VERSITA 10.2478/v10310-012-0031-4
Ovidius University Annals of Chemistry Volume 23, Number 2, pp.187-190, 2012

The behaviour of the oxo-biodegradable LDPE materials during the service life

Corina TEODORESCU*[a], Lica MITRANA and Anca-Corina TEIU

[a] *Ovidius University of Constanta, Department of Chemistry and Chemical Engineering , 124 Mamaia Blvd, 900527 Constanta, Romania*

Abstract. This is an experimental study on behaviour of oxo-biodegradable plastics containing additives during service life. Low density polyethylene is a most extensive used synthetic polymer with the largest production, because an important part of the production is converted into various products with short life cycle. The goal of this paper was to quantify the biodegradation of two low density polyethylene films containing 10% and 20% pro-oxidant AddiFlex in soil columns. Previously, the physical-mechanical properties and heavy metal content in polymer films have been determined. The obtained degree of mineralization was around 60% after 200 days of incubation for both studied polymer films (59.8% for 10% additive and 64.3% for 20% additive).

Keywords: oxo-biodegradable, LDPE, pro-oxidant

1. Introduction

European environmental regulations and concerns growing about environment led to the diversification of polymeric materials which are compatible with the environment. Use of biodegradable polymers has grown considerably. Both synthetic and natural polymers aren't biodegradable, unless they are converted into low molecular mass species that can be assimilated by microorganisms [1].

Low density polyethylene is the most extensive used synthetic polymer with the largest production. An important part of the polyethylene production is converted into various products with short life cycle such as different packaging films, bags, sheeting for covering widely used in agriculture. At the end of their life, in best case plastics reach the landfills or the environment, as part of "garbage in plastic"[1, 2].

Polyethylene is submitted to oxidative degradation by light and temperature, leading to deterioration of its mechanical properties and finally to the fragmentation of the product. Therefore, producers modify polyethylene by adding antioxidant additives in order to allow the processing of the melt without the risk of oxidation and providing the stability of the product obtained, especially if it has to support a longer exposure to direct sunlight. All polyethylene materials contain certain amounts of antioxidants that make the waste more stable than is desirable.

Because the use of polymers is inevitable, must be found some ways in order to:

- Enhance biodegradability of polymers by blending with natural biodegradable polymers, as starch or cellulose;
- The addition of pro-oxidants, because they are easily degraded;
- Utilization of microorganisms that can efficiently degrade these polymers.

Polyethylene degradation occurs when negative results of a chemical reaction changes the characteristics of a specimen. The term “degradation” is often adopted for the polymer chain breaking, but in addition it may also include: colour changes, embrittlement, loss of clarity, the increase of power dissipation factor and variations of viscosity. The polymer degradation can be induced by thermal, photo, mechanical, chemical, UV or biological action. Degradation is generally regarded

ISSN-1223-7221

as an undesired event. However, once the useful life of an item has expired and its specific properties are no longer required, environmental degradation can become attractive [3].

In a compost environment the present temperature and oxygen will initiate the molecular breakdown of the polymer and these results in:

- microbial digestion of the direct biodegradable components providing greater surface for the bio-process;
- thermo-oxidative breakdown of the polymer chains. Thus weakening the mechanical properties and makes the surface hydrophilic to assist direct microbial digestion;
- microbial digestion of the polymer fragments to H_2O, CO_2 and biomass. No toxic breakdown components are created [1].

The goal of this paper was to quantify the biodegradation of two polymer films of Low Density Polyethylene (LDPE) containing 10%, respectively 20% pro-oxidant AddiFlex in soil columns. Previously, their physical-mechanical properties and heavy metal content have been determined.

2. Experimental

In the experiments there were used samples of 40 μm thick polyethylene films, prepared in the laboratory from commercial LDPE with 0.691 g/min melt flow index and 0.921 g/cm^{3}density, resistant to oxidation and degradation due to the presence of antioxidants and stabilizers.

Two types of polyethylene – pro-oxidant additive mixture were studied: samples containing 10% pro-oxidant, respectively 20% pro-oxidant.

As pro-oxidant additive it was used a commercial thermo-oxidative additive for polyolefins known as AddiFlex. By using pro-oxidant additive, samples became oxo-biodegradable. Most active pro-oxidant are those based on metal combinations capable of producing two metal ions with similar stability and oxidation numbers that differ only by one unit (Mn^{2+}/Mn^{3+}).

Before starting the biodegradation experiment, the next properties of samples were determined: the melt flow index, elongation and tensile strength. Physical and mechanical properties of LDPE films were determined according to ASTM D 882/2010 on Instron Universal Tester [4].

In order to assess the soil pollution with metals, the content in heavy metals was analyzed for polymer film sample with 20% pro-oxidant by ICP-MS. Heavy metals analyses of the polymer film samples were done according with the DIN 54900 standard [5].

Active soil was composed of 90% plant substrate of peat and 10% mature compost. Mature compost contained a large number of different microorganisms that normally occur in compost and are able to degrade different types of biodegradable compounds. Active soil was preconditioned for 4 weeks at a temperature of 29^{o}C, before being used in biodegradation tests.

The mineralization of the materials occurred in soil columns at an incubation temperature of 60°C. The mineralization was monitored by measuring the produced carbon dioxide. The polymer films were mixed with microbial activated soil, which itself contained very low amounts of easily degradable carbon compounds.

Molecular weight of polyethylene samples used was: 79.994kg/mol for film with 10% pro-oxidant and 74.982kg/mol for film with 20% pro-oxidant.

Glass columns were filled by this mixture, as it can be seen in **Fig.1.**

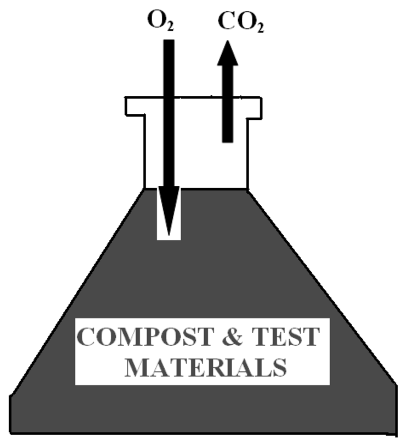

Fig.1. Experimental installation for the mineralization of materials in soil column

The microorganisms in the soil utilized the organic component, thereby producing new biomass. The samples were continuously aerated with oxygen.

The gas at the outlets of the columns transported the carbon dioxide, produced by the microorganisms, out of the glass columns. The gas was then washed in an adsorbent solution.

The carbon dioxide produced was trapped as sodium carbonate in a sodium hydroxide solution. Periodically a sample of the sodium hydroxide solution was taken and the carbonate content measured by titration. The carbon content of identical samples of test materials was analysed before starting the mineralisation test by total CO_2 production after burning.

$$2NaOH+CO_2=Na_2CO_3+H_2O \quad (1)$$

$$Na_2CO_3+2HCl=Na_2CO_3+2H_2O \quad (2)$$

The degree of mineralisation of the test materials was calculated from the carbon dioxide produced by material balance on carbon.

Thermal oxidation was investigated in well-defined conditions. In the oxidation processes were used high temperatures (50 - 70°C). The oxygen content in the compost decreases due to oxygen consumption by microorganisms.

3. Results and Discussions

The results concerning the melt flow index, elongation and tensile strength of the studied LDPE film samples are presented in **Table 1**.

Table 1. Physical and mechanical properties of films used in the test of mineralisation

Film type	**The melt flow index** [g/10min]	**Strain** [%]		**Tensile strength** [MPa]	
		Long	Transv	Long	Transv
without pro-oxidant	0.691	404	600	20.9	20.1
10% pro-oxidant AddiFlex	0.699	420	644	21.6	20.5
20% pro-oxidant AddiFlex	0.703	444	568	22.7	17.8

Films are anisotropic materials, so that resistance tests are tensile strength in the longitudinal direction (long.) and transverse (transv.).

The results presented in Table 1 show that AddiFlex pro-oxidants don't influence greatly the mechanical properties of the films.

The heavy metals content in 20% pro-oxidant sample determined by ICP-MS method are presented in **Table 2.**

Table 2. Metal content of LDPE film, with 20% pro-oxidant AddiFlex sample

Heavy metals	**20% pro-oxidant AddiFlex sample [mg / kg]**	**Tolerated values (Pre-Standard DIN 54900) [mg / kg]**
Lead	3.00	30.00
Chromium	1.50	30.00
Nickel	2.50	15.00
Zinc	25.00	100.00
Cadmium	0.15	0.30
Copper	2.00	22.50
Mercury	0.25	0.30

Table 3 presents the amount of CO_2 produced from mineralisation of two polymer films containing 10%, respectively 20% pro-oxidant AddiFlex samples during the incubation period.

The results of the investigation show that the materials degrade quickly at the temperature used.

After 200 days of incubation the degree of mineralisation was 59.8% for 10% pro-oxidant AddiFlex sample and 64.3% for 20% pro-oxidant AddiFlex sample.

Mineralisation of sample containing 10% pro-oxidant was slow, which indicates that some additional oxidation takes place during the period of mineralisation method, and is listed in Table 3.

The degree of mineralisation was calculated from the CO_2 produced as a percentage of the theoretical value of CO_2 that could be produced.

Table 3. The amount of CO_2 produced from mineralisation of two polymer films containing 10%, respectively 20% pro-oxidant AddiFlex samples during the incubation period

Incubation period (days)	Film with 10% pro-oxidant AddiFlex [% CO_2]	Film with 20% pro-oxidant AddiFlex [% CO_2]
0	0.0	0.0
6	5.0	7.1
13	13.1	13.3
22	18.9	19.0
32	23.2	23.1
43	28.0	27.5
54	32.1	31.5
62	33.8	33.3
81	38.3	38.6
95	42.5	42.1
109	45.2	46.0
123	47.3	49.0
137	50.5	52.1
150	53.0	55.9
165	55.1	58.5
180	57.5	61.6
200	59.8	64.3

5. Conclusions

Plastics must have a default life before physical degradation. Physical and mechanical properties of plastics should not change during their service. However, after the material has mainly served the purpose, it should be rapidly degraded. Thus, all biodegradable polymers have a delicate balance between achieving performance during their service life and being biodegradable after.

The goal of this paper was to predict the behavior of two polymer films of Low Density Polyethylene (LDPE) containing 10%, respectively 20% pro-oxidant AddiFlex in soil columns from the point of view of their life time of mineralization.

The physical-mechanical properties and heavy metals content, determined previously the experiment show that AddiFlex pro-oxidants don't influence greatly the mechanical properties of the films and the concentrations of heavy metals in 20% AddiFlex polymer film were below those tolerated by the standard DIN 54900.

The obtained degree of mineralization was around 60% after 200 days of incubation for both studied polymer films. The sample containing 10% pro-oxidant AddiFlex had a 59.8% mineralization rate and the sample with 20% pro-oxidant AddiFlex reached 64.3% mineralization rate, that means a percent of 10% pro-oxidant should be enough to assure the biodegradation process.

5. References

* E-mail address: cteo@univ-ovidius.ro

[1]. I. Jakubowicz, Polymer Degradation and Stability **80**, 1 (2002)

[2]. A. Koutsandreas, *Oxo-Biodegradable plastics: addressing the problem of plastics persistence in the environment,* Ed. Chemical Institute of Canada, 2009, pp. 18-20.

[3]. N.B. Vogt, E.A. Kleppe, Polymer Degradation and Stability, **94**, 4 (2009)

[4]. *** ASTM D 882/2010 – *Standard Test Method for Tensile Properties of Thin Plastic Sheeting.*

[5]. *** DIN V 54900-*Testing of Compostability of Plastics*;

Submitted: July 17th 2012
Accepted in revised form: November 21th 2012