RADIOLUMINESCENCE DEGRADATION OF SCINTILLATORS ON A BASIS OF POLYSTYRENE AND POLY-2,4-DIMETHYLSTYRENE, THE WAYS OF THEIR RADIATING STABILITY INCREASING

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Spectra of radioluminescence of plastic scintillators on a basis of polystyrene and poly-2,4-dimethylstyrene under an influence of γ-radiation are obtained. It is shown that the most effective quenchers are macroradicals, on which a transmission of excitation energy from "initial" luminescent additives occurs. The ways to increase PS radiating stability are proposed.

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1. INTRODUCTION

It is known that many factors have an influence on decrease of the plastic scintillators (PS) light output due to ionizing radiations; these factors are: type and rate of radiation, temperature, environment, etc. Therefore, it is difficult to compare data on PS radiation resistance given in literature. Besides, different authors give values of PS light output change, measured after different time since the termination of irradiation. "Post-radiation" transformation can occur to some extent in scintillators in that period [1].

In order to estimate the influence of radiation on PS scintillation properties more correctly, degradation of PS radioluminescence (RL) from the absorbed doze is investigated in present work on radioluminescence spectra which were registered under continuous γ-irradiation by a specially created installation.

The installation consists of a drum with samples, placed near ^{60}Co-source (60,000 g-equivalent radium activity, the absorbed doze rate being 3 Gy/s.) in canyon; systems of fibers transmitting scintillation signal from the sample on photomultiplier-100, located behind a lead shield; systems of device communication SKVU-100 from the PC. Concentration of macroradicals was determined by EPR spectra, spectra of absorption with the help of "Specord-M40" spectrophotometer.

2. RESULTS AND DISCUSSION

As active additives p – diphenyl phenylene (PT) of 2% mass and 1,4-di/2-(5-fenyloxazolyl)/benzene (POPOP) of 0,1% are used in them. Series of samples of various structures have been measured. Degradation of radioluminescence was estimated on curves of spectra relative intensity dependence on the absorbed doze (Fig.2). (PBD – 2-(4-diphenylyl)-5-phenyl-oxazole-1,3,4; TPB 1,1,4,4 – especially if one takes into account smaller density of tetraphenylbutadiene; MBD – 2-metyl-5(p-diphynylyl)-oxadiazole-1,3,4).

Apparently, this dependence has a complex character and depends on PS structure and γ -irradiation doze. It is established that RL degradation is strongest at dozes up to 40 kGy. For larger absorbed dozes, the curves of degradation of PS with various luminescent additives (LA) differ insignificantly but depend on a polymeric matrix nature. PS based on poly-2,4-dimethylstyrene show more radiation resistance than that on the basis of polystyrene with the same LA.

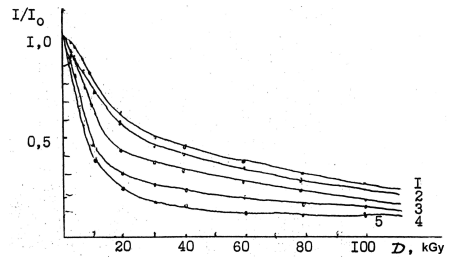

Fig.1. Curves of degradation of scintillation compositions radioluminescence: p-dmst (1, 2) and pst (3, 4, 5): 1 – PBD(5%)+POPOP(0,1%); 2 - PT(2%)+POPOP(0,1%); 3 - PT(2%)+POPOP(0.1%); 4 - PBD(2%)+TPB(0.1%); 5 – MBD(2%)+POPOP(0.1%)

Mechanisms of radiochemical processes resulting in damages of polymers and scintillators on their basis have been already investigated. It has been shown that primary products formed by radiolysis (ions, ions - radicals, short-lived radicals, and captured electron) turn into long-living (about several months) macroradicals under the action of temperature and light quanta. It was revealed that basically macroradicals with a broken chain (an end radical R_e) are stabilized in polystyrene, and alkyl-type macroradicals of "middle" type are in p-2,4-dmst [2, 3].

During the research of absorption spectra of the irradiated polymers we observed an increase in optical density in the 310…350 nm range. The comparison of dependences of paramagnetic centers accumulation, the increase in optical density and intensity of luminescence from the absorbed doze, and also a symbate decrease of these parameters during the "post-radiating" period have allowed identification of the strips of absorption caused by various macroradicals. Apparently, absorption of macroradicals lies in the field of luminescence of initial LA and in the field of absorption of secondary LA. Thus, the probability of transmission of energy of electronic excitation (TEE) from initial LA on macroradicals instead of secondary LA is large.

According to known Ferster-Galanin's formulas TEE calculations in the investigated polymeric systems have been carried out taking into account products of radiolysis.

$$k_{dd}(R) = 1/\tau_{0D}(R_0/R)^6,$$

$$R_0^6 = \frac{9000 \ln 10 \Phi^2 q_{0D}}{128\pi^5 n^4 N} \int I_D^u(\nu)\varepsilon_A(\nu)\nu^{-4} d\nu \ .$$

Table 1. *Absorption spectra of macroradicals in PST and p-2,4-dmst*

Polymer	λ_{max}	ε, M^{-1},sm^{-1}
Polystyrene	316. (e) 328.344 (m) 470.522	10^4 ~130
Poly-2,4-dimethylstyrene	330-340 (m) 482	$2 \cdot 10^3$ ~200

Table 2. *Calculated average critical radii of electronic excitation energy transport in γ-irradiated PS*

Polystyrene			Poly-2,4-dimethyl-styrene		
Donor	Acceptor	R_o, Å	Donor	Acceptor	R_o, Å
M^*	$R_c^\cdot$, $R_к^\cdot$	0,6	M^*	$R_c^\cdot$, $R_к^\cdot$	18,6
PT	$R_к^\cdot$	22,3	PT	$R_c^\cdot$	17,8
M^*	Op	28,2	M^*	Op	28,2
Op	PT	7,6			

where M*– the excited macromolecule; Op – oxygen-containing products of radiolysis; q_{oD}^- – [4]

As follows from the calculations, TEE from the excited macromolecules of polystyrene effectively occurs in oxygen-containing products of radiolysis by the inductive - resonant mechanism. TEE on macroradicals occurs from initial LA. In p-2,4-dmst TEE on macroradicals effectively occurs both from the excited macromolecules and from initial LA.

The probability of TEE on macroradicals increases according to their accumulation with absorbed doze (τ_{0PT} = 1.43·ns) [4].

As macroradicals have a competitive affect on excitation energy capture, it is logical to assume that the increasing of concentration of the initial additive will promote the increase of PS radiation resistance

Table 3. *Dependence of speed constant of energy transfer from PT on macroradicals from a dose*

D, kGy	$C_R \cdot 10^3$, M	$K \cdot 10^{-9}$, $m^{-1} \cdot c^{-1}$
5	0.5	0.7
20	1.0	6.3
45	5.0	140.0
60	10.2	720.0

We have carried out an experiment with LA which is well dissolved in polystyrene. Apparently the dependence has maximum at 4…6% of weights; the further increase in concentration of the additive reduces increasing in a system degradation, probably because of concentrating quenching.

A large role in formation and disappearance of macroradicals plays a molecular oxygen participating in intermediate reactions by the scheme:

$$R^\cdot + O_2 \rightarrow ROO,$$
$$ROO + HR \rightarrow ROOH + R,$$
$$ROO + R \rightarrow \text{products of radiolysis},$$
$$R + R \rightarrow \text{products of radiolysis}$$

Results of researches on influence of the molecular oxygen dissolved in polymeric matrix are presented in [3]. The induction period, which we have found out in accumulation of macroradicals, indicates a positive role of O_2 in preservation of stability of scintillation properties. Reactions with the participation of oxygen are diffusion-limited and depend on the permolecular structure of matrix that is on the density of molecular balls and on the mobility of macrochains. After the expenditure of the oxygen dissolved in the polymeric matrix, there is an intensive accumulation of macroradicals with the simultaneous diffusion of O_2 from air with small speed $D \sim 1.5 \cdot 10^{-9} sm^2 s^{-1}$. For acceleration of the diffusion processes before the reaction of oxygen with macroradicals, we incorporated various plasticizers (stearin, palmitic, threedecan acids) into PS with a standard set of LA. We have received PS with substantial increasing of radiation resistance up to 30…40 kGy doze (Fig.2) under the investigated doze rate. At low doze rates the range of preservation of high radiation resistance will extend, if the velocity of radicals formation will be comparable to that of diffusion of O_2 from air.

To increase radiation resistance of PS irradiated by large dozes, we incorporate 10% of isopropyldiphenyl (IPD). Under ionizing radiation this combination easily forms radicals (it is less radiation-resistant than luminescent additives), which recombine with macroradicals, thus protecting the polymer from destruction. The results, which prove such a protective mechanism, are shown in Fig.2. Interaction of radicals of isopropyldiphenyl with macroradicals of polystyrene proves to be true by comparison of luminescence spectra of superprecipitate samples of PS before and after γ-irradiation (Fig.2).

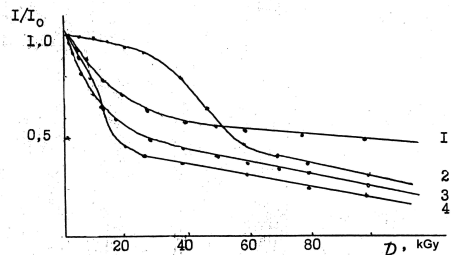

Fig.2. Curves of degradation of scintillation compositions radioluminescence:
1) pst+PT(2%)+POPOP(0.1%)+IPD(10%);
2) pst+PT(2%)+POPOP(0,1%)+TDA (0.2%);
3) p-2,4-dmst+PT(2%)+POPOP(0.1%);
4)pst+PT(2%)+POPOP(0.1%)

In fluorescence spectra of samples with IPD a typical for biphenyl groups spectrum is observed, spectra are not found out in standard PS from this area, as during the superprecipitate luminescent additives are washed out from the polymer.

Thus, we have proved that basic centers of PS radioluminescence quenching are macroradicals, especially the end radical R_e: ~CH_2-C_6H_5-CH. Rather large radiation stability of PS based on p-2,4-dmst is explained by the fact that in p-2,4-dmst macroradicals of "middle" type are stabilized in a greater degree: ~CH_2-$C_6H_5(CH_3)_2$-C~, which are conformationally more accessible to reactions with oxygen and other radicals.

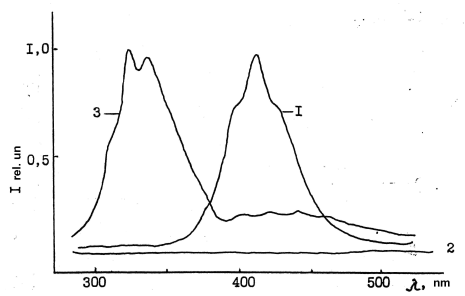

Fig.3. Spectra of fluorescence of γ-irradiated scintillation compositions on the basis of polystyrene:
1 - PT(2%) + POPOP(0.1%) before superprecipitate;
2 – the same after superprecipitate;
3 - PT(2%)+POPOP(0.1%)+IPB(10%) after superprecipitate

CONCLUSION

The experimental data obtained and their interpretation enable to draw the following conclusions regarding the increase in radiation resistance of polymeric scintillation compositions:

1. In the region of absorbed dozes up to 20… 30 kGy:

- Selection of LA, which luminescence area is not blocked by the area of absorption of the formed macroradicals;

- Increasing of diffusion rate of molecular oxygen by plasticizer substances in optimal concentrations.

2. In the region of the absorbed dozes 40…100 kGy:

- Increase in concentration of "initial" luminescent additive essentially exceeding concentration of macroradicals formed at these dozes;

- Introduction to PS structure of low-molecular combinations, which during irradiation easily form radicals capable to recombination with incipient stable macroradicals.

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ДЕГРАДАЦИЯ РАДИОЛЮМИНЕСЦЕНЦИИ СЦИНТИЛЛЯТОРОВ НА ОСНОВЕ ПОЛИСТИРОЛА И ПОЛИ-2,4-ДИМЕТИЛСТИРОЛА, СПОСОБЫ ПОВЫШЕНИЯ ИХ РАДИАЦИОННОЙ СТОЙКОСТИ

Н.И. Воронкина, В.Г. Сенчишин, В.К. Милинчук, И.П. Шелухов

Получены спектры радиолюминесценции пластмассовых сцинтилляторов на основе полистирола и поли-2,4-диметилстирола при воздействии на них γ-излучения. Показано, что наиболее эффективными тушителями являются макрорадикалы, на которые происходит перенос энергии возбуждения с первичной люминесцирующей добавки. Предложены способы повышения радиационной стойкости ПС.

ДЕГРАДАЦІЯ РАДІОЛЮМІНЕСЦЕНЦІЇ СЦИНТИЛЯТОРІВ НА ОСНОВІ ПОЛІСТИРОЛУ ТА ПОЛІ-2,4-ДИМЕТИЛСТИРОЛУ, СПОСОБИ ПІДВИЩЕННЯ ЇХ РАДІАЦІЙНОЇ СТІЙКОСТІ

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Одержано спектри радіолюмінесценції пластмасових сцинтиляторів на основі полістиролу та полі-2,4-диметилстиролу під дією γ-випромінювання. Показано, що найбільш ефективними гасниками є макрорадикали, на які відбувається перенос енергії збудження з первинної люмінесціючої домішки. Запропоновано способи підвищення радіаційної стійкості ПС.