameters, and the existence of compensation effect of activation parameters[15] make impossible the discrimination of the correct mechanism of this complex process only by using non-isothermal data[16]. For this reason in the past, together with my co-authors, we studied by using both isothermal and dynamic condition, the degradations of different sets of polymers: very thermally stable polyetherketones (PEK) and polyethersulfones (PES)[17–19] and well known polymer as polyethylene (PE), polystyrene (PS), polycarbonate (PC) and poly(methyl methacrylate) (PMMA)[20, 21]. The data obtained through literature kinetic methods, showed agreement each other only when a single degradation step occurred[17] while significant difference in the kinetic parameters were found in the case of multiple degradation stages (like for instance in the case of polyethylene degradation)[20]. Even though the biggest disadvantage of isothermal experiments is a limited temperature range, especially at lower temperatures it may be very difficult to reach complete conversion over a reasonable time period, we carried out, also, long-term (about 3 years) isothermal degradations. The results of these experiments were compared with those obtained by short-term degradations and suggested that kinetic parameters extrapolated from measurements at higher temperatures appear not sufficiently reliable, as well as the lifetime predictions so determined[17, 20, 21].

In this work a long-term (nine months) isothermal degradation of two different commercial polylactide (PLA) samples used for food packaging was carried out in a static air atmosphere, at 423 K. A set of short-term isothermal degradation experiments were also carried out in static air atmosphere, in the 453−523 K temperature range. The degradation activation energy values were determined through an isothermal literature method and the results obtained were compared with those obtained with an isothermal method set up in our laboratory. PLA was selected because it is, in these two forms, one of the most used polymeric materials in food packagings and represents one of the major domestic waste materials, but above all PLA has a low glass transition temperature, in respect to the polymers examined in the past, which suggests the possibility of a sizable degradation during the long-term measurements.

The aims of this work were: (1) to find a possible correlation between the data obtained from the long-term isothermal degradation performed at 423 K (temperature lower than the melting temperature of PLA and closer to the glass transition temperature) with those obtained from the short-term degradations at higher temperatures and then to verify the validity of lifetime predictions of polymers in service made by degradation experiments at higher temperatures; (2) to have information about the time needed to reach appreciable mass loss near the melting temperature of PLA, in order to explore the possibility of performing degradation experiments below the glass transition temperature (and then near the service temperature) in reasonable time; and (3) to extrapolate, in case of a positive correlation between the data obtained from the long-term isothermal degradation and those from the short-term experiments, these values at room temperature and then predict, eventually, the end life-service and, mostly, the end life-expiration of the material in order to allow, in the next future, a better management of waste from food packaging.

EXPERIMENTAL

Materials

Two polylactide samples used for commercial food packaging, one in the form of film and the other in the form of pan (Fig. 1), were studied as purchased without any special preliminary treatments.

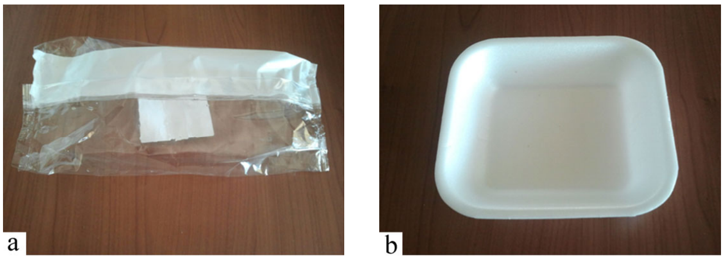

Fig. 1 Image of PLA sample **1** (a), sample **2** (b).

DSC Measurements

Differential Scanning Calorimetry (DSC) experiments were performed by a Mettler DSC 20 calorimeter in order to determine glass transition temperature (T_g) and onset melting temperature (T_{onset}) of our samples. Instrument calibration was made following the manufacturer instructions reported in a previous work[22]. Samples of about 6.0×10^{-3} g, held in sealed aluminium pans, a heating rate of 10 K·min^{-1} and a static air atmosphere were used for measurements.

Long-term Degradation

For the long-term oxidative isothermal degradation, weighed quantities of the two PLA samples in alumina open crucibles were put into an oven at (423 ± 1) K and there kept in isothermal conditions for about nine months (261 days). Samples were weighed once a day (first two months of heating), then three times a week (for three months) and successively once a week, using a Mettler AE 240 electronic balance ($\pm 1 \times 10^{-5}$ g). To this aim, crucibles were extracted from oven, cooled in a desiccator at room temperature for 1 h, weighed and then immediately put again into the oven.

Short-term Degradations

A Mettler TA 3000 thermogravimetric analyser coupled with a Mettler TC 10A processor as control and evaluation unit was used for short-term degradations. The temperature calibration of thermobalance was made according the procedure suggested by the supplier and reported in previous works[23–25], based on the change of magnetic properties of three metal samples (isatherm, nickel and trafoperm) at their Curie points (415.6, 630.1 and 1022.1 K, respectively). Isothermal experiments were performed in static air atmosphere as follows: samples (4×10^{-3}–6×10^{-3} g), held in alumina open crucibles, were quickly heated (20 K·min^{-1}) into the thermobalance from room temperature to the selected one and then maintained at this temperature for 900 min. The weight of sample at the start of isothermal heating was considered the initial one. The short-term isothermal degradations of polymers were repeated three times, and the D average values, where $D = (W_o–W)/W_o$, and W_o and W were the weights at the starting point and during scanning, at various times were in agreement with the experimental ones within ± 3% in every case. All methods, used to calculate the degradation activation energy of the studied polymers, assume that degradation occurs through a single stage kinetics, and then the process is characterized by a single kinetic triplet.

RESULTS AND DISCUSSION

Glass transition temperatures (T_g) and onset melting temperatures (T_{onset}) of PLA samples were at first calorimetrically determined, and the results are reported in Table 1.

The long-term isothermal degradations of samples **1** and **2** were performed for nine months at 423 K, a temperature slightly higher than the melting ones of the samples, and the weight losses were determined at various heating times.

Table 1. Glass transition temperature (T_g) and onset melting temperature (T_{onset}) for PLA samples

Samples	T_g (K)	T_{onset} (K)
1	333.2	413.6
2	336.7	413.1

In Fig. 2 the percentage of undegraded sample (1−*D*)% for both polymers are plotted as a function of heating time. Sample **1** started to degrade immediately differently than compound **2**, which showed an initial “induction period” (τ) of about 10 days, during which only 1% of mass loss was observed compared with 10% of compound **1** in the same time. An exponential degradation trend, much more pronounced for sample **1**, followed by a linear one was observed for both polymers. The overall mass losses in about 261 days of the two PLA samples, in isothermal heating conditions (423 K) and in a static air atmosphere, were 98% and 71% for compounds **1** and **2** respectively. Due to their simplicity and to the consistent time saving, TGA experiments in the scanning mode are more frequently used than those in isothermal heating conditions for determining kinetic parameters associated with the degradation of polymers.

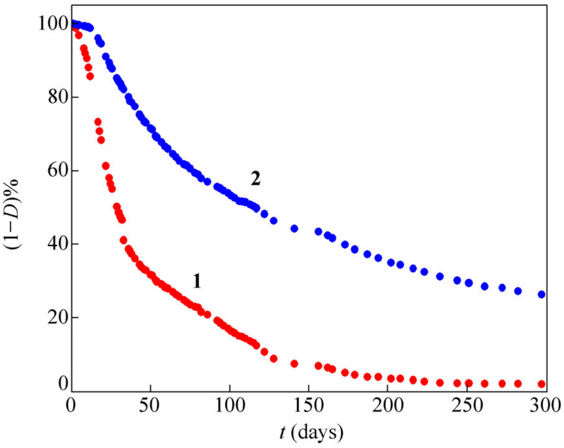

Fig. 2 Percentage of undegraded sample (1−*D*)% at 423 K as a function of heating time (*t*) for PLA samples **1** and **2**

Since my purpose was to compare the data from long-term experiments with those from the short-term ones, in order to verify if they were coherent with each other, I was forced to perform short-term degradations in isothermal heating conditions. TGA experiments were carried out at various temperatures, in the range 453–523 K, in ten degrees interval, in order to obtain E_a values for the degradation degrees (*D*%) included in the 5%–15% range about. This range was chosen because above this percentage about, polymer is usually not suitable to be used. The mass losses in 900 min of investigated polymers at the various temperatures are listed in Table 2. The isothermal degradation at 453 K and 463 K were not considered for sample **2** because of the low mass loss observed at these temperatures. The set of short-term experimental isothermal data was used to estimate the degradation activation energy of PLA samples through the MacCallum[26] and the Abate-Blanco[17,18] isothermal methods. The MacCallum method, extensively reported by Hill *et al*[27], is based on the following linear equation:

$$\ln t = a + b/T_{\mathrm{iso}} \tag{1}$$

where t = time employed to reach a fixed degree of degradation D, $a = \ln[\mathrm{F}(1-D)] - \ln \mathrm{A}$, $b = E_a/\mathrm{R}$, T_{iso} = temperature of isothermal degradation and $\mathrm{F}(1-D)$ is a function of degree of degradation. Thus the apparent activation energy, at each degree of degradation, can be obtained by the slope of the $\ln t$ versus $1/T_{\mathrm{iso}}$ straight line. The experimental isothermal data ($\ln t$ and $1/T_{\mathrm{iso}}$) obtained in the investigated temperature range (453–523 K) were treated according to the equation (1), giving rise, for each polymer, to linear $\ln t = \mathrm{f}(1/T_{\mathrm{iso}})$ relationships at the various selected degrees of degradation. The corresponding linear regression coefficients are reported in Table 3 for samples **1** and **2** respectively, together with the calculated degradation E_a values.

Table 2. Mass loss % observed in 900 min for PLA samples at the various temperatures of isothermal degradations (T_{iso})

T_{iso} (K)	**1**	**2**
453	15.6	1.5
463	27.2	7.9
473	30.9	14.9
483	41.5	17.8
493	60.3	37.6
503	69.7	52.6
513	82.8	57.4
523	85.8	60.9

Table 3. Regression coefficients and apparent activation energies by MacCallum equation for the isothermal degradation of PLA samples at various degrees of conversion (*D*%)

	1				**2**			
D%	*a*	$b \times 10^{-3}$ (K)	*r*	E_a (kJ/mol)	*a*	$b \times 10^{-3}$ (K)	*r*	E_a (kJ/mol)
5	−18.1 (± 1.3)[a]	10.8 (± 0.6)[a]	0.9893[a]	90 (± 5)[a]	−19.7 (± 1.9)[b]	12.1 (± 0.9)[b]	0.9859[b]	101 (± 7)[b]
7.5	−17.6 (± 1.3)[a]	10.7 (± 0.6)[a]	0.9893[a]	89 (± 5)[a]	−19.9 (± 2.1)[b]	12.3 (± 1.0)[b]	0.9831[b]	102 (± 8)[b]
10	−17.4 (± 1.3)[a]	10.7 (± 0.6)[a]	0.9894[a]	89 (± 5)[a]	−19.7 (± 3.4)[c]	12.4 (± 1.7)[c]	0.9656[c]	103 (± 14)[c]
12.5	−17.3 (± 1.3)[a]	10.8 (± 0.6)[a]	0.9886[a]	90 (± 5)[a]	−19.7 (± 3.6)[c]	12.5 (± 1.8)[c]	0.9602[c]	104 (± 15)[c]
15	−17.2 (± 1.4)[a]	10.8 (± 0.7)[a]	0.9807[a]	90 (± 6)[a]	−19.1(± 2.2)[c]	12.2 (± 1.1)[c]	0.9877[c]	101 (± 9)[c]

[a] Determined in the range 453–523 K; [b] Determined in the range 463–523 K; [c] Determined in the range 473–523 K

The experimental values at 423 K of studied polymers, at the same selected degrees of degradation, were later considered for linear regressions.

As shown in Fig. 3 the values at lower temperature, included into the corresponding single MacCallum straight lines, gave rise to a marked deviation of linearity, thus suggesting a higher degradation apparent activation energy at 423 K. The same set of data was used to derive degradation E_a values according to the Abate-Blanco method. The experimental weight loss data at various times of isothermal degradations were simply transformed all together in *D* values and then fitted into appropriate *D* = f(*t*) equations. The corresponding degradation curves at 473 K, in the considered degradation ranges (5%–15%), are reported as examples in Fig. 4.

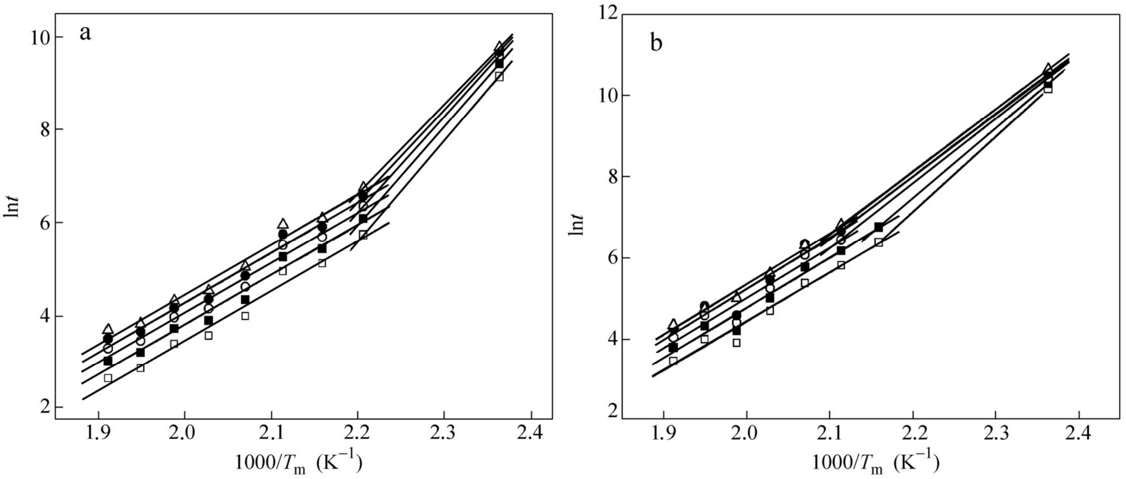

Fig. 3 MacCallum straight lines for sample **1** (a) and sample **2** (b) at various *D* values: 5% (□), 7.5% (■), 10% (○), 12.5% (●) and 15% (Δ)

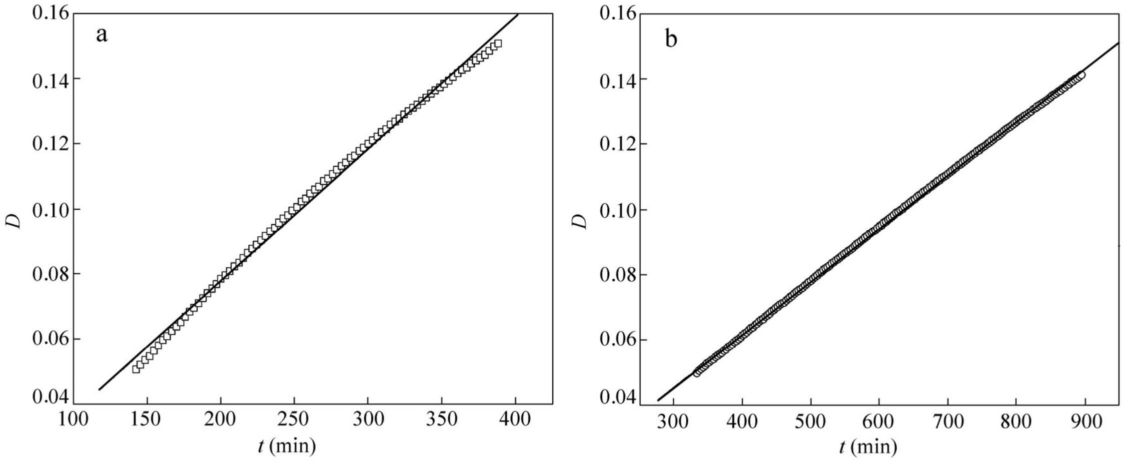

Fig. 4 Experimental D values as a function of heating time (t) and corresponding smoothed $D = \mathrm{f}(t)$ degradation straight line at 473 K for sample **1** (a) and sample **2** (b)

$$D = D_o + \beta t \tag{2}$$

Linear relationships were obtained for both polymers and the regression coefficients at various temperatures are reported in Table 4. The coefficient of time β, whose dimensions are t^{-1}, then representing a measure of decomposition rate, increased exponentially as a function of $-1/T_{\mathrm{iso}}$, thus giving rise to Arrhenius type equations.

$$\ln \beta = \ln\mathrm{A} - \mathrm{B}/T_{\mathrm{iso}} \tag{3}$$

Table 4. Regression coefficients of the $D = D_o + \beta t$ equations at the various temperatures of isothermal experiments for the ($5\% \le D \le 15\ \%$) degradation stage of PLA samples

	1			2		
T_{iso} (K)	D_o	$\beta(\mathrm{min}^{-1})$	r	D_o	$\beta(\mathrm{min}^{-1})$	r
423	−5.2756	0.0011	0.9831	−11.284	0.0006	0.9981
453	−0.6014	0.0184	0.9998	–	–	–
463	−0.9741	0.0366	0.9995	–	–	–
473	−0.3502	0.0406	0.9980	−0.3488	0.0163	0.9998
483	0.0559	0.0967	0.9992	1.0482	0.0201	0.9982
493	−1.0272	0.1736	0.9998	−1.4496	0.06	0.9998
503	−1.4122	0.217	0.9999	−2.6018	0.1545	0.9999
513	−1.2208	0.3559	0.9999	−0.4569	0.1056	0.9990
523	−0.3232	0.3838	0.9999	−0.7752	0.1884	0.9995

In Figs. 5(a) and 5(b) were reported the Arrhenius plots for both **1** and **2** samples, respectively, where the used β values were those obtained by Abate-Blanco method in the short-term degradation experiments at higher temperatures ($453\ \mathrm{K} \le T \le 523\ \mathrm{K}$) and that obtained by the same method in the long-term degradation at 423 K. Differently from what was observed for the MacCallum relationships (Figs. 4a and 4b), the point at 423 K fell on the same straight line obtained with the points at higher temperatures, thus suggesting the same kinetics of degradation.

The corresponding linear regression coefficients for the considered degradation degree ranges are reported in Table 5.

The E_a values calculated both excluding and including the point at 423 K seem to confirm a unique kinetic of degradation only for the compound **2**, for which an activation energy of degradation of 106 (± 13) $\mathrm{kJ \cdot mol^{-1}}$ was obtained on considering only the β values from short-term experiments compared to a E_a value of 109 (± 7) $\mathrm{kJ \cdot mol^{-1}}$ calculated by including the coefficient achieved at 423 K. By contrast the E_a values of sample **1** were quite different, 90 (± 6) $\mathrm{kJ \cdot mol^{-1}}$ on considering only the β values from short-term experiments and

107 (± 7) kJ·mol^{-1} by including the point at 423 K, making questionable the linearity between β values at higher and lower temperatures reported in Fig. 5(a), and then indicating different (lower) degradation rate values than those predictable on the basis of the experiments at higher temperatures. In Table 6 the degradation E_a values determined by MacCallum and Abate-Blanco methods are listed.

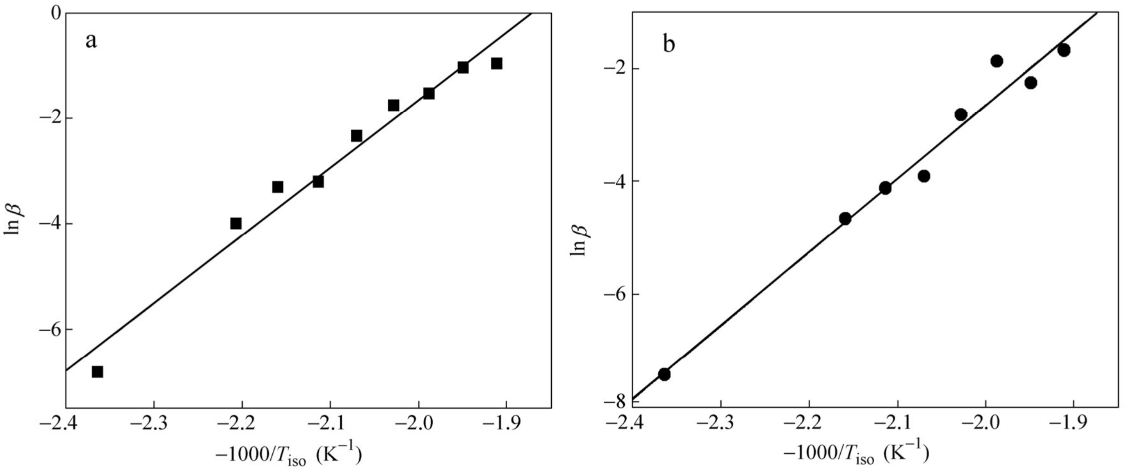

Fig. 5 Arrhenius plot of β values obtained by Abate-Blanco method for sample **1** (a) and sample **2** (b) from short- and long- term experiments

Table 5. Correlation coefficients of the lnβ= lnA–B/T_{iso} Arrhenius type equation obtained according to the Abate-Blanco method for PLA samples, and corresponding degradation E_a values

Sample	lnA	B × 10^{-3}	r	E_a (kJ/mol)
1[a]	20.0 (± 1.5)	10.8 (± 0.7)	0.9872	90 (± 6)
1[b]	24.1 (± 1.8)	12.9 (± 0.8)	0.9851	107 (± 7)
2[a]	23.0 (± 3.0)	12.8 (± 1.6)	0.9611	106 (± 13)
2[b]	23.5 (± 1.8)	13.1 (± 0.9)	0.9870	109 (± 7)

[a] Determined in the range 453–523 K; [b] Determined in the range 423–523 K

Table 6. Degradation E_a values (kJ·mol^{-1}) for PLA samples determined by Abate-Blanco and MacCallum (average values) methods

Sample	Abate-Blanco[a]	MacCallum[a]	Abate-Blanco[b]
1	90 (± 6)	90 (± 5)	107 (± 7)
2	106 (± 13)	102 (± 11)	109 (± 7)

[a] Determined in the range 453–523 K; [b] Determined in the range 423–523 K

The degradation E_a values reported for the MacCallum method were averaged from those obtained at various degrees of conversion in the considered D range. It appears correct because the differences among the values at various degrees of degradation are substantially all within the standard deviations. The data in Table 6 concerning the different samples of PLA indicate that the degradation E_a values obtained through the two methods, in the same temperature range, are in good agreement with each other, confirming the validity of the simple and fast Abate-Blanco method to obtain degradation E_a values of polymers exclusively by fitting the experimental TGA curve in the desired degradation range. In Table 6 is then highlighted the difference between the degradation E_a values of samples **1** and **2**, obtained with the Abate-Blanco method, calculated by including or less the point at 423 K. On the one hand the activation energy of sample **2**, calculated in the whole experimental temperature range, almost equal to that obtained by short-term measurements would seem to suggest an agreement, and then the possibility to extrapolate the degradation behavior of the polymer at lower temperatures and a lifetime prediction. By contrast the difference of 17 kJ·mol^{-1} found, for sample **1**, in the two different temperature range makes chancy this type of prediction.

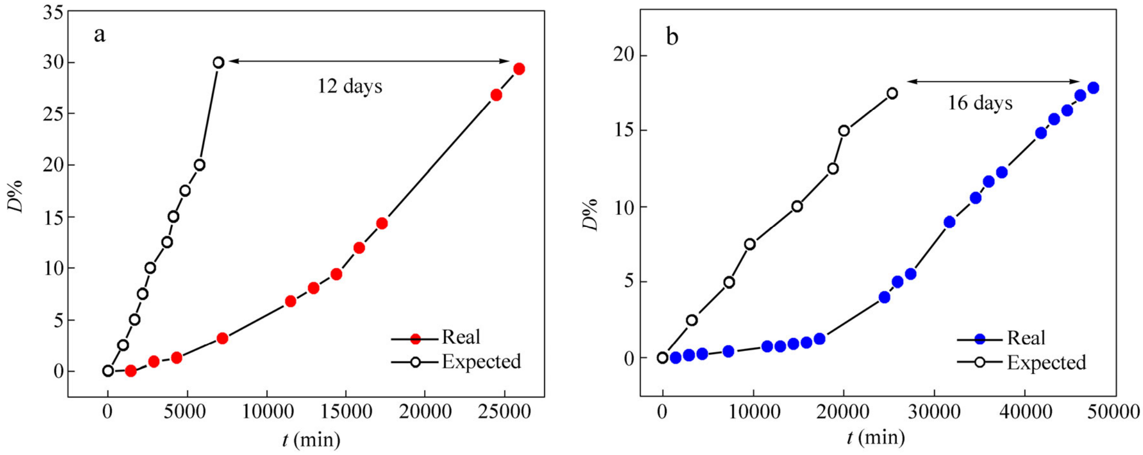

Fig. 6 Real and expected (extrapolated from MacCallum equations) percentage of degradation for sample **1** (a) and sample **2** (b)

In order to quantify the uncertainty in the lifetime prediction of the studied polymers, in Fig. 6 the trends of the real degradation and that extrapolated from the MacCallum equations, obtained through the short term experiments at the same degree of degradation, are shown for samples **1** and **2** respectively. It is quite evident the difference between the real and the expected trend of degradation, it is worth to note, at 30% of degradation degree, a difference of about 12 days for sample **1** (Fig. 6a) and about 16 days for sample **2** (Fig. 6b) at 20 % of degradation degree.

CONCLUSIONS

The examined commercial samples of PLA have reached a degree of degradation of 15% at a temperature near their melting after approximately 12 (Sample **1**) and 30 (Sample **2**) days respectively, thus suggesting the impossibility of performing degradation experiments below the glass transition temperature in a reasonable time.

Without going into the merits of what could be the predominant mechanism of degradation in the temperature range investigated, the results of the present study demonstrate, for commercial PLA polymers used in food packaging, the questionability of degradation E_a values extrapolated to lower temperatures from measurements at higher ones and then of degradation rates and lifetime predictions based on measurements at higher temperatures. In the future, through real measurements of degradation, carried out at a relatively low temperature, it could be possible to create a database of the degradation times of the most commercially used polymers, so as to obtain a series of correction factors for the kinetic parameters achieved through short-term measurements.

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