Thermal and radiation stability of polyolefins modified with silica nanoparticles

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The comparative behavior of low-density polyethylene, polypropylene and ethylene-propylene diene rubber subjected to γ-irradiation is presented for technological purposes in radiation processing. The investigation by nonisothermal chemiluminescence, FTIR-ATR spectroscopy and electrical conductivity were accomplished on SiO_2 nanoparticle composites loaded with 2 and 5 wt% filler. The differences between studied polyolefins spring from the unlike configurations, which contain various proportion of tertiary and quaternary carbon atoms. The two concentrations of silica nanoparticles change adequately the material behavior under γ-radiation.

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1. Introduction

The radiation processing of materials asks detailed knowledge on the complex radiolysis mechanisms. The behaviors of similar materials under identical irradiation conditions were scarcely reported [1-4]. The durability of polymer materials depends strongly on the intensity and duration of stressor action, as well as on the composition characteristics. The potential and limits of applications for polyolefins in ionizing radiation fields are related to the structural features, which are defined through the evolution of degradation level. The evolution in the functional properties of irradiated polymers reflects the direct connection between the amounts of oxygenated radiolysis products and the material behavior under operation conditions of nuclear applications.

The radical mechanism applied to radiolysis of polyolefins is based on the identification of their oxidizable sites. The free radicals involved in the progress of oxidative degradation are the sources of oxygenated final products, which deteriorate the functional properties, especially electrical characteristics. The factors those are responsible by the level of degradation, namely dose, material structure and formulation, irradiation environment, control the progress of oxidative ageing. The description of oxidation in polyolefins can be satisfactorily done by chemiluminescence based on the proportionality between light emission intensity, as well as infrared spectroscopy and the concentrations of oxidation initiators, hydroperoxides [5, 6], are proportional with the amount of free radicals resulting during radiolysis.

The effects induced in polyolefins by ionizing radiation were intensively studied because of their large economical interest. However, in the most of cases the irradiation conditions were different so the evaluation of degradation is not easy to be compared.

Considerable efforts were focused on the characterization of nanocomposites, which offer improved material alternatives [for example, 7-9]. In many cases their stability modified by the presence of nanoparticle filler and irradiation exposure can be improved due to the intimate interaction between the two phases or the adsorption of radicals protecting them against oxidation. Thermal and radiation strengths of nanocomposites depend on the chemistry of components (polymer matrix and inorganic compound) [10-12], as well as on the modification conditions [13-17].

The prediction of polymer stability in the correlation with material properties is the main goal for the complete understanding of the responsibility of the oxidation intermediates. The hydroperoxide generation and decomposition [18] are followed by the accumulation of oxygenated final products [19-22]. The increase in the amounts of oxygenated radiolysis products changes all material features, because the presence of oxygen modifies the bulk molecular interactions. In the similar sense the contribution of filler nanoparticles turns the course of material degradation [23-28].

The present paper describes comparatively the progress in oxidation states of three polyolefins, LDPE, PP and EPDM, which are degraded by γ-irradiation. The differences that appear between them are ascribed to the contribution of peroxyl radicals. They are responsible for the initiation of oxidation and their amounts and interaction with filler determined the degradation profile. The evaluation of hydroperoxidation according with the Bolland and Gee scheme envisages the further modifications occurred in material properties. Thermal stability and electrical characteristics are monitored for γ-exposed polyolefins, which are basic information for the diagnosis of insulating materials applied in nuclear field [29].

2. Experimental

Low density polyethylene was produced by ROMPETROL PETROCHEMICALS (Romania) as type B 21/2 with the following characteristics: density – 0.9077 g.cm^{-3}, crystallinity – 42 %, melting index 3.25 g/10 min (190 ^{0}C/2.16 kg), number of CH_3 per 100 carbon atoms – 3.05. Polypropylene was purchased from ROMPETROL PETROCHEMICALS (Romania) as type TATREN HG 10.07. Its main features are: density – 0.8994 g.cm^{-3}, melting index 1.498 g/10 min (190 ^{0}C/2.16 kg). Ethylene-propylene diene rubber (EPDM) was provided by ARPECHIM Pitești (Romania), whose ethylene/propylene ratio was 3/2. The diene, ethylidene 2-norbornene (EBN), was initially in the concentration of 3.5 phr. All polymeric materials were used as received products. SiO_2 nanoparticles were provided by Degussa, as fumed silica, Aerosil 380 with specific surface 380 m^2.g^{-1}, particle diameter range 3 – 15 nm. Three levels of nanofiller concentration (0, 2 and 5 wt.%) were tested.

Films of 100 μm thickness and sheets (0.5 mm thickness) were obtained by mixing basic polymer and nanofiller (SiO_2) in a Brabender Plastograph for 15 minutes at 180^{o}C. Specimens were pressed at 180 bars in an electrical device for 10 minutes after a preheating for 15 minutes. The pressing temperatures were adapted to the type of polymer. Neat materials were processed at 122 ^{o}C (LDPE), 155 ^{o}C (EPDM) and 170 ^{o}C (PP); the samples containing 2 % and 5 % silica were pressed at temperatures higher with 15 ^{o}C and 25 ^{o}C, respectively.

The exposure of polymer samples was achieved in air at room temperature in a γ-irradiator M-38 GAMMATOR (USA) equipped with a ^{137}Cs source. The dose rate is 0.4 kGy.h^{-1}. The values of received γ-dose were 0, 10, 20, 50 and 100 kGy.

Chemiluminescence measurements were performed applying nonisothermal procedure with LUMIPOL 3 (Slovak Academy), whose temperature value error was ± 0.5 ^{o}C. A convenient value for all formulations and doses, while the rate of heating applied for nonisothermal determination was 2 ^{o}C.min^{-1} over the temperature range from room temperature to 250 ^{o}C.

Fourier-Transform infrared (FTIR) spectra were collected in a JASCO 4200 FTIR spectrometer, in the attenuated total reflection mode (ATR) to elucidate the surface composition and radio-induced modifications to functional groups. The spectra resulted from averages of 48 scans at a resolution of 4 cm^{-1} between 600 and 4000 cm^{-1}. From the spectra the carbonyl index (CI) and hydroxyl index (HI) were determined using the absorbance between 1700 - 1760 cm^{-1} (for C=O), 3300-3600 cm^{-1} (for OH) and the CH_2 scissor bond between 1390-1500 cm^{-1} as reference band. The carbonyl index and hydroxyl index were defined as ratio of the integrated oxidation bands (CI: 1710-1760 cm^{-1} and HI: 3300-3600cm^{-1}) and the reference band (1390-1500cm^{-1}).

The electrical tests were performed on electrometer Keithley 6517A connected with a Keithley 8009 test fixture and a computer. The samples, plaques of square shape (10 x 10 cm^2) having the thickness of 0.5 – 0.6 mm, were placed between the two plane electrodes of the test fixture and a voltage step of 1000 V was applied for 60 minutes. For each sample one thousand values of the absorption current were recorded during voltage application, each point at every 3.6 seconds. All the measurements were performed at ambient temperature (27 ºC) and humidity (~ 50 %).

3. Results and discussion

The formation of hydroperoxides as the result of oxygen uptake leads to the accumulation of various oxygenated products [30], whose evolution determined the degradation kinetics. The presence of filler turns the rate of degradation because of the interaction between polymer matrix and nanoparticles, mainly the formation of bridges and the adsorption of radicals on the particle surface.

In Fig. 1 examples regarding the evolution of CL intensities measured at increasing temperature are illustrated. The increase in the stability of polymers especially on the high temperature range can be correlated with the modification in the concentration of filler. However, the presence of diene in EPDM causes the formation of a significant amount of peroxyl radicals around 100 ^{o}C, while peaks around 200 ^{o}C would be related to the scissions at tertiary and quaternary carbon atoms in EPDM and PP. The activation energies involved in the thermal oxidation of studied polyolefins correspond to the picture suggested by the present CL results. These values are 92.4 kJ.mol^{-1} for polypropylene, 130.2 kJ.mol^{-1} for ethylene-propylene copolymer and 138.8 kJ.mol^{-1} for low density polyethylene [30].

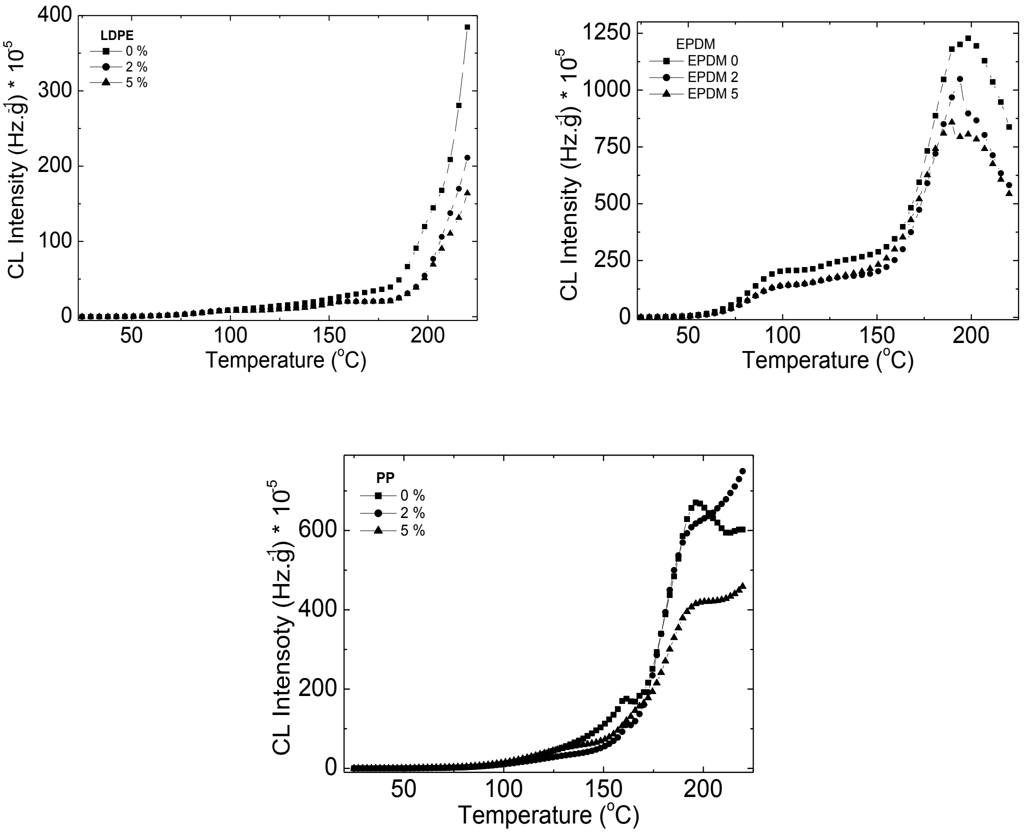

Fig. 1. Nonisothermal CL spectra recorded on three polymers modified with silica nanoparticles irradiated at 100 kGy. (■) neat, (●) 2 %, (▲) 5 %.

The configuration of molecules represents the main factor which influences the stability of backbones. During radiolysis the initiation of oxidation is described by the initial amount of radicals, which further scavenge molecular oxygen for the generation of peroxyl intermediates according with Bolland and Gee scheme [18]. The existence of free radicals in irradiated polyolefins formed during -exposure is revealed by the values of initial CL intensity (Table 1). The propagation of oxidation is related to the rate of secondary peroxyl radical disproportionation and, finally, the onset oxidation temperatures (Table 1) takes values corresponding to this process accompanied by the decomposition of hydroperoxides. The thermal stability of irradiated nanocomposites of polyolefins depends on the autocatalytic initiation step followed by the accumulation of alkoxyl and alkyl precursors.

Table 1. Changes in initial CL intensities and onset oxidation temperatures for irradiated SiO_2 nanoparticle modified polyolefins.

Dose (kGy)	EPDM			LDPE			PP		
	Initial CL intensity (Hz.g^{-1}) . 10^{-7}								
	0 % SiO_2	2 % SiO_2	5 % SiO_2	0 % SiO_2	2 % SiO_2	5 % SiO_2	0 % SiO_2	2 % SiO_2	5 % SiO_2
0	0.15	0.23	0.75	0.08	0.41	1.79	0.15	0.08	0.10
10	4.62	8.45	6.06	0.30	0.60	2.11	0.67	0.13	0.15
20	7.73	13.76	9.91	0.67	0.71	2.06	1.09	0.31	0.38
50	9.48	14.70	14.50	1.48	1.03	1.02	2.71	2.07	2.10
100	16.75	15.07	18.08	1.92	1.42	1.28	3.82	3.21	2.44
Oxidation onset temperature (° C)									
0	232	225	226	225	210	208	219	220	216
10	164	165	166	214	206	206	208	204	206
20	163	161	165	213	207	204	196	200	198
50	163	158	162	213	207	203	188	176	180
100	156	152	154	213	205	205	165	159	166

The main both oxygenated groups (hydroxyl, carbonyl) underwent an increase with irradiation time in a traditional way, when a very broad hydroxyl absorption region (3700 - 3200 cm^{-1}) with a maximum centered at about 3350 cm^{-1} attributed to the associated alcohols was observed. The absorbances at 1712, 1722 and 1740 cm^{-1} have been assigned to carboxylic acid, ketone and ester, respectively [31]. The recorded ATR/FTIR spectra are characteristic for neat polyethylene, polypropylene and ethylene propylene diene monomer rubber, respectively. The FTIR spectra for neat polyethylene and polyethylene filled with 2 % and 5 % nano silica filler is shown in the Fig. 2. The nano-SiO$_2$ filler addition leads to the increasing of peaks of about 1100 cm^{-1} and 800 cm^{-1}, which are attributed to the asymmetric stretching vibrations, and bending vibrations of Si-O-Si bonds of silica, respectively. The absorption peaks of about 3350 and 1640 cm^{-1} could be ascribed to the symmetric stretching vibrations of O-H. The 955 cm^{-1} is assigned to stretching vibration of Si-OH [32-36].

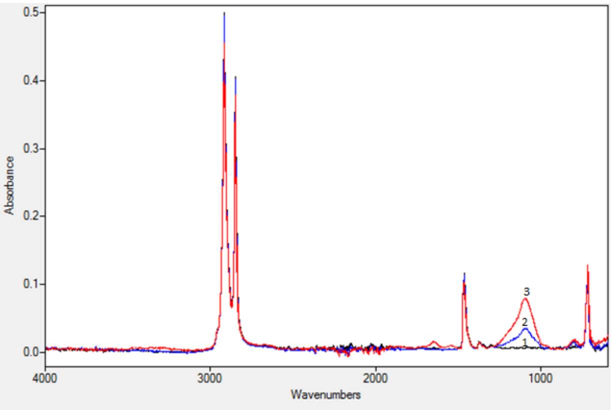

Fig. 2. FTIR Spectra of unfilled LDPE (1) and filled with 2 wt. % (2) and 5 wt. % (3) nano-SiO$_2$.

The oxidation of studied polyolefins takes place in organic components and the higher content of silica restricts the penetration of oxygen into the inner zones of bulk. Neat PP and EPDM present closed values either of HI and CI, because of the presence of reactive places, substituted carbon atoms or unsaturation (Fig. 3). The composites with 2 and 5 % of silica show differentiate curves whose values increase with absorbed dose. The sequence of radiation stability found from spectral investigations is the following:

LDPE > EPDM > PP

even the samples are pristine ones or they are modified with silica nanoparticles.

The absorption current i_a(t) appears when a step voltage is applied to a condenser. The typical time variation of the current in the condenser presents an asymptotic shape and has the following components:

$$i_a(t) = i_i(t) + i_p(t) + i_{ss}(t) + i_c(t),$$

where i_i(t) is the charging current of the capacitor with vacuum dielectric, i_p(t) is the polarization current, i_{ss}(t) is the space charge current and i_c(t) is the conduction current. The component i_i(t) is due to the charging of vacuum dielectric condenser and decreases to zero very quickly [37]. The component i_p(t) is given by the electric polarization phenomena that consist in very small motions of a large number of attached charges. The current i_{ss}(t) corresponds to the movement of space charge, which usually build up in polymer samples during their fabrication (by molecule fracturing, etc.), by charge injection from the electrodes and due to the degrading agents (heat, electric field, high energy radiation, etc) [38]. In a certain time, depending on dielectric properties, the component currents i_p(t) and i_{ss}(t) become zero. The conduction current i_c(t) corresponds to the convection of electrons, ions and molecular ions and depends on the chemical and physical structure of polymer nanocomposites.

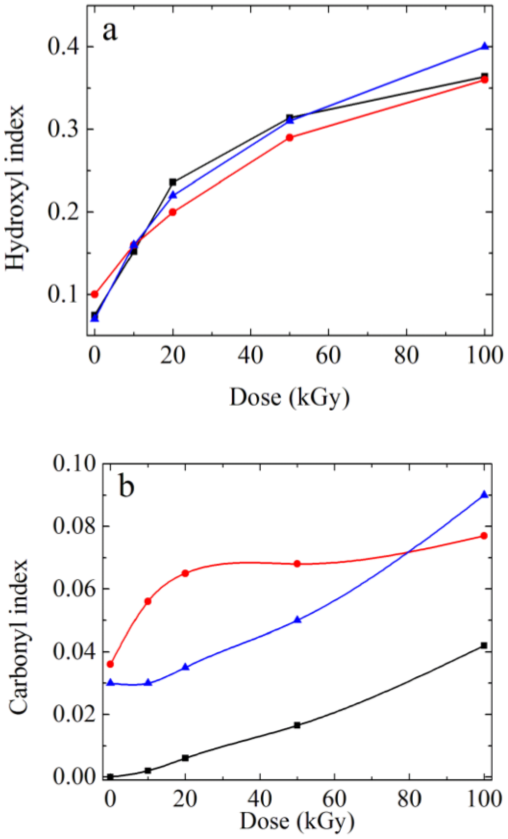

Fig. 3. Changes in hydroxyl index (a) and carbonyl index (b) obtained for polyolefins modified with n-SiO$_2$ 2 %: (■) PE, (▲) EPDM, (●) PP

Absorption currents in the samples of neat EPDM and nanocomposites based on EPDM with 2 and 5 wt.% nanoSiO$_2$, unirradiated and irradiated at a dose of 100 kGy, are presented in Fig. 4. If the gamma-irradiation dose increases at 100 kGy, it can be seen that the maximum values of currents increase and the slope of the curves becomes smaller. The enhance in dipoles concentration within polymer bulk is the reason of the changes in electrical characteristics as the consequence of scissoring bonds. The further oxidation of free radicals induces noticeable increases in the $i_p(t)$ and $i_{ss}(t)$ components values after the accomplishment of irradiation.

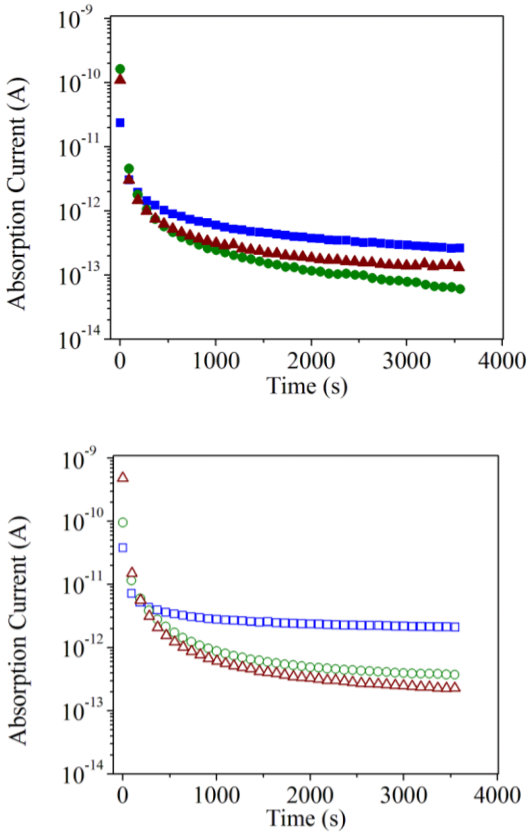

Fig. 4. Time variations of the absorption currents in unfilled EPDM at 0 kGy (■) and 100 kGy (□), EPDM/nanoSiO_2 with 2 wt.% at 0 kGy (●) and 100 kGy (○), 5 wt.% filler concentration exposed at 0 kGy (▲) and 100 kGy (Δ).

Fig. 5 shows that on the range of lower filler concentration (2 and 5 wt. % nano-SiO_2) in the EPDM host matrix, the presence of oxide determines a decrease in absorption current values relative to the neat polymer, due to the decrease of the polarization and the space charge current components. In the interface zone between nanoparticles and polymer chains are formed physical and chemical bonds due to the presence of hydroxyl groups (polar groups) on the surface of filler [39]. SiO_2 nanoparticles and polymer chains become inter-linked in the interface, due to active positions of crosslinking present in EPDM chains [39]. This behaviour would reduce the movement of the space charge in the nanocomposite structure leading to the decrease in $i_{ss}(t)$ absorption current component. According to Wolf and Wang [39-40], the polar surface of silica enhances filler–filler interactions, resulting in strong intermolecular hydrogen bonds between hydroxyl groups of silica. Such strong interactions could produce poor dispersion of the nanoSiO_2 in the rubber compound [39], which explains the decrease in the $i_p(t)$ component with the increase of silica filler in EPDM.

Even if the nanocomposites samples are irradiated at a dose of 100 kGy, the absorption currents values are smaller compared to the unfilled polymer. The higher values of electrical resistivity describe better insulating properties for the polymer nanocomposites.

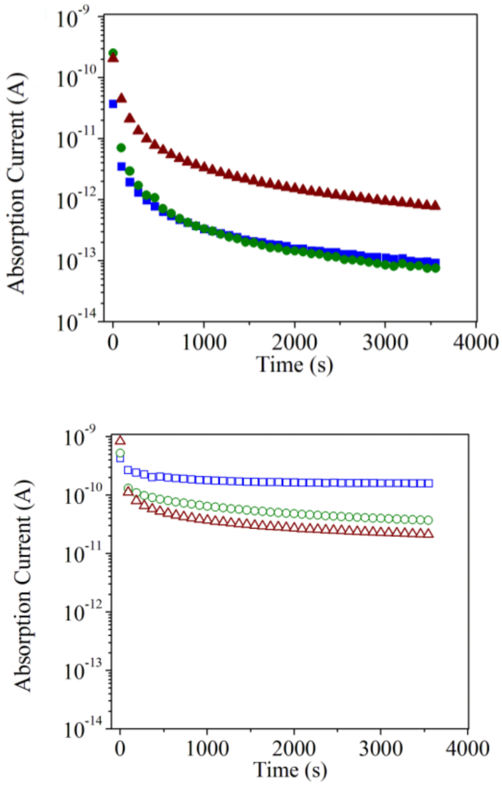

Fig. 5. Time variations of the absorption currents in unfilled LDPE at 0 kGy (■) and 100 kGy LDPE/nanoSiO_2 with 2 wt.% at 0 kGy (●) and 100 kGy (○) and LDPE/nanoSiO_2 with 5 wt.% filler concentration exposed at 0 kGy (▲) and 100 kGy (Δ).

The variations of medium absorption currents recorded on a group of 3 samples from each combination of nanocomposite neat LDPE and LDPE/nanoSiO_2 with 2 and 5 wt.% filler concentrations, unirradiated and irradiated at a dose of 100 kGy are presented in Fig. 5. It can be observed that by the increasing in gamma dose at 100 kGy, the values of absorption currents increase compared to the values of unirradiated nanocomposites. This behaviour may be correlated with irradiation process, which causes the increase of dipoles concentration as a result of structural degradation accompanied by an increase in polarization current $i_p(t)$ and space charge $i_{ss}(t)$ currents.

According to Tanaka's multi-core model for polymer nanocomposite dielectrics [41], the interface zone polymer – spherical nanoparticle is formed by three distinct layers. In the third layer of the interface it can be produced a crosslinking of polymer chains, which reduce the mobility of space charge, through the nanocomposite structure and may lead to a decrease $i_{ss}(t)$ values. Polarization current $i_p(t)$ could decrease because of the hydroxyl and carbonyl groups formed between the ends of polyethylene chains from the second layer of interface and the surface of polar nanoparticles, which could reduce the mobility of polymer chains. This could explain why the values of absorption currents are smaller in the case of unirradiated LDPE with 2 wt. % nanoSiO_2. For irradiated nanocomposites, the same behaviour is observed in both cases of 2 and 5 wt % nanoSiO_2 filler concentration in the LDPE matrix. The irradiation process brings about a pronounced polymer crosslinking in the third layer of interface, so a reduction of polymer chains and space charge mobility within the nanocomposites structures.

In Fig. 6 the absorption currents curves for neat PP and its nanocomposites based on PP/nanoSiO_2 with 2 and 5 wt. % filler concentrations unirradiated and irradiated samples at a dose of 100 kGy are shown. First of all, it can be observed that the presence of nanoparticles in the polymer matrix determines the increase of absorption currents with the filler concentration compared to the neat PP. The increase in polarization current $i_p(t)$ follows the accumulation of electric dipoles, especially inside nanoparticles and/or inside the polymer-nanoparticle interface layers. The increase in space charge current $i_{ss}(t)$ takes place simultaneously with the space charge accumulation in the huge area interface polymer - nanoparticles according to the nanocomposites models from literature [41, 42].

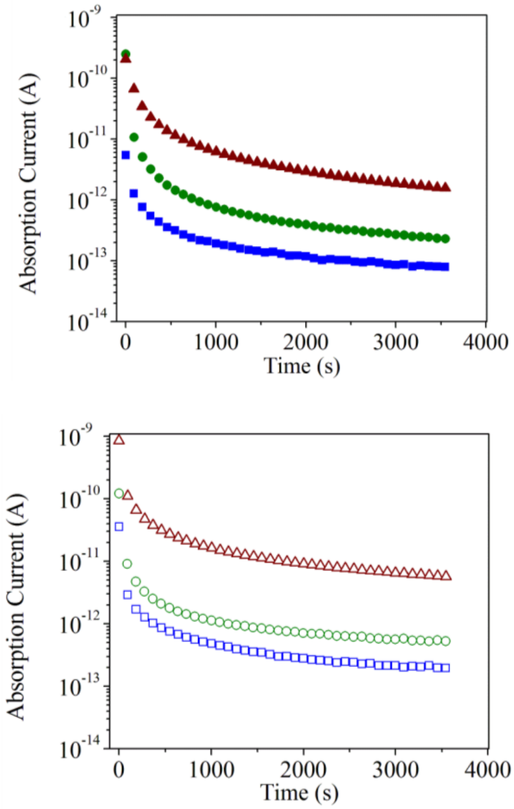

Fig. 6. Time variations of the absorption currents in unfilled PP at 0 kGy (■) and 100 kGy (□), PP/nanoSiO_2 with 2 wt.% at 0 kGy (●) and 100 kGy (○) and PP/nanoSiO_2 with 5 wt.

4. Conclusion

The exposure of engineering polyolefins to □-radiation causes the modifications in the structural features of studied polyolefins modified with SiO_2 nanoparticles. While nonisothermal determinations prove the improvement in their thermal stabilities, the formation of electrical dipoles affects the absorption current values. The decrease in these figures is the consequence of polarization, which becomes more important factor that demonstrates the interaction between inorganic filler and polymer phase. The structural characteristics influence all functional properties and the comparison between the three polyolefins, low density polyethylene (LDPE), polypropylene (PP) and ethylene-propylene-diene monomer (EPDM), by the different contribution of substituted carbons atoms and the presence of unsaturation. Nanoparticles of silica bring about an enhance in the radiation resistance; the investigated formulation can be used as technological materials on the field of nuclear energetics.

References

[1] B. Bartoníček, V. Plaček, H. Hnát, Radiat. Phys. Chem. **76**, 857 (2007).
[2] S. Cheng, Phillips, Ed, Parks, L., Radiat. Phys. Chem. **79**, 329 (2010).
[3] T. Seguchi, K. Tamura, T. Ohshima, A. Shimada, H. Kudoh, Radiat. Phys. Chem. **80**, 268 (2011).
[4] T. Zaharescu, I. Pleşa, S. Jipa, Polym. Bull. **70**, 2981 (2013).
[5] L. Matisova-Rychlá, J. Richlý, Inherent relations of chemiluminescence and thermoluminescence of polymers. In: Clough, R.L., Billingham, N.C., Gillen, K.T. (eds), Polymer durability, degradation and stabilization, advances in chemistry. ACS series 249, Washington DC, p. 175, (1996).
[6] N.C. Billingham, E.T.H. Then, A. Kron, Polym. Degrad. Stab. **53**, 339 (1997).
[7] J.K. Pandey, K. Raghunatha Reddy, A. Pratheep Kumar, R.P. Singh, Polym. Degrad. Stab. **88**, 234 (2005).
[8] A. Leszczyńska, J. Njuguna, K. Pielikowski, J.R. Banerjee, Thermochim. Acta **453**, 75 (2007).
[9] Zaharescu, Jipa, Radiochemical modifications in polymers. In K.F. Arndt, M.D. Lechner, Landolt-Börnstein Series, vol. **VIII**/6 C2, Polymer Solids and Polymer Melts, Springer, Heidelberg, p. 95 (2013)
[10] H.J. Gläsel, E. Hartmann, D. Mehnet, D. Hirsch, R. Böttcher, J. Holmes, Nucl. Instrum.Meth. B **151**, 200 (1999).
[11] S.J. Ahmadi, Y-D. Huang, N.Q. Ren, A. Mohaddespour, S.Y. Ahmadi-Brooghani, Compos. Sci. Technol. **69**, 997 (2009).
[12] S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, R. Kumar, Prog. Polym. Sci. **38**, 1232 (2013).
[13] C.G. Chen, D. Curlis, Polym. Bull. **49**, 473 (2003).
[14] O. Güven, Radiat. Phys. Chem. **76**, 1302 (2007).

[15] A. Nowicki, G. Przybytniak, E. Kornacka, K. Mirkowski, Z. Zimek, Radiat. Phys. Chem. **76**, 893 (2007).

[16] J. Sharif, K.Z. Mohd Dahlan, W.M. Zin, W. Yunus, Radiat. Phys. Chem. **76**, 1698 (2007).

[17] L. Zaidi, S. Bruzaud, M. Kaci, A. Bourmaud, N. Gautier, Y. Grohens, Polym. Degrad. Stab. **98**, 348 (2013).

[18] M. Koutný, T. Václavková, L. Matisová-Rychlá, J. Rychlý, Polym. Degrad. Stab. **93**, 1515 (2008).

[19] A. Singh, Radiat. Phys. Chem. **56**, 375 (1999).

[20] T.M. Alam, M. Celina, R.A. Assink, R.T. Clough, K.T. Gillen, Radiat. Phys. Chem. **60**, 121 (2001).

[21] D.M. Mowery, R.A. Assink, D.K. Derzon, S.B. Klamo, R. Bernstein, R.L. Clough, Radiat. Phys. Chem. **76**, 864 (2007).

[22] T. Zaharescu, M. Giurginca, S. Jipa, Polym. Degrad. Stab. **63**, 245 (1999).

[23] A.Tidjani, C.A. Wilkie, Polym. Degrad. Stab. **74**, 33 (2001).

[24] T. Tanaka, IEEE T. Dielect. El. In. **9**, 704 (2002).

[25] M. Khalid, A.F. Ismail, C.T. Ratnam, Y. Faridah, W. Rashmi, M.F. Al Khatib, Radiat. Phys. Chem. **79**, 1279 (2010).

[26] E. Planes, L. Chazeau, G. Vigier, T. Stuhldreier, Compos. Sci. Technol. **70**, 1530 (2010).

[27] N.T. Dintcheva, S. Alessi, R. Arrigo, G. Przybytniak, G. Spadaro, Radiat. Phys. Chem. **81**, 432 (2012).

[28] F. Ciuprina, T. Zaharescu, I. Pleşa, Radiat. Phys. Chem. **84**, 145 (2013).

[29] Z.A. Tamus, J. Electrostat. **67**, 154 (2009).

[30] S.S. Stivala, J. Kimura, S.M. Gabbay, S.M, Thermal degradation and oxidative processes. In N.S. Allen (ed), Degradation and stabilisation of polymers, ch. 3, Applied Science Pubs., London (1983).

[31] J.C. Suarez, E.E. da Costa Monteiro, E.B. Mano, Polym. Degradat. Stab. **75**, 143 (2002).

[32] T. Özdemir, Radiat. Phys. Chem. **77**, 787 (2008).

[33] J. Tai, J.S. Qian, Y. Zhang, J. Huang, Chem. Eng. J. **141**, 354 (2008).

[34] H. Zou, S. Wu, J. Shen, J., Chem. Rev. **108**, 3893 (2008).

[35] M. Liu, L. Gan, D. Chen, Z. Xu, Z. Hao, L. Chen, Int. J. Pharm. **427**, 354 (2012).

[36] X. Tai, J.H. Ma, Z. Du, W. Wang, J. Wu, Powder Technol. **233**, 47 (2013).

[37] P.V. Notingher, S. Busoi, L.M. Dumitran, C. Stancu, G. Tanasescu, E. Balescu, World Acad. Sci., Eng. Technol. **25**, 648 (2009).

[38] I. Pleşa, F. Ciuprina, P.V. Notingher, D. Panaitescu, Revue Roumaine des Sciences Techniques Série Électrotechnique et Énergétique, 277 (2011).

[39] M. Madani, Mol. Phys.: An International Journal at the Interface Between Chemistry and Physics **106**, 849 (2008).

[40] S. Wolf, M.J. Wang, Rubber Chem. Technol. **65**, 329 (1992).

[41] T. Tanaka, M. Kozako, N. Fuse, Y. Ohki, IEEE T. Dielect. El. In. **12**, 669 (2005).

[42] T.J. Lewis, J. Phys. D App. Phys. **38**, 202 (2005).

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