

Lifetime prediction of food and beverage packaging wastes

Ignazio Blanco¹

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Abstract Two different types of commercial polyethylene terephthalate (PET) and polypropylene (PP) samples used for beverage and food packaging were degraded for 25 months in isothermal oxidative condition at relatively low temperature (423 K). The results of this long-term experiment were compared with thermooxidative degradations of the same polymers that were carried out in a thermogravimetric (TG) analyzer, at higher temperatures ($443 \leq T \leq 623$ K), in 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 with the aim to verify the validity of lifetime predictions of polymers made by degradation experiments at higher temperatures. The results that were discussed and interpreted suggest caution in the extrapolation at lower temperature of degradation kinetics parameters obtained at high temperatures.

Keywords Lifetime prediction · Degradation activation energy · Kinetics of polymer degradation · Thermogravimetry

Introduction

Since its starting in the nineteenth century, food packaging industry has made great advances linked to global trends and above all to the consumer preferences. Over the last 30 years about, the use of polymers as food packaging

materials has exponentially increased, because of their availability in large quantities at low cost, light mass, favorable functionality and good barrier properties [1, 2]. In the polymer global market that has increased from some 5 million tonnes in the 1950s to nearly 100 million tonnes today, the 42 % is covered by packaging, with the packaging industry itself worth about 2 % of Gross National Product in developed countries [3]. Unfortunately and in spite of the above-mentioned advantages, many of these polymers are traditionally designed to resist microbial attack and to become recalcitrant to the environment [4]. The growing interest in environmental impact of discarded plastics has directed research on the development of materials that degrade more rapidly in the environment, leading to their complete mineralization or bioassimilation [5], but leaving unchanged the problem of final disposal of the enormous amount of plastic used previously. The envisaged direction is to look at the complete life cycle of the packaging (raw material selection, production, analysis of interaction with food, use and disposal) integrating and balancing cost, performance, health and environmental considerations [6, 7]. The modern food packaging industry is therefore divided, to the present day, between the need to extend and implement the principal packaging functions—containment, protection and preservation—and the need to be easily disposed of or recycled after use. Polyethylene terephthalate (PET) and polypropylene (PP), because of their low cost, durability and structures that resulted in wide ranges of strengths and shapes, are definitely the two petroleum-derived polymers most used for this purpose. Anyway, the protection of packaged food or beverage against external agents is one of the most important requirements, and it can be obtained by the use of additives, thus leading to difficulties in the recycling and degradation of these materials and consequently to a waste

✉ Ignazio Blanco
iblanco@dii.unict.it

¹ Department of Industrial Engineering, University of Catania, V.le a. Doria 6, 95125 Catania, Italy

increase. In this context, the study of the thermal properties of the materials used in food packaging [8–10] and more [11] is therefore crucial to improve the recyclability or provide a viable alternative. In particular, the studies of the lifetime prediction play a key role in facilitating both the design phase and the final disposition. Lifetime prediction is based on the identification of the critical reaction which limits the life of a material [12], and since there is a strong need for accelerated lifetime characterization methodologies, it is generally evaluated by thermogravimetric analysis (TG). Through this technique, it is possible to derive proper kinetic equations and the corresponding apparent activation energy (E_a) of degradation values that can be used to predict the thermal lifetime of polymeric materials. Obviously, it is about an extrapolation of reaction kinetics at high temperatures that should allow a fair estimation of the polymer lifetime.

Since several years, our group was engaged in the kinetic analysis of a complex process, like polymer degradation, by studying, in isothermal conditions, the degradations of different sets of polymers: very thermally stable polyetherketones (PEK) and polyethersulfones (PES) [13–15] and well-known polymer as polyethylene (PE), polystyrene (PS), polycarbonate (PC), poly(methyl methacrylate) (PMMA) and polylactide (PLA) [16–18]. Aware of the biggest disadvantage of isothermal experiments (e.g., the difficult to reach complete conversion over a reasonable time, especially at lower temperatures), we tried to compare the results of these short-term degradations with those obtained by long-term experiments. On continuing our contribution in this field, a long-term (25 months) isothermal degradation, at relatively low temperature (423 K), of commercial PET and PP (two of the most used polymer for food and beverage packaging), is carried out and compared with classical TG scans at higher temperature. The aim was to correlate the different sets of data (long term and short term) and extrapolate these values at room temperature to predict the end life-service and, mostly, the end life-expiration of the material in order to allow a better management of waste from food packaging.

Experimental

Materials

Two different types of commercial polyethylene terephthalate and polypropylene used for food and beverage packaging (Fig. 1) were studied after washing and drying to remove any food or water debris and will be indicated by the corresponding numbers as follows:

PET bottle for water	(1)
PET bottle label	(2)
PP fruit snack tray	(3)
PP lid of fruit snack tray	(4)

DSC measurements

A Mettler DSC 1 Star System was used for glass transition (T_g) and onset melting (T_{onset}) temperature determinations. The procedure suggested by the manufacturer was followed to calibrate the response of apparatus in enthalpy and temperature. To this purpose, two methods of instrument, which use the fusion of indium for the enthalpy calibration and the melting points of indium and zinc for that of temperature, were employed. The calibration of enthalpy was thus checked by the melting of fresh indium, showing an agreement with the literature standard value of $3.273 \text{ kJ mol}^{-1}$ [19] within 0.25 %, while the accuracy of temperature, checked by several scans with fresh indium and tin, was within 0.08 % in respect to literature values of 429.7 K for indium and 505.0 K for tin [19]. The calibrations were repeated every 2 weeks. Samples of about $5.0 \times 10^{-3} \text{ g}$, held in sealed aluminum crucibles, and a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, were used for measurements. The experiments were performed in triplicate, and the considered values were averaged from those of three runs, the maximum difference between the average and the experimental values being within $\pm 0.5 \text{ K}$.

Long-term degradation

For the long-term oxidative isothermal degradation, weighed quantities of PET and PP samples in alumina open crucibles were put into an oven at $(423 \pm 1) \text{ K}$ and there kept in isothermal conditions for about 25 months (736 days). Samples were weighed once a day (first 2 months of heating), then three times a week (for 3 months), successively once a week (for 3 months) and finally once a month, using a Mettler AE 240 electronic balance ($\pm 1 \times 10^{-5} \text{ g}$). 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 Shimadzu DTG-60 simultaneous DTA-TG apparatus was used for short-term degradations. The calibrations of temperature and mass were performed following the



Fig. 1 Image of (a) PET bottle sample 1 (b) PET bottle label sample 2 (c) PP fruit snack sample 3 (d) PP lid of fruit snack tray sample 4

Table 1 Glass transition temperature (T_g) and onset melting temperature (T_{onset}) for PET bottle sample 1, PET bottle label sample 2, PP fruit snack sample 3, PP lid of fruit snack tray sample 4

Samples	T_g /K	T_{onset} /K
1	350.0 (± 0.3)	502.3 (± 0.1)
2	306.1 (± 0.2)	413.9 (± 0.3)
3	320.9 (± 0.4)	424.1 (± 0.3)
4	332.0 (± 0.3)	404.7 (± 0.3)

procedure reported in our previous work [20] using as standard materials: indium (NIST SRM 2232), tin (NIST SRM 2220) and zinc (NIST SRM 2221a) for temperature and a set of exactly weighed samples supplied by Shimadzu for mass. All calibrations of equipment were repeated every 2 weeks. Isothermal experiments were performed in static air atmosphere as follows: samples (4×10^{-3} – 6×10^{-3} g), held in alumina open crucibles, were heated ($10 \text{ }^\circ\text{C min}^{-1}$) into the thermobalance from room temperature to the selected one and then maintained at this temperature until complete degradation or for 600 min. The mass 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 $D = (W_0 - W)/W_0$, and W_0 and W were the masses at the starting point and during scanning, at various times were in agreement with the experimental ones within $\pm 2.5 \%$ in every case. Both methods, used to calculate the degradation activation energy of the studied polymers, assume that degradation

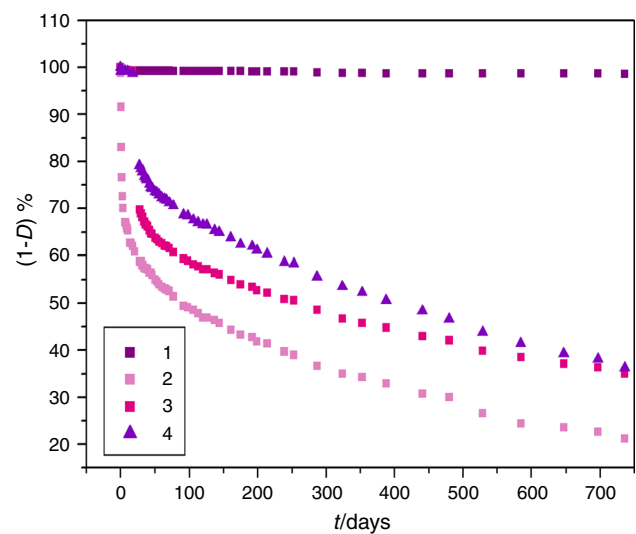


Fig. 2 Percentage of undegraded sample ($1-D$) at 423 K as a function of heating time (t) for PET bottle sample 1, PET bottle label sample 2, PP fruit snack sample 3, PP lid of fruit snack tray sample 4

occurs through a single stage kinetics, and then, the process is characterized by a single kinetic triplet.

Results and discussion

All samples were at first calorimetrically characterized by measuring the glass transition temperatures and onset melting temperatures, whose data are reported in Table 1.

Table 2 Regression coefficients and apparent activation energies by MacCallum equation for the isothermal degradation of samples **1** and **2** at various degrees of conversion (D %)

D %	1				2			
	a	$b \times 10^{-3}/K$	r	$E_a/kJ mol^{-1}$	a	$b \times 10^{-3}/K$	r	$E_a/kJ mol^{-1}$
5	$-17.3 (\pm 2)^a$	$11.8 (\pm 1.2)^a$	0.9685^a	$98 (\pm 10)^a$	$-23.3 (\pm 0.6)^b$	$12.7 (\pm 0.3)^b$	0.9979^b	$106 (\pm 2)^b$
7.5	$-16.4 (\pm 1.5)^a$	$11.8 (\pm 0.9)^a$	0.9844^a	$98 (\pm 7)^a$	$-21.2 (\pm 0.7)^b$	$11.8 (\pm 0.3)^b$	0.9969^b	$98 (\pm 2)^b$
10	$-17.3 (\pm 1.6)^a$	$12.6 (\pm 0.9)^a$	0.9838^a	$105 (\pm 7)^a$	$-19.6 (\pm 0.7)^b$	$11.1 (\pm 0.3)^b$	0.9965^b	$92 (\pm 2)^b$
12.5	$-16.2 (\pm 1.4)^a$	$12.2 (\pm 0.8)^a$	0.9873^a	$101 (\pm 7)^a$	$-18.5 (\pm 0.7)^b$	$10.6 (\pm 0.3)^b$	0.9960^b	$88 (\pm 2)^b$
15	$-15.8 (\pm 1.5)^a$	$12.1 (\pm 0.9)^a$	0.9844^a	$101 (\pm 7)^a$	$-17.6 (\pm 0.7)^b$	$10.3 (\pm 0.3)^b$	0.9960^b	$86 (\pm 2)^b$

^a Determined in the range 553–623 K

^b Determined in the range 443–533 K

Table 3 Regression coefficients and apparent activation energies by MacCallum equation for the isothermal degradation of samples **3** and **4** at various degrees of conversion (D %)

D %	3				4			
	a	$b \times 10^{-3}/K$	r	$E_a/kJ mol^{-1}$	a	$b \times 10^{-3}/K$	r	$E_a/kJ mol^{-1}$
5	$-29.9 (\pm 2)^a$	$15.8 (\pm 1.0)^a$	0.9852^a	$131 (\pm 8)^a$	$-26.5 (\pm 2)^b$	$14.2 (\pm 1.1)^b$	0.9810^b	$118 (\pm 9)^b$
7.5	$-28.7 (\pm 2)^a$	$15.3 (\pm 1.0)^a$	0.9844^a	$127 (\pm 8)^a$	$-24.1 (\pm 2)^b$	$13.2 (\pm 1.0)^b$	0.9814^b	$110 (\pm 8)^b$
10	$-27.5 (\pm 2)^a$	$14.9 (\pm 1.0)^a$	0.9849^a	$124 (\pm 8)^a$	$-23.1 (\pm 2)^b$	$12.8 (\pm 1.0)^b$	0.9793^b	$106 (\pm 8)^b$
12.5	$-27.2 (\pm 1.8)^a$	$14.8 (\pm 0.9)^a$	0.9872^a	$123 (\pm 7)^a$	$-21.9 (\pm 1.9)^b$	$12.3 (\pm 0.9)^b$	0.9808^b	$102 (\pm 7)^b$
15	$-26.8 (\pm 1.7)^a$	$14.7 (\pm 0.8)^a$	0.9882^a	$122 (\pm 7)^a$	$-21.6 (\pm 2)^b$	$12.2 (\pm 1.0)^b$	0.9785^b	$101 (\pm 8)^b$

^a Determined in the range 453–533 K

^b Determined in the range 453–533 K

The long-term isothermal degradations of both PET and PP samples were performed for 25 months at 423 K; this temperature was chosen because it was comparable (except for sample **1**) with the melting ones of most of the tested samples. The mass losses % were determined in isothermal conditions and plotted as a function of heating time (Fig. 2). Sample **2** started to degrade immediately differently than compounds **3** and **4**, which showed an initial “induction period” (τ) of about 20 days, during which only 1 % of mass loss was observed compared with 30 % of compound **2** in the same time. An exponential degradation trend, much more pronounced for sample **2**, followed by a linear one was observed for these polymers. The overall mass losses in 736 days, in isothermal heating conditions (423 K) and in a static air atmosphere, were 79, 64 and 65 % for compounds **2**, **3** and **4**, respectively. Differently than the others, and as predictable due its T_{onset} is higher than those of the other samples and the temperature of long-term experiments, sample **1** did not showed appreciable mass loss (~ 1.5 %) for the whole time of the experiment.

Kinetic parameters associated with the degradation of polymers are frequently determined through TG experiments in the scanning mode that, due to their simplicity and

to the consistent time saving, are more used than those in isothermal heating conditions. Moreover, as reported by Vyazovkin et al. [21] strictly isothermal experiments are not possible, because there is always a finite non-isothermal heat-up time (usually a few minutes) and anyway these experiments are rather time-consuming. Nevertheless, since the aim of this work was to compare data from long-term experiments with those from the short-term ones, in order to verify whether they were coherent with each other, it was, obviously, chosen to operate in isothermal heating conditions. TG short-term experiments were carried out at various temperatures, in the range 443–623 K, in 10° interval, in order to obtain E_a values for the degradation (D %) included in the 5–15 % range, on considering that above this percentage about, polymer is usually not suitable to be used. The set of experimental short-term isothermal data was used to calculate the degradation activation energy of PET and PP samples through the MacCallum method [22] and an Arrhenius-type isothermal method that we developed in recent years [14–18]. The MacCallum method, extensively reported by Hill et al. [23], is based on the following linear equation:

$$\ln t = a + b/T_{iso} \quad (1)$$

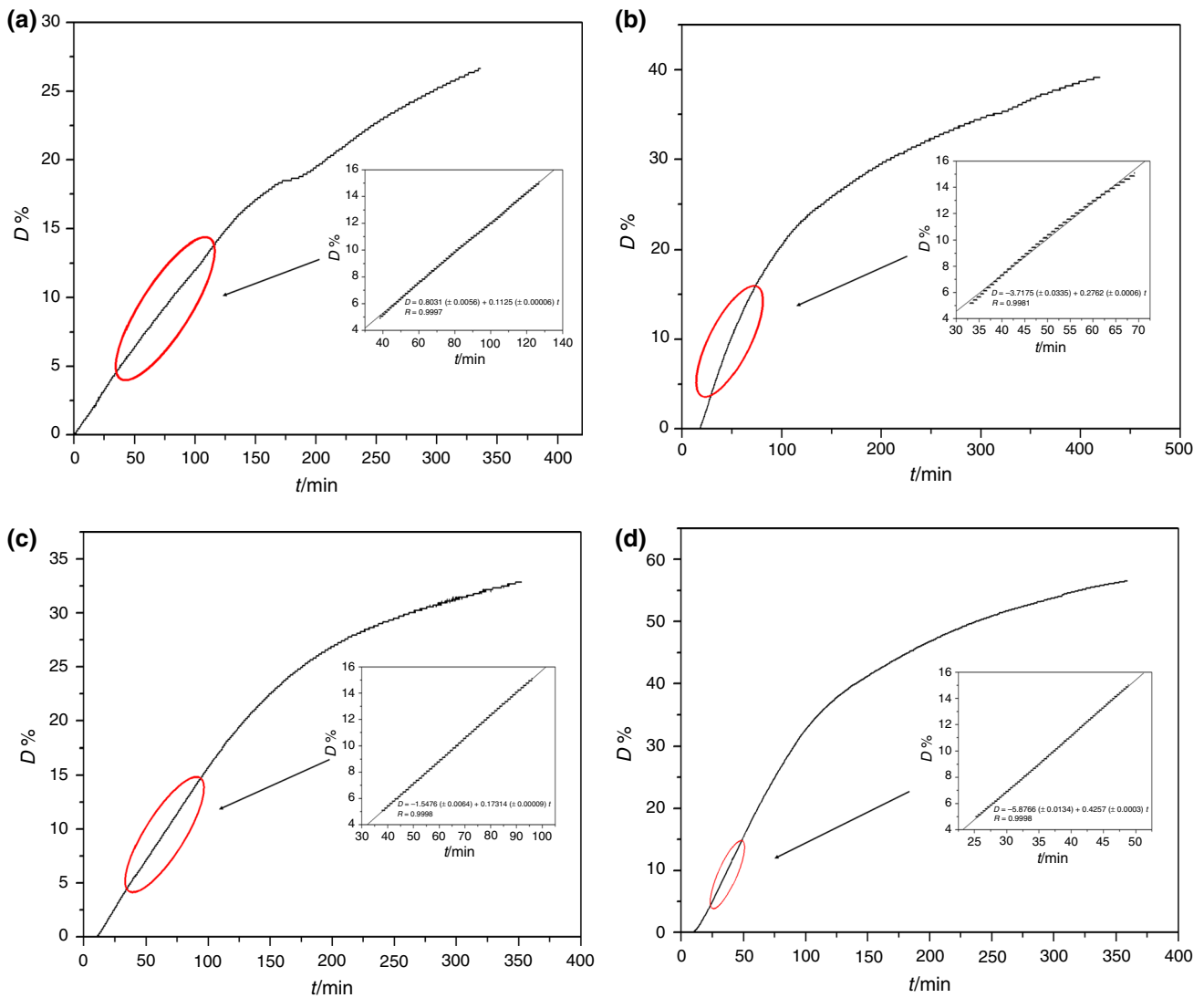


Fig. 3 Isothermal degradation at 593 K for sample **1** (a) and at 473 K for sample **2** (b), **3** (c) and **4** (d)

Table 4 Regression coefficients of the $D = D_0 + \beta t$ equations at the various temperatures of isothermal experiments for the ($5 \leq D \leq 15\%$) degradation stage of sample **1**

T_{iso}/K	1		
	D_0	β/min^{-1}	r
553	1.0156	0.0412	0.9973
563	3.9026	0.0483	0.9956
573	5.1552	0.0715	0.9869
583	3.9924	0.0982	0.9964
593	0.8031	0.1125	0.9997
603	2.8258	0.2293	0.9971
613	2.5529	0.3007	0.9982
623	2.4100	0.3473	0.9990

where t = time employed to reach a fixed degree of degradation D , $a = \ln[F(1 - D)] - \ln A$, $b = E_a/R$, T_{iso} = temperature of isothermal degradation, and $F(1 - D)$ is a function of degree of degradation. The isothermal data ($\ln t$ and $1/T_{\text{iso}}$) obtained in the investigated temperature range (553–623 K for sample **1**; 443–533 K for sample **2**; 453–533 K for samples **3** and **4**) were treated according to the Eq. (1), giving rise, for each polymer, to linear $\ln t = f(1/T_{\text{iso}})$ relationships at the various selected degrees of degradation. The apparent activation energy obtained by the slope of the $\ln t$ versus $1/T_{\text{iso}}$ straight line, at each degree of degradation, and the corresponding linear regression coefficients are reported in Tables 2 and 3 for PET and PP samples, respectively.

Table 5 Regression coefficients of the $D = D_0 + \beta t$ equations at the various temperatures of isothermal experiments for the ($5 \leq D \leq 15$ %) degradation stage of samples **2**, **3** and **4**

T_{iso}/K	2			3			4		
	D_0	β/min^{-1}	r	D_0	β/min^{-1}	r	D_0	β/min^{-1}	r
443	-14.645	0.0861	0.9998	-	-	-	-	-	-
453	-8.6413	0.1591	0.9991	-9.8885	0.0585	0.9991	-12.724	0.0921	0.9995
463	-5.6514	0.2301	0.9991	-11.347	0.1231	0.9997	-8.2392	0.2332	0.9996
473	-3.7175	0.2762	0.9981	-1.5476	0.1731	0.9998	-5.8766	0.4257	0.9998
483	-1.7924	0.3838	0.9994	-4.4240	0.5814	0.9998	-5.8234	0.8468	0.9995
493	-0.9970	0.5395	0.9998	-3.6025	1.2768	0.9998	-2.8487	0.9941	0.9999
503	-0.1317	0.7326	0.9998	-3.3009	1.4458	0.9998	-3.4772	1.1196	0.9997
513	1.2919	1.0461	0.9982	-1.3250	2.2969	0.9995	-1.1561	2.0274	0.9998
523	0.5666	1.9215	0.9994	-0.2423	4.9156	0.9991	0.5863	3.0584	0.9994
533	1.6105	2.5708	0.9982	-2.0846	6.5105	0.9996	-0.6558	4.6391	0.9998

Table 6 Correlation coefficients of the $\ln \beta = \ln A - B/T_{\text{iso}}$ Arrhenius-type equation and corresponding degradation E_a values

Sample	$\ln A$	$B \times 10^{-3}$	r	$E_a/\text{kJ mol}^{-1}$
1 ^a	17.2 (± 1.3)	11.3 (± 0.8)	0.9867	94 (± 7)
2 ^b	16.6 (± 0.8)	8.4 (± 0.4)	0.9919	70 (± 3)
3 ^c	29.3 (± 1.5)	14.5 (± 0.7)	0.9908	120 (± 6)
4 ^c	21.9 (± 1.4)	10.8 (± 0.7)	0.9851	90 (± 6)

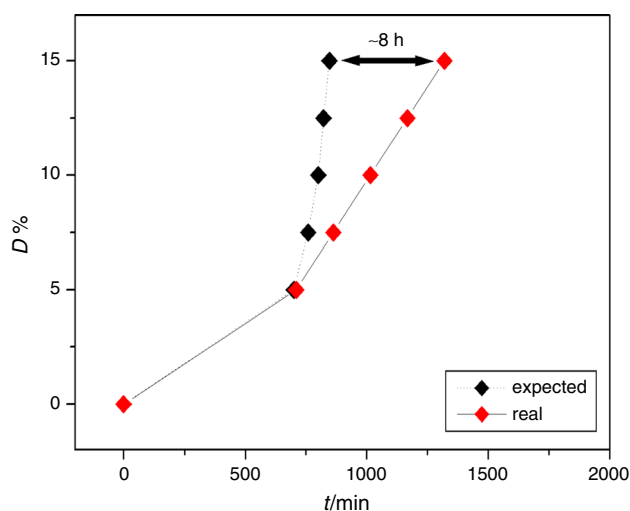
^a Determined in the range 553–623 K^b Determined in the range 443–533 K^c Determined in the range 453–533 K**Table 7** Degradation E_a values (kJ mol^{-1}) for the studied samples determined by Arrhenius and MacCallum (average values) methods

Sample	Arrhenius	MacCallum
1	94 (± 7)	101 (± 8)
2	70 (± 3)	94 (± 2)
3	120 (± 6)	125 (± 8)
4	90 (± 6)	107 (± 8)

The same experimental mass loss data at various times of isothermal degradations were used to calculate degradation E_a values according to the method we set up in the past [14–18]. These data were, at first, simply transformed all together in D values and then fitted into appropriate $D = f(t)$ equations; in Fig. 3 are reported as example the isothermal degradations of sample **1**, **2**, **3** and **4** at 593 and 473 K, respectively. The obtained linear relationships

$$D = D_0 + \beta t \quad (2)$$

at various temperatures are reported in Tables 4 and 5, for all samples, together with the corresponding regression

**Fig. 4** Real versus expected (extrapolated from MacCallum equations) percentage of degradation for sample **2**

coefficients. The coefficient of time β , whose dimensions are t^{-1} , then representing a measure of decomposition rate, increased exponentially as a function of $-1/T_{\text{iso}}$, thus giving rise to

$$\ln \beta = \ln A - B/T_{\text{iso}} \quad (3)$$

Arrhenius-type equations. E_a degradation values, thus derived, and the corresponding linear regression coefficients for the considered degradation degree ranges are reported in Table 6.

In Table 7, the degradation E_a values determined by both MacCallum and Arrhenius methods are listed for comparison. The apparent activation energy values reported for the MacCallum method were averaged from those obtained at various degrees of conversion in the considered

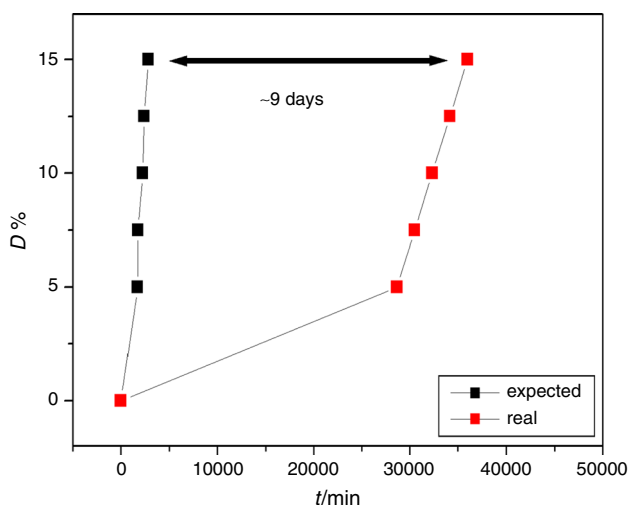


Fig. 5 Real versus expected (extrapolated from MacCallum equations) percentage of degradation for sample 3

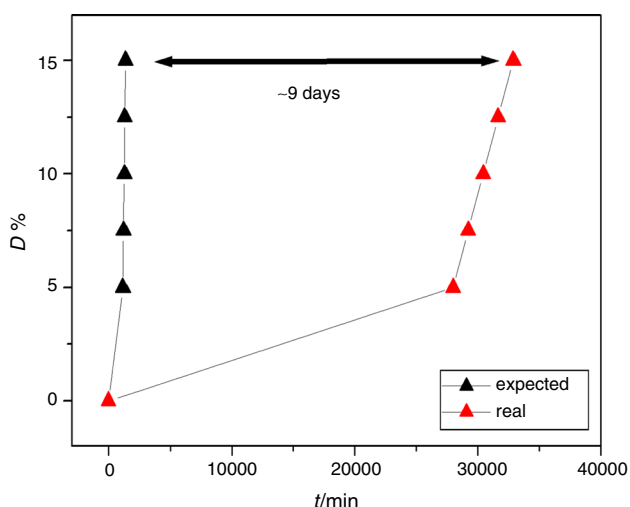


Fig. 6 Real versus expected (extrapolated from MacCallum equations) percentage of degradation for sample 4

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 7 are conflicting, indicating good agreement between the values obtained, with the two different methods, for two of the four polymers tested (samples 1 and 3), while quite different E_a of degradation values were obtained for samples 2 and 4. It is worth noting that increasing the activation energy value increases the agreement between the two methods, while for low E_a values, the gap between the two methods widens. Then, one can hastily conclude that the possibility to extrapolate the degradation behavior of the polymer at lower temperatures, and perform a lifetime prediction, it is more likely to succeed at the highest values of E_a and thus on decreasing the degradation

kinetics. By contrast, the difference of 24 kJ mol^{-1} found for sample 2, with the two methods, may suggest a chancy prediction in this case.

In order to try to make things clear about the possibility to realize polymer lifetime prediction, the data extrapolated from the MacCallum equations were compared with the degradation data measured in the last 25 months. The trend of the real degradation and that extrapolated by MacCallum equations, obtained through the short-term experiments at the same degree of degradation, is shown in Figs. 4–6 for samples 2, 3 and 4, respectively. The same trend was not reported from sample 1 for which the higher glass transition and onset temperatures in respect to those of the other studied samples and to temperature of long-term experiment make comparison not possible. From the above-reported figures, it is possible to note that very different results have been obtained for the various studied polymers. If the PET bottle label sample shows a certain reliability in the lifetime prediction (Fig. 4), the PP samples show instead a huge time lag from the forecast (Figs. 5 and 6), in the same considered degradation range (5–15%). Similar differences between the real and the expected trend of degradation were observed for samples 3 and 4. Indeed, both the PP tray sample (Fig. 5) and that of the lid (Fig. 6) show 9 days of deviation from the prevision based on extrapolations from tests performed at higher temperatures. These results show that it is far from easy to quantify the uncertainty in the lifetime predictions, ranging from the acceptable 8 h of difference to the daunting 9 days.

Conclusions

The examined commercial samples of PP have reached a degree of degradation of 15 %, in the neighborhood of their melting temperature, after approximately 25 days, thus suggesting the impossibility of performing degradation experiments below the glass transition temperature in a reasonable time. PET bottle label (sample 2) showed the 15 % of mass loss after only 36 h, while PET bottle (sample 1), which, however, has an onset temperature much greater than that used for the isothermal measurement, did not show appreciable degradation after 736 days of experiment, thus indicating caution in the comparison of measurements made above and below the polymer melting. 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 PET and PP polymers used in food and beverage packaging, the questionability of lifetime predictions based on measurements at higher temperatures. It seems evident that extreme caution is necessary in the use of degradation E_a values extrapolated

to lower temperatures from measurements at higher ones in doing ruminations about the polymer degradation rate. Finally in the future, through this kind of experiments (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, and, why not, obtain a series of correction factors for the kinetic parameters achieved through short-term measurements.

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