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EFFECT OF THERMOOXIDATION ON TINUVIN 783 IN LDPE FILMS : CHARACTERIZATION BY UV AND FTIR SPECTROSCOPY

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Abstract : The effect of thermooxidation on Tinuvin 783 which is a hindered amine light stabilizer in LDPE films has been investigated by UV and FTIR spectroscopy. Initially, a standard curve describing the variation of the concentration of Tinuvin 783 in LDPE films was plotted using the method of integration of the band area . The relation obtained was : band area = 19.6249 x [Tinuvin 783]. This equation was then applied to measure the variation of the concentration of Tinuvin 783 in the $0.2\%_{wt}$ stabilized samples which have undergone thermooxidation at 90°C for 98 days. The results showed a considerable decrease in the concentration of Tinuvin 783 by 35% during the first 30 days due to probably the formation of nitroxyl radicals. After this, the concentration was observed to be unchanged and may correspond to the phase of nitroxyl radical regeneration. On the other hand, no chemical change in the stabilized LDPE films was observed by FTIR spectroscopy at 90°C during 98 days while the band characteristic of ketone groups (1720 cm^{-1}) was detected for the unstabilized samples after only 11 days. (LDPE: low density polyethylene; HALS: hindered amine light stabilizer)

1. INTRODUCTION

The development of the plastic industry has motivated the use of plastic films in place of glass in greenhouses. Lower cost of plastic films coupled with easy handling, flexibility and optical properties have made plastic utilization as covering material successful 1). However, the plastic materials have the disadvantage that they are not sufficiently durable. Thus, when films of LDPE are exposed to heat or UV light, they undergo a process of oxidation which leads to the competing reactions of chain scission and cross-linking 2). In this context, considerable work has been devoted to the understanding of the mechanisms involved in the oxidative degradation of LDPE induced by various means such as heat, UV light, natural weathering and ionizing radiations 3-6). On the other hand, many papers concerning the mechanisms of stabilization of phenolic antioxidants and hindered amines (or HALS) in polyolefins have been published 7-9).

More recently, it has been established the effectiveness of hindered amines as heat stabilizers for polypropylene at temperatures below 100°C 10). In spite of this intense activity of research carried out for several decades, there are not yet enough data available in the literature on

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the stabilizing activity of HALS in LDPE films at low temperatures and particularly, that of Tinuvin 783 which is a combination of two polymeric hindered amines, Tinuvin 622 and Chimassorb 944.

In this paper, we discuss the first results dealing with the behavior of Tinuvin 783 in films of LDPE produced by the algerian company ENIP and commercialized under the grade name of B 24/2, which have undergone thermooxidation at 90°C. Consideration of the stabilizing activity of Tinuvin 783 in LDPE films is included here. The determination of the concentration of Tinuvin 783 in LDPE films during thermooxidation is carried out using UV spectroscopy. The degradation is evaluated on the basis of the formation of carbonyl groups detected and dosed by FTIR spectroscopy.

2. EXPERIMENTAL

LDPE used in this study is manufactured by the Algerian Company of Petrochemical Industries (ENIP) under the grade name of B 24/2. The main characteristics are : density = 0.923 g/cm^3 and melt flow index = 0.3 g/10 min.
The stabilizer tested is Tinuvin 783 which is a combination of two hindered amines of high molecular weight, i.e., Tinuvin 622 and Chimassorb 944 , kindly supplied by Ciba-Geigy.
The LDPE films of 80 µm of thickness, were prepared by blown extrusion process at 160 °C. One film contained Tinuvin 783 in the proportion of 0.2 % by weight, while, the other film was free of additives. The samples were placed in an oven at temperature of 90°C with a circulation of air . FTIR spectra and UV spectra were taken on a Shimadzu FTIR 8001 spectrophotometer and a Shimadzu UV-visible 2001 spectrophotometer, respectively.
The carbonyl index ($I_{C=O}$) was calculated from equation (1) :

$$(I_{C=O}) = A_{1720} / A_{720} \qquad (1)$$

The carbonyl index, used as a measure of the degree of degradation, has been evaluated as the ratio between the absorbance at 1720 cm^{-1} and the absorbance at 720 cm^{-1} , which is indicative of the CH_2 groups, to avoid the influence of variations of thickness 11).

3. RESULTS AND DISCUSSION

3.1. Unstabilized LDPE films

Fig.1 shows the UV absorption spectra of unstabilized LDPE films exposed to thermooxidation at 90 °C at different times.
The band having λ_{max} = 275 nm is observed for all the samples except the reference one. The band absorption increases with time and is attributed to the formation of carbonyl groups as expected.

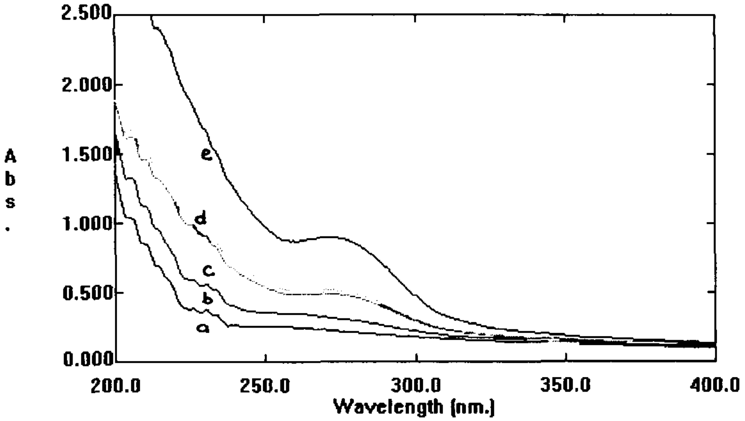

Fig. 1 UV spectra of unstabilized LDPE films exposed to thermooxidation at 90°C as a function of exposure time. a : non oxidized film ; b : 11 days ; c : 21 days ; d : 32 days ; e : 38 days.

In fact, infrared studies of LDPE films subjected to thermooxidation at 90°C have indicated the formation of carbonyl groups with an absorption peak located at 1720 cm^{-1}, characteristic of ketone groups as shown in fig. 2. Furthermore, it has been observed that the rate of carbonyl index increases very slowly at the begining of thermooxidation (< 10 days), then grows rapidly and finally, falls off as it can be seen in fig.3. This finding is in agreement with that reported by Marchal et al. [3] who explained that ketones are produced by a chain reaction in which the consumption of hydroperoxides followed by their regeneration takes place.

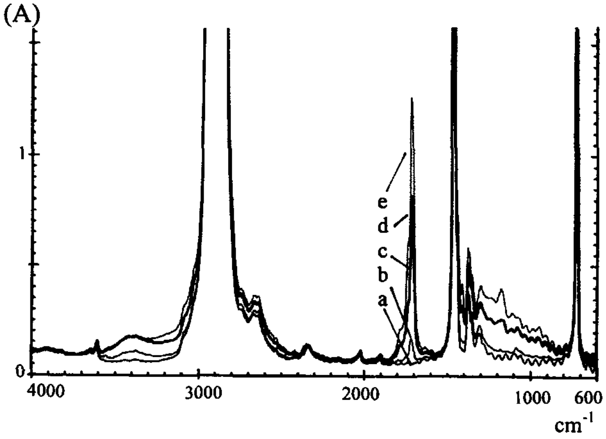

Fig. 2 FTIR spectra of unstabilized LDPE films exposed to thermooxidation at 90° C a: reference sample; b: 11 days; c: 21 days; d: 32 days; e: 38 days.

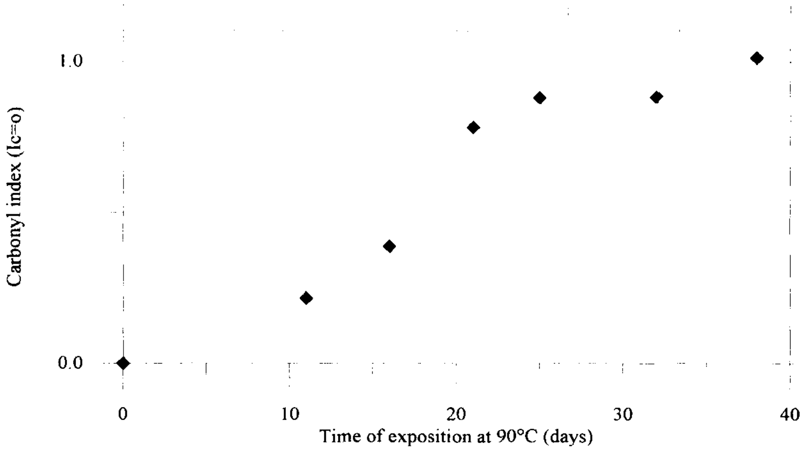

Fig.3 Variation of carbonyl index as a function of time for unstabilized LDPE films exposed to thermooxidation at 90°C.

3.2. Stabilized LDPE films by Tinuvin 783

Various methods have been reported in the literature for the determination of the concentration of stabilizers in polyolefins. Among them, we can cite especially, the IR spectrometry utilized by Zehnacker and Marchal [12)] to determine the concentration of Tinuvin 770 in LDPE films. Another method based up on HPLC was used by Gijsman et al. [13)] to measure the UVA concentration in polyethylene. The results obtained from these methods seem to be acceptable. In our study, the method of band area was applied with the use of a UV-visible spectrophotometer. The method consists of integrating the internal surface of the absorption band, characteristic of Tinuvin 783 in LDPE films for various concentrations, i.e., 0%, 0.1%, 0.2%, 0.4% and 0.6% by weight. From UV spectra as shown in fig.4, the absorption band of Tinuvin 783 in LDPE films is located at $\lambda_{max} = 225$ nm (characteristic band of ternary amines). The baseline was taken between $\lambda_1 = 213$ nm and $\lambda_2 = 238$ nm and all the mathematical calculations were done by a computer.

Although, HALS are generally known to be not constrained by Beer's law [14)], the plot of variation of the band area against the concentration of Tinuvin 783 in LDPE films shows a linear relationship as illustrated in fig.5. This linearity can be expressed by the relation (2):

$$\text{band Area} = 19.6249 \times [\,\text{Tinuvin } 783\,] \qquad (2)$$

where, the band area is calculated in nm^2 and [Tinuvin 783] is the concentration of the stabilizer in LDPE films and given in $(\%)_{wt}$.

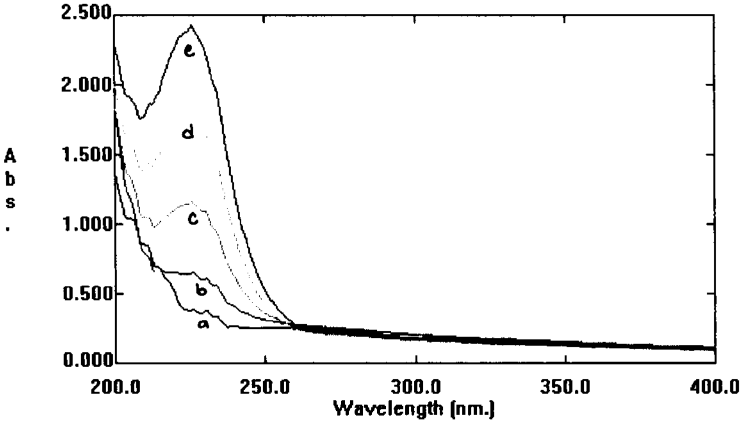

Fig.4 UV spectra of stabilized LDPE films by Tinuvin 783
a : (0% $)_{wt}$, b : $(0.1\%)_{wt}$, c : $(0.2\%)_{wt}$, d : $(0.4\%)_{wt}$, e : $(0.6\%)_{wt}$

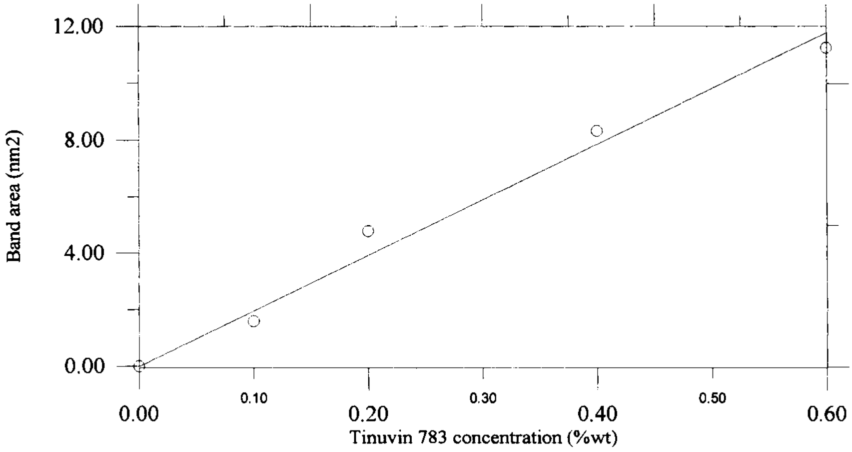

Fig.5 Standard curve of Tinuvin 783 concentration in LDPE films.

The equation (2) allows us to follow the variation of the concentration of Tinuvin 783 occuring during degradation. An application of this relation was carried out on the $(0.2\%)_{wt}$ stabilized sample taking into account the experimental errors owing to the industrial preparation of the films and assuming that the amount of Tinuvin 783 in LDPE which might have been lost by migration was negligible. In fact, this hypothesis was made on the basis of TGA thermograms as shown in fig.6 where the plot of loss of weight (in %) vs temperature recorded for both the reference sample and the samples subjected to thermooxidation at 90°C for 30 and 98 days respectively, was found to be similar.

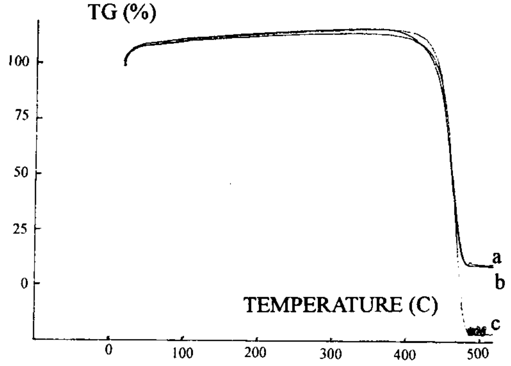

Fig.6 ATG thermogram for the stabilized samples.
a : reference sample, b : 26 days at 90°C, c : 98 days at 90°C

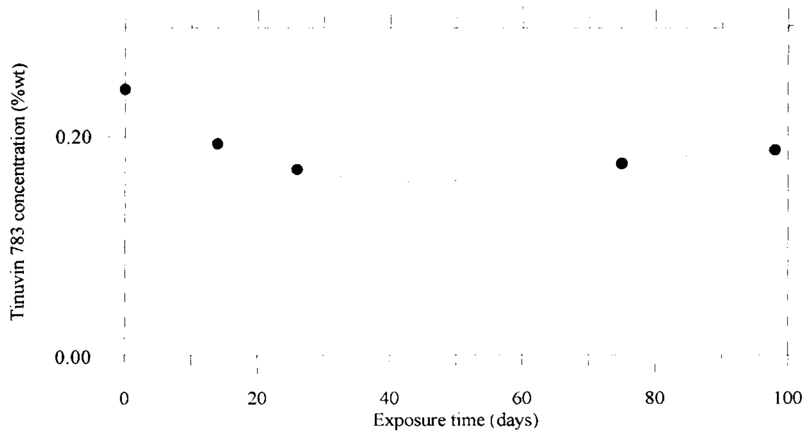

Fig.7 Evolution of Tinuvin 783 concentration in LDPE films as a function of time at 90°C.

From fig.7, it can be seen that after 98 days of heating , the curve is characterized basically by two distinct periods. In the first period of thermooxidation (< 30 days), the concentration of Tinuvin 783 decreases considerably by 35% while, in the second phase it becomes unchanged. It can be suggested thus, that in the first period, Tinuvin 783 was probably subjected to oxidation process leading to the formation of nitroxyl radicals as reported in the literature [8-9] . Although, there are not many data available on thermooxidation, the stabilizing activity of HALS was generally attributed to the nitroxyl radical regeneration from their reaction products, i.e., hydroxylamines >NOH and hydroxylamine ethers >NOR as described in the following scheme [9)] :

$$>NH \rightarrow >NO^{\cdot} \qquad [1]$$

$$>NO^{\cdot} + R^{\cdot} \rightarrow >NOR \qquad [2]$$

$$>NO^{\cdot} + PH \rightarrow >NOH + P^{\cdot} \qquad [3]$$

$$PO^{\cdot}_2 + >NOH \rightarrow PO_2H + >NO^{\cdot} \qquad [4]$$

$$>NOR \xrightarrow{\Delta} >NO^{\cdot} + R^{\cdot} \qquad [5]$$

Scheme 1. Regeneration cycle of nitroxyl radical

The second phase in which the concentration of Tinuvin 783 appeared to be unchanged may be explained by the fact that the amount of stabilizer converted to nitroxyl radical was enough to block the thermooxidation process. This phase may correspond to the regeneration cycle of the nitroxyl radical.

On the other hand, FTIR spectra of the stabilized samples showed no change in the molecular structure of LDPE films as illustrated in fig.8. No noticeable absorption of carbonyl groups was detected during all the heating treatment of the samples at 90°C.This result makes in evidence the effectiveness of Tinuvin 783 as a good antioxidant.

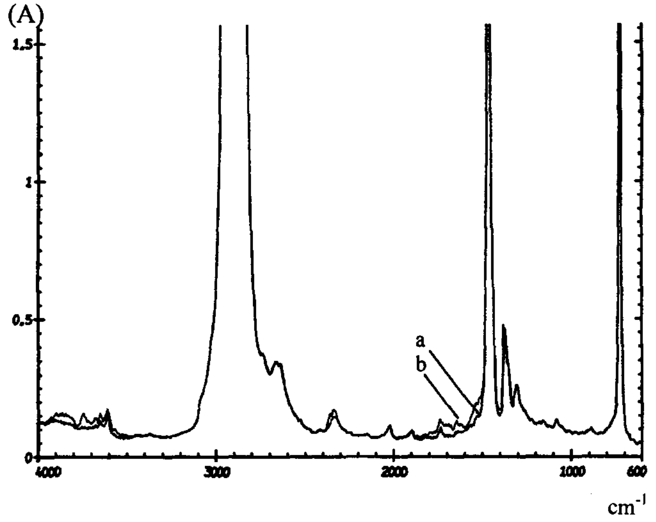

Fig.8 FTIR spectra of stabiliozed LDPE films by Tinuvin 783 under the concentration of $(0.2\%)_{wt}$ as a function of time. a : reference sample ; b : 98 days at 90°C.

4. CONCLUSION

Based up on the experimental work, the results obtained confirm the fact that Tinuvin 783 behaves as antioxidant since no absorption band of hydroperoxide groups nor ketone groups was observed in LDPE films during thermooxidation. On the other hand, the mechanism of stabilization of Tinuvin 783 remains still unsolved. However, further work in this field is expected in the near future to explore this problem.

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