IMPROVEMENT IN THE RADIATION STABILITY OF SYNTHETIC ELASTOMER EPDM MODIFIED WITH METALLIC SELENIUM

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Abstract

This study presents the antioxidant effects induced by metallic selenium in ethylene-propylene terpolymer (EPDM) subjected to accelerated ageing by γ-irradiation. Several doses were applied up to 100 kGy in order to qualify this material for nuclear applications. Three concentrations (0.25, 0.50, and 1% w/w) of Se in elastomer were prepared. FTIR spectroscopy and chemiluminescence were performed for characterization of oxidation progress. Kinetic parameters expressed in a function of received dose are assessed for emphasizing the stabilization efficiency of selenium.

1. Introduction

The industrial applications of radiation processing have been growing rapidly caused economical interest and ecological technologies. The main fields are the manufacturing of radiation crosslinked heat-shrinkable materials, wire, cables, automobile parts, and medical goods [1–3].

Copolymers of ethylene and propylene have a wide range of commercial applications, one of which is in the manufacture of some goods, such as syringes, catheters, gaskets, membranes, and corrosion sheet protection. They require advanced sterilization for long term use. This feature can be carried out by the application of different processing procedures, some of them being chemical treatments, but they present inherent disadvantages in the case of polymeric materials. For example, autoclaving can lead to oxidation of a polymer, and ethylene oxide is a known carcinogen and can be retained in the polymer matrix. Therefore, radiation sterilization is becoming the preferred method for sterilization of many polymeric goods [4].

The degradation mechanisms and lifetime prediction of materials exposed to high energy radiations are relevant problems which must be solved [5]. The important changes in polymers resulting from radiation-induced reactions must be studied for any application in nuclear power plants. Energetic requirements imposed on polymeric materials that are used in various areas of nuclear power plants for sealants, gaskets and electrical insulators stimulate the assays on material integrity. The action on a long lifetime of polymeric materials can be achieved by the addition of antioxidants, whose efficiency determines the extended period for the service of material. Several compounds exhibiting antioxidant properties exist in the market, but only some of them are compatible with human body. One example is metallic selenium, the stabilization of activity of which is remarkable [6–9] in comparison with several synthesis antioxidants.

The addition of stabilizers for the recycling of waste tire rubber is a worldwide environmental and economic problem facing the polymer industry. In addition, ionizing radiation offers possibilities of recycling polymers due to the ability to cause cross-linking and/or chain

scission of a wide range of materials without introducing any chemical initiators. Though the application of radiation for rubber recycling is not widespread, gamma irradiation of EPDM was shown to increase gel content and improve mechanical properties [10].

The activity of natural antioxidants was studied for the evaluation of competitive choice in respect with commercial antioxidants [11-14].

In this work, the efficiency of metallic selenium was assessed for the application of ethylene-propylene elastomers, EPDM, as a high stabilized product. The structural modifications are revealed by the change in IR spectra, which are sustained by the results obtained by means of testing and chemiluminescence.

2. Materials and procedure

Metallic selenium was provided by Merck in a powder form. The selected concentrations for addition of elementary selenium to EPDM manufactured by ARPECHIM Pitesti, Romania, were 0.25, 0.5, and 1 wt %. Specimens were prepared by solvent (CH_3Cl) removal from polymer solutions on aluminum round trays. Thin pristine films with about the same thickness were obtained to assess the contribution of a stabilizer to the inhibition of oxidation. The polymer was not previously purified to meet manufacturing conditions. The exposure of polymer samples was performed inside a GAMMATOR (USA) irradiation machinery provided with a ^{137}Cs source. Exposures were accomplished in air at room temperature and a dose rate of 0.4 kGy/h.

For chemiluminescence investigation, specimens were placed in aluminum trays. The isothermal chemiluminescence measurements were carried out in LUMIPOL 3 (SAS, Slovakia). From the time dependences of CL intensity, three main kinetic parameters, namely, oxidation induction time, initial chemiluminescence intensity, and maximum oxidation time, were obtained according to early reported procedure [15].

FTIR spectra were recorded using a JASCO 4200A spectrophotometer at 50 scans and 4 cm^{-1} resolution for extreme compositions.

3. Results and discussion

All radiochemical studies performed on polymers demonstrated that free radicals created during γ-irradiation can react with each other or with molecular oxygen according to the Bolland and Gee's mechanism for thermal degradation of these polymers, but it is usually extended for high energy irradiated polyolefins. The main reactions occurred under irradiation are gathered in Fig. 1. The rate of oxidation depends on the free radical concentration that is achieved at a certain irradiation dose.

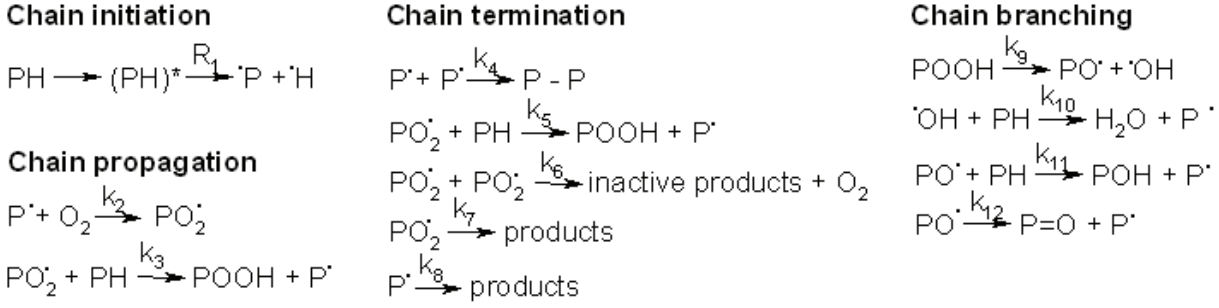

Fig. 1. Scheme of the mechanism of radiation induced oxidation in polyolefins.

Oxidative degradation can never be entirely eliminated because molecular oxygen is present in the majority of environmental conditions. Technological application of this class of polymers in the radiation processing field must take into account the effect of oxygenated products accumulated during the start step of irradiation on material stability.

The effects of different selenium concentrations at various radiation doses are shown in Fig. 2. The table lists the effects of various concentrations of elementary selenium on kinetic parameters obtained for EPDM samples at different radiation doses.

Kinetic parameters obtained for gamma-exposed EPDM samples stabilized with different concentrations of Se.

Se conc. (%)	0 kGy			50 kGy			100 kGy		
	$I_0 * 10^6$ (Hz/g)	t_i (min)	t_{max} (min)	$I_0 * 10^6$ (Hz/g)	t_i (min)	t_{max} (min)	$I_0 * 10^6$ (Hz/g)	t_i (min)	t_{max} (min)
pure	2.50	196	298	10.72	5	26	18.94	2	25
0.25%	0.67	862	1076	4.02	400	445	30.53	141	872
0.5%	0.59	1410	1572	2.16	1179	1515	31.34	803	2258
1%	0.50	2075	2148	0.44	1919	3251	12.02	2599	4994

The availability of selenium for increasing oxidation induction time (thermal stability) is proved by the enhanced values of t_i at higher Se concentrations. It can be observed that the oxidation induction periods for EPDM containing 1% metallic Se are of 1.5 to 8 times higher than the corresponding values for the samples with lower Se content. This behavior is based on the possibility exhibited by selenium oxide for the scavenging of radicals. It means that either metallic selenium or its oxide has the ability of the protection of radicals. The further chemical state of selenium, selenium acid causes oxidation, because it is a pro-oxidant compound.

The stabilization mechanism that is involved in the protection of thermal oxidation of polyolefins is presented in Fig. 2

$$Se + ROOH \longrightarrow RH + SeO_2$$

$$SeO_2 + 2\ ROOH \longrightarrow R\text{ - }R + H_2SeO_4$$

Fig. 2. The protection mechanism offered by metallic selenium.

The accumulation of oxidation products describes the evolution of progress in the stability of material. It may be depicted by the variation in the absorbencies of characteristic functions, mainly carbonyl and hydroxyl groups.

The increase in the selenium concentration brings about not only the oxidation inertness of polymer during the prolonged heating illustrated by initial values of CL emission intensities (I_0), but also by the extremely extended time when the sample is completely oxidized. The rate of oxidation was not properly determined because the propagation of oxidation at this stage of thermal degradation runs very fast. It can suggest that for a long time of processing, the conversion of metallic into selenium dioxide is beneficial for material stability, while selenic acid causes oxidation. Figure 3 shows that the increase of CL intensity on this period of oxidation is very sharp.

The structure of CL curves (Fig. 3c) demonstrates the reaction sequence illustrated in Fig. 2. The most important feature of the usage of this stabilizer, even for radiation stabilization, is the extraordinary long period in which oxidation does not start.

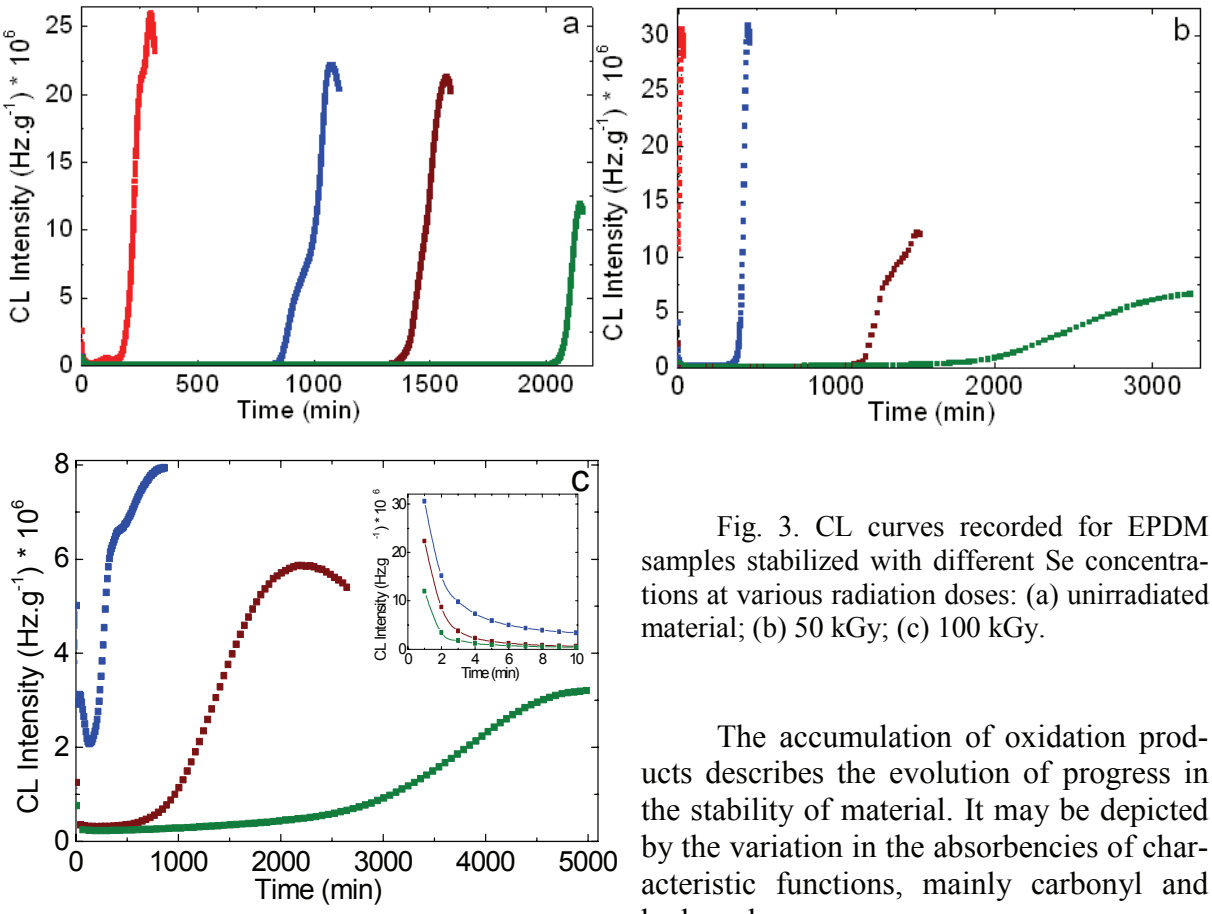

Fig. 3. CL curves recorded for EPDM samples stabilized with different Se concentrations at various radiation doses: (a) unirradiated material; (b) 50 kGy; (c) 100 kGy.

The accumulation of oxidation products describes the evolution of progress in the stability of material. It may be depicted by the variation in the absorbencies of characteristic functions, mainly carbonyl and hydroxyl groups.

The modifications induced in FTIR spectra over the first 50 kGy are not significant. The absorbance in the 3350 cm^{-1} band remained almost constant. This aspect is probably related on the low specific depositing energy. It means that, in the case of nuclear power stations, outside the active area where dose rate is extremely low, the chemical transformations induced in time are not relevant (Fig. 3).

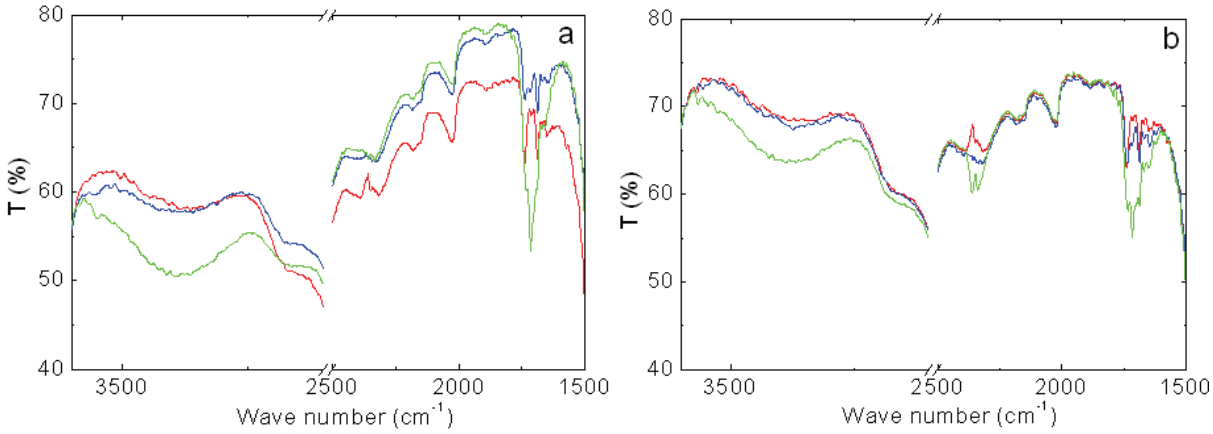

Fig. 4. FTIR spectra recorded for EPDM samples stabilized with different Se concentrations: (a) pure sample and (b) 0.5% metallic Se.

The presence of metallic Se in the composition of the elastomer brings about a sustained stabilization (Fig. 4b). In addition, the inhibition of oxidation is assured by the antioxidant, which does not allow further oxidation. The characteristic vibration bands are more strongly

modified in pristine elastomers than in the stabilized material. For protected EPDM in the presence of metallic selenium the spectral differences between unirradiated material and the 100 kGy exposed elastomers are very low. It means that the concentration of 1% Se may be used as radiation protection of elastomers, in particular, and of polyolefins, in general.

4. Conclusions

Selenium represents an ecological choice for the stabilization of polymeric materials not only for its effects on the oxidative aging process, but also for its favorable interaction with the user. High concentrations of metallic selenium promote advanced stabilization evidenced by both experimental methods. This additive can be associated with other antioxidant additives to increase the stabilization for long-term applications. Experimental data of this paper demonstrate the ability of metallic selenium to protect polymeric materials subjected to radiosterilization.

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