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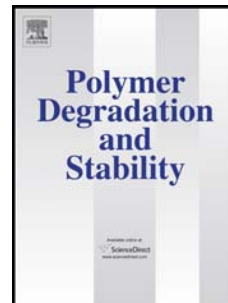
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THERMAL CHARACTERISATION OF THE OXO-DEGRADATION OF POLYPROPYLENE CONTAINING A PRO-OXIDANT/PRO- DEGRADANT ADDITIVE

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Abstract

The oxo-degradation process of polypropylene (PP) samples containing different concentrations (4% and 10% w/w) of pro-oxidant/pro-degradant additive EnvirocareTM AG1000C was investigated under accelerated test conditions. Samples were initially exposed to UV radiation for 300 hours. The tendency to biodegradation in soil medium of these UV-aged samples was then indirectly assessed by an indirect method for a period of 6 months. The entire degradation process of these materials was first examined by monitoring changes in their morphological properties (melting temperature, maximum lamellar thickness and crystallinity) with the aging time, by Differential Scanning Calorimetry (DSC). Then, changes in the thermal properties (onset temperature and maximum decomposition temperature) of these materials with the aging time were analysed by Thermogravimetric Analysis (TGA). Furthermore, the kinetics of the thermal decomposition of these PP samples with pro-oxidant/pro-degradant was also studied during the oxo-degradation process, by means of the Chang differential method. During exposure to UV radiation, the more significant changes in the morphological and thermal properties that were detected in PP samples containing

pro-oxidant/pro-degradant additive compared to pure PP, clearly suggest a higher level of oxidation in these samples, confirming the effectiveness of this pro-oxidant/pro-degradant additive in promoting the abiotic oxidation of polypropylene during UV-irradiation. Moreover, the level of oxidation observed in UV-aged samples seems to be dependent on the additive load.

On the other hand, during incubation in soil medium, changes in the morphological and thermal properties of previously photo-oxidized PP samples with pro-oxidant/pro-degradant were detected that indirectly support a certain progress of oxidation, indicating that previous abiotic oxidation can promote further degradation of the polypropylene matrix by soil microorganisms. In general, both morphological and thermal properties exhibit a non-linear dependency with the incubation time in soil, supporting the idea that biodegradation is a complex process that occurs in different stages. Furthermore, the extent of the changes in these properties during soil incubation was found to be proportional to the pro-oxidant/pro-degradant load and the previous photo-oxidation level.

Keywords:

Polypropylene (PP); pro-oxidant/pro-degradant additive; photo-oxidation; soil biodegradation; Differential Scanning Calorimetry (DSC); Thermogravimetric Analysis (TGA)

1. Introduction

The use of degradable polyolefins is an approach that has been recently developed to try to contribute to solve the environmental problem caused by the large quantities of these

plastic wastes [1-4]. These materials are designed to retain functionality during their processing, storage and service life, but to rapidly degrade to non-toxic products, once they are discarded. Degradable polyolefins can be obtained using special additives, called pro-oxidant/pro-degradants, that can be various complexes of transition metal ions, especially, Fe^{3+} , Co^{2+} and Mn^{2+} , in the form of salts of fatty acids [4,5]. Pro-oxidant/pro-degradants can accelerate the abiotic oxidation rate by catalyzing chain scission by light and/or heat. In particular, photo-oxidation can be initiated by Fe^{3+} , and thermo-oxidative degradation can be promoted by Co^{2+} and Mn^{2+} . As a consequence, low molecular weight oxidation products are rapidly formed [6-10], which are claimed to be easily biodegraded by microorganisms [3,4,11]. This degradation mechanism is called oxo-degradation. This term refers to a two stage process consisting of an initial oxidative degradation (which is normally abiotic), followed by the biodegradation of the oxidation products [12]. Although the abiotic and biotic degradative processes occur simultaneously, the abiotic oxidation is considered to be the rate-determining stage of the entire process. With an appropriate selection of the pro-oxidant/pro-degradant additive and its loading, it is expected to control the induction time required for a specific application.

The oxo-degradation process of polyethylene containing pro-oxidant/pro-degradant additives (especially LDPE formulations) is now well documented [13-34]. In contrast, studies on the abiotic [35-39] and biotic [40-43] degradability of polypropylene (PP) with pro-oxidant/pro-degradant additives are scarce as yet, although being this polyolefin one of the most widely used commodity polymers.

This work is aimed at investigating the entire degradation process of polypropylene containing a commercial pro-oxidant/pro-degradant additive, by first subjecting it to UV-irradiation and subsequently to an accelerated soil burial test. The oxo-degradation

process was examined by monitoring changes on the morphological and thermal properties of the polypropylene matrix, as a function of the aging time (both abiotic and biotic) and the additive load.

2. Material and methods

2.1. Materials

Test samples were injection-molded seedboxes of a commercial grade of polypropylene homopolymer (Moplen HP548S) manufactured by Basell with MFR = 35g/10min (230°C/2.16Kg ISO1133), containing different concentrations (4% and 10% w/w) of pro-oxidant/pro-degradant additive Envirocare™ AG1000C (samples A and B, respectively). Envirocare™ is an additive developed and marketed by Ciba Specialty Chemicals, which is based on the proprietary TDPA™ (Totally Degradable Plastic Additive) technology from EPI Environmental Products Inc. [4]. The TDPA™ technology utilizes a combination of transition metal carboxylate and an aliphatic poly(hydroxyl-carboxyl) acid as pro-degradant system, as disclosed in US patent 5854304 [44].

Additive-free polypropylene seedboxes were used as control samples (PP). All the samples were kindly supplied by SanSan Prodesing (Valencia, Spain). Test samples were cut into ~ 0.5 x 8 cm strips and subjected to accelerated abiotic and biotic degradation tests.

2.2. Accelerated photo-oxidation test

Samples containing pro-oxidant/pro-degradant and additive-free control samples were subjected to an accelerated photo-oxidation test using an Atlas XLS+ Suntest, equipped

with a xenon lamp emitting ultraviolet radiation at solar radiation wavelengths. The black body temperature was kept at 55°C. Samples were exposed to an average radiation of 478 W/m² for 100, 200 and 300 hours.

2.3. Accelerated soil burial test

Photo-oxidized and pristine samples containing pro-oxidant/pro-degradant additive were subjected to an accelerated soil burial test during 6 months, according to the DIN EN ISO 846:1997 European standard norm [45]. This is a method which merely assesses biodegradability of polymers indirectly, by monitoring changes in their physical properties due to the action of microorganisms. It is only valid therefore to confirm indirect biodegradability, intended as a change in the structural properties of the pristine polymer with the incubation time.

Samples were buried in biologically active soil in rectangular plastic boxes, which were kept opened to ensure a continuous fresh oxygen supply. The soil was a 50/50 % by weight mixture of a soil extract picked up from a culture field and a soil typically used in tree-nurseries for pine growth. The soil burial test was carried out in a Hereaus B12 culture oven at a constant temperature of $28 \pm 0.5^\circ\text{C}$, with periodical control of the pH and the water content of the soil. Photo-oxidized samples were removed every month, and pristine samples were removed every 3 months. After removal, samples were carefully washed with a soap solution to stop the degradation process and stored at room temperature in a desiccator before any analytical measurement.

2.4. Differential Scanning Calorimetry (DSC)

DSC measurements were carried out using a DSC-820 Mettler Toledo Calorimeter previously calibrated with indium standard. Three consecutive scans were performed

under nitrogen atmosphere with 5-7 mg of samples at a heating/cooling rate of 10°C/min. During the first scan, samples were heated from 0 °C to 200 °C to completely erase their thermal history. Then, samples were cooled from 200 °C to 0 °C and finally, samples were heated from 0 °C to 200 °C. Measurements were repeated at least twice with different samples. Thermal properties such as melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity (χ) were calculated from DSC traces recorded during the second heating scan. The melting temperature was determined as the maximum of the main endotherm. The crystalline content was obtained by dividing the melting enthalpy by the enthalpy of 100% crystalline polypropylene (ΔH_m^0), reported as 209 J/g [46]:

$$\chi = \frac{\Delta H_m}{\Delta H_m^0} \quad (1)$$

The maximum lamellar thickness (l_{\max}) of polypropylene was also determined according to the method proposed by Wlochowicz and Eder [47], based on the Thomson equation:

$$T = T^0 \cdot \left(1 - \frac{2\sigma_e}{\Delta H_m \cdot l} \right) \quad (2)$$

where T is the melting temperature of lamella of thickness l , T^0 is the equilibrium melting temperature of an infinite crystal, σ_e is the surface free energy of the basal plane and ΔH_m is the melting enthalpy per unit volume. Considering the values of these parameters for polypropylene [46] $T^0 = 460.7$ K, $\sigma_e = 49.6 \times 10^{-3}$ J/m² and $\Delta H_m = 1.34 \times 10^8$ J/m³, the maximum lamellar thickness corresponding to the melting temperature T_m can be calculated for each sample.

2.5. Thermogravimetric Analysis (TGA)

Thermogravimetric experiments were carried out using a Mettler Toledo TGA/SDTA 851e module. Dynamic measurements were performed from 25 °C to 600 °C at a heating rate of 10°C/min under Argon atmosphere (flow rate = 200ml/min). Measurements were repeated at least twice with 8-10 mg of different samples.

Thermogravimetric parameters such as residue and the extrapolated onset temperature (T_{onset}) [48] were directly calculated from TGA traces. The onset temperature corresponds to the temperature at which the weight loss begins and it is associated therefore to the beginning of the thermal decomposition of the material.

DTG curves were also obtained from the first derivative of the thermogravimetric curve. The maximum decomposition temperature (T_{max}) was determined as the maximum of the DTG curve, which corresponds to the maximum slope of the thermogravimetric curve, that is, to the temperature at which thermal degradation occurs with maximum degradation rate.

The characterization of the thermal decomposition of these materials was completed by performing a kinetic analysis. The kinetic of the reaction is usually described by the basic rate equation of chemical reactions:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

where α represents the degree of conversion, $k(T)$ is the rate constant and $f(\alpha)$ is the conversion function that depends on the reaction mechanism.

The degree of conversion is defined in terms of the mass loss as:

$$\alpha = \frac{\omega_0 - \omega}{\omega_0 - \omega_\infty} \quad (4)$$

where ω_0 , ω and ω_∞ are, respectively, the initial weight, the weight at time t and the final weight, measured at the end of the decomposition process.

Assuming that the temperature dependence of the rate constant is satisfactorily described by the Arrhenius equation, the kinetic of the reaction can often be given by the following rate equation:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot f(\alpha) \quad (5)$$

where A is the pre-exponential factor, R is the gas constant, T is the absolute temperature and E_a is the activation energy.

The simplest model used to describe the kinetic function $f(\alpha)$ is:

$$f(\alpha) = (1 - \alpha)^n \quad (6)$$

where n is the order of reaction, and its substitution to equation (5) gives:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot (1 - \alpha)^n \quad (7)$$

Methods that are based on equation (7) are denoted as differential methods, since they are directly deduced from a kinetic equation in its derivative form. In this study, the kinetic analysis of the thermal degradation of polypropylene was performed with the differential method proposed by Chang [49], which is based on the logarithm of equation (7):

$$\ln \left[\frac{\frac{d\alpha}{dt}}{(1-\alpha)^n} \right] = \ln A - \frac{E_a}{RT} \quad (8)$$

According to the Chang model, the plot of $\ln \left[\frac{d\alpha/dt}{(1-\alpha)^n} \right]$ against $1/T$ gives a straight line with a slope equals to $(-E_a/R)$ for each process, from which it is easy to obtain the corresponding activation energy, if the order of reaction is selected correctly. In that respect, Gao et al. [50] have shown that a first-order reaction model cannot be applied to properly describe thermal degradation of polypropylene. In contrast, the appropriate order of reaction for both, dynamic and isothermal thermal degradation of polypropylene, was determined by these authors to be $n = 0.35$.

3. Results and discussion

3.1. Characterization of pristine PP samples with pro-oxidant/pro-degradant

Pristine PP samples containing pro-oxidant/pro-degradant additive were initially characterized by DSC and TGA and compared to pure PP control samples, in order to assess the effect of this additive on the morphological and thermal properties of the polypropylene matrix.

3.1.1. Morphological properties

Initially, all the pristine samples display the typical DSC thermogram of polypropylene, consisting of a main endotherm with maximum around 160 °C and an overlapped shoulder at lower temperatures (around 140 °C). In general, the pro-oxidant/pro-

degradant additive does not modify substantially the calorimetric curve of polypropylene. Only a slight shift of the DSC thermogram towards higher temperatures is observed, that results in a slight increase of the melting temperature and, in turn, of the maximum lamellar thickness (Table 1). Furthermore, pristine samples containing pro-oxidant/pro-degradant additive also exhibit a slightly higher crystalline content (Table 1). The crystallization rate of polypropylene is increased by the presence of foreign particles in the melt (i.e. additives), that act as nucleation sites, and around which the polypropylene chains can crystallize [51]. Such a nucleating effect of the pro-oxidant/pro-degradant additive could explain the increased crystallinity of pristine samples A and B, compared to pure PP.

3.1.2. Thermal properties

Initially, all the pristine samples show the typical TGA runs of polypropylene, consisting of a single-step process. The thermal decomposition of pure PP starts at approximately 450°C, reaches its highest rate at 466°C and is almost completed at 600°C (residue <1%) (Table 2). Compared to pure PP, both the maximum decomposition temperature and the onset degradation temperature of PP with pro-oxidant/pro-degradant additive are reduced (Table 2). Particularly, the decrease in the onset degradation temperature is more significant. This indicates a lower thermal stability of these materials, probably as a result of the pro-degradative effect of this additive during processing. Similar results were obtained by Pablos et al. for LDPE and LLPDE samples containing Fe and Ca-stereate [14] and by Corti et al. for commercial LLDPE mulch films with pro-oxidant/pro-degradant additives [28]. Although the thermal decomposition of samples A and B also occurs with almost no residue remaining (~4%), the amount of residue is higher than for pure PP (Table 2). This suggests that the

origin of the residue of these samples is mainly the additive, which may not completely decompose in the temperature range of these experiments due to its inorganic components.

On the other hand, from the kinetic analysis performed using the Chang model, two different processes, with different activation energies, were found to be involved in the thermal degradation of polypropylene. These were denoted as stage 1 (from 359°C to 406°C) and stage 2 (from 412°C to 468°C), in order of increasing temperature. For pure PP, activation energy of 145 kJ/mol and 319 kJ/mol was obtained for stages 1 and 2, respectively (Table 3). The thermal decomposition of polypropylene is a very complex radical chain mechanism initiated by random chain scission and followed by radical transfer process, including midchain β -scission, end-chain- β -scission, radical addition, radical recombination and disproportionation [52,53]. Moreover, the presence of methyl side groups with low steric hindrance in polypropylene favours intramolecular hydrogen transfer [54] and intermolecular hydrogen abstraction [55] during its thermal degradation. All the aforementioned reactions have low activation energies since they are associated to the breakdown of less stable bonds [52,56]. Stage 1 displays similar activation energy and can consequently be ascribed to these low activation energy reactions. In contrast, activation energy of stage 2 is similar to carbon-carbon bond dissociation energy [52,56], and can therefore be assigned to random chain scissions in the carbon backbone, requiring higher activation energies.

Kinetic results also show that the pro-oxidant/pro-degradant additive causes a drop in the activation energy of the kinetic stage associated to the thermal breakdown of the carbon backbone (stage 2) (Table 3), confirming the idea that this additive promotes the thermal decomposition of polypropylene during processing, resulting in less thermally stable materials.

3.2. Abiotic degradation: photo-oxidation

3.2.1. Morphological changes

DSC experiments were performed to study first the morphological changes undergone by PP samples with and without pro-oxidant/pro-degradant additive during UV-irradiation. It was found that photo-oxidation only leads to slight changes in the DSC thermogram of pure PP. The DSC curve shape is qualitatively not modified, however it is slightly shifted towards lower temperatures [37,57-60]. In consequence, the melting temperature and the maximum lamellar thickness of pure PP tend to slightly decrease during photo-oxidation (Table 1). It is generally accepted that oxidation, although mainly occurring in the amorphous phase due to its higher oxygen permeability, may also take place in the interface of crystallites [61]. This process can be assumed to cause an increase in the surface free energy of the crystals (σ_e) which, in accordance with the Thomson equation (eq. 2), results in the subsequent lowering of the melting temperature [62]. Furthermore, a slight increase of the original crystalline content is also observed for pure PP during exposure to UV radiation (Table 1). It is well evidenced that the crystalline content of polypropylene increases at the beginning of oxidation [35-37,57,59,60,63-65]. This phenomenon has been explained as due to chain scission, which initially is the major driving force of the oxidative process, and leads to increasing segment mobility and chain arrangements, favouring further crystallisation [58].

These calorimetric results suggest that pure PP has only reached low level of oxidation, since the morphological changes that were noted during its photo-oxidation are characteristic phenomena that can be assigned to the chain scission effect that prevails at short-term UV exposure times.

In contrast, an appreciable modification of the DSC thermogram is observed during photo-oxidation of PP samples containing pro-oxidant/pro-degradant additive (Fig. 1). Basically, UV-irradiation leads to a multimodal and more heterogeneous DSC curve [37,57-59,66]. Regardless of the additive content, as the exposure time increases, there is a shape transition in which the maximum shifts to the lowest temperature contribution, while the original high temperature contribution vanishes. These morphological changes lead to a significant drop of the melting temperature [37,57,59,62] that occurs concurrently with a considerable decrease of the maximum lamellar thickness of these photo-oxidized PP samples, suggesting that as photo-oxidation proceeds, crystals are progressively becoming thinner (Table 1). Furthermore, this evidences that the crystalline phase, despite its lower permeability to oxygen, is also affected by the photo-oxidation process.

On the other hand, results also reveal that during photo-oxidation, crystallinity of PP samples containing pro-oxidant/pro-degradant additive tends to decrease with the exposure time to UV radiation (Table 1). It is generally accepted that when photo-oxidation spreads, the increasing impurity concentration (like oxygenated groups, double bonds, etc.) limits the secondary crystallization of polypropylene by reducing its molecular regularity. Thus, at high UV exposure times, the large number of chemical defects in the polymeric chain becomes the major driving force that prevents further crystallization [57,58,60,66].

In general, the aforementioned morphological changes, although being similar for both PP samples with pro-oxidant/pro-degradant, were found to take place at different time scales, being faster for the sample with a higher additive load (sample B).

It can then be concluded from the analysis of these calorimetric results that, as expected, photo-oxidation of polypropylene is enhanced by the pro-oxidant/pro-degradant

additive. In contrast to what was observed for pure PP, PP containing pro-oxidant/pro-degradant seems to have reached a higher level of oxidation. Furthermore, morphological changes during UV-irradiation were found to be accelerated for higher additive loads.

3.2.2. *Changes in thermal properties*

Changes in the thermal properties of PP samples with pro-oxidant/pro-degradant and additive-free control PP samples during accelerated photo-oxidation were next studied by TGA. In general, the shape of the TG traces of pure PP is substantially not modified during UV-irradiation, displaying similar one-step degradation. However, the onset temperature and the maximum temperature decomposition were found to slowly decrease with the UV exposure time, indicating a slight trend towards thermal destabilisation (Table 2). This trend is also confirmed by the decrease of the activation energy of the two identified kinetic stages that is observed as photo-degradation proceeds (Table 3). This lowering in thermal stability could be attributed to the low molecular weight oxidation products, with lower decomposition temperatures, resulting from chain scission reactions during photo-oxidation.

On the other hand, the exposure to UV radiation leads to a considerably lowered onset degradation temperature and maximum decomposition temperature in PP samples with pro-oxidant/pro-degradant additive compared to pure PP (Table 2). Furthermore, this decrease is more significant for higher additive loads (sample B). A similar trend was reported for both naturally and artificially photo-degraded polyethylene formulations with pro-oxidant/pro-degradant additives compared to pure polymers [15,17,23,28,34]. This lowering in thermal stability is also confirmed in this case by the decrease of the activation energy of the two identified kinetic stages that is observed during photo-

degradation of PP samples with pro-oxidant/pro-degradant (Table 3). This decrease of thermal stability observed in these UV-aged samples can probably be explained by the greater amount of low molecular weight fractions and chemical impurities (mainly oxygenated groups) resulting from photo-oxidation, which decompose at relatively lower temperatures, indicating that samples containing pro-oxidant/pro-degradant additive have undergone previous degradation [15,28,34]. Additionally, a concomitant decrease in the residue upon thermal degradation of these photo-oxidized samples is also apparent (Table 2).

Thermogravimetric results confirm that photo-oxidation of polypropylene is promoted by the pro-oxidant/pro-degradant additive, as previously suggested by calorimetric results. Compared to pure PP, photo-oxidation of PP containing pro-oxidant/pro-degradant results in less thermally stable materials. Furthermore, the level of oxidation observed in UV-aged samples seems to be directly proportional to the additive load.

3.3. Biotic degradation: biodegradation in soil

3.3.1. Morphological changes

Photo-oxidized samples containing pro-oxidant/pro-degradant additive were subjected to a subsequent soil burial test, in order to mimick the whole degradation process of these materials. Controls containing UV-unexposed PP samples with pro-oxidant/pro-degradant were also incubated in soil medium under identical conditions. Morphological changes undergone by these samples were first investigated as a function of the incubation time in soil. Pristine samples do not exhibit substantial changes in the shape of their DSC traces as a consequence of incubation in microbiologically active soil. As a result, no significant changes in the calorimetric parameters of pristine

samples A and B were detected during the soil burial test (Tables 4, 5). These results indicate that pristine samples containing pro-oxidant/pro-degradant additive, but not previously photo-oxidized, exhibit almost no biodegradation when aged in soil.

In contrast, a different behaviour is observed in the case of UV-exposed PP samples containing pro-oxidant/pro-degradant additive submitted to incubation in soil medium. A slight shift of the DSC traces towards lower temperatures, without substantial modification of their shape, is noted after 6 months of soil burial, suggesting that the crystalline phase of polypropylene is only slightly affected during biodegradation, in contrast to what was observed during photo-oxidation. This leads to a slight decrease of the melting temperature which, in turn, results in a slight decrease of the crystals thickness with the incubation time in soil (Tables 4, 5). A similar decrease of the melting temperature was found by Miyazaki et al. and Fehine et al. during biodegradation in soil of previously photo-oxidized PP samples containing different pro-oxidant/pro-degradant systems [42,43]. However, it is interesting to note that, in this case, this trend was found not to be linear, but in contrast, to occur in different stages. Moreover, a similar non-linear tendency was observed for the evolution of the crystalline content of both samples with the incubation time in soil, being such changes more significant for higher photo-oxidation times and higher additive contents (Tables 4, 5). Similarly, in a previous work, it was shown that changes in the calorimetric parameters of PP containing starch-based biodegradable additive naturally aged in soil, also take place in different stages [67]. This behaviour is also in good agreement with the idea originally proposed by Albertsson et al. that biodegradation of polyolefins is a complex process consisting of various stages [68]. In this case, crystallinity successively increases and decreases slightly with the incubation time in soil. In semicrystalline polymers, biodegradation is expected to start in the amorphous phase where

microorganisms are more active, due to its higher oxygen permeability [69], leading to an initial increase in crystallinity. Although oxygen is usually insoluble in the crystalline phase and biodegradation cannot be expected to be initiated in this phase, changes occurring in the amorphous phase due to the degradation process, are likely to also subsequently affect the crystalline phase [67]. This could explain the further slight decrease in crystallinity [70,71]. Furthermore, it was found that this decrease in the crystalline content occurs concurrently with a slight increase in the maximum lamellar thickness (Tables 4, 5), suggesting that once biodegradation proceeds, thinner crystalline entities are firstly being affected. Manzur et al. reported similar results for physico-chemically aged LDPE films submitted to biodegradation by a fungi consortium [71].

Therefore, the analysis of DSC results reveals slight calorimetric changes in the UV-aged PP samples with pro-oxidant/pro-degradant during incubation in soil medium that can be associated with a certain progress of degradation of these samples by the action of soil microorganisms, promoted by previous photo-oxidation. In general, calorimetric properties were shown to exhibit a non-linear dependency with the incubation time in soil, suggesting that biodegradation occurs in different stages. Furthermore, the extent of the morphological changes undergone by the polypropylene matrix was found to be dependent upon the additive load and the previous photo-oxidation level.

3.3.2. *Changes in thermal properties*

Polypropylene samples submitted to the accelerated biodegradation test were also characterized by TGA, in order to investigate changes in their thermal properties with the incubation time in soil. Pristine samples do not display substantial changes in the shape of their TGA traces as a result of their incubation in microbiologically active soil.

Regardless of the incubation time in soil, the thermal decomposition of pristine samples A and B occurs in a one-step process with almost no residue remaining ($\leq 5\%$) (Tables 6, 7). As a consequence, no significant changes in the thermogravimetric parameters were detected during incubation in soil medium of these samples (Tables 6, 7). These results confirm that pristine samples containing pro-oxidant/pro-degradant additive, but not previously aged, show almost no biodegradation when subjected to the accelerated soil burial test.

However, the thermal stability of previously photo-oxidized PP samples with pro-oxidant/pro-degradant additive was found to further change upon the incubation time in soil. In particular, both the onset degradation temperature and the maximum decomposition temperature were found to vary non-linearly during incubation in soil medium (Tables 6, 7). These results are in good agreement with the previous calorimetric analysis and support the idea that biodegradation of polyolefins is a complex process that takes place in different stages [68]. In general, initially a slight increase of the thermal stability is observed with respect to the corresponding values attained before incubation in soil. Roy et al. also found the thermal stability of UV-aged LDPE films with pro-oxidant/pro-degradant additive to increase after incubation with bacterial consortium [34]. Nevertheless, at longer incubation times, the onset temperature and the maximum degradation temperature were found to further slightly decrease. Furthermore, changes in the thermal stability with the incubation time in soil are more appreciable for higher additive contents and higher previous exposure times to UV radiation. This complex trend in thermal stability is also confirmed by the non-linear evolution of the activation energy of the two identified kinetic stages that is observed as degradation in soil proceeds (Tables 6, 7). Moreover, the activation energy of both processes alternatively increases and decreases with the incubation time in soil,

in a similar way and time scale as the onset degradation temperature and the maximum decomposition temperature do, for a given UV-exposure time and additive load. In a first step, preferential bioassimilation by soil microorganisms of low molecular weight polymer fractions generated during abiotic oxidation could explain the initial increase of thermal stability [23,34]. As a result, it is expected that smaller hydrocarbon fragments are released, which can in turn be further utilised by microorganism as carbon and energy sources [72]. The accumulation of these smaller polymer fractions would subsequently lead to a decrease of the thermal stability of the resulting polymeric matrix. Additionally, a concomitant decrease in the residue upon thermal degradation of photo-oxidized samples is also apparent (Tables 6, 7).

The analysis of these thermogravimetric results shows changes in thermal stability of photo-oxidized PP samples with pro-oxidant/pro-degradant additive during the accelerated soil burial test that can be related to a certain extent of oxidation, thus supporting the idea that previous abiotic oxidation of polypropylene promotes further biotic degradation. All the thermogravimetric parameters under study exhibit similar and concurrent non-linear changes with the incubation time in soil. Moreover, such changes were found to be accelerated for higher additive loads and longer previous UV exposure times.

4. Conclusions

The oxo-degradation process of PP samples containing pro-oxidant/pro-degradant additive was investigated by monitoring their morphological and thermal properties under abiotic and biotic accelerated degradative conditions.

During exposure to UV radiation, the more significant changes in the morphological and thermal properties that were detected in PP samples containing pro-oxidant/pro-degradant additive compared to pure PP, clearly suggest a higher level of oxidation in these samples. These results indicate that, as expected, the pro-oxidant/pro-degradant additive can promote the abiotic oxidation of polypropylene during UV-irradiation. In particular, photo-oxidation was found to lead to a reduction of crystallinity and a drop of the melting temperature that are accompanied by the formation and subsequent predominance of thinner crystalline entities. It was also shown that these morphological changes occur concurrently with a significant lowering of the thermal stability of these materials during exposure to UV radiation. These calorimetric and thermogravimetric changes are in good agreement and can be both explained by the greater concentration of lower molecular weight products and chemical impurities that are formed during photo-oxidation in its more advanced stages. Moreover, the level of oxidation observed in UV-aged samples seems to be dependent on the additive load.

On the other hand, in contrast to pristine control samples, changes in the morphological and thermal properties were detected in previously photo-oxidized PP samples with pro-oxidant/pro-degradant when subjected to a subsequent soil burial test that can be associated with a certain progress of oxidation. These results suggest that previous abiotic oxidation is responsible for further extent of degradation of the polypropylene matrix by soil microorganisms. In general, both morphological and thermal properties were found to exhibit a non-linear dependency with the incubation time in soil, confirming the idea that biodegradation of this polyolefin is a complex process that occurs in different stages. Changes in crystallinity suggest that although the degrading activity of the soil microorganisms starts in the amorphous phase, this seems to later also affect the crystalline phase, starting from thinner crystals. Changes in thermal

stability can be related to bioassimilation of the low molecular weight polymer fractions generated during abiotic oxidation. Furthermore, changes in both the morphological and thermal properties of the polypropylene matrix during soil incubation were found to be proportional to the additive load and the previous photo-oxidation extent. At this point, it should be noted that all the aforementioned results supporting a certain extent of biodegradability are merely indirect, in so far as they have been assessed by an indirect method.

It can then be concluded that the synergetic effect of abiotic degradation (due to UV exposure) and biotic degradation (as a consequence of the metabolic activity of the soil microorganisms) promotes the extent of the whole degradation of the PP samples containing pro-oxidant/pro-degradant additive studied in this work, confirming the potential of this additive in producing environmentally degradable polypropylene via combination of abiotic and biotic oxidizing agents.

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Table captions

Table 1. DSC parameters of photo-oxidized samples.

Table 3. Activation energies of photo-oxidized samples calculated with the Chang model.

Table 4. DSC parameters of pristine and photo-oxidized sample A aged in soil.

Table 5. DSC parameters of pristine and photo-oxidized sample B aged in soil.

Table 6. TGA parameters of pristine and photo-oxidized sample A aged in soil.

Table 7. TGA parameters of pristine and photo-oxidized sample B aged in soil.

Table 1.

time (h)	PP			A			B		
	T_m (°C)	χ (%)	l_{\max} (Å)	T_m (°C)	χ (%)	l_{\max} (Å)	T_m (°C)	χ (%)	l_{\max} (Å)
0	158.4	48.5	117	162.2	53.3	135	162.3	55.4	135
100	158.0	51.5	115	162.3	53.1	135	161.5	54.3	131
200	158.0	52.0	115	161.6	51.2	131	141.5	53.5	74
300	157.7	52.4	114	140.8	50.6	73	141.2	51.9	74

Table 2.

time (h)	PP			A			B		
	T_{onset} (°C)	T_{max} (°C)	residue (%)	T_{onset} (°C)	T_{max} (°C)	residue (%)	T_{onset} (°C)	T_{max} (°C)	residue (%)
0	448.6	466.0	0.6	440.2	465.0	4.5	439.0	463.5	4.3
100	446.4	465.4	0.1	438.6	464.9	3.9	435.8	463.2	3.8
200	446.6	465.0	0.1	435.1	463.0	3.7	431.1	461.4	3.1
300	442.4	463.7	0.1	433.4	462.8	3.8	427.8	460.9	3.1

Table 3.

time (h)	PP		A		B	
	Ea (Stage 1) (kJ/mol)	Ea (Stage 2) (kJ/mol)	Ea (Stage 1) (kJ/mol)	Ea (Stage 2) (kJ/mol)	Ea (Stage 1) (kJ/mol)	Ea (Stage 2) (kJ/mol)
0	145	319	143	238	142	234
100	142	313	140	225	138	219
200	130	310	128	209	123	192
300	126	295	123	204	118	174

Table 4.

UV exposure time (hours)	time in soil (months)	T_m (°C)	χ (%)	l_{\max} (Å)
0	0	162.2	53.3	135
	6	162.4	53.2	136
100	0	162.3	53.1	135
	2	161.2	53.9	129
	4	161.9	53.5	133
	6	161.4	55.3	130
200	0	161.6	51.2	131
	2	161.1	53.7	129
	4	161.4	53.3	130
	6	160.6	52.6	126
300	0	140.8	50.6	73
	2	139.4	53.3	70
	4	139.9	52.0	72
	6	138.0	54.1	69

Table 5.

UV exposure time (hours)	time in soil (months)	T_m (°C)	χ (%)	l_{\max} (Å)
0	0	162.3	55.4	135
	6	162.1	55.0	134
100	0	161.7	54.3	132
	2	161.1	54.5	129
	4	161.4	53.5	130
	6	160.4	55.2	126
200	0	141.5	53.5	74
	2	139.9	54.0	71
	4	140.5	51.1	73
	6	138.9	51.7	70
300	0	141.2	52.0	74
	2	139.7	54.2	71
	4	140.7	52.6	73
	6	138.5	53.0	69

Table 6.

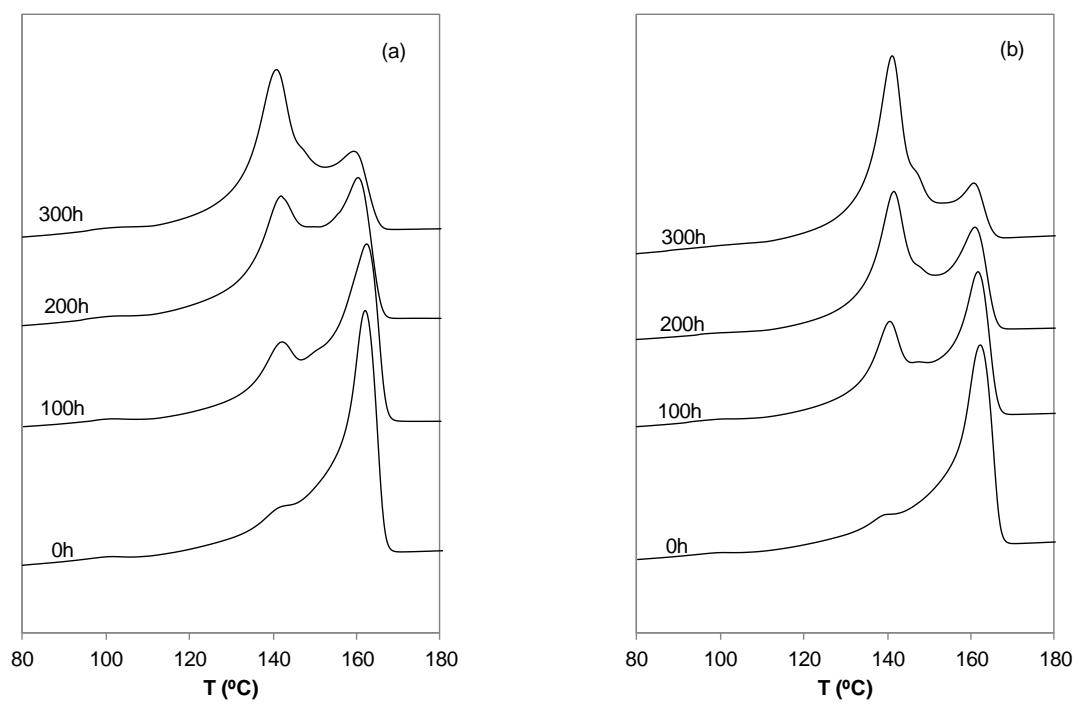
UV exposure time (hours)	time in soil (months)	T_{onset} (°C)	T_{max} (°C)	Residue (%)	Ea (Stage 1) (kJ/mol)	Ea (Stage 2) (kJ/mol)
0	0	440.2	465.0	4.5	143	238
	6	441.1	464.5	4.5	141	234
100	0	438.6	465.0	3.9	140	225
	2	439.3	465.6	3.9	142	226
	4	437.8	464.3	3.6	134	206
	6	434.7	463.9	3.1	138	205
200	0	435.1	463.0	3.7	128	209
	2	436.5	465.0	3.7	140	216
	4	435.3	464.2	3.5	132	202
	6	437.0	464.8	3.5	139	207
300	0	433.4	463.3	3.8	123	204
	2	439.3	465.2	3.7	139	217
	4	430.8	463.7	3.8	123	186
	6	435.7	464.7	2.6	131	204

Table 7.

UV exposure time (hours)	time in soil (months)	T_{onset} (°C)	T_{max} (°C)	Residue (%)	Ea (Stage 1) (kJ/mol)	Ea (Stage 2) (kJ/mol)
0	0	439.0	463.5	4.2	142	234
	6	439.3	463.1	4.0	145	231
100	0	435.8	463.2	3.8	138	219
	2	439.0	465.8	3.7	148	224
	4	435.8	463.2	3.5	137	203
	6	436.0	463.4	2.9	139	206
200	0	431.1	461.4	3.1	123	192
	2	434.1	463.5	3.3	135	207
	4	433.4	462.7	3.4	125	197
	6	434.2	464.6	2.9	126	195
300	0	427.8	461.8	3.1	118	174
	2	429.5	462.8	3.4	130	182
	4	425.8	460.9	3.4	114	162
	6	428.3	461.4	2.8	122	170

Figure captions

Fig. 1. DSC thermograms of PP with pro-oxidant/pro-degradant additive as a function of the exposure time to UV radiation: (a) sample A and (b) sample B.

**Fig. 1**