

RADIOTHERMOLUMINESCENCE OF THE γ -IRRADIATED COMPOSITIONS OF THE ULTRA-HIGH-MOLECULAR-WEIGHT POLYETHYLENE WITH NANO- α -SiO₂

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Radiothermoluminescence (RTL) of the ultra-high-molecular-weight polyethylene (UHMWPE) and nanocomposites obtained on its base via introduction of nanofiller α -SiO₂ (aerosil) to its volume is studied. Two relaxation processes (α - and β -relaxations) are observed in these composites, whose maximums of thermoluminescence appear at temperatures 205 and 212 K, correspondingly. Features of the RTL spectra in dependence from the α -SiO₂ concentration at the absorbed radiation dose $1 \cdot 10^4$ Gr are highlighted.

INTRODUCTION

At present, a lot of industry branches are interested on the development and application of active polymer composite materials with a complex of improved properties that can change their parameters and characteristics under the external conditions and influences. Addition of the dispersed fillers to the bulk polymer is one of the effective methods for obtaining of such materials [1]. Thanks to modification by the nano-dispersed additives of the initial polymers such as ultra-high-molecular-weight polyethylene (UHMWPE) [2], it is possible to manage the structure and properties of materials over a wide range due to existence of the nucleation and orientational effects, change of the macromolecule conformation, their chemical bonding to the surface of nanosized particles and “healing” of the structure defects. Introduction of additives of highly-dispersed nanosized inorganic particles such as aerosil, talc, aluminum oxides is accompanied by an improvement in the physico-mechanical properties of the polymer [2–5]. Processing of the polymers with various ionizing radiation sources is another approach for their modification and creation of the materials with improved properties based on them [6, 7]. At the same time, problems related with the dispersion property of the filler up to several nanometers are also important. During introduction of the fillers into polymers, it is necessary to overcome number of difficulties associated with the surface activity of the filler. In addition, influence of the fillers on electroactive and relaxation processes in a wide temperature range up to 77 K is also less studied process.

It is well known that thanks to processing of composite materials by ionizing radiation new possibilities appear in this direction [6–8]. On the other hand, the stability of the electroactive properties of polymer composites is determined both by relaxation processes that occur during heating of the sample and are associated with molecular mobility, as well as by including the movement of individual large and small kinetic units of polymers. In this regard, it is interesting and important from both a theoretical and a practical point of view to study the effect of polar organic and

inorganic additives on relaxation processes and the electroactive properties of composites.

There are number of existing methods for study of the structure-phase transitions in nanostructured polymer composites. Radiothermoluminescence (RTL) along with other methods being used successfully to analyze the dynamic structure of polymer composites, as well as to detect relaxation α , β , γ , λ and etc. processes, is one of such methods. It should be especially noted that at present, the role of nanofillers in stabilizing the structure and electret properties of nanocomposites at 77 K based on crystallizing polymers when they are filled with fillers of dispersion up to 50 nm and below is also unsatisfactorily clear [6, 9, 10].

Main goal of current paper is to study the features of stabilization of excess charges in composites based on UHMWPE and the effect of α -SiO₂ dioxide (up to 5 vol.%) on these properties by the RTL-method.

1. EXPERIMENT

Samples as films with thickness (180 ± 10) μ m have been obtained by method of the hot pressing (at pressure 15 MPa during 5 min and at temperature 190 °C) of the initially mixed powders of UHMWPE and silicium dioxide filler (α -SiO₂). The size of the powders of (α -SiO₂) filler is 20 nm. This filler is radiation resistant and is widely used in nuclear technologies [11–14]. Samples for RTL analysis in the form of disc with 8 mm diameter and 180 μ m thickness have been prepared from the films and after they were placed at the bottom of a stainless cup and covered with a stainless mesh to allow light output. Before irradiation, the samples in the cups passed degassing in a glass ampoule to a pressure of $1.33 \cdot 10^{-3}$ Pa, the ampoule was sealed and cooled to a temperature of 77 K by immersion in a Dewar flask with liquid nitrogen. Irradiation has been performed by the γ -radiation of ⁶⁰Co on the RXM- γ -20M equipment at the liquid nitrogen temperature. The dose rate was $3.3 \cdot 10^{-3}$ Gr/h. Absorbed dose was $1 \cdot 10^4$ Gr. RTL spectra have been prepared by the use of the equipment TLG-69M. The method is described in [15] at velocity 18°/min in the temperature range from 100 to 300 K. As usually, the

reproducibility of the positions of the RTL maxima was 2...3 degrees. Luminosity of the sample was registered in the range 300...820 nm by the use of photomultiplier FEU-51 and signal was recorded to the line of the electronic line recorder TZ-4620. Sample temperature was registered by the use of thermocouple type T (copper-constantan).

2. RESULTS AND THEIR DISCUSSION

RTL spectra of the UHMWPE (curve 1) as well as samples containing α -SiO₂ nanodispersed filler of the various volumes (curves 2–4) are presented at Fig. 1. It can be observed that RTL lighting of the initial UHMWPE in the 100...250 K temperature range has two maximums at temperatures 116 and 205 K as well as one inflection around temperature 139 K. Low-temperature maximum at the temp 116 K (γ -relaxation) and high-temperature maximum at the temperature 205 K (β -relaxation) appear due to the recombination of trapped electrons by positive ions. Activation energy W_a of these relaxation processes is computed by employing the method of the initial velocities. Thanks to the temperature position and values of the activation energy being equal correspondingly to 0.05 and 0.184 eV/K, these maximums belong to local relaxation of the methylene groups in amorphous regions or end groups with weak dependence from the features of the supramolecular structure of the UHMWPE and motion of the individual kinetic units on the surface of the polymer crystals.

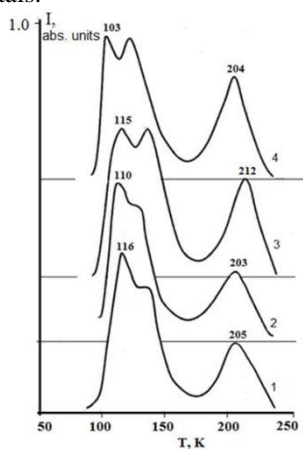


Fig. 1. RTL of UHMWPE and its composites: 1 – UHMWPE; 2 – 1; 3 – 3; 4 – 5 vol.% α -SiO₂

Position of the second RTL maximum (see Fig. 1, curve 1) corresponds to glassing process (β -process) of the UHMWPE and it is the reason of the segmented mobility of CH₂-groups at amorphous phase (collective relaxation at regions with disordered structure). Moreover, modification of the UHMWPE by adding α -SiO₂ silicium dioxide filler leads to the following change of RTL curves: content of UHMWPE consisting up to 5 vol.% of filler in fact does not have any influence to intensity of the luminosity at the low-temperature region. Increase of filler in fact does not change the position of the high-temperature peak, but, for case 3 vol.%, the position of the maximum of the high-temperature peak is observed at temperature

212 K, i.e. the maximum in this case shifts 8 °C towards high-temperature region. Observed inflection after low-temperature maximum at clean UHMWPE and UHMWPE +1 vol.% α -SiO₂ disappears for composites with nano- α -SiO₂ concentration of 3 and 5 vol.% and doublet with currently unknown nature is observed in these samples. For clarification of nature of this doublet, it is necessary to perform complete model experiments that is our future main goal.

The introduction of filler in polyolefins leads to a conformational (physical) change in the molecular structure of the polymers. In particular, macromolecules in filled polyolefins can have a certain amount of over potential bonds. The nature of the change in certain properties in the composition depends mainly from the proportion of the polymer located in the boundary layers, on the degree of intermolecular interaction in this system and the flexibility of the polymer chains.

Let's consider possible reasons of the change in RTL spectra of the composite UHMWPE + α -SiO₂ in dependence on the volume content of nanofiller.

Dependence of the β -maximum of the intensity from the content of the silicium dioxide filler in UHMWPE is presented in Fig. 2. One observes that introduction of silicium dioxide to UHMWPE up to 3 vol.% leads to intensity of the β -maximum, but amplitude of the maximum in fact does not change for 5 vol.% concentration of the α -SiO₂. Such a behaviour of the $J = f(\Phi)$ dependence is explained as follows: it is known that light intensity is proportional to electron recombination rate [16]:

$$J \sim \psi \frac{dn}{dt},$$

where ψ is rate of electrons causing light emission. Values of activation energy W corresponding to maximum of the luminosity of the polymer and composite are presented in Table. W is computed by both methods of the initial velocities [15] and partial half-width of the peak [17] via the following formula:

$$W = G_- \frac{kT_m(T_m - \Delta T)}{\Delta T},$$

where coefficients $G_- = 1.45$; $k = 1.38 \cdot 10^{-23}$ J/K; ΔT is a half-width of the luminosity peak in the region of the increase of the intensity and T_m is the temperature of the luminosity maximum.

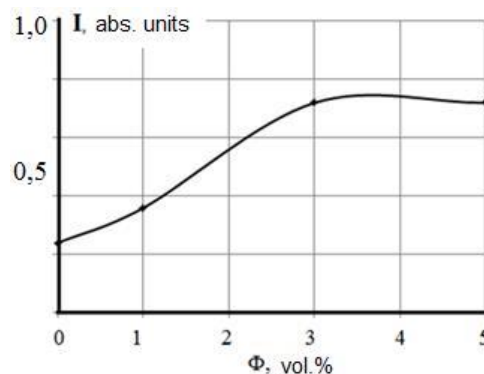


Fig. 2. Dependence of the intensity of the high-temperature peak of RTL from the volume content of the UHMWPE

It can be observed from the table that increase of the filler Φ leads to decrease of the activation energy W corresponding to relaxation process of UHMWPE. Observed decrease of W may be connected with the increase of overvoltages at the amorphous regions of UHMWPE. At low contents of the filler (1%), radiation crosslinking (at dose 10^4 Gr) causes a slow change in activation energy W , but fillers play the role of the formation structure. volume content of nanofiller.

With increase of the volume content of the nanofiller and as a consequence of UHMWPE polymer rate located in border layers, molecular mobility of the polymer chains and their kinetical units responsible for the RTL formation will decrease. This causes a shift in the low-temperature peak of the luminosity.

Shift of the glassing peaks towards high temperature region at higher content of the filler is connected with the increase of the number of the overvoltage chemical bonds as well as with the strength of the processes of the decrease of the segmental mobility of the macromolecules around the solid surface of the nanofiller.

CONCLUSION

1. It is obtained that changes of the molecular structure of UHMWPE by introduction silicium dioxide nanofiller and radiation modification exhibit themselves in the changes of the RTL spectra.

2. It is shown that one can predict changes of the segmental mobility by studying β -relaxation (205...212 K) of the nanocomposites.

The temperature range ΔT_{max} and value of the activation energy W , eV of UHMWPE and composites on the base of UHMWPE

UHMWPE		α -SiO ₂					
		1%		3%		5%	
T_{max} , K	W , eV	T_{max} , K	W , eV	T_{max} , K	W , eV	T_{max} , K	W , eV
116	0.05	110	0.38	115	0.072	103	0.042
205	0.184	203	0.12	212	0.17	204	0.32

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РАДИОТЕРМОЛЮМИНЕСЦЕНЦИЯ γ -ОБЛУЧЕННЫХ КОМПОЗИЦИЙ СВЕРХВЫСОКОМОЛЕКУЛЯРНОГО ПОЛИЭТИЛЕНА С НАНО- α -SiO₂

А.М. Магеррамов, Р.С. Исмайилова, М.М. Кулиев, Р.Л. Мамедова

Изучены радиотермолюминесценции (РТЛ) сверхвысокомолекулярного полиэтилена (СВМПЭ) и нанокompозиты, полученные на его основе введением в объем полимера нанонаполнителя α -SiO₂ (аэросил). В этих композитах наблюдаются два релаксационных процесса (α -, β -релаксации) с максимумами термолюминесценции при температурах 205 и 212 К соответственно. Выявлены особенности спектров РТЛ в зависимости от концентрации α -SiO₂ при поглощенной дозе облучения в $1 \cdot 10^4$ Гр.

РАДІОТЕРМОЛЮМІНЕСЦЕНЦІЯ γ -ОПРОМІНЕНИХ КОМПОЗИЦІЙ НАДВИСОКОМОЛЕКУЛЯРНОГО ПОЛІЕТИЛЕНУ З НАНО- α -SiO₂

А.М. Магеррамов, Р.С. Исмайилова, М.М. Кулієв, Р.Л. Мамедова

Вивчено радіотермолюмінесценції (РТЛ) надвисокомолекулярного поліетилену (НВМПЕ) і нанокompозитів, отриманих на його основі введенням в обсяг полімеру нанонаповнювача α -SiO₂ (аеросил). У цих композитах спостерігається два релаксацийних процеса (α -, β -релаксації) з максимумами термолюмінесценції при температурах 205 і 212 К відповідно. Виявлено особливості спектрів РТЛ у залежності від концентрації α -SiO₂ при поглиненій дозі опромінення в $1 \cdot 10^4$ Гр.