

## Abiotic degradation of plastic films

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**Abstract.** Degradable plastics have been promoted as an option to mitigate the environmental impacts of plastic waste. However, there is no certainty about its degradability under different environmental conditions. The effect of accelerated weathering (AW), natural weathering (NW) and thermal oxidation (TO) on different plastics (high density polyethylene, HDPE; oxodegradable high density polyethylene, HDPE-oxo; compostable plastic, Ecovio ®; metalized polypropylene, PP; and oxodegradable metalized polypropylene, PP-oxo) was studied. Plastics films were exposed to AW per 110 hours; to NW per 90 days; and to TO per 30 days. Plastic films exposed to AW and NW showed a general loss on mechanical properties. The highest reduction in elongation at break on AW occurred to HDPE-oxo (from 400.4% to 20.9%) and was higher than 90% for HDPE, HDPE-oxo, Ecovio ® and PP-oxo in NW. No substantial evidence of degradation was found on plastics exposed to TO. Oxo-plastics showed higher degradation rates than their conventional counterparts, and the compostable plastic was resistant to degradation in the studied abiotic conditions. This study shows that degradation of plastics in real life conditions will vary depending in both, their composition and the environment.

### 1. Introduction

Plastics are polymers constituted mainly by atoms of carbon and hydrogen. The versatility of their applications has significantly increased production and consumption of plastics. In 2013 production of plastics worldwide reached 299 million of ton; a 46% increase from 2002 [1]. Plastic carrier bags occupy an important place on the plastic market. An European citizen uses an average of 198 plastic bags per year [2]. In Mexico, 41% of the plastic industry produces bags and flexible films, employing 49 000 people in the country and manufacturing 600 000 tons per year of these commodities [3].

Plastics can be classified, according to their origin, in synthetic or biobased. Synthetic plastics are manufactured from petroleum or natural gas, both non-renewable resources; for instance, polyethylene



(PE), polypropylene (PP), polyvinyl chloride (PVC) and polyethylene terephthalate (PET). Biobased polymers can be natural or synthetic. Natural biobased polymers are synthesized by a living organism (starch, cellulose and bacterial polyhydroxyalkanoates) and synthetic biobased polymers are chemically transformed naturally occurring monomers. One example is the production of polylactic acid (PLA): starch is hydrolyzed to lactic acid, then lactic acid is transformed to polylactic acid, PLA. Some synthetic plastics have their bio-based equivalent, some examples are bio-PE and bio-PVC.

Accelerated consumption, inadequate disposal and difficulties in achieving recycling targets of plastic bags made chemical stability of these polymers an issue when they are discarded. Oxo- and bio-degradable plastic bags have been promoted to reduce environmental impacts of this commodity. Oxodegradable bags are manufactured from conventional synthetic polymers, such as polyethylene, and an additive that promotes oxidation. The pro-oxidant additive catalyzes the natural degrading process of plastics, and it is activated through ultraviolet radiation, temperature, humidity, mechanical tension or a combination of them. In the other hand, biodegradable plastics are capable of being degraded by living organisms. Biodegradability is independent of the origin of the plastic; bio-PE and PE from petroleum will degrade at the same rate. One biodegradable plastic commercially available in Mexico is Ecovio®, a biobased plastic film produced by BASF® that is designed biodegrade through composting.

Plastic industry has evolved to produce materials compatible with environmental aspirations of consumers, such as oxo and biodegradable films. However, it is not clear how these environmental credentials will affect the functionality of plastics during their useful life. This study investigates the effect of three oxidation processes (accelerated weathering, AW; natural weathering, NW; and thermal oxidation, TO) on five types of plastic films (high density polyethylene, HDPE; high density polyethylene with an oxidant additive, HDPE-oxo; compostable plastic film, Ecovio®; metalized polypropylene, PP; and metalized polypropylene with an oxidant additive, PP-oxo). Its aim is to assess if their degradability through oxidation or biological processes will affect its functionality.

## 2. Methodology

This study was carried out in the laboratory of Sustainable Technologies at the Autonomous Metropolitan University, Campus Azcapotzalco. The main stages of methodology were: preparation of plastic films, exposure of plastic films to oxidation processes, characterization of plastic films and determination of the kinetics of oxidation processes.

### 3. Preparation of plastic films

HDPE, HDPE-oxo and Ecovio® were obtained from commercial plastic film rolls, whereas PP and PP-oxo were obtained from post-consumer potato chip bags. Post-consumer films were cleaned with deionized water and paper towels to remove residuals. Finally, all types of plastics were cut into probes (1 x 15 cm).

### 4. Exposure of plastic films to the oxidation processes

Oxidation processes were studied for different periods; AW for 110 hours, NW for 90 days and TD for 30 days. Table 1 presents the sampling times for each oxidation process. Experiments were run with 20 replicates for each sampling time, type of oxidation process and type of plastic film.

**Table 1.** Sampling times for each oxidation process.

| Oxidation process      | Symbol | Units of time | Sampling times |    |    |     |     |
|------------------------|--------|---------------|----------------|----|----|-----|-----|
| Accelerated weathering | AW     | Hours         | 50             | 70 | 80 | 100 | 110 |
| Natural weathering     | NW     | Days          | 30             | 45 | 60 | 75  | 90  |
| Thermal oxidation      | TO     | Days          | 3              | 6  | 12 | 18  | 30  |

*4.1.1. Accelerated weathering.* An accelerated weathering test chamber was custom made by the Laboratory of Development in Professional Automation at the Autonomous Metropolitan University [4]. The chamber has a volume of 0.145 m<sup>3</sup>, and eight ultraviolet lamps with wavelength between 350 nm and 400 nm. The internal walls of the chamber are covered with stainless steel sheets AISI 304 with mirror finish. The chamber has a heating system capable of regulating temperature from 55 °C to 70 °C, and relative humidity can be set up to 50%. For this experiment temperature and humidity were set at 70 °C and > 50 %, respectively. In the chamber, samples are placed in a carousel to ensure all plastic film probes are exposed to similar conditions (radiation, temperature and humidity).

*2.2.2 Natural weathering.* Plastic films probes were placed on a metal rack. They were set parallel to the floor and held to the rack with adhesive tape. The rack was installed outdoors, facing south, on the roof of a four story university building.

*2.2.3 Thermal oxidation.* Plastic film probes were placed on a metal rack in a laboratory room with controlled temperature and humidity. Room conditions were set with a Norit humidifier at 30 °C and 80% relative humidity.

### 5. Characterization of plastic films

Elongation at break, weight and carbonyl index were used as indicators of degradation. Percentage of elongation at break and weight were measured before the oxidation process and for each sampling time, while carbonyl index was calculated only before and after the oxidation process. The average and standard deviation for 20 samples is reported for each sampling time.

*2.3.1 Percentage of elongation at break.* Elongation at break reflects the capability of plastics to resist changes of shape without formation of cracks. It is a direct indication of the loss of mechanical properties due to plastic degradation. Elongation at break was measured with a universal testing machine (UTM), model LP Plus from Lloyd instruments [5]. Plastic film probes were placed in the grips of the UTM, gauge length was set at 50 mm and velocity of the mobile grip was set at 50 mm/min.

*2.3.2 Weight.* Loss in weight is also produced through degradation processes. It was measured with an analytical balance, model DV114C from Ohaus, with a precision of  $\pm 0.1$  mg.

*2.3.3 Carbonyl index.* It is a measure of the presence of carbonyl groups (C=O), a product of oxidation of photodegradable polymers such as oxo-polyethylene and oxo-polypropylene. Carbonyl index was

determined with an infrared spectrometer FT-IR model Nicolet iS10 from Thermo Scientific, dividing the height of the peak at a wavelength of  $1751\text{ cm}^{-1}$  (C-O and C=O bonds) by the height of the peak at a wavelength of  $1895\text{ cm}^{-1}$  (C-C bonds).

#### 6. *Kinetics of oxidation processes*

Kinetics for each oxidation process was determined with the integrated rate equations, percentage of elongation at break was the parameter used to follow the reaction rate.

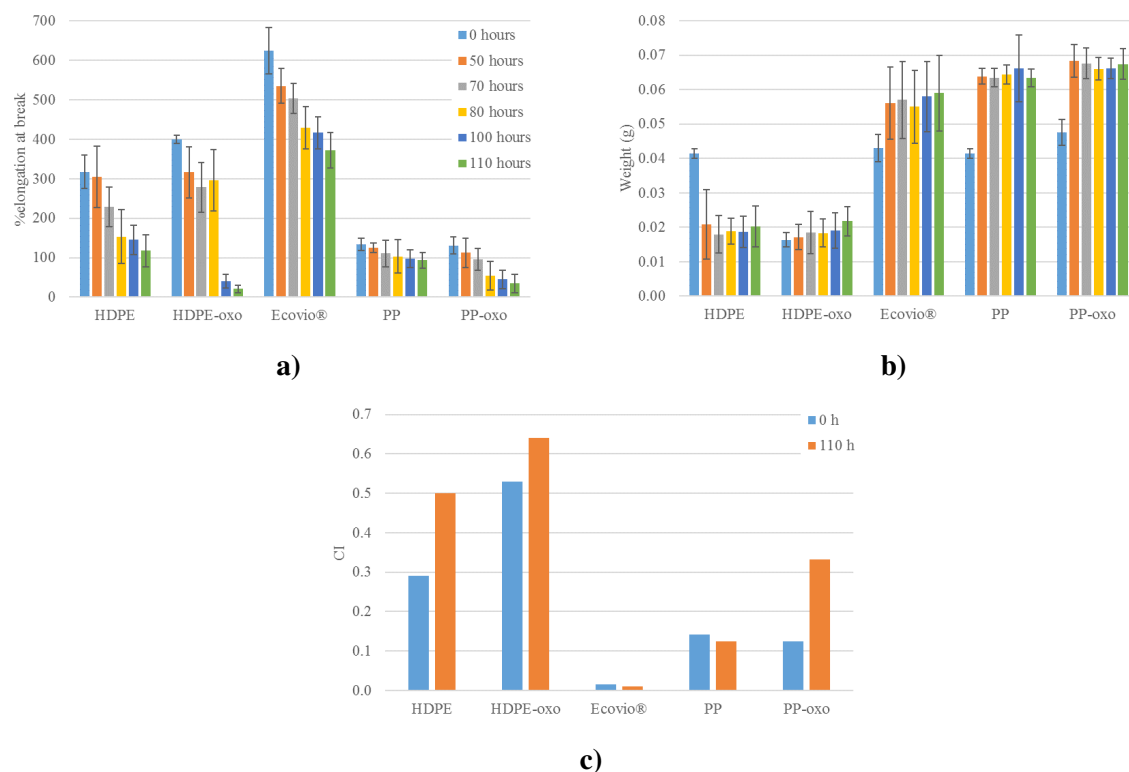
### 7. Results

#### 8. *Accelerated weathering*

All types of plastic films showed a decrease in percentage of elongation at break (figure 1a). The highest loss occurred for HDPE-oxo (95% loss, from 400.4% to 20.9%) the smallest loss occurred for PP (30% loss, from 133.4% to 93.3%). The decrease in elongation at break was higher for the polymers with the oxidant additive; i.e. higher for HDPE-oxo than for HDPE and higher for PP-oxo than PP.

Weight of plastic films is shown in figure 2b, the only plastic film that presented a loss in weight was HDPE. Increase of weight on HDPE-oxo, Ecovio, PP and PP-oxo can be explained by adsorption of water.

There was an increase on the carbonyl index for HDPE, HDPE-oxo and PP-oxo (figure 1c), this reflects an increase on the carbonyl groups due to oxidation. Also, Ecovio® and PP showed only marginal changes on the carbonyl index. Since Ecovio® degradation process begins with hydrolysis, instead oxidation, no changes were expected on the carbonyl index for Ecovio®.



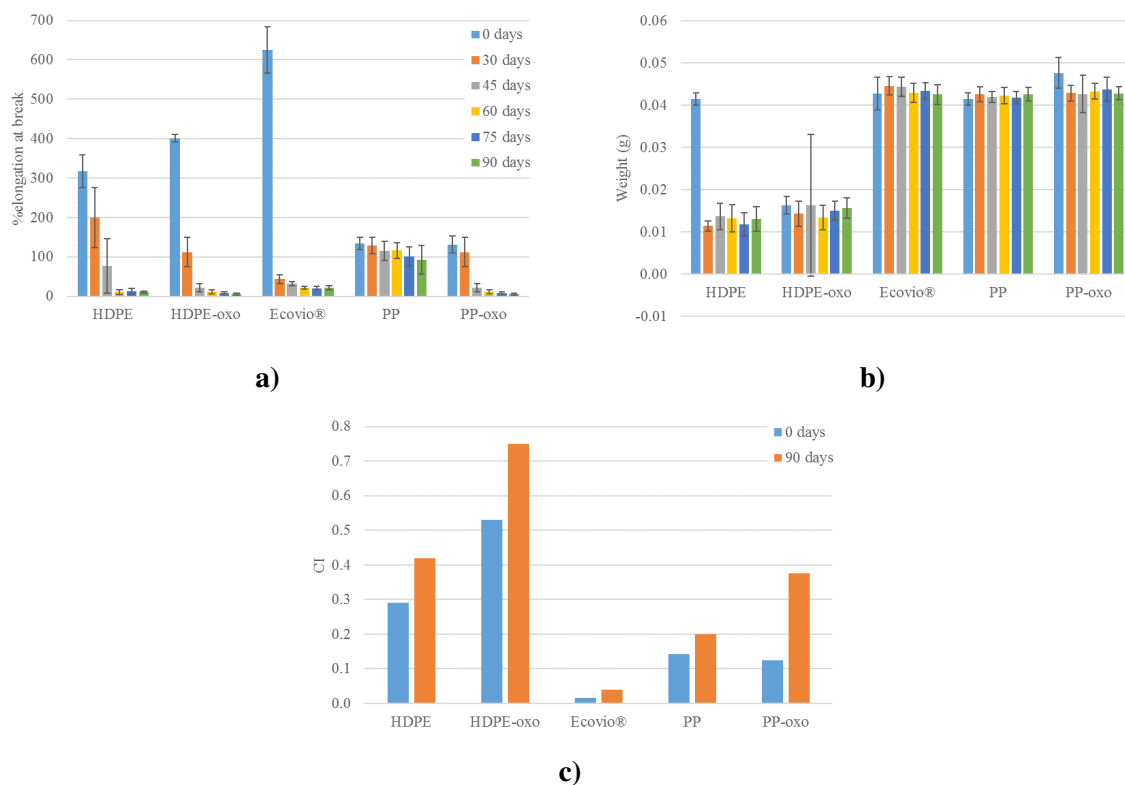
**Figure 1.** Accelerated weathering, a) % elongation at break, b) loss of weight, and c) carbonyl index (CI) for HDPE, HDPE-oxo, Ecovio®, PP and PP-oxo.

### 9. Natural weathering

During the 90 days that natural weathering of plastic films was carried out, average temperature varied from 15 °C to 22 °C and average relative humidity from 30 % to 80 %. Percentage elongation at break decreased in all types of plastics (figure 2a). The loss in elongation at break was higher than 90% for HDPE, HDPE-oxo, Ecovio® and PP-oxo., and was 30.4% for PP. In this oxidation process, loss of elongation at break was also higher for the polymers with the oxidant additive.

Weight of plastic films in natural weathering is presented in figure 2b; HDPE, HDPE-oxo and PP-oxo showed a decrease in weight, while Ecovio® and PP showed a slight increase.

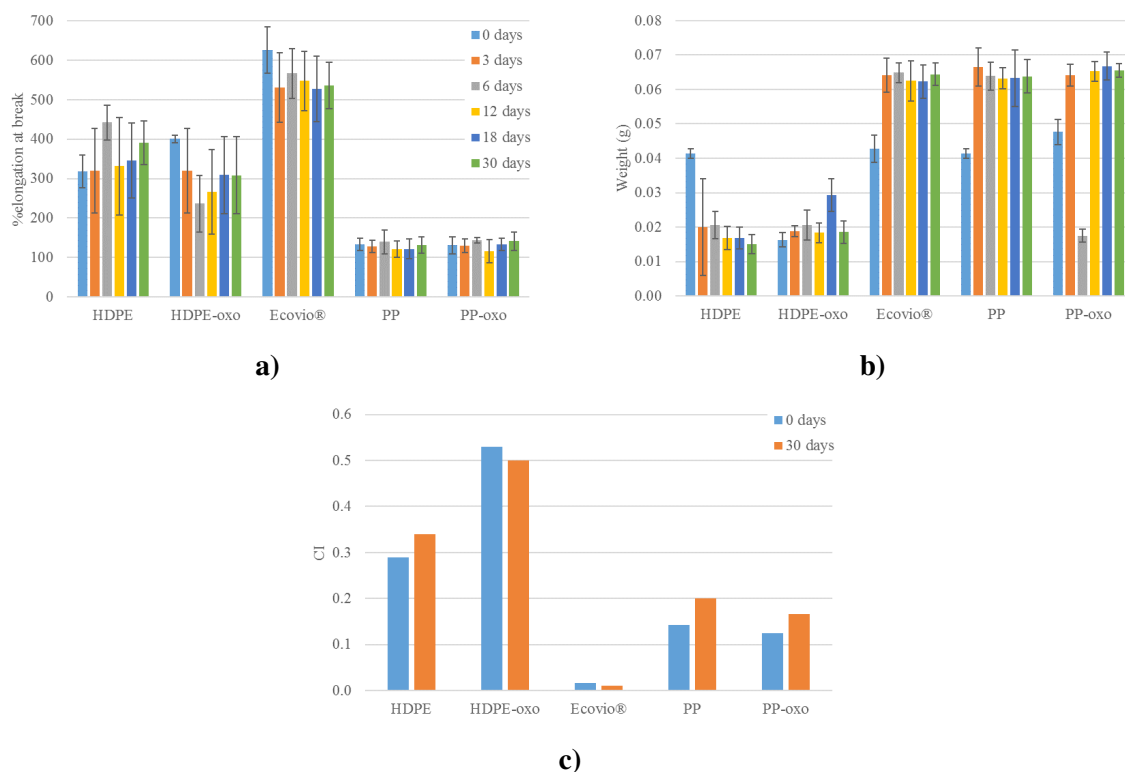
There was an increase on the carbonyl index on all types of plastic films, increase was higher in PP (200%, from 0.125 to 0.375) and Ecovio® (150%, from 0.016 to 0.040).



**Figure 2.** Natural weathering, a) % elongation at break, b) loss of weight, and c) carbonyl index (CI) for HDPE, HDPE-oxo, Ecovio®, PP and PP-oxo.

#### 10. Thermal oxidation

Average temperature varied from 19 °C to 23 °C and relative humidity from 90% to 100% during the 30 days that this experiment lasted. Percentage of elongation at break did not present any significant change (figure 3a). HDPE was the only type of plastic film that presented a decrease on weight (figure 3b). Finally, HDPE, PP and PP-oxo showed a slightly increase on the carbonyl index.



**Figure 3.** Thermal oxidation, a) % elongation at break, b) weight and c) carbonyl index (CI) for HDPE, HDPE-oxo, Ecovio®, PP and PP-oxo.

### 11. Kinetics of degradation processes

Table 2 presents the reaction order and the kinetic constant by type of plastic for the oxidation process of accelerated and natural weathering. Kinetics parameters were not calculated for thermal oxidation because there were no significant changes in elongation at break for this oxidation process. In AW -elongation at break followed a zero order reaction for all plastic films studied. Kinetic constants were higher for HDPE-oxo than for HDPE, and for PP-oxo than for PP. In NW a zero order reaction was followed by HDPE and PP and a first order reaction was followed by HDPE-oxo and PP-oxo.

**Table 2.** Kinetics of degradation for accelerated and natural weathering.

| Oxidation process      | Plastic film type | Reaction order | Kinetic constant | Units                                      | Correlation coefficient |
|------------------------|-------------------|----------------|------------------|--------------------------------------------|-------------------------|
| Accelerated weathering | HDPE              | 0              | 1.980            | % Elongation h <sup>-1</sup>               | 0.8395                  |
|                        | HDPE-oxo          | 0              | 3.438            | % Elongation h <sup>-1</sup>               | 0.7573                  |
|                        | Ecovio®           | 0              | 2.28             | % Elongation h <sup>-1</sup>               | 0.9563                  |
|                        | PP                | 0              | 0.39             | % Elongation h <sup>-1</sup>               | 0.9367                  |
|                        | PP-oxo            | 0              | 0.93             | % Elongation h <sup>-1</sup>               | 0.8723                  |
| Natural weathering     | HDPE              | 0              | 0.154            | % Elongation h <sup>-1</sup>               | 0.8822                  |
|                        | HDPE-oxo          | 1              | 2.11E-03         | h <sup>-1</sup>                            | 0.9509                  |
|                        | Ecovio®           | 2              | 2.23E-05         | % Elongation <sup>-1</sup> h <sup>-1</sup> | 0.9178                  |
|                        | PP                | 0              | 1.90E-02         | % Elongation h <sup>-1</sup>               | 0.9153                  |
|                        | PP-oxo            | 1              | 1.67E-03         | h <sup>-1</sup>                            | 0.9069                  |

## 12. Conclusions

During accelerated and natural weathering processes occurred a loss of mechanical properties of all types of plastic film studied (HDPE, HDPE-oxo, Ecovio®, PP and PP-oxo), evidencing their degradation. No substantial evidence of degradation was found on thermal oxidation. The loss of mechanical properties on accelerated and natural weathering was higher on HDPE-oxo than on HDPE and higher in PP-oxo than on PP. This was expected since oxo additives catalyse oxidation of synthetic plastics.

Ecovio®, a bio-degradable and bio-based polymer, presented loss of mechanical properties. However, this plastic film is designed to degrade through hydrolysis. High relative humidity and temperature may have triggered degradation of Ecovio®; loss of mechanical properties was higher in natural weathering (15 °C – 22 °C and 30 % - 80% relative humidity) than in accelerated weathering (70 °C and > 50% relative humidity).

Kinetics was found of zero order for HDPE, HDPE-oxo, Ecovio®, PP and PP-oxo for AW and only for HDPE and PP for NW. The value of the zero order kinetic constant of HDPE and PP was higher for AW than for NW, as expected. In AW reaction rates were higher for oxo equivalents of conventional polymers (HDPE-oxo > HDPE and PP-oxo > PP). Kinetic reaction of oxo polymers was found of first order for NW, hence reaction rate depends directly on elongation at break. Kinetic constant is on the same magnitude order for both, HDPE-oxo and PP-oxo.

Although synthetic, synthetic with oxidant additives and bio-based bio-degradable polymers showed evidence of degradation on accelerated and natural weathering conditions. The results show that the extent and rate of degradation are dependent on the type of plastics and the environment conditions. Thus, the benefits of using degradable plastics must be assessed for each specific situation where they will be used.

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