

EFFECT OF METAL OXIDE FILLERS ON THE RADIO THERMOLUMINESCENCE (RTL) PROPERTIES OF POLYOLEFINS

N.Sh. Aliyev, M.M. Guliyev, M.N. Bayramov, R.S. Ismayilova

Institute of Radiation Problems, MSE AR
nabi.aliyev.1958@mail.ru

Abstract: The effect of TiO₂, ZnO, and BeO metal oxide fillers on the radiothermoluminescence spectra of polyolefins (polypropylene and high-density polyethylene) was studied using the radiothermoluminescence (RTL) method. It was determined that depending on the chemical structure and volume fraction ($\Phi\%$) of the fillers, the nature of the low-temperature relaxation transitions differs, and the nature and depth of the traps change during the radiolysis at a dose of 10 kGy. TiO₂, ZnO, and BeO fillers have a modifying effect on polyolefins (PP and HDPE) that results in a fall in the polymer's glass transition temperature (T_g); modifications to the supramolecular structure (SMS) of the polymer cause the spherulites' size to decrease; and a reduction in internal stress is also observed. The γ -, β_1 , and β -relaxation peaks in polypropylene are strongly impacted by TiO₂ and BeO fillers, according to a comparison of RTL spectra. Furthermore, it can be seen from the HDPE and HDPE+3%ZnO spectra comparison that the ZnO filler lowers the radiation intensity across the whole temperature range. On the other hand, the β -maximum has shifted from 243K to a (10-15)^oC higher temperature range. This suggests a shift towards a high temperature range in the processing temperature of the specified composite.

Keywords: radiothermoluminescence, polyolefin, filler, polymer, polypropylene, composite, electron, relaxation, radical, modification, spectrum.

1. Introduction

By applying ionizing radiation to polyolefin-based composite materials with regulated electrophysical properties, novel materials for electronic engineering can be produced. The primary benefits of the recently developed polymer composites are their improved functionality and electrostability as compared to their polymer counterparts.

Newly developed materials exhibit a higher integration density of electronic devices in the contemporary development of electronic equipment, owing to their extensive range of functional capabilities. The unique characteristics of materials utilized in hybrid composite materials — which are composed of organic polymers (polyethylene, polypropylene, polyvinyl chloride, polyvinylidene fluoride, etc.) and inorganic dispersed particles (Fe₂O₃, Fe₃O₄, TiO₂, Al₂O₃, ZnO, SiO₂, CuO, BeO, ZrO₂, BaTiO₃, etc.) — determine success in this industry [9, 19, 25].

The electronics industry represents a significant area of use for polymer materials. Due to their excellent insulative qualities, most polymers are employed extensively. It is noteworthy that polymer materials (PVC plastics) modified with oxides (eg. Al₂O₃ and SiO₂) exhibit a 1.5–2 fold increase in volume resistivity (ρ_v) and a 1.3–1.9 fold decrease in dielectric loss ($\text{tg}\delta$). This contributes significantly to the material's insulation as well [24].

The radiothermoluminescence (RTL) method is widely used to analyze the structure,

molecular mobility, and relaxation processes in polymer and polymer composite materials, in addition to dielectric and thermal activation (TSD) spectroscopic methods. Based on this method, it is possible to determine the relaxation transition temperature, as well as the glass transition temperature (T_g), the activation energy of the relaxation, and the degree of crystallization according to the shape of the RTL glow curve.

The majority of the thorough and methodical research on radiothermoluminescence was done by Nikolsky and Bubin [1-3]. In this regard, the work of Charez Patric can be mentioned [4-6].

The essence of radiothermoluminescence is completed by the following: organic and inorganic compounds radiated at low temperatures glow when heated. The luminescence signal grows, passes through one or more maxima, and slowly fades. The temperature dependence graph of luminous intensity is called RTL curves or glow curves. The set of experiments confirms that the RTL maxima are closely related to the structural transition of the β -maximum vitrification. In the RTL curves, the β -maximum for low-density polyethylene manifests itself similarly at the glass transition temperature. Thus, as a result of cross-linking, cold stretching, and increasing the heating rate of the polymers, this maximum is shifted towards high temperatures. A more plausible cause of RTL in a polymer is the recombination of electrons with positively charged ions during heating of pre-irradiated samples at 77K, i.e., upon heating after irradiation, the process $M^+ + e - M + h\nu$ takes place, where e^- is the trapped (stabilized) electron.

The reliability of the RTL method allows for determining the high sensitivity of the β -transition and using it to study small amounts (a few mg) of polymers. This distinguishes the RTL method from other methods, as the β -relaxation transition (in dilatometry, methods of mechanical and dielectric losses, etc.) decreases with decreasing common sensitivity temperature.

The radiothermoluminescence (RTL) technique was used to examine how the structure and characteristics of polymers and composites made of them changed after being exposed to ionizing radiation. [10-13]. Structure at low temperatures (up to 77–293 K), molecular relaxation processes and the effect of ionizing γ -irradiation on these processes were examined in the systems studied according to RTL spectra. It is known that at low doses of γ -irradiation (up to 5 kGy), in the crystalline regions of polyolefins, there are regular areas and traps that form crystallites for charges of radiation origin, that is, consisting of methylene groups in the main chain of the macromolecule. [11]. The formation of radicals during the radiolysis of polyethylene occurs both as a result of the dissociation of excited macromolecules and as a result of secondary reactions of radicals with hot atoms and ions. Electrons, alkyl, allyl, and polyenyl radicals can be stabilized in irradiated polyethylene at liquid nitrogen temperature (77K) [14, 15]

The presence of thermoluminescence at low temperatures indicates that both positive and negative charges can be trapped in polymers. It is believed that there are primarily three types of electron traps: dielectric gaps (e.g., a certain space bounded by molecular chains arranged in a certain order), electron-hungry neutral molecules, and free radicals.

It is known from studies of many polymers that all maxima of thermoluminescence are related to the mobility and structure of different kinetic units of the material.

Oxidation, destruction, and chain-growth processes occurring in polymers during ionizing radiation affect the relaxation and structural transitions of polymer dielectrics. Therefore, in the study of these processes at the molecular level, along with the TSD method, the RTL method is of great importance [7].

It should also be noted that the transition of the polymer from the state of high elasticity to the next viscous state is called the α -process, and the transition from high elasticity to the

glassy state is called the β -process. We refer to transitions known as γ and δ that are seen at temperatures below the glass transition temperature (T_g). The γ -transition is related to the oscillations of several carbon atoms of the main chain of the polymer during the movement of the individual crystalline segments of the polymer surface, and the δ -transition is related to the rotation of the bonds around the polymer connected to the main chains with short side chain groups [4, 8].

2. Experimental part

Experimentally, RTL studies were carried out by irradiating the samples at a temperature of 77K in an MPX-25M type γ -irradiator with a radiation source of ^{60}Co at a dose of 10 kGy (1 mrd) in a vacuumed ampoule and using a TLQ-69M radiothermoluminograph.

In one of the main blocks of the TLQ-69M device, liquid nitrogen circulated in a closed circuit is used to cool the cryostat. Circulation is achieved by the fact that the liquid nitrogen droplets poured from the reservoir into the cryostat are partially vaporized and then discharged back into the reservoir together with the vapor through the outlet channel. Nitrogen circulation allows the cryostat to quickly cool down to 77 K. The outlet tap is closed to stop circulation. The steam pressure forces liquid nitrogen into the reservoir. The cryostat's heating element then activates. A nichrome wire heating element is connected to a step-up autotransformer, which provides smooth heating of the cryostat in the 77-380K range at a rate of 5 to 50 deg/min. The heating rate of the cryostat due to the actual heat flow does not exceed 1-2 deg/min.

Figures 1-6 show the radiothermoluminescence curves of high-density polyethylene (HDPE), ultra-high molecular weight polyethylene (UHMWPE), polypropylene (PP), HDPE/3%ZnO, HDPE/5%ZnO, and HDPE/10%ZnO samples.

Figure 1 demonstrates the RTL curve of a high-density polyethylene (HDPE) sample. As can be seen from the curve, γ , γ' , and β relaxation peaks were observed at temperatures of 133, 163, and 225K, respectively. It should be noted that with the gradual increase in temperature, various types of molecular motions associated with dipoles are activated. In this case, the relative intensities of γ , γ' , and β relaxation processes occurring at the indicated low temperatures are determined by the degree of orientation of the dipole groups.

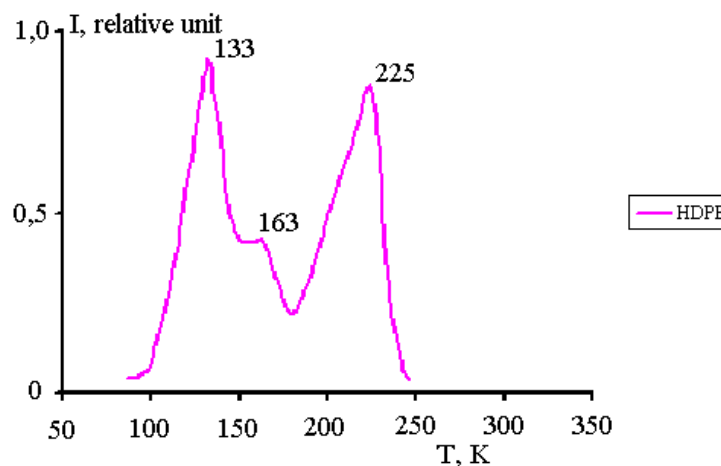


Fig. 1. RTL curve of high-density polyethylene (HDPE) sample.

Figure 2 shows the RTL curve of the ultra high molecular weight polyethylene

(UHMWPE) sample.

As can be seen from the figure, γ , and β relaxation transition peaks appeared at temperatures of 133 and 234 K. When the RTL curve of the UHMWPE sample is compared with the RTL curves of the other HDPE and PP samples, we see that the picture is completely different. So, if two relaxation transition peaks appeared in the UHMWPE sample, three peaks were observed in the other HDPE and PP samples. These differences may be related to the supramolecular structure (MSS), chemical, and physical-mechanical properties of the polymers whose RTL curves we compare and the effect of α -irradiation (Figs. 1, 2, and 3).

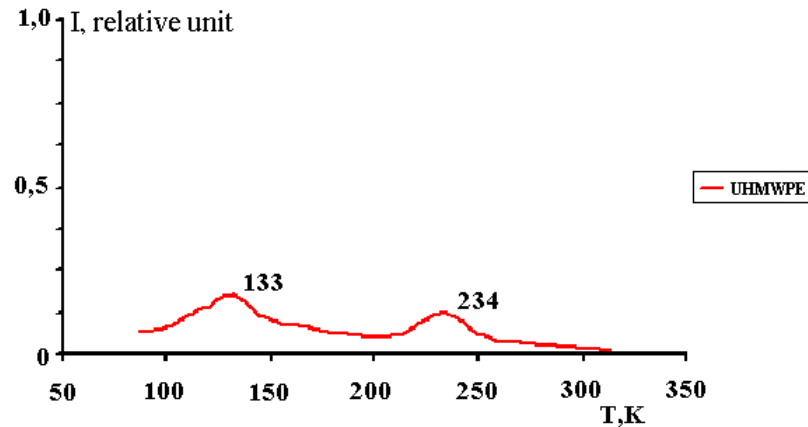


Fig. 2. RTL curve of ultra-high molecular weight polyethylene (UHMWPE) sample.

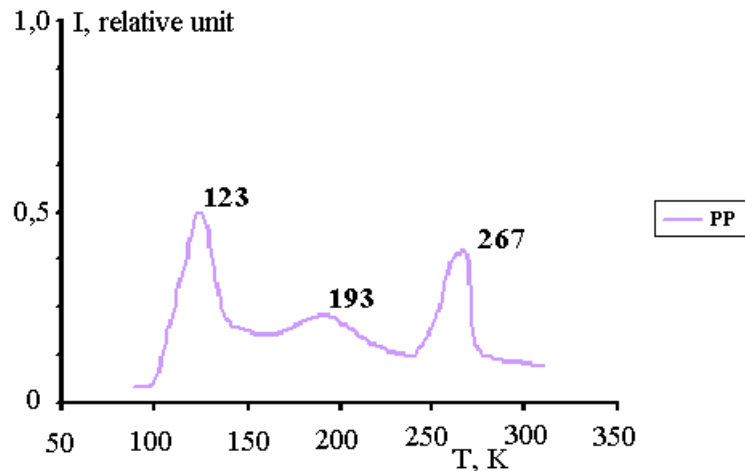


Fig. 3. RTL curve of polypropylene(PP) sample.

Four and five relaxation peaks may be seen in Figures 4, 5, and 6, depending on the ZnO filler's volume fraction ($\Phi\%$). These relaxation peaks were observed at 131K, 181K, 240K, and 282K in the HDPE/3%ZnO composite sample, at 120K, 163K, 181K, 233K, and 267K in the HDPE/5%ZnO composite sample, and at 133K, 173K, 193K, 240K, and 273K in the HDPE/10%ZnO composite sample. Here, it is observed that the volume fraction of ZnO filler has a significant effect on the generation of relaxation peaks at different temperatures and the temperature shift. It was determined that depending on the chemical structure and volume fraction ($\Phi\%$) of the filler, the characteristics of low-temperature relaxation transitions differ, and the nature and depth of the traps change during the radiolysis at a dose of 10 kGy.

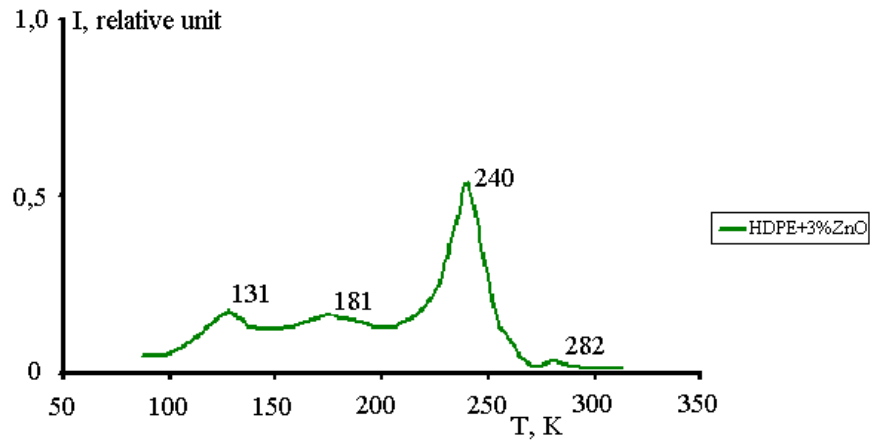


Fig. 4. RTL curve of HDPE/3%ZnO composite sample.

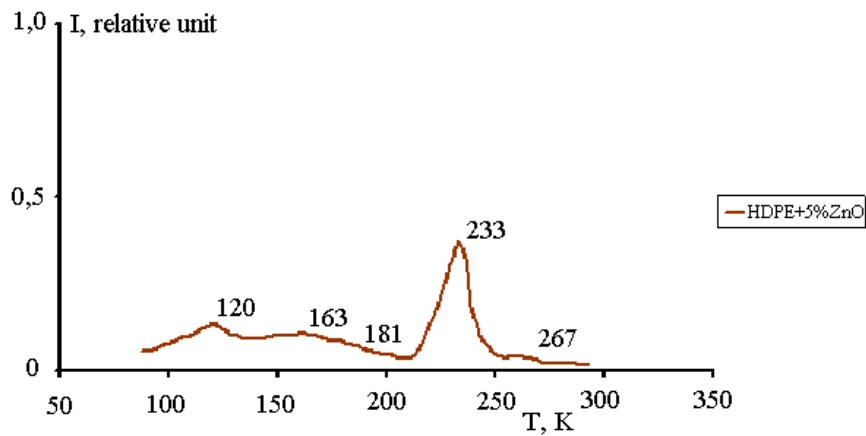


Fig. 5. RTL curve of HDPE/5%ZnO composite sample.

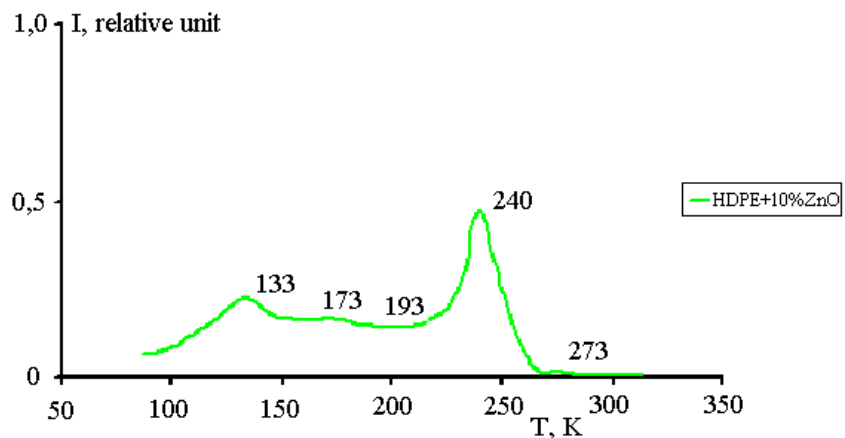


Fig. 6. RTL curve of HDPE/10%ZnO composite sample.

Comparative RTL curves for HDPE (1) and HDPE+3%ZnO (2) samples that were cooled to 273K are shown in Figure 7. From the comparison of these spectra (curves 1, 2), it can be seen that the ZnO filler lowers the radiation intensity in the entire temperature range. On the other

hand, β -maximum shifted from 243K to a (10–15) °C higher temperature range. This indicates that the processing temperature of the given composite has shifted toward the high-temperature range. This process can be related to the change of the crystallization level and the shift of the crystallite sizes in a small region. Another auxiliary explanation is related to the relaxation (reduction) of internal stress due to the effect of the filler. It should also be noted that the α -peak in the RTL spectrum of pure HDPE is related to the molecular mobility of bigger crystallites [8]. Changes in the molecular structure of the polymer as a result of the effect of γ -irradiation significantly affect the dielectric properties and relaxation processes. The relaxation of charges accumulated at the interphase boundary also affects the electrophysical properties of composite samples[23].

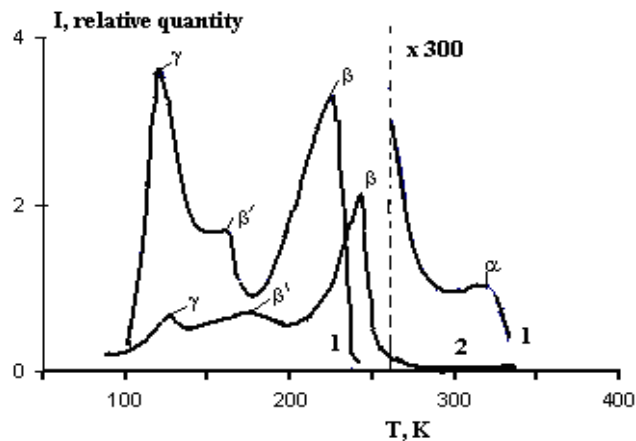


Fig. 7. Comparative RTL curves of HDPE (1) and HDPE/3%ZnO (2) samples.

Figure 8 shows the RTL curves of the PP+TiO₂ and PP+BeO samples (1, 2, 3, 4, 5 curves). Here's a side-by-side comparison. The RTL spectrum of the PP+TiO₂ composite sample demonstrates four peaks in the low-temperature range (100-300)K, as shown in Figure 8. If the RTL curves of isotactic polypropylene are characterized by three maxima at temperatures of 123, 193, and 267K (curve 1), then, in composites, the amplitude of the maxima at 123 and 267K is reduced, and the maximum at 193K is divided into two very weak intensity maxima (curves 2-4). We presume that this effect is due to the effect of the filler; an additional weak peak appears in the temperature range of 173-235K (curves 2-4). It is known that [18] is the β -maximum due to the relaxation in the vitrification region, which is more sensitive to the structural change when fillers are added to PP. Figure 8 illustrates how the characteristic β -relaxation peak of pure PP at 193K (activation energy $W=0.16$ eV) decreases to 181K when the volume fraction of TiO₂ filler increases to $\Phi =3\%$ ($W=0.18$ eV), increases to 195K at $\Phi =5\%$ ($W=0.23$ eV), and at $\Phi =10\%$ it has the same value as pure PP ($T_m=193$ K and $W=0.16$ eV).

In the PP+TiO₂ composite samples, the appearance of new peaks in the temperature range of 200÷300K with activation energies of 0.40, 0.29, and 0.25 eV, the $T_m=218$ K peak at $\Phi=3\%$, and $T_m=224$ K at $\Phi=5\% \div 10\%$ is probably related to the chemical properties of TiO₂ oxide and the modifications in the supramolecular structure (SMS) that result from its incorporation into the polymer. The glow peak at 267K ($W=0.68$ eV) shifts towards the high-temperature range of $T_m=269$ K ($W=0.37$ eV) and then falls to $T_m=265$ K at $\Phi=5\%$ ($W=0.43$ eV), and the luminescence maximum ($W=0.49$ eV) at $T=261$ K at $\Phi=10\%$ shifts towards lower temperatures. Dissimilar to the PP+TiO₂ composite, depending on the quantity of BeO in the low-temperature range of PP+BeO samples characteristic of β -relaxation, PP+BeO samples exhibit RTL peaks at

$T_m=224\text{K}$ ($\Phi=3\%$, $W=0.55\text{ eV}$), $T_m=221\text{K}$ ($\Phi=5\%$, 0.45 eV), and $T_m=219\text{K}$ ($\Phi=10\%$, 0.37 eV). In the composite samples with BeO volume fraction of $\Phi=3\% \div 10\%$ in the β -transition region, the maximum shift values are 14, 19, and 9K, respectively. The RTL curves for pure BeO include four peaks, primarily at 155, 203, and 276K temperatures, with a minor one at 290K, as was previously demonstrated in [22]. However, studies [16, 17, 20-22] demonstrate that thermoluminescence curves in the $77 \div 300\text{K}$ temperature range are typified by two principal peaks at 155 and 290K, respectively, that have activation energies of 0.59 and 0.87 eV.

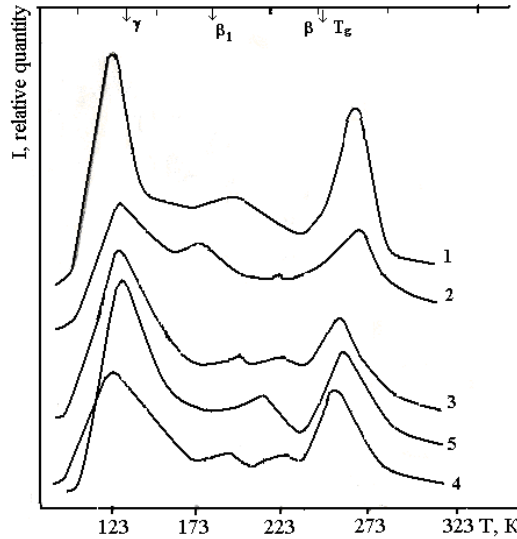


Fig. 8. RTL spectra of PP+TiO₂ and PP+BeO composite samples for different volume fraction of fillers. 1-PP; 2-3%; 3-5%; 4-10% TiO₂; 5-10% BeO.

As can be seen from Fig. 8, for PP+TiO₂ and PP+BeO compositions (curve 5 given for comparison in the figure is the RTL spectrum of the PP+10%BeO sample), corresponding low-temperature luminescence peaks coincide with the luminescence region related to β -relaxation processes of pure PP, and in the $250 \div 290\text{K}$ temperature range are related to TiO₂ and BeO metal oxides. In this instance, with an increase in the amount of TiO₂ and BeO, the luminous intensity for TiO₂ falls at $\Phi=3\% \div 5\%$ and rises at $\Phi=10\%$ in the $T \leq 290\text{K}$ low-temperature ranges, whereas BeO shows a drop. Based on information in [22], the glow peak at 290K ($W=0.87\text{eV}$) is associated with specific and heterovalent doping defects in BeO and is collected in the 4.9eV band.

Table 1 lists the values of the activation energy W corresponding to each luminescence maximum of the polymer and composite.

The activation energy W was calculated using the partial peak half-width method [19] with the following formula:

$$W = G_- \frac{kT_m(T_m - \Delta T_-)}{\Delta T_-}, \quad (1)$$

Here, G_- is the coefficient, 1.45 is taken for the first-order relaxation kinetics, T_m - the temperature of the luminescence maximum, ΔT_- - half-width of the peak on the side of increasing intensity; $k=1,38 \cdot 10^{-23}\text{ C/K}=0,86\text{ eV/K}$ - Boltzman constant.

The table indicates that the maximum of the spectrum for the β -relaxation in the PP+TiO₂ composite is observed when the amount of TiO₂ is $\Phi=10\%$ ($W=0.49\text{ eV}$). The observed change

of W is probably due to the increase in the internal stress of PP in the amorphous domains. Cross-linking by radiation with small doses of filler (10 kGy) causes a weak change in the activation energy W , and the filler acts as a structural builder [20].

Table 1

Values of W (eV) - activation energy for pure PP, HDPE sample, and PP+TiO₂ and HDPE+3% ZnO composites with different volume fractions Φ (%) of fillers at T_m -maximum luminescence temperature for β -transition

Material	Characteristics	
	T_{max}, K	W, eV
PP	193	0,16
	267	0,68
PP+3% TiO ₂	181	0,18
	218	0,40
	269	0,37
PP+5% TiO ₂	195	0,23
	224	0,29
	265	0,43
PP+10% TiO ₂	193	0,16
	224	0,25
	261	0,49
HDPE	162	0,17
	228	0,41
HDPE+3% ZnO	173	0,12
	243	0,71

As can be seen from Fig. 9, the considered fillers affect the glass transition temperature T_g of the PP/metal oxide composite in a different manner, for which the dependences of $T_g=f(\Phi)$ are significantly different in form.

When the amount of TiO₂ is $\Phi=3\%$, the glass transition temperature of the composite shifts towards a high-temperature range of 2°C compared to the glass transition temperature of pure PP, and when the amount of BeO is $\Phi=5\%$, it shifts towards a low-temperature range of 19°C. This allows us to conclude that depending on the chemical structure of the fillers, the characters of the low-temperature relaxation transitions differ, and the nature and depth of the traps change during the radiolysis at a dose of 10 kGy.

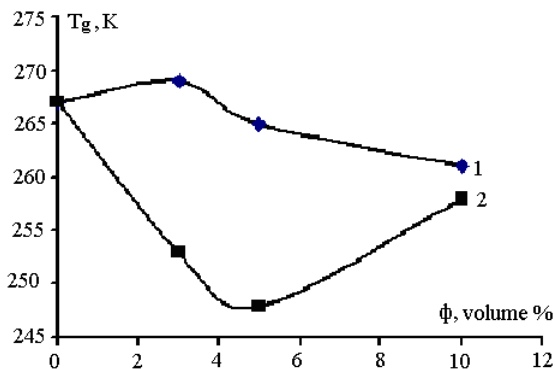


Fig 9. Dependences of $T_g=f(\Phi\%)$ in PP/ TiO₂ (1) and PP/ BeO (2) composites.

The modifying effect of both TiO₂ and BeO fillers on polypropylene (due to a decrease in the value of the polymer's glass transition temperature T_g) is associated with modifications in the polymer's supramolecular structure (by reducing the size of spherulites), as well as a decrease in internal stress. A comparison of the RTL spectra in Fig. 8 shows that both fillers (TiO₂ and BeO) significantly affect the γ -, β_1 - and β -relaxation peaks in polypropylene. T_g

Thus, the inclusion of TiO₂ dispersed oxide in the PP matrix, as with BeO oxide [9], leads to a change in the intensity of peaks γ -, β_1 -, and β - in the RTL curves and the maxima of the realization temperature, and these can be used to predict the electrophysical, dielectric, and physical-mechanical properties of the composites obtained on the basis of those fillers.

3. Result

1) It was determined that the characteristics of low-temperature relaxation transitions differ depending on the chemical structure and volume fraction ($\Phi\%$) of the fillers, and the nature and depth of the traps change during the radiolysis at a dose of 10 kGy. The modifying effect of TiO₂, ZnO, and BeO fillers on polyolefins (PP and HDPE) (due to the fall in the T_g value of the polymer's glass transition temperature) is related to the modifications in the polymer's supramolecular structure (by reducing the size of the spherulites) as well as to the decrease in internal stress. A comparison of RTL spectra shows that TiO₂ and BeO fillers significantly affect the γ -, β_1 -, and β -relaxation peaks in polypropylene.

2) Comparing the HDPE and HDPE+3%ZnO spectra, it is clear that the ZnO filler reduces the radiation intensity in the entire temperature range. On the other hand, β -maximum shifted from 243K to a (10–15)°C higher temperature range. This indicates that the processing temperature of the given composite has shifted toward the high-temperature range.

References

1. V.G. Nikolsky. N.A. Mironov. Thermoluminograph for the study of organic substances. // Factory laboratory, 1973, vol. 39, No. 10, pp. 1272-1275.
2. V.V. Filippov. Development of the RTL method for studying the structural features and kinetics of oxidation of polymer materials. Abstract dissertation of a candidate in physical and mathematical sciences M., MIPT, 1984, p. 25.
3. V.G. Nikolskij. The Application of the Radiothermo-luminescence Method to the Analysis of Polymers and Polymer Composites, Pure and Appl. Chem., 1982, v. 54, №2, p. 493-506.
4. M. Dole. Radiation chemistry of macromolecules, translation from English. edited by Doctor of Technical Sciences Finkel E.E. Moscow-Atomizdat 1978, p. 328.
5. V.G. Shevchenko. Fundamentals of the physics of polymer composite materials. Moscow 2010, p. 99.
6. V.G. Nikolskij, The Application of the Radiothermo-luminescence Method to the Analysis of Polymers and Polymer Composites, Pure and Appl. Chem., 1982, v. 54, №2, p. 493-506.
7. M.M. Guliyev. Study of Polymer-Pieroceramic Composites by the Radio-Thermoluminescence Method. Surface Engineering and Applied Electrochemistry, 2007, v. 43, No.6, pp. 508-511.
8. A.M. Maharramov. Structural and radiation modification of electrets, piezoelectric properties of polymer composites. Baku: Elm, 2001, p. 327.

9. A.V. Kruzhalov, I.N. Ogorodnikov and S.V. Kudyako, Radiative relaxation of low-energy electronic excitations and point defects in beryllium oxide, *Izvestia University, Physics*, No. 11 (1996), 76-93.
10. N.Sh. Aliyev, A.M. Maharramov, M.N. Bayramov, I.K. Aliyeva, and E.G. Hajiyeva Radiothermoluminescence of γ -irradiated polypropylene compositions with titanium dioxide and beryllium oxide. *NEWS of ANAS, series of physical, technical and mathematical sciences, physics and astronomy 2015 #2*, pp. 89-93
11. V.A. Aulov, I.O. Kuchkina, A.N. Ozerin. Dependence of intensity of radiothermoluminescence of crystalline regions of polyethylene on radiation dose. *High energy chemistry*, 46 (2012), pp. 433-436.
12. I.V. Kuleshov, V.G. Nikolsky. *Radiothermoluminescence of polymers*, M.: Chemistry, 1991, p. 128
13. A.M. Maharramov, M.K. Dashdamirov and I.M. Ismayilov. Radiothermoluminescence of electroactive polymer-piezoceramics composites, *News. Baku State University, Ser. physics and mathematics Sciences*, No. 1(2006), pp. 158-168.
14. S.Z. Allahyarov, L.D. Kisper, V.G. Nikolsky, D.P. Kiryukhin, D.A. Gordon, A.I. Mikhayilov, D.A. Dixon. Radiolysis of thermoplastic polymers. 2. Comparative characteristics of low-temperature radiation destruction of polyethylene and n-heptane for the accumulation of stable radicals. *Plastics*, No. 2, 2009, pp. 20-27.
15. V.D. Kulikov. Features of filling capture centers with electrons in dielectric materials under intense electron irradiation. *ZhTF*, 2007, volume 77, issue 5, pp. 23-29.
16. A.M. Maharramov, F.I. Ahmadov, M.A. Nuriyev, Kh.B. Baghirbeyov. Influence of γ -irradiation on the dielectric properties of composites based on polyolefins with BeO filler. Abstract. report at the 6th Intl. Conf., Nuclear and Radiation Physics, Almaty, (2007), pp. 210-211.
17. A.M. Maharramov, F.I. Ahmadov, M.A. Nuriyev and I.M. Ismayilov. Radiothermoluminescence of γ -irradiated polypropylene compositions with dispersed oxides. *Electronic processing of materials*, 2009, No. 5, pp. 105-108.
18. A.M. Maharramov, M.A. Nuriyev, F.I. Ahmadov, N.Sh. Aliyev, A.A. Shukyurova and T.S. Mehdiyeva. Effect of electron irradiation on the charge states of polymer composites. *ANAS RPI, an international conference dedicated to the 40th anniversary of RPI, November 3-5, 2009, Baku*
19. A.M. Maharramov, E.M. Gojayev. Charge state of composites based on polyethylene with semiconductor filler TiInS_2 . *Electronic processing of materials*, 2007, No. 2, p. 84-88.
20. F.Y. Ahmadov, Y.M. Ismayilov, H.V. Baghirbeyov, A.M. Maharramov and N.Sh. Aliyev. Dielectric properties and peculiarities of the radiothermoluminescence of compositions polypropylene-metal oxides. *The fourth Eurasian conference on Nuclear Science and its application. Oct. 1-3, November. Baku-Azerbaijan, (2006)*, pp. 534-536.
21. F.Y. Ahmadov, Y.M. Ismayilov, H.V. Baghirbeyov, A.M. Maharramov, E.M. Hamidov, N.Sh. Aliyev. Dielectric properties and radiothermoluminescence features of compositions of polypropylene-oxides of metals. *The fourth Eurasian conference on "Nuclear science and its application" Baku-2006*, p.188.
22. N.N. Hajiyeva, M.A. Nuriyev and A.M. Maharramov, The Features of radiothermoluminescence of the thermally processed beryllium oxide. *Abst. 8th Intern. Conf. "Solid st. physics" Almaty, (2004)*, pp. 317-318.
23. A.A. Nabiyeu Influence of gamma radiation on the electrophysical properties of nanocomposites obtained on the basis of high-density polyethylene and nano-size SiO_2 /

- Journal of Radiation Researches, ANAS Institute of Radiation Problems, Volume 6, N2, 2019, pp. 97-104.
24. V.L. Chuleev, V.M. Zolotarev, V.A. Pakharenko, E.V. Chuleeva. Dependence of the properties of PVC-based polymer composites on the composition. *Plastics*, No. 5-6, 2014, pp. 13-17.
25. R.H. Young, J.J. Fitzgerald. Effect of Polar Additives on Dielectric Properties and Charge Transport in a Molecularly Doped Polymer: A Test of Dielectric Polarization Models. *J.Cem.Phys.* 1995, 102(15), pp. 6290-6300.

ВЛИЯНИЕ ОКСИДНЫХ НАПОЛНИТЕЛЕЙ МЕТАЛЛОВ НА РАДИОТЕРМОЛЮМИНЕСЦЕНТНЫЕ (РТЛ) СВОЙСТВА ПОЛИОЛЕФИНОВ

Н.Ш. Алиев, М.М. Гулиев, М.Н. Байрамов, Р.С. Исмаилова

Резюме: Методом радиотермолюминесценции (РТЛ) изучено влияние металлооксидных наполнителей TiO_2 , ZnO и BeO на радиотермолюминесцентные спектры полиолефинов (полипропилена и полиэтилена высокой плотности). Установлено, что в зависимости от химического строения наполнителей и их объемной доли ($\Phi\%$) различаются характеры низкотемпературных релаксационных переходов, а в процессе радиолитического разложения при дозе 10 кГр изменяются характер и глубина ловушек. Модифицирующее действие наполнителей TiO_2 , ZnO и BeO на полиолефины (ПП и ПЭВП) приводит к снижению значения температуры стеклования (T_g) полимера, изменению надмолекулярной структуры (НМС) полимера обуславливая уменьшение размеров сферолитов, а также проявляется снижение внутренних напряжений. Сравнение спектров РТЛ показывает, что наполнители TiO_2 и BeO оказывают заметное влияние на пики релаксации γ -, β_1 - и β в полипропилене. Также из сравнения спектров ПЭВП и ПЭВП+3% ZnO видно, что наполнитель ZnO снижает интенсивность излучения во всем диапазоне температур. С другой стороны, ИК-максимум сместился с 243К на (10-15)К в область высоких температур. Это показывает, что температура обработки данного композита сместилась в область высоких температур.

Ключевые слова: радиотермолюминесценция, полиолефин, наполнитель, полимер, полипропилен, композит, электрон, релаксация, радикал, модификация, спектр.

METAL OKSİD DOLDURUCULARININ POLİOLEFİNLERİN RADİOTERMOLÜMİNESSENSİYAYA (RTL) XASSƏLƏRİNƏ TƏSİRİ

N.Ş. Əliyev, M.M. Quliyev, M.N. Bayramov, R.S. İsmayılova

Xülasə: Radiotermolüminessensiya (RTL) metodu ilə TiO_2 , ZnO və BeO metal oksid doldurucularının poliolefinlərin (polipropilen və yüksək sıxlıqlı polietilen) radiotermolüminessensiya spektrlərinə təsir tədqiq edilmişdir. Müəyyən edilmişdir ki, doldurucuların kimyəvi quruluşundan və həcmi payından ($\Phi\%$) asılı olaraq aşağı temperaturlu relaksasiya keçidlərinin xarakterləri fərqlənilir və 10 kQr dozada radioliz prosesi zamanı təhlələrin təbiəti və dərinliyi dəyişir. TiO_2 , ZnO və BeO doldurucularının poliolefinlərə (PP və YSPE) modifikasiyaedici təsiri polimerin şüşələşmə temperaturunun (T_g) qiymətinin azalmasına səbəb olur, polimerin üstmolekulyar quruluşundakı (ÜMQ) dəyişikliklər sferolitlərin ölçülərinin kiçilməsini şərtləndirir və həm də daxili gərginliklərin azalması da özünü göstərir. RTL spektrlərinin müqayisəsi göstərir ki, TiO_2 və BeO doldurucuları polipropilendə γ -, β_1 - və β -relaksasiya piklərinə nəzərə çarpacaq dərəcədə təsir edirlər. Həm də, YSPE və YSPE+3% ZnO spektrlərin müqayisəsindən aydın olur ki, ZnO

doldurucusu bütün temperatur intervalında şüalanma intensivliyini azaldır. Digər tərəfdən, β -maksimum 243K-dən (10-15) $^{\circ}$ C yüksək temperatur oblastına sürüşmüşdür. Bu onu göstərir ki, verilmiş kompozitin işlənmə temperaturu yüksək temperatur oblastına sürüşmüşdür.

Açar sözlər: radiotermolüminessensiya, poliolefin, doldurucu, polimer, polipropilen, kompozit, elektron, relaksasiya, radikal, modifikasiya, spektr.