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Oxo-biodegradable full carbon backbone polymers – biodegradation behaviour of thermally oxidized polyethylene in an aqueous medium

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Abstract

Several demonstrations of the effective biodegradation in soil of pro-oxidant activated polyethylene (PE) have been reported recently. Nevertheless a comprehensive understanding of the ultimate fate in the environment of the oxidized fragments of oxo-biodegradable polyethylene materials needs the extension of the studies to other natural environments and in particular to aqueous media (river, lake, brackish and marine waters) where accidental plastic littering and the resulting degraded fragments eventually may end up.

In this respect, as part of our continuing activity in the area of oxo-biodegradable polymeric materials, in the present paper we wish to report on the results attained in an ongoing investigation on the biodegradation in a water medium of thermally pre-oxidized low density polyethylene (LDPE) film samples containing pro-oxidant additives.

Thermally oxidized LDPE-film samples and corresponding acetone extractable fractions were submitted to the effect of microorganism flora present in river water. The effective biodegradation was assessed by monitoring the amount of CO_2 developed over time in a respirometer apparatus. Levels of biodegradation up to 12 and 48% for the degraded fragments and corresponding fractions extracted with boiling acetone were detected on a 100-day time frame.

Keywords: Thermally degradable LDPE; Oxo-biodegradation; Alkane biodegradation; River water

1. Introduction

The extremely low propensity to oxidation and further degradation followed by biodegradation of conventional polyethylene is widely accepted. However, more than 30 years ago it was suggested that pre-aging treatment (UV, heat exposure, oxidation with nitric acid), as well as the addition of pro-degradant systems acting as initiators of thermal and photo-oxidation of polyethylene films promote the fragmentation of the tested samples eventually followed by microbial attack [1–5].

In particular, it was repeatedly demonstrated that abiotic oxidation produces functional macromolecules susceptible to random cleavage with the formation of low molecular weight oxygenated products including aliphatic carboxylic acids, alcohols, aldehydes and ketones [6–9].

The rate of biodegradation of polyethylene, even under prolonged exposure time (10–32 years) to microbial consortia of soil, was found to be very low, thus accounting for less than 1% carbon mineralization [10,11]. Nevertheless, more recently it has been demonstrated that the use of suitable pro-oxidants as dopants of conventional LDPE or MDPE film induces substantial oxidation of the tested specimen with consequent fragmentation, drop of molecular weight and wettability increases ultimately followed by a fairly-high mineralization extent (60–70%) and fixation of carbon into cell biomass (8–10%) [12] in soil burial tests [13,14].

Most of the studies of the biodegradability of polyolefins containing pro-oxidant have been carried out on complex solid media like soil and compost [13–15], indeed very few studies have been carried out in aqueous media as well as in the

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Table 1
Characteristics of thermally degradable PE film samples used in thermal degradation tests [20]

Test sample[a]	Thickness (μm)	Sample code	Mw[b] (kDa)	ID[b]
Lupolen 3026 HK with 15% DCP540™	32	LDPE-DCP540	147.7	3.78
French compost bags with 10% ZSK 1314™	34	FCB-ZSK10	157.6	4.36
French compost bags with 15% ZSK 1314™	34	FCB-ZSK15	157.6	4.36

[a] The percent figures (%) are referred to the amount of EPI-masterbatch in the PE granule blends submitted to melt blown extrusion.
[b] Determined by HT-GPC.

presence of selected microbial species. In this respect the assimilation of organic acids derived from polyethylene oxidation by *Arthrobacter paraffineus* was observed by Albertsson et al. [16] as well as the direct assimilation of thermo-oxidized polyethylene by *Penicllium pinophilum*, even though at a very low mineralization rate (0.37% in 31 months) [17], and UV irradiated LDPE by a thermophilic bacterium [18].

The use of selected bacterial strains in liquid cultures demonstrated their capability to biofilm formation on the assayed PE film samples [19,20]. In particular a *Rhodococcus ruber* strain is found to utilize polyethylene films as sole carbon source as established by an 8% weight loss within 30 days of incubation, in a burial test [19]. More recently metabolic studies using ATP/ADP nucleotide assays revealed, after an initial fast growth due to the assimilation of low molecular fractions from thermally oxidized samples of LDPE, that the energetic status of some microbial strains, such as *Rhodococcus rhodochrous* and *Nocardia asteroides*, were compatible with the continuous assimilation of the polymer even though at a fairly low rate [20].

In the present study, aimed at the assessment of the mineralization level in river water medium, LDPE samples doped with pro-oxidant, formerly submitted to a prior investigation of the effects of different degradation conditions in term of either temperature or relative humidity on the oxidation behaviour, were utilized [21]. Accordingly thermally oxidized films at maximum and medium levels of oxidation, as determined by carbonyl index (CO*i*), as well as the relevant acetone extractable fractions, were used to feed aqueous cultures of microorganism consortia present in river water. A respirometric procedure [22] based on the determination of the carbon dioxide evolved from the different cultures was utilized to assess the extent of the mineralization of the analyzed films and fractions extracted with acetone.

A fairly high biodegradation of these latter fractions, as well as the positive influence of the achieved oxidation level on the biodegradation propensity of the film samples was clearly demonstrated.

2. Experimental part

2.1. Thermally degradable polyethylene films

Poly(ethylene) film samples containing thermal pro-oxidant additives (LDPE-DCP540, FCB-ZSK15, and FCB-ZSK10) were kindly supplied by EPI Environmental Plastics Inc. (Vancouver, Canada).

Thermal degradation conditions and solvent extraction procedures of the analyzed films have been reported previously [21].

Compositions and characteristics of film samples utilized in accelerated thermal degradation tests are reported in Table 1 whereas in Table 2 is reported the data relevant to the recorded oxidation levels as assessed by the carbonyl index (CO*i*) and the amount of the low molecular weight oxidized LDPE fractions as extracted with boiling acetone.

2.2. River water respirometric biodegradation test

The biodegradation tests were carried out in 300-ml Erlenmeyer flasks equipped with a silicone rubber stopper, hanging a 40 ml capacity plastic vial filled with 20 ml of a 0.05 M KOH solution for trapping CO_2 evolved from the microbial culture. Each flask contained 100 ml sterilised low concentration salt solutions having the following composition per litre of distilled water: KH_2PO_4 85 mg, K_2HPO_4 218 mg, Na_2HPO_4 334 mg, $(NH_4)_2SO_4$ 10 mg, NH_4NO_3 10 mg, $CaCl_2$ 36 mg, $MgSO_4 \cdot 7H_2O$ 23 mg, and $FeCl_3 \cdot 6H_2O$ 0.3 mg, pH 7.4 ± 0.2 [23].

Table 2
LDPE-film samples thermally treated at 70 °C and relevant fractions extractable with acetone tested in the river water biometer assay

Test sample	Film			Acetone extract			
	CO*i*[a]	Mw[b] (kDa)	ID[b]	Film weight (%)	CO*i*[a]	Mw[c] (kDa)	ID[c]
LDPE-DCP540	2.3	9.7	2.59	11.3	6.4	1.49	1.41
	4.6	4.5	1.27	21.1	20.7	1.08	1.37
FCB-ZSK15	2.8	7.6	2.44	9.2	6.1	1.67	1.52
	4.4	5.1	1.32	21.8	10.9	1.27	1.42
FCB-ZSK10	2.3	10.1	2.47	10.2	9.5	1.37	1.45
	4.1	4.4	1.25	18.8	12.7	1.27	1.39

[a] Evaluated by FT-IR as $D_{B1640\text{-}1840}/D_{B1435}$.
[b] Determined by HT-GPC.
[c] Determined by GPC.