Characterization by FTIR spectroscopy of degradation of polyethylene films exposed to CO2 laser radiation and domestic composting

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Abstract. Polyethylene (PE) is a non-biodegradable polymer and accumulate easily on environment due its high molecular weight. In order to reduce this problem low-density (LDPE), high-density (HDPE) and biodegradable (BIO-PE) polyethylene films were exposed to CO2 laser radiation at different fluences and to domestic composting, the effects of CO2 laser radiation and domestic composting were characterized by FTIR spectroscopy. LDPE, HDPE and BIO-PE exposed to CO2 laser radiation underwent thermodegradation reactions causing changes in LDPE, HDPE and BIO-PE chemical and physical properties due to chain scission. LDPE, HDPE and BIO-PE biodegradation reactions leading to the formation of carbonyl (C=O), vinyl (CH2=CH) and hydroxyl (OH) groups.

1. Introduction
Plastics are one of the most used materials around the world and their demand has increased throughout the years, moreover, most of these plastics are single use plastics and their wastes accumulate on the environment causing serious environmental problems; only in 2015, there were about 4.9 billion metric tons of plastic wastes in landfills [1]–[3].

Polyethylene (PE) is widely used for plastic bags due to its excellent properties and high durability, packing represents the 62.2% of plastic wastes in the world; even though, PE is not a biodegradable polymer due to its high molecular weight, long carbon chain molecular structure and hydrophobic behavior [4], [5]. Some authors have reported that PE undergoes thermodegradation reaction when is exposed to CO2 laser radiation modifying the molecular weight, reducing the polymeric chain size, and increasing its degradability and hydrophilicity [6]–[11].

Biodegradable polyethylene, produced to accelerate the degradation process and reduce their accumulation in the environment, decompose into CO2, methane, water, inorganic components or biomass as a result of the microbial degradation process under appropriate environmental conditions. Moreover, under suitable physical and/or biological treatments, some synthetic polymers may undergo biodegradation reactions [12].

In the present study, it is described the characterization by FTIR spectroscopy, of degradation of commercial LDPE, HDPE, and BIO-PE exposed to CO2 laser radiation and composting at ambient conditions.

2. Experimental
2.1. Materials
Films of commercial LDPE, HDPE and BIO-PE bags of 13x20cm of 0.05, 0.07 and 0.01mm thickness, respectively, were used. LDPE, HDPE and BIO-PE molecular weight and exact composition are commercially confidential, because they were synthesized and manufactured under trademark.

2.2. Laser CO2 irradiation
LDPE, HDPE and BIO-PE films were exposed to CO2 laser radiation using a CO2 laser Engraver C120H at 10.6μm, with 1.8cm laser spot diameter, expanded using a zinc selenide (SeZn) with a negative meniscus lens. PE samples were mounted on racks at 20cm from the lens at different fluences, F [=] J/cm² (Table 1).

| Film     | Power (W) | Time (min) | Fluence (J/cm²) |
|----------|-----------|------------|-----------------|
| LDPE     | 9.5 W     | 10min      | 2240            |
|          |           | 20min      | 4480            |
|          |           | 30min      | 6720            |
|          |           | 10min      | 1297            |
| HDPE     | 5 W       | 20min      | 2594            |
|          |           | 30min      | 3891            |
| BIO-PE   | 5 W       | 20min      | 2594            |
|          |           | 30min      | 3891            |

2.3. Domestic Composting
LDPE, HDPE, and BIO-PE films unexposed and exposed to laser CO2 radiation were exposed to domestic composting at ambient conditions between April and July 2019, average temperature of 24°C and average relative humidity (RH) of 26.2%. Compost contained mainly fruit and vegetable peels, dried leaves and tree waste, and was placed into plastic containers in Aguascalientes City, Mexico, 21° 52’ 56” N Lat., 102° 16’ 57” W Long.

2.4. Infrared Spectroscopy (IR)
Structural changes of PE films exposed to CO2 laser radiation and to domestic composting were characterized by Fourier Transform Infrared Spectroscopy, FTIR. The FTIR spectra were recorded on a Thermo Nicolet spectrophotometer model iS10 with Germanium mirror, Ge, with a resolution of 4cm⁻¹ and scanning of 64, in the range of 690-4000cm⁻¹. IR spectra were normalized to maximum absorbance.

2.5. Carbonyl Index (Ico)
Carbonyl index was calculated by the ratio of the IR absorbance band at 1715 cm⁻¹ \((A_{1715})\), stretching vibration of the carbonyl group (C=O), and the IR absorbance at 1465 cm⁻¹ \((A_{1465})\), of the methylene band; see equation (1) [13].

\[
I_{co} = \frac{A_{1715}}{A_{1465}} \tag{1}
\]

2.6. Vinyl Index (Iv)
Vinyl index was calculated by the ratio of the IR absorbance at 909 cm⁻¹ \((A_{909})\), stretching vibration of the vinyl group (CH=CH), and the absorbance at 1465 cm⁻¹ \((A_{1465})\) of the methylene band; see equation (2) [13].

\[
I_{v} = \frac{A_{909}}{A_{1465}} \tag{2}
\]

1.1. Hydroxyl Index (IOH)
Hydroxyl index was calculated by the ratio of the IR absorbance at 3400 cm⁻¹ \((A_{3400})\), stretching vibration of the hydroxyl group (O-H), and the absorbance at 3100 cm⁻¹ \((A_{3100})\) as reference; see equation (3) [14].

\[
I_{OH} = \frac{A_{3400}}{A_{3100}+0.0018} \tag{3}
\]
2. Results
IR bands characteristics from LDPE, HDPE and BIO-PE films unexposed to CO2 laser radiation are stretching vibration of carbon-hydrogen bond (CH) of the main chain at 2772–3038 cm⁻¹, the scissoring and bending vibration of methylene (CH₂) and methyl (CH₃) groups, respectively, as an overlapped band at 1440–1490 cm⁻¹, and rocking vibration of methylene (CH₂) groups at 700–750 cm⁻¹ [Socrates]. IR spectra from LDPE, HDPE and BIO-PE exposed to CO2 laser radiation to domestic composting show bands in the carbonyl group region (1715 cm⁻¹), in the hydroxyl group region (3100–3520 cm⁻¹) and in the region of polysaccharides (1088 cm⁻¹) [15], [16].

Carbonyl index was used to measure the oxidation rate from LDPE, HDPE, and BIO-PE films exposed to CO₂ laser and to domestic composting, see Figure 1. LDPE and HDPE carbonyl index exposed to CO₂ laser radiation increase due to free radicals produced during thermodegradation reactions interact with ambient oxygen, nevertheless, BIO-PE films has not significant changes in the carbonyl index on exposure to laser radiation. Carbonyl index of LDPE, HDPE and BIO-PE samples increase and decrease randomly during domestic composting process, due to oxidation rate depends on the microbial activity presented at each composting phase [17], [18].

Vinyl index was used as an indicator of degradation rate of LDPE, HDPE, and BIO-PE samples exposed to CO₂ laser radiation and to the domestic composting, see Figure 2. Vinyl index of LDPE, HDPE and BIO-PE increases with exposure to CO₂ laser radiation due to chain scission is produced by thermodegradation reactions.

Vinyl index from LDPE, HDPE, and BIO-PE vinyl index increases and decreases randomly during domestic composting process; the increase of vinyl index is due to the biodegradation of LDPE, HDPE, and BIO-PE, and the decrease is due to metabolization of double bonds by microorganisms [18]. Vinyl index is higher in BIO-PE than LDPE, and HDPE due to it is a biodegradable polymer.

![Figure 1](image1.png)

**Figure 1.** Carbonyl index of a) LDPE, b) HDPE and c) BIO-PE, exposed to different fluences of CO₂ laser radiation and to domestic composting.

![Figure 2](image2.png)

**Figure 2.** Vinyl index of a) LDPE, b) HDPE and c) BIO-PE, exposed to different fluences of CO₂ laser radiation and to domestic composting.
Biodegradation, oxidation and fermentation of polymeric substances by microorganisms, produces the formation of polysaccharides and hydroxyl group is the polysaccharides characteristic functional group; therefore, the hydroxyl index was used to measure polysaccharides concentration and the rate of LDPE, HDPE, and BIO-PE biodegradation, see Figure 3. The increase of hydroxyl index from LDPE, HDPE, and BIO-PE films exposed to different fluences and domestic composting is an indicative of their biodegradation.

Figure 3. Hydroxyl index of a) LDPE, b) HDPE, and c) BIO-PE exposed to different fluences of CO2 laser radiation and to domestic composting.

3. Conclusions
LDPE, HDPE, and BIO-PE were exposed to CO2 laser radiation in order to increase their degradability and hydrophilicity, through chain scission. Carbonyl and vinyl index from LDPE, HDPE, and BIO-PE films exposed to CO2 laser radiation and domestic composting increase and decrease randomly throughout exposure to the domestic composting due to the microbial activity; the carbonyl and vinyl indexes increase due to films biodegradation and decrease due to the metabolism of the double bonds by microorganisms producing polysaccharides.

LDPE, HDPE, and BIO-PE films exposed and unexposed to CO2 radiation underwent biodegradation during domestic composting. Hydroxyl index in LDPE, HDPE and BIO-PE films exposed and unexposed to CO2 radiation did not show a constant behavior during all the exposure time in the domestic composting, due to the different kind of microorganisms in different phases of the domestic composting; the decrease of the hydroxyl index indicates that LDPE, HDPE, and BIO-PE begin to mineralize into smaller molecules.

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