



Degradation Study of the Blue Polyethylene Film Oxo-Degradable in the Landfill

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Abstract A very visible portion in the landfill consist polyethylene (PE) films utilized for packaging which are disposed of in short time. In the landfill there are anaerobic and aerobic process and growth of the microorganisms that are responsible for biodegradation. Common pro-oxidants presently being used for preparation of “oxo-degradable” films are stearates of transition metals. The mechanisms of polymers degradation involve the use of polymer and/or additives as a source of carbon and energy for microorganisms. The work was study and presented the analysis structural, thermal and morphologic determinations of the blue PE film (mixture LDPE/HDPE recycled) formulated with pro-oxidant additives in the landfill, after 4 and 8 months. The results indicate that blue PE films showed structural changes, reduction of thermal stability and physical deterioration of the surface.

Keywords oxo-degradable, landfill, degradation, PE

Introduction

The study of polymers degradation is currently a topic that has attracted attention mainly because it allows planning the lifetime of a material during and after use, and also the possibility of designing environmentally friendly products that are more acceptable, less aggressive in terms of environment. The polymer degradation, regardless of the mechanism, promotes changes in material properties, such as mechanics, optics, and may cause cracks, erosion, discoloration and separation of phases [1]. Some phenomena combined can accelerate the synthetic polymers degradation, they are: photo-degradation, thermo-degradation, thermo-oxidation, and biological degradation, this one promoted by the action of bacteria, fungi and algae. And these phenomena may have the contribution of some factors such as humidity, impurities of the polymer, polymer blends, presence of co-monomers and others [2]. Some degradation studies may occur at various stages, the first may be not biotic, involving the material oxidative degradation, and a second step biotic, degradation by the action of microorganisms, such as the oxo-biodegradable polymers [3-5].

The polyolefin has good mechanical properties during its use, but they must embrittle and fragment much more quickly in landfill conditions after disposal than do ordinary PE bags and films. Initiation of oxidative degradation (peroxidation) is the result of heat generated microbial in landfills. Disintegration of these plastics follows molar mass reduction as a result of the mechanical actions that occur during normal landfill operations. The fragmentation of the films and bags allows the vertical flow of liquids and gases which enhances the aerobic biodegradation of food and green garden wastes, paper and similar [6]. In the last few years, polyethylene (PE) film contain pro-oxidant additives has been introduced into the market as a new material promising biodegradability, in conjunction with the continual use of existing production and processing technologies and with reasonable prices of products. Primary applications are in agricultural greenhouse construction, mulching film, packaging film as well as in other products with a limited lifetime, e.g. bags [7]. Polymeric materials containing pro-oxidant substances are known as oxo-biodegradable polymers. Those materials require oxidative degradation (normally by the action of ultraviolet radiation and/or heat) in order to reduce the molar mass and to form oxygenated groups, which are more easily metabolized by microorganisms [8]. The oxo-biodegradable additives are typically incorporated into the polymeric chain in conventional plastics such as Polyethylene (PE), Polypropylene (PP), Polystyrene (PS), Polyethyleneterephthalate (PET) and sometimes also Polyvinylchloride (PVC) at the moment of conversion into final products. Pro-oxidant additives



are added at low concentrations (typically 1 – 5% weight) in the formulation of conventional polymer resins, or even of hydro-biodegradable resins, almost without changing their original mechanical and optical properties [3]. These additives are based on chemical catalysts, containing transition metals such as cobalt, manganese; iron, etc., which cause fragmentation as a result of a chemical oxidation of the polymer chains triggered by ultraviolet irradiation (UV) or heat exposure. In a second phase, the resulting fragments are claimed to eventually undergo biodegradation. In addition to additives that trigger the fragmentation process, the oxo-biodegradables include stabilizers, which are added to limit the unwanted fragmentation of the polymer chains while the plastic is still used by consumers [9]. The pro-oxidant into polyethylene initiates polymer degradation by producing free radicals which react with molecular oxygen to create peroxides and hydroperoxides. The oxidation may be enhanced by biodegradation which results a porous structure and enhances the accessibility of the polymer molecules to oxygen and microorganisms [10].

The aim of this study is to evaluate the degradation in the landfill of the blue PE film original from the mixture of low density polyethylene (LDPE) with high density polyethylene (HDPE), recycled with pro-oxidant additive, by the structural properties, thermal and morphological characteristics.

Experimental Work

The blue PE films with pro-oxidant additive were placed in the landfill of Farroupilha city, for 4 and 8 months. The landfill of Farroupilha city, RS/Brazil (Figure 1) is situated in an area of approximately 11,000 m² and it contains 63,300 t of urban solid residues.

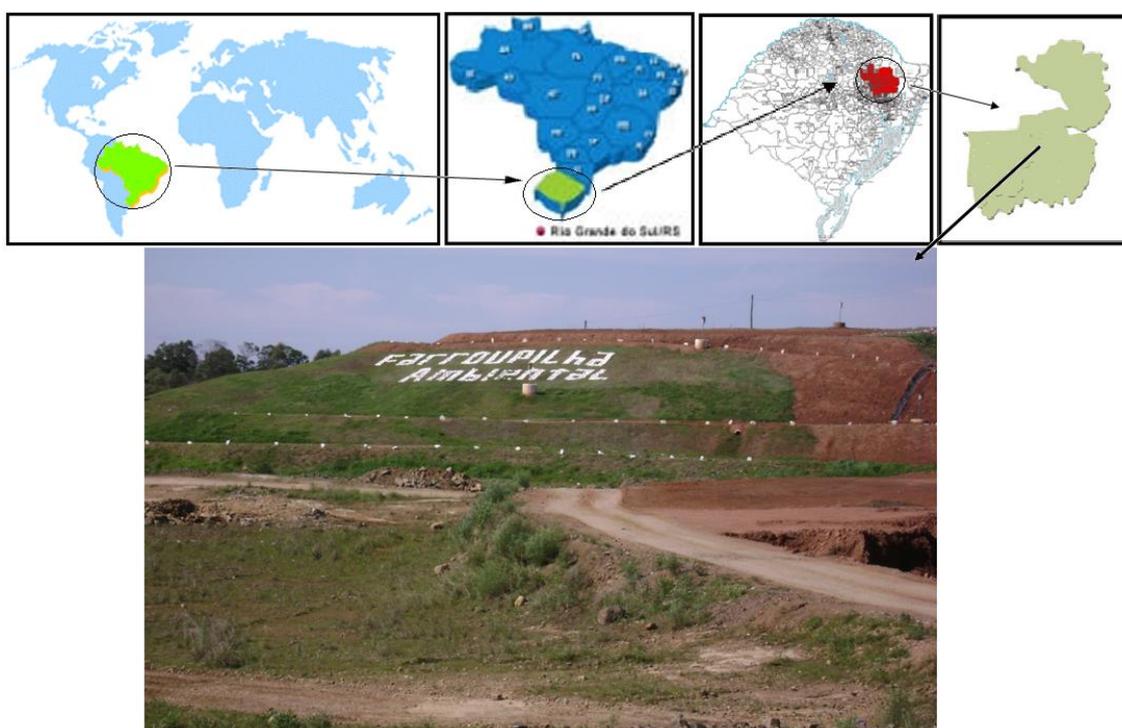


Figure 1: The landfill of Farroupilha city in south of Brazil

Materials

The blue PE films were prepared by a mixture of 1.0% wt of the pro-oxidants, mixture of LDPE and HDPE recycled - (LDPE/HDPE)r with pigment blue in an industrial extruder, single screw with double fillet, with a diameter of 45 mm and 1.3 m high. The temperature profile used in the extruder was 134, 185, 185, 183 e 160 °C.

The blue PE films with dimensions of 13 x 13 x 5x10⁻⁴ cm with pro-oxidants in triplicate were placed in 20x20 cm nylon packaging in the landfill of Farroupilha city in south of Brazil buried at a 2m deep. The samples after 4 and 8 months of disposition were collected, washed according to standard ASTM D6288-98, adapted, Standard Practice for Separation Washing of Recycled Plastics Prior Testing (1998).

Structural analysis, thermal and morphological characteristics were subsequently carried out.



Spectroscopy Characterization

The Fourier transform infrared (FT-IR) spectroscopy analysis was carried out with 32 scans, in the range of 4000 cm^{-1} to 400 cm^{-1} , at a resolution of 4 cm^{-1} , transmission analysis on samples in film form.

Thermal analysis (TGA and DSC)

The TGA analysis (TGA50 – Shimadzu) was carried out under N_2 ($50\text{ mL}\cdot\text{min}^{-1}$) atmosphere, from ambient temperature up to 750°C . Approximately 10mg of each sample was used in a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

The DSC (DSC50 – Shimadzu) analysis was performed under N_2 atmosphere ($50\text{ mL}\cdot\text{min}^{-1}$) using approximately 10mg of each sample. Initially, the samples were heated until 180°C ; after that, cooled from temperature ambient to -100°C and then re-heated at 180°C . Those experiments were performed in a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) was carried out using a Superscan S-550, with a secondary electron detector and an acceleration voltage of 15,0 kW. The scanning was carried out at a magnification of x 1500 (10 μm). The samples were previously covered with gold.

Results and Discussion

A sanitary landfill is predominantly an anaerobic biological system, in which the treatment of the deposited domestic solid residues occurs through the interaction of different microbial species [11].

Degradability of polymeric materials is a function of the structures of polymeric materials, the presence of degradative microbial population and the environmental conditions that encourage microbial growth [12].

A significant reduction in absorption by FT-IR between 1710 and 1740 cm^{-1} , PEBD samples in the land, was observed by Chiellini et al.,(2003)[13], which has attributed to assimilation of the polymer oxidized by microorganisms.

The blue PE films show no evidence of peroxidation in FT-IR (Figure 2) but this suggests a period of fast growth on the beginning of incubation caused by consumption of additives, stearates from pro-oxidants and/or low molecular oxidation products of PE. [9].

The structural analyses of the blue PE films in the landfill (Figure 2) showed decrease the absorption on the pro-oxidant additive in region amorphous of the polymer (1300 cm^{-1}) and molecular oxygen present. The oxidation takes place there predominantly whereas the crystalline zones remain intact [14].

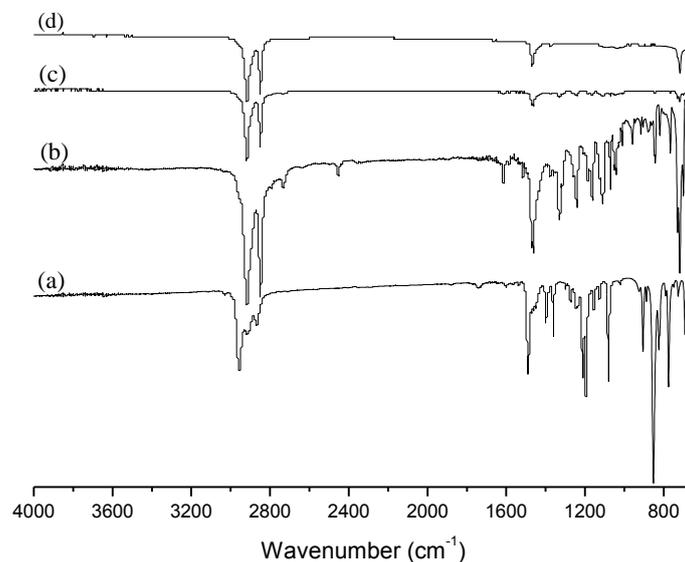


Figure 2: Spectroscopy FT-IR the (a) additive pro-oxidant, (b) blue PE film virgin, (c) blue PE film after 4 month and (d) blue PE film after 8 month of exposure in the landfill

As structural changes in the polymer chain may reflect the stability of the material, Figure 3 shows the thermogravimetric TGA by assessing changes around $400^\circ - 500^\circ\text{C}$ region characteristic of polyethylene degradation [15].



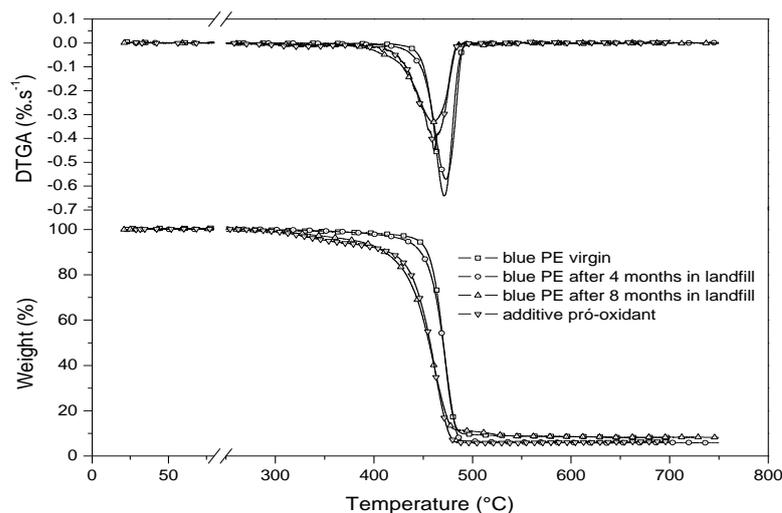


Figure 3: Thermograms the additive pro-oxidant, the blue PE film virgin and after 4 and 8 month of exposure in the landfill

The additive pro-oxidant, blue PE film virgin and blue PE film, after being submitted to further degradation in landfill after 4 months showed a single event of mass loss in the thermo gravimetric. The degradation of the additive pro-oxidant and blue PE film, after 8 months of exposure, initiated at temperatures below the blue virgin PE and blue PE after 4 months later. This difference at the beginning of the degradation can be characterized by the division chain of PE [16,4], accelerated by the action of pro-oxidant that degraded in the same range (300 to 500°C).

Figure 4 illustrates the curves of the exothermic DSC thermogram of the first and second heating of the blue virgin PE film and after 4 and 8 months of exposure in the landfill.

In Figure 4 we observed the presence of two melting peaks attributed to fusion of LDPE and HDPE both at temperatures below the literature that is 120 to 135°C respectively. This reduction in T_m of the polymers is due to the fact that both are recycled polymers with degradation process started.

The heterogeneity of this material is due the presence of co-monomers and/or mixture of PEs. The literature attributes the first peak melting $\approx 110^\circ\text{C}$ which refers to the polymer LDPE with thick plates with the highest amount of branches. The second endothermic phenomenon $\approx 130^\circ\text{C}$ can be attributed to the HDPE, characteristic of thin plates, due to few branches [17-19].

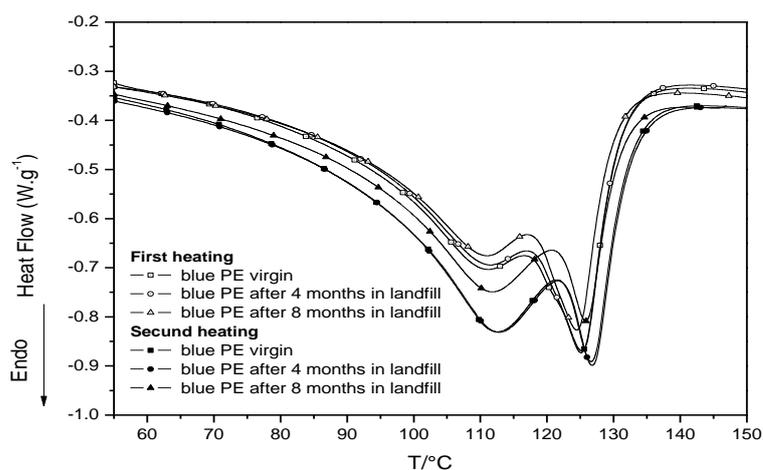


Figure 4: Thermograms by DSC the blue PE film virgin and after 4 and 8 month of exposure in the landfill for first and second heating.



Figure 5 shows the crystallization of the blue virgin PE film and after 4 and 8 weeks of exposure in the landfill. It is observed the presence of two crystallization peaks, one at about $\sim 118^\circ\text{C}$ attributed to the crystallization of HDPE and the other one at $\sim 95^\circ\text{C}$ attributed to the crystallization of LDPE.

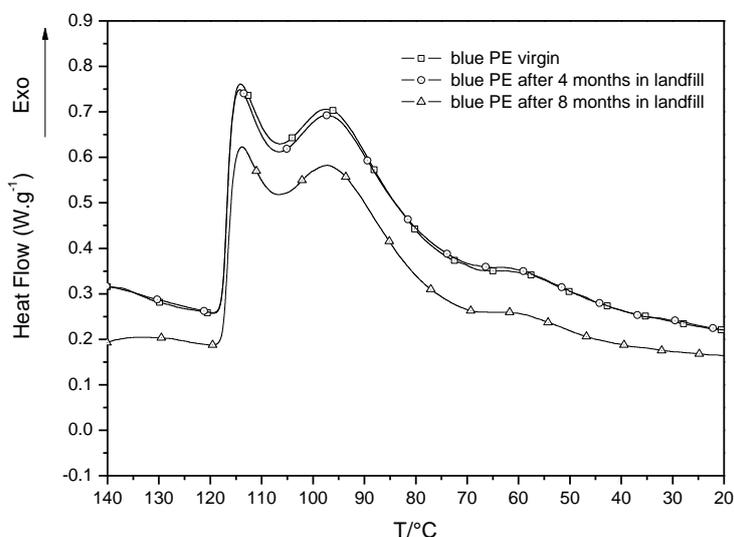


Figure 5: Thermograms by DSC the blue PE film virgin and after 4 and 8 month of exposure in the landfill for first and second heating coolind crystallization.

Complementing the Figures 4 and 5, were calculated their enthalpies of the films studied. Table 1 shows the peak melting (T_m) and enthalpy of fusion (ΔH_f) of polymers in the first heating and the crystallization temperature (T_c) and enthalpy of crystallization (ΔH_c) of polymers. It can be seen by examining Table 1 that both T_m and T_c of blue PEs remained stable, however, changing from 8 months of exposure in the landfill the films showed a significant reduction of enthalpy ΔH_f and ΔH_c . This reduction is directly related to the loss of stability's degradation, and processes of chain scission promoted in the films that influence the energy needed to melt and order the polymers.

Table 1: Enthalpies and temperatures of heating/coolind thermograms obtained by DSC the blue PE film virgin and after 4 and 8 month of exposure in the landfill.

samples	1 ^o T_m	1 ^o ΔH_f	T_c	ΔH_c	2 ^o T_m	2 ^o ΔH_f
Blue PE	124.7	-96.8	113.8	81.8	126.2	-1111
4months	124.7	-96.1	113.8	80.3	126.5	-111.2
8months	123.9	-81.7	113.4	67.7	125.4	-90.2

Figure 6 illustrates the SEM micrographs of the blue virgin PE film surface after 4 and 8 months of exposure in the landfill.

Figure 6 (A) shows the morphology of the blue PE film before exposure in the landfill. It can be observed that the film remains stable, without features that demonstrate degradation processes. In Figure 6 (B) and (C) referring to the blue PE films collected in landfill after 4 and 8 months, there is the presence of biofilm. Microorganism attack on PE is a secondary process, after an abiotic process of degradation with structural changes in films with physical deterioration of the surface, including phenomena such as fissures, cracks, erosions, globules and destroyed zones and consequently the stability of these ones [6,10,20]. They are able to absorb and grow on the surface of polyethylene film containing the pro-oxidant additives and the initiation of oxidative degradation is the result of heat generated in landfill microbial [6, 21-23].



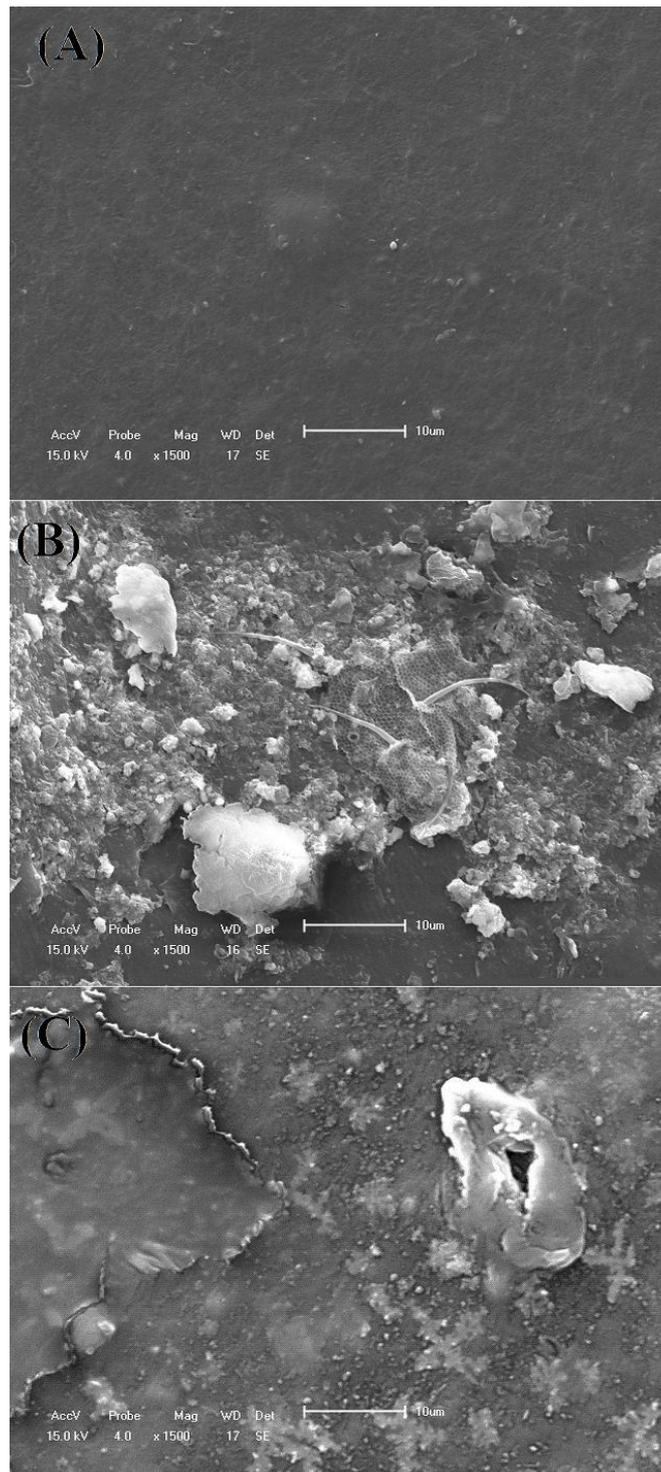


Figure 6: SEM micrographs of (A) blue virgin PE film, (B) blue PE film after 4 months in the landfill and (C) blue PE film after 8 months in the landfill

The existing publications, so far, describing the oxi-biodegradation of polymers as a process that occurs in two steps, involving oxidative damage (usually abiotic) followed by oxidative degradation product [1,3-5]. This suggests that after 8 months of exposure in the landfill, the structure of the blue PE films, recycled, with pro-degrading additive may have pores in the structure, which may be responsible for the accessibility of polymer molecules in the dissemination of microorganisms, looking for nutrients to continue their metabolism and also responsible for the accumulation of water that penetrates the polymer matrix, causing swelling of the same [10, 24].

These results can be demonstrated by the Figures 4 and 5 thermograms where there was a reduction of thermal stability in the film submitted for 8 months in the landfill with degradation beginning at lower temperatures. It is also consider the possibility of the degradation process beginning by the attack of microorganisms seen at Figure 6 (B) and blue PE film surface structure damaged seen at Figure 6 (C). This justifies the reduction of enthalpies, fusion and crystallization of the sample of blue PE film after 8 months of exposure in the landfill.

Conclusion

The pigments and pro-oxidant additives accelerate the catalytic oxidation and the adhesion of microorganisms in oxo-degradable polymers after exposure in landfill, facilitating the attacks which induce microbiological degradation/ biodegradation of the polymer environment in complex microbial community.

The structural analyses the blue PE films in the landfill showed decrease absorbencies on the pro-oxidant additive, after 4 and 8 months of exposure and biofilm formation when incubated with microorganisms.

Regarding the crystalline melting temperature (T_m) and crystallization temperature (T_c) of the films of blue PEs remained stable, however, changing from 8 months in the landfill the films showed a significant reduction of enthalpy ΔH_f and ΔH_c . This reduction is directly related to the loss of degradation stability and exposure time of samples in the landfill.

Acknowledgments

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