

# SYNERGISTIC EFFECT OF STABILIZER COUPLES SELENIUM-HINDERED PHENOLS IN EPDM UNDER IONIZING RADIATION

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This paper presents the synergistic effect of two antioxidant couples Se-Irganox 1076 and Se-Irganox 1010 induced in ethylene-propylene terpolymer (EPDM). Oxygen uptake was applied at 19°C and normal air pressure. This investigation was performed on irradiated polymer samples at three doses: 100, 200 and 300 kGy. Co-operative factors reveal values between 2,8 and 5,3.

## Introduction

The quality of polymeric materials determines the lifetime (endurance) of various products under different operation conditions. Several environmental factors like oxygen, humidity, sunlight, ionizing radiation, chemical reagents induce a progressive damage after energy transfer onto macromolecular materials. This degradation process consists of changes in mechanical, thermal or electrical properties. In fact, incidental high-energy radiation produces structural modifications by scission of weaker bonds that exist in macromolecules. Degradation products are formed simultaneously with decrease in gravimetric molecular weight. If damaging process takes place in the presence of oxygen, ketones, aldehydes, alcohols acids, esthers, peracids and so on are produced. The structure of polymer, the intensity of degradation factor, the level of material stress, the value of oxygen diffusion coefficient influences their accumulation rate.

Un important role in the durability extension of polymer materials is played by optimal amount of stabilizers. The addition of antioxidants to polymers induces retardation of oxidation. It means that oxidation induction time becomes longer in comparison with the same parameter of unstabilized polymer. In the same time oxidation rate decreases significantly [1].

General mechanism applied to the oxidative degradation of polyolefins was reported by Bolland and Gee [2]. If this process occurs in radiation field it progresses with high rate. Accelerated electrons or  $\gamma$ -radiation split macromolecules and free radicals are formed. They will be involved in recombination or oxidation reactions. The simultaneity and the contribution of crosslinking and scission will determine specific behaviour of radiation processed polymer [3].

Ethylene-propylene elastomers (EPDM and EPR) show remarkable stability against the action of high-energy radiation, comparable with the strength of polyethylene; they belong to the radiation crosslinkable type of polymers. Tertiary carbon atoms and low amount of

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unsaturation due to the technology of manufacture (the presence of diene for example hexadiene or ethylidene norbornene) get into these compounds some availability towards oxidation. The mechanistic features of oxidative degradation are based on typical reactions of ethylene and propylene units [5].

The assessment of polymer stability by measurement of kinetic characteristics, namely oxidation induction period, propagation rate of oxidation can be performed using proper methods: IR spectroscopy [5,7], thermal analysis [8], chemiluminescence [9], oxygen uptake [10,11], and so on. These parameters that depict the degradation level may be invoked for strength investigations.

In this paper radiation behaviour of stabilized EPDM is presented. The effect of antioxidant couples Se-Irganox1076 or 1010 are discussed.

## Experimental

Ethylene-polypropylene-diene terpolymer, EPDM (Terpit C<sup>®</sup>) was provided by ARPECHIM Pitesti. Molecular structure is presented in Fig. 1.

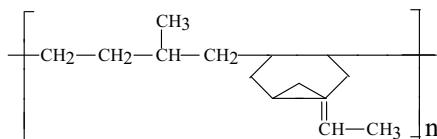


Fig. 2: EPDM molecular structure.

In Table 1 main characteristics of raw material are listed.

Property	Value
Propylene content (%)	39.8
Number of CH <sub>3</sub> for 100 C atoms	0.983
Unsaturation (C=C/1000 C atoms)	0.184
Numerical average molecular weight	80,800
Gravimetric average molecular weight	155,500
Viscosimetric average molecular weight	129,300
Viscosity index	1.38
Ethylidene norbornene content	3.5

Polymer was previously purified in order to remote the low amounts of antioxidants added during manufacture. EPDM was taken into *o*-xylene by gentle heating. Then polymer was precipitated with cold methanol. After separation of supernatant by filtration residual solvent was removed by abundant wash with cold acetone till the smell of *o*-xylene can't be felt. Separated solid was dried in an oven at 35°C.

Pure elastomer was resolved in CHCl<sub>3</sub> for easy sample preparation by solvent remote. Additive concentration was 0.1 phr for each compound. Chloroform solutions of Irganox 1010 or 1076 and Se suspension were added to polymer solution in proper amounts to

respect the selected concentration. Solvent evaporation was carried out on Al-trays at room temperature. Samples of 0.025 g were prepared.

Polymer samples were exposed to  $\gamma$ -radiation in GAMMATOR (USA) equipment provided with  $^{137}\text{Cs}$  source. Dose rate was 0.4 kGy/h.

Thermal stability of irradiated samples was carried out under isothermal ( $190^{\circ}\text{C}$ ) and isobaric conditions (normal air pressure) in a laboratory unit (Fig. 2).

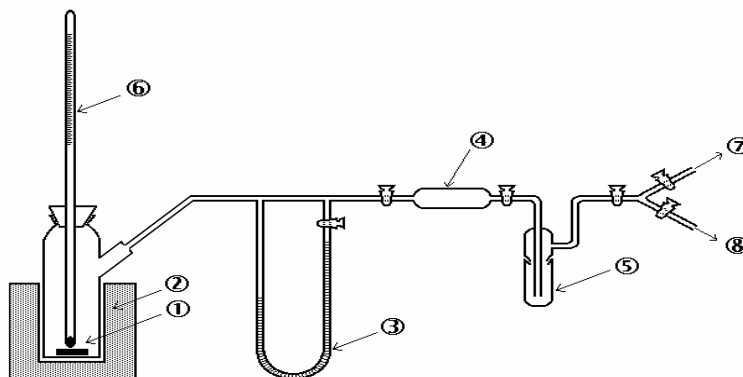


Fig. 2: *Oxygen uptake unit sheet:*

- (1) sample; (2) isothermally operated electrical oven; (3) Hg manometer; (4) oxygen flashing buffer vessel;  
(5) drying vessel; (6) control thermometer; (7) outlet to vacuum; (8) gas inlet.

## Results and discussion

Permanent action of destructive environmental factors is described by scission of some weak bonds that link atoms in macromolecules. Multiple bonds and sites with high substitution number increase thermal and radiochemical degradation probability. Changes in product formulations by addition of proper stabilizers are a good way to achieve high durability of polymers.

The stabilization of polymers is remaining one of constant area through the topics of polymer characterization. Various economic activities in chemical industry, electrotechnics and electronics, transport and nuclear energy supplying require high material strength on the intensive attack of energy and reagents. Many investigations were performed to assess the antioxidant activity of sterically hindered phenols [13÷15] or amines [16÷18] in oxidative protection.

Few papers [19÷21] firstly described the stabilizing behaviour of elementary selenium. The detailed characterization demands the study on synergistic effects of antioxidant couples like selenium and commercially available hindered phenols (Irganox 1076 and 1010). In Fig. 3a oxidographs obtained for monostabilized EPDM are shown. It may be noticed a clear difference between unstabilized and added polymer. The presence of elementary selenium increases oxidation induction period by 5 times, activity of Irganox 1076 delayed the start of oxidation with a factor of 6.2 while Irganox 1010, an efficient additive ensures a thermal stability 11.5 times longer than pure EPDM. The efficiency of

studied additive systems in retardation of oxidative degradation is well reveal by the evaluation of damaging rate (Fig. 3b).

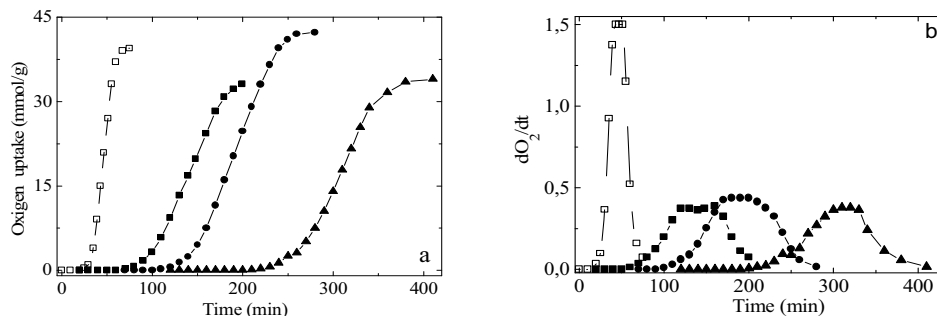


Fig. 3: (a) Oxidographs and (b) their first derivatives drawn for EPDM in different stabilization states.

(□) control, (■) elementary selenium, (●) Irganox 1076, (▲) Irganox 1010.

Intermediates that are formed from phenolic compounds differentiate the efficiency of these stabilizers. This class of oxidation retardants presents many active intermediates, especially in quinone form while selenium acts as oxidation protector in metallic or dioxide states [21]. In this sense Fig. 3b proves an activity of selenium similar to hindered phenols. It means that selenium exhibits proper characteristics not only in biological environment but also in polymer materials.

Radiation exposure produces radicals that react more or less quickly to each other or with oxygen. The rate of degradation depends on the concentration of these radicals that is proportional with dose rate and total dose. However if a stabilizer is added to radiation processed polymer irradiation can promote crosslinking instead of degradation. In Table 2 there are listed the induction times and oxidation rates for  $\gamma$ -irradiated samples. Because gel dose of EPDM is 55 kGy [22] and the amount of oxygen previously dissolved in polymer is low the radiation effects induced in macromolecular substrate are more important at higher doses, namely 200 and 300 kGy. Thus, diffusion of molecular oxygen towards the inner zones of specimens promotes an advanced oxidation.

**Table 2. Oxidation induction time and oxidation rate of additivated EPDM at various doses**

Stabilizer	Dose (kGy)	Oxidation induction time (min)	Oxidation rate ( $\text{mol}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ ). $10^6$
Se	100	92	7,8
	200	78	9,3
	300	60	10,9
Irganox 1076	100	153	5,2
	200	130	6,8
	300	96	7,5
Irganox 1010	100	289	4,8
	200	235	5,5
	300	196	6,3

In Table 3 there are presented the main kinetic parameters that describe the stabilization activity of elementary selenium and phenolic antioxidant. The co-operation between the two compounds simultaneously added to EPDM can be evaluated by the following relationship:

$$\varrho = \frac{t_{ij}}{t_i + t_j}$$

where  $\varrho$  is co-operative factor,  $t_i$ ,  $t_j$  and  $t_{ij}$  are the values of oxidation induction times for additive i, additive j and their couple, ij. It can be observed that increasing dose lowers co-operative factor value.

**Table 2. Oxidation induction time and and co-operative factors determined for addittivated EPDM at various doses**

Dose (kGy)	Se – Irganox 1076		Se – Irganox 1010	
	Induction period (min)	Co-operative factor	Induction period (min)	Co-operative factor
0	1337	4,8	2319	5,3
100	1176	4,5	2155	5,3
200	811	3,9	1440	4,6
300	437	2,8	870	3,4

The contribution of antioxidant couples does not depend only on polymer material but also on radiation damage of additive. Elementary selenium activity is less affected by irradiation and modification of co-operative factors of studied antioxidant pairs may be explained by radiation instability of phenolic component. The selected doses did not produce a retrogression of thermal stability less than unirradiated and unstabilized ethylene-propylene elastomer.

## Conclusion

The experimental data presented in this paper reveal a synergistic effect of selenium and phenolic antioxidants, Irganox 1010 and 1076, in ethylene-propylene terpolymer. Though irradiation obviously induced drastic modification of thermal strength of polymer the Se/Irganox couples get a good protection to macromolecular material. The co-operative factors take satisfactory values in order to prove their availability for enhancing polymer lifetime.

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