

Identification of carbonyl species of weathered LDPE films by curve fitting and derivative analysis of IR spectra

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ABSTRACT

We describe the examination of the weathering degradation of LDPE (low density polyethylene - locally produced B24/2 and imported LDPE 2100T), supplied by two different manufacturers and processed into films for greenhouse coverings, over several months in a sub-Saharan region of Algeria.

The IR spectral region most affected by the aging process is the carbonyl region. Curve fitting combined with derivative spectroscopy revealed that the composite carbonyl band encompasses more than 10 different oxidation products. The most significant among these in terms of absorbance are carboxylic acids, ketones, aldehydes and esters. The oxidation kinetics with respect to the type of LDPE film shows that B24/2 LDPE undergoes less oxidation than LDPE 2100 T. Calculating the concentrations of different carbonyl species compared to their respective absorbance's indicates that the aldehydes are the predominant component of the final compound, rather than the carboxylic acids.

OBJECTIVES

The local production of raw material (polyethylene) for the plastics industry is often insufficient to meet industrial demand. Additionally, it has been observed that some batches of film do not last for the entire growing season compared to others that appear to withstand aging better.

For this reason, an aging protocol was applied to a pair of films produced using different batches of raw material (locally produced B24/2 and imported LDPE 2100T).

The experiments were performed so that the respective aging behavior for each material was examined using FTIR by following the types and kinetics of the photoproducts produced.

A more precise identification of all of the carbonyl species remains very difficult because the corresponding signals often overlap. Only by separating their corresponding signals can an exhaustive identification of all of the components be made.

MATERIALS AND METHODS

- The first batch of LDPE used in this investigation was commercial raw material produced by the ENIP Company, Skikda, Algeria under the reference B24/2. The second batch of LDPE was supplied by the Saudi Basic Industries Corporation (Sabic) as "LDPE 2100 T N00W". The films (180 mm thick) did not contain any stabilizing agents.
- Film cuts were mounted on wooden frames facing south in accordance with ISO 4607. Exposure outdoors took place in Laghouat, Algeria (3348°N, 256° E) from March to November for both derived films.
- The absorbances over the range from 1680-1800cm⁻¹ strongly overlap into a single signal with multiple shoulders. To determine the oxidation products, mathematical curve fitting was performed to deconvolute the carbonyl bands. The curve-fitting analysis of this band was performed using the second derivative method in the OriginPro software package (version 8.6).
- The concentrations of carbonyl compounds were calculated from their absorbance integrated intensity (area) IA and their molar extinction coefficients ϵ (l.mol⁻¹cm⁻¹).

RESULTS

The weathering processes that the polyethylene films are exposed to over the eight-month testing period lead to rapid degradation in which the films become excessively brittle.

The degradation appears to progress similarly for both material types (Fig. 1). A comparison of the part of the spectrum containing carbonyl shows that these compounds are more developed in the LDPE 2100 T material than in the B24/2 material (Fig. 2).

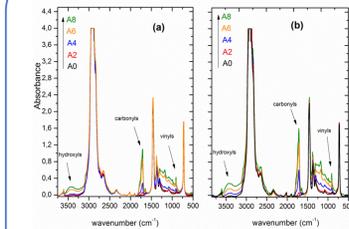


Figure 1: IR spectra of LDPE for different ageing times (0, 2, 4, 6 and 8 months): a) B24/2 b) LDPE 2100T

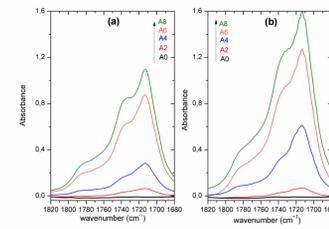


Figure 2: Progression of the carbonyl band as function of ageing time: a) B24/2; b) LDPE 2100T.

The identification of all of the different oxidation species constituting this broad absorption band is very important for understanding the oxidation mechanism. In Figure 3, deconvolution by curve fitting reveals a number of different sub-peaks. The curve fitting is mathematically non-unique. For the same IR band with the same curve of the second derivative, two groups of sub-peaks are mathematically acceptable (Fig.4).

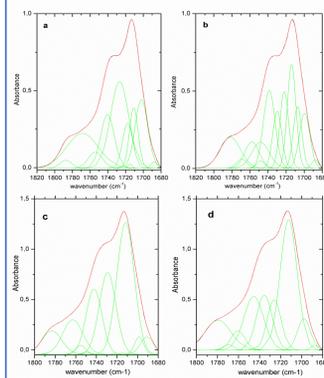


Figure 3: Curve fitting of the carbonyl band of the most aged film a) B24/2: first fit b) B24/2: second fit. c) LDPE 2100T: first fit d) LDPE 2100T: second fit.

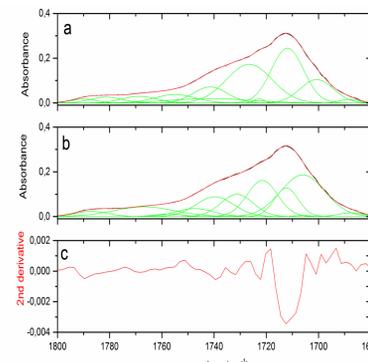


Figure 4: Deconvolution by curve fitting: (a) first fit $R^2 = 0.9994$ and $\chi^2 = 5.34 \cdot 10^{-5}$; (b) second fit $R^2 = 0.9993$ and $\chi^2 = 6.25 \cdot 10^{-5}$; (c) second derivative of the band of the IR spectrum of the LDPE sample considered.

The fourth derivative enhances the resolution and enables the separation of signals that are very close to each other but separated from those of the second derivative. The results obtained from this method for all of the spectra (B24/2 and LDPE 2100T) are in good agreement with previous results. The same sub-peaks exist for the different aging times and differ only in their increasing amplitude (Fig.5).

The peak positions separated by the two treatments and their corresponding carbonyl species are reported in Table 1.

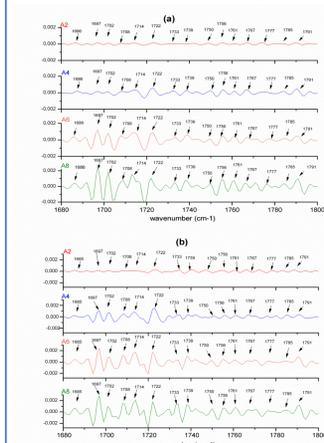


Figure 5: Identification and progress of the different carbonyl species by means of the 4th derivative: a) B24/2; b) LDPE 2100T

Table 1
Different carbonyl species identified by fourth derivative for all aged films.

Component n°	Peak position (cm ⁻¹)	B24/2	Sabic	Assignment
1	1686	+	+	Ketones, acids, β unsaturated ^{a,b}
2	1697	+	+	γ -Ketoacids, keto group ^{a,b}
3	1702	+	+	Conjugated ketones ^{a,c}
4	1708	+	+	γ -Ketoacids, acid group ^{a,b}
5	1714	+	+	Carboxylic acids (associated) ^{a,b,c}
6	1722	+	+	Ketones ^{a,b,c}
7	1733	+	+	Aldehydes ^a
8	1739	+	+	Esters ^{a,b}
9	1750	+	+	Peracids ^{a,b}
10	1756	+	+	Free carboxylic acids ^{a,c}
11	1761	+	+	not identified ^a
12	1767	+	+	Carboxylic acids (isolated) ^{a,b}
13	1777	+	+	Peresters ^{a,b,c}
14	1785	+	+	γ -Lactones ^{a,b}
15	1791	+	+	not identified ^a

^a Separated by derivative analysis in this work.

^b Assignment according to Ref. [3].

^c Assignment according to Ref. [9].

The peak separation allows the determination of the absorbance and permits the calculation of the concentration of each species by applying Beer Lambert's law.

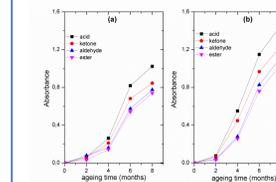


Figure 6: Variation of the carbonyl absorbance versus exposure time: a) B24/2; b) LDPE 2100T.

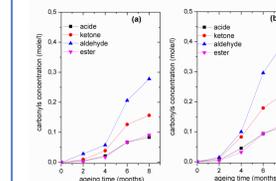


Figure 7: Comparison of the kinetics of formation of the oxidation products for the B/24 and the LDPE 2100T for the same period of exposition.

Figure 6 shows the variation in absorbance for the most active oxidation species versus the exposure time for both products. The curves show that the carboxylic acids are predominant in the materials.

In Figure 7, the plot of the calculated concentration of these carbonyl compounds versus the exposure time, for both products, shows other priorities.

The aldehydes are shown to be the prevalent species. This is contrary to that observed in previous work, in which the acids are the predominant carbonyl group.

CONCLUSIONS

The exposure of polyethylene films to a natural environment leads to the unavoidable oxidation of the original molecular structure. The goal of this work was to compare the aging behavior of two different commercial LDPE base materials used for the production of greenhouse covering films. More than 10 different oxidation products have been identified. Deconvolution by curve fitting associated with the fourth derivative permitted the reinforcement of the determination of the existence of the peaks pertaining to the carbonyl envelope.

Carboxylic acids have always been considered to be the largest population of final oxidation products. The calculated concentration of the carbonyl compounds reveals that the aldehydes are the most predominant compound after aging.

Curve fitting combined with derivative spectroscopy appears to be a very powerful tool for the qualitative and quantitative evaluation of different chemical species existing in an unaged or aged material. In conclusion, a detailed analysis of the entire IR spectrum is considered to be a very interesting method, which may provide better insight on global photo oxidation mechanisms.

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