



## FTIR AS A TOOL TO EVALUATE THE PHOTOOXIDATIVE DEGRADATION OF POLYETHYLENE

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### Abstract

Polyethylene has well-defined chemical reactions within the photooxidation. The products formed, including molecular fragments containing carbonyls, hydroxyls and terminal vinyl groups, are responsible for changes in the properties of the polymeric material. Many techniques and methods can be used in the evaluation of the accelerated oxidation process by UV radiation incidence on polyethylene, including Fourier Transform Infrared Spectroscopy, which allows, from the creation of indices, to verify the appearance of the functional groups produced. In this work, the carbonyl, terminal vinyl and hydroxyl index allowed evaluating the photooxidative degradation of polyethylene in HDPE/LDPE films processed with and without a pro-oxidant. It was observed that the additive provided greater chain scission and oxygen increase in the fragments produced in the photochemical reactions in the presence of air, leading to greater fragility, which was confirmed by micrographs obtained by SEM.

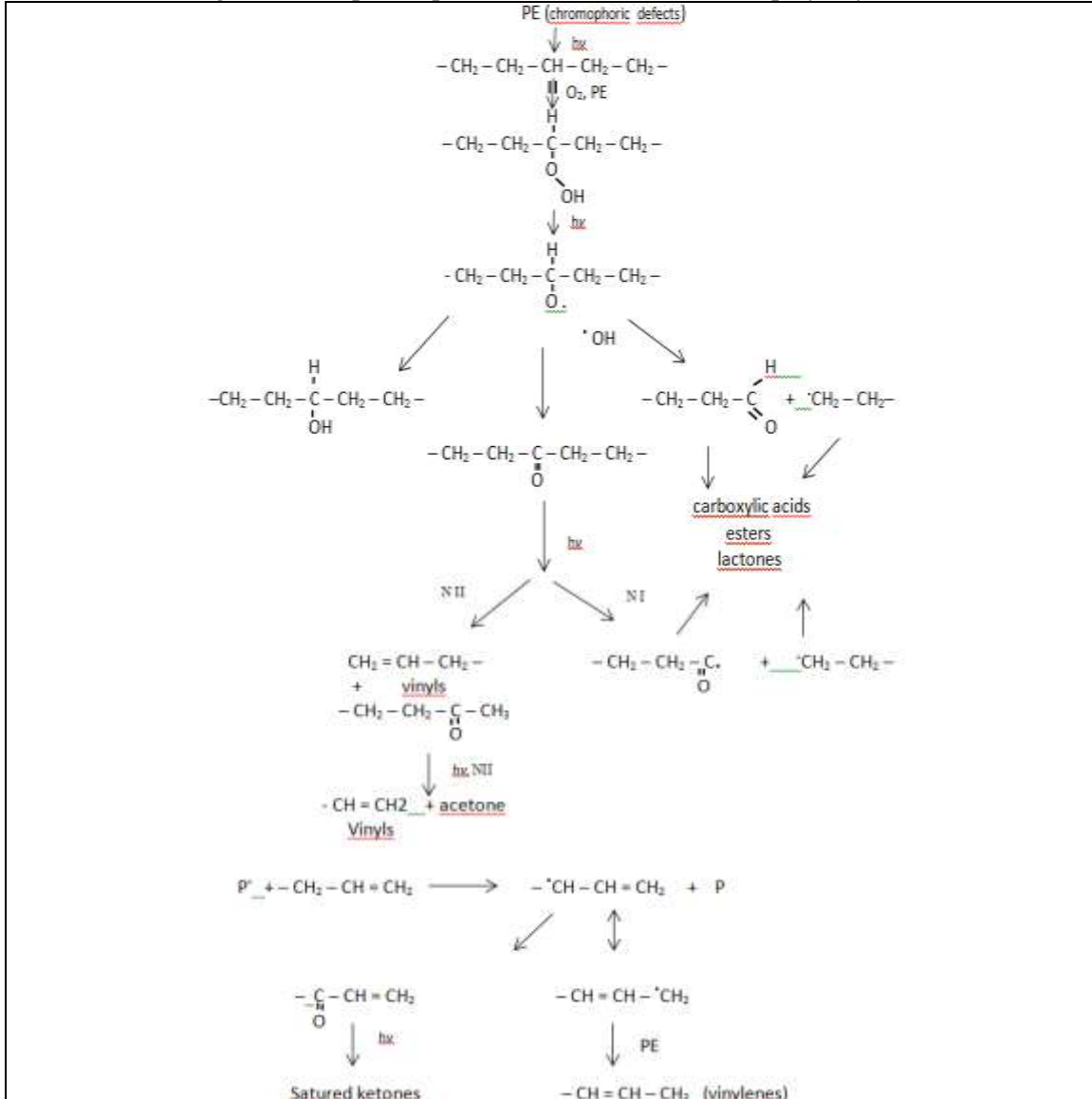
*Keywords: FTIR, polyethylene, degradation, carbonyl index, vinyl index.*

### Introduction

Polyethylene (PE) is one of the most widely used resins in the world, with several applications in the plastics industry, either in the production of artifacts such as toys and household items, or in the production of films used as various packaging, such as supermarket bags. In 2015, the production of PE was 116 million tons, and 97 tons of waste of the same polymer were generated [1], much of it discarded incorrectly and unconsciously, becoming a major environmental problem due to its accumulation in oceans, rivers and soils [2]. Processing polyethylene with pro-oxidant additives has been one of the alternatives to accelerate the process of waste degradation by thermal and photo-oxidation [3], producing oxygenated fragments that can be assimilated by microorganisms [4]. The study involving pro-oxidant agents has been growing in research centers and involves the submission of PE processed with these additives to different aging environments, requiring the characterization of the material by various types of analysis. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy are examples of such techniques. FTIR allows verification of the insertion of functional groups into the PE during the photo-oxidation process that is well known and leads to the production of fragments containing carbonyls ( $>C=O$ ), hydroxyls ( $-OH$ ) and terminal vinyl unsaturations ( $>C=CH_2$ ), which can be traced from indices. The insertion of these functional groups into the PE chains, as well as the

reduction of the molar mass of the polymer, leads to its yellowing and brittleness, with the appearance of micro-cracks in aged films. Fig. 1 shows the chain of chemical reactions in the photooxidation of PE [5], with production of fragments containing the screened groups.

Figure 1 - Simplified photooxidation mechanism of polyethylene.



Source: Adapted from Gardette and collaborators (2013) [5].

The objective of this work was to demonstrate how FTIR can be used to evaluate the degradation of High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE) blend films, in mass percentages of 90 and 10%, respectively, processed without and with a transition metal organic salt pro-oxidant additive, d2w<sup>TM</sup>, and subjected to accelerated aging for 144 hours in a UV chamber.

## Experimental

### Materials

The polymers HDPE (HE-150) and (LDPE - EB-853/72), both produced by Braskem S.A; d2w<sup>TM</sup> additive, in masterbatch, were used.

### *Obtaining of tubular films*

The mixture of HDPE and LDPE polymers, 90 and 10%, was processed in a single-screw extruder, model ES 35-FR (Seibt), producing films with an average thickness of 30µm, without and with 1% of the pro-oxidant additive d2w<sup>TM</sup>.

### *Accelerated aging by UV radiation incidence*

The film was exposed to 144 hours of UVA/UVB radiation in a Comexin (C-UC) chamber, according to ASTM G-154 standards.

### *Characterization*

#### *Fourier Transform Infrared Spectroscopy (FTIR)*

The Fourier transform infrared spectroscopy (FTIR) analyses were performed in Perkin Elmer equipment, Frontier model. All films were evaluated in ATR (Attenuated Total Reflectance) mode. The spectra were obtained at an ambient temperature of 25°C, air humidity controlled at 30%, in an absorption region ranging from 650 to 4000 cm<sup>-1</sup>, with 10 scans for each sample.

The carbonyl functional group, produced in the photooxidation of PE, has absorption of infrared radiation in different bands, dependent on the organic function, which are: carboxylic acids (1712 cm<sup>-1</sup>), ketones (1723 cm<sup>-1</sup>), aldehydes (1730 cm<sup>-1</sup>) and lactones (1780 cm<sup>-1</sup>) [6,7]. From the absorption, it is possible to calculate the oxidation level of the polymeric material through the carbonyl index, CI, using Eq. 1:

$$CI = \frac{A_1}{A_2} \quad (1)$$

in which A<sub>1</sub> is the absorption area of the band between 1700 and 1780 cm<sup>-1</sup>, referring to the peaks of the carbonyl-containing groups, and A<sub>2</sub> is the area the band with a peak at 1463 cm<sup>-1</sup> ( 1450 – 1468 cm<sup>-1</sup>), considered invariable for polyethylene [7].

The terminal vinyl index, VI, was determined using Eq. 2. As observed in Fig. 1, photooxidation of PE produces fragments with terminal vinyl groups.

$$VI = \frac{A_3}{A_2} \quad (2)$$

in which A<sub>3</sub> is the absorption area of the band at 908 cm<sup>-1</sup>, referring to vinyl groups, and A<sub>2</sub> is the area the band with a peak at 1463 cm<sup>-1</sup> ( 1450 – 1468 cm<sup>-1</sup>), which is relatively invariant for polyethylene [7].

The hydroxyl index, OHI, was determined using Eq. 3. Polymeric fragments containing hydroxyls are also produced in the photooxidation of PE.

$$OHI = \frac{A_4}{A_2} \quad (3)$$

where A<sub>4</sub> is the absorption area of the band between 3400-3230 cm<sup>-1</sup> [8], referring to the hydroxyl in polymer chain.

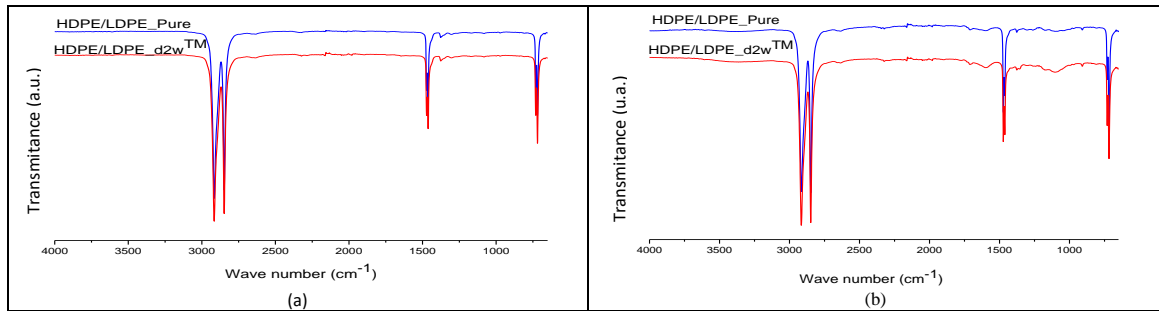
#### *Scanning Electron Microscopy (SEM)*

The analyses were performed in the following equipment: Jeol Scanning Electron Microscope, model JSM6510LV and Denton Vacuum Metallizer, model Desk V. The samples were metallized with gold. The electron beam used contained 10 kV of energy and magnifications of 1,500 and 5,000x.

## **Results and Discussion**

The FTIR spectra of the evaluated films, without and with pro-oxidant, before and after accelerated aging, are presented in Fig. 2.

Figure 2 - FTIR spectra of HDPE/LDPE films: (a) before and (b) after accelerated aging in UV chamber.



Visually, it is possible to observe changes in the spectra of the films before and after exposure to UV radiation, indicating the appearance of functional groups due to photooxidation.

Table 1 shows the area of the specified bands as calculated by OriginPro 8.5.1.

Table 1 - Band areas of the spectra specified for subsequent calculation of the indices.

Film	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>
HDPE/LDPE_Pure_t=0	47.10	328.50	14.00	83.91
HDPE/LDPE_d2w <sup>TM</sup> _t=0	84.10	359.50	23.61	198.30
HDPE/LDPE_Pure_144h_UV	127.40	340.60	39.17	568.20
HDPE/LDPE_d2w <sup>TM</sup> _144h_UV	159.20	355.90	58.94	350.30

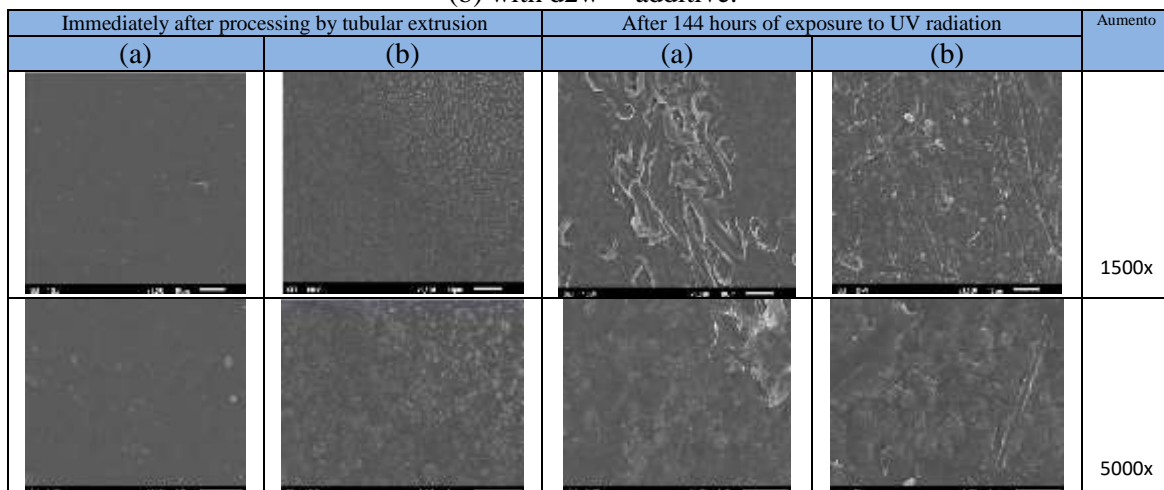
Table 2 presents the CI, VI and OHI values. Both HDPE/LDPE films showed an increase in CI, VI and OHI after exposure to UV radiation, evidencing the oxidation process of PE by radiation incidence.

Table 2 - CI, VI and OHI calculated for the films evaluated.

Film	CI	VI	OHI
HDPE/LDPE_Pure_t=0	0.1434	0.04262	0.2554
HDPE/LDPE_d2w <sup>TM</sup> _t=0	0.2339	0.06567	0.5516
HDPE/LDPE_Pure_144h_UV	0.3740	0.1150	1.6682
HDPE/LDPE_d2w <sup>TM</sup> _144h_UV	0.4473	0.1656	0.9843

Fig. 3 shows the micrographs of the surfaces of the HDPE/LDPE films, without and with the additive, before and after exposure to UV radiation, magnified 1500 and 5000x.

Figure 3 - Micrographs of HDPE/LDPE films after processing: (a) without additive, (b) with d2w<sup>TM</sup> additive.



The surface of HDPE/LDPE films with and without additive showed regular surface before exposure to UV radiation. After 144 hours exposed to accelerated aging, both films showed morphological changes, with the appearance of cracks that indicate the fragility of both. The cracks were clearer for the film with d2w<sup>TM</sup>, for which higher increments of IR and CI were observed, indicating that the degradation was more severe in the film containing the pro-oxidant.

## Conclusions

The determination of the carbonyl, terminal vinyl and hydroxyl indices from the FTIR spectra of the HDPE/LDPE films facilitates the evaluation of the photooxidative degradation process of polyethylene, since the higher the indices, the greater the presence of polymeric fragments containing the traced functional groups. The micrographs obtained by SEM confirm the appearance of microcracks in the material, indicating severe degradative process that was more intense for the additived film.

## Acknowledgements

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