

EFFECTIVENESS OF CERTAIN STABILIZERS ON THE
AGEING OF POLYETHYLENE FILMS

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ABSTRACT

The effectiveness of different phenolic antioxidants on high density polyethylene (HDPE) and low density polyethylene (LDPE) has been studied by the isothermal chemiluminescence method. The decreasing order of the antioxidant efficiency for these polymers is as follows:

Irganox 1010 >> Etanox 330 > Irganox 1076 (Hostanox 016) > Topanol OC

RESUMO

*Foi estudada a eficiência de vários antioxidantes fenólicos sobre polietileno de alta densidade (PEAD) e polietileno de baixa densidade (PEBD) usando técnicas de quimi-luminescência isotérmica. A ordem decrescente de eficiência antioxidante para os dois polímeros foi a seguinte:
Irganox 1010 >> Etanox 330 > Irganox 1076 (Hostanox 016) > Topanol OC.*

Keywords: polyethylene ; thermal - oxidative destruction ; phenolic antioxidants; chemiluminescence

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INTRODUCTION

The study of heat stabilization of polyethylene films by commercial antioxidants is not merely of great practical importance but it is also of scientific interest. Extrusion and blowing of polyethylene films expose them to severe degradative conditions, and the need for effective stabilization is therefore an absolute necessity. Stabilizers for this purpose must themselves be heat-resistant and should not sublime or decompose below processing temperature. Approximately 60 antioxidants are marketed in the world for the manufacturing and polyethylene - using industries¹. The choice of stabilizer for a particular type of polyethylene is governed by the specific nature of the changes which occur in it during the primary working up stage and in storage.

The chemiluminescence (CL) method has been recognised as a useful tool for the evaluation of stabilizers²⁻⁶. In this work, the CL method was applied to evaluate the thermal oxidative stability of low density polyethylene (LDPE) and high density polyethylene (HDPE), containing certain phenolic antioxidants.

EXPERIMENTAL

Both polyethylene types (films of 0.1 mm thickness) with the characteristics specified in Table 1, were kindly supplied by ARPECHIM Pitesti, Romania.

Table 1. Some characteristics of the polymers studied

| Type | Sort | Branching (CH ₃ /1000 C) | Crystallinity (%) | MFI (g / 10 min) | Stabilizer concentration (%) |
|------|-----------------|--|----------------------|---------------------|------------------------------------|
| LDPE | A-2-2-FMA / 002 | 20 | 52 | 0.33 | 0.02 |
| HDPE | A-5-3-MB / 064 | 0.5 | 72 | 5.09 | 0.03 |

The compounds chosen for study were tetrakis (methylene - 3,5 - di - tert - butyl - 4 - hydroxyphenyl) methane propionate (Irganox 1010), 1,3,5 - trimethyl - 2,4,6 - tris (3,5 - di - tert - butyl - 4 - hydroxy benzyl) benzene (Etanox 330), octadecyl - 3 - (3', 5' - di - tert - butyl - 4 hydroxyphenyl) propionate (Irganox 1076 or Hostanox 016) and 2,6 - di - tert - butyl - 4 - methyl phenol (Topanol OC).

Chemiluminescence spectra of the films samples were recorded on a OL - 94 chemiluminescence apparatus manufactured by ICPE, Romania. Chemiluminescence intensity versus time was recorded at constant temperature (190°C) under air flow (1.12 l / min).

RESULTS AND DISCUSSION

Figures 1 and 2 show the chemiluminescence of LDPE and HDPE respectively, both unstabilized and stabilized with the above mentioned antioxidants. As can be seen, some S-shaped CL curves present small shoulders that denote two consecutive antioxidation processes. This observation is in a good agreement with Chien's conclusions⁷ about two stages of the decomposition of hydroperoxides in polyethylene.

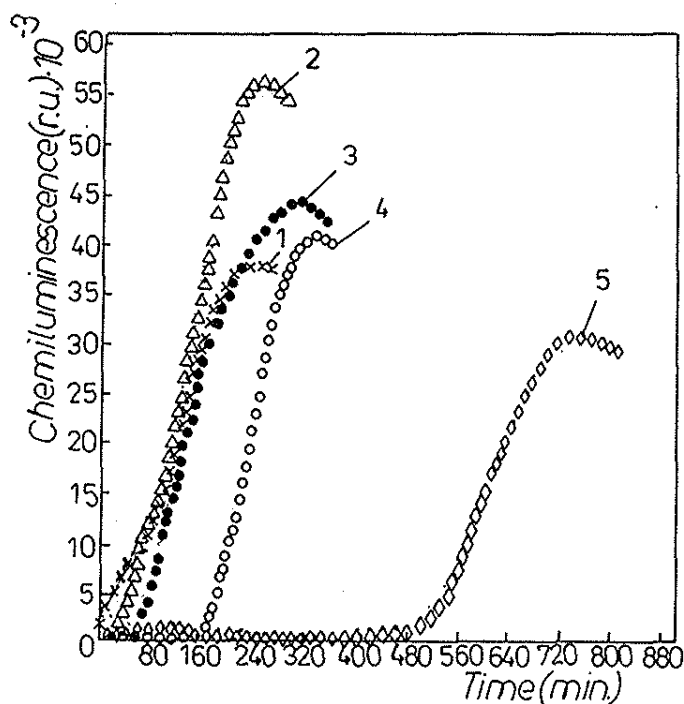


Fig.1. Chemiluminescence intensity as a function of time for oxidation (190°C, air) of LDPE unstabilized (1) and stabilized with Topanol OC (2), Irganox 1076 (3), Etanox 330 (4) and Irganox 1010 (5)

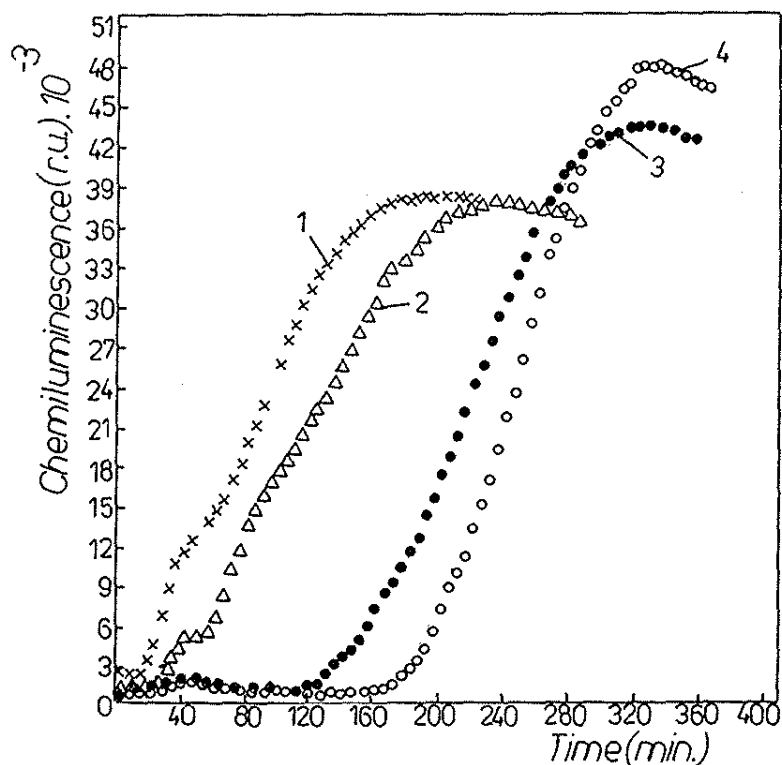


Fig. 2. Chemiluminescence intensity as a function of time for oxidation (190°C, air) of HDPE unstabilized (1) and stabilized with Topanol OC (2), Hostanox 01 (3) and Etanox 330 (4)

Table 2. Values of the kinetic CL parameters (190°C, air) for LDPE and HDPE

| Antioxidant | LDPE | | | | HDPE | | | |
|---------------------------------|-----------------|-------------------------------|---------------------|---------------------|-----------------|-------------------------------|---------------------|---------------------|
| | t_l (min.) | V_{ox}^{max} (r.u./min.) | I_{max} (r.u.) | t_{max} (min.) | t_l (min.) | V_{ox}^{max} (r.u./min.) | I_{max} (r.u.) | t_{max} (min.) |
| none | 19 | 226 | 37768 | 258 | 28 | 338 | 42008 | 210 |
| Irganox 1010 | 526 | 171 | 30458 | 765 | 704 | 165 | 28327 | 600 |
| Etanox 330 | 185 | 354 | 40565 | 345 | 192 | 477 | 48039 | 340 |
| Irganox 1078 or Hostanox 016 | 71 | 311 | 44236 | 315 | 155 | 370 | 43443 | 330 |
| Topanol OC | 52 | 302 | 55903 | 259 | 43 | 384 | 37601 | 235 |

The kinetic analysis of chemiluminescence data was made using the following parameters (Table 2): the induction period (t_i), the maximum oxidation rate (V_{ox}^{max}), the CL emission maximum intensity (I_{max}) and the time for reaching the CL maximum emission value (t_{max}).

Table 3. The antioxidant effectiveness parameters for LDPE and HDPE (190°C, air)

| Antioxidant | LDPE | | HDPE | |
|---------------------------------|------|------|------|------|
| | A | S | A | S |
| Irganox 1010 | 15.4 | 0.76 | 45.1 | 0.49 |
| Etanox 330 | 5.0 | 1.57 | 10.9 | 1.41 |
| Irganox 1076 or Hostanox 016 | 1.6 | 1.38 | 8.5 | 1.09 |
| Topanol OC | 1.0 | 1.34 | 1.0 | 1.14 |

Table 3 shows the antioxidant activity (A) expressed by the relation^{8,9}:

$$A = (t_x - t_0) / (t_s - t_0)$$

where t_0 , t_x and t_s are, respectively, the induction periods graphically deduced from chemiluminograms for pure polymer, for polymer with the particular antioxidant and with Topanol OC, which was taken as a standard.

The relative stability (S) was calculated using the following relation⁶:

$$S = (V_{ox})_x / (V_{ox})_0$$

where $(V_{ox})_0$ and $(V_{ox})_x$ are the maximum oxidation rate for pure and antioxidant-protected polymer, respectively. This parameter is also given in Table 3.

As can be seen, all stabilizers studied inhibited LDPE and HDPE degradation in air at 190°C by trapping the radicals formed in the matrix. This is confirmed by the increased values of the time parameters t_i and t_{max} in comparison to the blank sample. The V_{ox}^{max} parameter decreased only slightly, due to the high temperature of the oxidation reaction, when the most analysed antioxidants cannot be active after the induction period has ceased. A similar trend was observed for I_{max} parameter.

The product Irganox 1010 exhibits the highest protection capability among the antioxidant studied. For this antioxidant the highest increase in the length of the induction period was obtained and the lowest V_{ox}^{max} parameter was recorded. This means that the oxidation products of Irganox 1010 are still able to participate as protecting agents in the propagation period. This is also proved by the lowest I_{max} value recorded in the case of this stabilizer (i.e. minimum quantities of hydroperoxide are formed).

On the other hand, as can be seen in Table 3, the antioxidant efficiencies for HDPE samples were much higher than that for LDPE ones. Judging from the time chemiluminescence parameters the decreasing order of the antioxidant efficiency in both polymers is as follows:

Irganox 1010 >> Etanox 330 > Irganox 1076 (Hostanox 016) > Topanol OC

This antioxidant ranking is in a good agreement with the order obtained by the other methods¹⁰⁻¹². This fact apparently indicates that the isothermal chemiluminescence method can be used for evaluating of thermal oxidative stability of the polyolefinic films. One of the advantages is that only a very small amount (ca. 35 mg) is required for the measurement of the chemiluminescence.

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