

Photo- and thermal oxidation of polyethylene: comparison of mechanisms and
influence of unsaturation content

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Abstract

The behaviour of polyethylene with different contents in vinyl and t-vinylene groups have been studied by photooxidation with $\lambda > 300$ nm light or by thermooxidation at a temperature of 100 °C. The oxidation was studied by infrared spectroscopy and it was shown that the same oxidation products were obtained, but with different relative concentrations depending on the conditions of ageing, i.e. photochemical or thermal conditions. The mechanisms by which the oxidation products are formed were recalled. The differences between photo- and thermooxidation were evidenced on the basis of the stability of ketones that do not accumulate in photochemical conditions, as a result of Norrish reactions. The influence of the initial amount of unsaturated groups on the rates of oxidation was characterized. It was shown that the concentration of unsaturations had no effect on the rate of photooxidation but dramatically influenced the stability in thermooxidative conditions.

1. Introduction

The photo and thermooxidation of polyolefins have long been of interest to scientists and engineers. In the last 50 years, many investigations have been undertaken to elucidate the degradation mechanisms of polyolefins. Polyethylene (PE) is one of the most common, widespread and most inexpensive commodity thermoplastic polymers used for industrial as well as medical applications. Despite the numerous papers published in the literature that deals with the thermally or photochemically induced oxidation of polyethylene^{1,2,3,4,5,6,7,8,9,10, 11,12,13,14}, several basic aspects of the mechanism of oxidation remain unclear. The basic differences between photo and thermo-oxidation are ignored and the role played by the structure of the polymer and its chemical defects is not totally clear.

The aim of this paper is to study the thermal and UV degradation of ethylene/ α -olefin copolymers and to compare the mechanisms of thermooxidation at moderate temperature (100 °C) to that of photo oxidation at wavelengths above 300 nm. Different catalysts result in differences in the type and concentration of unsaturations, mainly in vinyl, trans-vinylene and vinylidene groups. The influence of the concentration of unsaturations on both the photo- and the thermo-oxidation of PE is reported in this article. The polyethylenes have been studied by FTIR and UV spectroscopy, in order to follow the degradation of the samples.

2. Experimental

2.1. Materials

The materials used in this work were two types of polyethylene (PE) produced by TVK. Sample (A), an ethylene/1-hexene copolymer, was synthesized with a Phillips type catalyst (Tipelin FA 381 grade of TVK), and sample (B), an ethylene/1-butene copolymer, with a Ziegler-Natta type catalyst (Tipelin 7000 F grade of TVK). These two samples contained different number of vinyl and *trans*-vinylene groups and similar amounts of vinylidene unsaturations.

2.2. Preparation of the films

The additive-free polymer powders were pelletized using a Rheomex S ¾" type single screw extruder attached to a Haake Rheocord EU 10 V driving unit at 50 rpm and barrel temperatures of 180, 220, 260 and 260 °C, then compression-moulded to films at 150 °C using an Agila PE20 hydraulic press (processing conditions: low pressure for 120 s, followed by a high-pressure cycle at 150 bar for 90 s and finally cooling with tap water). The thickness of the obtained films was between 90 and 105 µm. To extract the residual degradation products of low molecular masses, samples were purified with Soxhlet extraction in methanol at 150 °C.

2.3. UV light and thermal ageing

The samples were irradiated in the form of the films as described above. UV-light irradiation was carried out under polychromatic light with wavelengths longer than 300 nm in a SEPAP 12.24 unit¹⁵, in the presence of air, at 60 °C. This accelerated weathering device was equipped with four medium pressure mercury lamps of 400 W (a borosilicate envelope filters wavelengths below 300 nm) and the samples were placed on a rotating carousel positioned in the centre. Thermal oxidation of PE samples was carried out in an air-circulation oven at 100 °C.

2.4. Characterisation

Infrared spectra in transmission mode were recorded with a Thermo Scientific Nicolet 6700 FTIR spectrometer, with OMNIC software. Spectra were obtained using 32 scan summations and 4 cm⁻¹ resolution. The rates of polymer oxidation were determined by monitoring the rate of formation of non-volatile carbonyl oxidation products. The intensity of the absorbance maximum at 1713 cm⁻¹ was taken as a measure of the concentration of carbonyl compounds (mainly carboxylic acids). Slight differences in film thicknesses were corrected by adjusting the absorbance at 720 cm⁻¹ for a film with a thickness of 100 microns.

UV/Visible spectra were recorded on a Shimadzu UV-2550 scanning spectrophotometer equipped with an integrating sphere.

3. Results and discussion

Fig. 1 shows the FTIR spectra of PE (A) and PE (B) recorded before aging in the absorption range of unsaturations (vinyl, *t*-vinylene and vinylidene). One can see that the absorption bands of *t*-vinylene (965 cm⁻¹) and vinyl (909 and 991 cm⁻¹) defects are more intense for PE (A) than for PE (B). For both PE, the vinyl group absorption at 909 cm⁻¹ is the most characteristic.

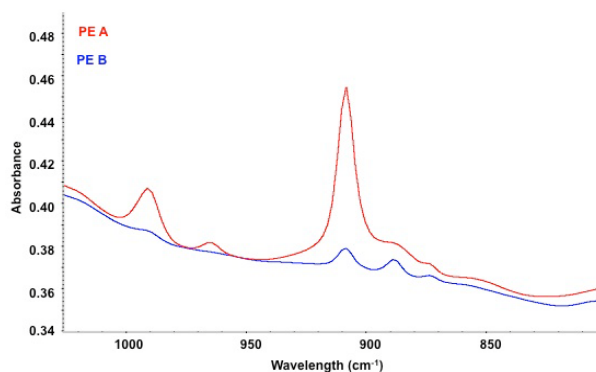


Fig. 1 Infrared spectra of PE A and B in the absorption range of unsaturations

The concentrations of vinyl, *t*-vinylene and vinylidene unsaturations can be determined using average molar extinction coefficients determined on the basis of average molar absorption coefficients of model compounds such as hexenes, heptenes, octenes, etc.

Table 2

Composition of PE A and PE B

Function		Wavenumber at the absorption maximum (cm ⁻¹)	ϵ (M ⁻¹ cm ⁻¹)	Concentration in PE A (M)	Concentration in PE B (M)
Vinylidene	CH ₂ =CR ₂	888	158	0.063	0.054
Vinyl	CH ₂ =CHR	909	122	0.803	0.075
Vinylene	CH=CH	965	100	0.047	0.005

3.1 Photooxidation of Polyethylene

Infrared spectroscopy has proven to be a useful and frequently used analytical technique for monitoring the oxidation process of polyethylene¹¹. Fig. 2 illustrates the modification of PE spectra during photooxidation in the range of carbonyl absorption. The same modifications were observed for both PEs. As the same modifications were noted, only PE (A) is shown here. As frequently reported in the literature, the modification of the spectrum indicates that ketones (1718 cm⁻¹) are formed in the initial steps, and carboxylic acids (1713 cm⁻¹)

¹), esters (1735 cm^{-1}) and lactones (1780 cm^{-1}) form in secondary processes. One can also notice the formation of isolated double bonds (1640 cm^{-1}). In the range of hydroxyl frequencies, not shown here; a broad band with a maximum at 3420 cm^{-1} and a sharp absorption band at 3550 cm^{-1} appear in the spectrum. These bands are known to come from the formation of monomeric hydroperoxides (3550 cm^{-1}) and hydrogen-bonded alcohols and hydroperoxides (3420 cm^{-1}). The intensities of both bands remain very low, confirming that the stationary concentrations of hydroperoxides are rather small under the conditions of photo oxidation¹.

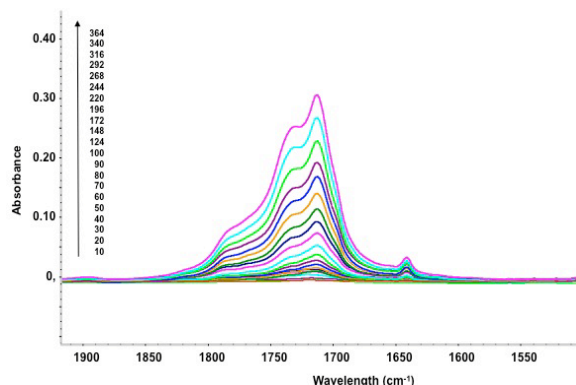


Fig. 2 Changes in the infrared spectra of PE A with irradiation time in the range of carbonyl absorption

Fig. 3 shows the modifications that occur in the absorption range of the unsaturations. The three unsaturated groups of PE, namely vinyl, *t*-vinylene and vinylidene, behave differently during photooxidation.

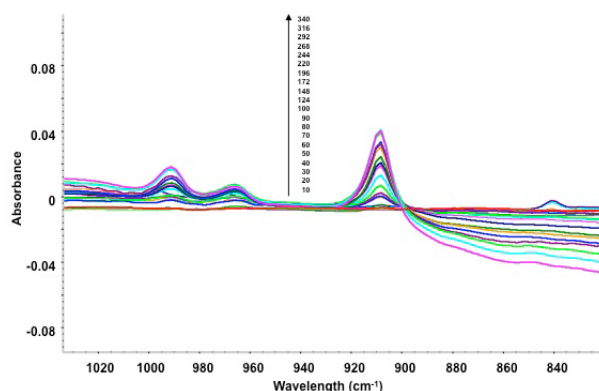
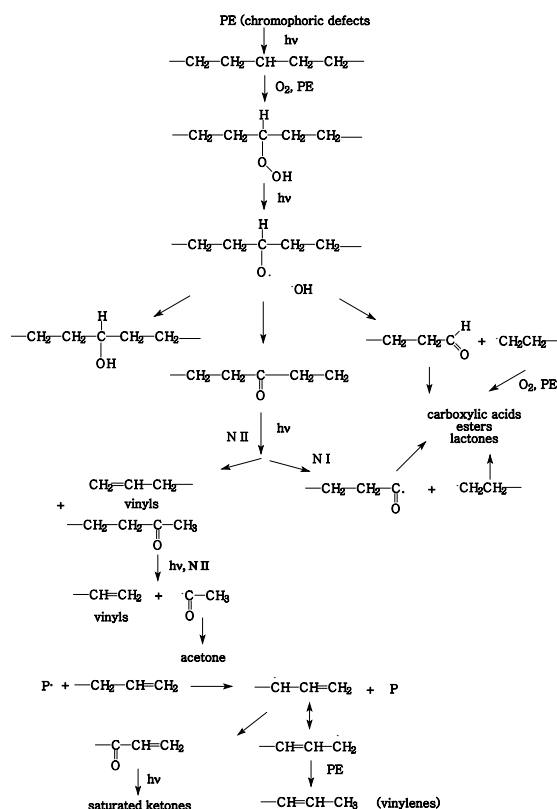


Fig. 3. Subtracted spectra of PE A with irradiation time in the absorption range of unsaturations

One can notice an increase in the intensity of the bands at 909 and 991 cm^{-1} , which indicates the formation of new vinyl unsaturations, and at 965 cm^{-1} characteristic of the *t*-vinylene group. No modification is observed in the intensity of the vinylidene group at 888 cm^{-1} .

At present the mechanism of photooxidation accounting for the main routes of degradation of PE is well understood and can be summarized as shown in Scheme 1. PE is a non-absorbing polymer in the sense that it does not contain chromophoric species that can absorb in the range of the solar light. Light absorption is necessary to provoke photochemical reactions, although this basic law of photochemistry is sometimes forgotten^{16,17}. In the case of non-absorbing polymers, the absorption of light is attributed to unidentified chromophors that can vary from one PE to another. Extensive work has been devoted to the nature of chromophoric species, and it is well admitted that oxidized species formed during processing, like hydroperoxides or ketones, are potential candidates. Light absorption by chromophoric defects results in the formation of radicals, which can either abstract a hydrogen atom or add to an unsaturated group. The investigated PE types have about 5-6 branching points per 1000 carbon atoms, which means as many tertiary carbons. Nevertheless, it is expected that most hydrogen abstraction occurs at secondary carbon atoms, despite the much larger reactivity of hydrogen atoms attached to tertiary carbon atoms¹⁸.



Scheme 1 Simplified photo oxidation mechanism of polyethylene

Chemical derivatizations performed on oxidized samples have permitted the identification of the various oxidation products¹⁹. Hydroperoxides are formed as primary photoproducts and

can be chemically titrated using several methods²⁰. Once formed, they can decompose by the scission of the weak O-O bond, which gives a macro-alkoxy and a hydroxyl radical HO•. The alkoxy macroradical is the key intermediate in the reaction. This radical can react by several routes: β -scission with cleavage of the main chain to form aldehydes, abstraction of hydrogen without cleavage of the chain to form hydroxyls, cage reaction between the pair of the radicals formed, i.e. macro-alkoxy radical and hydroxyl radical HO•¹. The latter reaction produces chain ketones. Ketones photochemically react by Norrish type I or type II reactions. It has to be recalled that Norrish reactions are photochemical reactions²¹ and it is sometimes forgotten that these reactions cannot occur under the conditions of thermo-oxidation²². Photolysis of ketones by Norrish II processes results in the formation of vinyl-type unsaturations with absorption bands appearing at 909, 991, and 1640 cm⁻¹, and produces a chain-end ketone, which also reacts by a Norrish II reaction and forms a vinyl unsaturation and acetone. The formation of carboxylic acids, esters and lactones comes from the various reactions involving both the aldehydes and the keto radicals formed by Norrish I reactions. The formation of *t*-vinylenes results from the mesomerism of allylic radicals formed by hydrogen abstraction from the carbon atom in α -position to the double bonds of vinyl groups.

Under irradiation, no modification of the UV visible spectra of the exposed samples was observed in the visible domain, even for long irradiation times of up to 400 h. Only a shift of the absorption in the UV region is noticed, which indicates the formation of unsaturated groups.

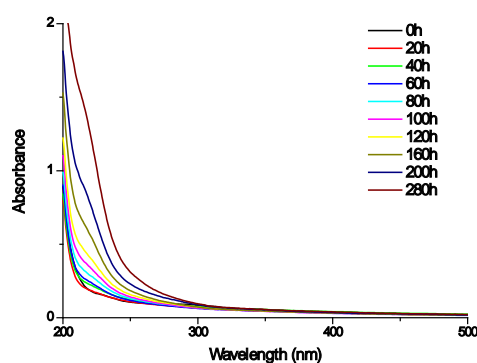


Fig. 4. UV-visible spectra of PE A with irradiation

The rate of photooxidation of the two PEs can be compared by measuring the increase of absorbance at 1713 cm⁻¹ with irradiation time. Changes in the concentration of unsaturations were also compared (Figure 5) by plotting the increase in the absorbances at 909 cm⁻¹ (vinyl)

and 965 cm^{-1} (*t*-vinylene) as a function of irradiation time. It is worth to note that the rate of the formation of vinylenes is approximately one-tenth that of the rate of vinyl formation.

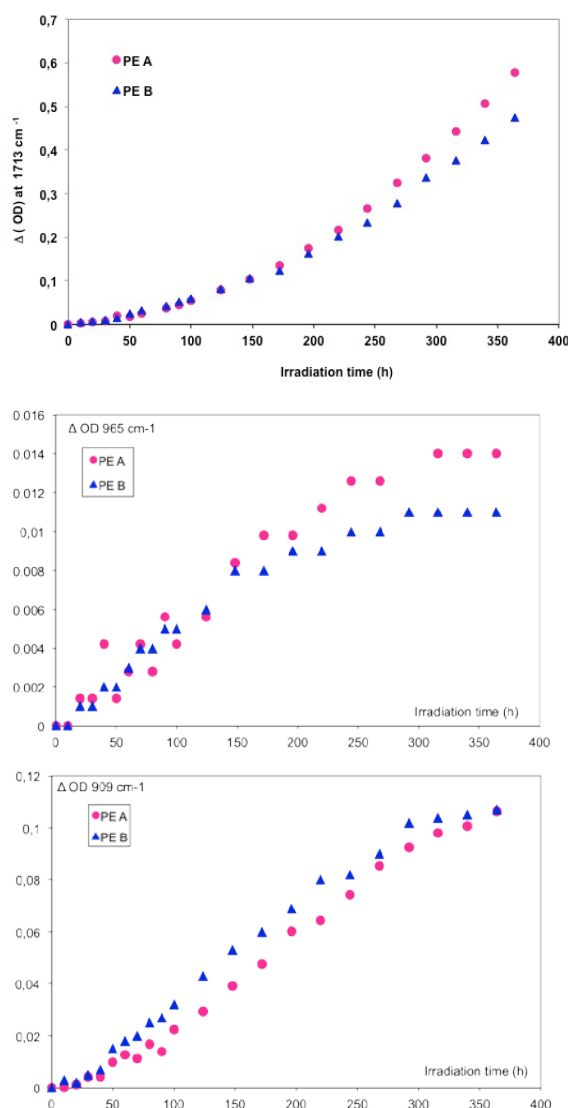


Fig. 5. Changes in the absorbances at 1713 cm^{-1} , 965 cm^{-1} and 909 cm^{-1} for PE (A) and PE (B) exposed to artificial accelerated ageing in UV light.

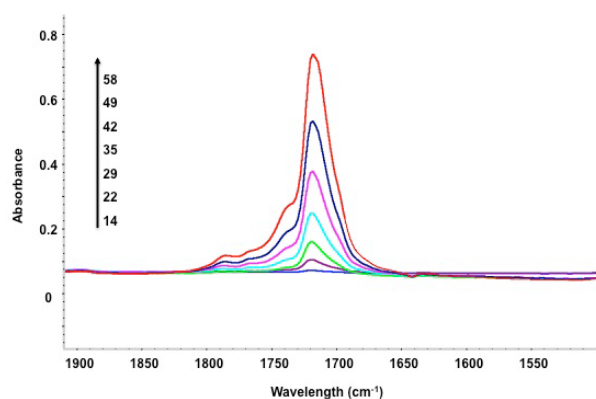
On the basis of these results, several comments can be made. The most important result concerns the influence of the initial concentration of unsaturations on the rates of PE photooxidation. As the kinetic curves of PE A and PE B are similar, one can conclude that the initial amount of unsaturations does not affect the formation rate of oxidation products resulting from the photooxidation process. This is true as well for carbonyls as for vinyl groups formed by the photolysis of the ketones, the formation of which parallels that of acid groups. The formation of vinyl groups should compete with their disappearance through reactions

with radicals yielding vinylene groups. The kinetics determined reflects the competition between the formation and disappearance of vinyl groups, which shows that the rate of formation is much more important than the rate of disappearance. It is also interesting to note that the concentration of *t*-vinylene groups formed by this reaction does not depend on the initial quantity of vinyl group contained by the matrix. Concerning the vinylidene groups, not shown here, no modification in their concentration was observed during photooxidation.

3.2 Thermooxidation of polyethylene

Figs. 6a and b shows the changes in the infrared spectrum of PE (A) in the absorption range of carbonyl and unsaturated groups. The changes observed in the carbonyl range in the case of PE B were very similar, thus not presented. As discussed below, the differences between the two polymers affect the kinetics of oxidation.

In the range of $1900\text{--}1500\text{ cm}^{-1}$, one can see the formation of absorption bands at frequencies similar to those reported above for photo oxidation (1718 cm^{-1} , 1713 cm^{-1} , 1735 cm^{-1} , 1780 cm^{-1}), which indicates that the same products are formed. However the shape of the complex carbonyl band differs strongly, which reflects dissimilar relative concentrations of the products formed by thermo- and photo-oxidation, respectively. It is worthy to note that the main absorption maximum is observed at 1720 cm^{-1} , which is characteristic of ketones, whereas it appeared at 1713 cm^{-1} in the case of photo oxidation. Ketones are then the main products formed by thermal oxidation. In the range of $1000\text{--}800\text{ cm}^{-1}$, one can note a dramatic decrease of vinyl concentration. The concentration of vinylidene unsaturations also decreases, but very slightly. For PE B, not shown here, no detectable decrease was observed in the intensities of the absorption bands characteristic of unsaturations. The attention must be called here to the fact that the initial concentration of unsaturations in PE B was very weak.



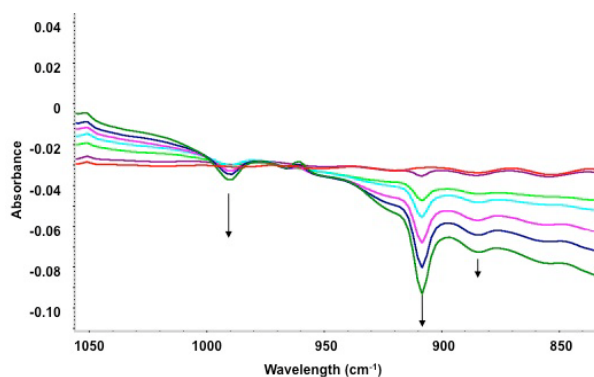


Fig. 6 Infrared spectra of PE A in the range of carbonyl absorption (a) and subtracted spectra for PE A in the range of the absorption of unsaturated groups (b) as a function of the time of oxidation (100 °C)

Whereas no modification of the UV-visible absorption characteristics was observed during photooxidation, some notable changes appear on the spectra as a result thermal oxidation. Fig. 7 presents the modifications of the UV-visible spectrum of PE A as a function of aging time at 100 °C.

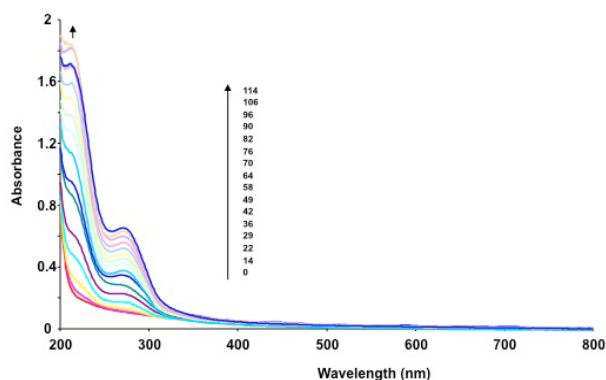


Fig. 7 Changes in the UV-visible spectra of PE A with thermal oxidation (100 °C)

One can observe an absorption maximum at 275 nm that develops during the oxidation (the maximum at 215 nm is not taken into account, since the response of the detector cannot be considered as relevant below 250 nm). The maximum at 275 nm, which is characteristic of $\pi\pi^*$ transition in α - β unsaturated ketones, indicates the formation of conjugated ketones as already observed in the case of PVA²³. These products are not stable under UV-light irradiation, and as shown in figure 8, disappear in only a few hours of exposure.

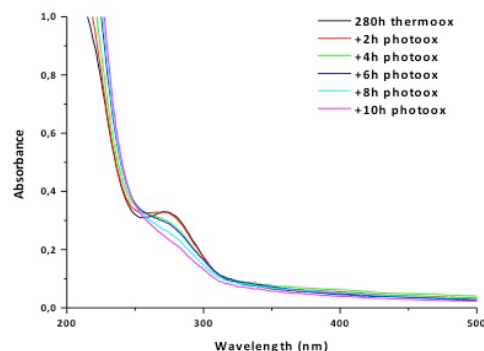
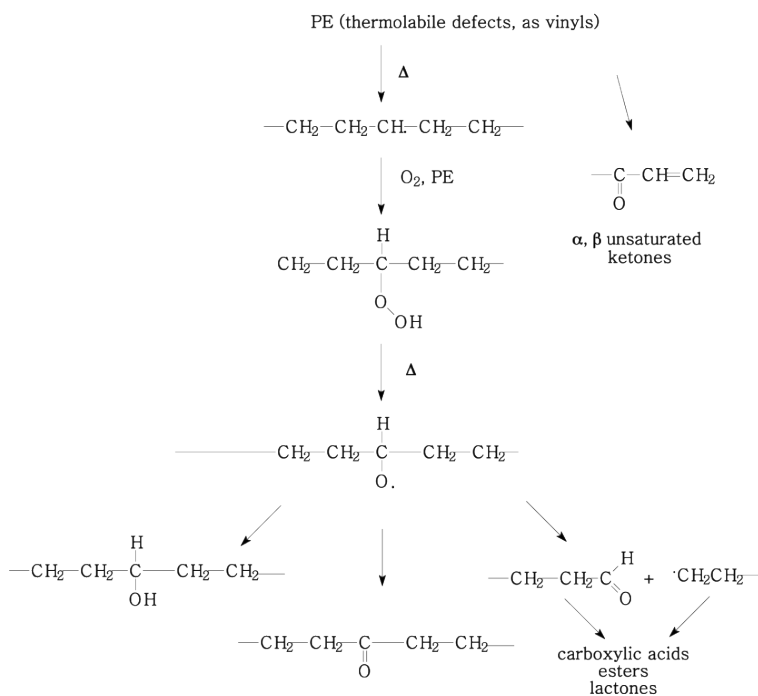


Fig. 8. Photo oxidation of sample PE A after thermal oxidation at 100 °C for 60 h

In the case of PE B, only weak modifications in the UV-visible range were observed. The degradation of polyethylene at 100 °C occurs by a similar way as photodegradation, but without Norrish reactions. As a direct consequence, ketones can accumulate as oxidation products and vinyl (and then *t*-vinylenes) groups do not form. One observes only the disappearance of the unsaturations, which can be directly related with the formation of α - β unsaturated ketones. This is reported in scheme 2 that represents a simplified mechanism of polyethylene thermal oxidation.



Scheme 2. Simplified mechanism of the thermal oxidation of polyethylene

From a kinetic point of view, the two polymers A and B behave rather differently. As shown in Figs. 9a and b, PE A oxidises much faster than PE B. The larger reactivity of PE A reflects the influence of the concentration of vinyl groups on thermal oxidation. Similar conclusions are derived from the increase of absorbance at 275 nm with the time of oxidation. Moreover one can observe in these figures the good correlation between the IR and UV absorbances. Fig. 9c presents the rate of concentration change for vinyl groups. The figure clearly shows that the concentration of vinyl groups rapidly decreases in the case of PE A (starting from 0.803 M), whereas only a slight modification is observed for PE B (starting from 0,075 M).

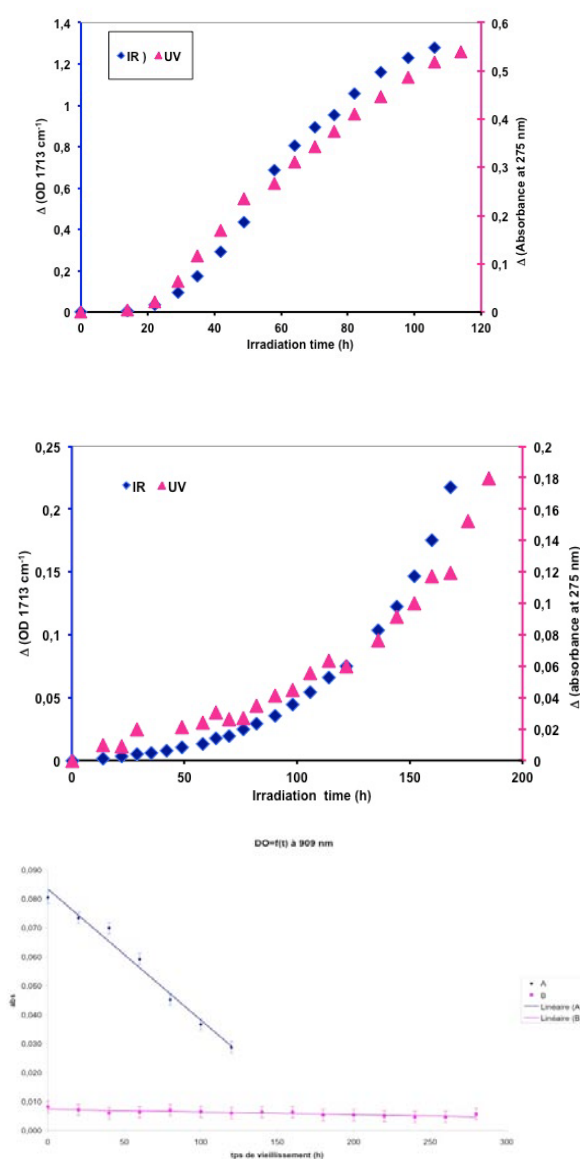


Fig. 9 Changes in the absorbances at 1713 cm^{-1} and 275 nm with time in the thermal oxidation ($100 \text{ }^{\circ}\text{C}$) of PE A (9a) and PE B (9b), and at 909 cm^{-1} for both samples (9c)

3.3 Comparison between photo- and thermo-oxidation of polyethylene

On the basis of the many results previously published in the field of photo oxidation of polyolefins, one can deconvolute the complex spectrum in the carbonyl domain in order to highlight the main bands that contribute to the broad absorption of carbonyls. This deconvolution was performed by taking into account the vibration frequencies of the bands associated with the various products, which have been identified by chemical derivatization or by physical treatments¹¹. The absorption maxima that were chosen for analysis are given in table 3.

Table 3

Absorption maxima of the different products formed during the oxidation of polyethylene^{24,25,26}

Product	Conjugated ketone	Carboxylic acid	Ketone	Ester	Peracids	Lactone
Absorption maximum (cm ⁻¹)	1696	1713	1720	1735	1765	1785

Figure 10 shows an example of a spectrum deconvoluted into the various absorption maxima given in table 3.

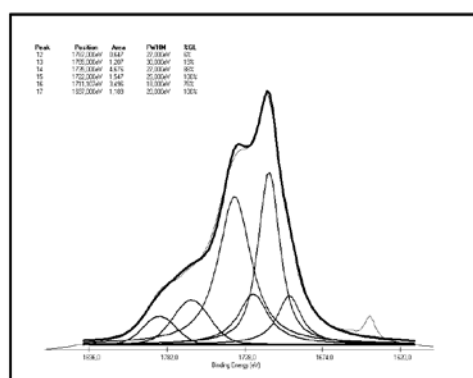


Fig. 10 Deconvoluted FTIR spectrum in the absorption range of carbonyl groups for PE A recorded after 150 hours exposure to UV light

All the spectra recorded after photo- or thermo-oxidation of PE A and B were deconvoluted following the same procedure, with the same set of data. It is worth to note that nice fits were obtained between the recorded “experimental” spectra and the spectra rebuilt after deconvolution. The molar absorption coefficients of the various oxidation products that were considered for spectral deconvolution are known from the literature. The values are reported in table 4.

Table 4

Infrared characteristics of the oxidation products formed in PE

Product	Wavenumber at the absorption maximum (cm ⁻¹)	Molar absorption coefficient (M ⁻¹ cm ⁻¹)
lactones	1785	720 ²⁷
esters	1735	500 ²¹
ketones	1720	350 ²¹
carboxylic acids	1713	680 ²¹

Considering these values and the series of deconvoluted spectra, one can plot the kinetics of oxidation for the different products. This is presented in Figures 11a and b showing changes in the concentration of oxidation products for polymer A submitted to photo- and thermal oxidation, respectively.

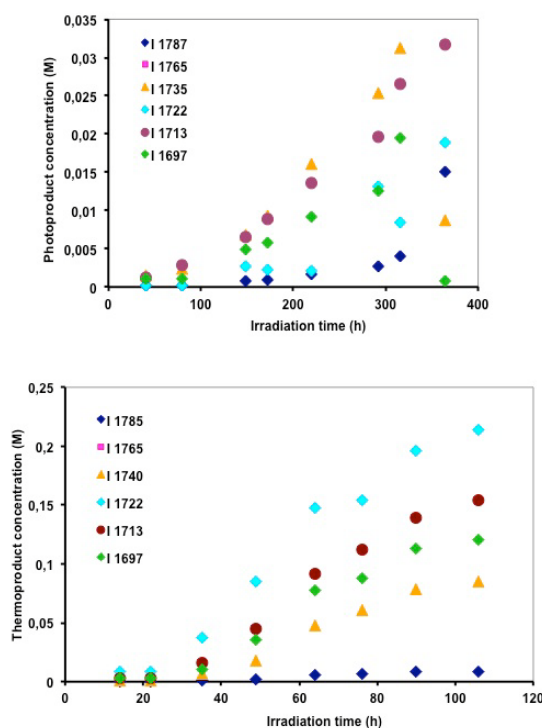


Fig. 11 Concentrations of the main oxidation products for polymer A as a function of increasing exposure time; A: photooxidation, B: thermal oxidation

Photooxidation and thermooxidation of polyethylene produces almost the same oxidation products, but their relative concentrations are different. The Norrish reactions that occur in photooxidation are responsible for these differences. The same carbonyl products form in both cases, but not in the same quantities: ketones and conjugated ketones accumulate during thermodegradation, whereas they disappear to yield new unsaturations in photodegradation. Vinyl and vinylenic unsaturations can appear in photo degradation through Norrish reactions. Under the conditions of photooxidation, the initial concentration of unsaturations has no influence on the rate of oxidation (PE A vs. PE B), which suggests that unsaturations do not play an important role in the initiation of oxidation, in other terms unsaturations are not the chromophoric species initiating the photochemical oxidation of PE. One can expect that unsaturations disappear during the oxidation process by a mechanism involving hydrogen abstraction from the carbon atom in α -position to a double bond. However, experimental results indicate that the rate at which unsaturations form in Norrish II reactions is much faster than the rate at which they disappear by oxidation processes. Under the conditions of thermooxidation (100 °C), unsaturations play a decisive role, shown by differences in oxidation rates determined for PE A and B. It is very probable that the thermal lability of the hydrogen atom located on the carbon atom in α -position to the double bond is responsible for the reactivity of the unsaturated groups. These unsaturations disappear, but they do not form by any of the reactions occurring during thermal oxidation.

4. Conclusion

This study of the photo- and thermal oxidation of two PE samples containing different amount of unsaturations has shown two main results: the influence of the initial number of unsaturated groups on the rate of photo oxidation and the dramatic differences between thermal and photo oxidation. Unsaturated groups behave as thermolabile groups, but not as chromophoric species. Samples with high vinyl content degrade much faster under the conditions of thermal than photooxidation. The concentration of unsaturations does not influence the rate of photo oxidation. Photo and thermal oxidation result in the same products, apart from unsaturations that form only by photochemical processes, but the relative concentrations of these products are dramatically different in the two processes.

5. Acknowledgements

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