Thermo-Oxidation and Biodegradation Study of Low-Density Polyethylene /Starch Films by IR Spectroscopy

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ABSTRACT: *This article reports a study of the thermo-oxidation and biodegradation in the soil of low-density polyethylene/starch films (LDPE/starch) by infrared spectroscopy: Films of LDPE/Starch blends of different composition (starch content range from 0 to 15% w/w), were prepared and exposed to thermo-oxidation at different temperatures at 80, 90 and 100°C, and buried in the soil of public dump during 300 days. The oxidation, for films subjected to thermal oxidation, was revealed by the appearance of absorption bands of carbonyl groups centered at 1715 cm^{-1}. After the induction period, which varies from 12 to 14 days according to the concentration of starch incorporated in the films, the indication of carbonyl croup increases with time and temperature of exposition. During the first 30 days, the rate of oxidization is the weaker, the larger percentage of starch in the film of LDPE. The biodegradation of films buried in the soil for 300 days, was followed by infrared spectroscopy. The carbonyl index calculated at 1715 cm^{-1} and at 1744 cm^{-1} showed the oxidation of films LDPE/starch. This index increases with time of burial and starch percentage incorporated into LDPE films during the first 180 days in soil burial, then decreases.*

KEY WORDS: *Low-density Polyethylene (LDPE); Starch; Biodegradation; Thermo-oxidation; Blends.*

INTRODUCTION

The problems of accumulation of plastic wastes in the environment and implementation of legislation on non-final waste have provoked since the last time a growing interest for the biodegradable materials [1, 2]. Much of waste thermoplastics consisted of polyethylene, used extensively in packaging and agricultural application [3-6]. Polyethylene is an inert polymer to chemical and biological attacks. This resistance is mainly related to its hydrophobicity, high molecular weight and its lack of functional groups recognizable by microbial enzymatic systems [7-10]. All of these properties limit applications in which biodegradation is a desirable attribute [10]. The direct incorporation of natural biodegradable polymers, such as starch, to enhance the potential biodegradability of polyethylene has also been evaluated [10-12]. The major degradation effect promoted by the microbial assimilation of the natural polymers in the blends was the increase of the surface area of the synthetic bulk

Table 1: The abbreviation of blends.

Formulations	F0	F1	F2	F4	F7	F9	F12	F15
LDPE Wt%	100	99	98	96	93	91	88	85
Strach Wt%	0	1	2	4	7	9	12	15

material rendering it more susceptible to abiotic oxidation. Hence, this is only an example of indirect oxidative degradation of polyethylene afforded by the biodegradation processes of natural polymers [13].

The study of polymer degradation in natural environments has shown that it occurs in two stages. The first step is abiotic degradation, these processes result in functional macromolecules, which thermally and/or photo-chemically cleave repeatedly to low molecular weight fragments. The second step is biotic, it consists biodegradation by microorganisms of low molecular weight oxygenated products include aliphatic carboxylic acids, alcohols, aldehydes and ketones formed in the first stage of degradation [13–16].

Approximately 50% of the annual word global production of plastics is destined for use as packaging materials and 90% of these materials end-up in municipal burial sites [10]. In these sites the conditions are mainly aerobic with temperatures reaching up to 70 °C for the first few days of burial, falling to about 50 °C after two months [17], thus the thermo-oxidative degradation of plastics is greatly accelerated. Several works have been done on the study of thermo-oxydation films of LDPE and little work on the study of thermo-oxidation mixtures of LDPE /starch. To see if the thermal degradation is followed by biodegradation of the films LDPE/starch, in this study, we compared the evolution-products of oxidation films of LDPE/starch exposed to thermal oxidation at different temperatures (80, 90 and 100 ° C), and the LDPE/starch films subjected to burial in the soil of discharge for a duration time of 300 days. The change of chemical structure of the films was followed by IR spectroscopy.

EXPERIMENTAL SECTION
Materials

The Low-Density Polyethylene (LDPE) used is manufactured by the Basell Company, (Holland), commercialized under the grade name of B24. It has a melt flow index (MFI) of 0.75 g (10 min)$^{-1}$ and a density of 0.923.

Native soluble starch used in this study was supplied by Prolabo Company. It contained 90% amylose, 10% amylopectin. The densities of this starch ranged between 1.514 and 1.520.

Preparation of blend films

The blends were prepared by extrusion on a GUIPPE Crespi extruder (screw diameter: 45 mm and length 20 D). The barrel temperatures were sequentially 150, 160, and 170°C and the screw speed was 50 rpm. They were transformed to films of 0.3 mm thickness by compression molding using a Davenport Hydraulic press at 200 kg/cm^2 and 160°C, the compression was maintained for 03 min. The different samples were coded as indicated in Table 1.

Thermal oxidative-degradation

LDPE/starch films were exposed in an air circulation oven at different temperatures (80, 90 and 100°C) during 60 days. The samples were removed from the oven at regular time intervals for a total incubation time of up to 60 days. After removal from the oven the samples were placed in desiccators until needed for measurements. The oxidized samples were analyzed by infrared spectroscopy.

Sample burial

Samples in a form of thin films (0.3 mm thickness) were buried in the soil of Boulimat public dump (Bejaia-Algeria) at 10 cm depth [18] during 300 days. Individual samples were taken out periodically for examination. Prior before analysis by IR spectroscopy, the films were rinsed with distilled water and then dried at 50°C during 48 hours. The characteristics of the soil are presented in Table 2.

Analysis by Fourier Transform Infrared Spectroscopy (FT-IR)

The infrared spectra of different films were recorded using a Shimadzu FTIR 8001 Spectrometer, in the wave number region 4000-600 cm^{-1}. The spectra were taken as an average of 40 consecutive scans at 4 cm^{-1} resolution.

Table 2: Main characteristics of the soil.

Physical characteristics of the soil used	
Clay	8%
fin silt	3%
Coarse silt	9,6%
fin sand	16,1%
Coarse sand	24,5%
texture	Silty Sand (balanced)
Moisture	10,48%
Chemical characteristics of the soil used	
pH (water)	5.45
pH (KCl)	5.34
Total limestone	4.45%
Active limestone	0%

In the FT-IR spectra, special interest was focused on the carbonyl region. The oxidation degree, i.e. carbonyl index, C I., under the different oxidation conditions were obtained by calculating the carbonyl absorption at 1715 cm^{-1} for LDPE/starch films subjected to thermal oxidation, and at 1715 and 1744 cm^{-1} for the samples submitted to burial in soil.

Relative absorbance intensities of the ester carbonyl band at 1744 cm^{-1}, keto carbonyl band at 1715 cm^{-1}, to that of the methylene band at 1464 cm^{-1} were evaluated using the following formulae [12, 15,16, 19- 22].

$$CI_{1715} = A_{1715}/A_{1464} \qquad (1)$$

Where A_{1715} is the carbonyl absorbance at 1715cm^{-1}, and $A_{1450}$is the reference absorbance band of methylene groups at 1464cm^{-1}).

$$CI_{1744} = A_{1744}/A_{1464} \qquad (2)$$

Where A_{1744} is the carbonyl absorbance at 1744 cm^{-1}

Before exposure, the samples exhibit a low absorption at 1715 cm^{-1} attributed to carbonyl groups formed during the implementation, we noted that A^0_{1715}. The correction of the carbonyl index defined as [15]:

$$CI_{1715} = \left(A_{1715} - A^\circ_{1715}\right)/A_{1464} \qquad (3)$$

RESULTS AND DISCUSSION
Evolution of chemical structure of LDPE/starch blends exposed to thermo-oxidation at different times by FT-IR spectroscopy

Infrared spectroscopy was carried out to study the change of the chemical structure of the films exposed to thermal degradation.

Fig. 1 depicts the FT-IR spectra of some LDPE/Starch blends with 0, 2, 4, 7, 9, and 15wt% starch containing. The only differences observed are in the hydroxyl region, between 3600 and 3100 cm^{-1} [15, 17, 23], where there is an increase in absorbance with increasing starch content. There is also an increase in the 1640 cm^{-1} and between 1190 and 950 cm^{-1} region, attributed, respectively, to protein of starch [24-26] and to C-O bond stretching of Starch [27].

The FT-IR spectra of a pure LDPE (F_0), incubated for various time periods at 80°C, are shown in Fig. 2. It is easily observable that significant changes in the hydroxyl and carbonyl regions. Representative FT-IR spectra of F_0, at different aging times, recorded in the carbonyl (1800-1600 cm^{-1}) and hydroxyl (3600-3100 cm^{-1}) regions are shown in Figs. 3(a) and 3(b), respectively.

In Fig. 3a the appearance of broad absorption band localized at 1715 cm^{-1}, which belongs to mixture of different carbonyls species such as carboxylic acid, ketones, aldehydes, esters and lactones is observed [28,29]. This can be explained by the fact that in the presence of oxygen, free radicals formed as a result of the thermal oxidation reaction are converted to peroxides and hydroxides, and subsequently to carbonyl compounds.

Fig. 3b shows the evolution of the FT-IR spectra of F0 films recorded in the hydroxyl region before and after incubated for different times at 80°C. All spectra of thermal samples exhibit a large absorption band peaking up at 3100 cm^{-1} corresponding to formation of hydroperoxides, alcohols and carboxylic acids [30].

The FT-IR spectra of the LDPE/Starch films, subjected to thermal oxidation at 80°C for 60 days, showing the evolution of the bands in the same regions observed in the spectra of F0 films submitted at 80°C for different times. For the comparison between spectra of F15 films after and before incubation at the thermal oxidation, we are mainly interested in the hydroxyl region (3600-3100 cm^{-1}) and carbonyl region (1800-1600 cm^{-1}).
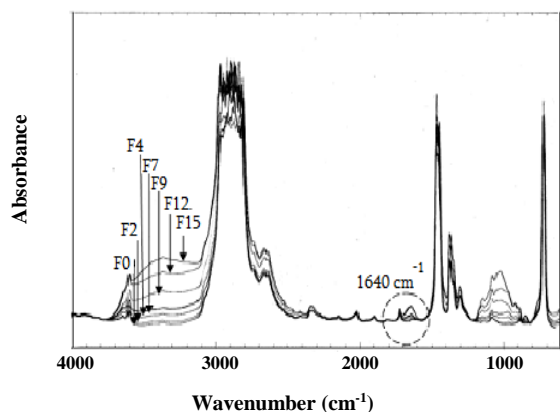
Fig. 1: FT-IR of LDPE/starch, recorded between 4000 and 600 cm⁻¹.
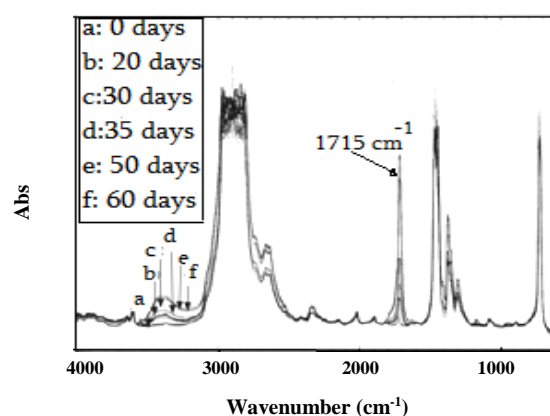

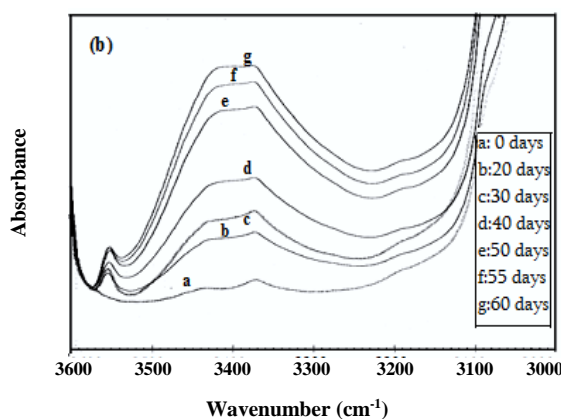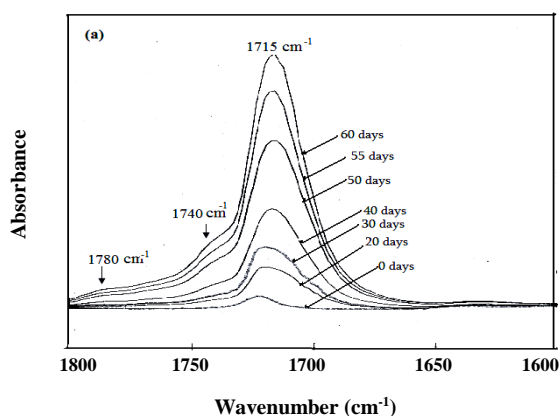*Fig. 2: FT-IR spectra of F0 films for different incubation times at 80°C.*

Fig. 3: FT-IR spectra of F0 films for different incubation times at 80°C. (a): Carbonyl and (b): Hydroxyl regions.

Fig. 4 shows the FT-IR spectra of F15 films before and after 60 days of heating at 80°C, in the hydroxyl region. Were we noted, an increase in absorbance as function of heating times, this is probably due to hydrogen banding between the various groups (hydroxyl, carboxyl, etc).

Moreover, the FT-IR spectra of F15 Samples (Fig. 5) exhibit similar shape of carbonyl band as that observed for the neat LDPE (F0, Fig. 2), this result suggests that the presence of starch does not affect the mechanism of thermo-oxidation of the polymer matrix. The band intensity at 1640cm⁻¹, attributed to the presence of starch in the LDPE films [24-26], decreases as function of heating times. We explain this phenomenon by the disappearance of starch in the blends.

Carbonyl index

The rates of oxidation of LDPE in the different materials submitted at thermal oxidation are followed by determining the Carbonyl Index (CI) at 1715cm⁻¹ (Eq. (3)), and the results obtained are plotted in Fig. 6.

The evolution of carbonyl index follows same kinetic for all formulations, and it can be decrease in oxidation rate of LDPE/Starch blends compared to oxidation rate to neat LDPE (F0), the oxidation rate lower than percentage of starch in LDPE films is larger. Moreover, a higher induction period is noted for the F15 samples. As reported in the literature [31], the induction period is associated to the tendency of material to undergo degradation. Materials with higher induction period are more resistant to degradation. From these results, the F15 has both higher induction period and lower slopes than the other samples. Thus, in first approach it seems that starch actually inhibits the oxidation rate of LDPE; it acts as a rather effective antioxidant.

The evolution of carbonyl index of F0 and F15 films, subjected to thermal oxidation at 80, 90 and 100° C as a
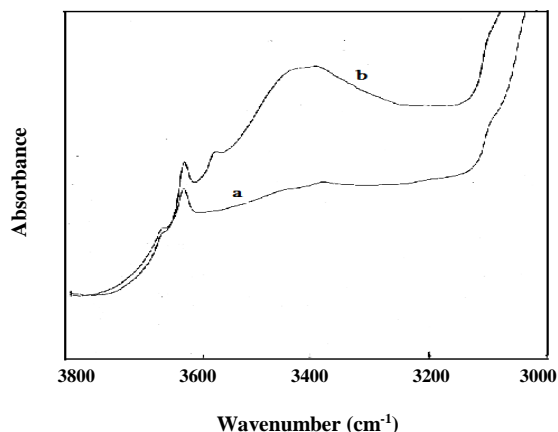
Fig. 4: Hydroxyl region of FT-IR spectra of F15, (a) after, (b) before 60 days of incubation at 80°C.
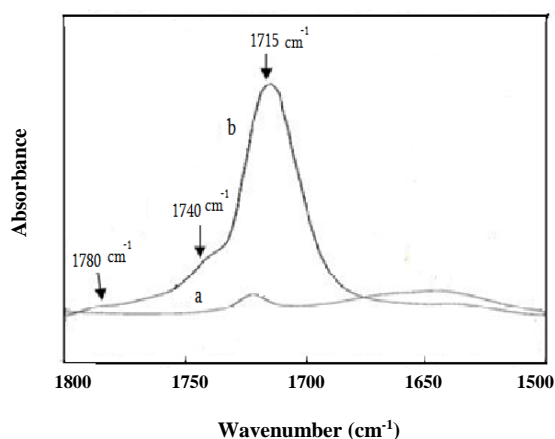

Fig. 6: Evolution of carbonyl index of F0, F4, F7, F9 and F15 films, versus incubation times at 80 ° C.

Fig. 5: FT-IR spectra of theF15film recorded in the carbonyl region(a) reference, (b) before 60 days of incubation at 80 °C.

Fig. 7: Evolution of the index of carbonyl at 1715 cm^{-1} of F0 and F15 Films, depending on the heating time at 80, 90 and 100 ° C.

function of times of exposure, are shown in Fig. 7. It found that rate in the carbonyl index is more important than temperature is larger.

Hydro peroxides are usually major's products of thermo-oxidation. These are highly reactive, interact (cage effect) to give the final products (carbonyl) [12] (Figs. 8, and 9).

Evolution of chemical structure of LDPE/starch films subjected to burial in soil for 300 days by IR spectroscopy

Structural changes, such as an oxidation level of LDPE/starch blends due to biological treatment, can be accurately detected by IR spectroscopy.

The comparison between the FT-IR spectrum of F15 films before and after 180 days of burial in the soil (Fig. 10),
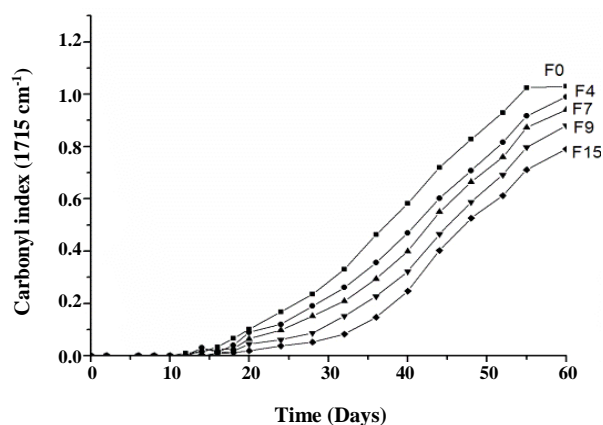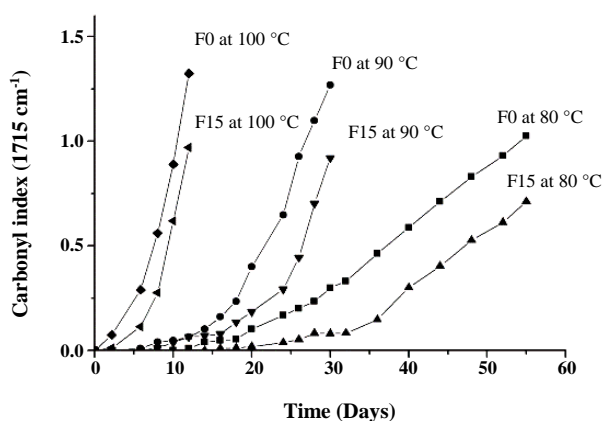
shown the decrease in intensity of the broad band between 3600 -3100 cm^{-1} attributed to the stretching vibration of hydroxy groups from the starch [15] and bands between 1190 and 950 cm^{-1} assigned to the C-O bonds of starch. This may be due to the consumption of the starch by various microorganisms of the soil. However, the decreases of these bands, can be compensated by the presence of hydro-peroxides on LDPE chains due to abiotic and / or biotic oxidation of LDPE / starch blends films buried.

Fig. 11 present, as examples, the FT-IR spectra, recorded in the carbonyl region 1800-1600 cm^{-1} of F15 films at 0, 120, 180 and 300 days of soil burial. It is observed a gradual increase in intensity of absorption band of the carbonyl at 1715 cm^{-1}, during the first months
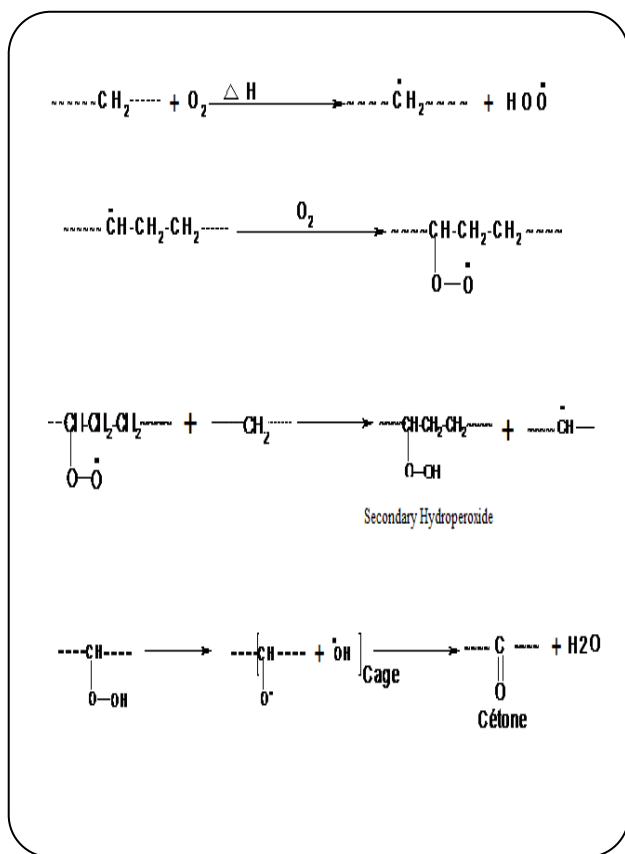
Fig. 8: Decomposition mechanism of hydro peroxides to ketones [32].

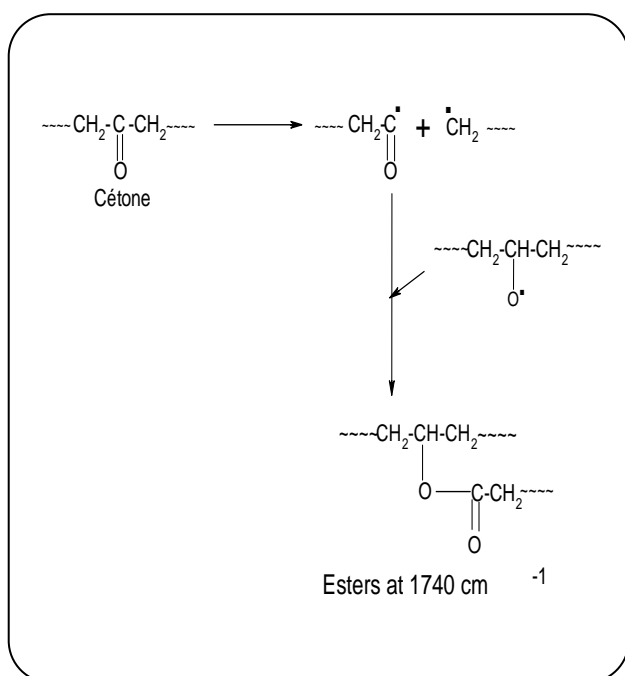**Fig. 9: Abiotic conversion mechanism of ketones to esters [12].**

of burial, with the formation of an absorption band located at 1744 cm^{-1}, attributed to the carbonyl ester group, and a shoulder at 1700 cm^{-1} after 120 days of burial. This shoulder, located at 1700 cm^{-1}, attributed to carboxylic acid.

If we compare the FTIR spectra, recorded in the carbonyl region of F15 Films subjected to thermal oxidation (Fig. 5) and those of the F15 films submitted to soil burial (Fig. 11) we see that does not follow the same oxidation mechanism. In addition the amount of ester formed for films submitted to the burial is larger than that of the films subjected to thermal oxidation. This may indicate that the presence of esters is not only due to abiotic oxidation but may be due also to the biotic oxidation of polyethylene fragments according to the mechanism of biodegradation proposed by Schlegel [33] for hexadecane (C$_{16}$H$_{34}$).

To obtain quantitative information of the structural modification of the LDPE/starch blends films after burial in the soil, the carbonyl index was estimate. Figs. 12 and 13 show the carbonyl index at 1715 and at 1744 cm^{-1}, respectively, of the LDPE/starch blends films at different times of soil burial.

After an induction period (15 to 20 days), the carbonyl index at 1715 cm^{-1} of the LDPE / starch blends films subjected to soil burial, increases rapidly and linearly during the first180 days of burial, beyond which a slowdown of rate carbonyl index is observed for the blends that contain a quantity of starch less than 9%. The carbonyl index of degradation F12 and F15 samples, decreased after 180 days burial in the soil. However, the increase in the index at 1715 cm^{-1}during the180 days of burial is more important than percentage of starch into the blends (LDPE/Starch) is higher. The same evolution is observed for the carbonyl index at 1744cm^{-1}. The F0 samples have a lower evolution of carbonyl index at 1715cm^{-1}. However, the carbonyl index of F0 films increases gradually during soil burial.

Indeed, the consumption of the starch incorporated into the LDPE films, by the various microorganisms of the soil, requires reduction of molecular weight of the LDPE matrix (fragments) and increases introduction of the oxidized groups into the chain [5]. Of this fact the oxidation of LDPE/starch blends films, during the first times burial is much more important than the quantity of starch incorporated into the LDPE film is large.
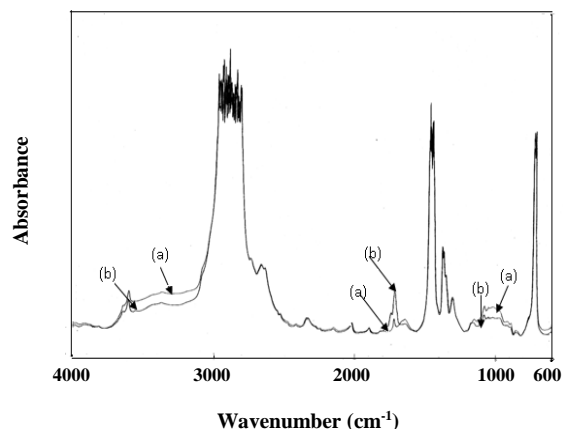
Fig. 10: FTIR spectra of F15 films, (a) before, (b) after 180 days of burial in soil.
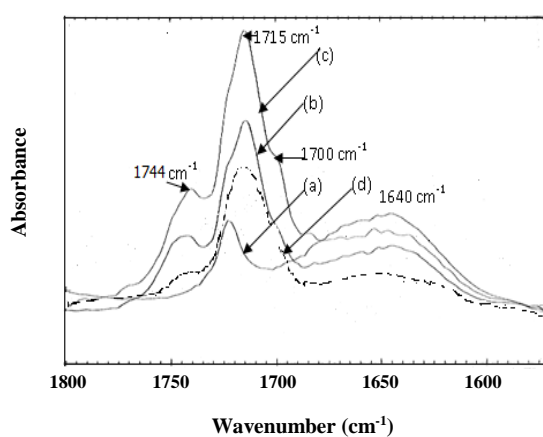

Fig. 12: Evolution of the carbonyl index at 1715cm⁻¹, as a function of burial times.

Fig. 11: FTIR spectra of F15 film recorded in the carbonyl region between 1800 and 1600 cm⁻¹, a): 0 days, b) 120 days c) 180 days and d) 300 days of burial in the soil.
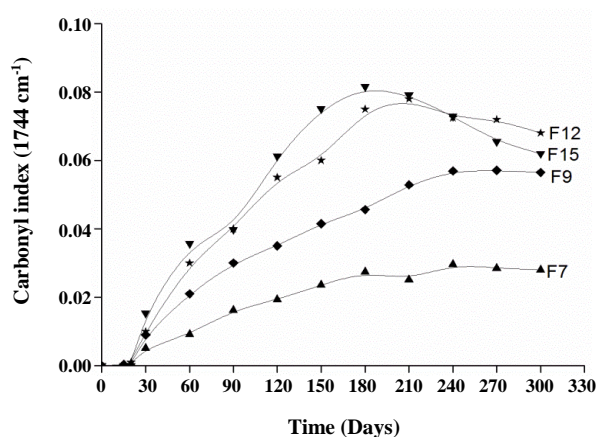
Fig. 13: Evolution of the carbonyl index at 1744 cm⁻¹, as a function of burial times.

Beyond 180 days of burial, the carbonyl index decreases gradually as a function of times of burial from F12 and F15 simples. Biotic reduction of the carbonyls groups abioticaly introduced to the LDPE was previously reported [34, 35]. *Weiland & Daro* [36] observed a reduction in the carbonyl group concentration after 150 days of incubation the LDPE thermallytreated with a mixed fungal culture. Analogously, this phenomenon has already been observed by *Hasan* [34] and *Sahebnazar* [35] for LDPE films exposed to UV radiation then soil incubation in the presence of Aspergillus terreus and Aspergillus fungatus, indicating that the microorganisms use the carbonyl group of LDPE abiotic oxidation products for degradation LDPE films [16].
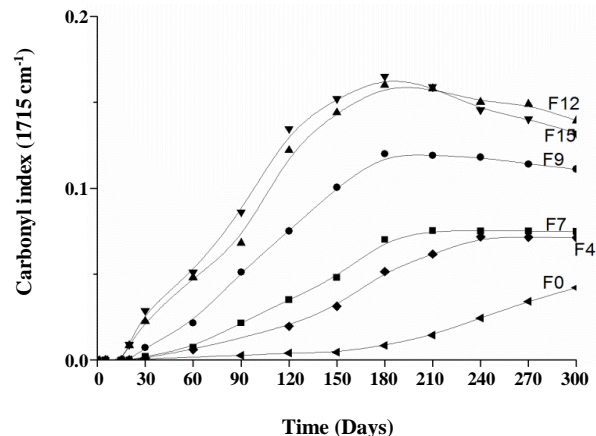
In the biodegradation of polyethylene, the first step is abiotic degradation implies the photo-oxidation and/or thermo-oxidation [13-16]. This degradation leads to formation of low molecular weight fragments and thus increases the hydrophilicity of the polymer, by consequence, the susceptibility of the polymer to microbes increases. Indeed, the resulting carboxylic acid from the oxidation abiotic of long chain hydrocarbons (similar to the biotic degradation of paraffin $-C_{10}H_{20}$ [12, 33]) undergoes β.oxidation which, by reaction with coenzyme A (CoA), removes two carbon fragments from the carboxylic molecule. The tow carbon fragments, acetyl-ScoA, enter the citric acid cycle and get completely converted into carbon dioxide and water (Fig. 14).
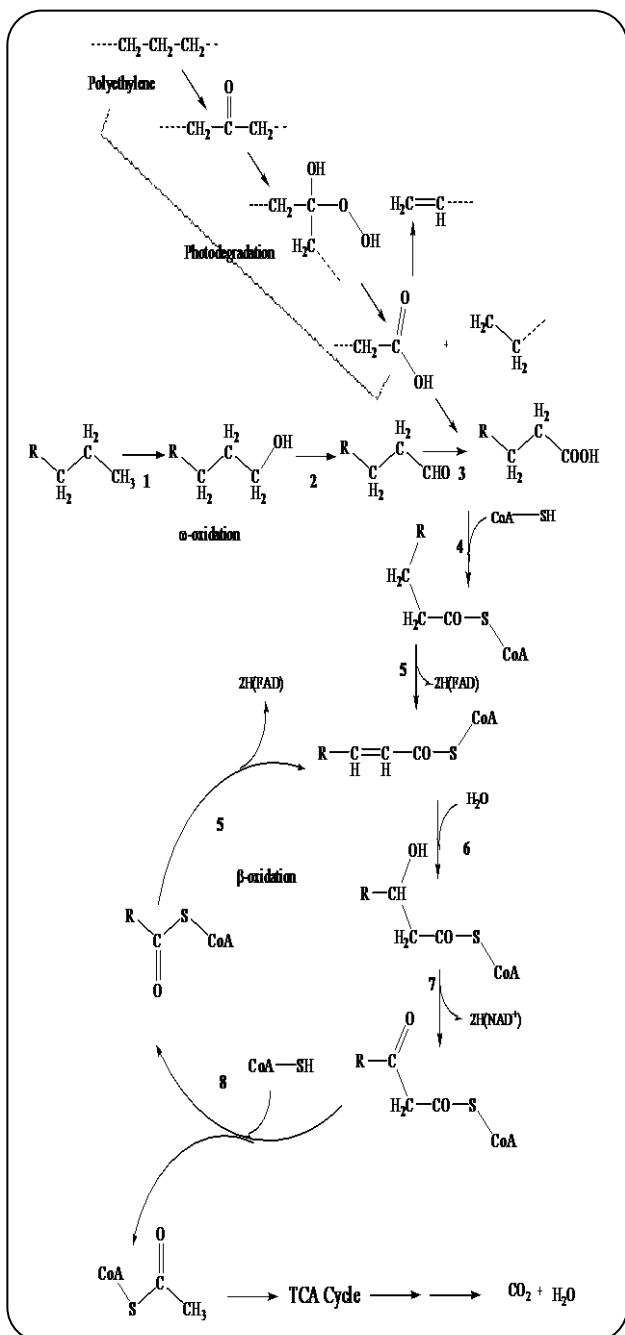
Fig.14: Mechanism of biodegradation of polyethylene [37].

CONCLUSIONS

In the present study, the effect that starch has upon thermal and biological degradation of low density polyethylene films was studied using IR spectroscopy.

The measurement confirms that starch inhibits the thermo oxidative degradation of LDPE. A possible explanation is that this behavior is due to presence of various leftovers which remain in starch after its extraction from

natural resources [17]. Since native starch is usually extracted from plants, it also contains a plentitude of additives (proteins, phospholopides, phosphoric...etc) [6]. Some these additives may act as radical blocking.

The analysis by infrared spectroscopy shows a change in the structure of LDPE/starch blends films after burial in the soil, which is indicated by the decrease in the intensity of the bands located at 3600-3100 cm^{-1} and at 1190-950 cm^{-1}, due to the consumption of starch by the microorganisms. Abroad band in the carbonyl region between 1800-1600 cm^{-1}, the intensity this band increases with times, and the quantity of starch included in the LDPE films during the first month of incubation in the soil. This shows that the consumption of starch by the microorganisms is accompanied by oxidation of LDPE films. After 180 days burial, the carbonyl index, of blends witch a quantity of starch superior to 12 Wt% decreases. The reduction of carbonyl after a burial indicates the use of oxidation products of LDPE by the microorganisms for degrading LDPE films.

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