J Therm Anal Calorim (2009) 97:853–858
DOI 10.1007/s10973-009-0355-2

Thermal analysis of soil-buried oxo-biodegradable polyethylene based blends

Sílvia Maria Martelli · Elizabeth Grillo Fernandes · Emo Chiellini

AICAT2008 Conference

Abstract Low-density polyethylene (LDPE) blended with poly(3-hydroxybutyrate) (PHB) and additivated with pro-oxidant were soil buried for 180 days and characterized using thermogravimetry (TG) and differential scanning calorimetry (DSC). TG data showed that both onset and maximum rate degradation temperatures decreased as a function of biodegradation time. Apparent activation energies (E_a) using the Broido integral method decreased with the burial time increasing. PE crystallinity degree values increased in general up to 2 months of biodegradation. At the end of the soil burial (SB) test these values decreased principally for samples that were previously thermo-oxidized in an oven.

Keywords Oxo-biodegradable · Poly(ethylene) · Poly(3-hydroxybutyrate) · Soil burial

Introduction

Polyethylene (PE) has achieved a very important position in several sectors due to its low cost and high versatility as a consequence of its good processability and mechanical properties, high thermal stability and light-weight. Nevertheless, PE waste persists for many years after disposal causing a serious environmental problem. In this respect the need to create alternatives in the development of more friendly materials drove many researches especially in packaging and agricultural fields [1, 2]. An approach to increase PE biodegradability is its blend with natural biodegradable polymer such as starch [3–5]. This strategy leads to the attack of the microorganisms, such as fungi and bacteria, in the biodegradable polymer phase. As a consequence, the polyolefinic matrix weakens and increases the surface area, hydrophilicity and permeability [4]. Another way to accelerate PE degradation is with the addition of additives, which will facilitate photo and/or thermal decomposition. These reactions bring about the formation of free radicals, which catalyze the break of PE chains [5]. A new approach to increase PE biodegradability could be its blend with poly(3-hydroxybutyrate) (PHB). This polymer is natural polyester produced by several microorganisms [6]. In the last decades PHB has attracted much interest in medical and agricultural applications owing to its biocompatibility and biodegradability [7].

In the present study it was applied the two approach afore mentioned to modulate PE environmental degradability. Formulations of PE-PHB blends additivated with two different pro-oxidant were submitted to a soil burial (SB) biodegradation test for 180 days. Changes on thermal properties at different stages of SB test were accessed using thermogravimetry (TG) and differential scanning calorimetry (DSC).

Experimental

Materials

Riblene® FF33 a low density polyethylene (LDPE that will be simplified to PE) pellet with a melt flow index (MFI) [at 190 °C/2.16 kg] = 0.8 g 10 min^{-1} and density (d) = 0.92 g cm^{-3} at 23 °C was kindly supplied by Polimeri

---

S. M. Martelli · E. G. Fernandes · E. Chiellini (✉)
Laboratory of Bioactive Polymeric Materials for Biomedical and Environmental Applications, Department of Chemistry and Industrial Chemistry, University of Pisa, Via Vecchia Livornese 1291, 56010 Pisa, Italy
e-mail: emochie@dcci.unipi.it

Europa, Italy. Biocyle poly(3-hydroxybutyrate) (PHB) pellet with average molecular weight (Mw) = 425 kDa and polydispersity (Mw/Mn) = 2.51 was kindly supplied by PHB Industrial S.A., Brazil. Lotader AX 8840 a poly(ethylene-*co*-glycidyl methacrylate) (EGMA) with 8 wt% of glycidyl methacrylate and $d = 0.94$ g cm^{-3} at 23 °C was supplied by Arkema, Italy.

Totally Degradable Plastics Additives (TDPA®) DCP562 (T6), MFI [at 125 °C/2.16 kg] = 23–28 g 10 min^{-1} and DCP571 (T7), MFI [at 125 °C/2.16 kg] = 25–30 g 10 min^{-1} (is a proprietary masterbatch containing pro-oxidants, mainly of cobalt and manganese stearate, stabilizers and fillers into a PE matrix) were kindly supplied by EPI Environmental Technologies Inc. ("EPI"), Canada.

Formulation and processing

All formulation components were previously dried at 50 °C for 24 h in a vacuum oven. Extrusion was performed in a bench type compounder ZK 25 T co-rotating twin-screw extruder with diameter of 25 mm and L/D = 18 and comprising three heating zones (Teach Line® from Dr Collin GmbH-Germany). The rotation of the twin-screw was 15 rpm whereas feeding was 4.7 rpm. The temperatures from hopper to die were set to 150, 180, 180, 180 °C, respectively. PE-PHB based blends preparation followed two stage. Firstly, 90 wt% of PE and 10 wt% of EGMA compatibilizer was blended and the resulting pellets was called PEL. The second stage was the blending of the formulations presented in the Table 1.

Soil burial (SB) experiment

SB experiments employed loam from Pine and Quercia trees taken from Marina di Pisa woods (Italy) (total nitrogen 1.34 g kg^{-1} and soil organic matter (SO) 2.95%) and perlite (PER) ($d = 80$–120 g cm^{-3} and granulometry = 1–3 mm). PER was used in order to provide aeration and moisture retention during tests. The procedure of aerobic biodegradation of samples in SB was carried out in two steps. The first step consisted in the preparation of soil. Initially, stones, plant remains, etc. from loam were removed manually and after was left in an static oven at 50 °C by ca. 48 h. Dried loam was sieved through a 2 mm mesh. Following, the moisture content of the soil was adjusted to 50 wt% and then it was mixed with PER in the proportions of 2:1 soil:PER (WSP). The second step corresponded to the assembly of the biometers of 750 mL (Fig. 1), which were filled with the following three layers: 15 g of PER:50 g of WSP:15 g of PER. In the middle of WSP, it was placed a piece of sample (ca. 250 mg). The final system was wetted with 10 mL of distilled water and biodegradation followed in the dark at room temperature for 180 days. At specific times, pieces of buried film samples were removed from biometers and washed with distillate water. The excess of water in the film surface was removed with tissue paper and placed inside desiccators containing saturated solutions of magnesium nitrate for at least 48 h before testing [8].

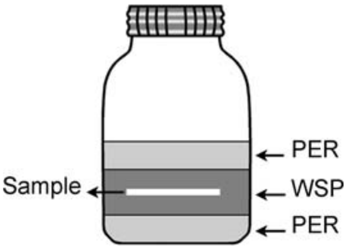

Fig. 1 Biometer used in soil burial experiments

Characterization

TG analysis was performed in a TA Thermogravimetric Analyzer Q500 using samples with 10–20 mg and a heating rate of 10 °C min^{-1} from 30 °C to 810 °C under a 60 mL min^{-1} nitrogen atmosphere.

DSC evaluations were carried out on a Mettler DSC822^{e} module with FRS5 sensor and controlled by the STAR^{e} software. The analysis under nitrogen flow rate of 160 mL min^{-1} was performed at 10 °C min^{-1} in the range of –50 to 150 °C with isotherm of at least 2 min at the end of each of the three cycles: 1st heating, 1st cooling, and 2nd heating.

Table 1 Composition and identification codes of PE-PHB based blends

Code	PHB/wt%	T6/wt%	PEL[a]/wt%	Code	PHB/wt%	T7/wt%	PEL/wt%
3T6	0	3	97	3T7	0	3	97
3T6t[b]	0	3	97	3T7t[b]	0	3	97
2B3T6	2	3	95	2B3T7	2	3	95
2B3T6t[b]	2	3	95	2B3T7t[b]	2	3	95

[a] PEL: 90 wt% PE/10 wt% EGMA. [b] Samples previously submitted to a thermal ageing in an oven at 50 °C for 60 days

Table 2 TG data of PE-PHB blends as a function of soil burial biodegradation test[a]

Sample	0^b		60 Days		120 Days		180 Days	
	T_d/ °C	R_{800}/ wt%	T_d/ °C	R_{800}/ wt%	T_d/ °C	R_{800}/ wt%	T_d/ °C	R_{800}/ wt%
3T6	386	0.7	348	0.8	355	1.1	327	2.6
3T6t	156	0.9	156	5.1	–	–	186	6.6
2B3T6	301	0.5	234	0.7	285	0.7	302	0.9
2B3T6t	152	0.8	172	4.2	–	–	168	1.4
3T7	377	0.4	357	0.7	364	0.8	354	1.3
3T7t	117	0.9	180	1.6	–	–	178	1.7
2B3T7	263	0.4	250	1.0	246	0.8	244	1.0
2B3T7t	131	0.6	185	7.4	–	–	187	3.8

[a] T_d is the decomposition temperature defined at 1 wt% weight loss; R_{800} is the residual weight at 800 °C; [b] Time 0 corresponds to samples before SB test

Results and discussion

Thermogravimetry

TG data of PE-PHB based blends as a function of SB time are summarized in Table 2. The decomposition temperature (T_d) was defined as the temperature at 1% weight loss and the residue was measured at 800 °C (R_{800}).

T_d values of 3T6 and 3T7 PE samples containing only pro-oxidant additives not previously pre-oxidized in oven were 386 and 377 °C, respectively. The difference of ca. 10 °C between their T_d values indicate that thermal-degradation of additivated PE depended on the kind of pro-oxidant. In both materials, thermal stability decreased with SB experiment time. The differences on T_d values of 3T6 and 3T7 as recorded at 0 and 180 days were of 59 and 23 °C, respectively. On the other hand, it was observed an increasing on the residual weight at 800 °C (R_{800}) with SB time. The sample 3T6 presented a R_{800} value of 0.7 wt% at time 0 day and 2.6 wt% after 180 days of SB, which corresponds to the significant increase on the char formation (ca. 4 times). In the case of the sample 3T7, R_{800} value changed from 0.4 wt% (0 day) to 1.3 wt% at (180 days), respectively that corresponds to an increase on char production of ca. 3 times as much. These results, suggest that the addition of pro-oxidant promoted some PE structural changes during melt processing and/or SB (in both case there is the presence of oxygen), which modified its pyrolysis mechanism.

The effect of previous oxidation of additivated PE materials on thermal stability as a function of SB time was more significant. The samples 3T6t and 3T7t, which were aged in an oven for 60 days at 50 °C, thermo-degraded at 156 and 117 °C, respectively, prior to SB experiment (0 days). The recorded T_d values corresponded to a decrease in the thermal stability by 230 and 260 °C in respect of the values recorded for the pristine 3T6 and 3T7, respectively. However, the T_d values of pre-oxidized materials increased with SB time, behaviour differently found to that previously verified for the samples not aged in oven. After 180 days of SB, 3T6t and 3T7t thermo-degraded at 186 and 178 °C, respectively, that represents an increase on thermal stability of 30 and 61 °C. Two hypotheses can be formulated to explain the observed behaviour. During pre-oxidation in oven, the principal reaction mechanism is chain scission forming chains with lower molecular weight (MW) and introducing oxygenated functional groups and double bonds in the PE chain [9]. The new functionalized low MW chains are then responsible by the lower thermal stability of pre-oxidized samples (3T6t and 3T7t). As these chains are better assimilated by the micro-organism present in soil, after 180 days of SB the material will present a lower amount of less stable moieties and, consequently, present higher T_d values. Another possibility could imply the formation of cross-link, which imparts higher thermo stability. Any way, both kinds of PE modified chains (functionalized and cross-linked) would be responsible of the increase in the char amount in the 180 day SB samples. The R_{800} value of sample 3T6t at 0 day of SB was 0.9 wt%, which increased to 6.6 wt% after 180 days. This change in the char formation represents a significant in increase (ca. 7 times). On the other hand, the increase of char content was less significant in the case of sample 3T7t, which changed from 0.9 wt% to 1.7 wt% at 0 days and 180 days, respectively corresponding to an increase lower than twice.

Some formulations of the PE based materials were prepared with PHB (Table 1) as another variable for the optimization of PE biodegradation. The amount of 2 wt% of PHB was defined in the author's study related to the PE-PHB compatibilization [10]. In general, the thermal stability of materials as a function of SB time was similar to that of materials containing only pro-oxidant discussed above. T_d values of 2B3T6 and 2B3T7 were 301 and 263 °C, respectively. Thermal stability temperature of melt processed PHB is around 275 °C [11, 12]. So, comparing these T_d values with that of their parent formulations 3T6 and 3T7, it can be supposed that the PHB would be the principal responsible for the decreasing in the thermal stability of the PE based blends containing both additives, pro-oxidant and PHB. During SB experiment, 2B3T6 T_d value decreased initially of ca. 70 °C, which increased again until reaching the initial value at the end of 180 days. Conversely, T_d value of 2B3T7 decreased slightly resulting a difference of 19 °C in relation to the original one at the end of SB experiment. These behaviours suggest that in the family of samples containing the pro-oxidant T6, at the content level used in the present work, there is a competitive effect. Samples that were previously pre-oxidized presented behaviour similar to that described above without PHB. This means that the T_d values of the PE-PHB-Tn blends increased with increasing of the SB experiment time. The increasing after 180 days of SB were of 16 and 56 °C for 2B3T6t and 2B3T7t, respectively.

Typical first derivative TG (DTG) traces as a function of SB time of PE based materials that were not previously thermo-oxidized in the oven are depicted in Fig. 2. The temperature of the maximum degradation rate (T_p) was defined at the peak of the DTG. PE samples additivated only with pro-oxidant showed a single weight loss step independently of the SB time (Fig. 2a). However, T_p values decreased with biodegradation time. For example, T_p values of 3T6 sample changed from 474 °C before SB test (0 day) to 466, 463 and 454 °C after 60, 120 and 180 days, respectively. Similar values were found for 3T7 sample. This suggests that pro-oxidants additives catalyzed degradation reactions of the PE chain at ambient temperature during the time of the SB experiment.

Thermo-degradation of PE-PHB blends additivated with pro-oxidant occurred in two steps. Moreover, the maximum degradation rate showed the same behaviour observed for samples without PHB. Thermal stability of both components PHB and PE decreased with SB time (Fig. 2b). The T_p values of PHB in 2B3T6 sample (insert in Fig. 2b) decreased from 224 to 217 °C, 218 and 210 °C after 60, 120 and 180 days of SB, respectively. T_p values of PE in 2B3T6 sample dropped from 473 to 469 °C, 469 and 466 °C after 60, 120 and 180 days of SB, respectively.

To resume the effects of factors such as time in SB, pre-oxidation, and PHB addition factors on T_d values, a 2^3 factorial design was elaborated considering respectively the following low (−) and high (+) levels: 0 day, 180 day; no, yes; 0 wt%, 2 wt%. It is possible from this kind of statistical experimental design (EXD) to establish what are the best settings and if there are interactions between factors (interdependence). A simple way to respond these questions is creating the "mean interaction plot" represented in Fig. 3.

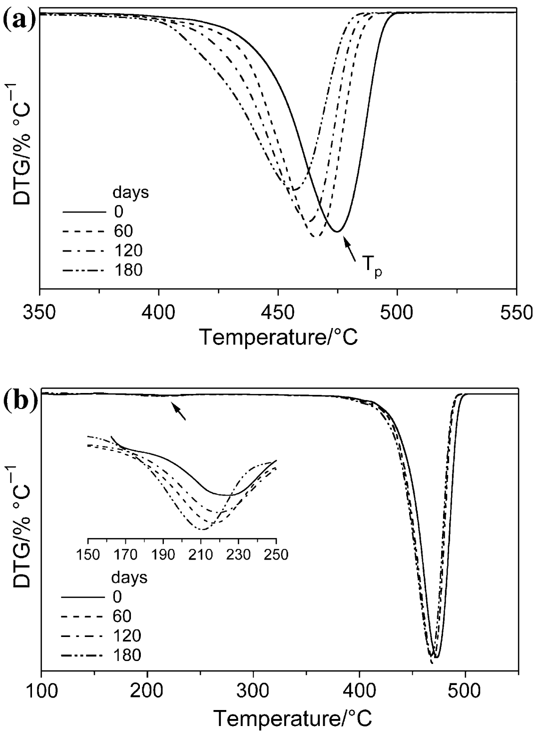

Fig. 2 DTG traces of 3T6 (a) and 2B3T6 (b) samples as a function of SB time

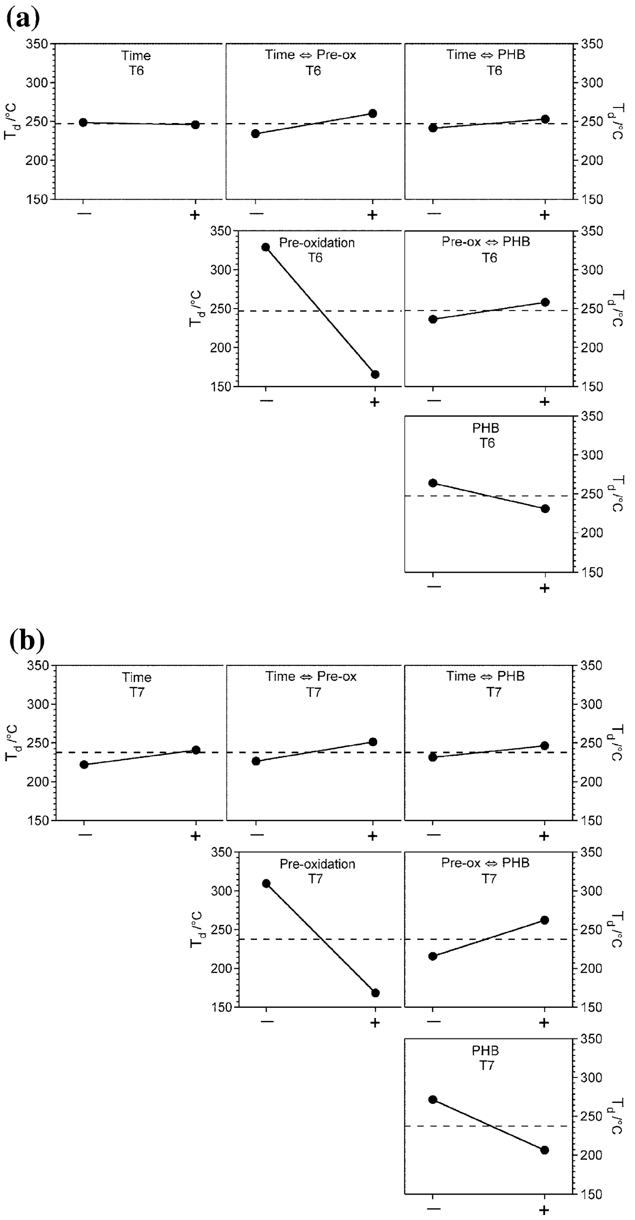

Fig. 3 EXD mean interaction plots for T_d of PE based materials containing (a) T6 and (b) T7 pro-oxidants

T_d behaviour as a function of the assessed factors is similar on both T6 and T7 family of PE based materials. The plots show that the most significant factor (steeper trace) is the pre-oxidation treatment prior SB, confirming the effective action of the pro-oxidants. Besides, the additive T6 is a slightly better than T7. SB time is not an important variable principally for formulations containing T6 considering that the mean values at low (−) ad high (+) levels are around the total mean (dashed line). However the addition of PHB seems to promote thermal degradation of PE based materials, principally in the presence of the pro-oxidant T7 (Fig. 3b–sub-plot PHB). The interactions between factors (Time⇔Pre-ox, Time⇔PHB, Pre-ox⇔PHB) showed to be so important however a different T7/PHB could promote a more significant effect on T_d taking into account that their interaction plot was more steep than the others interactions.

The kinetics of the thermal degradation was studied applying the Broido method [13] from which the apparent activation energies (E_a) can be obtained in the temperature range close to T_p and considering a first order model. The weight fraction of the molecules not yet decomposed (y) is defined by the equation

$$y = (w_t - w_r)/(w_0 - w_r) \tag{1}$$

where w_0, w_t and w_r are the sample weight taken initially, at time t, and at the end of thermal decomposition, respectively. The Broido equation is

$$\ln(\ln(1/y)) = (-E_a/RT) + \text{constant} \tag{2}$$

where R is the gas constant and T is the absolute temperature.

The plot of ln(ln(*1/y*)) versus 1/*T* gives a straight line and from the slope it is obtained the E_a of the pyrolysis reaction. The weight fractions used in the calculations were taken in the temperature range (Δ*T*) defined by the half of DTG peak (Fig. 4).

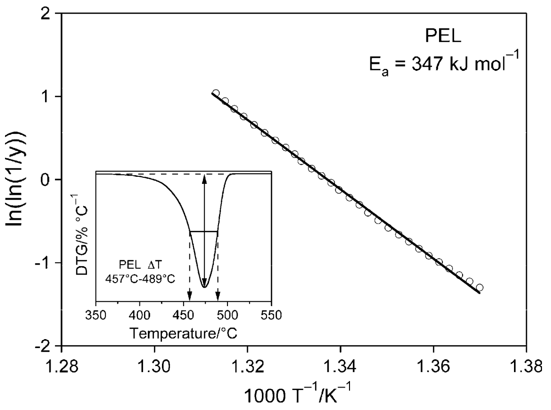

Fig. 4 Δ*T* definition and Broido plot of PEL (—— Eq. 2; ○ experimental points)

Table 3 Δ*T* and E_a of 3T6 and 3T7 blends as a function of biodegradation time

Sample	Δ*T*/°C	E_a/kJ mol^{-1}	Sample	Δ*T*/°C	E_a/kJ mol^{-1}
3T6-0d	456–489	378	3T7-0d	454–484	368
3T6-60d	448–477	370	3T7-60d	449–477	374
3T6-120d	442–474	339	3T7-120d	449–478	375
3T6-180d	433–470	282	3T7-180d	445–474	346

Table 3 reports the E_a values and Δ*T* of 3T6 and 3T7 PE materials as a function of biodegradation time. It can be observed that the apparent thermal degradation E_a of PE based materials tends to decrease slightly up to 120 days in presence of both pro-degradants. Moreover, after 180 days of SB the behaviour of 3T6 family was different of the 3T7 one. 3T6 showed a significant decrease of E_a, whereas the value for 3T7 changed little.

Differential scanning calorimetry

Typical DSC traces of the PE based materials from the first heating scan are represented in Fig. 5. The crystallinity degree of PE (X_{cPE}) in the samples was determined from melting enthalpy (the normalized area under the trace $-\Delta H_m$—Fig. 5), which was compared with the value of 290 J g^{-1} corresponding to the enthalpy of 100% crystalline PE with perfect crystal [14].

Table 4 records X_{cPE} values of PE from the first heating scan as a function of SB time. X_{cPE} values were dependent of the three variables studied: SB time, kind of pro-oxidant and oven pre-oxidation. It was found that with increasing of SB time the X_{cPE} value tend to increase. For example, X_{cPE} values of ca. 43 and 44% were found for 3T6 and 3T7, respectively, which increased of 2 and 4%, respectively at the end of 180 days of SB. Contat–Rodrigo et al. [15] found

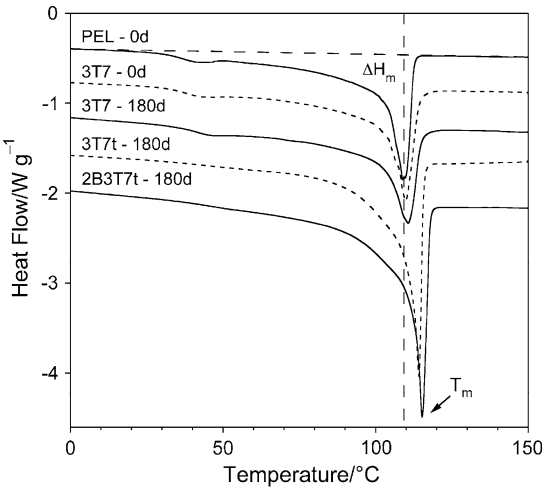

Fig. 5 Typical DSC traces of PE based materials

Table 4 PE crystallinity degree as a function of SB time

Sample	0 Days	60 Days	120 Days	180 Days	Sample	0 Day	60 Days	120 Days	180 Days
3T6	42.7	46.6	48.1	44.9	3T7	44.3	44.2	55.9	47.9
3T6t	56.3	60.4	–	55.5	3T7t	57.0	60.9	–	58.4
2B3T6	42.7	51.3	45.1	46.2	2B3T7	44.3	47.5	42.3	58.8
2B3T6t	54.4	57.2	–	60.6	2B3T7t	57.5	69.3	–	65.3

Table 5 Thermal properties of PE in the PE based materials as a function of SB time

Sample	0 Days		60 Days		120 Days		180 Days	
	T_m/ °C	X_{cPE}/ %	T_m/ °C	X_{cPE}/ %	T_m/ °C	X_{cPE}/ %	T_m/ °C	X_{cPE}/ %
3T6	109	44.5	110	46.4	110	47.4	110	46.2
3T6t	113	45.5	113	49.2	–	–	113	35.5
2B3T6	110	44.6	111	51.0	110	45.0	110	45.0
2B3T6t	113	46.1	113	45.5	–	–	113	48.1
3T7	110	43.3	110	44.5	111	55.1	111	45.4
3T7t	113	47.1	114	48.5	–	–	113	48.3
2B3T7	110	43.4	110	47.1	110	43.5	110	52.0
2B3T7t	112	47.4	113	57.5	–	–	109	48.2

equivalent behaviour in their SB studies of the polypropylene (PP). They explained this behaviour considering that the scission of the amorphous phase chains during degradation reactions allows the crystallization to proceed to a higher extent. The effect of oven pre-oxidation was more significant. For instance, 2B3T6 and 2B3T6t X_{cPE} values were 43 and 54% that represents an increase of 11%.

Table 5 list T_m and X_{cPE} values as a function of SB time obtained from the second heating traces. Basically, all T_m values remained constant after that the previous thermal history was cancelled, independently of SB time. The crystalline contents presented the same behaviour observed in the first heating traces.

Conclusions

Polyethylene/Poly(3-hydroxybutyrate) blends additivated with two kinds of pro-oxidants were submitted to soil burial biodegradation and thermal properties were evaluated. TG analysis showed that T_d values changed during soil burial and that thermal aged samples and kind of pro-oxidant has a significant influence on blend biodegradation. As T_d value decreases are related to the PE chain modification, it can be concluded that the best setting was the formulation of PE with T6. DSC evaluations pointed out that the same variables that have affected the pyrolysis behaviour of PE based materials had an effect on their degree of crystallinity.

Acknowledgements The work was performed within the framework of GFP EC-Funded Project Polyver. COOP-CT-2006-032967.

References

1. Roy PK, Surekha P, Rajagopal C, Chatterjee SN, Choudhary V. Accelerated aging of LDPE films containing cobalt complexes as prooxidants. Polym Degrad Stab. 2006;91:1791–9.
2. Koutny M, Lemaire J, Delort AM. Biodegradation of polyethylene films with prooxidant additives. Chemosphere. 2006;64: 1243–52.
3. Arvanitoyannis I, Biliaderis CG, Ogawa H, Kawasaki N. Biodegradable films made from low-density polyethylene (LDPE) rice starch and potato starch for food packaging applications: Part 1. Carbohydr Polym. 1998;36:89–104.
4. Shah PB, Bandopadhyay S, Bellare JR. Environmentally degradable starch filled low density polyethylene. Polym Degrad Stab. 1995;47:165–73.
5. Hakkarainen M, Albertsson A-C. Environmental degradation of polyethylene. Adv Polym Sci. 2004;169:177–99.
6. Ariffin H, Nishida H, Shirai Y, Hassan MA. Determination of multiple thermal degradation mechanisms of poly(3-hydroxybutyrate). Polym Degrad Stab. 2008;93:1433–7.
7. Siciliano A, Seves A, Demarco T, Cimmino S, Martuscelli E, Silvestre C. Miscibility and thermal and crystallization behaviors of poly(D-(-)-3-hydroxybutyrate)/atactic poly(methyl methacrylate) blends. Macromolecules. 1995;28:8065–72.
8. ASTM D 618. Standard practice for conditioning plastics for testing. In: ASTM Standard. ASTM International: West Conshohocken PA 2008.
9. Chiellini E, Corti A, D'Antone S, Baciu R. Oxo-biodegradable carbon backbone polymers—Oxidative degradation of polyethylene under accelerated test conditions. Polym Degrad Stab. 2006;91:2739–47.
10. Martelli SM, Fernandes E.G, Chiellini E. Compatibilization of polyethylene-poly(3-hydroxybutyrate) based blends (submitted).
11. Chiellini E, Fernandes EG, Pietrini M, Solaro R. Factorial design in optimization of PHAs processing. Macromol Symp. 2003;197: 45–55.
12. Fernandes EG, Pietrini M, Chiellini E. Bio-based polymeric composites comprising wood flour as filler. Biomacromolecules. 2004;5:1200–5.
13. Broido A. Simple sensitive graphical method of treating thermogravimetric analysis data. J Polym Sci Pol Phys. 1969;7:1761–73.
14. Munaro M, Akcelrud L. Polyethylene blends: A correlation study between morphology and environmental resistance. Polym Degrad Stab. 2008;93:43–9.
15. Contat-Rodrigo L, Ribes-Greus A, Diaz-Calleja R. Characterization by thermal analysis of PP with enhanced biodegradability. J Appl Polym Sci. 2001;82:2174–84.