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Impact of solar radiation effects on the physicochemical properties of polyethylene (PE) plastic film.

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Abstract

This study deals with the photodegradation of polyethylene films for greenhouse covering. The UV range of solar light appears as the most deleterious factor of plastic degradation in outdoor exposure. The reasons of this photosensitivity are structural defects which are light absorbing. The use of FTIR as an investigation tools has revealed that the material reacts with surrounding oxygen via a photooxidation process. Although, the photochemical process is quite complex it appears through this study that crosslinking and chain scissions are the most important events taking place during ageing. These two key reactions change irretrievably the average molecular weight affecting thus drastically the mechanical properties and reducing in the same way the service life time of the films.

Keywords: Polyethylene, films, FTIR, ageing

1. Introduction

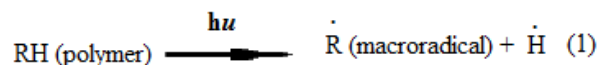
Aging of plastic material by photooxydation takes place via the combined action of UV light and oxygen, this is the main mode of plastic degradation (Chevalier, 1986). This type of aging belongs to the type of chemical aging involving oxydation of the molecular chains (Gugumus, 1990; Tidjani, & Arnaud, 1993).

Contrarily to physical aging, It leads to chemical changes of the polymeric chains, and this occurs mainly at the film surface. The progress of the oxydation through the thickness of the film is a decreasing function, since it depends on the oxygen absorption capacity (limiting factor) of the material (Douminge, 2010).

The basic reactions taking place during photooxidation has been described by the reaction process of Bolland (1949), consisting in three main steps: Initiation, propagation and terminaison (Geetha, & All ,1987).

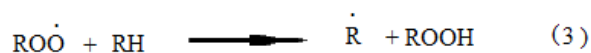
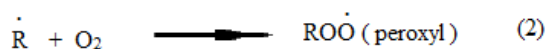
- *Initiation*

The UV-irradiation in the wavelength range between 290 and 400 nm is absorbed by the material. The initial presence of structural defects leads to the formation of polymer free radicals.



- *Propagation*

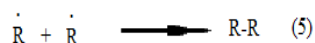
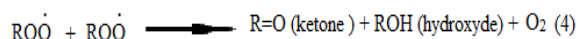
In this step occurs the formation of macroperoxy radicals.



The macro radical produced during initiation can readily react with oxygen to form peroxy. This peroxy can extract hydrogen from another polymeric chain, this leads to hydroperoxyde formation and to a new alkyl radical.

- *Termination*

Termination reactions can be of three (3) different types, combination between (1) two peroxy; (2) two alkyl radical or (3) an alkyl radical with a peroxy.



The degradation phenomena involved during photodegradation are common to all the other modes of aging and involve mainly chain scissions and crosslinking reactions (Torikai, & All, 1986)

Such information allow Algerian manufacturers to intervene in the material polymerization process to attempt either to reduce structural defects in order to increase the material lifetime or to introduce photosensitizers to make the material more sensitive towards UV light and thus to make it more degradable. In all the cases, this will drastically reduce plastic waste, thus preventing from an excessive environmental pollution.

2. Experimental

The study of the weathering of Low Density Poly (Ethylene) (LDPE) film used as greenhouse covering is performed with a polymer which is a neat grade exempt of stabilizing agent. The absence of a stabilizing system makes the film transparent (Peacock, & Andrew, 2000)

The chemical and morphological properties modifications undergone by the material have been characterized by mean of Fourier Transform Infrared spectroscopy (FTIR).

2.1. Material and exposure

The studied material is provided in the form of commercial film for agricultural use and it is processed by blow extrusion (Fig.1), (Combette, & Ernout, 2005).

The raw material is the “LDPE B24 / 2” polymerized by the ENIP of Skikda. The films without stabilizing system are produced by the SOFIPLAST Company of Setif. Film cuts were mounted within wooden frames facing south, inclined at 45°, according to the standard NF T51-165. The solar exposure took place at Laghouat, Algeria (38°, 48’ N) from Mars to November. The maximum time of 8 months corresponds to the time at which the films became too brittle to resist to the wind force.

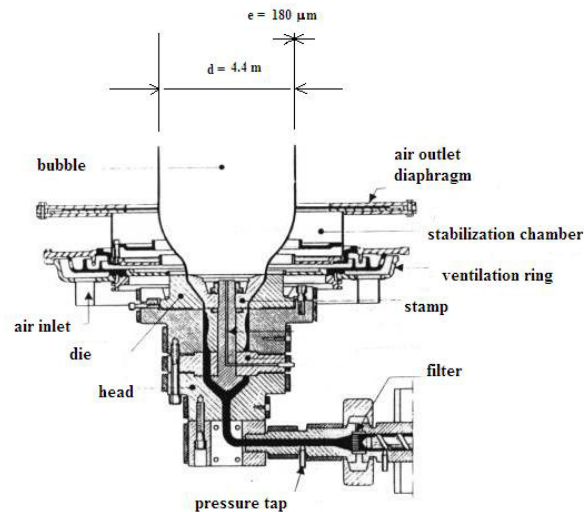


Fig.1. Blow extrusion process.

2.2. Microstructural characterization

Infrared spectroscopy was performed on an FTIR apparatus “Shimadzu FTIR-8400” coupled to a computer. The specific absorption peaks were analyzed from the spectra delivered by the equipment. For each peak the “optical density” (OD) was determined following the usual definition as:

$$OD = \ln(I_0/I) \quad (1)$$

Where (I_0) is the reference infrared intensity corresponding to the baseline of the spectrum at the peak wave number and (I) is the minimum intensity at the base of the peak.

3. Results and discussion

The analysis of the aged film spectra (Fig.2) lets us to see that the main changes occurs in the ranges of wave numbers between 1700 and 1800 cm^{-1} (corresponding to the vibrations of carbonyl groups), 900-1000 cm^{-1} (vibrations of unsaturations) and 3400-3600 cm^{-1} (corresponding to the vibration OH groups) (Mistry,2009 ; Hamid, & All,1988).

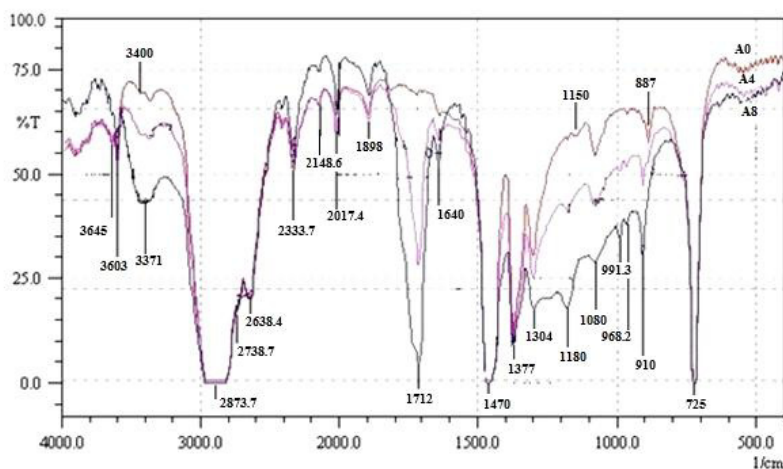


Fig.2. FTIR spectra of LDPE film; unaged (A0), aged for 4 months (A4) and 8 months (A8).

3.1. Kinetic approach of the formation or the disappearance of some photoproducts

From the OD of the absorption bands measured on the IR spectrum for each stage of ageing it is possible to plot their variation versus time. These give us a good insight on the kinetic of formation or disappearance of the photoproducts which intervene in the photochemical process of degradation. In figure 3, is reported the (OD) variation of carbonyl groups (1712 cm^{-1}) versus exposure time. Almost nonexistent in the beginning of ageing, carbonyl groups start a significant growth only after two months of exposure. Above this period of time, oxidation becomes auto-accelerated until the sixth month. Then, it stabilizes and knows a small decrease at the end of the ageing protocol.

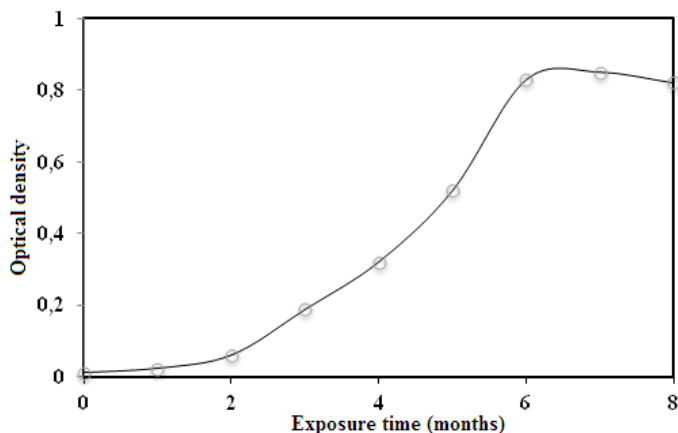


Fig.3. OD variation of carbonyl groups (1712 cm^{-1}) vs exposure time.

The s-shaped curve suggests that the oxidation obeys to an autocatalytic process. The strong intensity of the peak at 1712 cm^{-1} (Fig.2) shows well that carbonyls are the major photoproducts formed from those derived from all the photochemical reactions (Halim, & All, 2000). The main reason is probably the fact that the unformulated PE with stabilizer make it very sensitive toward given UV light wavelengths which can interact with structural defects such as unsaturations or hydroperoxydes (Lacoste, & All, 1991). The shape of the absorption band of carbonyls which points at 1712 cm^{-1} indicate that the main oxidation products formed during ageing are carboxylic acids (Lin, & Argon, 1994). This is the results of the combined action of light and oxygen which react with the structural defects.

The unsaturations are also the subject of great modifications since the base line of the IR spectrum of their corresponding region collapses drastically with exposure time. Among them the pics at 910 and 888 cm^{-1} , corresponding to vinyl (R-CH=CH_2) and vinylidene ($\text{RR}'\text{-C=CH}_2$) respectively, vary in a singular manner. In fact the first disappears while the second grows significantly (Fig.2).

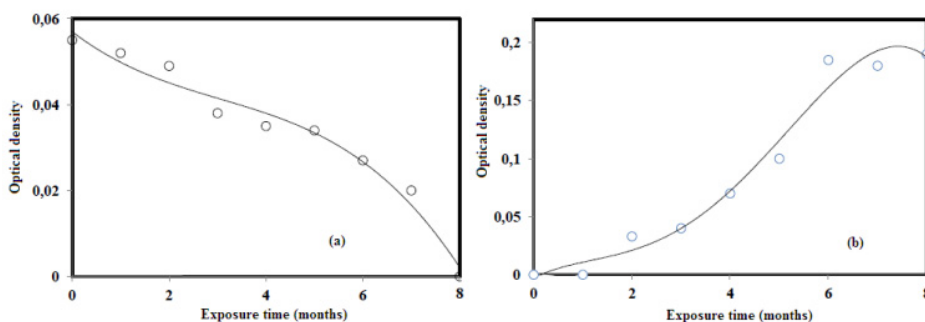


Fig. 4. (a) variation of the vinylidene concentration 888 cm^{-1} ; (b) Variation of the vinyl concentration at 910 cm^{-1} .

The kinetic of disappearance of vinylidenes is reported in figure 4 (a). Slow in the beginning the consummation of this chemical structure becomes accelerated at the end of the protocol. In fact, vinylidenes contribute to the formation of crosslinkings (Carrasco, & All, 2001 ; Candiera, & Ken Busfield, 1997).

Such a reaction is responsible of the average molecular weight decrease, leading to a drastic loss of the mechanical properties (Chabira, & All, 2008 ; Meinel, & Peterlin, 1971).

The vinylidenes identified in the starting product can react with an alkyl radical to produce crosslinking (Fig.7).Consequently to that the average molecular weight is temporally increased (Torikai, & All , 1986; Budtov,& All,1984).

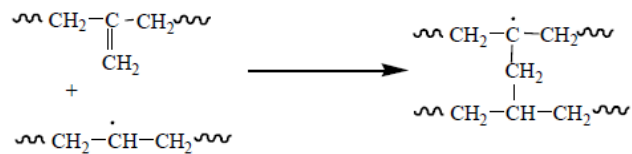


Fig7. Crosslinking reaction between a vinylidene and an alkyl radical.

This indicates that the main reactions taking place during outdoor exposure are crosslinking and chain scissions (Budtov, & All ,1984; Severini, & All , 1988).

4. Conclusion

Polyethylene is an important industrial product which has many applications in our daily lives. One of the most important application of polyethylene is greenhouse covering. However the structural defects of this material acquired during polymerization and processing make it very sensitive towards UV light. Unsaturation and hydroperoxides present in the manufactured product are both light absorptive substances leading to reaction with oxygen for the first or to the formation of macroradicals for the second.

This material photosensitivity promotes degradation, causing a drastic drop of the mechanical properties and reducing significantly the service life time of the films.

From practical point of view the use of FTIR as an investigation tool in such a field of research makes possible the understanding of the impact of UV light on the structural defects existing in unformulated PE film.

The analysis of the IR spectrum and the kinetic study of formation and/or disappearance of the chemical species help in understanding the very complex photochemical mechanisms of degradation.

By reducing the structural defects during polymerization or by adding adequate stabilizers to PE manufacturers might help in preventing excessive plastics wastes in the nature.

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