



Oxo-biodegradable carbon backbone polymers – Oxidative degradation of polyethylene under accelerated test conditions[☆]

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Abstract

Oxo-biodegradation of carbon-only backbone polymers is receiving ever increasing attention for the practical implications that some re-engineered thermoplastic polymer formulations based on conventional biostable polymeric materials may satisfy in terms of environmental friendliness and acceptance by commodity plastic manufacturers.

In this respect, as part of our continuing activity in the area of bioactive polymeric materials for biomedical and environmental applications, we report the results of an investigation of the effects of different degradation conditions on the oxidative degradation of polyethylene (PE) film samples containing pro-oxidant additives and formulated according to a proprietary technology. The effects of temperature and relative humidity have been evaluated by monitoring, with time, several parameters associated to oxidation and cleavage of the macromolecules, such as the weight variation due to oxygen uptake, film wettability, carbonyl index, molecular weight and the extractability with polar solvents of oxidized PE samples.

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1. Introduction

The world production and consumption of polymeric materials and relevant plastic items is increasing exponentially [1,2] and approaching the level of cellulose in the production and consumption of paper and cardboard.

If one considers the present global situation of synthetic polymeric materials production on the basis of the backbone structure of the macromolecular components, one can easily become aware of the overwhelming share (~90%) held by polymers with carbon-only backbones (vinyl and vinylidene polymers) [2] with only 10% of condensation polymers, with hetero-atom backbones.

If one then combines this situation with the fact that about 35–45% of the synthetic polymer production goes into single-use items (disposables, packaging, table ware, etc.), it is easy to envisage a catastrophic environmental impact as a likely consequence of the accumulation of plastic waste, due to the recalcitrance of carbon backbone high molecular weight compounds towards attack by environmental microflora.

The general policy and strategies nowadays in place are meant to recover the free energy content present in plastic items at the end of their service life and they should be structurally prone to allow for a cost effective recovery technology.

Options offered are based on mechanical (material feed-stock) or chemical (portable fuels and monomeric components) recycling, incineration (thermal revaluation) and bio-recycling comprising aerobic biodegradation with composting revaluation and anaerobic digestion with production of methane and cell biomass.

Given the wide variety of polymeric structural features, all options for the management of plastic waste should coexist in

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a harmonized vision as required by and applicable to municipal and industrial waste treatment.

All the recovery practices require economical support in terms of manpower and suitably dedicated infrastructures, as well as household separate collection which needs an efficient plan for civic education and training on the fundamental aspects and concepts of sustainable development [3,4].

This mission of vital importance can be in principle disseminated and eventually accomplished in industrialized countries, whereas in developing countries where populations are still struggling with the survival needs in everyday life, this is much more difficult to disseminate and comprehend [5,6].

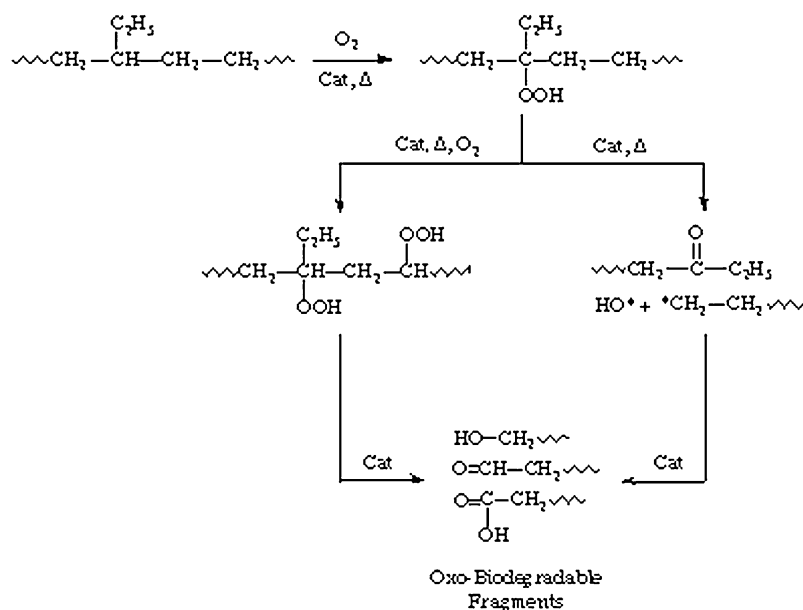
The idea of achieving low cost, environmentally degradable vinyl polymers with specific regard to polyolefins dates back to the second half of the 20th century [3,4]. Starting from the studies on the thermal and photolytic degradation of polyethylene (PE) and polypropylene (PP), the major strategies in order to overcome the intrinsic recalcitrance of PE to biological attack were focused on the introduction of functional groups and substances capable to promote the formation of free radical precursor moieties (e.g. hydroperoxides) by photo-physical and thermal decomposition, and to induce cleavage of the macromolecular backbone. Accordingly, copolymerisation with a small amount of monomers containing carbonyl groups such as carbon monoxide, methyl vinyl ketone or the incorporation of transition metal compounds such as dithiocarbamates as photoinitiators or photosensitisers, and pro-oxidants, were performed in order to enhance the oxidation of polyethylene

exposed to light and temperature, through the generation of free radicals reacting with molecular oxygen to produce peroxides and hydroperoxides [5,6]. These last, eventually decompose in the presence of heat, light and metallic ions, leading also to the formation of macro-alkoxy radicals, with auto-oxidation of polyethylene proceeding through classical free radical chain reactions [7,8]. As a result, main chain scission and cross-linking are the major consequences of thermal oxidation of polyolefins [9,10]. In the presence of oxygen, however, chain scission and macromolecules oxidation are the predominant reactions [11] (Scheme 1).

Several studies thus report on the significant reduction of molecular weight after thermal degradation of poly(ethylene) samples containing pro-oxidants [12], as well as on the identification of oxidation products including carboxylic acids, ketones, lactones and low molecular weight hydrocarbons [6].

Rate and extent of free radical oxidation of polyolefins are also affected by structural parameters such as chain defects (unsaturation) and branching, the latter being representative of relatively weak links susceptible to oxygen uptake to give hydroperoxides and bond cleavage. In this connection it has been stated that the hierarchy in the oxidation susceptibility of polyolefins is as follows: iPP > LDPE > LLDPE > HDPE [13,14].

Thermal oxidation reactions in polyethylene have been also studied in detail by chemiluminescence analysis [15,16]. It has been suggested that the major structures in the initial step of oxidation are α,γ - and α,δ -keto-hydroperoxides, whose acid-catalyzed transformation leads to chain scission with



Parameters to be monitored:

1. Weight increase;
2. Carbonyl index;
3. Wettability ;
4. Molecular weight;
5. Fractionation by solvent extraction

Scheme 1. Mechanism of radical oxidation of polyethylene.

simultaneous formation of carboxylic acids, aldehydes and methyl-ketone groups [17].

On the other hand, relatively little information on the influence of environmental parameters such as relative humidity, presence (aerobic) or absence (anaerobic) of oxygen, whole biological *consortia* on the propensity of thermal oxidation of degradable PE films, are available [18].

As a continuing part of our activity in the preparation of environmentally degradable/biodegradable polymeric systems and assessment of their propensity to degradation/biodegradation under different environmental conditions [19–24], the present paper is aimed at investigating the effects of different parameters such as temperature and relative humidity mimicking the environmental conditions associated with the composting processes, on the oxidation behaviour and hence degradation/biodegradation of different LDPE blown films containing pro-oxidant additives.

2. Experimental part

2.1. Thermally degradable polyethylene films

Polyethylene film samples containing proprietary TDPA[®] thermal pro-oxidant additives were kindly supplied by EPI Environmental Plastics Inc. (Vancouver, Canada).

The composition and characteristics of film samples, utilized in accelerated thermal degradation tests are reported in Table 1.

2.2. Degradation procedures

2.2.1. Thermal aging

Thermal oxidation of test samples was carried out in air in an oven at two different temperatures, 55 and 70 °C, under dry (uncontrolled humidity) and approximately 75% relative humidity (RH, saturated NaCl solution) conditions.

The oxidation behaviour at 55 °C of test samples floating in tap water was also studied.

2.3. Analytical characterization

2.3.1. Gravimetric analysis

Weight variation of film specimens submitted to thermal aging was recorded with time. Rectangular specimens

(9 × 9 cm) of each test sample were held up in glass tubes and weighed at time intervals with an analytical balance Alfacprecision AM 120 (±0.1 mg accuracy), after conditioning at room temperature in a desiccator. The results were averaged on 15 replicates.

2.3.2. Fourier transformed infrared spectroscopy (FT-IR)

FT-IR measurements were carried out with a Jasco model 410 FT-IR spectrophotometer. The spectra were taken as an average of 16 scans with 2 cm⁻¹ resolution. The carbonyl index (CO_i) was calculated as the ratio of the optical density of the absorption band at 1640–1840 cm⁻¹ (carbonyl peak), and the optical density of the absorption band at 1463 cm⁻¹ (CH₂ scissoring peak).

2.3.3. Contact angle

Wettability determinations of film surfaces submitted to thermal degradation were performed by contact angle measurements on samples supported on glass slide, carried out using a Camtel (Royston, UK) Goniometer mod. FT200. The wetting liquid was Millipore grade distilled water. Calculations were averaged on five measurements carried out at appropriate times.

2.3.4. Solvent extraction

The fractions of organic solvent extractable from original and thermally degraded specimen were also determined by extraction with boiling acetone. The extracts were dried to constant weight under vacuum.

2.3.5. Size exclusion chromatography (SEC)

The molecular weight (Mw) and molecular weight distribution (ID) of original and degraded samples were determined by means of a Waters model GPCV 2000 liquid chromatograph equipped with four Waters Styragel columns (HT6E; 2 HT4, HT3) and refractive index detector. 1,2,3-Trichlorobenzene stabilized with 1% 2,6-di-*tert*-butyl-4-methylphenol (BHT) was used as mobile phase at 1.0 ml/min flow rate at 140 °C.

Mw of acetone extracts were determined with a Jasco PU-1580 liquid chromatograph equipped with a Jasco 830RI refractive index detector and Perkin Elmer LC-75 UV–vis detector, using a PLgel guard column and two PLgel Mixed-D (30 cm, 10 μm) columns. Chloroform was used as mobile phase at 1 ml/min flow rate. Relative calibration was obtained by analyzing monodisperse polystyrene standards.

Table 1

Characteristics of thermally degradable PE film samples used in thermal degradation tests

Test Sample ^a	Thickness (μm)	Colour	Sample code
Lupolen 3026 HK with 15% DCP540 TM	32	Light brown	LDPE-DCP540
French compost bags with 10% ZSK 1314 TM	34	Green	FCB-ZSK10
French compost bags with 15% ZSK 1314 TM	34	Green	FCB-ZSK15

^a The percent figures (%) referred to the amount of EPI master batch in the PE granule blends submitted to melt blowing extrusion.

3. Results and discussion

As indicated in Scheme 1, the oxidative degradation of PE samples promoted by proprietary pro-oxidants loaded deliberately into PE, can be assessed by monitoring the increase of the weight of the samples, the carbonyl index (CO_i) due the oxygen uptake and the consequent increase of wettability, as well as the drop in Mw and extractability with solvent.

For efficiency and clarity the analysis of the mentioned parameters will be presented and discussed in specific sections.

3.1. Thermal aging of PE samples containing pro-oxidant

The oxidation propensity of PE samples containing pro-oxidant additives, as induced by heat was assayed in an oven at different temperatures (55 and 70 °C). The indicated temperatures were selected with the intention of mimicking the thermophilic phase of a composting process. The influence of the water vapour pressure was also investigated by comparing the thermal aging under dry condition and in controlled atmosphere as conditioned at approximately 75% relative humidity.

3.2. Determination of PE sample weight increase

Recording weight variations of test samples submitted to thermal aging in air in an oven at 55 and 70 °C showed an appreciable increase attributable to the oxygen uptake.

At 55 °C, the sample weight increase recorded after 8 days aging was appreciable in the case of LDPE-DCP540 film specimen, whereas in the FCB-ZSK15 and FCB-ZSK10 samples the oxygen uptake started after 15 and 23 days, respectively (Fig. 1). In any case, however, a weight increase corresponding to approximately 5% of the initial weight was reached in a sigmoidal profile after 42 days aging (Fig. 1). As expected, at 70 °C, the induction phase was significantly shorter, thus requiring 3, 6 and 8 days aging in the case of LPE-DCP540, FCB-ZSK15 and FCB-ZSK10 samples, respectively (Fig. 2). Also at this temperature, the overall weight increase, reached in a sigmoidal profile, corresponded to approximately 5.5%.

3.3. Determination of carbonyl index

The oxidation of the PE in the thermally aged samples was clearly shown by the FT-IR characterization. A sharp increase in absorption in the carbonyl region was recorded with time in all the samples aged at 70 °C (Fig. 3). Broadening in the

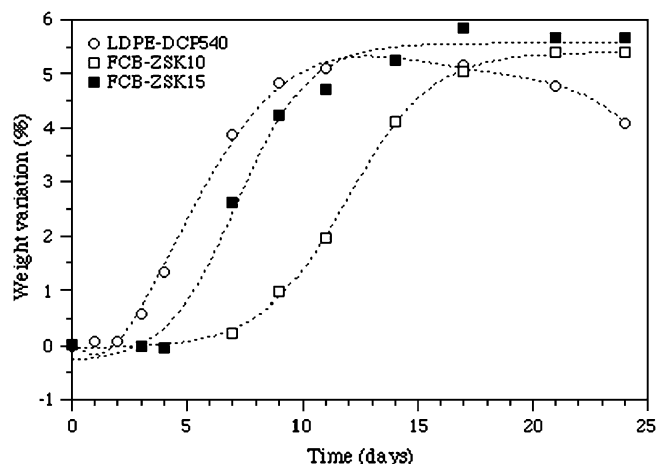


Fig. 2. Weight variation profile of LDPE samples containing pro-oxidant additives thermally treated in air in oven at 70 °C.

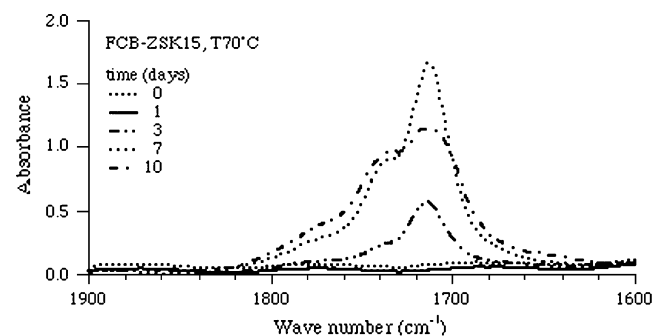
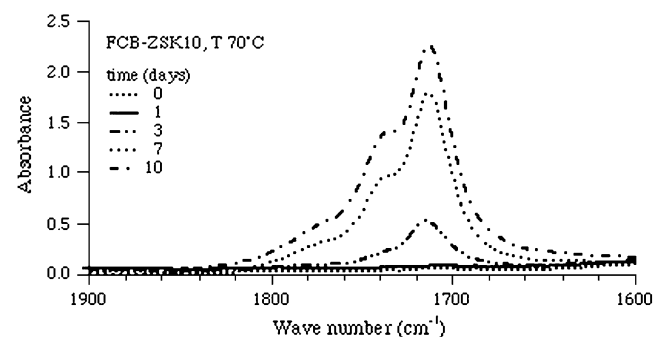
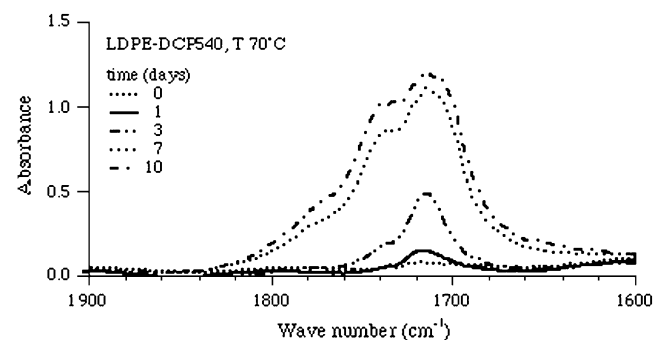


Fig. 3. Time variation of carbonyl absorption band of LDPE samples containing pro-oxidant additives thermally treated in air in oven at 70 °C.

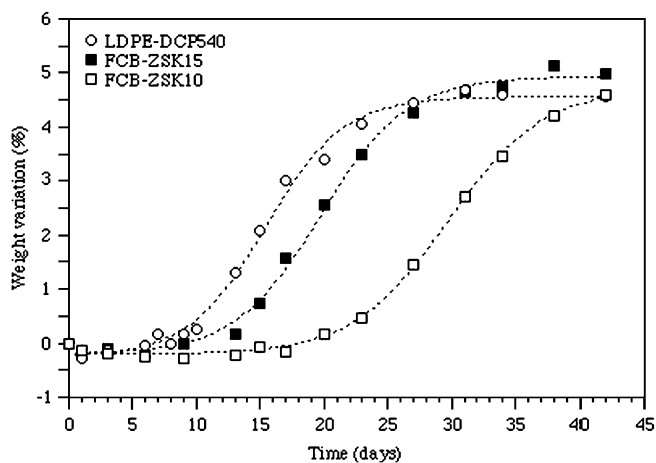


Fig. 1. Weight variation profile of LDPE samples containing pro-oxidant additives thermally treated in air in oven at 55 °C.

1680–1850 cm^{-1} range of carbonyl groups, as determined by the overlapping bands corresponding to acids (1712 cm^{-1}), ketones (1723 cm^{-1}), aldehydes (1730 cm^{-1}) and lactones (1780 cm^{-1}) [25] was observed, thus indicating the presence of different oxidized products, as previously reported (Fig. 3) [26]. On the basis of the absorption maxima, degradation products recognizable as carboxylic acid (ν_{max} 1712 cm^{-1}) were recorded as the major components in the early stage of oxidation, particularly in the LDPE-DCP540 sample. The broadening of the absorption band with time was attributable to the formation of ester groups (ν_{max} 1740 cm^{-1}) as recorded in all the treated samples. Carboxylic acid absorption bands were prevalent in the samples containing the ZSK1314 additive, whereas the relative intensity of ester groups and probably lactones (ν_{max} 1785 cm^{-1}) was higher in the LDPE-DCP540 sample.

As the carbonyl groups usually account for most of the products of thermooxidative degradation of polyethylene, their concentration, as determined by the carbonyl index (CO_i) can be used to monitor the progress of degradation [27]. CO_i determinations were therefore used to compare the thermal oxidation of test samples under dry and 75% relative humidity conditions at 55 and 70 °C.

In Fig. 4, the CO_i variation of LDPE-DCP540 samples recorded at 55 and 70 °C, are reported. A marked effect of the relative humidity on the thermal oxidation rate of this latter sample was observed at 70 °C as well as at 55 °C. In both cases, however, high CO_i values were recorded, even though at rather higher aging time under 75% RH (Fig. 5). In contrast, the

oxidation of LDPE samples containing the ZS K1314™ pro-oxidant additive, was not notably affected by the high humidity level, the delay in the degradation being almost exclusively attributable to the different aging temperatures (Figs. 5 and 6).

It is worth noting that, in all cases, the high humidity level, comparable to that occurring under real environmental conditions (e.g. aerobic composting), did not influence the overall extent of oxidation reached by all the tested samples.

The influence of moisture was also directly assessed by placing LDPE-DCP540 and FCB-ZSK15 film specimens directly on the surface of tap water in a beaker maintained at 55 °C. The disintegration of film samples occurred within 28 days aging. Afterwards the film debris sank to the bottom of the beaker. FT-IR analysis of the degraded materials confirmed the oxidation of the polymer in both analyzed samples. CO_i values of the tested samples after 28 days aging in water were 4.5 and 4.4, respectively, which were strictly comparable to the CO_i values recorded under dry condition at 55 °C.

3.4. Determination of wettability of oxidized sample

The increasing oxidation of the polymer was also shown by the change in the wettability of the surface of the samples. Contact angle values, recorded during the aging time in air at 70 °C, were found to decrease in all cases from 94.5° to 97.8° recorded at time zero to approximately 70° after 4 days aging. In the further 11 days aging the contact angle values remained basically constant (Fig. 7). After 15 days,

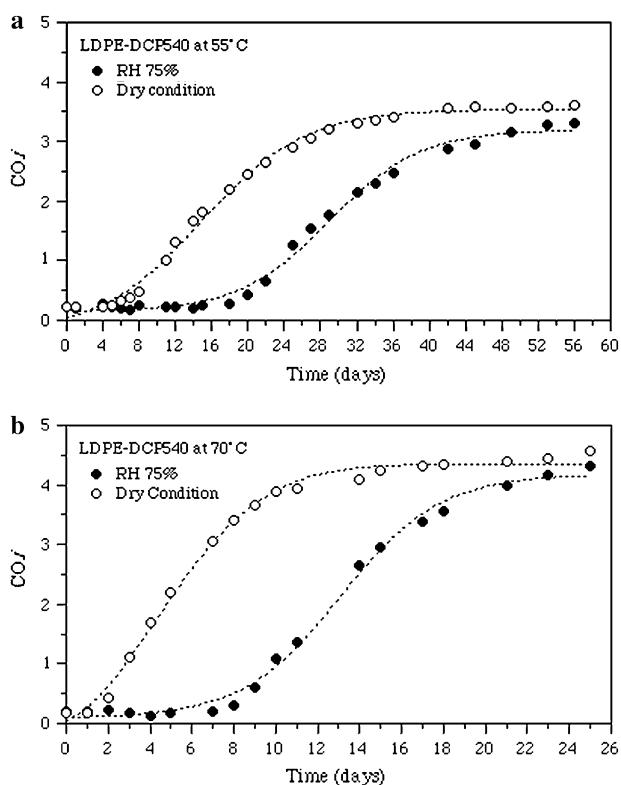


Fig. 4. Carbonyl index (CO_i) variation of LDPE-DCP540 film sample aged in oven at 55 (a) and 70 °C (b), under both dry and 75% RH atmosphere.

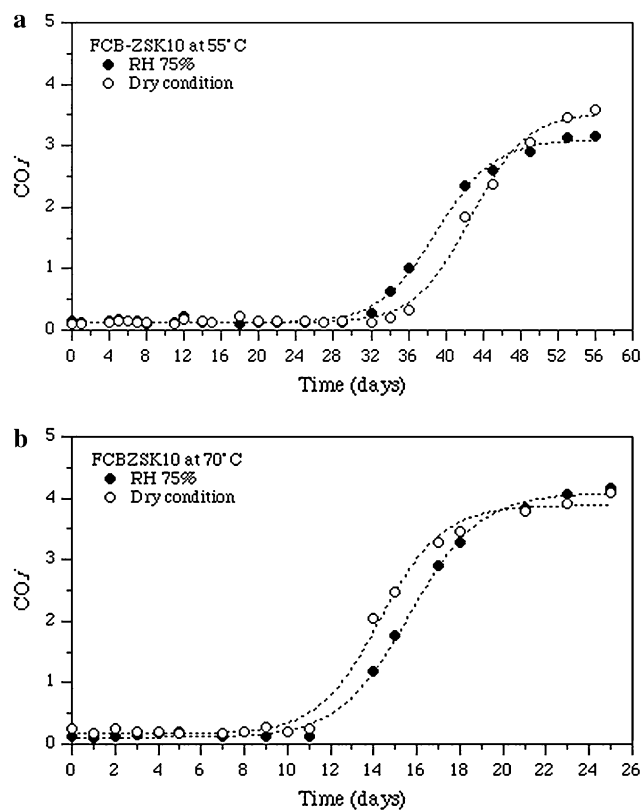


Fig. 5. Carbonyl index (CO_i) variation of FCB-ZSK10 film sample aged in oven at 55 (a) and 70 °C (b), under both dry and 75% RH atmosphere.

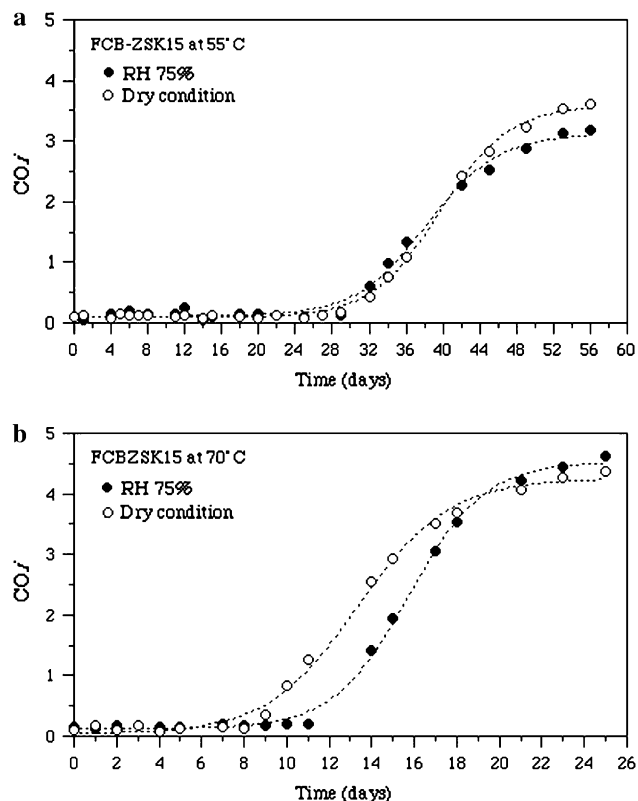


Fig. 6. Carbonyl index (CO_i) variation of FCB-ZSK15 film sample aged in oven at 55 (a) and 70 °C (b), under both dry and 75% RH atmosphere.

the measurement became impossible due to the complete disintegration of the films.

3.5. Fractionation of oxidized sample with boiling solvents

LDPE samples thermally treated in air in an oven, at different temperatures and aging time, were submitted to an extraction procedure with boiling acetone in order to evaluate the extractable fraction as a function of the level of polymer oxidation as assessed by the CO_i (Table 2).

Acetone was chosen as a moderately polar solvent that was able to dissolve the oxidized PE fragments which in principle

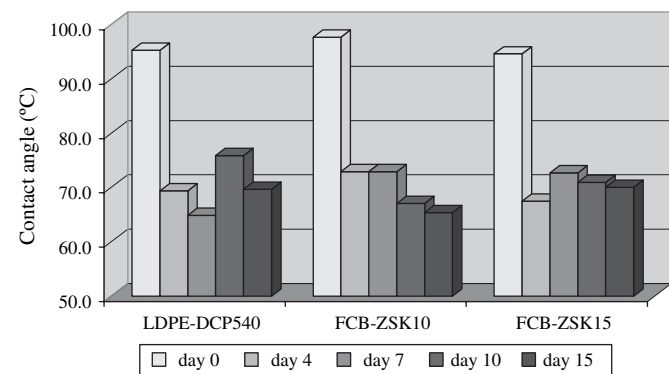


Fig. 7. Contact angle determinations with distilled water as wetting agent of LDPE samples containing pro-oxidant additives thermally treated in air in oven at 70 °C.

Table 2

Relationship between carbonyl index (CO_i) and percentage of fractions extractable with acetone from original and thermally treated LDPE film samples

Sample	CO_i^a	Acetone extract		
		(%)	Mw ^b (kDa)	ID ^b
FCB-ZSK10	0.453	6.5	1.52	1.49
	0.534	7.7	1.47	1.46
	3.583	17.9	1.30	1.39
	6.816	27.1	0.92	1.32
FCB-ZSK15	0.212	5.9	1.58	1.46
	2.864	9.2	1.67	1.52
	5.193	23.8	1.27	1.43
	7.256	22.6	1.03	1.36
LDPE-DCP540	0.627	5.5	1.08	1.27
	2.243	11.3	1.49	1.41
	4.818	21.1	1.08	1.37
	5.441	27.7	0.89	1.33

^a Evaluated by FT-IR as $D_{B1640-1840}/D_{B1435}$.

^b Determined by HT-GPC.

might be subjected to a higher diffusion in natural environments.

The recorded data clearly showed that the amount of acetone extractable fraction is positively correlated to the level of oxidation induced by the thermal treatment in oven, thus reaching fairly high amount corresponding to 25–30% of the sample weight (Table 2).

As expected acetone extraction allowed the oxidized PE fragments to be separated from those at limited level of oxidation. Therefore, the recorded data have to be considered as partially representative of the overall of low Mw fractions produced during the thermal oxidation of the test materials.

Mw of acetone extractable fractions were analyzed by gel permeation chromatography (Table 2). In all cases low Mw (800–1600Da) materials were detected in the solvent extracts. It is worth noting, however, that the level of oxidation, as related to the carbonyl index, promoted the increase of the amount of the extractable fraction as well as a significant decrease of the corresponding Mw.

Accordingly, from heavily oxidized test samples, about 25% by weight of acetone extracts were obtained, which also were showing very low Mw (850–1050 Da) (Table 2).

The recorded data suggest that cross-linking reactions do not notably affect the oxidative degradation behaviour of the analyzed samples, which seem to proceed with macromolecular cleavage to low Mw fractions capable of being assimilated by microorganisms [28–31]. Other studies have demonstrated that microorganisms are able to assimilate the oxidation products formed during thermal- and photo-oxidation of polyethylene [32,33].

3.6. Determination of molecular weight (Mw) of analyzed samples

Mw and molecular weight distribution of LDPE samples containing pro-oxidant additives submitted to thermal aging at 70 °C under different relative humidity conditions were analyzed by HT-GPC. The recorded Mw data were related with

Table 3
Relationship between carbonyl index (CO_i) and molecular weight (Mw) of LDPE-DCP540 sample thermally treated at 70 °C in dry and wet conditions

Test conditions				RH ~ 75 (%)			
Dry (open air)				RH ~ 75 (%)			
Time (days)	CO _i ^a	Mw ^b (kDa)	ID ^b	Time (days)	CO _i ^a	Mw ^b (kDa)	ID ^b
0	0.22	147.7	3.78	0	0.22	147.7	3.78
2	0.61	39.4	4.24	12	1.60	10.7	2.92
3	1.14	19.5	2.96	13	2.23	10.4	2.88
5	2.32	9.7	2.59	25	4.33	4.8	1.37
25	4.57	4.5	1.27	—	—	—	—

^a Evaluated by FT-IR as $D_{B1640-1840}/D_{B1435}$.

^b Determined by HT-GPC.

the CO_i values as determined by FT-IR spectroscopy on the same specimen (Tables 3–5).

In Table 3, the Mw analysis and CO_i values of LDPE-DCP540 sample are reported. It was evident that a few days of thermal degradation under dry and 75% RH conditions were sufficient to induce a dramatic decrease of Mw from 148 000 in the original film to a value lower than 5000 in the thermally treated film specimen. Also the polydispersity index (ID) was found to decrease significantly, from 3.78 to 1.27 (Table 3). Comparable results were recorded in the analysis of Mw of thermally treated FCB-ZSK10 and FCB-ZSK15 film samples (Tables 4, 5).

HT-GPC chromatograms, revealed the presence, at higher retention time, corresponding to the lowest Mw, of elution peaks having a bimodal shape, thus revealing the presence of very low (1700) Mw fractions (Fig. 8).

A dramatic reduction up to 8400 of the Mw was detected also in the case of LDPE-DCP540 and FCB-ZSK15 samples aged in water at 55 °C for 28 days.

The relationship between the Mw and CO_i was expressed by a monoexponential trend (Fig. 9). Accordingly, CO_i values may be used in order to predict the Mw decrease as a function of the oxidation level. Moreover, the recorded trend is in agreement with a statistical chain scission mechanism, as suggested in the photo and thermal degradation of polyolefins [7,8,11].

Table 4
Relationship between carbonyl index (CO_i) and molecular weight (Mw) of FCB-ZSK10 sample thermally treated at 70 °C in dry and wet conditions

Test conditions				RH ~ 75 (%)			
Dry (open air)				RH ~ 75 (%)			
Time (days)	CO _i ^a	Mw ^b (kDa)	ID ^b	Time (days)	CO _i ^a	Mw ^b (kDa)	ID ^b
0	0.25	157.6	4.36	0	0.25	157.6	4.36
11	0.63	45.7	3.94	12	0.57	28.6	3.63
13	1.40	16.4	2.75	16	2.54	9.9	2.59
15	2.33	10.1	2.47	25	4.16	4.9	1.33
25	4.09	4.4	1.25	—	—	—	—

^a Evaluated by FT-IR as $D_{B1640-1840}/D_{B1435}$.

^b Determined by HT-GPC.

Table 5
Relationship between carbonyl index (CO_i) and molecular weight (Mw) of FCB-ZSK15 sample thermally treated at 70 °C in dry and wet conditions

Test conditions				RH ~ 75 (%)			
Dry (open air)				RH ~ 75 (%)			
Time (days)	CO _i ^a	Mw ^b (kDa)	ID ^b	Time (days)	CO _i ^a	Mw ^b (kDa)	ID ^b
0	0.11	157.6	4.36	0	0.11	157.6	4.36
9	0.67	34.4	3.66	14	1.49	18.1	3.53
12	1.59	14.9	2.91	17	2.89	8.1	2.68
15	2.83	7.6	2.44	25	4.62	4.2	1.44
25	4.38	5.1	1.32	—	—	—	—

^a Evaluated by FT-IR as $D_{B1640-1840}/D_{B1435}$.

^b Determined by HT-GPC.

4. Conclusions

The proprietary prodegradant systems used in the formulation of the analyzed LDPE film samples were effective in inducing the oxidative degradation of the polymer backbone. As expectable, the rate of degradation directly depends upon the

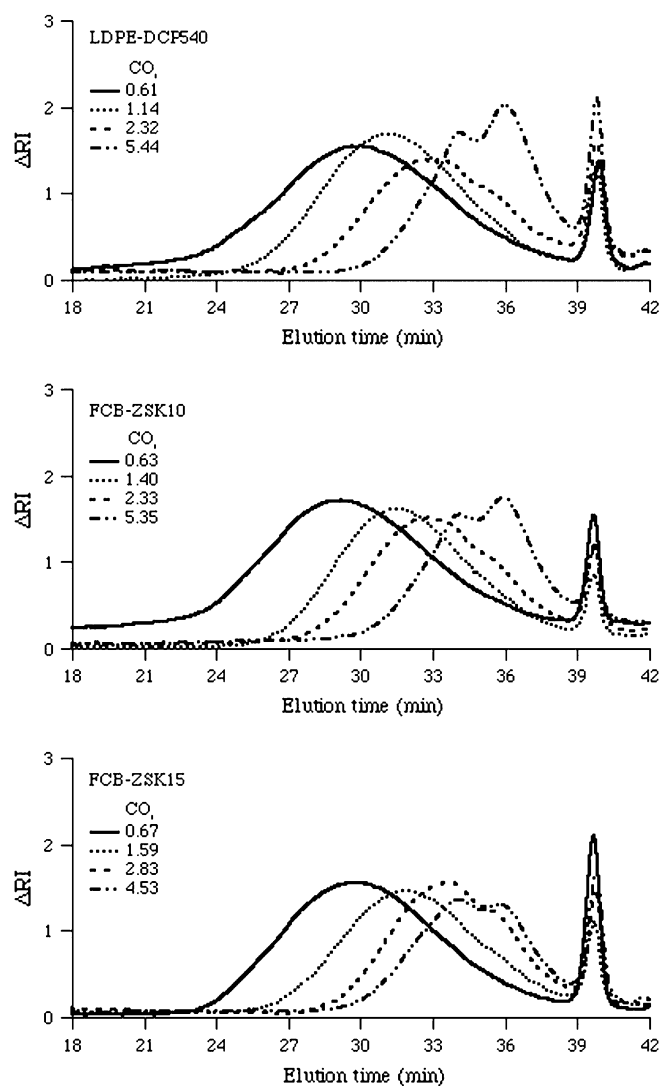


Fig. 8. HT-GPC chromatograms of LDPE samples containing pro-oxidant additives thermally treated in air in oven at 70 °C.

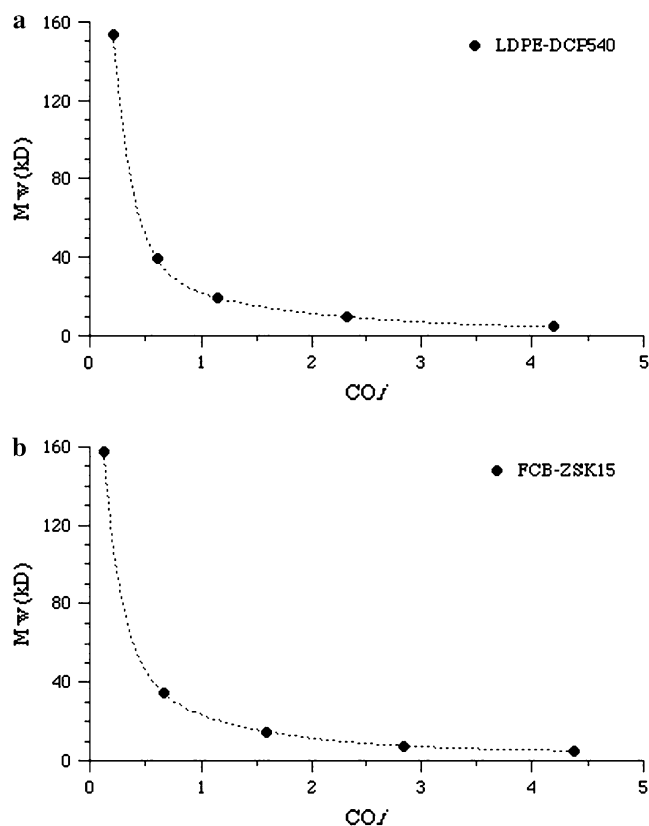


Fig. 9. Molecular weight Carbonyl index (COI) relationship in LDPE-DCP540 (a) and FCB-ZSK15 (b) film samples thermally treated in air in oven at 70 °C.

temperature with higher values achievable at higher temperatures.

During thermal pre-treatment in moisture saturated environments (75% RH) a variable delay in the start of oxidation was observed in a few cases relevant to the lower temperature pre-treatment (55 °C). The final level of oxidation, was, however, strictly comparable under dry and wet conditions.

Once the oxidation reached a plateau, a substantial drop in the molecular weight was detected, of more than one order of magnitude with respect to the thermally untreated samples. This was accompanied by the production of low molar mass, oxidized fractions, which due to their wettability and functionality, become vulnerable to microorganisms [19,20].

The changes of the molecular weights of the tested samples could be nicely reproduced with monoexponential decay, thus allowing a simple straightforward method for the assessment of the relative extent of degradation and, indirectly, to predict the potential assimilation by microorganisms.

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