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### Irradiation of Polyethylene in Presence of Several Additives as Studied by Chemiluminescence

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## IRRADIATION OF POLYETHYLENE IN PRESENCE OF SEVERAL ADDITIVES AS STUDIED BY CHEMILUMINESCENCE

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### ABSTRACT

The protecting effect against radiation induced oxidation of polyethylene provided by several additives, namely pyrene, Irganox 1222 and Irganox 1010 has been investigated by mean of FTIR spectroscopy and chemiluminescence (CL) technique. Pyrene appears to be more effective and more stable to irradiation than phenolic antioxidants. Thus, about half of initial pyrene seems to remain unchanged after an exposure of the material to  $\gamma^{60}\text{Co}$  rays at 240 kGy (dose rate 1 kGy/h) in presence of air. Under the same conditions, about 90% of initial Irganox 1010 seems to be consumed as indicate a comparison of induction oxidation times of initial and irradiated material. The stabilizing effect of the residues resulted by pyrolysis at 850°C in inert atmosphere of several polymers, such as polyacrylonitrile, polyvinylchloride and methyl cellulose is discussed as well.

## INTRODUCTION

The interaction of polymeric materials with ionizing radiation is involved in several modern technologies such as radiation processing, production of energy in nuclear plants a.s.o. It is well known that as a result of interaction of macromolecules with ionizing radiation, highly excited electronic states result within the polymer. These can lead to bond scission and formed free radicals are primary reactive species responsible for radiation induced chemistry in most organic systems. Oxidation during or subsequent irradiation is an undesired process because it can decrease the service life of the material. Therefore, important efforts are still made in order to suppress it by means of synthesis of new materials having inherently high radiation resistance and the use of effective additives [1]. Most of the additive molecules found to have an antirad activity can be grouped into two categories according to their mode of action:

(1) *Radical scavengers*. Some substances such as hindered phenols, amines, quinones, thiols and others have a great efficiency in trapping of radicals which result in polymer matrix. Among them, hindered phenols and secondary amines are also widely used as stabilizers, and they are quite stable under irradiation. These stabilizers can be used singly or combined to give synergistic effects [2];

(2) *Energy scavengers* can deactivate to their ground state the excited electronic states of the host polymer. It was found in studies on several model compounds that aromatic molecules are very effective in reducing radiation damage [3, 4, 5]. They act as scavengers for excited electronic states, but a charge transfer mechanism is also considered to play an important role [6]. Recent papers refer to the effectiveness of some polynuclear aromatic hydrocarbons on stabilization of polymers against radiation induced oxidation [1, 7, 8].

It is also known that pyrolysis of several polymers, such as polyacrylonitrile, polyvinylchloride, cellulose a.s.o. at 500-900°C lead to solid residues with condensed polycyclic structures [9, 10] consisting of graphite like lattices and high spin molecules [11].

The aim of this work was to compare the effectiveness in protection of polyethylene against radiation induced oxidation of a polynuclear aromatic hydrocarbon (pyrene) with those of two phenolic antioxidants, namely Irganox 1010 and Irganox 1222.

## EXPERIMENTAL

### Materials

Commercial grade low density polyethylene (LDPE) K322 type, a product of SC BRAZI SA ROMANIA and linear low density polyethylene (LLDPE) were used as polymers. LLDPE was kindly supplied by a Japanese company. It was specially synthesized to be free of additives. The antioxidant contained by LDPE (IRGANOX 1076) was removed by repeated operations consisting in hot o-xylene dissolution, methanol precipitation, filtration and washing.

Phenolic antioxidants, namely IRGANOX 1010 and IRGANOX 1222 or a polynuclear hydrocarbon, namely pyrene, were used as stabilizers.

The polymeric residues resulted from pyrolysis of polyacrylonitrile, polyvinyl chloride, or polyvinyl acetate were also used, single or as binary mixtures with IRGANOX 1076, to stabilize LDPE. Pyrolysis of polymer samples has been carried out for 2 hours at 850°C in argon .

The polyethylene samples were mixed with additives in the presence of ethyl alcohol or tetrachloroethylene, then the samples were kept in vacuum at room temperature for 24 hours, in order to remove the solvent. During solvent evaporation, the samples were repeatedly mixed . The obtained mixtures were hot pressed under vacuum to a film ca. 40 mm diameter and 120 (5 mm thickness, which were used for subsequent experiments after cut at suitable dimensions. Some samples, namely those containing LDPE and pyrolyzed polymers used in CL experiments for testing their thermal stability, were used as powders.

### Methods

Chemiluminescence spectra were recorded on a CL analyzer OX-7-TC (Tohoku Electronic Ind. Co. Ltd.) or on a Oxyluminograph OL 94 (ICPE) apparatus. The chemiluminescence analysers were coupled to computers that achieved CL, background, time and temperature data acquisition.

Measurement programs were chosen to record both CL in inert (nitrogen) and oxidative (oxygen) atmosphere.

Infrared spectra of the initial and  $\gamma$ -irradiated film samples were recorded on a Fourier Transform Infrared (FT-IR) spectrophotometer (JASCO FT IR Model MCT 5E type, JASCO Corp. Japan) and on a IR 75 Karl Zeiss Jena spectrophotometer.

TABLE 1. Kinetic Parameters of Oxidation of LDPE Containing Pyrene Calculated from CL curves. Conditions: Apparatus: Tohoku OX-7-TC; Temperature: 170°C; Oxygen Flow: 60 ml/min; Sample Size: 5 mm x 5 mm

| Pyrene (%) | $t_i$ (min) | $t_{0.5}$ (min.) | $t_{max}$ (min.) | $I_{mxx}$ (u.r./g) | $V_{ox}$ (%/min.) |
|------------|-------------|------------------|------------------|--------------------|-------------------|
| 0          | -           | 7.5              | 23               | 6 533              | 9.29              |
| 0.25       | 5.5         | 15               | 22               | 7 795              | 10.20             |
| 0.50       | 4.5         | 11               | 20               | 7 642              | 9.27              |
| 0.75       | 6.5         | 15               | 23               | 7 649              | 7.29              |

TABLE 2. Kinetic Parameters of Oxidation of LDPE Containing Pyrene Calculated from CL Curves. Conditions: Apparatus: OL 94; Temperature: 180°C; Air Flow: 300 ml/min; Sample Weight: 20 mg, Powder

| Pyrolyzed polymer     | $t_i$ (min) | $t_{0.5}$ (min.) | $t_{max}$ (min.) | $I_{mxx}$ (u.r./g) | $V_{ox}$ (%/min.) |
|-----------------------|-------------|------------------|------------------|--------------------|-------------------|
| -                     | -           | 93               | 186              | 63 350             | 0,65              |
| Polycellulose acetate | 20          | 104              | 235              | 88 450             | 0.51              |
| polyacrylonitrile     | 10          | 96               | 210              | 79 550             | 0.59              |
| polyvinylchloride     | 15          | 80               | 170              | 97 700             | 850               |

The samples were subjected to action of  $\gamma$ -rays in presence of air at room temperature, in a  $\gamma^{60}\text{Co}$  facility at the Japan Atomic Energy Institute-Takasaki Radiation Research Establishment and in a  $\gamma$ - $^{137}\text{Cs}$  Gammator M-38 facility at the University of Bucharest.

## RESULTS AND DISCUSSION

The thermal stability at 170°C of the LLDPE samples containing pyrene is rather similar to that of the "free of additives" sample. However, a slight reduction in oxidation rate and an increase in induction period of oxidation, described by  $t_{1/2}$  parameter (see Table 1), suggest a small increasing in stability caused by pyrene.

CL curves recorded from the samples containing pyrolyzed polymers lead to similar conclusions (see Table 2). It is known that the ionization potential decreases from benzene to graphite as the number of quinoidic rings in polynuclear

aromatic molecules [12-15] increases. On the other hand, the stability of the compounds provided by the charge transfer increases by increasing the conjugation [16]. Taking into account the aromatic polynuclear structure of both pyrene and these pyrolyzed compounds [9, 17], it can be assumed that the stabilizing effect of these compounds is due to a charge transfer from the aromatic compound to  $RO_2$  radical of the polymer.

The maximum of CL intensity is slightly higher in the presence of both pyrene and pyrolyzed polymers, perhaps due to changes induced by their condensed aromatic rings in photochemical yield of CL emission from polymer.

Irradiation in the presence of air resulted in an intense oxidation as suggested by the analysis of IR spectra (see Tables 3 and 4) and CL curves (Figure 1).

The effectiveness of Irganox 1010 is surprisingly low taking into account its high capability to suppress thermal oxidation. This fact could be explained by the lower mobility of its great molecule ( $M_w = 1144$  g/mol) as compared with that of Irganox 1222 ( $M_w = 372$  g/mol). It was also emphasized that the depletion of the phenolic antioxidants in polymeric materials subjected to ionizing radiations is caused not only by interactions with peroxy radicals, but also by radiation induced scission of their molecule [18]. On the other hand, the effectiveness of these additives is controlled by their mobility that decreases as the molecular weight [19] increases.

Pyrene appears to be the most effective of the low molecular weight additives studied. Its high effectiveness is due perhaps to a different mechanism of action based on both energy and charge transfer [3, 4, 6, 8].

IR spectra of the irradiated LDPE samples containing pyrolyzed polymers exhibit low concentrations of oxidation products suggesting the high protection capability of these compounds as compared with phenol antioxidants. On the basis of the absorbance at  $1720\text{ cm}^{-1}$ , the effectiveness of these piro-polymers could be ranked as follows:

**piro-MC > piro-PE (piro > CA (piro-PAN > Irganox 1076 > free of additives LDPE**

It should be noted that the structure of piro-PE (fullerene type) is different from those of other pyrolyzed polymers (graphite type) because it resulted as a cooled fraction in a low temperature zone of the furnace.

CL curves recorded under nitrogen from irradiated samples containing pyrene exhibit a higher intensity as compared to the signal from the corresponding free of additives sample (see Figure 2). It could be due to the fluorophore effect of

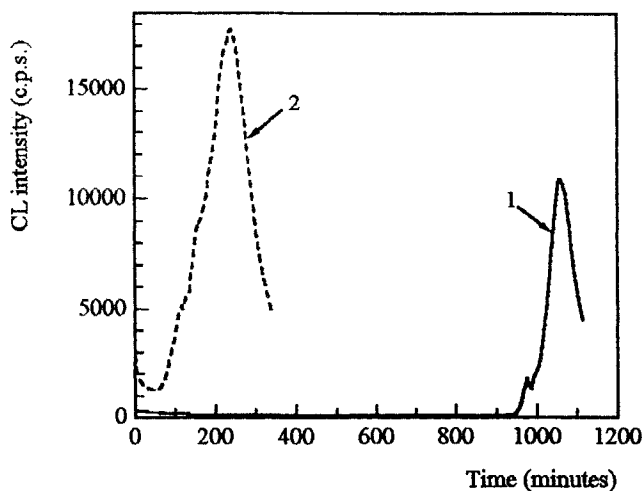
TABLE 3. IR Absorbance (A/d Values; A = Absorbance, d = Sample Thickness) of  $\gamma$ -Irradiated (240 kGy) LLDPE Samples Containing Various Additives. Conditions: Irradiation:  $\gamma^{60}\text{Co}$ , 10 kGy/h, in Air; IR Measurements: Spectrophotometer JASCO FT-IR

| Wavenumber<br>( $\text{cm}^{-1}$ ) | Assignment  | Initial,<br>unirradiated | Free of<br>additives | 240 kGy irradiated sample |                           |                           |                  |                  |       |
|------------------------------------|-------------|--------------------------|----------------------|---------------------------|---------------------------|---------------------------|------------------|------------------|-------|
|                                    |             |                          |                      | Irganox<br>(0.5%)         | Irganox<br>1010<br>(1.0%) | Irganox<br>1222<br>(1.0%) | Pyrene<br>(0.5%) | Pyrene<br>(1.0%) |       |
| 3,555                              | free ROOH   | 0.01                     | 0.93                 | 1.25                      | 1.03                      | 0.62                      | 0.50             | 0.59             | 0.43  |
| 3,410                              | assoc. ROOH | 0.83                     | 4.50                 | 5.32                      | 4.88                      | 2.60                      | 2.70             | 2.17             | 2.17  |
| 3,371                              | HO groups   | 1.17                     | 4.50                 | 5.32                      | 4.92                      | 2.88                      | 4.28             | 2.48             | 2.30  |
| 1,743                              | esters      | -                        | 11.47                | -                         | 11.47                     | 5.24                      | 4.96             | 4.65             | 4.08  |
| 1,733                              | aldehydes   | -                        | 13.64                | 13.59                     | 11.84                     | 7.25                      | 7.13             | 6.67             | 5.99  |
| 1,720                              | ketones     | -                        | 29.76                | 23.47                     | 17.98                     | 17.02                     | 16.43            | 16.43            | 13.89 |
| 1,712                              | acids       | -                        | 20.46                | 14.90                     | 10.85                     | 6.20                      | 6.26             | 6.45             | 5.16  |

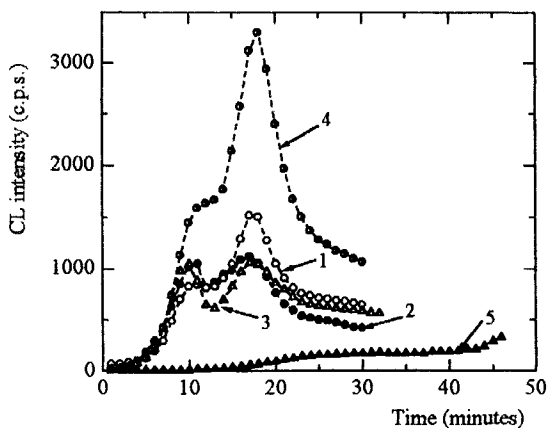
TABLE 4. IR Absorbances (A/d Values; A = Absorbance, d = Sample Thickness, in cm) of  $\gamma$ -Irradiated (40 kGy) LLDPE Samples Containing Irganox 1076 or Various Pyrolyzed Polymers. Conditions: Irradiation:  $\gamma$  137Cs, , 550 Gy/h, in air; IR measurements: IR 75 Spectrophotometer, Film Thickness ca. 110 $\mu$ m

| Wavenumber<br>(cm <sup>-1</sup> ) | none, 0 kGy | A/d of irradiated 40 kGy LDPE samples containing various additives (0.5%) |              |          |         |          |         |         |
|-----------------------------------|-------------|---|--------------|----------|---------|----------|---------|---------|
|                                   |             | none  | Irganox 1076 | piro-PVC | piro-PE | piro-PAN | piro-CA | piro-MC |
| 3,555                             | -           | 11.11   | 8.76         | 8.20     | 14.91   | 5.29     | 4.71    | 9.18    |
| 3,410                             | -           | 12.02   | 9.52         | 12.47    | 27.14   | 5.50     | 14.78   | 17.23   |
| 3,371                             | -           | 12.02   | 8.97         | 10.71    | 32.06   | 9.36     | 13.02   | 16.19   |
| 1,743                             | 2.78        | 7.53  | 3.30         | 4.38     | 3.79    | 5.31     | 3.55    | 2.79    |
| 1,733                             | 2.43        | 9.84  | 3.97         | 4.75     | 2.76    | 5.68     | 5.01    | 5.66    |
| 1,720                             | 4.93        | 9.84  | 8.83         | 8.19     | 4.86    | 8.46     | 6.49    | 2.37    |
| 1,712                             | 6.39        | 9.84  | 9.54         | 8.97     | 5.57    | 8.46     | 6.54    | 3.59    |





**Figure 1.** CL curves recorded in oxygen atmosphere from LLDPE stabilized with 1% IRGANOX 1330: 1- initial, unirradiated; 2- $\gamma$  irradiated 240 kGy. Conditions: Irradiation:  $\gamma^{60}\text{Co}$ , 10 kGy/h, in air; CL measurements: apparatus: Tohoku OX-7C; temperature: 170°C; oxygen flow: 60 ml/min; sample size: 5 mm x 5 mm.



**Figure 2.** CL curves recorded in inert atmosphere (nitrogen) from LLDPE samples containing several additives: 1-free of additives sample; 2-Irganox 1010 (0.5%); 3- Irganox 1222 (0.5%); 4 - Pyrene 0,5%; 5 - Pyrene 100%. Conditions: apparatus. Tohoku OX-7C; heating rate (25-170°C): 10°C/min.; nitrogen flow: 90 ml/min.; sample size: 5 mm x 5 mm; weight of pyrene sample: 10 mg.

the aromatic molecules. The relative weak signal recorded from irradiated pure pyrene supports this assumption.

CL curves in Figures 3 and 4 illustrate the changes in relative concentration of CL emitting species induced by irradiation in the case of LLDPE stabilized with Irganox 1010 and pyrene, respectively. The two CL maxima observed when an irradiated polymer sample is heated in inert atmosphere could be assigned to trapped peroxyradicals and hydroperoxides [20]. At low irradiation doses, the trapped radical seems to be the main emitting component, higher doses of hydroperoxides exceed trapped radicals which seem to reach a constant level, most of them leading to subsequent oxidation reactions [21]. The evolution of this maxima is similar in both cases, but the intensity of CL emission is considerably higher with pyrene samples.

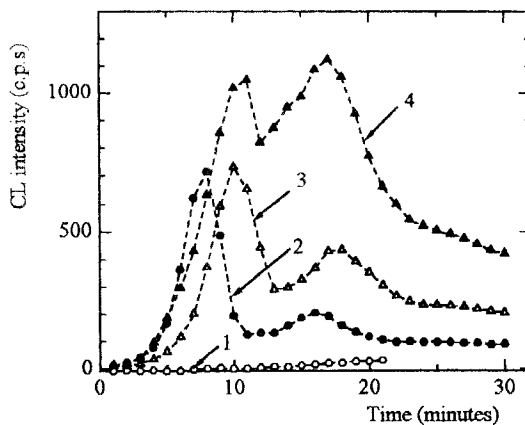
The thermal stability of irradiated polymeric materials is strongly affected by the subsequent reactions of trapped peroxy radicals and hydroperoxides induced by irradiation.. These species are usually destroyed by a thermal treatment in inert atmosphere. The stability of the resulting material depends on the nature and concentration of the remaining stabilizer.

This behavior could be explained taking into account the antioxidant consumption during irradiation and/or destruction of the reactive species upon heating under inert atmosphere.

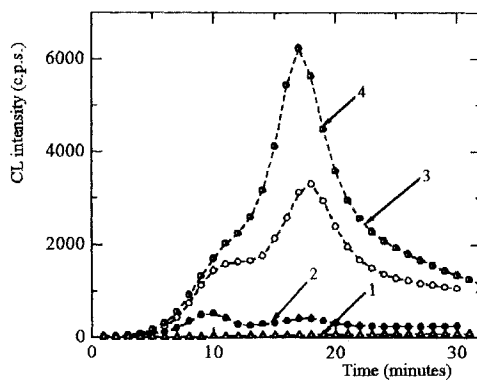
A comparison of the CL induction time values leads to the conclusion that more than 90% of the initial antioxidant is consumed upon irradiation (see Figure 1). On the other hand, above half of the pyrene seems to be unchanged as suggested the IR absorption band at  $840\text{cm}^{-1}$ . These conclusions are in good agreement to data reported by Clough and Gillen [1].

At higher pyrene concentrations (over 1%), the samples exhibited an enhanced stability (see Figure 5). A similar effect was observed in the case of irradiated samples containing pyrenols [8]. It was assigned to an interaction of a stable radical of pyrenol with peroxy radicals of polymer.

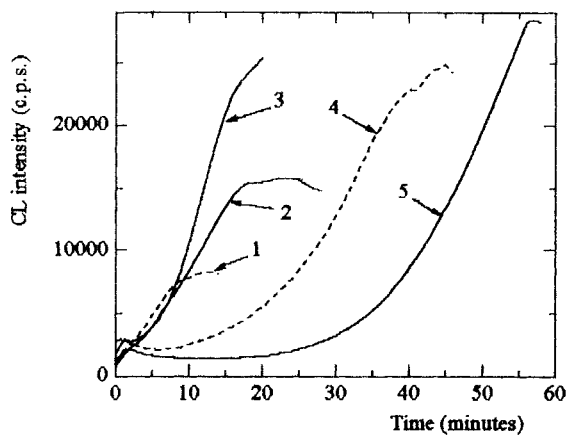
Binary mixtures of Irganox 1222 and pyrene exhibited antagonistic interaction in LLDPE, but the cooperative effect of Irganox 1010 with pyrene was found to be a synergistic one. Similar conclusions concerning the synergistic effects of various phenolic antioxidants and pyrene in protection of LDPE were reported in a previous paper [8]. A similar effect has been also observed in the case of a LDPE sample stabilized with a binary mixture of Irganox 1076 and pyrolyzed PVC (see Figure 6). These synergistic effects could be explained on the basis of either a non-chemical interaction that involves a filling compound [22, 23] or a charge transfer interaction involving polynuclear aromatic molecules [24].



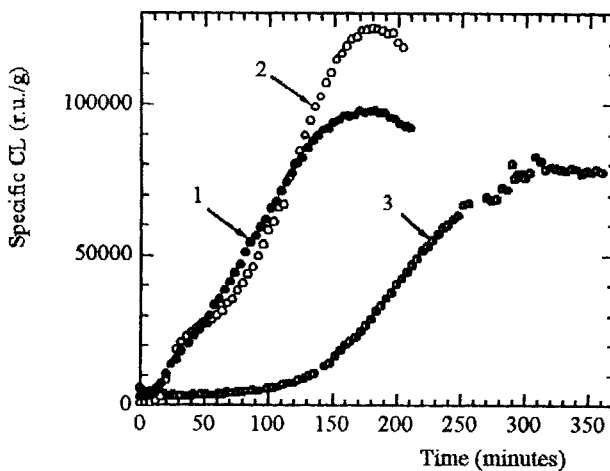
**Figure 3.** CL curves from  $\gamma$ -irradiated LLDPE samples containing 0,5% IRGANOX 1010: 1 - initial, unirradiated; 2 - 25 kGy; 3 - 80 kGy; 4 - 240 kGy. Conditions: Irradiation:  $\gamma^{60}\text{Co}$ , 10 kGy/h, in air; CL measurements: apparatus: Tohoku OX-7C; heating rate (25÷170°C): 10°C/min; nitrogen flow: 90 ml/min; sample size: 5 mm x 5 mm.



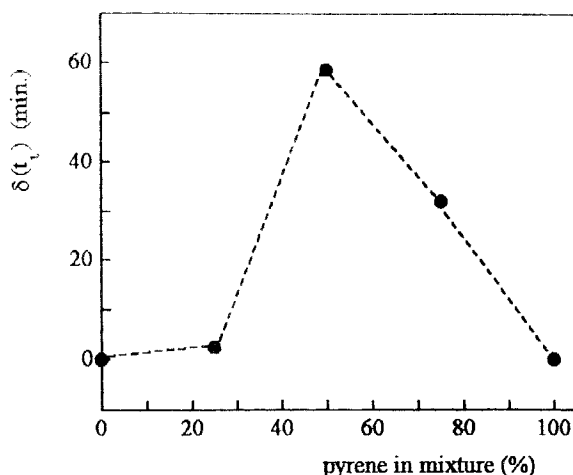
**Figure 4.** CL curves from  $\gamma$ -irradiated LLDPE samples containing 0.5% pyrene: 1 - initial, unirradiated; 2 - 25 kGy; 3 - 240 kGy; 4 - 480 kGy. Conditions: Irradiation:  $\gamma^{60}\text{Co}$ , 10 kGy/h, in air; CL measurements: apparatus: Tohoku OX-7C; heating rate (25÷170°C): 10°C/min; nitrogen flow: 90 ml/min. sample size: 5 mm x 5 mm.



**Figure 5.** CL curves from irradiated (240 kGy) LLDPE samples containing pyrene: 1 - free of additives; 2- 0.5 %; 3- 1 %; 4 - 2 %; 5 - 3%.



**Figure 6.** CL curves from LDPE stabilized with Irganox 1076 or/and piro-PVC: 1 - 0.5% piro-PVC; 2 - 0.1% Irganox 1076; 3 - 0.5% piro-PVC + 0.1% Irganox 1076. Conditions: apparatus: OL 94; temperature: 180°C; air flow: 330 ml/min; sample weight: 20 mg, powder.



**Figure 7.** Dependence of  $\delta(t_i)$  parameter ( $t_{i, \text{mixture}} - (t_{i, \text{Irganox 1010}} + t_{i, \text{pyrene}})$ ) on pyrene concentration for several LLDPE irradiated samples (240 kGy). Conditions: Irradiation:  $\gamma^{60}\text{Co}$ , 10 kGy/h, in air; CL measurements: apparatus: Tohoku OX -7-TC; temperature: 170°C; oxygen flow: 60 ml/min; sample size: 5mm x 5mm.

No effect of the Irganox 1222/pyrene mixture was observed upon subsequent oxidation at 170°C in oxygen of  $\gamma$ -irradiated samples, CL parameters being similar to those corresponding to the sample without additives irradiated and measured in the same conditions. A synergistic effect was observed in the case of the mixture of Irganox 1010 and pyrene. This effect exhibits a maximum of intensity at a weight ratio of 1:1 as Figure 7 shows. Similar behavior of mixtures of pyrolyzed polymers and phenol antioxidants was observed.

## CONCLUSION

Chemiluminescence under nitrogen or in oxidative atmosphere provides useful data for characterization of the radiation induced changes in polymers. Aromatic compounds containing fused rings such as pyrene or the residues resulting by pyrolysis of certain polymers in argon at elevated temperatures exhibit a protecting effect against thermal or radiation induced oxidation, perhaps acting by aenergy and charge transfer mechanism.

The synergistic effects observed in stabilization against both thermal and radiation induced oxidation could be of interest for practical appliances.

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