

# IR Spectroscopy and Scanning Electron Microscopy Studies of Natural Ageing of Polypropylene

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**Abstract-** In the present work we are concerned in the study by IR Spectroscopy and Scanning Electron Microscopy of the effect of solar radiation in two different regions on the natural ageing of the polypropylene (PP). The first region of Mohammedia and the second region of Talsint-Figug. The analysis showed a marked degradation of the surface, which is mainly caused by the contamination of the superficial structure by oxygen. This study was conducted with the aid of three samples of PP: the first was new, the second sample (M) old was exposed about four months the region of Mohammedia; and third, sample (t) old was exposed four about months the region of Talsint-Figug. Spectral analysis indicates that, for new sample, oxygen establishes single bonds with carbon. However, through the ageing process, spectral changes essentially occur in the regions of  $-3400$ ,  $-1712$ , and  $1170\text{ cm}^{-1}$  which correspond to hydroxyl and/or hydrogen peroxide groups, a carbonyl group, and C—O. The examin of the bands corresponding to a carbonyl group reveals the presence of a complicated mixture of oxidation products: aldehydes, ketones, esters, acids, peresters, and peracids. Spectral analysis also shows that the most favorable site for oxidation is at the methylene group. This result is a consequence of the increase of the reactivity of the reactions of oxidation which brings a breaking of the macromolecular skeleton of the formation of peroxide of under products which might act as catalysts of degradation.

**Key words:** Polymer, Polypropylene, Ageing, Oxidation, FTIR, SEM

## I. INTRODUCTION

The ageing of a polymer is shown by a slow, often irreversible deterioration of the properties of the material as a result of its own instability under the effect of the environment [1]. The polymer used in this study is the polypropylene (PP) in the form of low-thickness films (0.06mm). Polypropylene (PP) is a linear polyolefin having the formula  $(C_3H_6)_n$ , obtained by Ziegler-Natta polymerization or by polymerization catalyzed by a metallocene. There are a wide variety of properties and behavior of the PP depending on the chemical nature of its formulation and shaping conditions[2]. This polymer has been used in various applications for human life because of its low density, excellent thermal and mechanical properties and good process ability with its appropriate price[3]. Unfortunately, polymers (polyolefins) are subject to natural (outdoor) weathering; the latter giving rise to

degradation effects. Weathering is particularly severe for organic materials, because it combines the photophysical and photochemical effects of ultraviolet (UV) radiation, with the oxidative effects of the atmospheric oxygen and hydrolytic effects of water [4]. Weathering is commonly defined as the undesirable change produced by outdoor exposure [4]. In this paper, we have studied and compared the effect of aging on three samples of PP, including a new taken as reference; and other naturally aged in two different regions. In this regard, we have followed the evolution of the composition of the surface of PP samples under natural aging (in particular UV light of the sun) using ATR-FTIR spectroscopy. As photo-degradation occurs mainly in thin polymer samples of surface layers, reasonable experimental methods are commonly used to study changes in the surface structure (decomposition and formation of chemical bonds), such as attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), which is one of the most widely used non-destructive techniques in the polymers for the characterization of polymer industry.

In the present article, we present results obtained by means of IR Spectroscopy and Scanning Electron Microscopy. The study was undertaken on three samples: first, a new sample (N) taken as reference; the second sample (M) old was exposed about four months the region of Mohammedia; and third, sample (t) old was exposed about four months the region of Talsint-Figug.

## II. EXPERIMENTAL

### A. Materials

The study focused on three films of PP, thin (0.06) intended to be used as pockets and whose use is commonly answered. This is the PP, manufactured in France and marketed by Cambridge, numéro208873 reference. The samples were analyzed by ATR-FTIR Spectroscopy and Scanning Electron Microscopy.

### B. Natural ageing exposure

The two kinds of samples (PP (M) and PP (T)) were exposed to natural weathering (days and nights) for four months during the period from July to October. Natural ageing of these samples was carried out at the roof of a building in Mohammedia city and in Talsint Figug city,

Morocco. The support sample is inclined  $45^\circ$  from the horizontal and oriented towards the south in accordance with the norm (NF T51-165).

### C. Spectral analyses

#### a. IR Infrared Spectroscopy

ATR-FTIR spectra were recorded on citya Magna-IR 560 using ZnSe crystal. The spectra were recorded in the 400-4000  $\text{cm}^{-1}$  range, with a resolution of 4  $\text{cm}^{-1}$  and scan number of 400. All spectra were taken in logarithmic absorbance mode. Experiments are performed applying the ATR equipment with the FTIR spectrometer. The sample surface exposed to photo-oxidative conditions has been in contact with crystal. Indeed, ATR-FTIR spectroscopy is well known as a surface characterization and depth profiling technique. The advantage of ATR is the possibility of obtaining the spectra directly from the sheet without any further sample preparation. ATR is a very sensitive technique and is especially suitable for surface analysis. The utmost care should be taken in sample manipulation to avoid contamination.

The spectral bands of the investigated functional groups of the polymer were normalized with respect to a reference band and internal standard. Obviously, the reference band was present in three samples of polypropylene and its intensity and wavelength did not change upon the ageing time. The band characteristic of methylene groups (1378  $\text{cm}^{-1}$ ) was accepted as the reference band [5- 6- 7].

#### b. Scanning Electron Microscopy

Scanning Electron Microscopy is a technique of electron microscope capable of producing high resolution images of the surface of a sample by using the principle of electron-matter interactions.

The observation of the samples in cutting or in surface was realized on a device of method ESEM with a gas pressure in the room being able to go until 26 m bar. It is also the only allowing microscope to work in three methods of different emptiness: high vacuum (10-6 m bar), low vacuum (0,1 – 1,33 m bar), and environmental (1,33 – 26 m bar). And for each of these methods a detector of the secondary electrons that furnishes non-drivers without any preparation, it allows also to observe in a manner dynamic of the materials under a given environment (pressure, temperature, gas composition). It remains topographic on the sample. The method ESEM eliminates totally the effects of loads and allows the observation of samples non-drivers without any preparation, it allows also to observe in a manner dynamic of the materials under a given environment (pressure, temperature, gas composition). Equipped with a complete system of microanalyses X (detector edx-edax) and of a detector of the electrons retro diffused, it allows giving the chemical composition of his sample with a detection limit up to Bore [8].

## III. RESULTS AND DISCUSSION

### A. IR Infrared Spectroscopy

The IR Spectrum of the new PP sample is shown in Fig.1. It consists of the characteristic bands of PP [9]: a Broad and intense band That extends from 2860 to 3000  $\text{cm}^{-1}$  is attributed to the valence vibrations of the C–H bonds, a bands located at 1450  $\text{cm}^{-1}$  is characteristic of methylene –CH<sub>2</sub> Group, and a band at around 1377  $\text{cm}^{-1}$  is attributed to the methylene CH<sub>3</sub> group. There are two other types of bands present: C–C vibrations are found in the lower frequency region (from 700 to 1200  $\text{cm}^{-1}$ ), and another band of intensity comparable to the former, which characterizes dialkyl ether bonds, C–O–C [10], is found at 1168  $\text{cm}^{-1}$ . Note also the emergence of a very low intensity band at 1646  $\text{cm}^{-1}$  that corresponds to C=C bonds [12], as well as the existence of another band, also of very weak intensity, in the region of 3114 to 3255  $\text{cm}^{-1}$  that is attributed to the valence vibrations of an alkane C–H bond. The absence of a band at 1700  $\text{cm}^{-1}$  relating to the carbonyl, shows that the oxygen in the reference sample sets only single bonds with carbon.

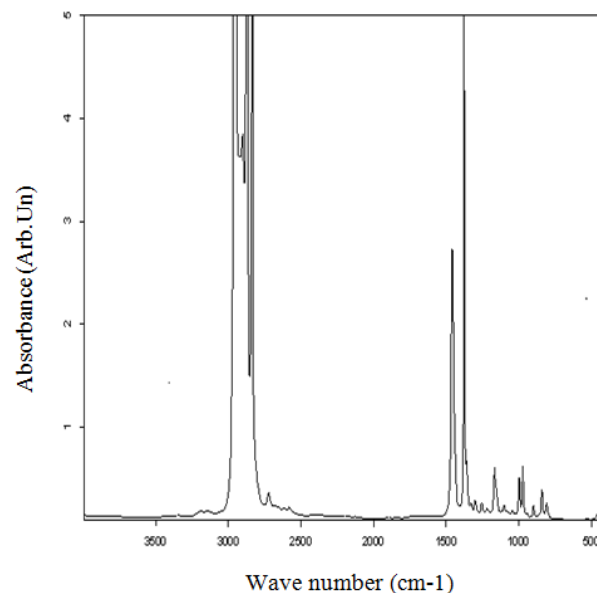


Fig.1 IR survey spectra of the new polypropylene sample

Fig.2 shows the spectrum of the old sample (M), about four months the region Mohammedia. In addition to the characteristic bands next to the bands corresponding to the PP bonds (C–H, CH<sub>2</sub>, CH<sub>3</sub>) [11], the Spectrum reveals the existence of a new band centered at 1712  $\text{cm}^{-1}$  that corresponds to a carbonyl bond C=O [12-13]. Also, another new band between 3100 and 3500  $\text{cm}^{-1}$  is attributed to a hydroxyl bond and/or a hydro peroxide bond [14-15]. The third band in very low intensity to 1646  $\text{cm}^{-1}$  corresponding to the C = C bond [16] which relates to groups located at the end of the polymer. Note the significantly increased intensity of the band located at 1168  $\text{cm}^{-1}$ , which characterizes the C-O bond, the decreased intensity of the band, corresponding to methylene –CH<sub>2</sub>– groups.

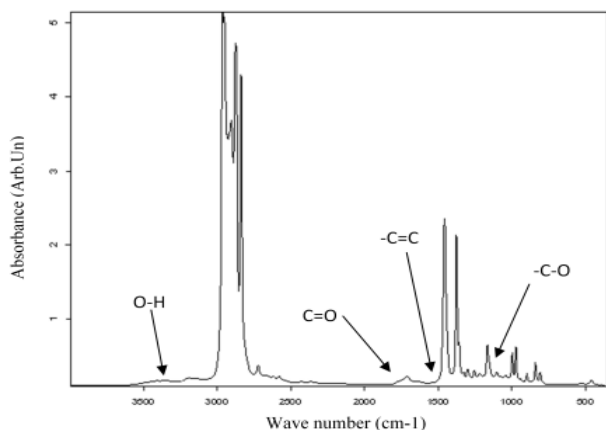


Fig. 2 IR survey spectra of the polypropylene sample (M) aged exposed about four months the region of Mohammadia

Fig.3 is the IR Spectrum of the old sample (T), about four months the region Talsint-Figug It shows an important increase of the bands attributed to C=O, C-O, and OH bands.

The changes that affect the three spectra of the corresponding PP samples essentially refer to these regions:  $3400$ ,  $1712$ , and  $1170$   $\text{cm}^{-1}$ . These regions respectively show the contributions from the alcohol and/or hydro peroxide groups, the carbonyl group (C=O), and OH bonds and a remarkable increase in the band at  $1646$   $\text{cm}^{-1}$  corresponding to the C = C bond [14]. Note also the increased intensity of the band at  $1166$   $\text{cm}^{-1}$ , characteristic of the ether bond CO [14].

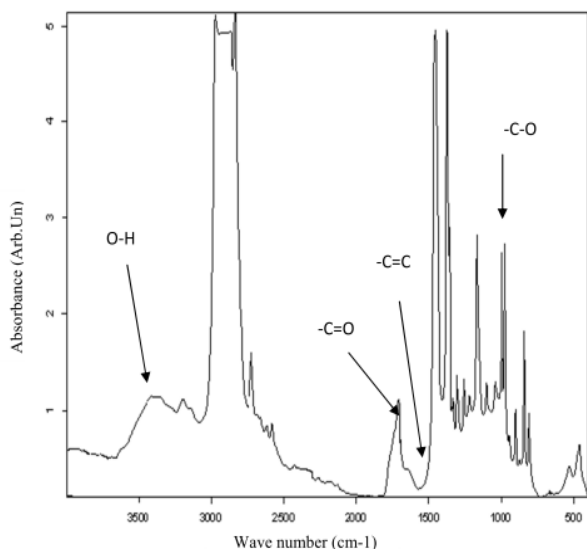


Fig. 3 IR survey spectra of the polypropylene sample aged exposed about four months the region of Talsint-Figug

The spectral changes between the three samples of PP occur mainly in the  $3400$   $\text{cm}^{-1}$ ,  $1700$   $\text{cm}^{-1}$ ,  $1646$   $\text{cm}^{-1}$  and  $1166$   $\text{cm}^{-1}$  respectively assigned to alcohol and / or hydroperoxide, carbonyl, ether and the alkene function. When studying the aging of PP, usually two regions of the IR spectra are examined: the hydroxyl region and / or hydroperoxides (POOH) and regions carbonyl (C = O) [15-16], we will focus especially in the second region, designated in the literature by the index of aging [16].

The superposition of the region located between  $1900$  and  $1600$   $\text{cm}^{-1}$  for the spectra of all These samples (Fig.5) shows in particular that the carbonyl group is absent from the spectrum for the new PP sample while the second sample offers a very significant C=O feature, which is even more remarkable for the third sample (aged about four months the region Talsint-Figug).

Whereas for the sample (M) and sample (T), the convolution shows the presence of a broad band centered at  $1712$   $\text{cm}^{-1}$  with two shoulders at  $1735$  and  $1780$   $\text{cm}^{-1}$  band to  $1712$   $\text{cm}^{-1}$  corresponds to an acid carboxylic acid in dimer form [14] or to a ketone. In a similar study [16], the comparison with the XPS spectra indicated that this band can be attributed largely to ketones [14]. The first shoulder at  $1935$   $\text{cm}^{-1}$  corresponds to a free acid and / or ester the second shoulder at  $1780$   $\text{cm}^{-1}$  corresponds to a peracid function and / or function perester or even  $\gamma$ -perlactone.

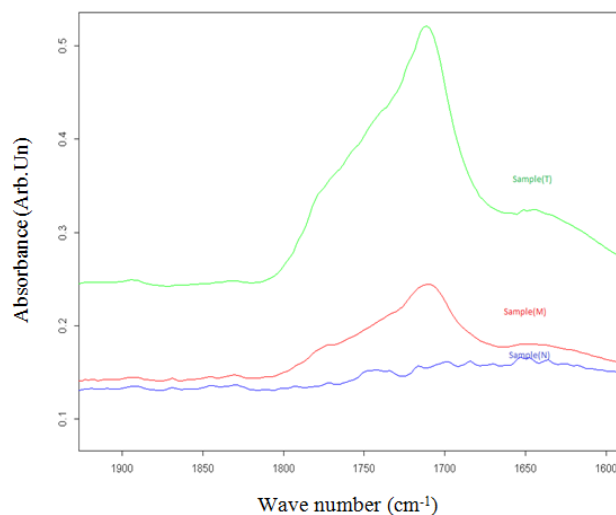


Fig. 4 IR spectra from CO groups' characteristic region for (a) a non treated polypropylene sample, (b) aged exposed about four months the region of Mohammadia, (c) aged exposed about four months the region of Talsint-Figug

In addition to the characteristic bands corresponding to the main groups found in the material ( $-\text{CH}$ ,  $-\text{CH}_2$ ,  $-\text{CH}_3$ ), the IR spectrum of the new PP sample also contains a band related to an ether's C-O bond.

The method proposed by Luongo[12].was used to determine the nature of the configuration of the chains forming the samples. This method is based on the characteristic absorption bands and those specific to the isotactic and atactic phases, its vantagead is that it is independent of the physical nature of the samples and the molecular mass distribution and it is also unaffected by minor constituents such as stabilizers. For mor information on the spectral differences characterizing the PP samples called 100% isotactic and 100 atactic, the reader may refer to Luongo[13].The IR spectrum of the new sample(Fig.1) closely resemble that of the 100% isotactic, in particular, the two bands at  $974$  and  $975$   $\text{cm}^{-1}$  have almost the same intensity(although these two bands show up in our instrument at  $972$  and  $997$   $\text{cm}^{-1}$ , they are essentially the same) and the band at  $1168$   $\text{cm}^{-1}$  with a shoulder at  $1554$   $\text{cm}^{-1}$

<sup>1</sup> is also similar to the bands found on the 100% isotactic spectrum.

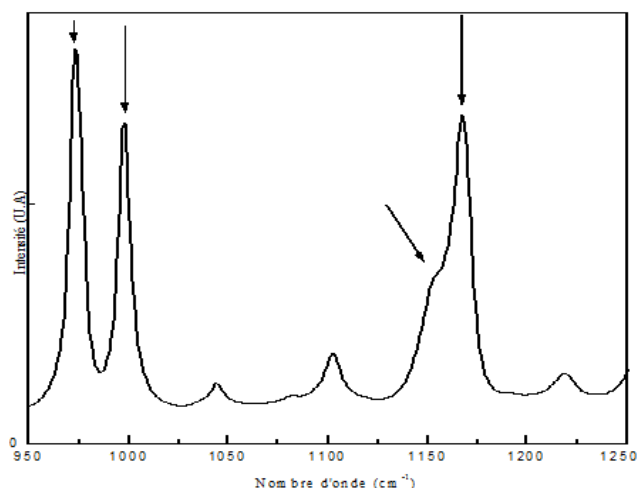


Fig.5 Determining the configuration of the PP by the method of Luongo

The fixation of oxygen on the polymer is caused by photooxidation reactions [14]. PP is susceptible to oxidation by several methods: heating, radiation, UV, and so forth [15-16]. Because the formation of carbonyl group is always significant, certain authors follow the evolution of the carbonyl group as a function of exposure time [17-18]. In this study the interest was on the nature of carbonyl-containing compounds. It looks as though the disappearance of the component located at  $1700\text{cm}^{-1}$  is caused by one of the following conjugation between the ketone group and the  $\text{C}=\text{C}$ , especially because this latter band is observed at  $1637\text{cm}^{-1}$  for the old sample (M), about four months the region Mohammedia and is seen at  $1640\text{cm}^{-1}$  on the Spectrum of the old sample (T), about four months the region Talsint-Figug. Second, the loss of the carboxylic acid existing as a dimer [17]. Displaces ketones [13]. By  $10\text{-}20\text{cm}^{-1}$  and consequently would force the component appearing at  $1700\text{cm}^{-1}$  to add to the component found at  $1710\text{cm}^{-1}$ . The concentration of the numerous oxidation products, other than for hydroperoxides and alcohols, are ordered according to the following decreasing order: carboxylic acids > ketones > esters > peracids, peresters > alkenes. These results are in agreement with those obtained by other authors who used chemical reactions to attain this goal [14-15-16].

The intensity of the band centered at  $842\text{cm}^{-1}$ , which is attributed to the  $\text{C}-\text{C}$  vibration, is merely affected by the aging phenomenon and hence it can be used as a reference band to normalize the carbonyl absorption band and to compare the aged sample [14]. On the contrary, the intensity of the methylene group shows an interesting alteration during oxidation. Actually, as the intensity of the methylene decreases, that of the carbonyl increases, thus confirming that the oxidative attack preferentially occurs on the methylene group.

Henceforth, IR spectroscopy allowed us to clearly determine the site of oxidative attack, as corroborated by our XPS results [12]. It permitted the detection of oxygen in the new sample, even though it was present in trace amounts. It also aided in visualizing the increasing degree

of oxidation (Fig.4). However, the closeness of the absorption bands in the complicated mixture of aldehydes, ketones, esters, acids, peresters, and peracids, along with the difficulties of differentiating between hydroperoxides and alcohols, rendered the qualitative analyses more difficult.

#### a. Degree of crystallinity

The infrared spectrums permitted us to calculate, in a quantitative manner, rate of crystallinity  $X_C$  of different samples starting from two specific picks of  $997$  and  $970\text{cm}^{-1}$ . The pick  $917\text{cm}^{-1}$  was taken as reference [15-16].

$$X_C = \left( \frac{109 \times (\mathcal{A}_{997\text{cm}^{-1}} - \mathcal{A}_{917\text{cm}^{-1}})}{\mathcal{A}_{972\text{cm}^{-1}} - \mathcal{A}_{917\text{cm}^{-1}}} - 31.4 \right) \times 100$$

#### b. Density

To calculate the density in function of the rate of crystallinity, we often use the following equation.

$$X_C = 100 \times (d - d_A) / (d_C - d_A)$$

We have the density of the samples  $\rho_a$  and  $\rho_c$  which are respectively the densities of PP of amorphous and crystalline phases. Different values of  $\rho_a$  are stated in the literature [14-16]. We took  $d_A = 0.850\text{g/cm}^3$  [14] and  $d_C = 0.936\text{g/cm}^3$  [14-15] We have taken the following.

Table-1 presents the density and rate of the crystallinity of three samples

(N, M and T)		
Samples	$X_C$ %	$d$ ( $\text{g/cm}^3$ )
Sample (N)	45,27	0,8889
Sample (M)	56,67	0,8987
Sample (T)	71,74	0,9116

According to the following picture observe us an increase of the rate of crystallinity and densities of the samples age this is hard to the replacement of the liaisons  $\text{C}-\text{H}$  by the liaisons  $\text{C}=\text{O}$  in the shapeless region [17].

#### B. Scanning Electron Microscopy

The results obtained by SEM micrograph have shown a difference between the morphology of its samples.

We remark that the micrograph of the sample (N), the surface is observed without cracks and with some white stains due to the existence of some vacuums from the liberation of gas during the treatment. But for the micrograph of the sample (M), the white stains were bigger with some equivalent cracks with appearance of oxygen in chemical composition of the sample which indicates the formation of some products of oxidation. The something was observed in the micrograph of the sample (T).

The surface showed some deeper and more numerous cracks than those observed in the sample (M), equivalency to the increase of the percentage of oxygen in their chemical composition, This result is a of the increase of the reactivity of the reactions of oxidation which brings a breaking of the macromolecular skeleton of the formation of peroxide of other products which might act as catalysts of degradation. We also observe the appearance of some metals like Mg, Al, Si, and K with different percentage. This is explained by the

existence of dust, polluted air because of the existence of cement – producing factory in that region (Talsint-Figug). These results show accordingly with that the sample(M) and sample(T) undergo a remarkable degradation regarding the climate factors of each region (O, UV, humidity.....) which confirms the results of infrared [18].

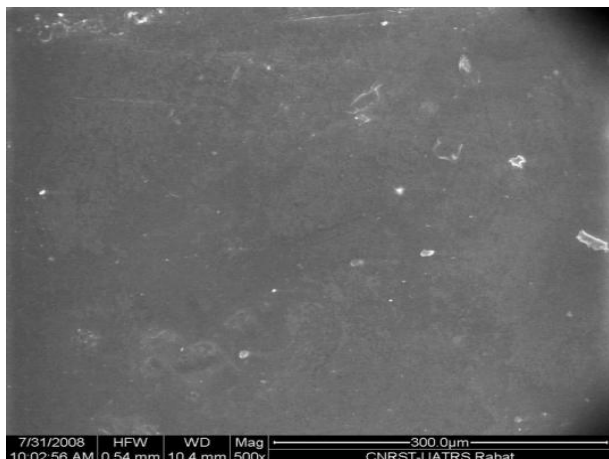


Fig.6 Scanning electron microscopy micrographs of polypropylene sample (N) new

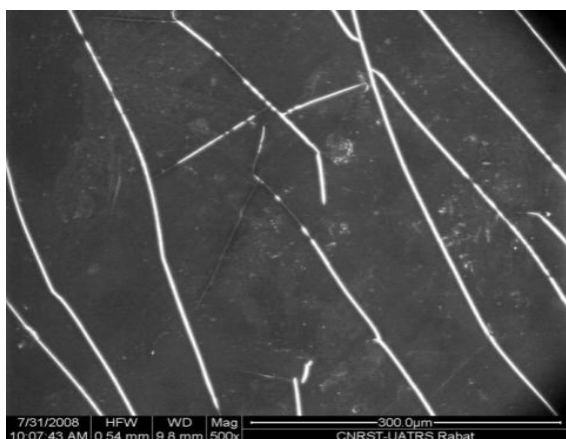


Fig.7 Scanning electron microscopy micrographs of polypropylene sample (M) aged exposed about four the region of Mouhammadia

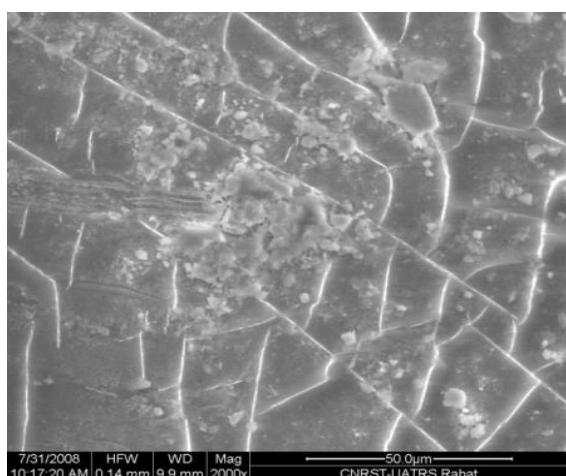


Fig.8 Scanning electron microscopy micrographs of polypropylene sample (T) aged exposed about four months the region of Talsint-Figug.

#### CONCLUSION

IR Spectroscopy and Scanning Electron Microscopy (SEM) were used to study aging natural PP.

The data obtained via IR Spectroscopy and Scanning Electron Microscopy was useful in determining the structural modifications brought about by aging of commercial PP samples. Indeed, three types of PP samples were analyzed: the first sample was absolutely new, the second had been exposed about four months the region of Mohammedia, while the third was exposed about four months the region of Talsint-Figug. The IR spectrum and Scanning Electron Microscopy of the new sample (N) (Fig.1, Mic.6) reveals the presence of oxygen, which is incorporated into the polymeric chain via single chemical bonds, and indicates that the commercial sample is isotactic. The IR spectrum and Scanning Electron Microscopy of the second sample (M) old was exposed about four months the region of Mohammedia, (fig. 2, Mic.7), the spectrum shows the presence of a carbonyl group. The examining of this peak indicates the presence of a complicated mixture of oxidation products: conjugated ketenes, aldehydes, esters, acids (carboxylic acids can exist as stable dimers, which absorb at  $1710\text{cm}^{-1}$ , or as free acids [18], which absorb at  $1755\text{cm}^{-1}$ ), peresters, and peracids. The decreased intensity of methylene confirms that it is the favourable oxidation site. The IR spectrum and Scanning Electron Microscopy of third sample (T) aged exposed about four months the region of Talsint-Figug (Fig3, Mic.8). However, the intensity of the carbonyl group is greater for the third sample, and the examining of this band shows the absence of the conjugated ketene. Also, the intensity of the numerous oxidation products is increased. These results show accordingly with that the sample (M) and sample (T) undergo a remarkable degradation regarding the climate factors of each region (O, UV, humidity.....).

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