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Degradation of polyethylene film samples containing oxo-degradable additives

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Abstract

The introduction of the so called oxo-biodegradable additives in the Argentine market motivated the assessment of the effects of abiotic and biotic factors on the structure and mechanical behavior of polyethylene (PE) with oxo-degradable additives (PE+AD). Samples of oxo-degradable packaging films found in local shops together with polyethylene films with and without $d_2w^{®}$ additive were annealed at different temperatures between 50 and 110ºC and submitted to ultraviolet radiation at different irradiances (0,35; 0,45; 0,89 and 1,20 W/m^2). Furthermore, aged oxo-degradable films were set in a controlled compost bioreactor in order to evaluate their biodegradation ability. Experimental results showed that elongation at break was the mechanical property more sensitive to the polymeric degradation. The structural changes determined by FT-IR remarked the importance of the UV degradation time over the irradiation rate; the carbonyl index of the degraded samples pointed out that chain scission was a thermally activated process. Regarding degradation due to UV radiation, at the same dose, the elongation at break is lower at lower irradiance both in PE and PE+AD samples. On the other hand, thermal degradation of PE without additive is more susceptible to degradation than PE + AD. At the beginning of the biodegradation tests, PE + AD showed a higher CO_2 production rate with respect to PE; however, this rate reduced along the first 30 days, reaching the CO_2 production of PE without additive. The maximum biodegradation observed for both PE and PE+AD samples was 24 % after 90 days of incubation.

Keywords: degradation; oxo-degradable; polyethylene

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1. Introduction

Shopping bags made of polyethylene (PE) with the so called totally degradable polymer additives (TDPA) have appeared in the Argentine market with the claim of being "oxo-degradable". The underlying technology is based on the special additives which, if incorporated into standard polyethylene resins, might accelerate the degradation of the products made with them (http://www.degradable.com.ar, accessed February 2012). Abiotic agents such as solar ultraviolet radiation (UV), heat or mechanical stresses could initiate the first stage of degradation: an oxidation process promoted by the additives. Once oxidized, polyethylene should exhibit a significant reduction of its molecular weight, and thus low molecular weight compounds could be easily assimilated by the microorganisms in the ecosystem where the films were disposed (biotic mechanism); Koutny et al. (2006) provided a comprehensible review for both micro-biologist and polymer scientists.

Although the technology of the oxo-degradable products is not new but their first appearance on the market in the 80's, it is still doubtful (Davis, 2006) whether these products provide what they promise according to international standards of biodegradation (Krzan et al., 2006). Moreover, there are still concerns about the potential toxicity of the additives as well as their possible negative effects on the recycling of conventional polymers (Kyrikou et al., 2007; Roy et al., 2011). Furthermore PE biodegradation is confronted with methodological problems, because of long-term experiments that interfere with the established research funding system and the tendency of industry to launch new products in the shortest possible time (Kotny et al., 2006).

Therefore, in order to assess whether PE with oxo-degradable additives can be safely inserted in the Argentine market, we studied how abiotic (temperature and UV radiation) and biotic (aerobic biodegradation) factors affect mechanical behavior and degrade the structure of these materials.

2. Experimental

Three types of plastic films were studied: polyethylene (PE), polyethylene with the d2w® oxo-degradable additive (PE + AD) and several shopping bags collected from shops in Buenos Aires City labeled as "oxo-degradable".

UV degraded samples were exposed to UV radiation in a Q-Lab Model QUV environmental chamber under irradiances between 0,35 and 1,20 W/m^2 and temperatures between 50 °C and 70 °C. Thermal aging was performed in a gravity convection oven "Techno Dalvo" at different temperatures between 50 °C and 110 °C, according to the ASTM D-5208 and ASTM D-5510, respectively. Four samples (20±0,5 x 80±0,5 mm and 50±2 μm thickness) were tested for each condition at different aging times.

Degradation of the films was followed, on one hand, by measuring their tensile properties: tensile modulus (E), stress at break (σ_b) and elongation at break (ε_b). Stress-strain tests of films were performed at room temperature using an Instron 5500 testing machine, at a strain rate of 2 x 10^{-3} s^{-1}, according to the ASTM D-3826.

On the other hand, the formation of carbonyl groups produced along the degradation of polyethylene, was measured by a Fourier transform infrared (FT-IR) spectrophotometer (Nicolet Magna IR 560). The spectra were taken as an average of 256 scans with 2 cm^{-1} resolution. The Carbonyl Index (CI) was calculated as the ratio of absorbance values at 1715 (carbonyl peak) and 1460 cm^{-1} (-CH$_2$-scissoring peak).

Aerobic biodegradation tests were carried out in 1000 ml glass vessels filled with defined amounts of mature compost (20 g). Polymer samples (6,5 x 9,5 cm and 50±2 μm thickness) were placed in the middle layer at 70 mg/g mature compost concentrations. The vessels were kept in the dark and incubated at 55±1 °C. A small glass with a 0,05 N KOH solution inside the vessel was used to absorb the CO$_2$ produced by the biodegradation. At regular intervals the cumulative production of CO$_2$ was determined by titration of the solution with 0,1 N HCl (Chiellini et al., 2003). Three samples were tested for each type of plastic films together with a positive control performed with quantitative filter paper (cellulose) and a blank.

The biodegradation percentage (D_t) of the test material for each measurement interval determined from the released cumulative amounts of CO_2 was calculated according to Equation *(1)*:

$$D_t = \frac{(CO_2)_T - (CO_2)_B}{ThCO_2} \times 100 \tag{1}$$

Where $(CO_2)_T$ was the cumulative amount of carbon dioxide evolved in each composting vessel; $(CO_2)_B$ was the mean cumulative amount of CO_2 evolved in the blank vessels; $ThCO_2$ was the theoretical amount of CO_2 produced by the test material.

3. Results and discussion

3.1. Degradation of "oxo-degradable" shopping bags

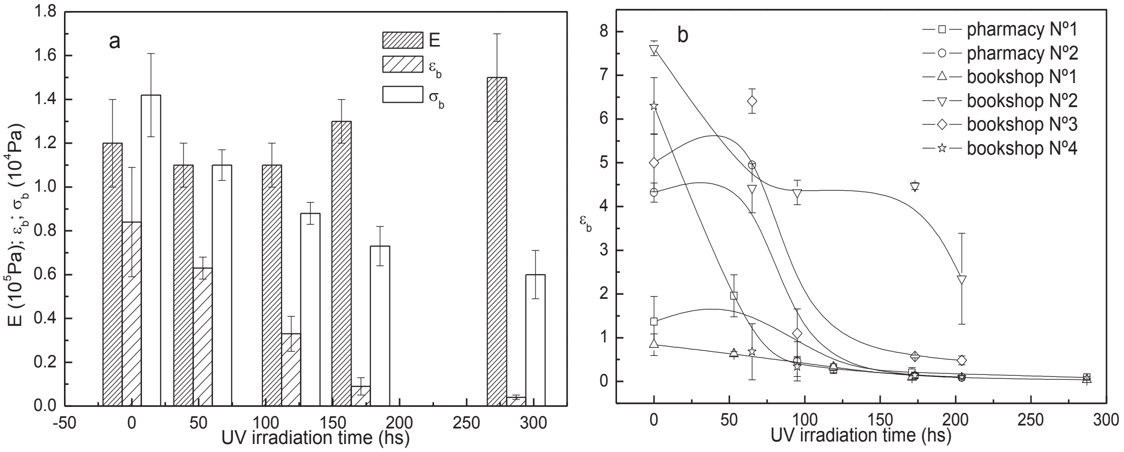

Fig. 1. (a) Mechanical degradation of "oxo-degradable" bags from bookshop Nº1, Buenos Aires after UV irradiation at 0,89 W/m^2, 50 ºC vs. irradiation time; E, elastic modulus, ε_b and σ_b, deformation and stress at break, respectively. (b) Elongation at break vs. irradiation time for several "oxo-degradable" shopping bags from Buenos Aires (the lines are only visual guides).

Shopping bags labelled "oxo-degradable", submitted to UV irradiation at 0,89 W/m^2 irradiance and 50 °C, showed a decrease in the elastic modulus as well as the elongation and stress at break, as illustratred in Fig. 1a. Particularly, the ε_b, turned out to be the property more sensitive to the UV degradation. This result, also observed by Reddy et al. (2008), is characteristic of the polymer degradation submitted not only to UV but also to gamma irradiation (Goulas et al., 2002; Hermida et al., 2008). Because of this, only the dependence of ε_b with the irradiation time is plotted in Fig. 1b for different shopping bags. In this figure, two different degradation profiles were observed. On one hand, some samples showed a slight increase of ε_b during the first 55 to 65 hours of treatment, followed by a fast decrease that might be due to a sort of plasticisation exerted by the low molecular weight chains produced in the first stage of the abiotic degradation. On other hand, other samples revealed a dramatic decrease in ε_b even for low doses of UV radiation. This completely different behaviour might be due to physico-chemical differences in the material of the shopping bags. Thus, in what follows the abiotic and biotic degradation of oxo-degradable materials were measured using samples of the same PE film with and without oxo-degradable additives (gently provided by Res Argentina).

3.2. Abiotic degradation of PE and PE+AD films

In order to evaluate the UV degradation of PE films as well as the influence of the oxo-degradable additive (d2w®) in this response, both the decrease in the mechanical properties as well as the increase in the carbonyl index (CI) were determined. These data were illustrated in Figs. 2 and 3 for PE and PE+AD.

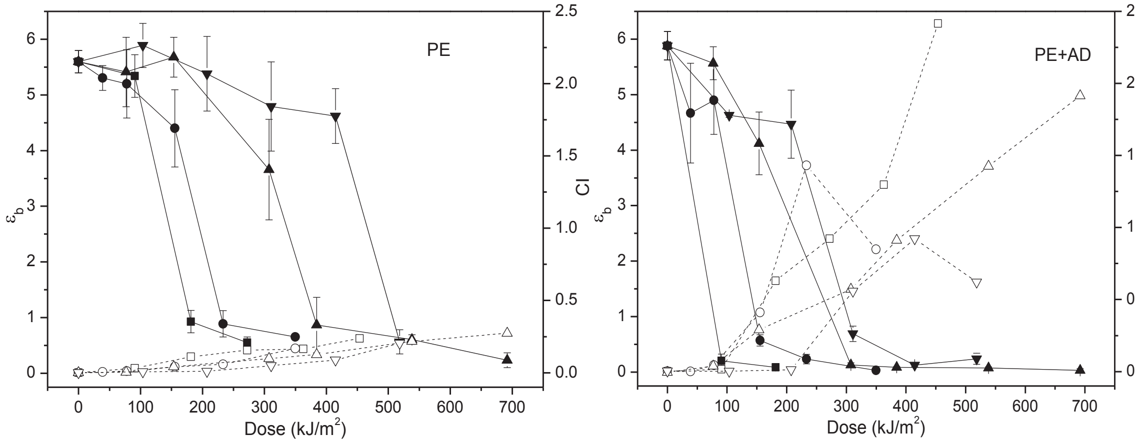

Fig. 2. ε_b (—) y CI (---) vs. dose at 50 ºC and the following UV irradiances: ■,□ 0,35 W/m^2; ●,○ 0,45 W/m$^{2;}$ ▲,△□ 0,89 W/m^2 and ▼,▽ □1,20 W/m^2) for PE and PE+AD films.

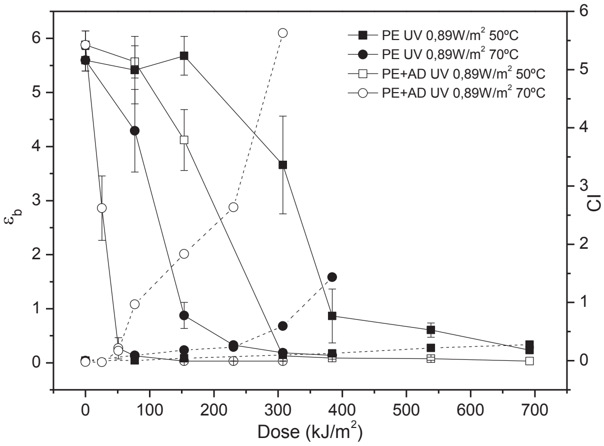

Fig. 3. CI (---) and ε_b (—) of PE and PE+AD samples exposed to UV radiation at 0,89 W/m^2 and 50 ºC or 70 ºC.

Figure 2 shows changes in the carbonyl index and the elongation at break for the PE and PE+AD films exposed to UV radiation at different irradiances (0,35 W/m^2; 0,45 W/m^2; 0,89 W/m^2 y 1,20 W/m^2) at 50 °C. For both PE and PE+AD, at any irradiance, an increase in the UV radiation dose (exposure time x dose rate) produced the increase in the CI, that is, the polymer chains were cleaved giving rise to carbonyl groups. Due to the cleavage of polymeric chains, also ε_b decreased as the exposure time (dose) increases.

It is remarkable that for a given dose, the lower the irradiance the higher the degradation; in fact, the lower ε_b or the higher CI (higher degradation) correspond to the lower irradiance. This means that the cleavage of polymer chains depends on the time of exposure to the UV radiation rather than to the dose. Moreover, at a given dose, the CI of PE+AD is higher than for PE, emphasizing the proto-degrading effect of the additive.

On the other hand, Figure 3 presents the influence of the temperature on the degradation of PE and PE+AD samples irradiated at 0,89 W/m^2, measured by the increase of CI and the decrease of ε_b at 50 and 70 °C. This remarks the thermally activated behavior of the chain scission mechanism. It is noticed that at lower irradiances the UV degradation was so severe that samples disintegrate after the thermal aging; after thermal aging of samples irradiated at 1.20W/m^2 similar results were obtained.

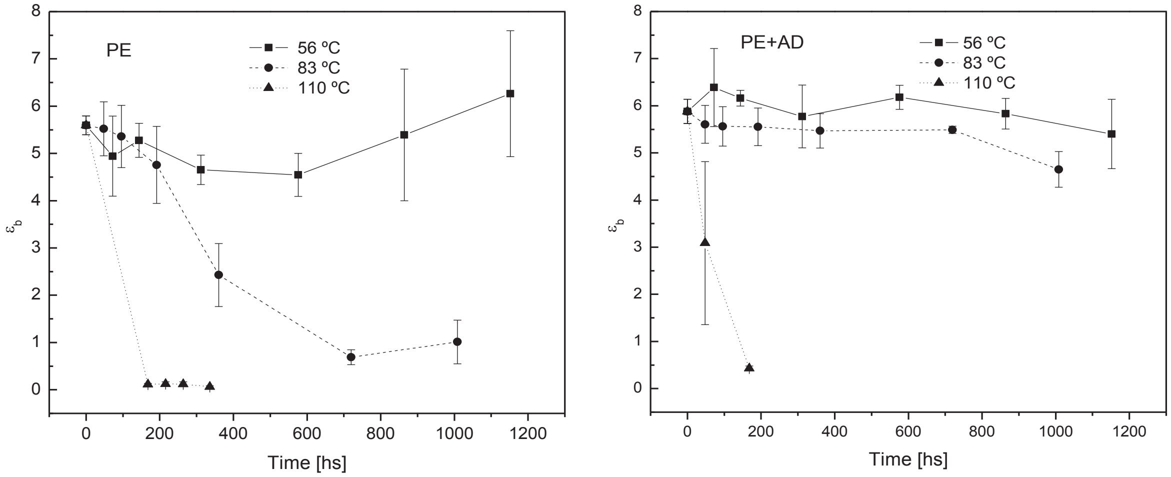

Fig. 4. ε_b vs. time of isothermal treatment at 56 ºC, 83 ºC and 110 ºC for PE and PE+AD films.

To assess the thermal degradation PE and PE+AD samples were aged at 56, 83 and 110 ºC and the deformation at break measured as a function of the annealing time. Figure 4a shows a noteworthy drop in the ε_b of PE as the degradation temperature increases; this behaviour agrees with a thermally activated process. Instead, ε_b of the PE+AD films exhibited only a slight decrease when the temperature rose from 56 to 83 ºC, as illustrated in Figure 4b. However, when annealed at 110 ºC both PE and PE+AD samples became so brittle that after 200 h they just broke during manipulation before the tensile test.

3.3. Biotic degradation of PE and PE+AD films

Aerobic biodegradation was measured by the differential accumulation of CO_2 between vessels with samples of PE and PE + AD and vessels containing only compost (blank experiment) during 90 days of incubation (Fig. 5).

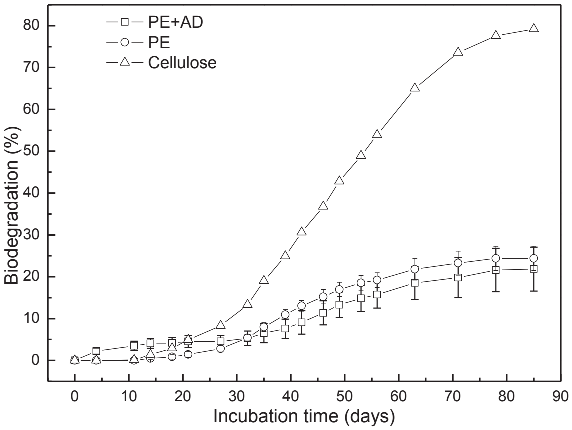

Fig. 5. Aerobic biodegradation degree of PE and PE+AD films samples in mature compost.

Before the biodegradation assessment, samples were UV irradiated at 0,89 W/m^2 and 70 °C for 96 hours (dose = 307 kJ). The experiment was performed in triplicate. The effectiveness of the incubation conditions for microorganisms in the compost was evaluated using the high level of CO_2 production in the vessels with cellulose (positive control). At the beginning of the experiment it was observed a similar CO_2 accumulation in vessels with cellulose and PE samples, while the biodegradation rate was faster in the vessels with PE + AD. In fact, after the first 14 days of biodegradation of PE and PE + AD samples 14,1 mg and 50,6 mg of CO_2 were accumulated; this means biodegradation rates 0,8 % and 5,0 %, respectively, as shown in Fig. 4. We claimed that the high microbial activity in the vessels with the PE + AD samples could be attributed to the presence of low molecular weight chains, as shown by the high value of CI after the abiotic treatment; this agrees with previous results (Jakubowicz, 2003; Corti et al., 2010).

After 20 days of incubation, however, the biodegradation in the vessels with PE + AD reached a plateau that lasted 10 days, and then the biodegradation matched the curve of the PE samples. After 90 days of incubation, about 24 % of biodegradation took place for both types of samples; this value agreed with the CO_2 accumulation in the blank experiment.

These results might be attributed to two different sources of nutrients for the microorganisms: the additive and the PE chains of lower molecular weight. In fact, the first plateau in the curve of biodegradation of PE + AD samples might be associated to an increase of the microbial activity due to the presence of the additive, as suggested by Davis (2006). In the vessels with pieces of PE film without additive, the microorganisms has no additive as source of nutrients so, the biochemical chain scission took place slowly until the density of low molecular weight chains (or equivalently the carbonyl index) reached the values for the UV irradiated PE + AD. When this happened, the biodegradation rate has the same dependence on time for both materials.

4. Conclusions

The elongation at break was the most suitable mechanical parameter to quantify the abiotic degradation. Due to the disparity in the mechanical response of shopping bags labelled "oxo-degradable", a set of samples cut from PE and PE+AD films were used to standardize the study effects of the additive on the degradation. From the experimental results it was observed that films with the oxo-degradable additive showed more mechanical damage than those without additives, especially when irradiated with UV light. In addition, the elongation at break was more sensitive than the carbonyl index, which characterizes the chain scission produced by thermal or ultraviolet irradiation ageing.

On the other hand, an increase in the time of exposure to UV radiation produced a higher mechanical and structural degradation than an increase in the irradiance. Furthermore, UV irradiation at different temperatures allowed determining that UV degradation is a thermally activated process.

As the temperature of an isothermal annealing was increased, a remarkable reduction of the elongation at break was measured for the PE samples, whereas for the PE + AD samples appreciable differences were not observed except at 110 °C.

Finally, the additive promoted degradation by abiotic factors and increased the microbial activity in the early stages of the biodegradation. However, the additive is not sufficient to produce a complete mineralization of polyethylene. In fact, after 90 days of incubation at 55±1 °C only 24 % of PE or PE+AD had been biodegraded.

Acknowledgements

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