



## Material properties

## Evaluation of the rate of abiotic and biotic degradation of oxo-degradable polyethylene

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## ABSTRACT

The recent introduction of oxo-degradable additive in the Argentinean market has motivated the study of the effect of abiotic (temperature and ultraviolet (UV) radiation) and biotic (aerobic in compost) degradation on the structure and mechanical behavior of films of polyethylene (PE) and oxo-degradable polyethylene (PE+AD).

Physico-chemical tests show that the failure strain and the carbonyl index of degraded PE and PE+AD samples depend on the UV irradiation dose. Furthermore, the additive plays a crucial role in the degradation and subsequent decay of the molecular weight.

It was observed that, for the same dose, the most deteriorated material was the one exposed to the lowest irradiance, emphasizing the importance of the time of exposure to UV radiation. The ratio between the irradiance and the critical dose, is a characteristic time associated to the sharp decay on the failure strain. The critical dose decreases significantly when increasing the temperature of the photodegradation assay.

PE is more susceptible to thermal degradation than PE+AD; the latter only degrades under thermal aging at the highest temperature.

Initially biotic degradation in compost showed an increasing production of carbon dioxide for both previously UV-degraded and untreated PE+AD. It is also remarkable that UV-degraded samples of PE and PE+AD with differences in their abiotic degradation level, reached the same final biotic degradation level. It was observed that although the additive increased the abiotic photodegradation, the molecular weight reduction in compost was not enough to reach the maximum biotic degradation level established by international standards for biodegradable materials.

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## 1. Introduction

Plastics are very versatile materials that enable many applications due to properties such as flexibility, hardness, lightness; they are also excellent as a barrier against the permeation of gases, present various mechanical and physical properties, good optical properties (transparency) and ease of manufacture and molding of complex parts. Its increase in various applications (such as packaging, medical products and disposable items, auto parts, clothing, toys, etc.) has become a topic of vital importance in terms of its impact on the environment [1]. Firstly we must consider that these

materials are produced from oil, natural gas and coal; despite being secondary products, their origin remains dependent on non-renewable sources such as fossil fuels. Second, the accumulation of waste of some inert plastics such as polyolefins, although not posing risk of ecotoxicity, generate major drawbacks [2].

It is worrying the longtime of plastic waste disposal, whose volume has increased dramatically in recent years (in the United States the generation of plastic solid waste increased 1500% in 30 years) [3]. 12.5% of the municipal solid waste (MSW) generated in the world are plastics (United Nations Program for the Environment UNEP, 2002), approximately 25 million tons per year; 50% of this amount comes from packaging [4]. In Argentina more than 12 million tons of municipal solid waste are generated annually (or an equivalent of 0.91 kg of waste per capita per day) of which 14± 4% are plastics. More than 25% of the waste generated is deposited in

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open dumps and 30% in partial controlled landfills [5].

As already stated, the generation of solid waste is a conflict in every city in the world. In particular this work is based on the situation of plastic waste of the province of Buenos Aires, where more than 4 million tons/year of MSW (17%) are plastics [5]. To reduce their impact on the environment, in September 2008, the law 13868 of the Province of Buenos Aires (effective October 2009) was enacted. This legislation prohibits the use of plastic bags in supermarkets, warehouses and shops in general, and promotes such bags are replaced by those made of degradable materials so to reduce their environmental impact [6]. Under this legislation, traditional polyethylene bags were replaced by bags made from polyethylene and oxo-labeled as biodegradable, oxo-degradable or oxy-degradable. This attribute stems from the addition of special additives to standard thermoplastics in order to accelerate the degradation products. The first stage of degradation may be initiated by abiotic mechanisms including ultraviolet light (UV) of sunlight, heat or mechanical stress to promote the oxidation process. The hypothesis is that on breaking the molecular chain by oxidation the molecular weight becomes low enough to allow the action of microorganisms of the ecosystem where the plastic product was laid (biotic degradation or biodegradation).

Although the technology of oxo-degradable additives is not new, its appearance on the market raised questions about whether they are truly biodegradable according to international standards, such as EN13432 [7], EN14855 [8] and D5338 [9] for biodegradation in compost, for example. Recent contributions [10,11] remark disadvantages of oxo-degradable polymers: environmental fate of the polymer residues and possible accumulation of toxins, negative effect for polymer recycling—because the presence of oxo-degradable additives determines the life time of recycled products. Answers to these and other questions have to be established prior to accepting these polymers as environmentally friendly options.

Based on the problem of plastic waste management, this paper aims to determine whether the mechanical and structural properties are appropriate to characterize the kinetics of abiotic UV-degradation of polyethylene films with and without an oxo-degradable additive. Furthermore, another goal of the paper is to evaluate the susceptibility to biotic degradation, once these materials were subjected to abiotic degradation processes. In order to achieve these objectives, the effect of UV irradiation on the structure and mechanical behavior of polyethylene films with and without pro-degradant additives and its subsequent degradation in compost will be studied.

## 2. Materials and methods

### 2.1. Tested materials

For this work, polyethylene films (PE) and polyethylene films with the oxo-degradable additive  $d_2w^{\text{®}}$  (PE+AD), both provided by RES Argentina, were considered. Films are white, and their thickness is about 50  $\mu\text{m}$ .

Elemental analysis of samples was performed by X-ray fluorescence (XRF). A X-ray spectrometer wavelength dispersive flag 200 Panalytical Venus was used to evaluate the nature of the oxo-degradable additive by XRF. Fig. 1 shows the spectra of the blank, the PE and the PE+AD; the presence of titanium in both films is due to the addition of  $\text{TiO}_2$  as a white pigment. Moreover the presence of manganese is observed only in the sample of PE + AD. Individual spectra for lighter elements in PE and PE+AD samples show a significant presence of Ca, and traces of K and Mg, as indicated in Table 1.

### 2.2. Photodegradation

Photodegradation was carried out in an environmental chamber Q-Lab Model QUV. This equipment simulates the harmful effects of solar radiation by UV fluorescent bulbs. It should be noted that although UV radiation accounts for only 5% of the sunlight that reaches the earth, it is responsible for the majority of solar degradation of polymeric materials exposed to the weather. Solar UV radiation can be divided into UVA, UVB and UVC, corresponding to long, medium and short wavelengths, respectively. This solar radiation reaching the earth 90% of UVA radiation, 10% of UVB, while 100% of the UVC radiation is filtered by the ozone layer. Therefore, in order to reproduce the long-wave UV radiation (UVA) for degradation testing. We use UVA-340 lamps, which offer the best correlation with the damage resulting from exposure outdoors, and simulating the solar spectrum between 295 nm and 365 nm with a maximum at 340 nm [12,13]. No condensation step was included.

PE and PE+AD films were cut into strips ( $250 \pm 1$ ) mm long ( $20 \pm 1$ ) mm wide and placed in sample holders into the environmental chamber for photodegradation at the temperatures and irradiances indicated in Table 2; these parameters were based on previous work [14–16] and can be set directly from the control panel of the chamber. Tests were carried out according to ASTM D-5208 [17]; samples were removed at different times in order to evaluate the physico-chemical changes due to the aging treatment.

### 2.3. Biotic degradation

Test samples of PE and PE+AD previously aged by UV radiation at  $0.45 \text{ W/m}^2$  and  $50^\circ\text{C}$  for 9 days (which the molecular weight was determined) and others aged at  $0.89 \text{ W/m}^2$  and  $70^\circ\text{C}$  for 96 hs (more degraded samples) were considered to assess the biotic degradation. Photodegraded samples ( $6.5 \times 9.5$ )  $\text{cm}^2$  were placed in compost stabilized bird guano in static 1000 ml glass containers at a constant temperature ( $55 \pm 1$ )  $^\circ\text{C}$ . Three samples were tested for each type of plastic films together with a positive control performed with quantitative filter paper (cellulose) and a blank; errors correspond to the standard deviation. In all containers cumulative production of  $\text{CO}_2$  relative to the target was measured at regular intervals using the discontinuous method of determining  $\text{CO}_2$  absorption in a potassium hydroxide solution and subsequent titration with hydrochloric acid.

### 2.4. Evaluation of the degradation effects

#### 2.4.1. Cumulative carbon dioxide amount

The biodegradation percentage ( $D_t$ ) of the test material for each measurement interval determined from the released cumulative amounts of  $\text{CO}_2$  was calculated according to Eq. (1), where  $(\text{CO}_2)_T$  was the cumulative amount of carbon dioxide evolved in each composting vessel;  $(\text{CO}_2)_B$  was the mean cumulative amount of  $\text{CO}_2$  evolved in the blank vessels;  $\text{ThCO}_2$  was the theoretical amount of  $\text{CO}_2$  produced by the test material.

$$D_t = \frac{(\text{CO}_2)_T - (\text{CO}_2)_B}{\text{ThCO}_2} \times 100 \quad (1)$$

#### 2.4.2. Fourier transform infrared spectroscopy (FTIR)

The formation of carbonyl groups, typical feature of the polyethylene degradation, was evaluated by FTIR on a Nicolet Magna IR 560 equipment with a resolution of  $2 \text{ cm}^{-1}$  and 256 scans and dry air purge in the range of  $600 \text{ cm}^{-1}$  and  $4500 \text{ cm}^{-1}$ . Carbonyl index (CI) was determined as the ratio between the areas of the peaks at

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