Effect of ultraviolet radiation in the photo-oxidation of High Density Polyethylene and Biodegradable Polyethylene films

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Abstract. One of the most widely used plastics in the world is the High density polyethylene (HDPE), it is a stable material due to its carbon-carbon bonds, causing their slow degradation; which is why we are looking for alternative ways to accelerate the degradation process of this polymer. An alternative is the addition of oxidized groups in its molecular structure, which results in the development of polymers susceptible to biodegradation (PE-BIO). In this paper, HDPE and PE-BIO films were exposed to UV-B radiation (320-280 nm) at different exposure times, 0-60 days. The effects of UV radiation in samples of HDPE and PE-BIO were characterized using infrared spectroscopy with attenuated total reflectance (ATR). The results show that the exposed materials undergo changes in their molecular structure, due to the infrared bands formed which corresponds to the photo-oxidation of HDPE and PE films when submitted to UV-B radiation.

1. Introduction
Nowadays, plastics are products widely used and manufactured in large quantities, their difficult process of degradation causes these materials are the most frequent contaminants in soils and oceans [1, 2]. The high density polyethylene (HDPE) is one of the most commonly used plastics in everyday life [3], its widespread use is due to its low manufacturing cost, in addition to its excellent mechanical and chemical properties; its low rate of degradation is one of the reasons that new alternatives for disposal reduction are studied. One of the proposed alternatives is the manufacture of self-biodegradable polyethylene (PE-BIO), which is an oxidized material, containing carbonyl groups (C=O) in its molecular structure; whose important feature is that they are susceptible to microbial attack. Another alternative is the use of UV-B radiation, in order to degrade and to incorporate plastics as harmless material to the environment [3].

2. Theory
Plastics are synthetic materials derived from petroleum, so the problems caused by their indiscriminate use and their persistence in the environment, has resulted in a worldwide established system of coding to identify them. Plastic products have a distinctive symbol to identify each type of polymer. The HDPE is identified with the number two.
The high density polyethylene (HDPE), is a semicrystalline thermoplastic, which is obtained by the addition polymerization mechanism of the monomer ethylene; its structure is a linear chain of CH₂-CH₂ with few branching, its density is 96 g/cm³ and its melting point is 135 °C. The HDPE is not toxic, has a lower stiffness compared with the polypropylene, its chemical resistance is acceptable, also, has good mechanical strength; these properties have made from HDPE an attractively material for the production of plastic bags, toys, cases (elbow, knee), household items; also is widely used in the automotive and food packaging industry. The widespread use and high persistence in the environment of HDPE, have led to seek solutions to reduce the presence of this polymer in the environment. The biodegradable polyethylene (PE-BIO) has been proposed as a solution to the problem of environmental pollution by HDPE. The PE-BIO is a synthetic polymer including carbonyl groups in its molecule, so that, microorganisms are able to metabolize the chains of this materials; however for microorganisms perform their function is necessary for the PE-BIO exposed to weather with temperature and humidity controlled [4].

The degradation of the polymers is mainly due to photo-oxidation reactions [5, 6, 7] and thermo-oxidation reactions [8, 9]; causing breakage and cross-linking of the polymer chains, the formation of carbonyl (C=O) and vinyl (CH=CH₂) groups, as well as changes in the conformation of the polymer [10, 11, 12]. These effects have been characterized by other authors with techniques such as differential scanning calorimetry (DSC), electron microscopy (SEM), X-ray diffraction (XRD) and Infrared Spectroscopy (FTIR) [13, 14, 15, 16, 17]. In the present work, the effect of UV-B radiation on the photo-oxidation of HDPE and PE-BIO films were characterized using FTIR spectroscopy.

3. Materials and methods

3.1 Material
High density polyethylene (HDPE) and biodegradable polyethylene (PE-BIO) films of dimensions 40x50 mm with a thickness of 0.5 mm.

3.2 Exposure to UV-B radiation
The samples of HDPE and PE-BIO, were exposed to UV-B radiation for a period of time from 0 to 60 days, at a distance of 5 cm between the sample and the radiation source, using a UV-B BYTEK lamp model Ultraviolet Multiprom Eraser in a 320-280 nm range emission.

3.3 FTIR spectroscopy
The effects of UV-B radiation in the films of HDPE and PE-BIO, were characterized by infrared spectroscopy (FTIR), using a spectrophotometer Thermo Nicolet iS10, equipped with ATR, Germanium mirror and a Potassium bromide beam splitter.

4. Results
In figure 1, the infrared spectra of HDPE and PE-BIO unirradiated are shown, which have the same set of IR absorption bands; stretching vibration of the carbon-hydrogen bonds (CH) of the main chain occurs at 2772-3038 cm⁻¹; the regions of 1440-1490 cm⁻¹ and 700-750 cm⁻¹ correspond to the vibration of wagging and rocking methylene (CH₂), respectively [18]. The IR spectrum of PE-BIO, figure 1, has an absorption band at 1640 cm⁻¹ which is due to stretching vibration of the carbonyl group (C=O), indicating that this material is oxidized from manufacturing.

Photo-oxidation of PE films exposed to UV-B radiation is developed according to the reaction mechanism Norrish Type II [19, 20], which is considered a homolytic process consisting of four stages: initiation, propagation, chain branching and termination [21]. The stage of initiation is mainly caused by hydroperoxides formed during the polymerization reactions of PE.
Hydroperoxides when decomposed by the effect of UV-B radiation, allow the formation of functional groups such as hydroxyl, anhydrides and carbonyl. As the dose of UV-B radiation increases in the films of HDPE and PE-BIO, the breaking bond between tertiary carbons and branch leading to the formation of vinyl groups [22, 23]; when increasing dose of UV-B radiation, the carbonyl and vinyl groups releasing from main chains causing crosslinking of the same [24].

![Figure 1. Infrared spectra of HDPE and PE-BIO unirradiated films](image)

In figures 2a and 2b, the IR spectra of HDPE and PE-BIO films are shown, respectively, from 0 to 60 days of exposure to UV-B radiation. The infrared absorption band located in the range of 1600-1800 cm\(^{-1}\) corresponding to stretching vibration of the carbonyl functional group (C=O). During the first 30 days of exposure of the films of HDPE to UV-B radiation, it is observed the increase in band intensity of IR absorption of carbonyl, due to the photo-oxidation of plasticizers and stabilizers that HDPE contains [16]. From 30 to 60 days of exposure to UV-B radiation, the photo-oxidation of the chains of HDPE occurs and IR absorption band tends to wide, due to the simultaneous formation of groups such as esters, ketones, anhydrides and vinyl groups (see table 1).

| Photo-oxidation products | Wavenumber (cm\(^{-1}\)) |
|--------------------------|--------------------------|
| Vinlylidene              | 888                      |
| Terminal vinyl           | 909                      |
| Trans-vinylene           | 965                      |
| Ketones                  | 1715                     |
| Esters                   | 1730                     |
| Anhydrides               | 1770                     |

PE-BIO films are in oxidized state from its manufacture and, during the first 5 days of exposure to UV-B radiation, the presence of oxidized groups decreases, since the carbonyl group is more susceptible to experiment cleavage by action of UV-B radiation [23]. However, after 5 days of
exposure to UV-B radiation, the intensity of the IR absorption band is increased due to photo-oxidation of PE-BIO stabilizers and plasticizers.

Figures 2a and 2b shows the IR region from 1750-2000 cm\(^{-1}\) which corresponds to different types of vinyl groups of HDPE and PE-BIO films exposed to UV-B radiation from 0 to 60 days. For both types of polymeric materials, the intensity of IR absorbance is increased as the exposure time of the material to UV-B radiation progresses, due to the formation of vinyl groups from the reaction of tertiary carbons by effects of UV-B radiation [21].
5. Conclusions
In the presence of UV-B radiation and oxygen, chains of HDPE and PE-BIO experiment structural changes at molecular level, forming vinyl and carbonyl groups, which are considered the main products of photo-oxidation.

The broadening of IR absorption band of carbonyl and vinyl groups is due to the simultaneous formation of different products of photo-oxidation such as ketones, esters, anhydrides, vinylidenes, terminal vinyl and trans-vinylenes groups during exposure of the HDPE and PE-BIO films to UV-B radiation.

The formation of oxidation products occurs mainly in HDPE films, because the presence of the carbonyl group in the PE-BIO from manufacturing slows down the photo-oxidation reaction of this polymer; so that, it is found that the final disposition of PE-BIO must be satisfied with the conditions of disposal of solid waste, temperature and humidity, stipulated for this type of polymeric material.

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