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Determination of biochemical and physical conditions of plastics denominated as "biodegradable" subjected to anaerobic conditions

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Abstract

The main objective of the study was to determine the biochemical and physical conditions of two different types of polymeric materials (HDPE with oxo-additive and PLA) when subjected to conditions similar to those presented inside a sanitary landfill. These materials are commercialized within the country claiming to be biodegradable under certain conditions. However, the conditions in which such degradation may occur are completely unknown from those presented inside a solid waste final disposal site (sanitary landfill).

The experiment simulated the general conditions to which the materials would be subjected once inside a sanitary landfill, (absence of molecular oxygen, absence of light, constant temperature, high humidity, among others). Changes in biochemical and physical conditions were monitored as well as the container. These changes may indicate degradation of the polymers. Along the experiment, not enough evidence could be observed that doubtlessly showed actual biodegradation in any of the plastic materials tested.

Keywords: polylactic acid (PLA), HDPE with additive, anaerobic biodegradation, biodegradability, landfill, oxo additives.

1. INTRODUCTION

Plastic materials are of great use and versatility thanks to their chemical and physical properties, including resistance to degradation. However, when these materials become waste those same properties make them a complex environmental problem (Aboud-Zeid et al. 2001). To solve this problem two fundamentally different solutions, among others, have been proposed: the addition of chemical catalysts to the actual polyolefin or the use of polymers developed from substances susceptible to biodegradation. In the first case, adding a metallic salt, as catalyst during the manufacture of the polymer, leads to the claim (according to the manufacturers of the additive) that complete degradation/biodegradation of the polymer will occur when complying with the standard procedures ASTM D882-02, D883-08, D3826-98 and D6954-04. To fulfill the requirements stated in the standards certain controlled conditions such as presence of molecular oxygen, high temperature, light intensity and physical stress should be guaranteed in order to obtain the first step of degradation and to facilitate biological attack (Itävaara et al. 2002). These conditions never occur within a regular waste management facility (sanitary landfill) like the ones in operation in developing countries like Colombia. Furthermore, the manufacturer´s statement confuses the public, who ignores the specific chemical, physical and biochemical differences between the conditions of the standard tests and those presented in the landfill, causing them to believe that the degradation will occur even within the sanitary landfill.

For the second case, some studies have demonstrated the occurrence of biodegradation phenomena. However, there has not been any previous research that proves its occurrence with materials and products sold within developing countries.

The main intention of this study is to investigate the chemical and physical behavior of the referred materials when subjected to anaerobic conditions simulating those presented within a sanitary landfill similar to the ones existing in Bogotá, D.C.

The polymeric materials used in this work were blown film extruded high-density polyethylene (HDPE) with a suitable synthetic oxo-catalist and a "biodegradable" polymer derived from starch, in this case polylactic acid (PLA), also blown film extruded. Both of them are available in the local market.

Changes in mass, coupled with gas generation and changes in mechanical properties, were taken into account, primarily to observe a possible degradation of the samples. Other complementary and supplementary measurements were taken in order to confirm the occurrence of chemical processes in the bulk.

2. MATERIALS AND METHODS

Two types of plastic materials were chosen for this study: Polylactic Acid also known as PLA and High-Density Polyethylene (HDPE) with Oxo-additive.

2.1 Polylactic Acid, PLA

PLA is a thermoplastic polyester with a molecular structure as represented in figure 1, with its main building block being lactic acid. This polymer is manufactured from renewable resources such as corn, beets, wheat and other starch-rich products, where its denomination "of natural origin" comes from. It has been extensively used in the food, chemical and pharmaceutical industries as well as in agriculture, animal food and plastic sectors, among others (Serna et al.2003). The samples taken for this particular study were taken from bags made for the food packaging industry.

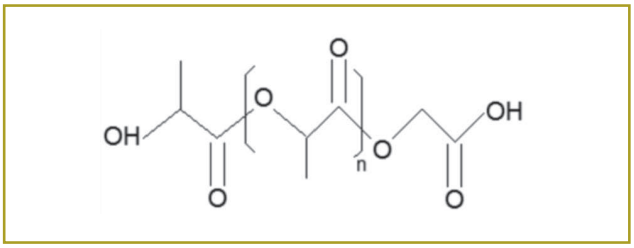

Figure 1. Molecular structure of Polylactic Acid – PLA.

2.2 High Density Polyethylene (HDPE) with oxo-additive, Oxo-HDPE

HDPE is a polyolefin from synthetic origin. It is represented by its repetitive unit $(CH_2\text{-}CH_2)_n$, (see figure 2). It is obtained from the polymerization of ethene (ethylene) (chemical formula $CH_2{=}CH_2$), from which

it derives its name. The polymer used here has been additivated and it is commercially available as Oxo-HDPE. This denomination of oxo-degradable, according to the manufacturers, comes from the addition to the polymeric structure of a metallic salt that acts as an oxo-catalyst for the degradation of the polymer itself

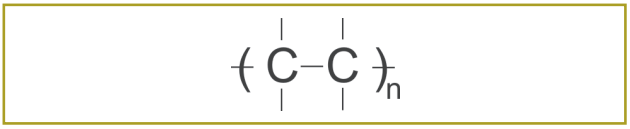

Figure 2. Molecular structure of HDPE.

2.3 Plastic Samples

For both types of plastic material, several standard size samples were made.

Each sample was 2.54 cm wide by 25.4 cm long (1x10 inches), according to the stated requirements of standard test ASTM D882. This particular size configuration is used to determine the modulus of elasticity for this kind of material under mechanical stress-strain – tension tests. These same pieces allowed us to check the evolution of mass.

Other plastic samples were made in the form of small circles of 5.0 mm diameter. These samples were used to monitor the variation in the Chemical Oxygen Demand (COD) of the plastic itself and to make visual inspections of the polymeric structure under optical microscope.

2.4 Anaerobic Sludges

The anaerobic sludge (biomass) used within the experiment was monitored with identical periodicity, as the plastic material, in order to assess biodegradation of the samples. The parameters observed were dissolved and total COD; Total and Volatile Suspended Solids (TS and VSS, respectively); nitrates NO_3–; sulfates, SO4= and biogas production were determined according to similar methodologies taken from several researchers. (Aboud-Zeid et al. 2001; Agamuthu et al. 2005; Imam et al. 1999; Itävaara et al 1996; Itävaara et al. 2002; Massardier-Nageotte et al 2006; Mohee et al. 2008; Sha et al. 2008).

2.5 Experiment

Both PLA and Oxo-HDPE were subjected to anaerobic conditions by submerging them into anaerobic sludge inoculated with biomass taken from a primary sludge digester from the local wastewater treatment plant. This methodology is similar to those reported in the literature (Aboud-Zeid et al. 2001; Agamuthu et al. 2005; Imam et al. 1999; Itävaara et al 1996; Itävaara et al. 2002; Massardier-Nageotte et al 2006; Mohee et al. 2008; Sha et al. 2008; Serna et al. 2003).

250 ml Erlenmeyer flasks were used as reactors. Each flask was filled with sludge (6000 mg/l initial TS concentration), mineral media (See tables 1 and 2), and then the plastic samples were introduced; an identical procedure was followed to make a replicate set and two controls were also prepared. The first control set (positive control) contained sludge and mineral media, but no plastic; the second control set (negative control) contained sterile mineral media and plastic samples but no biomass. The flasks were sealed with rubber stoppers from which a plastic PVC tube was connected to the gas collection system. For every single set (experimental, replicate and both controls) almost all parameters were

Table 1
Composition of the Mineral Media

Component	Initial Concentration (mg/l)	Component	Initial Concentration (mg/l)
MgCl2•6H2O	1000	NaHCO3	4200
CaCl2•2H2O	143	NaCl	1000
KCl	1200	NaNO3	2740
KH2PO4	205	Na2S•9H2O	370
Na2SO4	2840	Trace*	1,0 ml/l
NH4Cl	270		

*Trace Solution

Table 2
Trace Solution Composition

Component	Initial Concentration (mg/l)	Component	Initial Concentration (mg/l)
C6H9NO6	3500	CuCl2•6H2O	130
H3BO3	62	ZnCl2	68
MnCl2•4H2O	98	Na2MoO4•2H2O	24
FeCl2•4H2O	1500	Beef Extract	1000
CoCl2•6H2O	120	NiCl2•6H2O	240

measured every other week, excepting gas production and temperature readings that were taken daily.

The experiment was carried out for a period of six months. The gas production was measured through the inverted cylinder method consisting in two graduated cylinders (one 500 ml and the other 250 ml) in which the small one is put upside down inside the big one, with the plastic tubing going inside the small submerged cylinder. The cylinder system was filled with an acid solution saturated with sodium chloride in order to avoid dissolution of the carbon dioxide from the biogas. The gas was then confined and the production was measured by means of the displaced liquid volume inside the small cylinder. The accumulated biogas production was recorded daily.

To guarantee absence of light and complete anaerobic conditions all sets were introduced in glass chambers covered with aluminum foil and depleted of air. Three chambers were prepared, one containing the Oxo-HDPE tests, one with PLA tests and one holding the control sets for both materials.

The experiment was set to simulate the conditions presented within a sanitary landfill in the city of Bogotá, D.C., which meant that the temperature was kept close to 20 ºC or slightly below in the psychrophilic range.

Sixty days after the beginning of the experiment a sludge addition was made given the fact that the data recorded up to that moment suggested inhibition of the biomass.

All parameters were measured following standard procedures (Standard Methods for the Characterization of Water and Wastewater, 20th Ed.) and the experimental procedure was performed following indications of the ASTM5526. 1994; ASTM D5511. 2002 and ASTM D882. 2002 specific for this type of systems.

3. RESULTS AND DISCUSSION

To determine the extent of degradation/biodegradation of the plastic materials the parameters of mass, modulus of elasticity, stress and deformation as well as visual inspection under the microscope were monitored with respect to time.

At the same time, the sludge (in charge of the potential biodegradation) was monitored for total and dissolved COD, Total Solids (TS); Volatile suspended solids (VSS); nitrate concentration, sulfate concentration and biogas production.

3.1 Biodegradation analysis

In order to be able to determine the extent of biodegradation (if any) it is important to know the initial conditions in which the experiment began to compare them to the data recovered over time, and assess the occurrence of the phenomenon and the extent to which it occurred.

Initial conditions PLA

Sample Measurements	:	2.54 cm x 25.4 cm x 0.023 mm
Initial mass	:	156 ±3.4 g
Modulus of elasticity	:	2636 MPa
Deformation (Max)		5,08 %

Initial conditions oxo-HDPE

Sample Measurements	:	2.54 cm x 25.4 cm x 0.018 mm
Initial mass	:	95 ±5 g
Modulus of elasticity	:	417 MPa
Deformation (Max)	:	144 %

Initial conditions Biomass

Dissolved COD	:	323 mg/L
Total Solids	:	6323 mg/L
Volatile suspended solids	:	3250 mg/L
Nitrates	:	1370 mg/L
Sulfates	:	1420 mg/L

3.2 Mass Variation

Figure 3 shows the relative mass variation for the PLA samples. The results suggest a coupled physical and biological effect, since a greater variation of mass has been observed with respect to the time in the samples subjected to biological activity, as compared to the same parameter variation in the negative control. It can be said that there is a physical effect by the submersion in the media (observations of the negative control) and an additional effect given by the biological activity. The samples subjected to biological activity showed a variation of mass of 3.8 g, a net loss of 2.4% of the initial mass. The negative control showed a cumulative mass loss of 0.8 g, equivalent to a 0.84% loss compared to the initial mass.

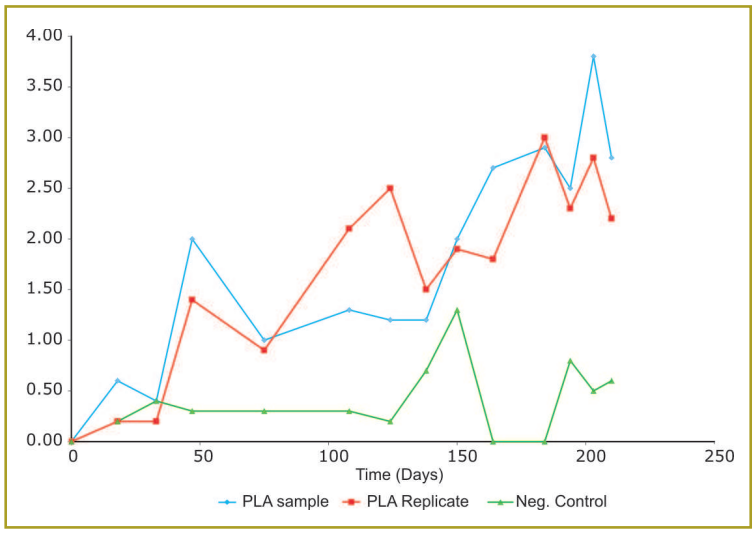

Figure 3. Mass variation for PLA.

Observations made for the Oxo-HDPE samples (see figure 4) do not show a behavior similar to the one reported for PLA. Both the tested samples and the negative control show a very small and practically identical mass variation that could be due more to side effects of the recovery and cleaning procedures than actual degradation. According to this analysis it is considered that no effect was observed for this kind of material.

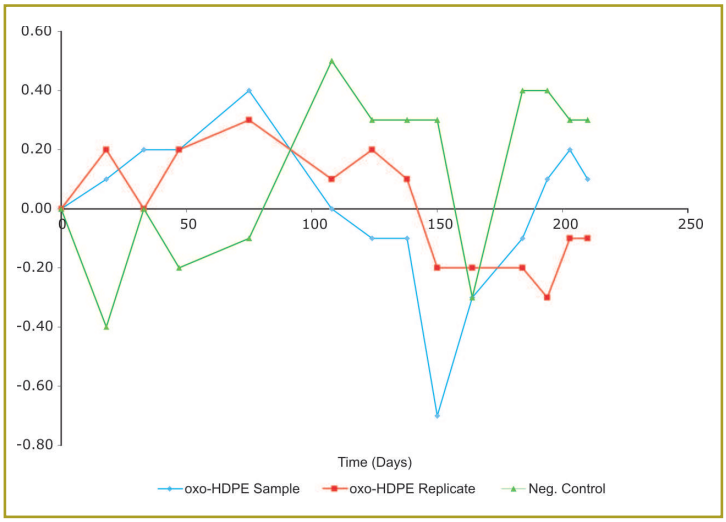

Figure 4. Mass variation for Oxo-HDPE.

3.3 Correlation Between the Measured COD and Materials Degradation

A correlation between the development of the dissolved COD against the mass loss of the plastic samples was to be established. The working hypothesis considered the solubilization of parts of the polymer as the first step for biological degradation, implying that an increase in the dissolved COD concentration must be coupled with a loss of mass from the plastic samples.

As shown in figure 5 the dissolved COD has an upward tendency during the first 164 days of the experiment. However, this tendency is observed for both PLA and Oxo-HDPE samples as well as for the positive control. Although PLA showed a small but significant mass loss that might have been correlated with this result, Oxo-HDPE and the positive control showed no significant difference in their variation of the same parameter when compared with the PLA experiment, suggesting that another effect should have to be considered. As it will be shown later, endogenous decay is the probable phenomenon describing this behavior. From day 164 on, the decrease in the concentration of

dissolved COD for all samples and controls is consistent with the late stages of endogenous decay rather than actual plastic substrate utilization. This observation also correlates to the behavior of Total and Volatile Suspended Solids.

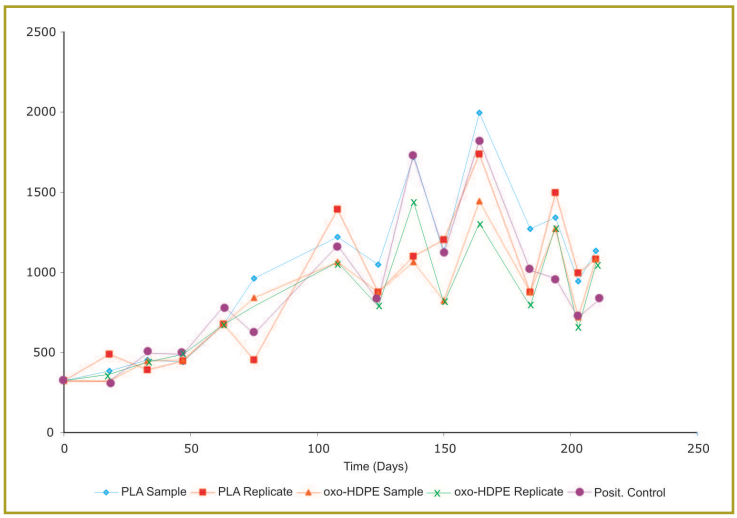

Figure 5. Development of the dissolved COD.

3.4 Solids Behavior (TS y VSS)

With the development of TS and VSS parameters, what is happening with the biomass can be addressed. During the first two months of the experiment the volatile fraction of the solids decreases significantly, indicating a decrease in the bacterial population, consistent with endogenous decay. Bacteria is not using the plastic material as carbon source but themselves (see figure 6). After day 60 more biomass was added to the systems, reflected in the measured concentrations of both parameters (see figures 6 and 7). The addition of biomass was aimed at increasing the overall observed rate of degradation of the plastic material (if any). The overall effect observed was a confirmation of the endogenous decay hypothesis.

3.5 Development of the Electron Acceptors

Nitrate and sulfate are electron acceptors essential for facultative and anaerobic cellular respiration respectively. Figure 8 shows that during the first 60 days the

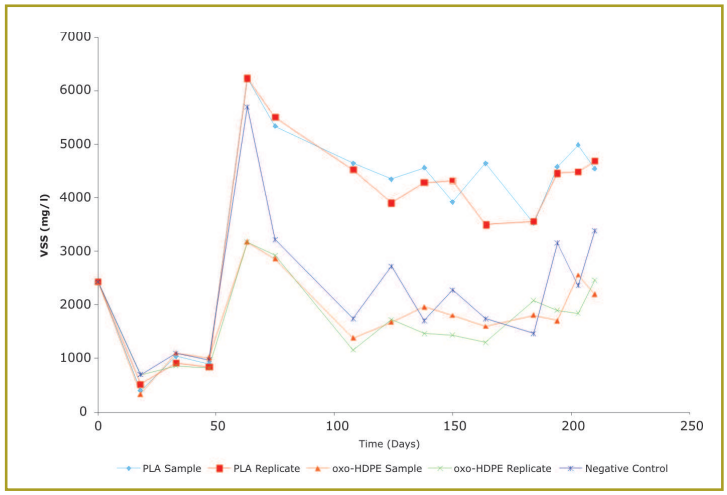

Figure 6. Development of Volatile Suspended Solids (VSS).

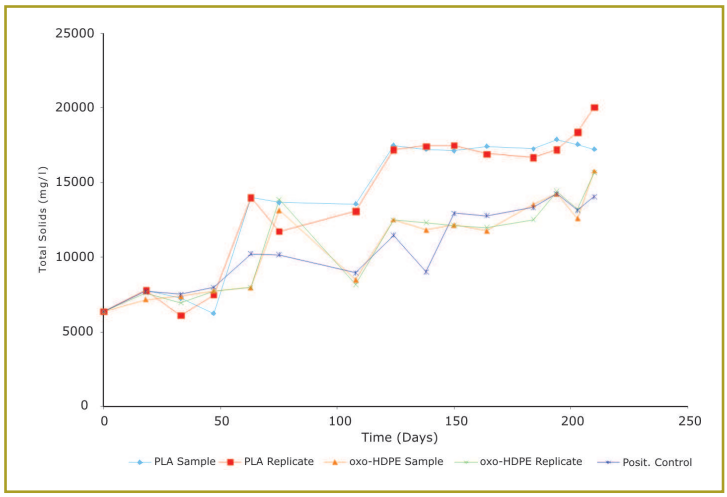

Figure 7. Development of Total Solids (TS).

concentration of nitrate remains rather constant, suggesting the absence of facultative denitrifying bacteria. After the sludge addition, there is an evident nitrate consumption, even to the edge of depletion, indicating heavy denitrifying conditions.

Sulfate (figure 9) shows a similar behavior as the one seen for nitrate, in this case, however, the sulfate reduction occurred at all times during the length of the experiment. At around day 110 an addition of both nitrate and sulfate at levels close to those of the initial condition was performed. The purpose of the addition was to address the possibility of system inhibition caused by lack of electron acceptors.

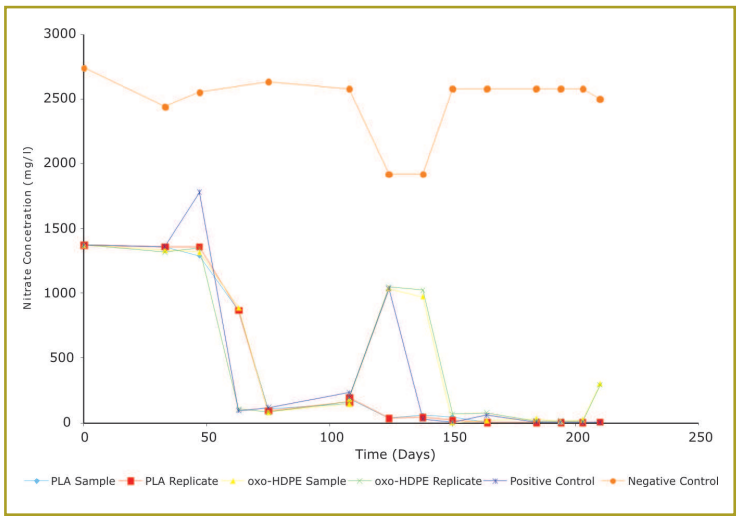

Figure 8. Development of Nitrate Concentration.

The observed consumption of electron acceptors coupled with gas production demonstrated that the systems were alive and active but the carbon source was not the plastic material being tested.

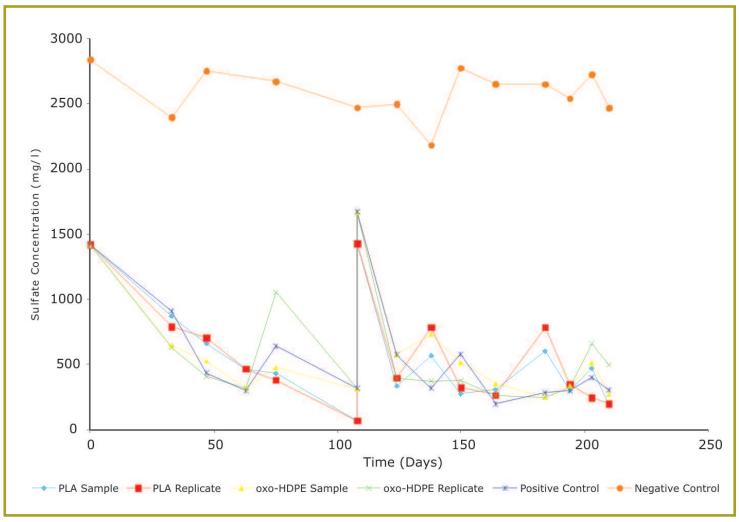

Figure 9. Development of Sulfate Concentration.

3.6 Biogas Production

The conditions under which the biomass was to perform the degradation were very strict. The only source of carbon (besides the biomass itself) was the plastic material being tested (either PLA or Oxo-HDPE). There was no co-substrate, only mineral salts and some electron acceptors available for their vital functions. If any degradation was to occur, bacteria should be converting those complex polymeric substances into biogas (mainly methane and carbon dioxide).

Figure 10 depicts the development of biogas production. The acclimation phase can be observed to have lasted close to two months (low gas yield). After the sludge addition, the gas production rate greatly increased, mainly due to the presence of organic matter in the sludge itself at the time of the addition. After a while, the gas production rate decreased entering a stagnant phase similar to a second lag phase. Finally a behavior consistent with endogenous decay was shown, in which the gas production rate increased measurably but could not be associated to anything different but the loss of biomass.

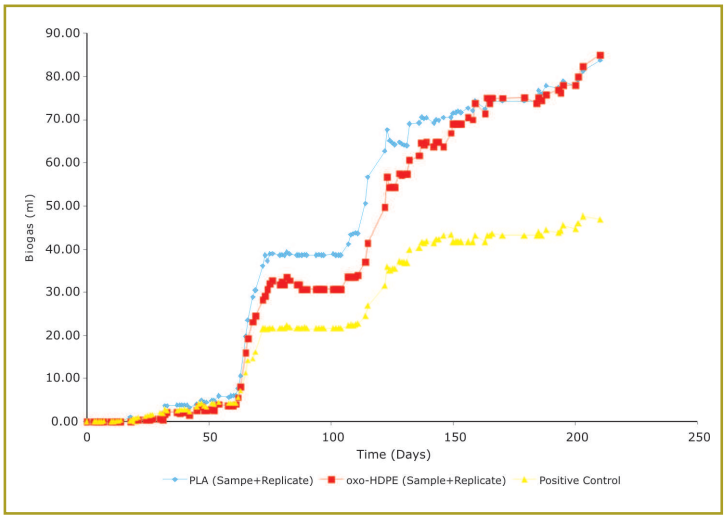

Figure 10. Cumulative Biogas Production.

3.7 Mechanical properties

Figures 11 through 14 depict the tendency to maintain a constant value of the modulus of elasticity; therefore, showing no sign of degradation. If any degradation had happened, the material should have become stiffer and more fragile, due to the fact that the polymeric chains would have fractured and the resulting fractions, being under chemical disequilibrium, would have bound with other fractions of carbon chains originating three-dimensional interchaining, reducing the molecular weight of the polymer. This degradative behavior is observed

by a stiffening of the polymeric structure (reduction of the modulus of elasticity). At the same time, had the degradation occurred, a significant reduction in the ductility of the material should have been observed. None of the cases shows results in favor of the previously stated argument, which means that no distinguishable degradation could be observed.

The high dispersion of the data can be explained by the difference in the position of the plastic sample when subjected to the tensile stress test, internal holes in the plastic sheet due to manufacturing processes and to errors in cutting the sample in an exact and accurate manner.

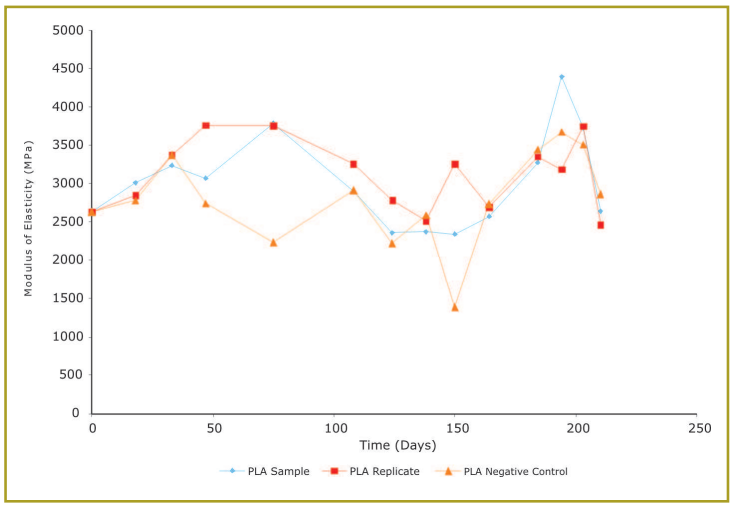

Figure 11. Modulus of Elasticity (PLA).

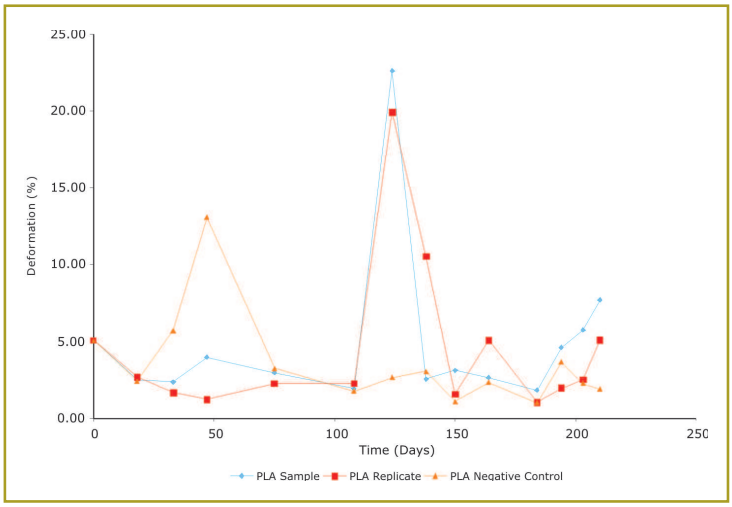

Figure 12. Maximum Deformation (PLA).

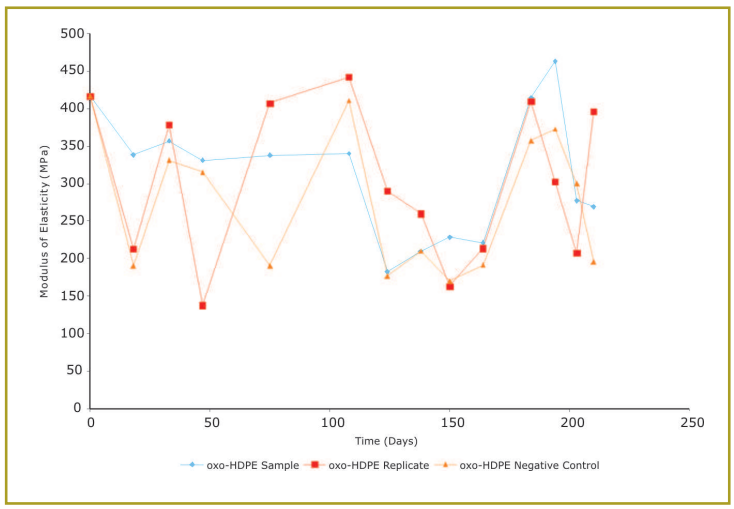

Figure 13. Modulus of Elasticity (Oxo-HDPE).

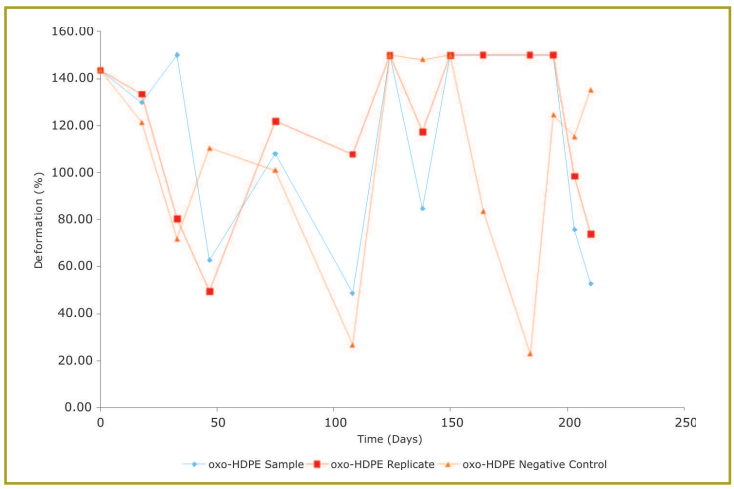

Figure 14. Maximum Deformation (Oxo-HDPE).

3.8 Optical Micrographs

Observation under optical microscope of the PLA samples (figures 15 through 17) shows that the structural integrity of the material is intact even though the material was subjected to the experimental conditions a couple of weeks (figure 15); two and a half months (figure 16) and six months (figure 17). There was no visual evidence of degradation.

The optical microphotographs allow to see that the Oxo-HDPE is semicrystalline. Little spherules, characteristic of this type of material, are clearly distinguishable. There are no holes or microvoids or cracks within the material indicating biodegradation or biological attack during the length of the experiment (see figures 18through 20).

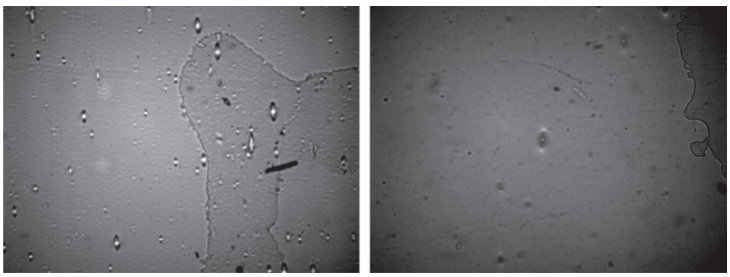

Figure 15. Optical micrographs of PLA. Initial Conditions. Left (10x), Right (40x).

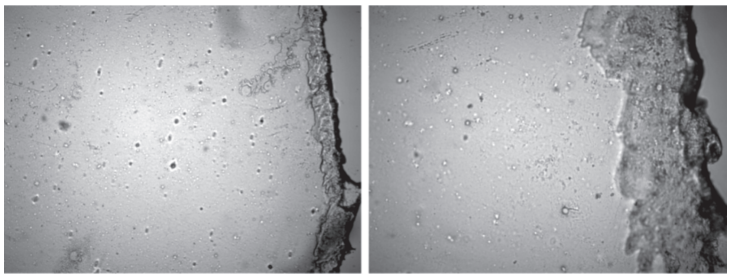

Figure 16. Optical micrographs PLA, 75 days under anaerobic conditions. Left (10x), Right (40x).

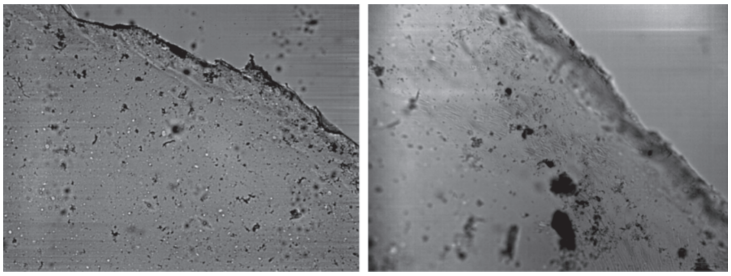

Figure 17. Optical micrographs PLA, 210 days under anaerobic conditions. Left (10x), Right (40x).

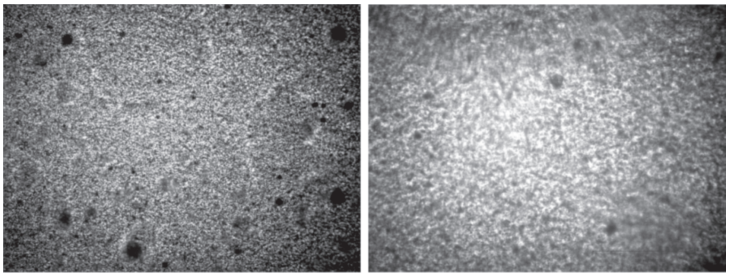

Figure 18. Optical micrographs Oxo-HDPE. Initial Conditions. Left (10x), Right (40x).

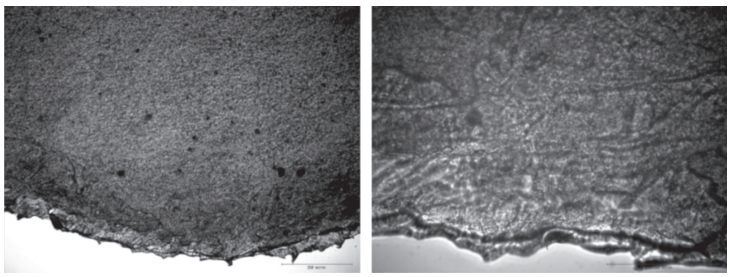

Figure 19. Optical micrographs. 75 days under anaerobic conditions. Left (10x), Right (40x).

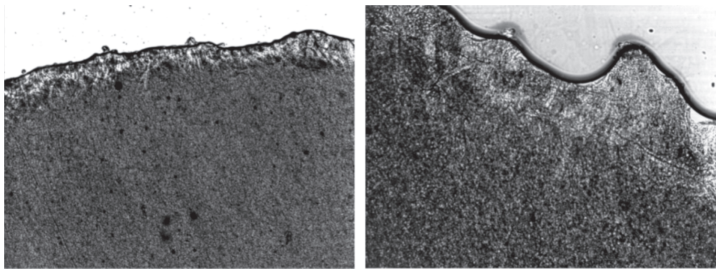

Figure 20. Optical micrographs. 210 days under anaerobic conditions. Left (10x), Right (40x).

4. CONCLUSSIONS

The analysis of the data gathered during the experimental phase gives, as a result, that there was no considerable loss of mass, low rate of biogas production and no apparent change in the mechanical properties of the materials. This conducts to a lack of evidence in supporting the occurrence of biological degradation for either of the polymeric substances under study.

Depletion of the mineral salts nitrate and sulfate (electron acceptors) implies respiratory processes by the biomass, evidencing biological activity. However, based upon the data gathered it is suspected that endogenous decay was the principal biological process involved. Additionally, the modulus of elasticity for both plastic materials tested remained practically constant, without variations that may indicate degradation.

As a general conclusion, it can be said that the materials under study when subjected to conditions similar to those encountered within a sanitary landfill will not show a biological degradation in short periods of time, i.e. six months. However, it is recommended for these materials' chemical and biological processes to be studied for longer periods to be considered and merchandised as truly "biodegradable".

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