

Kinetic Effects of Selenium on Degradation of Ethylene–Propylene Copolymer

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ABSTRACT: The antioxidation protection of elementary selenium added to an ethylene–propylene copolymer (EPR) at different concentrations (0.1, 0.2, and 0.5 phr) was studied. Oxygen uptake measurements were isothermally performed at 180°C on polymer samples stabilized with increasing concentrations of Se. Experimental data have revealed the enhancement in induction periods and the decrease in oxidation rates for unaged elastomer samples. Stabilized polymer specimens exposed to γ -radiation have presented the highest effects at 0.5 phr of selenium concentration for all irradiation doses (50, 100, 150, and 250 kGy). Influence of selenium on the competition between crosslinking and oxidation occurred in γ -irradiated ethylene–propylene elastomers discussed on the basis of kinetic treatment on studied thermal degradation process. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2053–2057, 2001

Key words: ethylene–propylene copolymer; selenium; thermal degradation; γ -irradiation

INTRODUCTION

The aging behavior of commercial polymer products is principally influenced by the presence of stabilizers. Beside the effects of material properties such as molecular structure, morphology, trace amounts of manufacture impurities on the long-term stability, environmental conditions such as temperature, light, or high energy radiation exposure, service surrounding and the concentration of selected additives play a decisive role on the kinetics of the degradation process. The importance of the stabilization activity is emphasized by the safety operation of products over a long period of time. Furthermore, the degrada-

tion level achieved by polymer items during service changes mechanical properties and the life time is thus diminished.

Various stabilizer types including hindered phenols^{1–5} and hindered-amine light stabilizers^{6–10} are commonly used in the prevention of thermo- and photo-oxidative degradation. Other kinds of compounds: triazine derivatives,^{11–13} organic sulphites,¹⁴ metal chelates,¹⁵ and so on were previously tested as antioxidants.

The efficiency of selenium in the inhibition of thermal aging has received little attention. A low number of papers were published on the antioxidant behavior of selenium in polymers.^{16–23}

Due to the practical purposes, some general requirements—appropriate solubility, advanced compatibility with the host polymer, low tendency of migration, own high thermal stability—have to be the characteristics of the compound used as the antioxidant in the polymer matrix. Elementary

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selenium displays more or less these characteristics. They have been not yet studied in detail.

The purpose of this article is the assessment on antioxidant behavior of elementary selenium loaded at three concentrations in ethylene-propylene copolymer and the underlining of its effects on the competition between crosslinking and degradation on γ -irradiated EPR samples. The antirad activity of selenium over sterilization dose range is also reported.

EXPERIMENTAL

The polymer used in this investigation was an ethylene-propylene copolymer provided by ARPECHIM Pitești (Romania). The initial composition of this material corresponds to a ethylene/propylene ratio of 3/2. The preliminary protection additives were removed by precipitation from hot *o*-xylene by pouring cold methanol. Then, elastomer was taken in a CHCl_3 solution. Elementary selenium as a fine powder material (Merck) was added under vigorous stirring to solutions of purified ethylene-propylene copolymer in appropriate amounts to obtain three concentrations: 0.1, 0.2, and 0.5 phr. Each new solution was equally distributed by means of a 500- μL micropipette on aluminium trays to prepare thin films ($\sim 30 \mu\text{m}$ thickness) after fast removal of solvent by natural evaporation.

Irradiation was performed in air at room temperature in a ^{137}Cs GAMMACELL (USA) facility to a maximum dose of 250 kGy. The dose rate was 0.054 kGy/h.

The thermal stability of unexposed or γ -irradiated samples was determined by oxygen uptake measurements under isothermal (180°C) and isobaric (normal pressure) conditions. Air was selected as the oxidative environment. The equipment used in the determination of kinetic parameters (oxidation induction time and oxidation rate) was made in our laboratory.²⁴ All measurements were promptly carried out after the end of irradiation, unless otherwise mentioned.

RESULTS AND DISCUSSION

When ionizing radiation loses a part of their energy on macromolecules, scission of weaker bonds takes place. Different types of free radicals are formed, and their subsequent reactions will de-

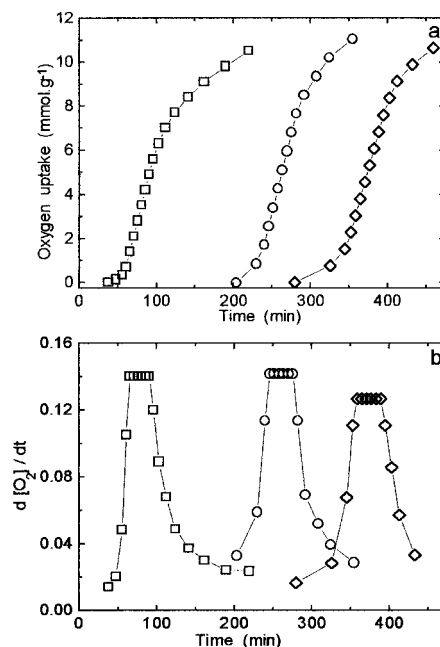


Figure 1 (a) Oxygen uptake of unirradiated EPR samples containing different amounts of Se. (b) First-order derivatives of oxygen uptake dependencies of unirradiated and stabilised sample. (\square) 0.1 phr; (\circ) 0.2 phr; (\diamond) 0.5 phr.

termine the structures and concentrations of degradation products.

Because of the great interest on the thermal and/or radiation degradation behavior of polymers, the addition of various stabilizers is deeply investigated. The interest in commercial products is explainable, but it does not exclude any search on other materials. Elementary selenium is one of the unusual stabilizers. Experiments on the stabilization of ethylene-propylene copolymer with respect to radiochemical degradation under oxidizing conditions can point out the capacity of this element to promote the augmentation in oxidation resistance.

Figure 1(a) shows the stabilization effect of increasing concentration of metallic selenium on the ethylene-propylene copolymer. This additive acts very efficient at the concentrations exceeding 0.2 phr. The linear dependency of oxidation induction time on selenium concentration could be proven. Figure 1(b) presents the rate of oxygen consumption. Despite the lack of any difference between the oxidation rates for the first chosen concentrations (0.1 and 0.2 phr), the induction period values are very unalike (Table I). It seems that the concentration of 0.1 phr Se would not be

Table I The Main Kinetic Parameters for Thermal Oxidation of EPR-Se Systems

Se Concentration (phr)	Irradiation Dose (kGy)	Oxidation Induction Time (min)	Maximum Oxidation Rate (mol O ₂ · g ⁻¹ · s ⁻¹) · 10 ⁶
control	—	66	3.51
0.1	—	70	2.58
	50	74	2.84
	100	80	1.98
	150	75	2.78
	250	75	2.78
0.2	—	126	2.24
	50	182	2.01
	100	225	1.25
	150	198	1.53
	250	148	2.37
0.5	—	242	1.96
	50	316	1.42
	100	601	0.58
	150	425	1.25
	250	235	2.85

sufficient to attain satisfactory stabilization effect in the ethylene-propylene copolymer.

A relevant example regarding the stabilization activity of selenium is the evaluation of thermal behavior of EPR added with 0.5 phr Se at various irradiation doses. Dependencies of oxygen uptake [Fig. 2(a)] and rates of oxidation [Fig. 2(b)] on thermal degradation time demonstrate the high efficiency of Se on oxidation prevention in unirradiated samples and the stabilization action over low irradiation dose range. The remarkable enhance in the oxidation induction time for the EPR-0.5 phr Se irradiated at 100 kGy (Table I) suggests the involvement of the additive in the hindrance of oxidation. The balance between crosslinking and degradation is modified by selenium. The minimal effect at the low concentration (0.1 phr) indicates a slight contribution of the additive to the decreasing oxidation rate of elastomer. Moreover, the oxidation stability of EPR doped with 0.1% Se is diminished at the exposure of 100 kGy in comparison with the same type of sample irradiated at 50 kGy [Fig. 3(a)]. The same values of oxidation rates [Fig. 3(b)] but lowering oxidation induction times for EPR-0.1 phr Se samples underlines the limitation in stabilization behavior of selenium.

The susceptibility of ethylene-propylene elastomer to crosslinking is confirmed by the data listed in Table I. The main contribution to the decrease in maximum oxidation rate (the last column) is due to gamma irradiation as it was pre-

viously reported for unstabilized elastomes.²⁵ The conversion of macromolecules in free radicals is possible by the transfer of radiation energy onto

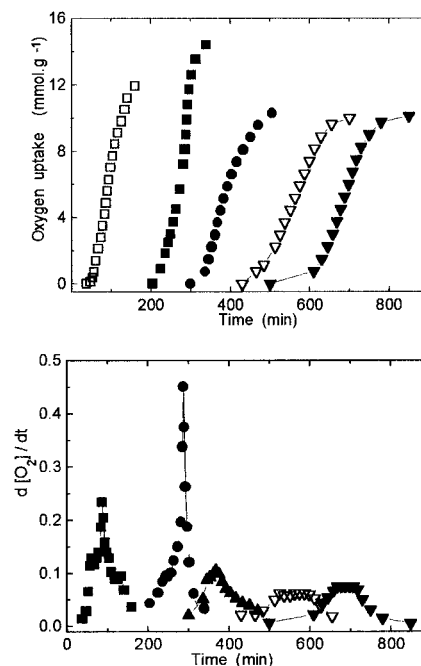


Figure 2 (a) Oxygen uptake of irradiated EPR samples containing 0.5% Se at various doses. (b) First-order derivatives of oxygen uptake dependencies of irradiated EPR-Se 0.5 phr samples. (□) control; (■) unirradiated; (●) 50 kGy; (▼) 100 kGy; (○) 150 kGy; (▽) 250 kGy.

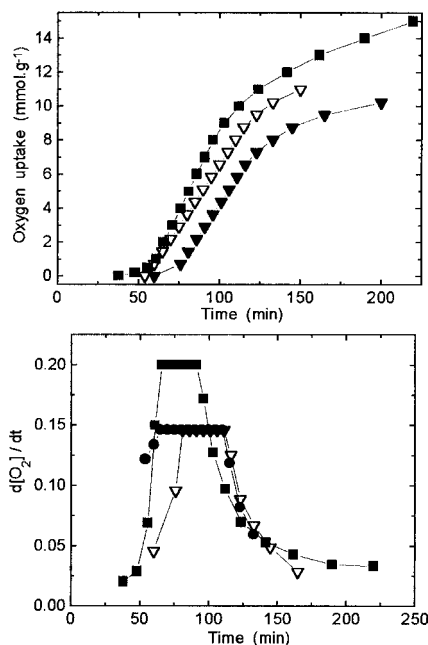


Figure 3 (a) Oxygen uptake of irradiated EPR samples containing 0.1% Se at various doses. (b) First-order derivatives of oxygen uptake dependencies of irradiated EPR–Se 0.1 phr samples. (■) unirradiated; (▼) 50 kGy; (▽) 100 kGy.

molecules. Subsequently, these intermediates can recombine to increase gel fraction or react with oxygen to promote degradation. The presence of antioxidant—in this case elementary selenium—protect free radicals against oxidation. The elastomer samples irradiated at 50 and 100 kGy present more favorable kinetic characteristics than the same parameters determined on unexposed samples. The irradiation doses exceeding 100 kGy generate higher amounts of free radicals, but selenium is not entirely able to screen the degradation process. Thus, the decrease in oxidation induction times and the promotion of oxidation on higher rates emphasize the disability of selenium to carry out an efficient oxidative protection. It can be assumed that selenium acts as free radical scavenger. At the lower concentrations of these intermediates corresponding to low irradiation doses selenium can successfully retard degradation process and the yield of crosslinking is enhanced. Contrarily, a significant improvement of radical amounts rises the probability of oxidation because the additive is not efficient even at high concentrations, for example 0.5 phr Se. Thus, the antirad activity of selenium can be reported for the doses up to 100 kGy.

However, this dose range is sufficient for sterilization of polymer materials.

CONCLUSIONS

In the course of this investigation we found that elementary selenium displays an antioxidative effect in the ethylene–propylene elastomer. Moreover, the irradiation of a stabilized polymer confirms the antirad behavior of selenium up to a dose of 100 kGy of absorbed dose. The kinetic parameters of thermal oxidation performed on unirradiated or on radiation-exposed EPR containing various concentrations of selenium point up the availability of selenium to hinder oxidative degradation.

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