

Prevention of degradation of γ -irradiated EPDM using phenolic antioxidants

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The mitigation of oxidative degradation under γ -irradiation promoted by eight commercial antioxidants: Ethanox 330, Hostanox O3, Irganox 1010, Topanol OC, Ionox 220, Santonox R, Santowhite, Cyanox 2246 loaded onto ethylene–propylene terpolymer at the concentration of 0.5 phr in respect of a pristine polymer was studied. The polymer samples were exposed to various doses up to 500 kGy. The kinetic parameters of oxidations: oxidation induction times, onset oxidation temperature, oxidation rates were evaluated by CL measurements. They validated the differences in the stabilisation activities by limitation of the oxidation gradient. The high efficiency of some of the antioxidants studied, such as Ionox 220 and Santowhite, ensured the delay in degradation even at a high irradiation dose (500 kGy). For the environments with γ -radiation exposure, a relevant sequence in the increasing protection efficiency could be established: Topanol OC; Hostanox O3; Irganox 1010; Cyanox 2246; Santonox R; Ionox 220; Santowhite. The FT-IR spectra were recorded for the calculation of the radiochemical yields resulting from the modifications occurring in the concentrations of oxygenated structures. The accumulations of hydroxyl- and carbonyl-containing products were calculated to evaluate the irradiation effects in EPDM-based products during a severe accident. The options for EPDM stabilisation are discussed based on chemiluminescence and FTIR analyses. © 2015 Institute of Chemistry, Slovak Academy of Sciences

Keywords: EPDM, radiation degradation, oxidation, stabilisation, FT-IR, chemiluminescence

Introduction

The addition of a stabiliser to the formulation of polymer material is a satisfactory conscious option for improving the product life-time. The profusion of antioxidant structures makes it difficult to compare a large part of them in the same matrix and under similar conditions. However, the presence of a radical scavenger in nuclear energetic polymeric materials is strongly required, because any exposure to radiation induces the irreversible process of oxidative degradation in the polymer bulk as a result of oxygen diffusion (Yilmaz Kaptan & Güven, 1997; Suljovrujic,

2013). Typical additives providing an efficient delay in oxidation belong to phenolic structures, because the reaction of the free radicals with oxygen is blocked (Zaharescu et al., 2006; Navarro et al., 2011). The differences in efficiency between oxidation protectors are caused by the different mobilities of hydroxyl protons, which can be replaced by free radicals. The preservation of a low oxidation state in the polymer is effectively assisted by the chain-breaking and hydroperoxide decomposition activities of phenoxy radicals (Ahmad et al., 2014).

The radiation degradation is initiated by bond cleavage and progresses by a chain process. The initia-

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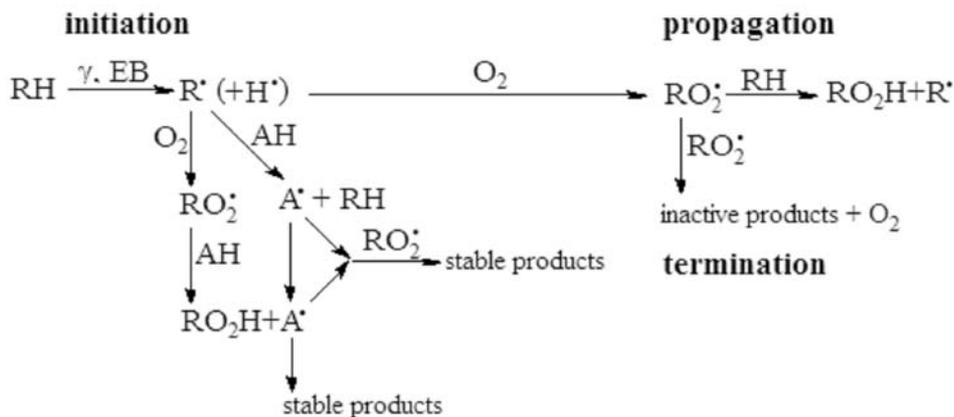


Fig. 1. General scheme of competition between stabilisation and progress of oxidation.

tors are peroxy radicals produced by the reaction of diffused molecular oxygen with newly generated radicals. A scheme of the radiochemical degradation mechanism and stabilisation activity is presented in Fig. 1.

The competition between the propagation of oxidation and the stabilisation action must lead to protection of the polymer as long as the additive is not entirely decayed. The stabiliser consumption and its loss cause an accelerated ageing of the polymer, because the high concentration of initiators determines a certain oxidation level (Jipa & Zaharescu, 2013). Effectively, the rate of oxidation in polymer materials depends on the formulation and the irradiation conditions (dose absorbed, dose rate, exposure environment, processing temperature). The oxidation profile is related to the diffusion-limited process according to the physical features, sample size or surrounding pressure (Hoyos et al., 2006; Ohtake et al., 2013).

The prediction of antioxidant capacity for delaying oxidation is explored for assessment of the material resistance in direct connection with the energy transfer from a degrading environment (Zaharescu et al., 2013a). The durability of stabilised products related to material failure is the main characteristic that indicates the limit of chemical transformations occurring during ageing (Beißmann et al., 2014). The migration of the antioxidant is of great importance (Lundbäck et al., 2006; Reinas et al., 2012) because it would be expelled from the material without any efficiency. This is directly connected with the size of the protector molecules, which affects the depletion of the additive and the history of the environmental conditions.

The ranking of stabilisation activity can be established after investigation of the effects of different structures under similar conditions: polymer matrix, processing parameters, selection of the same testing procedure. In evaluation of the protection action, the appropriate procedures must be selected in relation to the measurement accuracy (Pospíšil et al., 2003). This study is based on the results obtained by two accurate and complementary methods: FT-IR spectroscopy and chemiluminescence. They provide reliable information

on the structural changes occurring in the polymer and on the material resistance against oxidation (Zaharescu et al., 2014). The selection of hindered phenolic structures was based on their ability to scavenge the oxidation promoters and, consequently, on delaying the premature ageing.

The protective action of selected compounds can be regarded as an antirad activity, which involves the intrinsic radiation stability of additives and diminution of the negative effects of the energetic factors of degradation. Their presence can retard the start of oxidation and the material lifetime can be significantly increased. This is an essential feature of polymer materials operating in radiation environments, because safety involves high-performance materials (Celina, 2013). The prevention mechanism involved in the activity of antioxidants is based on the temporary blocking of the chain initiation of degradation, the scavenging free radicals or peroxy intermediates, if the additive belongs to the classes of primary stabilisers or to the chain-breaking antioxidants, respectively. The chemical protection afforded by antioxidants ensures not only the security of equipment by the integrity of items but also the low frequency of maintenance breaks.

A large volume of information is available on the protection activity shown by antioxidants. Unfortunately, the correlation between the efficiency of a large category of additives has hardly been reported for similar investigation parameters. According to the international standards, the security reports on the operation of nuclear units (nuclear power plants, electron beam accelerators, industrial radiation processing enterprises, equipment for medical treatments, sterilisation, vulcanisation, and polymer-waste recycling) require a high radiochemical stability of plastics spare parts. This paper sought the validation of the protection activities for different antioxidants in order to prevent advanced degradation in γ -radiation-exposed EPDM products. The manufacture of high stability items such as gaskets, fittings, O-rings, buffers, separation membranes, electrical cable insulations intended

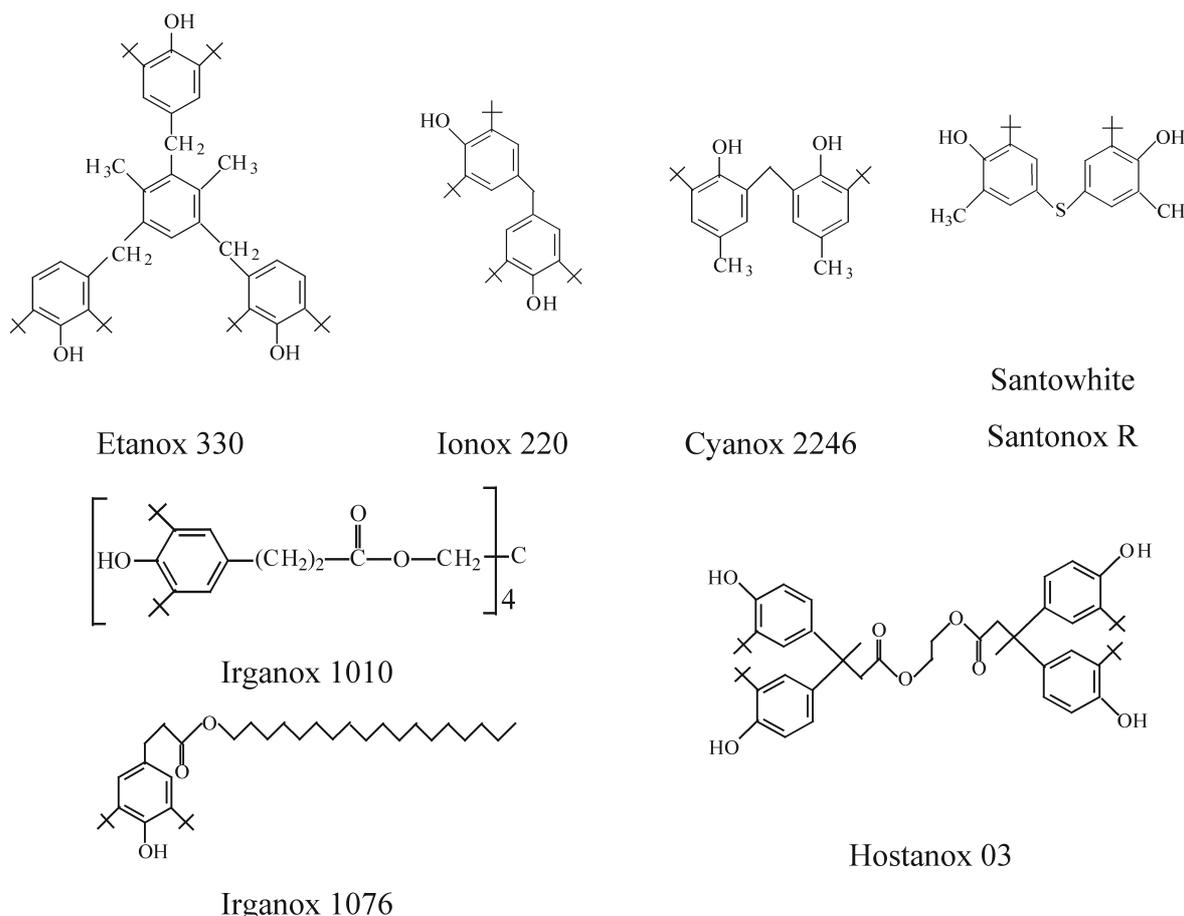


Fig. 2. Molecular structures of additives.

for use in nuclear power stations, accelerators, and high-activity irradiators raises the question of their reliability in service when exposed to any dose.

Experimental

The host polymer, ethylene-propylene terpolymer (EPDM), was provided by APRCHIM Pitești (Romania) as Terpit C[®]. It consists of ethylene (64.5 mass %), propylene (32 mass %), and diene, 5-ethylidene-2-norbornene (3.5 mass %). The main initial properties are: number of CH₃ for 100 carbon atoms: 0.983, unsaturation (C=C/1000 carbon atoms): 0.184, melt index (dl g⁻¹): 1.38. The material was used as received.

The powdered additives, the molecular structures of which are presented in Fig. 2, are: Ethanox 330 (1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene), Irganox 1010 (pentaerythritol tetraakis(3-*t*-butyl-4-hydroxyphenyl)propionate), Topanol OC (octadecyl 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate), Ionox 220 (2,6-di-*t*-butyl-4-[(3,5-di-*t*-butyl-4-hydroxyphenyl)methyl]phenol) were provided by Ciba Geigy (USA), Hostanox O3 (ethylene bis[3,3-bis(3-*t*-butyl-4-hydroxyphenyl)butyrate] was produced by BOC Sciences (USA), Santonox R (5-*t*-butyl-

4-hydroxy-2-methylphenyl sulphide) was manufactured by Monsanto (USA), Santowhite (2-*t*-butyl-4-(5-*t*-butyl-4-hydroxyphenyl)sulphonyl-5-methylphenol) was delivered by Alfa Aesar (USA), and Cyanox 2246 (2,2'-methyl bis(4-methyl-6-*t*-butylphenol)) was offered by CYTEC Ind. Inc (USA). This group consists of antioxidants with different stabilisation capacities providing a detailed image on the diversity of options for the additive selection by plastics manufacturers and customers. These antioxidants were used as received.

The solid polymer was first dissolved in chloroform and then the residual gel was removed by filtration. Eight solutions with 0.5 phr of each antioxidant were prepared by the addition of a due amount of stabiliser into an EPDM chloroform solution. Films of 100 μm thickness for spectral determinations were cast in stainless steel moulds by solvent evaporation at ambient temperature. The films were collected from the mould and embedded in a solid frame in order to ensure the FT-IR investigation at the same point. Aliquots of 100 mL (approximately 0.3 mg of dry material) of each antioxidant/EPDM solution were transferred onto aluminium trays for chemiluminescence determinations.

The exposure of pristine and modified polymer

samples was performed inside a GAMMATOR M 38 (USA) γ -irradiation machine equipped with a ^{137}Cs source. The exposures were performed in air at ambient temperature at a dose rate of 0.4 kGy h^{-1} . Irradiation was performed by accumulation avoiding the errors deriving from differences between the samples.

The dose range begins with small values, which are characteristic of standard endurance testing in nuclear energetics and also includes high doses that are specific for nuclear accidents and LOCA events, such as Chernobyl.

FT-IR spectroscopy was performed on a JASCO 4200A (Japan) spectrophotometer at 50 scans and 4 cm^{-1} resolution. The infrared spectra of all samples were measured in the transmission mode. The light beam passed through the films at the same place, because the holders facilitate identical positioning during spectrum recording. The carbonyl and hydroxyl indices were calculated as the ratios between the absorbances measured at 1718 cm^{-1} and 3390 cm^{-1} , respectively, and the absorbance at 2920 cm^{-1} (Chiellini et al., 2006). The molar extinction coefficients, $310 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $90 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, were used for calculating the radiochemical yields of carbonyl- and hydroxyl-containing products (Escobar Barrios et al., 2012).

Chemiluminescence (CL) measurements were carried out on a LUMIPOL 3 (Polymer Institute of Slovak Academy of Sciences, Bratislava, Slovakia) equipment under isothermal and non-isothermal regimes, which provide reliable information on the progress of oxidative degradation from the emission of one photon for each de-excitation event of the carbonyl intermediate (Cerutti et al., 2009). The chemiluminescence measurements were based on the proportionality between the amounts of the primary intermediate and the recorded emission intensities. Oxidation induction times and oxidation rates were calculated from CL spectra recorded at 170°C . Errors of less than $\pm 0.5^\circ\text{C}$ were observed in temperature measurements. The CL results are expressed in Hz g^{-1} because the frequency unit is related to the number of counted photons and the mass unit represents the normalisation mass values.

All determinations were performed immediately after irradiations to minimise the decay consequence for short- and medium-lived radicals.

Results and discussion

FT-IR investigation

Hydroperoxides, the initiators of the chain process of oxidation, decay into various stable structures by the interaction with hydrocarbon macromolecules or with each other (Cerutti et al., 2009; Zaharescu et al., 2013b). An increase in oxidation product concentrations is properly described by the corresponding

modification of two main bands in the FT-IR spectra: 1714 cm^{-1} for carbonyl units and 3350 cm^{-1} for bound hydroxyls. The energy considerations on stabilisation efficiency concern not only the resistance of a material to oxidation but also the availability of an antioxidant to scavenge free radicals to prevent their reaction with oxygen. This assertion is related to the hydroxyl proton mobility, which depends on the intramolecular electronic interactions and on the hindering effect of *t*-butyl groups (Rychlý et al., 2000).

The contribution of additives is essential for the delay of degradation for the polymer continuously subjected to the action of various stressors (heat, sunlight, high energy radiation). The specificity of each stabiliser determines the suppression of oxidation up to a certain ageing state. The evolution of the bands in the FT-IR spectra describes the susceptibility of the polymer to resist an oxygen attack during irradiation. In the vicinity of the 1714 cm^{-1} band ascribed to carbonyl-stretching, several other vibrations at 1725 cm^{-1} (saturated ketones), 1740 cm^{-1} (esters) and 1755 cm^{-1} (γ -lactones) (Rivaton et al., 2006), which are not clearly resolved, can be noted in the records of medium-dose irradiated films. This means that there is no preferential degradation route when the concentrations of primary free radicals are low. At doses not exceeding 100 kGy , the overlapping of these bands does not permit their deconvolution and the calculation of specific quantities of stable products appeared as the result of oxidation promoted by γ -irradiation. At the same time, the band at 808 cm^{-1} ascribed to the double bonds from 5-ethylidene-2-norbornene (Rivaton et al., 2006) is correspondingly diminished. This proves that the third component (diene) of the polymer contributes by splitting, to the formation of further amounts of free radical which along with the peroxy radical initiate additional oxidation chains.

The differences between the antioxidant activities in delaying oxidative degradation are conclusively shown by the increase in the transmission values of the carbonyl and hydroxyl bands (Fig. 3). The hindered phenol structures are able to protect the polymer by the proton substitution, the mobility of which is influenced by the substituents on the benzene rings. Concomitantly, the number of available mobile protons is an important factor that determines an advanced stabilisation activity. For example, Hostanox 03 and Irganox 1010, which include in each of their molecules four mobile protons, have the greatest efficiency in the protection of EPDM against oxidation, while Topanol OC, having only one hydroxyl proton per molecule, does not notably protect the host polymer.

Other antioxidants studied exhibit an intermediate protection capacity due to their structural features. They restrict their reactions with free radicals appearing at all stages of oxidation according to their own reactivity, even though they appear by radiochemical

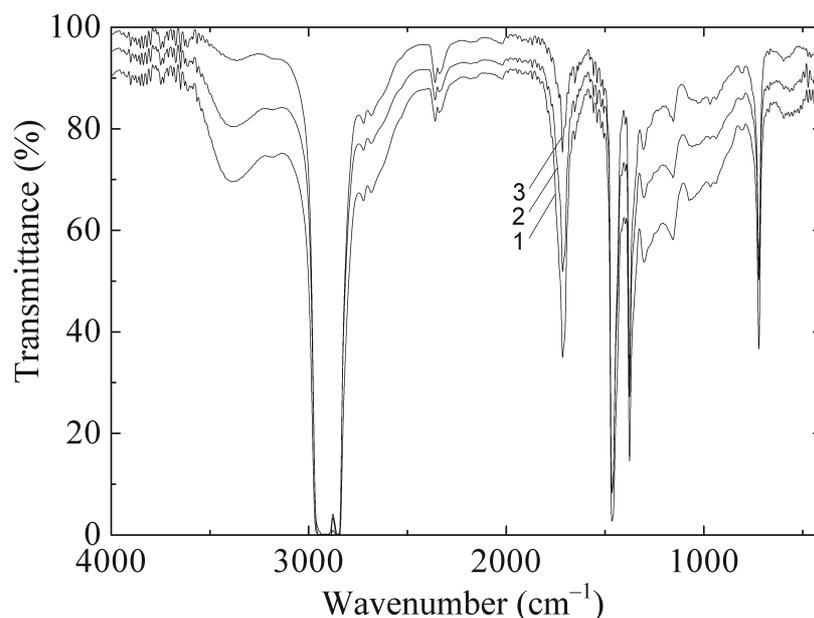


Fig. 3. FT-IR spectra of EPDM films in different oxidation states. Total dose: 500 kGy pristine EPDM (1), EPDM + Irganox 1076 (2), EPDM + Santonox R (3).

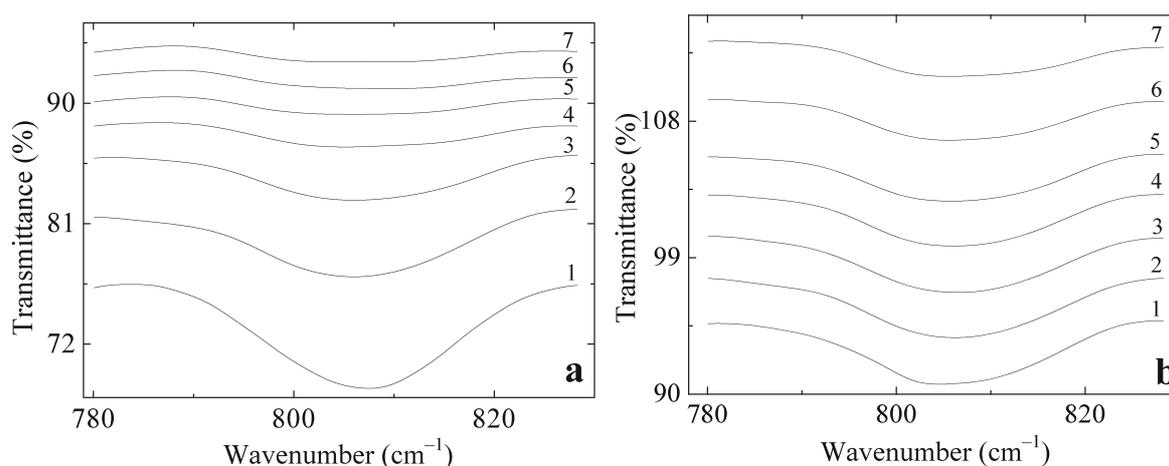


Fig. 4. Variation in transmittance intensities at 808 cm^{-1} for two EPDM films: neat EPDM (a); EPDM modified with Santowhite (b): 0 kGy (1), 10 kGy (2), 20 kGy (3), 50 kGy (4), 100 kGy (5), 200 kGy (6), 300 kGy (7).

scission followed by oxidation, or they are generated by monomolecular and dimolecular reactions involving hydroperoxides (Richaud et al., 2006). A certain specificity of antioxidants in respect of the accumulation rates of oxygenated radiolysis products was reported (Ghaffari & Ahmadian, 2007). This issue is related to the efficiency of radical scavenging which can be correlated with the mobility of hydroxyl protons.

In the recorded FT-IR spectra of EPDM films, slight transmittance values were registered in the regions of $3400\text{--}3200\text{ cm}^{-1}$ because of the presence of antioxidants, which contain OH functions or slow degradation over the shelf-life. Unfortunately, it is not possible to evaluate the consumption of antioxidants by this method, due to the accumulation of ra-

diolysis products. The modifications in the bands at 965 cm^{-1} of *trans*-vinylene (Gheysari & Behjat, 2001), 1170 cm^{-1} ascribed to the C—O bond (Rjeb et al., 2000), 1462 cm^{-1} representing the bending vibration of C—H in the methylene groups (Bykova et al., 2014), 1658 cm^{-1} attributed to C=O stretching (Sibeko & Luyt, 2014), 2683 cm^{-1} and 2725 cm^{-1} describing C—H bond stretching (Bykova et al., 2014) are minor. Significant differences were observed between the transmittances measured at 808 cm^{-1} (Figs. 4a and 4b). The diminution in each transmittance of this band depicts the consumption of diene (Rivatton et al., 2006), which has a specific rate for each formulation. It can be readily noted that the stabilisers presented protect this part of the molecules because the diene con-

Table 1. Carbonyl and hydroxyl indices radiation oxidation of stabilised EPDM; stabiliser concentration: 0.5 phr

Dose (kGy)	free	Hostanox 03	Topanol OC	Irganox 1010	Ethanox 330	Ionox 220	Cyanox 2246	Santonox R	Santowhite
Carbonyl index									
0	0.068	0.043	0.081	0.100	0.104	0.092	0.094	0.069	0.019
50	0.093	0.063	0.105	0.111	0.107	0.095	0.097	0.075	0.019
100	0.127	0.089	0.130	0.125	0.109	0.098	0.104	0.087	0.023
150	0.173	0.116	0.160	0.138	0.118	0.102	0.116	0.098	0.037
200	0.237	0.142	0.211	0.154	0.135	0.110	0.137	0.106	0.056
250	0.293	0.182	0.267	0.169	0.151	0.122	0.155	0.120	0.070
300	0.344	0.222	0.322	0.184	0.171	0.134	0.173	0.132	0.090
350	0.393	0.256	0.380	0.209	0.193	0.147	0.186	0.146	0.118
400	0.445	0.318	0.423	0.242	0.209	0.158	0.213	0.169	0.135
450	0.479	0.378	0.466	0.272	0.231	0.170	0.228	0.196	0.148
500	0.501	0.440	0.501	0.307	0.252	0.181	0.242	0.238	0.167
Hydroxyl index									
0	0.050	0.050	0.029	0.033	0.053	0.054	0.053	0.067	0.038
50	0.060	0.054	0.037	0.036	0.058	0.055	0.060	0.068	0.041
100	0.081	0.065	0.055	0.062	0.067	0.060	0.069	0.069	0.048
150	0.095	0.080	0.075	0.071	0.080	0.070	0.080	0.077	0.053
200	0.115	0.095	0.101	0.098	0.103	0.079	0.092	0.085	0.061
250	0.136	0.111	0.124	0.102	0.126	0.095	0.104	0.094	0.073
300	0.158	0.126	0.142	0.142	0.146	0.112	0.113	0.102	0.083
350	0.170	0.138	0.164	0.159	0.160	0.126	0.123	0.116	0.097
400	0.189	0.154	0.185	0.180	0.170	0.138	0.131	0.123	0.107
450	0.196	0.175	0.201	0.198	0.178	0.148	0.138	0.138	0.113
500	0.208	0.190	0.221	0.204	0.185	0.158	0.146	0.156	0.122

sumption occurs faster (Fig. 4a). Consequently, in the presence of phenolic antioxidants, the radiation degradation of the ethylene–propylene terpolymer can preferentially be ascribed to the breaking of the C–C and C–H bonds by homolytic and heterolytic scissions, respectively. The additional contributions to the generation of peroxy intermediates are supplied by the decay of diene, which is the third but weak molecular component.

Accordingly, the progress in the radiochemical oxidation vs the stabilisation activities can be quantified by calculating the carbonyl and hydroxyl indices (Table 1). An appropriate order of the increasing protection efficiency can be established: Topanol OC; Hostanox 03; Irganox 1010; Cyanox 2246; Santonox R; Ionox 220; Santowhite.

The different abilities in the delaying oxidation can be attributed not only to the facility of proton remoteness but also to their radiation stability and to the contribution of their quinone descendants. Unfortunately, Santonox R and Santowhite, the antioxidants with similar molecular structures, show slight differences in their protection actions.

The irradiation effects on traces of impurities may alter the behaviour of the basic compound, which does not regularly happen in conventional chemistry.

The radiochemical yields (Fig. 5) were calculated by applying the Lambert–Beer law followed by the conversion of absorbances into the numbers of func-

tions existing at certain irradiation doses:

$$G = 9.63 \times 10^3 \frac{1}{\varepsilon \rho d} \frac{A}{D} \left(\frac{\text{events}}{100 \text{ eV}} \right) \quad (1)$$

where G is the radiochemical yield (events per 100 eV), ε is the extinction coefficient for each spectral band ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), ρ is the material density (g cm^{-3}), d is the film thickness (cm), A is the absorbance measured at each dose, and D is the irradiation dose (kGy). The constant value 9.63×10^3 is the result of the conversions of units for concentration, dose, and density.

The radiochemical yields characterise the peculiar process feature which describes the development of degradation as the result of various reactions which occurred during irradiation. Their values are the general consequences of the contributions due to the sequential extent of product concentrations either by the accumulation of corresponding intermediates or by their decay following the oxidation mechanism controlled by each type of antioxidant (Zaharescu et al., 1999).

The linear dependence of G on the absorbed dose is not rigorously observed. This means that the upper curvature illustrates the preponderance of the built-up generation, while the slower increase defines the higher consumption rate in respect of the accumulation rate.

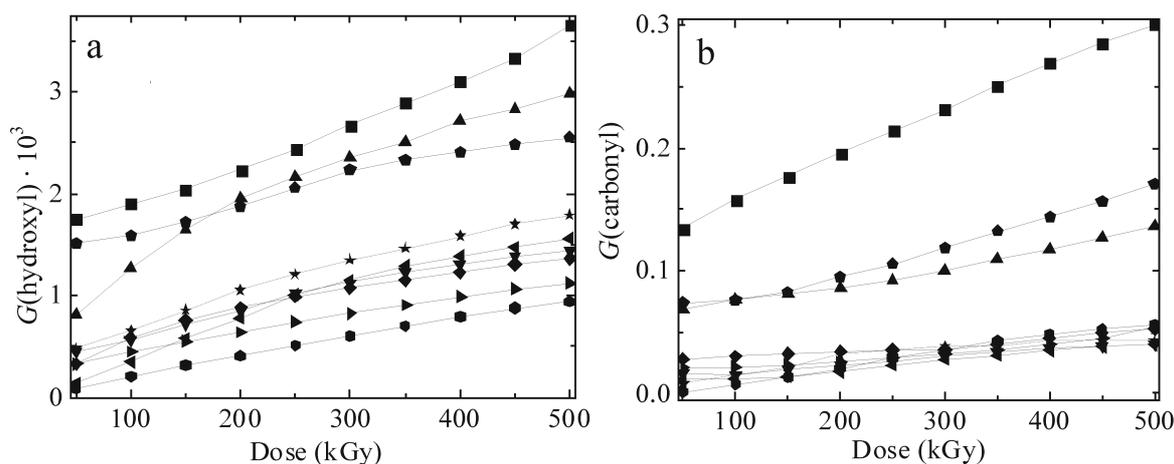


Fig. 5. Radiochemical yields, hydroxyl (a) and carbonyl (b) indices, calculated for each stabilisation state of EPDM as the function of dose: neat (■), Topanol OC (●), Hostanox 03 (▲), Cyanox 2246 (▼), Irganox 1010 (◆), Ionox 220 (◄), Santonox R (►), Santowhite (●), Ethanox 330 (★).

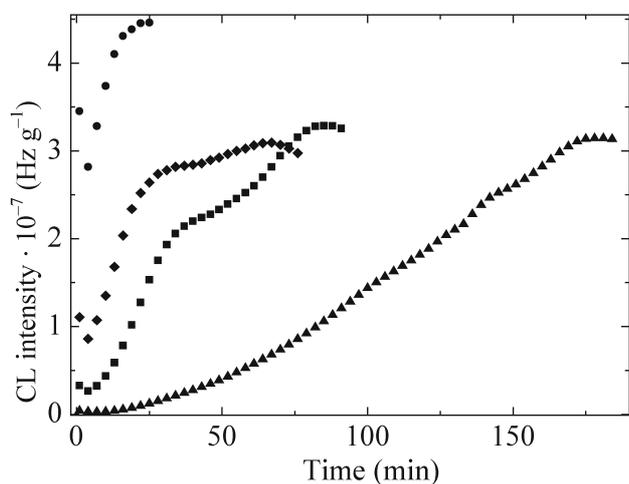


Fig. 6. Isothermal CL spectra recorded on pristine EPDM: 0 kGy (▲), 50 kGy (■), 100 kGy (◆), 300 kGy (●).

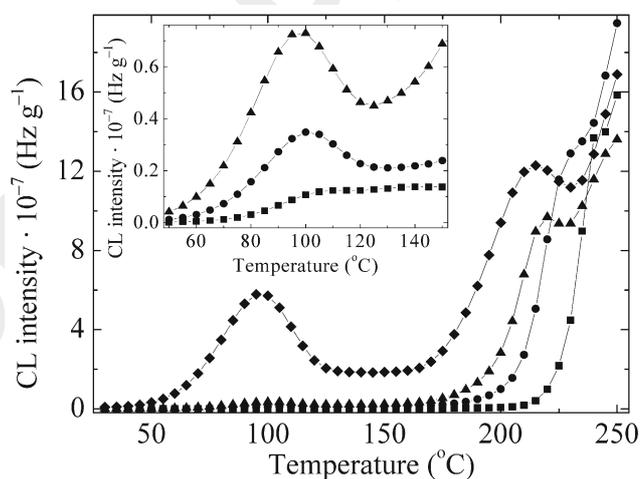


Fig. 7. Non-isothermal CL spectra recorded on pristine EPDM: 0 kGy (■), 50 kGy (●), 100 kGy (▲), 300 kGy (◆).

Chemiluminescence investigation

The behaviour of irradiated polymer samples subjected to heating in a chemiluminescence oven follows the history of degraded materials. In these cases, the pre-existing oxidation initiators, such as hydroperoxides, induce more rapid oxidation. The pristine EPDM undergoes oxidation during radiolytical exposure, when the polymer accumulates hydroperoxides which appear according to the chain mechanism. The oxidation induction times are significantly reduced as the dose effect is mirrored by the accumulation of initiators, RO_2 . In Fig. 6, the isothermal CL spectra indicate the necessity for stabilisation, because the decreasing oxidation induction times for the irradiated EPDM samples would result in unacceptable values for any application in a radiation environment. The non-isothermal determination of thermal stability for

the irradiated neat EPDM reveals a significant decrease in onset oxidation temperatures as the absorbed dose increases (Fig. 7). The presence of the CL intensity peak at around 100°C, which increases at higher γ -doses, confirms the formation of peroxy radicals by the scission of the double bonds in the first stage of radiation degradation (Zaharescu et al., 2013b). In Table 2, it may be noted that the onset oxidation temperatures illustrate the delayed start of thermal degradation when the antioxidant is added to the formulations of irradiated EPDM.

The additives which protect the polymer from its radiolysis also played their role during the chemiluminescence measurements. The main kinetic parameters of material oxidation, oxidation induction time (OIT) and rate of oxidation (v_{ox}) in the propagation step of oxidation, depict the strength of the formu-

Table 2. Onset oxidation temperatures for improved EPDM (heating rate: 5 °C min⁻¹)

Stabiliser	Onset oxidation temperatures (°C)			
	0 kGy	50 kGy	100 kGy	300 kGy
free	213	205	192	172
Topanol OC	215	206	198	182
Hostanox 03	216	210	203	190
Irganox 1010	220	216	210	196
Cyanox 2246	222	219	212	197
Santonox R	225	220	214	200
Ionox 220	227	222	215	205
Ethanox 330	230	225	215	210
Santowhite	230	217	218	212

Table 3. Main kinetic parameters for radiochemical oxidation of stabilised EPDM (testing temperature: 170 °C)

Stabiliser	Oxidation induction time (min)				Oxidation rate · 10 ⁻⁷ (Hz g ⁻¹ min ⁻¹)			
	0 kGy	50 kGy	100 kGy	300 kGy	0 kGy	50 kGy	100 kGy	300 kGy
free	93	62	32	15	6.51	3.22	1.76	0.93
Topanol OC	102	88	41	23	5.82	2.85	1.39	0.75
Hostanox 03	105	91	63	34	5.44	2.71	1.45	0.70
Irganox 1010	130	103	75	49	4.88	2.15	0.97	0.31
Cyanox 2246	152	121	94	56	4.25	2.16	0.93	0.28
Santonox R	171	144	111	61	4.04	1.79	0.88	0.30
Ionox 220	180	156	108	68	3.99	1.65	0.81	0.22
Ethanox 330	174	145	102	81	4.08	1.56	0.92	0.20
Santowhite	203	188	124	73	3.75	1.48	0.74	0.20

lation against oxidative ageing. Table 2 summarises the values of OIT and v_{ox} whose evolution is in good agreement with the spectral results of this investigation. While the neat polymer is readily oxidised, the efficient antioxidants such as Santowhite, Ionox 220, Santonox R, and Cyanox 2246 have demonstrated that they are suited to improve the durability, when they are used for the stabilisation of EPDM or polyolefins with a similar structure. The stabilisation efficiency is closely related to the molecular structure of the antioxidant and the exposure dose.

From the analysis of results presented in Table 3, it may be stated that OIT is the important feature for characterisation of the antioxidant property, because it determines the duration of the material with no measurable changes, while the oxidation rate depicts the resistance of the product over long periods of operation. These kinetic parameters are inter-correlated with regard to stability improvement within the dose range. All the antioxidant loadings tested in this study can confirm the acceptable stability of these formulations in respect of γ -irradiation at low doses up to 100 kGy, the critical dose which would be received during severe nuclear events.

The calculated radiochemical yields for accumulation of the main oxidation products (Fig. 5) prove that the addition of an efficient antioxidant significantly decreases the level of degradation during irradiation incidents.

The efficient activity of Santowhite, Ionox 220, Santonox R, and Cyanox 2246 at very high irradiation doses warrants the application of these formulations in the production of items intended for nuclear equipment. The oxidation is fed by the diffusion of oxygen, but ionising radiation provides the energy for structural damage. The irradiation dose is the determining factor, which can be considered as an essential operation parameter in the oxidative degradation of polymers. The decrease in the material stability determined by the energy transfer from incidental radiation accompanied by the simultaneous diffusion of oxygen can be mitigated by an efficient protector. This process occurs in various ways (Sibeko & Luyt, 2014), the transition of α -hydroxyl structures by the abstraction of proton into hydroperoxides, the inner molecular decomposition of vicinal hydroxyls or the bimolecular elimination of neighbouring protons. The last two routes are always followed by a chemiluminescence emission.

During the radiation processing of EPDM (Steltescu et al., 2013) and the accidental events of hazardous exposure (Rajini & Udayakumar, 2007; Plaček et al., 2009), the accumulation of degradation oxidation products restricts the duration of rescue operations. The adequate selection of a stabiliser is dependent on chemical and mechanical resistance adjust-

ment. The effect of the scission rate must be controlled by the antioxidant activity and the integrity of the material is directly correlated with the radio-oxidation level attained.

Conclusions

This study sought to present a comparative evaluation on the basis of the stabilisation efficiencies of several phenolic antioxidants, which significantly improve the resistance of the ethylene-propylene terpolymer to oxidation for applications in the nuclear industry for the fabrication of gaskets, membranes, sealing rings, buffers, connections, fittings, electrical cable insulations. It was demonstrated that the addition of proper compounds conferred long-term durability; even though the absorbed dose is very high, at around 500 kGy, while the irradiation is accomplished in air. For doses of less than 100 kGy all of the antioxidants tested satisfactorily maintained the oxidation stability of EPDM. At higher doses, the most efficient additives were the compounds containing several hydroxyl groups in their molecules. The evolution of radiochemical yields, as well as of carbonyl and hydroxyl indices, reflects the damage trends in respect to irradiation conditions. The structure of the antioxidant in relation to the mobility of the hydroxyl proton accurately defines the protection potential of the compound. The durability of EPDM under γ -irradiation is correlated with the antioxidant activity, which can be expressed by the evolution of the radiochemical yields of carbonyl and hydroxyl units. The effect of the additive incorporated in the formulation of EPDM products is a significant reduction in minimising the level of the oxidation state. The incorporated stabilisers reduce by half the number of oxidation events accounted for by radiochemical yields. The elimination of the oxidation peak noted in the pristine material increases the durability of the stabilised EPDM by preservation of the initial molecular configuration. The results reported here are useful for the selection of stabilisers for the manufacture of spare parts used in radiation fields and they are a guarantee of low damage effects in nuclear incidents.

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