Research Article

LDPE Oxidation by CO₂ Laser Radiation (10.6 μm)

A. Martínez-Romo, R. González-Mota , J. J. Soto-Bernal, and I. Rosales-Candelas

Instituto Tecnológico de Aguascalientes, Aguascalientes, AGS, Mexico

Correspondence should be addressed to R. González-Mota; rgmota40@gmail.com

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Thermooxidation of LDPE films by CO₂ laser radiation, 10.6 μm, was characterized by Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR). The formation of carbonyl and hydroxyl functional groups onto LDPE films was dependent on the fluency of CO₂ laser. IR absorption of vinyl groups and C-O bond present in alcohols showed a decrease and an increase, respectively, indicating that CO₂ laser radiation causes simultaneous formation and accumulation of hydroperoxides in LDPE films; furthermore, crystallinity of LDPE films irradiated with CO₂ tends to increase. So, CO₂ laser radiation is able to oxidize the LDPE films, obtaining a PE with similar spectroscopic properties to that of PE-BIO by a physical process.

1. Introduction

Polyethylene (PE) is one of the most extensively used thermoplastic polymers [1, 2]; its mechanical properties, electrical insulation, chemical resistance, being odorless and nontoxic, toughness and flexibility, low cost, and easy processability have led to a widespread use in diverse applications [3, 4]. These properties make PE suitable material for use as packaging films, enabling the production of mechanically strong films [5]. These films are usually discarded after only single use and then finally accumulate in a sanitary landfill, due to their low degradability caused by their high molecular weight and the absence of hydrophilic functional groups [6].

Biodegradable polymers may be classified into two groups, those that are intrinsically biodegradable, whose molecular structure allows the action of microorganisms, and those that, after being subjected to aging treatment (UV radiation, heat exposure) or due to the addition of prodegradant additives, like organosoluble transition metal ions, dithiocarbamates, acetylacetonates and ketones, which act as initiators of the degradation process, may undergo a microbiological attack [7–9].

In general, PE is not a biodegradable polymer; therefore, the main strategies to increase their biodegradability are focusing on developing a PE susceptible to hydrolysis reactions, biodegradable PE, PE-BIO, and incorporating oxygen

into the backbone polymer, like carbonyl group (C=O) [10]. Commonly, the incorporation of this chromophore group into the polymer backbone is carried out adding chemical additives, like ester, ketones, or lactones, during the polymerization process [11]. The oxidized polymers change the behavior from hydrophobic to hydrophilic, resulting in the fact that polymers could be metabolized by some microorganisms [12, 13].

In this work, we have studied the oxidation of LDPE when it is irradiated with CO₂ laser radiation (10.6 μm), obtaining an oxidized PE, by a physical process, with similar spectroscopic properties to those of PE-BIO obtained by chemical process.

2. Methodology

2.1. Materials. LDPE and PE-BIO films were obtained from commercial bags samples from different supermarkets in Aguascalientes, Mexico; these bags, used for dry-cleaning, newspapers, bread, frozen foods, fresh produce, and garbage, were made in Mexico and are commercialized in Latin America [14]. The molecular weight and exact composition were commercially confidential, because they were synthesized and manufactured under trademark. 32 samples of LDPE were cut into strips of 40 × 50 mm with a thickness of 0.05 mm.

2.2. Laser Treatment. Laser treatment of LDPE films was carried out with a CO₂ laser model Laser Engraver C120H at wavelength of 10.6 μm with a spot of 3.5 cm. The laser spot was expanded using a zinc selenide (SeZn) mirror and a SeZn meniscus negative lens with a wavelength transmission of 10.6 μm and focal length of -116.16 mm. LDPE films were mounted on racks at 20 cm from the radiation source and irradiated at three fluencies, F , ($\text{W}\cdot\text{s}/\text{cm}^2$): 1050, 2100, and 3050.

2.3. Carbonyl Index (I_{CO}). Structural changes of LDPE films irradiated by CO₂ laser were characterized by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of the films were recorded on a Thermo-Nicolet spectrophotometer model iS10 with attenuated total reflectance (ATR).

The carbonyl index (I_{CO}), used to characterize the oxidation of LDPE, is defined as the ratio of absorbance of the stretching vibration of carbonyl group ($\text{C}=\text{O}$), 1740 cm^{-1} ($A_{(1740)}$), and the absorbance at 1835 cm^{-1} ($A_{(1835)}$), used as reference. Consider the following [15]:

$$I_{\text{CO}} = \frac{(A_{(1740)} - A_{(1835)})}{(0.008 * t)}, \quad (1)$$

where t is the thickness of the LDPE films (mm).

2.4. Hydroxyl Group Index (I_{OH}). The hydroxyl group index (I_{OH}), used to characterize the degree of oxidation of LDPE, is defined as the ratio of absorbance of the stretching vibration of hydroxyl group, 3400 cm^{-1} ($A_{(3400)}$), and the absorbance at 2020 cm^{-1} ($A_{(2020)}$), used as reference. Consider the following:

$$I_{\text{OH}} = \frac{A_{(3400)}}{A_{(2020)}}. \quad (2)$$

3. Results

The infrared, IR, spectra of PE-BIO and LDPE films exposed to CO₂ laser radiation are shown in Figure 1. These spectra show the IR bands characteristics of PE: stretching vibration of carbon-hydrogen group (CH) of the main chain at $2772\text{--}3038\text{ cm}^{-1}$ and wagging and rocking vibration of methylene (CH_2) at $1440\text{--}1490\text{ cm}^{-1}$ and $700\text{--}750\text{ cm}^{-1}$, respectively [16, 17]. The IR spectra of the PE-BIO films without exposure to CO₂ laser radiation show an IR absorption band at 1740 cm^{-1} and stretching vibration of carbonyl group ($\text{C}=\text{O}$), whereas the IR spectrum of the LDPE films shows this band after being exposed to CO₂ laser radiation. IR spectra of PE-BIO show a single peak at $700\text{--}750\text{ cm}^{-1}$ and at $1440\text{--}1490\text{ cm}^{-1}$ because it is a linear polymer, while for LDPE these same bands are bifurcated due to being a branched polymer. See Figures 2(a) and 2(b).

IR band from rocking vibrations of methylene group (CH_2) from LDPE films irradiated with CO₂ laser tends to increase and form a doublet as CO₂ laser fluency increases (see Figure 2(a)), indicating that crystallinity is increasing, because this IR band shows a doublet when it is in crystalline

FIGURE 1: IR spectrum of LDPE and PE-BIO films exposed to CO₂ laser radiation.

phase [16]. These results are in agreement with those reported by Laycock et al., since they reported that crystallinity tends to increase at the early stages of PE photooxidation [18].

IR bands from asymmetric deformation of methyl group (CH_3) from LDPE irradiated with CO₂ laser tend to split and increase the formed shoulder as CO₂ laser fluency increases (see Figure 2(b)), indicating that LDPE irradiated with CO₂ laser radiation undergoes branches scission from polymer backbone, allowing the formation of short and low molecular weight polymer chains leading to a decrease in molecular weight and formation of $\text{C}=\text{O}$ groups. The $\text{C}=\text{O}$ bonds make the polymer surface ready for microorganism's attack [11, 16, 19].

LDPE exposed to CO₂ laser radiation undergoes thermooxidation reactions bringing on oxygen diffusion in polymeric chains of the LDPE films, causing polymer backbone scission, resulting in the formation of smaller molecular fragments. The incorporation of oxygen into the polymer chain results in the formation of functional groups like $\text{C}=\text{O}$ groups. See Figure 3(a). The inclusion of $\text{C}=\text{O}$ groups in the polymeric chain changes their behavior from hydrophobic to hydrophilic behavior [20]. PE-BIO is an oxidized material since its manufacturing, $I_{\text{CO}} = 3.75$, while I_{CO} of LDPE films without exposure to CO₂ laser radiation is 0.12; however, LDPE films exposed to CO₂ laser radiation show similar I_{CO} to that of PE-BIO; therefore, it is possible to oxidize LDPE when it is irradiated with CO₂ laser radiation. See Figures 3(a) and 3(b).

Figure 4(a) shows IR absorption bands of stretching vibration of the hydroxyl group (OH), $3600\text{--}3100\text{ cm}^{-1}$ of LDPE films exposed to CO₂ laser radiation at different fluencies and PE-BIO without exposure to CO₂ laser radiation. These bands tend to get broader and coalesce while increasing CO₂ laser fluency [21], indicating formation of hydroperoxides and OH groups during thermooxidation reactions. IR absorption band from OH groups increased during thermooxidation reactions because there is a disequilibrium in the formation and consumption of hydroperoxides

FIGURE 2

FIGURE 3

throughout the formation of carbonyls, esters, lactones, and ketones groups[22]. Hydroperoxides accumulate in the polymer matrix during thermooxidation reaction of PE, unlike the photooxidation reaction, where they do not accumulate [23–25]. Therefore, CO_2 laser radiation is able to oxidize LDPE films by thermooxidation reactions. Figure 4(b) shows I_{OH} from LDPE and PE-BIO films exposed to CO_2 laser. I_{OH} tends to increase with the increase of CO_2 laser fluency; it should be highlighted that I_{OH} from 2100 and 3151 F is almost the same as I_{OH} of the nonirradiated PE-BIO films.

Grassie and Scott reported that hydroperoxides and vinyl groups initially are present in LDPE films due to the remnants of additives used during polymerization process [26]. In Figure 5(a), IR absorption regions of vinyl groups, $900\text{--}800\text{ cm}^{-1}$, of LDPE films irradiated by CO_2 laser radiation are shown. The decrease in IR absorbance from the out-of-plane deformation vibration of CH_2 of vinylidene groups, $895\text{--}885\text{ cm}^{-1}$, is due to thermooxidation reaction of the LDPE films which causes the decomposition of vinylidene and hydroperoxides groups and the formation of free radicals.

FIGURE 4

FIGURE 5

These free radicals tend to react in presence of CO₂ laser radiation and oxygen forming C=O, C-O and OH. See Figures 3(a), 4(a), and 5(b) [12, 27].

Figure 5(b) shows IR absorption band of C-O groups present in alcohols, 1200–1010 cm⁻¹, of LDPE films irradiated by CO₂ laser radiation. LDPE exposed to CO₂ laser radiation undergoes an increase in this IR absorption band, indicating a simultaneous formation and accumulation of hydroperoxides in LDPE films; these results are consistent with the increase in the carbonyl and hydroxyl groups concentration, Figures 3(a)

and 4(a), respectively. Therefore, this result indicates that the LDPE is susceptible to oxidation when it is irradiated with CO₂ laser radiation.

4. Conclusions

In this work, we have shown that CO₂ laser radiation at 10.6 μm produces thermooxidation reactions onto LDPE, causing the oxidation of the polymer backbone and the formation of smaller molecular fragments. CO₂ laser radiation

induces the formation, accumulation, and decomposition of hydroperoxides groups causing the formation of oxidized groups such as ketones, lactones, and carboxylic acids into LDPE films. The higher degree of oxidation was obtained at a fluency of $1050 \text{ W} \cdot \text{s}/\text{cm}^2$. Therefore, it is possible to oxidize the LDPE when it is exposed to CO_2 laser radiation, obtaining, by physical process, a PE with spectroscopic properties similar to PE-BIO.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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