



# 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  $\lambda \geq 300$  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 thermo-oxidation 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.

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## 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 deal with the thermally or photochemically induced oxidation of polyethylene [1–16], 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/ $\alpha$ -olefin copolymers and to compare the mechanisms of thermooxidation at moderate temperature (100 °C) to that of photooxidation 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 PE A, an ethylene/1-hexene copolymer, was synthesized with a Phillips type catalyst (Tipelin FA 381 grade of TVK), and sample PE B, an ethylene/1-butene copolymer, with a Ziegler–Natta type catalyst (Tipelin 7000 F grade of TVK).

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**Table 1**  
Composition of PE A and PE B.

Function		Wavenumber at the absorption maximum (cm <sup>-1</sup> )	$\epsilon$ (mol <sup>-1</sup> L cm <sup>-1</sup> ) from Ref. [3]	Concentration in PE A (mol L <sup>-1</sup> )	Concentration in PE B (mol L <sup>-1</sup> )
Vinylidene	CH <sub>2</sub> =CR <sub>2</sub>	888	158	0.063	0.054
Vinyl	CH <sub>2</sub> =CHR	909	122	0.803	0.075
Vinylene	CH=CH	965	100	0.047	0.005

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 <sup>3</sup>/<sub>4</sub> " 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  $\mu$ m. To extract the residual degradation products of low molecular masses, samples were purified with Soxhlet extraction in methanol.

## 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 unit [17], 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<sup>-1</sup> 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<sup>-1</sup> was taken as a measure of the concentration of carbonyl compounds (mainly carboxylic acids). The molar absorption coefficients for the different products were obtained from the literature. Slight differences in film thicknesses were corrected by adjusting the absorbance at 720 cm<sup>-1</sup> for a film with a thickness of 100 microns.

Deconvolutions were performed using a deconvolution software Spectracorr (OMNIC 8.1) from ThermoOptek.

The concentrations of vinyl, *t*-vinylene and vinylidene unsaturations (Table 1) can be determined using average molar absorption coefficients determined on the basis of average molar absorption coefficients of model compounds such as hexenes, heptenes, octenes, etc. and given in the literature [3].

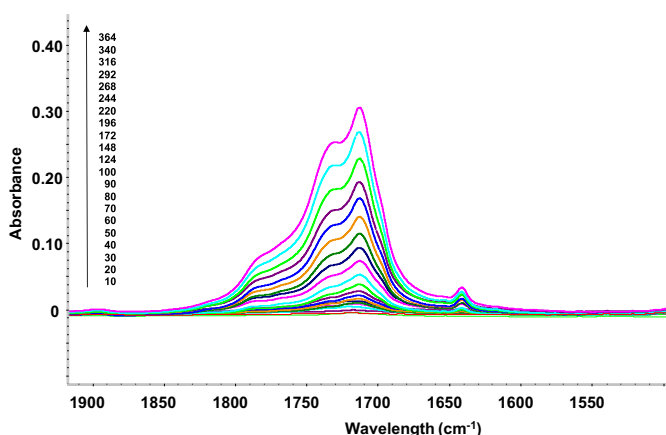
UV/Visible spectra were recorded on a Shimadzu UV-2550 scanning spectrophotometer equipped with an integrating sphere.

## 3. Results and discussion

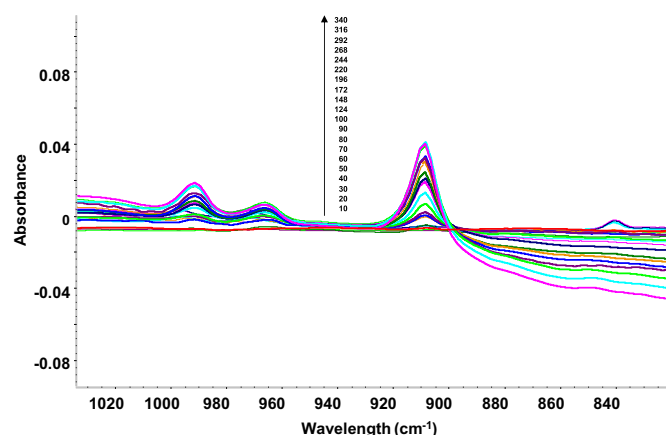
### 3.1. Photooxidation of polyethylene

Infrared spectroscopy has proven to be a useful and frequently used analytical technique for monitoring the oxidation process of polyethylene [12]. Fig. 1 illustrates the modification of PE spectra during photooxidation in the range of carbonyl absorption. The same modifications were observed for both PE samples. As the same modifications were noted, only PE A is shown here. As frequently reported in the literature [12], the modification of the spectrum indicates that ketones (1720 cm<sup>-1</sup>) are formed in the initial steps, and carboxylic acids (1713 cm<sup>-1</sup>), esters (1735 cm<sup>-1</sup>) and lactones (1780 cm<sup>-1</sup>) form in secondary processes. One can also notice the formation of double bonds (1640 cm<sup>-1</sup>).

In the range of hydroxyl frequencies, not shown here, a broad band with a maximum at 3420 cm<sup>-1</sup> and a sharp absorption band at 3550 cm<sup>-1</sup> appear in the spectrum. These bands are known to



**Fig. 1.** Infrared spectra of a PE A film during photooxidation in the absorption range of carbonyl.



**Fig. 2.** Subtracted IR spectra of a PE A film during photooxidation in the absorption range of unsaturations.

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