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The new radiation-hard plastic scintillators with diffusion enhancers and 3-hydroxyflavone derivatives

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New mechanically strong compositions of radiation-hard plastic scintillators with diffusion enhancers and primary dopants with the large Stokes shift are proposed. The new PS has 3 times greater radiation hardness in comparison with the analogues. In order to impart the mechanical strength, the PS are produced on spatially cross-linked polystyrene base.

Keywords:plastic scintillators, diffusion enhancers, radiation hardness, cross-linked polystyrene.

Предложены новые, механически прочные составы радиационно-стойких пластмассовых сцинтилляторов с усилителями диффузии и первичными добавками с большим сдвигом Стокса. Новые ПС имеют в 3 раза большую радиационную стойкость по сравнению с аналогами. С целью придания механической прочности ПС изготовлены на основе пространственно-сшитого полистирола.

Нові радіаційно стійкі пластмасові сцинтилятори з посилювачами дифузії та похідними 3-гідроксифлавону.

Запропоновано нові, механічно міцні склади радіаційно-стійких пластмасових сцинтиляторів з підсилювачами дифузії і первинними добавками з великим зміщенням Стокса. Нові ПС мають у 3 рази більшу радіаційну стійкість у порівнянні з аналогами. З метою надання (забезпечення) механічної міцності, ПС виготовлені на основі просторово-зшитого полістиролу.

1. Introduction

The present article continues the series of the works devoted to creation of plastic scintillators (PS) with the increased radiation hardness [1–3]. In the works [4, 5] it was shown that in order to increase the radiation hardness of PS ternary composition (luminescent polymer + primary (LD1) and secondary (LD2) luminescent dopants) it is necessary to input 20–30 wt.% of liquid substances, so-called diffusion enhancers (DE).

The radiation hardness is convenient to characterize by the magnitude of the radiation dose under influence of which the given PS light output is halved. This dose is also called the light output attenuation half-dose and it is signed as $D_{1/2}$. To allow comparison, radiation hardness measurements are performed with PS samples with cylinder shape of 30 to 16 mm in diameter and of 10 mm in height.

For the typical PS brand UPS-98RH with 20 wt.% of DE, the dose $D_{1/2}$ is 5.1 Mrad, which is in 4 times higher than the commercial PS without DE ternary composition marks SCSN-81T, BC-408 and UPS923A [5]. However the PS with DE have the low me-

Table 1. Compositions of PS based on polystyrene (wt.%), their microhardness (*HV*, MPa), light yield before (L_0, %) and after irradiation with dose of 3.3 Mrad (L, %), light yield ratio (L/L_0, %) and light yield attenuation half-dose ($D_{1/2}$, Mrad)

No. of PS sample	Diffusion enhancer	Cross-linking agent	Primary luminescent dopant	Secondary luminescent dopant	*HV*, MPa	L_0, % (D = 0 Mrad)	L, % (D = 3.3 Mrad)	L/L_0, %	$D_{1/2}$, Mrad
1334	25 % IPDP	15 % DPDMA	2 % PBD	0.1 % POPOP	72	65	46	70	6.4
1339	25 % IPN	15 % DPDMA	2 % PBD	0.1 % POPOP	78	76	51	67	5.7
1350	25 % MN	15 % DPDMA	2 % PBD	0.1 % POPOP	67	63	43	69	6.2
1360	25 % BMN	15 % DPDMA	2 % PBD	0.1 % POPOP	70	46	31	68	5.9
1399	25 % IPDP	5 % DVDP	2 % PBD	0.1 % POPOP	107	49	36	73	7.3
1400	25 % IPDP	8 % DVDP	2 % PBD	0.1 % POPOP	149	45	32	71	6.7
1402	25 % p-xylene	3 % DVDP	2 % PBD	0.1 % POPOP	105	80	63	79	9.7
1404	25 % p-xylene	8 % DVDP	2 % PBD	0.1 % POPOP	139	61	46	75	8.0
1452	–	–	2 % 3HF	–	122	64	49	76	8.3
1456	–	–	2 % BP-3HF	–	121	68	55	81	10.9
1457	–	–	2 % F-3HF	–	120	68	52	77	8.8
1458	25 % IPDP	8 % DVDP	1.5 % BP-3HF	–	148	66	57	87	16.4
1459	25 % IPDP	8% DVDP	1.5 % F-3HF	–	147	60	56	94	37.0
1460	25 % IPDP	8% DVDP	2 % p-TP	0.1 % BP-3HF	149	63	38	61	4.6
1461	25 % IPDP	8 % DVDP	2 % p-TP	0.1 % F-3HF	148	55	34	62	4.8
1462	25 % IPDP	8 % DVDP	2 % p-TP	0.1 % POPOP	147	51	33	65	5.3
UPS923A	–	–	2 % p-TP	0.1 % POPOP	122	100	51	51	3.0

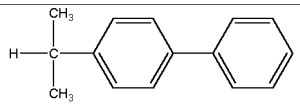
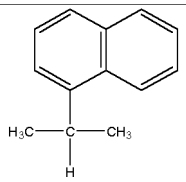
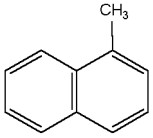
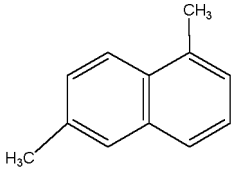
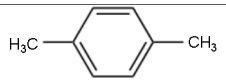
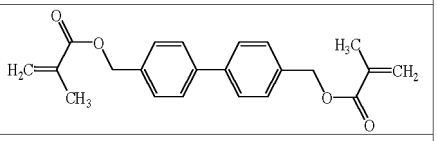
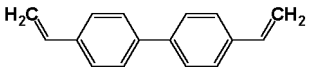
chanical strength (the microhardness by Vickers *HV* is in the range from 3 to 15 MPa) [1], that considerably complicates cutting and polishing of scintillating material and can lead to gradual change in the PS shape.

In [1, 2] it was proposed to increase the mechanical strength of PS material with different diffusion enhancers by creating the cross-linked structure in its polymeric matrix. Thus, in the work [1] PS on the base of cross-linked polystyrene, which contained 25 wt.% isopropylnaphtalene (IPN) as the diffusion enhancer, and 15 wt.% 4.4′-bismethylene-2-methacrylate-biphenyl (BPBMA) as the cross-linking agent, was obtained, that allowed to increase the PS material microhardness *HV* up to 78 MPa. Wherein the PS light yield decreased to L = 76 % relatively to not cross-linked PS with the same composition. In [2] cross-linked PS with the higher mechanical strength (*HV* = 105 MPa) and the higher light output (L = 80 %) was obtained. In this PS 3 wt.% of 4.4′-bivinylbiphenyl (BVBP) was used as the cross-linking agent, and 25 wt.% para-xylene — as the diffusion enhancer. As it will be shown below, the attenuation half-dose of this PS amounts $D_{1/2}$ = 9.7 Mrad.

In the work [3] investigation of the radiation hardness of PS with binary (base + LD1) and ternary compositions (base + LD1 + LD2), where 3-hydroxyflavone derivatives with the large Stokes shift were used as the radiating dopant, was performed. In the work it is shown, that PS with the binary composition with 3-hydroxyflavone derivatives have the higher radiation hardness relatively to PS with ternary composition. PS with the binary composition with 2 wt.% BP-3HF have the highest attenuation half-dose ($D_{1/2}$ = 10.9 Mrad).

In the present work investigations to PS with the increased radiation hardness creating were continued. As it was noticed before, two ways of PS radiation hardness increase are known. The first is based on diffusion enhancers input into PS composition [1, 2, 4, 5], the second — on use of scintillation dopants with the large Stokes shift [3, 6]. The idea of the present work is combination of these two ways. As the result, realization of this idea has leaded to creation of the new, radiation-hard and mechanically strong PS with diffusion enhancers and with 3-hydroxyflavone derivatives (3HF), which have the large Stokes shift. Besides the new PS properties studies, also in the present work measurements of the radiation hardness of the cross-linked PS with diffusion enhancers, obtained by us in [1, 2], are performed.

Table 2a. Chemical names, abbreviations and structural formulas of diffusion enhancers and cross-linking agents, used for PS obtaining

Compound (abbreviation)	Structural formula
4-Isopropylbiphenyl (IPBP)	
1-Isopropylnaphthalene (IPN)	
1-Methylnaphthalene (MN)	
1,6-Dimethylnaphthalene (BMN)	
1,4-Dimethylbenzene (*p*-xylene)	
4,4′-Bis-methylene-2-methacrylate–biphenyl (BPBMA)	
4,4′-Divinylbiphenyl (BVBP)	

2. Experimental

2.1 PS fabrication.

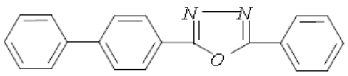
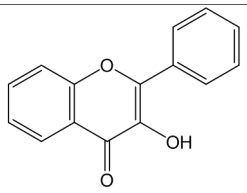
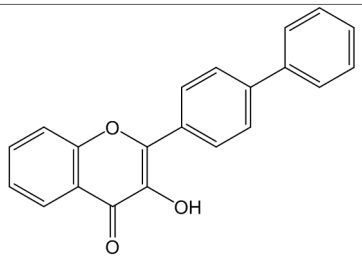
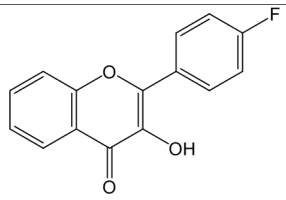
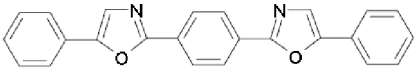
The PS samples were obtained by the process of copolymerization of styrene with the cross-linking agent 4.4′-bivinylbiphenyl (BVBP) with presence of the polymerization initiator 2.2′-azobisisobutyronitrile (AIBN) and one of diffusion enhancers. Cross-linking agent (BVBP) content in different samples varied from 3 to 10 wt.%. Wherein another additives amounted: as diffusion enhancer — 25 wt.%, the polymerization initiator (AIBN) — 0.02 wt.%, the primary luminescent dopant (LD1) — 2 wt.%, as secondary luminescent dopant (LD2) — 0.1 wt.%.

The prepared reaction mixtures were placed into glass vials with diameter 20 mm and dissolved at the temperature of 65°C. The reaction mixtures were saturated with argon for 15 min, for oxygen traces deleting, then the vials were sealed and placed into a thermostat at the temperature of 70°C. Polymerization was performed by the stepping temperature growth to 150°C for 150 h with following cooling at the rate of 5°C per hour. Then the vials were broken and PS workpieces were obtained, of which the samples with the shape of the polished cylinders with diameter of 16 and height of 10 mm were fabricated.

In Table 1 the compositions of all the studied PS samples (wt.%), their microhardness (HV, MPa), light yield before (L_0) and after irradiation with the dose of 3.3 Mrad (L_0) and light yield attenuation half-dose ($D_{1/2}$, Mrad) are presented. The sign "—" says about absence of a certain additive in the PS composition.

The structural formulas and abbreviations of all the chemical substances, used

Table 2b. Chemical names, abbreviations, and structural formulas and of scintillation dopants, used for PS obtaining

Compound (abbreviation)	Structural formula
2-(4-Biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD)	
3-Hydroxyflavone (3HF)	
2-([1,1'-Biphenyl]-4-yl)-3-hydroxy-4H-chromen-4-one (BP-3HF)	
2-(4-Fluorphenyl)-3-hydroxy-4H-chromen-4-one (F-3HF)	
Para-terphenyl (*p*-TP)	
2,2'-(1,4-Phenylene)bis-(5-phenyl-1,3-oxazole) (POPOP)	

for PS production, are shown in Table 2a and 2b.

In Table 1, the PS samples with the new compositions are shown with the numbers 1458–1462. The PS samples No. 1334, 1339, 1350, 1360 were obtained in the work [1], the PS No. 1399, 1400, 1402, 1404 — in [2] and the PS No. 1452, 1456, 1457 — in [3]. In these studies preparation methods, compositions, mechanical and scintillation properties of these PS are detailed.

2.2 The measurement methods.

The PS samples microhardness was determined by the Vickers method with a microhardnessmeter PMT-3 (Russian Federation).

The light yield was measured with the scintillation spectrometer, adapted to the CAMAC standard. A signal from the photomultiplier tube Hamamatsu R1307 was fed to the input of the charge digital converter QDC LeCroy 2249A. The PS light yield was determined by the peak of monoenergetic electrons with the energy of 975 keV from the radioisotope electron source Bi-207. For scintillation flash registration of the PS with the radiation maximum, located in the blue and green spectral range, PMT Hamamatsu R669 with the photocathode, which has the spectral sensitivity extended to the red spectral range, was used. The PS light yield was measured relatively to the "standard" PS sample UPS-923A, made on the base of linear polystyrene without fillers, containing two luminescent additives (2 % paraterphenyl and 0.1 % POPOP) [7].

For radiation-hardness measurement, the PS samples were subjected to gamma-radiation influence of Co-60 radionuclide with the dose rate of 47 rad/min in the air medium under the temperature of 18°C. The light yield of the irradiated PS samples was measured immediately after reach of the needed irradiation dose.

The light yield attenuation half-dose ($D_{1/2}$, Mrad) was calculated from obtained experimental data by with formula [8]:

$$L = L_0 \exp(\alpha D), \quad (1)$$

where L and L_0 — the PS sample light yield before and after irradiation, α — the degradation constant (Mrad^{-1}), D — irradiation dose (Mrad).

Since the attenuation half-dose $D_{1/2}$ is determined at $L/L_0 = 1/2$, so from equation (1) it results:

$$D_{1/2} = (\ln 2)/\alpha. \quad (2)$$

At this value, the degradation constant α is calculated by approximation of the experimental data with formula (1).

3. Results and discussion

3.1 Microhardness and light yield.

From Table 1 it is seen, if DVDP is used as the cross-linking agent, the PS with different diffusion enhancers have the high microhardness from 107 to 148 MPa, what is comparable with the PS without diffusion enhancer (HV = 122 MPa). Wherein, while the cross-linking agent is added, the light yields of the PS with different DE decrease not similarly and are located from 45 % to 76 % relatively to the PS type UPS-923A with standard ternary composition. In this range it is located the light yield of the PS with binary composition without the diffusion enhancer, which contain 3-HF or its derivatives as the scintillation dopant.

3.2 Radiation hardness.

Investigation results of the PS radiation hardness are shown in Table 1. Also, for comparison convenience, in Fig. 1. the light yield attenuation half-dose values of the PS samples, presented in Table 1, are shown. A group of the new radiation-hard cross-linked PS with diffusion enhancers and one luminescent dopant with the large Stokes shift (3HF derivatives) is signed in this figure as DE + 3HF. The PS light yield measurements were performed immediately after their irradiation.

It is seen from presented in Fig. 1 and Table 1 data, the group CL+DE of the cross-linked PS with LD1 and LD2 and the diffusion enhancer has the half-doses $D_{1/2}$ in the range from 4.6 to 9.7 Mrad. The attenuation half-dose of the not cross-linked PS with the diffusion enhancer mark UPS-98RH is equal to the value $D_{1/2}$ = 5.1 Mrad [5], i.e. it is located in the same range. This

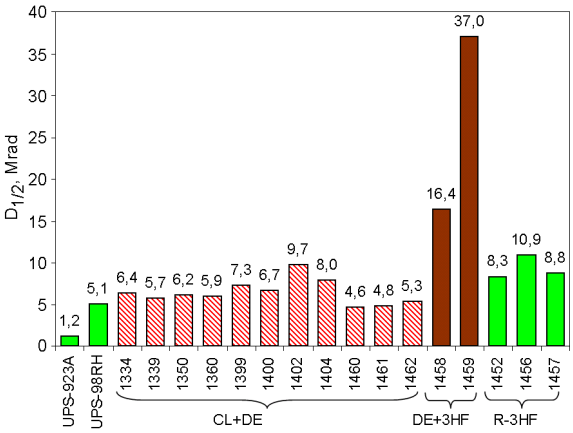


Fig. 1. Light yield attenuation half-dose of the PS samples, listed in Table 1: CL+DE — cross-linked PS with LD1 and LD2 and diffusion enhancers (DE); DE+3HF — new cross-linked PS with DE and single LD with the high Stokes shift (3HF derivatives); R-3HF — linear PS with single DE with the high Stokes shift (3HF derivatives). Light yield measurements are performed immediately after irradiation.

is an expected result, which confirms, that polystyrene matrix cross-linking does not significantly affect to the radiation hardness of the PS with diffusion enhancers [1, 2].

Also, it is seen in Fig. 1 and Table 1, the group R-3HF of the linear PS with the binary composition, in which 3HF-derivatives with the large Stokes shift are used as the luminescent dopant, has the attenuation half-dose in the range from 8.3 to 10.9 Mrad. This corresponds to some higher radiation hardness relatively to the previous group CL+DE DE of the cross-linked PS with diffusion enhancers.

How it is seen from Fig. 1, the group DE+3HF of new cross-linked PS with diffusion enhancers 3HF derivatives with high Stokes shift (Table 1, PS No. 1458 and 1459) demonstrates the extremely high radiation hardness. The light yield attenuation half-doses $D_{1/2}$ of these PS are equal 16.4 and 37 Mrad, respectively. Thus, the new type of PS, which contains 25 % IPDP, 8 % DVDP and 1.5 % F-3HF (Table 1, PS No. 1459), has the radiation hardness in 7.3 times higher, then the PS of mark UPS-98RH [5] and in 3.4 times higher, then the PS with binary composition with the luminescent dopant BP-3HF (Table 1, PS No. 1456).

Light yield regeneration of irradiated PS. Light yield regeneration of irradiated PS is well known. In [4, 5, 7] it was shown, that PS light yield gradually regenerates in

Table 3. Relative light yield (L/L_0, %) and light yield attenuation half-dose ($D_{1/2}$, Mrad), measured immediately and 2 months after irradiation of the PS with dose of 3.3 Mrad

No. of PS sample*	L/L_0, % immediately	L/L_0, % 2 months	$D_{1/2}$, Mrad immediately	$D_{1/2}$, Mrad 2 months
1452	76	86	8.3	15.7
1453	79	90	10.0	22.8
1454	61	81	4.6	11.0
1455	74	80	7.5	10.2
1456	81	89	10.9	19.5
1457	77	84	8.8	13.2
1458	87	91.8	16.4	26.7
1459	94	95.8	37.0	52.9
1460	61	90.3	4.6	22.5
1461	62	90.5	4.8	22.9
1462	65	94.0	5.3	37.0

* The PS compositions: 1452 — 2 % 3HF; 1453 — 2 % naphtalene-3HF; 1454 — 2 % 2-methyl-3HF; 1455 — 2 % CHF3-3HF; 1456 — 2 % BP-3HF; 1457 — 2 % F-3HF. The rest — polysterene [3]. The PS compositions No. 1458–1462 are presented in Table 1.

the air or another gas medium, containing oxygen. Light yield regeneration proceeds due to oxygen diffusion into the PS volume. However full regeneration does not occur, even after long time, when all the volume becomes to be filled with oxygen. Wherein, regeneration of PS with diffusion enhancers proceeds much faster.

In Table 3 and Fig. 2 the relative light yield and light yield attenuation half-dose values of the PS samples, irradiated with dose of 3.3 Mrad and measured immediately (light bars) and two months after the irradiation (dark bars) are presented.

In Table 3 and Fig. 2 it is seen, the light yield of all PS has significantly regenerated for two months after irradiation. The light yield of the PS with the ternary composition with a diffusion enhancer has regenerated especially well. Thus, the L/L_0 values of the PS 1460, 1461, 1462 immediately after irradiation were low, and amounted of 61, 62, 65 %, but for two months after the irradiation, they have regenerated to 90.3, 90.5, and 94.0 %, respectively. It is seen, the PS with the binary composition (group R-3HF) demonstrate lower light yield regeneration to $L/L_0 \leq 90$ %. The PS with the new composition with DE and F-3HF (Fig. 2, the PS 1459) demonstrates the highest radiation hardness with the regeneration effect accounting. Its L/L_0 ratio for two months delay since the irradiation, has amounted the record value 95.8 %, and the light yield attenuation half-dose $D_{1/2}$ has

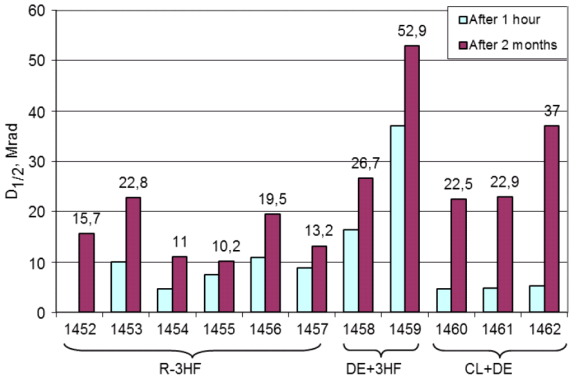


Fig. 2. Light yield attenuation half-doses of the PS samples, irradiated with dose of 3.3 Mrad and measured immediately after irradiation (light bars) and 2 months after irradiation (dark bars). The PS groups symbols are similar with Fig. 1.

growth to 52.9 Mrad. That is in 2.3 times more, than PS with the binary composition with Naphtalene-3HF (Table 3, Fig. 2, the PS 1453) and in 1.4 times more, than the PS with diffusion enhancers (Table 3, Fig. 2, the PS 1462).

3.3 The new PS light yield after irradiation with dose of 100 Mrad.

Let us estimate, how the radiation hardness of the proposed in this article PS meets modern requirements, and whether this PS can be used in the detectors, which are installed on the LHC beam (CERN, Switzerland). It is known, the total radiation effect

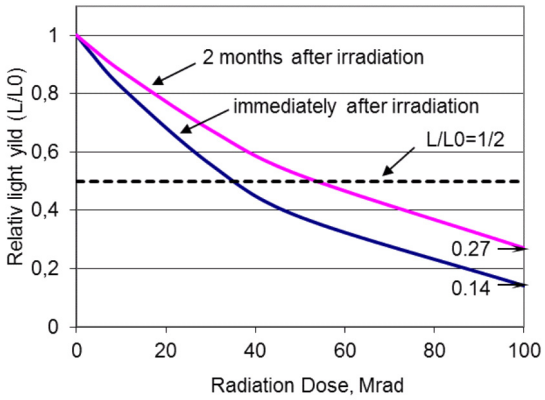


Fig. 3. Extrapolation dependence of light yield ratio (L/L_0) of the cross-linked PS with DE and F-3HF (Table 1, PS 1459) on irradiation dose in range from 3.3 Mrad to 100 Mrad. Extrapolation of data, obtained immediately after irradiation with dose of 3.3 Mrad (the lower curve), end after 2 months since irradiation (the higher curve).

on the closest to the beam PS can reach 10 Mrad for 10 years of CMS detector exploitation [9]. After the planned upgrade in 2016–2018 years the LHC beam the protons energy will double, and the luminosity will increase on the order [10]. Accordingly, the total dose of irradiation on mounted particle detectors will increase on the order.

In the current work, the PS radiation hardness was measured by the accelerated method, at which the PS irradiation dose amounted of 3.3 Mrad. So, for estimation of the relative light yield L/L_0 at the dose of 100 Mrad, the extrapolation method was applied, using the expression (1). In Fig. 3, two curves are shown, one of them is the extrapolation result of data, obtained immediately after irradiation with dose of 3.3 Mrad, and another — after 2 months since the irradiation. The extrapolation results show, after irradiation with the dose of 100 Mrad, the new PS (Table 1, the PS 1459) will have the light yield, equal to 14 % of the initial light yield without recovery effect account, and 27 % with recovery effect account.

4. Conclusions

Thus, accordingly to the previous estimations, at the irradiation dose of 100 Mrad, the light yield of the cross-linked PS with 25 wt.% DE and 1.5 wt.% F-3HF will amount 14 % and 27 % without and with recovery effect account, respectively. This is the good result, meeting the requirements, presented above. However, the investigations of the given PS radiation hardness must be continued at the irradiation dose about 100 Mrad, to decrease errors, occurring at using of the accelerated investigation methods.

Moreover, it is necessary to study the radiation hardness of wavelength shifting fiber, which will be used for signal reading from tiles, made of the new scintillation material. For this purpose the plastic fiber O-2(100) can be used [11] (http://kuraraypsf.jp/psf/ws.html), the absorption specter of which (max 535 nm) well matches with the new PS emission maximum, located on wavelength 530 nm.

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