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CONTRIBUTIONS OF ECOLOGICAL OXIDATION PROTECTORS IN THE STABILITY OF EPDM-BASED PACKAGING MATERIALS

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In the paper the effects of gallic acid and rosemary extract on the thermal and radiation stabilities were analyzed for polymer matrix, ethylene-propylene-diene monomer, EPDM. The complementary procedures, infrared spectroscopy and nonisothermal chemiluminescence were applied for the illustration of degradation kinetics. The resistance of stabilized polymer in three compositions (pristine material and EPDM added with each of protectors) was evaluated by the calculation of activation energy involved in the oxidative degradation of EPDM. The protection efficiencies of the two additives were compared and discussed.

Keywords: EPDM, stabilization, rosemary extract, gallic acid

1. Introduction

The deep interest concerning the manufacture of ecological products for the handling of fresh food is focused on several polymers, which satisfy the warranty demands for the safe heath of population. The most efficient procedure available for the attaining longer durability of packaging materials is the addition of protection compounds in the material composition [1-3]. The polymer degradation is described elsewhere [4], but the specific activities involved in the durability improvement are influenced by the filler chemistry. The delay of oxidation can be achieved by synthesis [5,6] and natural [7,8] phenolic structures, inorganic compounds [9,10] or by chemical modifications illustrated by crosslinking [11,12]. A special attention was focused on hybrid materials like polyhedral oligomeric silsesquioxane (POSS) [13], hydroxyapatite [14], biofillers [15], modified silica [16], which improve the thermal resistance of basic

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materials. The most important feature that can be remarked from the investigations on hybrid polymer materials is the involvement of filler in the degradation mechanism by their active surfaces [17] or by the scavenging free molecular fragments [18] prior their reactions with diffused oxygen. It must not be discarded the electronic interaction between particle surface [19] and free radicals that have un impaired electron capable to direct degradation intermediates towards the spots, where there is an electron deficit.

The packaging materials are subjected to the action of damaging agents: heat, sun light, humidity by raining, dirty dust. They are always associated with the everywhere existing oxygen. The progress of material ageing can be effectively delayed by the addition of some oxidation protector that acts implicitly on the molecular fragments appeared after scission of macromolecules. Naturally, they would react with diffused oxygen and initiate the self-catalytic chain according with the degradation mechanism [4]. The life time of packaging materials depends on the polymer structure, the intensity and duration of stressor action, the material formulation. The improvement of material durability is related on the stabilization efficiency, which must be assessed by an appropriate technique. The evaluation of efficiency due to the presence of stabilizing compounds is faithfully achieved by chemiluminescence by which the evolution of oxidation is accurately done [4]. According with the oxidation mechanism the main intermediates are the entities resulting from oxidation reactions [20], which are the start points for the chemiluminescence (CL) emission (Fig. 1):

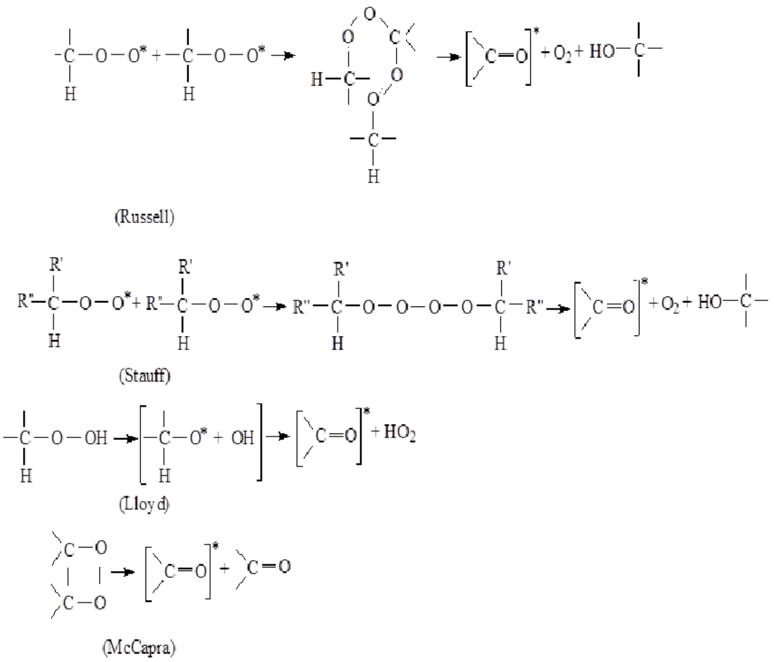

Fig. 1. Mechanisms of chemiluminescence emission.

The main goal of this study is the evaluation of the protection efficiency promoted by two natural antioxidants (gallic acid and rosemary extract) in EPDM products, which can be successfully used as packaging materials in the handling of food.

2. Experimental procedure

Ethylene-propylene-diene elastomer (EPDM), was produced by ARPECHIM Pitești (Romania) as TERPIT C®. Initial molecular structure was consisted of ethylene and propylene with composition ratio 2:1. This elastomer was produced with a third component, a diene (5-ethylidene-2-norbornene), whose concentration was 3 wt%. Gallic acid was provided by Sigma Aldrich (UK); the rosemary powder was obtained in our lab by Soxhlet extraction in ethanol from rosemary leaves. For the purification, our raw rosemary material was precipitated from ethanol solution by adding water drop by drop. Aliquot solutions of 25 mL were poured in separate bottles, where the appropriate antioxidant amount (1.0 wt% in dry state) were added. The CL samples were prepared in round aluminum caps by pouring 0.5 mL of stabilized material solution. Chemiluminescence (CL) investigation were achieved by LUMIPOL 3 (SAS, Bratislava, Slovakia) providing information through nonisothermal measurements. The selected heating rates were 3.7, 5, 10 and 15 °C min^{-1}. The values of onset oxidation temperature (OOT) were obtained from CL spectra and used as input results for the calculation of activation energies by Kissinger procedure [21]. FTIR films were obtained by solvent removing from stainless steel trays. FTIR spectra were recorded on the spectrometer JASCO A-4200, Japan over the whole range 4000–400 cm^{-1} by 50 scans. The γ-exposure of samples was done in air at room temperature inside an irradiator Ob Servo Sanguis (Hungary) equipped with a ^{60}Co source. The dose rate was 0.7 kGy h^{-1}. The weathering treatment was done with Xenotest 440 (Atlas, USA) equipment.

3. Results and discussion

The description on the progress of oxidation takes into consideration the competition between the formation and decay of hydroperoxides, which are the promoters of degradation. In the EPDM compositions modified with the antioxidants, this ratio is turned onto the inhibition of oxidation reactions that decreases the local concentrations of hydroperoxides. The most reactive positions in EPDM macromolecules [8] are shown in Fig. 2.

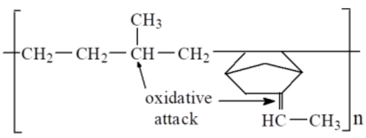

Fig. 2. The illustration of the most sensible points in EPDM molecules for oxygen attacks.

The antioxidants are able to break the degradation chain by blocking the reactivity of peroxyl ($RO_2^{\cdot}$) and alkoxyl ($RO^{\cdot}$) strongly bonded on the molecules of stabilizer by proton replacement.

3.1. Nonisothermal chemiluminescence

The efficient stabilization of oxidative ageing of EPDM is achieved by the action of studied protectors. In the unirradiated samples, the oxidation starts later in the presence of gallic acid and rosemary extract. The OOT values decreased from 220 °C for pristine polymer to 210 °C and 180 °C for samples containing rosemary and gallic acid, respectively (Fig. 3). The comparison of the emission intensities recorded at 200 °C illustrates the efficiency degrees of the additives Table 1. The evolution of Cl curves describes the scavenging effect of the additives, which block free radicals in respect with their reactions with oxygen. As it can be noticed from Fig. 3, the concentrations of free radicals generated from the removing methyls are much greater that the radicals formed by the splitting of double bonds. According to the history of radical intermediates, they may form a significant amount of unsaturation by their disproportion.

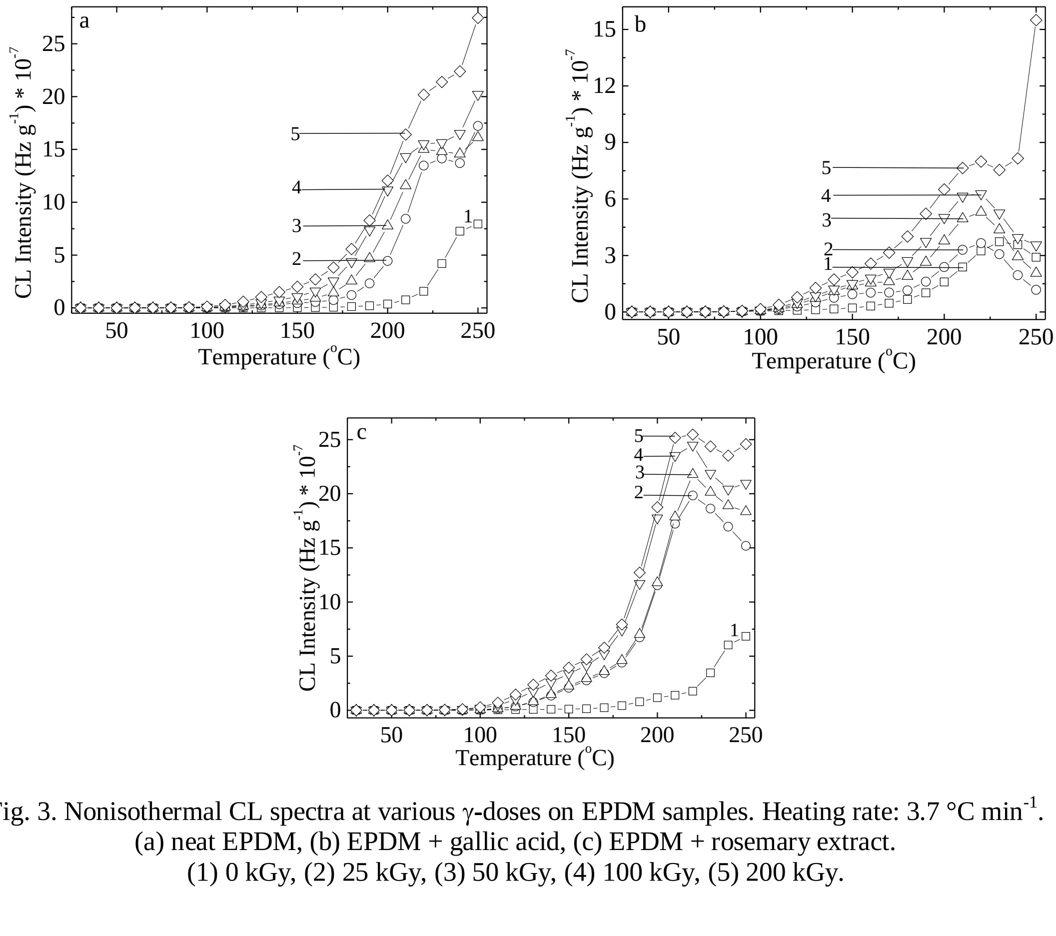

Fig. 3. Nonisothermal CL spectra at various γ-doses on EPDM samples. Heating rate: 3.7 °C min^{-1}.
(a) neat EPDM, (b) EPDM + gallic acid, (c) EPDM + rosemary extract.
(1) 0 kGy, (2) 25 kGy, (3) 50 kGy, (4) 100 kGy, (5) 200 kGy.

Table 1.

CL intensities recorded at 200 °C for the oxidation of EPDM samples

Dose [kGy]	CL Intensity [Hz g^{-1} s^{-1}] * 10^{-7}		
	Neat EPDM	EPDM + rosemary	EPDM + gallic acid
0	1.766	1.422	1.094
25	7.546	4.444	2.386
50	11.784	7.762	3.773
100	14.755	10.765	5.011
200	18.752	12.054	6.501

The gallic acid, that is a polyphenol (3,4,5-trihydrobenzoic acid) has a prominent contribution by the multiple proton positions capable to be substituted by free radicals. In contrast with gallic acid, rosemary extract exhibits a good protection over the low and medium temperature ranges. The low CL emission intensities measured in the cases of EPDM/gallic acid samples demonstrated that the reactions of peroxyl radicals with O_2 during degradation [4] did not occur. Consequently, the emission of CL photons according with the schemes presented in Fig. 1 is minimized due to the decrease in the concentration of $RO_2^{\cdot}$ Intermediates blocked by molecules of antioxidants.

The γ-exposed EPDM, where the local concentrations of radical became higher at increasing dose, presented different stabilization degrees. The nonisothermal CL spectra depicting the progress of oxidation in polymer matrix vs temperature present at 220 °C a shoulder in the case of pristine materials and well-defined peaks in the cases of modified EPDM. The peaks would be ascribed to the limitation of rate generation of $RO_2^{\cdot}$ intermediates because of the hindering action of antioxidant compounds. Because the scavenging activity of gallic acid is more effective than the corresponding feature of rosemary, the curve height at this temperature is lower for gallic acid than for rosemary. Similar behavior in the oxidation of organic phase was reported for the diminution of oxidation rates in the hybrid systems consisting of polyisobutylene succinic anhydride modified with silica and magnetite nanoparticles [21].

The thermal ageing of pristine EPDM has demonstrated its capability to extend the oxidation induction period due to presence of the unsaturation from the third component, the added diene [22]. The oxidation of elastomer takes place with an oxygen consumption of $7x10^{-12}$ mol g^{-1} s^{-1} at 40 °C, the value characterizing the oxygen diffusion polyethylene [23], the major structural component of the studied polymer. Some previous reports on the thermal stability of EPDM [24-26] revealed its susceptibility to generate oxygen-containing stable products during the long exposure in oxidative environments.

The evaluation of activation energy required for the oxidative degradation of EPDM [27] demonstrates the main role of propylene moieties involved in the fragmentation of EPDM molecules. The similarity of this energy values with the figure reported earlier [27] explains that the most sensible places in the studied polymers are the tertiary carbon atoms and the double bonds from the structure of added diene.

Table 2.

Onset oxidation values for the EPDM samples investigated by nonisothermal chemiluminescence

Sample	Dose [kGy]	Onset oxidation temperature [K]			
		3.7 °C min^{-1}	5.0 °C min^{-1}	10.0 °C min^{-1}	15.0 °C min^{-1}
neat EPDM	0	493	500	511	518
	25	488	491	503	513
	50	471	479	488	499
	100	453	459	473	481
	200	433	446	455	467
EPDM + gallic acid	0	495	498	511	518
	25	480	485	496	503
	50	471	475	488	495
	100	456	460	472	483
	200	443	452	466	473
EPDM + rosemary extract	0	499	504	515	523
	25	489	498	507	513
	50	481	483	494	503
	100	468	474	482	492
	200	459	468	476	484

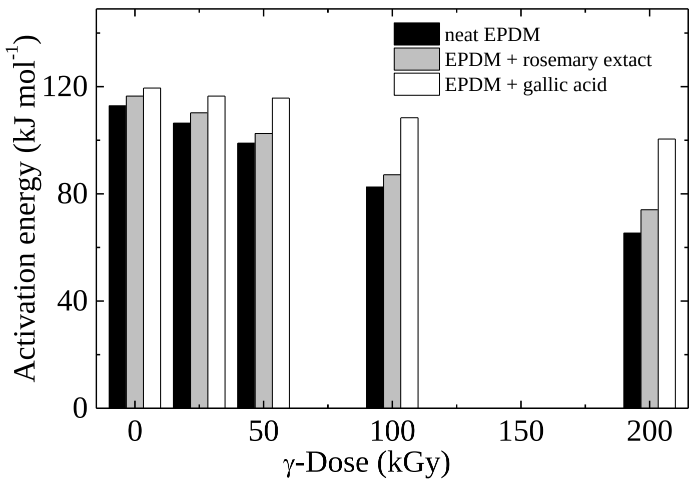

Fig. 4. Activation energies of radiation processed EPDM in the presence of the two stabilizers

The stabilization effect illustrated by Fig. 4 reveals a relevant aspect of protection. While the resistance to oxidation drops down significantly in pristine

EPDM, it is similarly followed by the polymer in the presence of rosemary extract particles. The alike trends in the modifications of activation energy for the oxidation in EPDM substrate, either for neat materials, or for EPDM/rosemary samples, suggest the light contribution of this additive even though it has a satisfactory concern in the improving durability of polymers [28, 29]. It is generally accepted that the efficiency of rosemary extracts depends on the additive composition [30] and the decomposition descendants have antioxidant features. This last aspect confirms the differences that exist between neat and rosemary-modified EPDM (Fig. 4). The addition of gallic acid improves the value of onset oxidation temperature of 1.54 times in respect with neat polymer at an advanced oxidation state achieved after the γ-irradiation dose of 200 kGy, while under the same condition this parameter increases only by 1.13 times for rosemary-containing sample. It may be assumed that the molecular structure of gallic acid would not be changed significantly under irradiation. During γ-processing, the conversion or the remove of any hydroxyl substituent on the benzene ring, the basic frame of these molecules, do not lead to a noticeable diminution of the protection activity of gallic acid.

The accelerated oxidation sustained by various radical intermediates [31] in γ-irradiated ethylene-propylene elastomers is conducted by the selectivity of the additive components, but the main final products of oxidation remain ketone-containing structures centered on the FTIR stretching band at 1720 cm^{-1}. The presence of gallic acid has a strong stabilization effect even at high temperatures (Fig. 3) due to the diminution of oxidation rates at all γ-irradiation doses. In the environmental ageing of EPDM packaging products, the presented results are useful for the evaluation of material durability subjected to an inherent degradation by synergistic effects of heat, sun light, biocomponents released by handled food, and mechanical charges. The stabilization assays for depicting the activities of studied additives indicated relevant contributions at temperatures exceeding 100 °C addressing the slower amelioration of evaluating oxidation state of basic polymer.

As it has been demonstrated by CL investigation, the development of ageing is tightly related to the availability of additive upon the scavenging oxidizing radicals, which are withdrawn from their reactions with oxygen. Accordingly, the residual amounts of reactive intermediates sustain the continuation of oxidation during strong hazardous exposure. For a general application of γ-sterilization, the protection activities evaluated at 25 kGy are optimized by the inclusion of gallic acid in the formulation of EPDM-based product.

The achieved stabilization especially by gallic acid proves the correlation between the proton availability for replacement by free intermediates and the jointing strength of carbon-centered radicals appeared by the scission of weaker bonds [32]. Thus, the concern of studied additives is a reliable proof for the extension of application area in the field of difficult operation conditions.

3.2. Infrared spectroscopy

The FTIR investigations emphasizes the protective effects of rosemary extract and gallic acid on the acceleration ageing (Fig. 5). The outdoor resistance illustrated by the results of weathering treatment is characterized by the material photolysis, when oxidizable centers are broken and the resulting fragments with high local concentrations follow the Bolland and Gee oxidation mechanism. The examined evolution of the changes occurred in our degrading EPDM samples shows the preferential accumulation of carbonyl-containing products, which attain a great concentration after 70 h of weathering exposure. The hindering effect on oxidation is more visible for the variation of carbonyl index that they are noticed

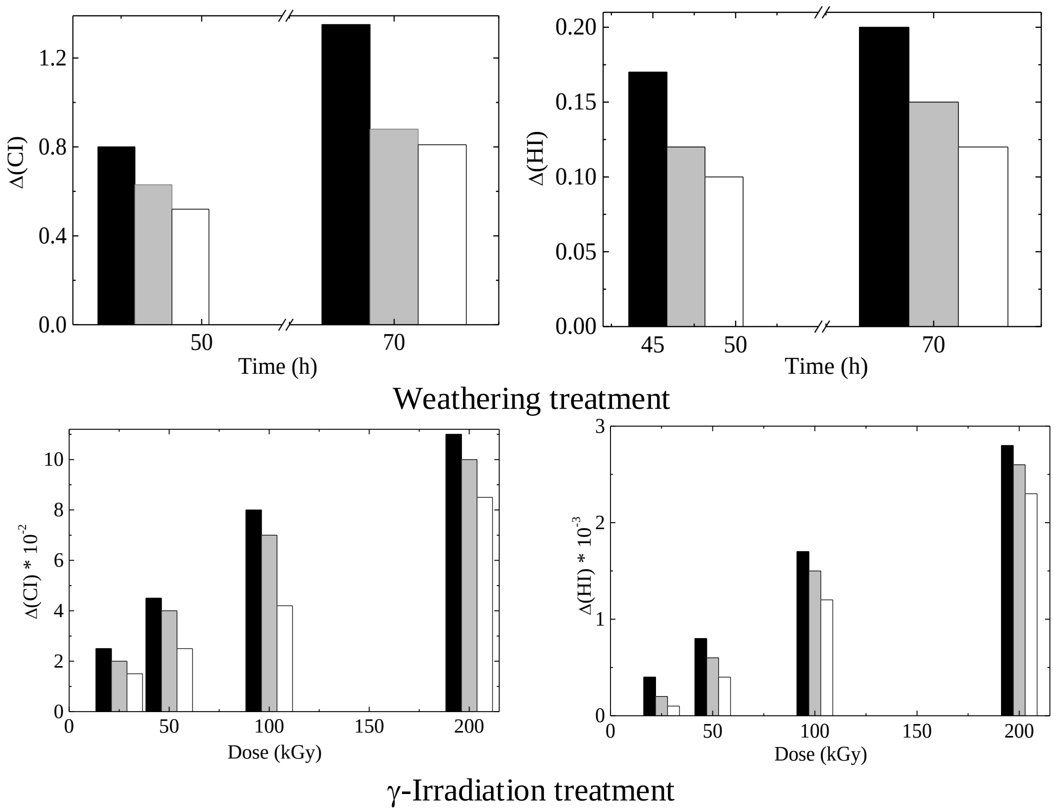

Fig. 5. The evolution of carbonyl (CI) and hydroxyl (HI) indices in the studied EPDM samples subjected to two different degradation processes.

for hydroxyl index. While the weathering exposure progresses, the higher amount of hydroperoxides is converted into C=O compounds [33], which are abundant in pristine EPDM.

The accelerated ageing occurred during γ-irradiation in air revealed the effective action of stabilizers, but the effects are less sustained that in the case of weathering. This aspect can be ascribed to the higher local concentration of radicals due to the higher energy of incidental radiation. It seems that the alkoxy forms of antioxidant molecules are less stable in the high energy exposure, when the α,δ-keto-hydroperoxides are decomposed with a high activation energy (240 kJ mol^{-1}) [33]. For the sterilization dose (25 kGy), the ageing is less developed that it is attained after 47 h of weathering. The oxidative degradation of γ-irradiated ethylene-propylene elastomers is modelled by taking into account all of the possible reactions involving hydroperoxides [34]. As the similar results obtained by the present investigation indicate the evolution of degradation, the stabilization activity of natural antioxidants like flavonoids (caffeic acid and naringenin) revealed their high efficiency and the influence of the preservation in molecular structure by the improvement of characteristic oxidation parameters [35]. In comparison with weathering treatment the γ-irradiation has a special feature consisting of the tendency onto crosslinking over a low dose range, where certain intermolecular bonds are formed [36]. This tendency is associated with the oxygen uptake, when the continuous diffusion of molecular oxygen controls the evolution of ageing [37]. Using reference structure (pentacontane), it was demonstrated that the most significant increase in the amount of bonded oxygen occurs just around 5 kGy, when the solubilized oxygen is totally consumed. After the irradiation dose of 20 kGy, the quantities of aldehydes and ketones, alcohol esters reach steady-states, while the amount of carboxylic acids increases linearly [37]. A slight modification of energetic conditions during γ-exposure of EPDM can be noticed from Fig. 6. The linear dependencies of activation energy on γ-dose were found for all investigated compositions. The change in the slopes that define the two different dose ranges would be ascribed to the abundancy of radicals that diminishes the distance between reacting fragments and O_2.

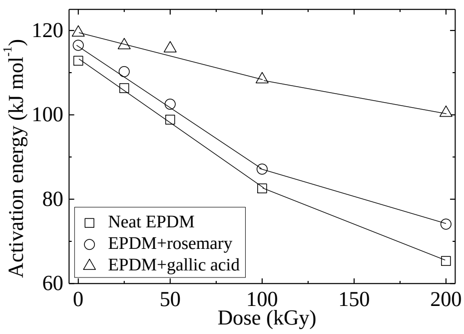

Fig. 6. The dependence of activation energy on γ-irradiation dose for EPDM samples

6. Conclusions

This paper provides useful information on the improving solution by ecological additives in plastics like ethylene-propylene elastomers. The comparison between the protection efficiency of gallic acid and rosemary extract reveals the higher effect of formerly mentioned antioxidant. The nonisothermal chemiluminescence measurements indicated either the relevant effect in the delay of oxidation during thermal degradation, or the high efficiency of gallic acid under the action of γ-radiation. The activation energies present higher values confirming the antioxidant activities of rosemary extract and gallic acid in EPDM matrices. The linear dependences of the degradation activation energy on exposure γ-dose and the change in the slopes over low/medium and high dose ranges confirm the influence of received energy, which conducts the scission of macromolecules. The formation of hydroperoxides by the replace of active proton of active hydroxyls of antioxidant structure, the precursors of final oxygenated products of degradation, is efficiently hindered as the calculated carbonyl and hydroxyl indices illustrate.

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