

# Thermal degradation of polypropylene/starch-based materials with enhanced biodegradability

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## Abstract

Blends of polypropylene (PP) and starch-based biodegradable materials were tested for biodegradability under soil burial test conditions. By means of thermogravimetric analysis, we evaluated the thermal stability of the PP matrix, of the additive and of the blends before and after the soil burial test. The kinetic parameters associated with thermal degradation were determined using integral isoconversional methods. We present a methodology that allows the kinetic triplet to be determined on the basis of non-isothermal experiments, and which gives results similar to those obtained in isothermal experiments. The kinetic parameters show the effect of degradation in soil on the blends studied. All the materials studied decompose by a type  $R_n$  mechanism in a nitrogen atmosphere and a type  $A_n$  mechanism in an oxygen atmosphere. The biodegradation was seen to affect the starch of the additive and not the PP matrix.

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## 1. Introduction

Most synthetic polymers are designed and manufactured to withstand environmental degradation. In general, these materials have a short useful life, in many cases of less than two years. These two facts have led, in recent years, to a significant increase in the amount of plastic waste. A number of strategies may be used to counter this problem.

A suitable option, from an ecological and economic perspective, would be to collect, separate and recycle some of these materials. Because of their excellent properties, polyethylene (PE) and polypropylene (PP)

are used in a wide range of applications, such as agriculture, the automobile industry, packaging, etc. They are generally recycled, although the process is complex and has one major drawback: the materials are degraded by use and by the recycling process [1,2]. The thermal and mechanical properties of recycled materials are inferior to those of virgin products. The recycled materials must therefore be treated and restabilised. It is therefore necessary to ascertain the thermal stability of the polymers before and after their use and after they are recycled [3,4]. Pyrolysis, combustion and gasification of carbon-rich waste are particularly important treatments for elimination and reuse. This procedure allows gaseous fuels and/or energy to be obtained with a notable reduction in waste. A first step in carrying out these processes is to ascertain the thermal degradation of these materials under a variety of conditions and to determine the kinetics. Thermogravimetric analysis is the technique

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most commonly employed to determine kinetic parameters and it has been widely used to ascertain the thermal decomposition of polyolefins [5–8].

Polyolefins are known to be sensitive to thermal oxidation, due to the impurities generated during their manufacture at high temperatures. Despite this fact, their slow abiotic oxidation rate means that they should be classed as non-biodegradable polymers [9,10]. A possible solution to the considerable amount of polyolefin waste would be to induce a certain level of biodegradability by adding biodegradable additives in the form of masterbatches [11] and/or pro-oxidants [12]. The most commonly employed additives are made of starch and other components.

The useful life of polyolefins with enhanced biodegradability is determined by the changes that their physical and chemical properties undergo during the degradation process. The changes observed in the structure, morphology and mechanical and thermal properties of these polyolefins must be analysed in order to elucidate the degradation mechanism.

Several authors have studied the accelerated degradation in soil of PE and PP with a variety of biodegradable additives, such as Bioeffect, Mater-Bi, etc. In general, the degradation process affects the thermal stability, mechanical properties, crystallinity and lamellar thickness distribution and begins in the amorphous/crystalline interface. In these systems, the properties of the polyolefin matrix suffer practically no modifications during the degradation process, which does, conversely, alter the properties of the starch in the additive [13,14].

For this paper, we studied the accelerated degradation in soil of blends of PP and a biodegradable additive commercially known as Mater-Bi AF05H. The biodegradability of this additive has been proved in various environments, although its slow degradation rate in humid environments means that it cannot be classed as compostable [15,16]. In a previous paper [17], this same system, PP/Mater-Bi, was studied by differential scanning calorimetry (DSC), and the process of degradation in soil was shown to increase the crystallinity of the material up until the fourth month, when it became stable or fluctuated slightly. During the degradation process, all the alterations take place in the starch of the additive and not in the polymeric matrix, which remains unchanged.

In the present paper, thermogravimetric analysis was used to assess the thermal stability of the PP/Mater-Bi blends before and after degradation in soil and of the pure components. The aim was twofold: firstly, to determine how the biodegradation process affects the thermal stability of the materials, and secondly, to gain any information on the potential ability of these materials to be recycled and/or used as fuel and therefore eliminated. The last thing may be deduced from the kinetics associated with the thermal and thermooxidative degradation processes.

## 2. Theoretical analysis

The rate of degradation or conversion, in thermogravimetric analysis,  $d\alpha/dt$ , can be defined as the variation in the degree of conversion with time or temperature. The degree of degradation or conversion is calculated in terms of mass loss as

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty} \quad (1)$$

where  $W_0$ ,  $W$  and  $W_\infty$  are, respectively, the initial weight, the actual weight at each point of the curve and the final weight measured at the end of the degradation process.

Accepting the Arrhenius equation, the kinetic of the reaction is usually described by the rate equation

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2)$$

where  $t$  is time,  $A$  is the pre-exponential factor,  $E$  is the activation energy,  $T$  is the absolute temperature,  $R$  is the gas constant and  $f(\alpha)$  is the differential conversion function.

In general, the kinetic analysis was carried out using an isoconversional method. The basic assumption of these methods is that the reaction rate at constant conversion is solely a function of the temperature [18].

### 2.1. Isothermal methods

By integrating the rate equation, Eq. (2), under isothermal conditions, we obtain

$$\ln t = \ln \left[ \frac{g(\alpha)}{A} \right] + \frac{E}{RT} \quad (3)$$

where  $g(\alpha)$  is the integral conversion function defined as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (4)$$

According to Eq. (3), the activation energy and the constant  $\ln[g(\alpha)/A]$  can be obtained, respectively, from the slope and the intercept of the linear relationship  $\ln t$  against  $T^{-1}$  for  $\alpha = \text{constant}$ .

### 2.2. Non-isothermal methods

By integrating the rate equation, Eq. (2), under non-isothermal conditions and then reordering it, the so-called temperature integral may be expressed as

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-(E/RT)} dT \quad (5)$$

where  $\beta$  is the heating rate.

By using the Coats–Redfern [19] approximation to solve Eq. (5) and considering that  $2RT/E \ll 1$ , this equation may be rewritten as

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[ \frac{AR}{\beta E} \right] - \frac{E}{RT} \quad (6)$$

For a given kinetic model, the linear representation of  $\ln[g(\alpha)/T^2]$  against  $T^{-1}$  makes it possible to determine  $E$  and  $A$  from the slope and the ordinate at the origin.

By reordering Eq. (6), we can write

$$\ln \frac{\beta}{T^2} = \ln \left[ \frac{AR}{g(\alpha)E} \right] - \frac{E}{RT} \quad (7)$$

The linear representation of  $\ln[\beta/T^2]$  against  $T^{-1}$  makes it possible to determine  $E$  and the kinetic parameter  $\ln[AR/g(\alpha)E]$  for every conversion degree. This isoconversional procedure is equivalent to Kissinger's method [20] and similar to Ozawa's method [21,22].

Once  $g(\alpha)$  is known, Eq. (7) can be applied to the temperature of the peak (maximum reaction rate). If the degree of conversion in the peak does not vary with the heating rate, the representation of  $\ln[\beta/T_p^2]$  against  $T_p^{-1}$  allows us to determine  $E$  and  $A$  [22].

The constant  $\ln[AR/g(\alpha)E]$  is directly related by  $R/E$  to the constant  $\ln[g(\alpha)/A]$  of the isothermal adjustment, Eq. (3). Thus, taking the dynamic data  $\ln[AR/g(\alpha)E]$  and  $E$  and applying Eq. (7), we can determine the isoconversional lines, Eq. (3), and simulate isothermal curing [23,24].

By combining Eqs. (2) and (6) without logarithms, as described by Criado [25], we can obtain reduced master curves of the type

$$\frac{z(\alpha)}{z(0.5)} = \frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)} = \left( \frac{T}{T_{0.5}} \right)^2 \frac{(d\alpha/dt)}{(d\alpha/dt)_{0.5}} \quad (8)$$

where 0.5 refers to the conversion of 0.5.

The left side of Eq. (8),  $f(\alpha)g(\alpha)/f(0.5)g(0.5)$ , is a reduced theoretical curve, which is characteristic of each reaction mechanism, whereas the right side of the equation associated with the reduced rate can be obtained from experimental data. A comparison of both sides of Eq. (8) tells us which kinetic model describes an experimental reactive process. Table 1 indicates the algebraic expressions of  $f(\alpha)$  and  $g(\alpha)$  for the kinetic models used.

Table 1  
Algebraic expressions for  $f(\alpha)$  and  $g(\alpha)$  for the kinetic models used

Models	$f(\alpha)$	$g(\alpha)$
A <sub>1.5</sub>	$2(1-\alpha)[- \ln(1-\alpha)]^{1/3}$	$[- \ln(1-\alpha)]^{1/3}$
A <sub>2</sub>	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
A <sub>3</sub>	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{2/3}$
R <sub>2</sub>	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R <sub>3</sub>	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
D <sub>1</sub>	$1/2(1-\alpha)^{-1}$	$\alpha^2$
D <sub>2</sub>	$-\ln(1-\alpha)$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D <sub>3</sub>	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)]^{-1/3}$	$[1-(1-\alpha)^{1/3}]^2$
D <sub>4</sub>	$3/2(1-\alpha)^{1/3}[1-(1-\alpha)]^{-1/3}$	$(1-2/3\alpha)(1-\alpha)^{2/3}$
F <sub>1</sub>	$(1-\alpha)$	$-\ln(1-\alpha)$
power	$2\alpha^{1/2}$	$\alpha^{1/2}$
n+m=2; n=1.9	$\alpha^{0.1}(1-\alpha)^{1.9}$	$[(1-\alpha)\alpha^{-1}]^{-0.9}(0.9)^{-1}$
n+m=2; n=1.5	$\alpha^{0.5}(1-\alpha)^{1.5}$	$[(1-\alpha)\alpha^{-1}]^{-0.5}(0.5)^{-1}$
n=1.5	$(1-\alpha)^{1.5}$	$2[-1+(1-\alpha)^{-1/2}]$
n=2	$(1-\alpha)^2$	$-1+(1-\alpha)^{-1}$
n=3	$(1-\alpha)^3$	$2^{-1}[-1+(1-\alpha)^{-2}]$

### 3. Experimental

#### 3.1. Materials

Polypropylene 1148-TC (PP) supplied by BASF (Germany) was blended with Mater-Bi AF05H supplied by Novamont North America (USA). Mater-Bi AF05H is a starch-based additive that contains highly complexed thermoplastic starch with ethylene-vinyl-alcohol copolymers (EVOH), with a starch content close to 50% in weight.

A homogeneous mixture with 50/50 PP/Mater-Bi AF05H by weight was initially prepared from the melt in a Brabender Plasticorder PL 2100 rheometer. Afterwards, the blend was cut as nut coal and compression-moulded into rectangular bars (68 × 12 × 1.8 mm) using an M Carver press. This methodology was followed in a previous work [13,17].

Samples of pure PP and Mater-Bi AF05H were also compression-moulded from pellets to be used as control materials. Both pure and blended samples were taken

apart to compare them with samples that were aged in soil.

### 3.2. Soil burial test

Soil burial tests were carried out according to the DIN 53739 International Norm [26] over a period of one year. The soil used in these tests was a red soil extract taken from a culture field in Alginet (Valencia). The boxes were kept in a Hereaus B12 culture oven at a constant temperature of  $28 \pm 0.5$  °C, and the pH and water content of the soil were controlled periodically. We measured the pH values of a soil extract dissolved in distilled water at a proportion of 1:20. The soil was maintained at approximately pH 7 and a relative humidity of 0.87 g water/g wet soil.

The samples were removed after different time periods: 20 days and 4, 6, 8, 10 and 12 months. The pure samples were only removed at the end of the test. After removal, all the samples were carefully washed with a soap solution in order to stop the degradation process and were blotted before analysis.

### 3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were carried out in a Mettler TG50 thermobalance linked to a Mettler TA4000 thermal analysis system. Isothermal degradations of PP were carried out for different times at temperatures of 300, 325, 350, 375 and 400 °C in a nitrogen atmosphere. Non-isothermal degradations of PP, Mater-Bi and PP/Mater-Bi were carried out at heating rates of 0.5, 0.75, 1.5, 2.5, 5, 10, 15, 25 and 50 °C min<sup>-1</sup>, between 25 and 600 °C, in nitrogen and oxygen atmospheres. The precision of reported temperatures was estimated to be  $\pm 2$  °C. The mass of the samples was approximately 10 mg and the gas flux 200 cm<sup>3</sup> min<sup>-1</sup> (measured under normal conditions).

## 4. Results and discussion

A preliminary analysis of the thermal stability of pure PP was carried out in order to establish an analytical methodology and to determine the behaviour of the polymeric matrix before blending and biodegrading. PP degraded in a single stage under both isothermal and non-isothermal conditions. Isoconversional kinetic parameters were obtained by isothermal experiments at different temperatures and by applying Eq. (3) at different degrees of conversion. Table 2 details these parameters. The continuity observed in the kinetic parameters during the thermal degradation process indicates that the process takes place in a single elemental stage. Fig. 1 shows the experimental degree of conversion–time curves,  $\alpha-t$ , at various temperatures, as well as those simulated from kinetic isothermal parameters (Table 2). The optimal regressions obtained (Table 2) and the effective simulation (Fig. 1) indicate that the methodology used is suitable for the purpose of describing the kinetics of degradation.

A drawback, however, is that this methodology does not provide the pre-exponential factor,  $A$ , but only the parameter  $\ln[g(\alpha)/A]$ , which contains  $A$  and the integral function of the degree of degradation  $g(\alpha)$ . Furthermore, it is difficult to establish optimum degradation temperatures in complex systems such as blends, which undergo various processes of degradation. If low temperatures are used, the more stable components do not degrade, whereas if high temperatures are used, all the components degrade simultaneously and so it is not possible to distinguish the components on the basis of their stability.

In an attempt to solve these two problems, the degradation of PP was studied by means of experiments at different heating rates. Fig. 2 shows the degree of conversion–temperature curves,  $\alpha-T$ , at various heating rates, and the derivative of these curves, referred to as the DTG curve. By applying Eq. (7) to different

Table 2

Isothermal and non-isothermal kinetic parameters associated with the thermal degradation of the polypropylene in a nitrogen atmosphere

$\alpha$	Isothermal			Non-isothermal <sup>a</sup>				
	$E$ (kJ mol <sup>-1</sup> )	$\ln[g(\alpha)/A]$ (min)	$r$	$E$ (kJ mol <sup>-1</sup> )	$\ln[AR/g(\alpha)E]$ (K <sup>-1</sup> min <sup>-1</sup> )	$\ln[g(\alpha)/A]$ (min)	$\ln A^b$ (min <sup>-1</sup> )	$r$
0.1	90	-15.0	0.996	91	5.9	-15.2	11.8	0.996
0.2	95	-15.2	0.999	94	5.9	-15.2	12.6	0.998
0.3	95	-15.0	0.999	95	5.7	-15.1	12.9	0.998
0.4	95	-14.8	1.000	95	5.5	-14.9	13.0	0.999
0.5	95	-14.5	1.000	96	5.6	-14.9	13.3	0.999
0.6	95	-14.4	1.000	97	5.6	-15.0	13.6	0.999
0.7	95	-14.3	1.000	98	5.6	-14.9	13.8	0.999
0.8	96	-14.2	0.999	99	5.6	-15.0	14.1	0.998
0.9	98	-14.5	0.999	101	6.0	-15.4	14.7	0.998

<sup>a</sup> To determine the non-isothermal parameters, thermogravimetric curves were used at heating rates of 0.5, 0.75, 1.5, 2.5 and 5 °C min<sup>-1</sup>, since it is within this range of rates that the temperatures of degradation are similar to those used isothermally.

<sup>b</sup>  $\ln A$  was determined for the kinetic model R<sub>2</sub>.

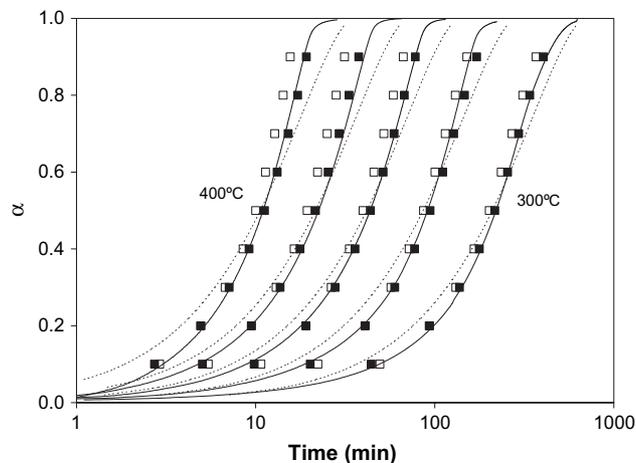


Fig. 1. Experimental and simulated degrees of conversion versus time for pure PP degraded in a nitrogen atmosphere at different temperatures (400, 375, 350, 325 and 300 °C). (—) Experimental isothermal curves. (■) Isoconversional isothermal data obtained by Eq. (3). (□) Isoconversional non-isothermal data obtained by Eq. (7). (—) Curves obtained by using function  $R_2$  and the non-isothermal kinetic parameters,  $E$  and  $A$ , obtained at the maximum of the DTG curve.

values of  $\alpha$ , the dynamic kinetic parameters and the isothermal parameters can be calculated from them by the combined application of Eqs. (3) and (7) (Table 2). As shown, the non-isothermal parameters  $E$  and  $\ln[g(\alpha)/A]$  are similar to the isothermal parameters. Fig. 1 shows the good results given by the isoconversional simulation of the isothermal curves  $\alpha-t$  from non-isothermal data.

To obtain a kinetic model we used the reduced master curves in Eq. (8). Fig. 3 compares the theoretical curves (left side of Eq. (8)) to the experimental curves (right side of Eq. (8)) obtained from the data in Fig. 2. PP degrades following a kinetic model of surface control type  $R_2$ . Knowing the kinetic model and the isoconversional data, the pre-exponential factor can be determined for each conversion (Table 2).

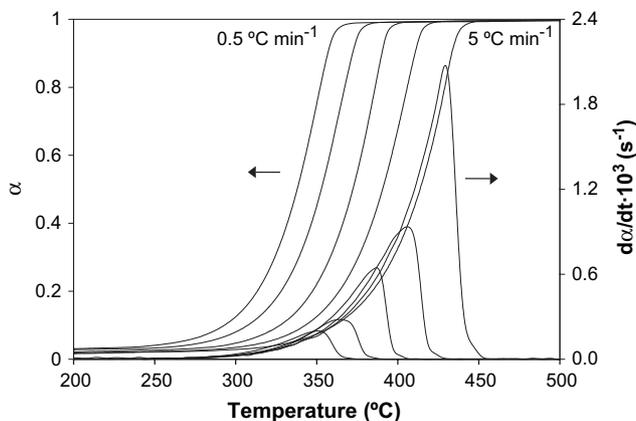


Fig. 2. Degree of conversion versus temperature and DTG curve in a nitrogen atmosphere for pure PP at 0.5, 0.75, 1.5, 2.5 and 5 °C  $\text{min}^{-1}$ .

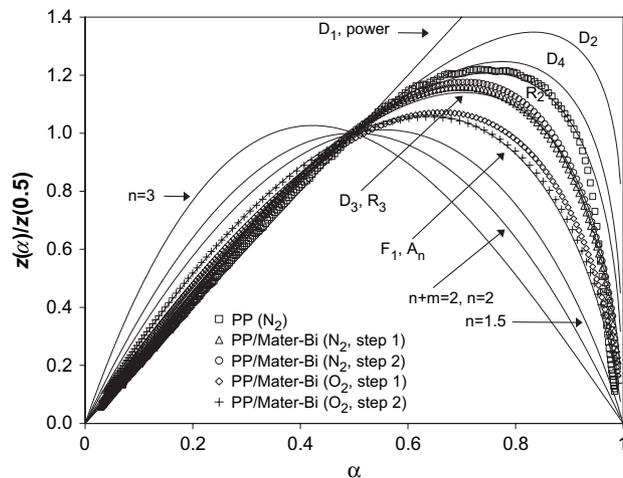


Fig. 3. Reduced master curves of different kinetic models and experimental data at different atmospheres at 10 °C  $\text{min}^{-1}$  calculated by Eq. (8) for PP without degradation in soil and for PP/Mater-Bi after 12 months of degradation in soil.

A quicker alternative for carrying out kinetic calculations is simply to determine the kinetic triplet ( $E$ ,  $A$ ,  $g(\alpha)$ ) for the conversion associated with the maximum rate of degradation. For PP, the application of Eq. (7) to the maximum of the DTG curve (Fig. 2) has allowed the following kinetic parameters to be obtained:  $E = 96 \text{ kJ mol}^{-1}$ ,  $\ln[AR/g(\alpha)E] = 4.8 \text{ K}^{-1} \text{ min}^{-1}$ ,  $r = 0.999$ ,  $\ln[g(\alpha)/A] = -14.2 \text{ min}$  and  $\ln A = 13.6 \text{ min}^{-1}$  (for a kinetic model of type  $R_2$ ). As the kinetic parameters only vary slightly on conversion, the isothermal degradation was simulated using only  $E$  and  $A$ , obtained from the maximum and the kinetic model  $R_2$ . Fig. 1 shows that, although the simulation is not as precise as the isoconversional, the degradation process can still be perceived in sufficient detail.

The latter procedure was employed to compare the thermal stability of the samples before and after the blending and biodegradation processes. Fig. 4 shows the  $\alpha-T$  and DTG curves in a nitrogen atmosphere, at different heating rates, for the PP/Mater-Bi system degraded in soil over a period of 6 months. Similar curves were obtained for the other blends studied (figures not shown). The existence of various overlapping degradation processes does not permit the use of isothermal procedures and complicates the non-isothermal determination of the complete kinetic triplets associated with each degradation process. Firstly, we separated the overlapping processes by deconvoluting the DTG curve. To do so, we used the Peak.fit programme by Jandel Scientific Software, which has a mathematical function known as “asymmetric logistic amplitude” [22]. Fig. 5 shows, by way of example, the separation of peaks of the DTG curve at 10 °C  $\text{min}^{-1}$  in an  $\text{N}_2$  atmosphere for the PP/Mater-Bi samples biodegraded over 12 months. The sum of the separated curves reproduces the

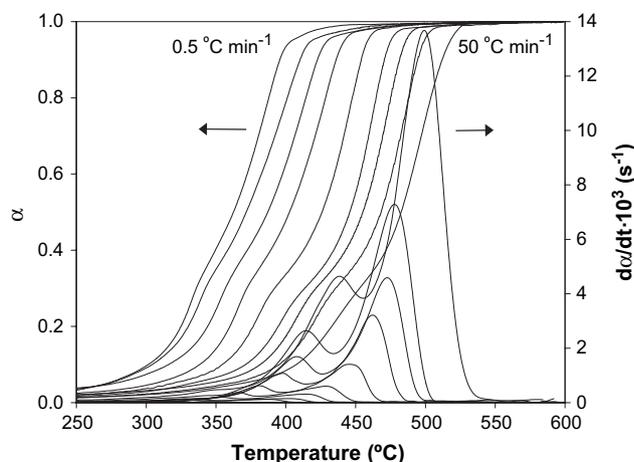


Fig. 4. Degree of conversion versus temperature and DTG curve in a nitrogen atmosphere at 0.5, 0.75, 1.5, 2.5, 5, 10, 15, 25, 50 °C min<sup>-1</sup> for PP/Mater-Bi after 6 months of degradation in soil.

experimental signal exactly. Similar results were obtained for all the systems studied, at various heating rates and in nitrogen and oxygen atmospheres. Once the peaks were separated, the kinetic model was determined by applying Eq. (8) to each peak. The rest of the kinetic triplet was determined for each degradation process by applying Eq. (7) to the maximum of the DTG curve at various heating rates. Table 3 contains the kinetic data obtained by following this procedure.

Fig. 3 shows, by way of example, some of the kinetic models that follow the separate processes in both nitrogen and oxygen atmospheres. We can see how it is not always possible to elucidate the exact reaction mechanism. For example, in a nitrogen atmosphere the degradation may be of type R<sub>3</sub> or D<sub>3</sub> and in an oxygen atmosphere of type F<sub>1</sub> or A<sub>n</sub>. In these cases, we used the Coats–Redfern method (Eq. (6)) to discern the kinetic model that the process follows. For the possible models,

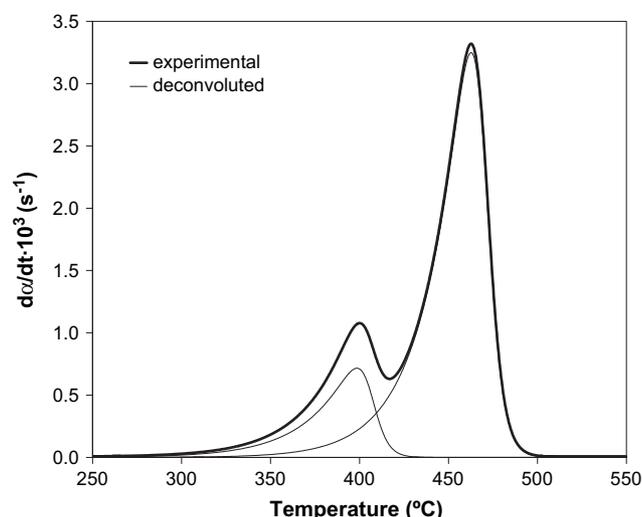


Fig. 5. Deconvolution of the overall kinetic process in different peaks. Thermal degradation in nitrogen at 10 °C min<sup>-1</sup> of PP/Mater-Bi after 12 months of degradation in soil.

Eq. (6) was represented and  $E$  and  $\ln A$  were determined from the slope and the coordinate origin. As all the models provide good regressions, we took that which gives a value of  $E$  similar to that obtained by isoconversional method at the maximum (Table 3). Table 4 exhibits the results obtained in an oxygen atmosphere by the Coats–Redfern method for the PP/Mater-Bi system degraded in soil over a period of 12 months. The models used for the first and second stage were A<sub>2</sub> and A<sub>1.5</sub>, respectively. Using other heating rates gives similar results. Following the same criteria, an R<sub>3</sub> model was set for the two stages in all the PP/Mater-Bi systems (in a nitrogen atmosphere). The D<sub>3</sub> model was ruled out because its  $E$  value is much greater than the isoconversional  $E$  value.

Fig. 6 shows the TG and DTG curves at 10 °C min<sup>-1</sup> of the pure components (PP and Mater-Bi) and of the

Table 3

The calorimetric and kinetic parameters associated with the thermal degradation and thermal oxidation of several of the systems studied

System <sup>a</sup>	Time	Step 1 <sup>b</sup>					Step 2 <sup>b</sup>						
		$T_p^c$ (°C)	$E$ (kJ mol <sup>-1</sup> )	$\ln[AR/g(\alpha)E]$ (K <sup>-1</sup> min <sup>-1</sup> )	Model	$\ln A$ (min <sup>-1</sup> )	$k_{400}^d$ (min <sup>-1</sup> )	$T_p^c$ (°C)	$E$ (kJ mol <sup>-1</sup> )	$\ln[AR/g(\alpha)E]$ (K <sup>-1</sup> min <sup>-1</sup> )	Model	$\ln A$ (min <sup>-1</sup> )	$k_{400}^d$ (min <sup>-1</sup> )
PP (N <sub>2</sub> )	0 days	—	—	—	—	—	—	440	121	9.5	R <sub>2</sub>	18.4	0.0417
Mater-Bi (N <sub>2</sub> )	0 days	320	184	26.7	R <sub>3</sub>	35.5	15.02	447	265	33.4	R <sub>3</sub>	42.5	0.0074
PP/Mater-Bi (N <sub>2</sub> )	0 days	322	189	27.8	R <sub>3</sub>	36.6	17.87	462	180	18.6	R <sub>3</sub>	27.6	0.0094
PP/Mater-Bi (N <sub>2</sub> )	20 days	326	177	25.2	R <sub>3</sub>	33.5	6.85	462	179	18.4	R <sub>3</sub>	27.3	0.0096
PP/Mater-Bi (N <sub>2</sub> )	4 months	394	142	15.0	R <sub>3</sub>	23.8	0.19	460	174	17.9	R <sub>3</sub>	26.6	0.0108
PP/Mater-Bi (N <sub>2</sub> )	6 months	397	144	15.2	R <sub>3</sub>	24.2	0.20	462	172	17.3	R <sub>3</sub>	26.1	0.0100
PP/Mater-Bi (N <sub>2</sub> )	12 months	399	145	15.3	R <sub>3</sub>	23.9	0.14	462	173	17.6	R <sub>3</sub>	26.2	0.0093
PP/Mater-Bi (O <sub>2</sub> )	12 months	283	73	5.6	A <sub>2</sub>	15.0	—	429	341	48.2	A <sub>1.5</sub>	59.1	—

<sup>a</sup> The atmosphere in which the samples were degraded by heating is shown in brackets.

<sup>b</sup> The two stages of degradation are referred to as 1 and 2 in increasing order of temperature. In the nitrogen atmosphere, the first stage corresponds to the degradation of the starch of Mater-Bi and the second to the joint degradation of the PP and EVOH of Mater-Bi.

<sup>c</sup>  $T_p$  is the temperature of the maximum of the DTG curve at a rate of 10 °C min<sup>-1</sup>.

<sup>d</sup> To compare the results of the samples degraded in a nitrogen atmosphere, we calculated the rate constant at 400 °C,  $k_{400}$ , from the values of  $E$  and  $\ln A$  using the Arrhenius equation.

Table 4  
Kinetic parameters obtained using the Coats–Redfern method (Eq. (6)) at the rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  for the oxidative degradation of the PP/Mater-Bi system, which had previously been degraded in soil over a period of 12 months

Model	Step 1		Step 2	
	$E$ (kJ mol <sup>-1</sup> )	ln $A$ (min <sup>-1</sup> )	$E$ (kJ mol <sup>-1</sup> )	ln $A$ (min <sup>-1</sup> )
F <sub>1</sub>	155	33.1	525	90.2
A <sub>1.5</sub>	100	20.8	346	59.1
A <sub>2</sub>	73	15.5	257	43.5
A <sub>3</sub>	46	8.2	167	27.8

blend of both in a nitrogen atmosphere without degradation in soil. Mater-Bi shows two degradation processes. By comparing these with the pure components and on the basis of data in the relevant literature we associated the first to starch and the second to EVOH [27]. There are also two processes in the blend; the first corresponds to starch and the second to the joint degradation of EVOH and PP. The increase observed in the thermal stability of the material subsequent to the blending process suggests some form of chemical or physical interaction between EVOH and PP. This fact suggests that the blends are suitable for recycling, even without restabilising them [28]. Table 3 shows the kinetic parameters associated with these degradation processes. The values of  $E$ , ln  $A$  and  $k_{400}$  associated with starch (Step 1) are almost identical in the blend and in the pure Mater-Bi, whereas the parameters associated with the PP + EVOH (Step 2) blends present intermediate values with respect to the pure components. To compare the thermal stability of various systems and/or processes  $E$  should not be used exclusively, because of the compensating effect that exists between  $E$  and  $A$ . An appropriate comparison, in systems that have the same reaction mechanism, would use the rate constant  $k$ , which would include both

parameters. In this paper, we used the rate constant at  $400\text{ }^{\circ}\text{C}$ ,  $k_{400}$ , for this comparison. In the blend without degradation in soil, the starch and the PP + EVOH processes show similar activation energies, which would suggest that their thermal stability is similar. In contrast, the  $k$  constant of starch is much higher than that of PP + EVOH, which is coherent with the fact that starch is much less stable.

Fig. 7 shows the thermogravimetric analysis in a nitrogen atmosphere of some of the blends degraded in soil over different periods. Table 3 shows, for these same systems, the kinetic data and the peak temperatures. The joint degradation of PP + EVOH always takes place at the same temperature. This result, together with the absence of carbonyl bands in the spectrum of FTIR after degrading the materials in soil, suggests that the PP matrix and EVOH are not affected by biodegradation. On the contrary, the thermal stability of starch increases considerably until the fourth month, after which it stays constant or increases slightly. This is in keeping with the fact that the biodegradation process basically takes place in the starch units, whilst PP and EVOH remain unchanged. Several authors obtained similar results for starch/poly(lactic acid) systems for degradation in soil over the period of one year. They demonstrated that the biodegradation process does not affect the poly(lactic acid) and only takes place in starch [29]. In a previous paper, for the PP/Mater-Bi system, we saw that increasing the degradation in soil period increases crystallinity, due to the fact that cracks begin in the amorphous region of starch [17]. Though the exact nature of the process undergone by starch was not determined, several of the processes that may compete during the degradation in soil are the following: crosslinking, hydrolysis due to the bonding  $\alpha(1-4)$  of amylose and amylopectin to produce cyclodextrins, the elimination of amylose units, which

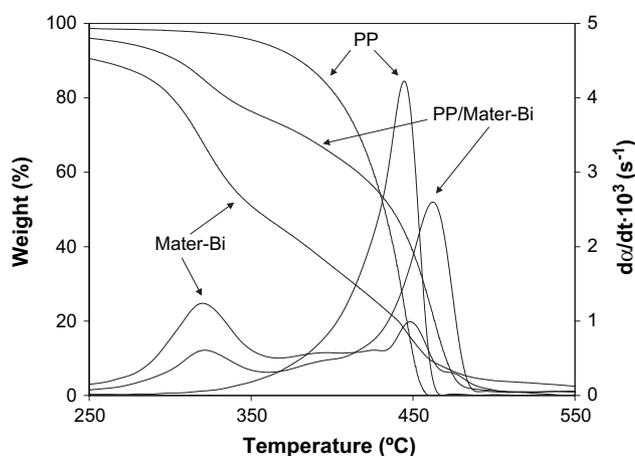


Fig. 6. TG and DTG curves in a nitrogen atmosphere at  $10\text{ }^{\circ}\text{C min}^{-1}$  for PP, Mater-Bi and PP/Mater-Bi without degradation in soil.

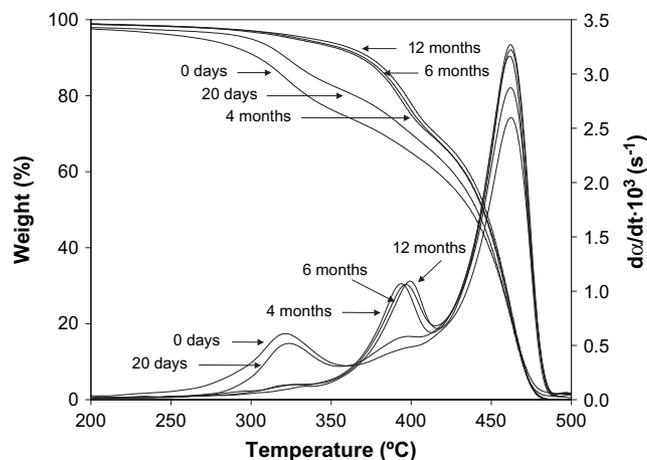


Fig. 7. TG and DTG curves in a nitrogen atmosphere at  $10\text{ }^{\circ}\text{C min}^{-1}$  for PP/Mater-Bi degraded in soil over different time periods.

increases the glass transition temperature of the material, etc. [30].

The kinetic parameters (Table 3) highlight the effect of the degradation in soil on the PP/Mater-Bi blends. The thermal degradation of PP + EVOH (Step 2) presents similar values for  $E$ ,  $\ln A$  and  $k_{400}$  for all the degradation times, since PP + EVOH is not affected by degradation in soil. The kinetic parameters for starch change until the fourth month and after this time remain almost constant, since the biodegradation only affects the thermal stability up until the fourth month. Once again, the magnitude of  $E$  cannot be taken as a comparative parameter;  $k_{400}$  should be used instead. For example, the decrease in  $E$  for starch up until the fourth month might be interpreted as an increase of the thermal degradation rate, when in reality the opposite happens. On the contrary, the decrease of  $k_{400}$  up until the fourth month is coherent with the decrease of the thermal degradation rate and therefore with the increase of the stability of starch. PP + EVOH presents a  $k_{400}$  value that is much lower than that of starch and are therefore more stable, despite their activation energy being of the same magnitude.

Fig. 8 shows the thermal oxidation of the blends. Over short periods of biodegradation, the process takes place in one sole stage at low temperatures, whereas over long periods a second stage appears at higher temperatures near the region where the material loses weight in a nitrogen atmosphere. These two stages cannot be attributed to the various components in the sample because they only appear in some cases. Therefore, the second stage should be associated with units that oxidised during the degradation in soil. These units have a high thermal stability and are not affected by oxygen until high temperatures are reached.

The kinetic parameters highlight the considerable differences between the degradation in a nitrogen

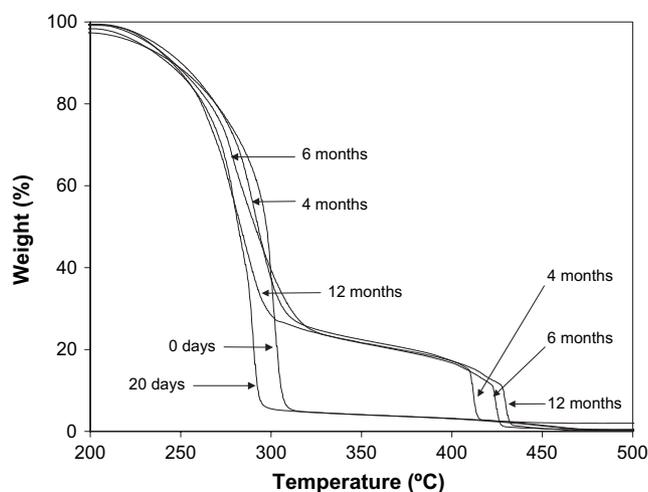


Fig. 8. TG curves in an oxygen atmosphere at  $10\text{ °C min}^{-1}$  for PP/Mater-Bi degraded in soil over different time periods.

atmosphere and an oxygen atmosphere and between the two stages in the oxygen atmosphere (Table 3). The pyrolysis in a nitrogen atmosphere follows a type  $R_n$  mechanism. This mechanism is decelerative and presents the maximum speed at the start, and then it decreases as the material runs out. Thermal oxidation presents a type  $A_n$  mechanism. This mechanism, which is typical of the autopropagation that exists in combustion, is sigmoidal and does not show the maximum rate at the start. Furthermore, the first stage of thermal oxidation presents very low values of  $E$  and of  $\ln A$ , whereas the second stage shows very high values of the same.

## 5. Conclusions

From the results, we can conclude that blends of PP and Mater-Bi subjected to biodegradation in soil undergo some type of transformation, which is demonstrated by an increase in their thermal stability in a nitrogen atmosphere.

The process of biodegradation essentially takes place in starch and does not significantly affect EVOH or PP. Until the fourth month of biodegradation, starch gains thermal stability and subsequently it remains practically unchanged.

In an oxygen atmosphere, the effect of the degradation in soil on the materials is made evident by the appearance, at high temperatures, of a second stage of degradation, in those samples subjected to long periods of biodegradation.

The thermal stability of the blends presents a synergic effect with respect to the pure components that does not obey any blending rules and which may be due to chemical and/or physical effects.

In a nitrogen atmosphere all the systems follow a kinetic model of surface control type  $R_n$ , whereas in an oxygen atmosphere the kinetic model is of sigmoidal type  $A_n$ .

In general, the kinetic parameters were a reflection of the following: (a) the influence of the atmosphere in which the experiment was carried out, (b) the composition of the blend, and (c) the process of degradation in soil.

The changes in the thermal stability and the kinetic data in nitrogen and oxygen atmospheres provided information on the three possible ways of eliminating waste: biodegradation, recycling and incineration.

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