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The mechanical strength advance of radiation-hard plastic scintillators with diffusion enhancers

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The mechanical strength of a radiation-hard plastic scintillator with diffusion enhancers was investigated by creating cross-linked structure in its polymeric matrix. The best result is reached, if 4,4′-divinylbiphenyl is used as a cross-linking agent, and *p*-xylene — as a diffusion enhancer.

Keywords:plastic scintillator, mechanical strength, 4,4*porime*-divinylbiphenyl, *p*-xylene

Исследована механическая прочность радиационно-стойкого пластмассового сцинтиллятора с усилителями диффузии путем придания его полимерной матрице пространственно-сшитой структуры. Лучший результат достигается, если в качестве сшивающего агента используется 4,4′-дивинилдифенил, а в качестве усилителя диффузии — пара-ксилол.

Підвищення механічної міцності радіаційно-стійких пластмасових сцинтиляторів з підсилювачами дифузії. *О.С.Вельможна, Ю.О.Гуркаленко, Д.А.Єлісєєв, П.М.Жмурін, В.М.Лебедєв, В.М.Переймак.*

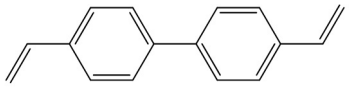
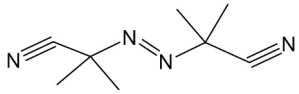
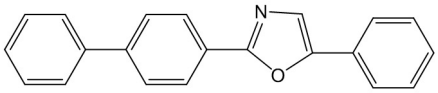
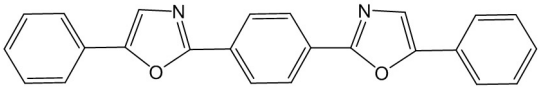
Досліджено механічну міцність радіаційно-стійкого пластмасового сцинтилятора з підсилювачами дифузії шляхом надання полімерній матриці просторово-зшитої структури. Кращий результат досягається, якщо в якості зшиваючого агента використовується 4,4′-дивінілдифеніл, а як підсилювач дифузії — пара-ксилол.

1. Introduction

The present article is a continuation of the work [1], which is devoted to creation of radiation hard plastic scintillator (PS) with increased mechanical strength. The problem is solved as follows. It was shown in the works [2, 3], the PS radiation hardness can be increased, if liquid substances, so called diffusion enhancers (DE), of 20–40 wt. % are input into PS composition. DE's increase radiolysis products and atmospheric oxygen movability into PS volume that leads to elimination of absorption centers, which are formed in PS material under ionizing radiation influence. However the diffusion enhancers have a strong plasticization effect on the PS material, that decreases its hardness up to viscous-flexible state (microhardness by Vickers HV < 50 MPa) [1]. With such low mechanical strength, PS material cutting and polishing becomes more difficult and even the shape of the PS loses stability.

It was shown in the work [1], that mechanical strength of PS material with DE percentage up to 25 wt. % can be increased by creating in its polymeric matrix spatially cross-linked structure. So, the microhard-

Table 1. Structural formulas, melting temperature ($T_{melting}$) and luminescent maximum (λ_{max}) of substances, which were used for spatially cross-linked radiation hard PS obtaining

Substance	Structural formula	$T_{melting}$, °C	λ_{max}, nm.
4,4′-Divinylbiphenyl (DVBP)		155	355
2,2′–Azobisisobutyronitrile (AIBN)		104	–
2-(4-Biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD)		167-168	365
1,4-bis-(5-phenyloxazolyl-2) benzene		245-246	415

ness of the PS with 25 wt. % isopropylnaphthalene (IPN) increases to 78 MPa, if 15 wt. % of 4,4′-bis-methylene-2-methacrylate-biphenyl (BPBMA) is used as a cross-linking agent. However, as performed by us tests show, the reached mechanical strength of 78 MPa is not enough for high quality cutting and polishing of the obtained PS material.

So, investigations to improve the mechanical strength of the radiation hard PS with diffusion enhancers are continued by us. In the present work, the mechanical and scintillation properties of the PS with DE and spatially cross-linked structure, obtained by means of the 4, 4′-divinylbiphenyl (DVBP) linking agent, are described.

2. Experimental

The spatially cross-linked PS with diffusion enhancers were obtained by the method of free-radical copolymerization of styrene with 4,4′-divinylbiphenyl (DVBP) with presence of different diffusion enhancers and scintillation additives. 2,2′-azobisisobutyronitrile (AIBN) was used as a polymerization initiator.

Right before the polymerization, styrene was passed through a chromatographic column, filled with aluminium oxide, then was distillated under reduced pressure ($P = 0.12$ bar) and at temperature of 85°C.

AIBN (from ALDRICH) was additionally purified by the method of recrystallization from isopropyl alcohol.

The cross-linking agent and diffusion enhancers (biphenyl and naphthalene derivatives) were synthesized and purified in ISMA NAS Ukraine [1].

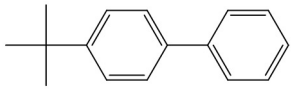
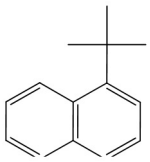
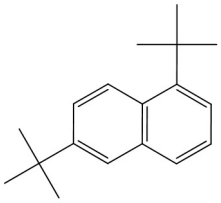
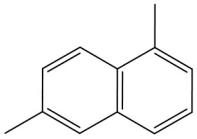
The scintillation additives (2-(4-phenyl)-5-(4-biphenyl) oxadiazol-1,3,4 (PBD) and 1,4-bis-(2-(5-phenyloxazolyl-2))-benzene (POPOP)) were produced at Kharkov chemical reagent plant (KCRP, Kharkiv, Ukraine).

The structural formulas of all substances, which were used in this work to obtain the radiation hard polymeric compositions, are given in Tables 1 and 2.

The PS samples were obtained in process of copolymerization of styrene with 4,4′-divinylbiphenyl (DVBP) monomer with one of the diffusion enhancers and 2,2′-azobisisobutyronitrile (AIBN) polymerization initiator presence. The divinylbiphenyl (DVBP) cross-linking agent content in the different samples varied from 3 to 10 wt. %. Wherein another additives content was constant, as in the work [1], and amounted: the diffusion enhancer — 25 wt. %, the polymerization initiator (AIBN) — 0.02 wt. %, the secondary luminescent additive (POPOP) — 0.1 wt. %.

Prepared reaction mixtures with the different cross-linking agent content were

Table 2. Structural formulas, brutto-formulas, boiling temperature ($T_{boiling}$), melting temperature ($T_{melting}$) of the diffusion enhancers

Diffusion enhancer	Structural formula	Brutto-formula	$T_{boiling}$, °C	$T_{melting}$, °C
4-Isopropylbiphenyl (IPBP)		$C_{15}H_{16}$	345	+11
1,4-Dimethylbenzene (*p*-xylene)		$C_6H_4(CH_3)_2$	138,3	13,26
1-Isopropylnaphthalene (IPN)		$C_{13}H_{14}$	-	-16
1,6-Diisopropylnaphthalene (1,6DIPN)		$C_{16}H_{20}$	306	-
1,6-Dimethylnaphthalene (1,6DMN)		$C_{12}H_{12}$	264	-17

placed into glass vials in amount of 10 g and dissolved at temperature of 65°C. The reaction mixtures were saturated with argon for 10 min, for oxygen traces deleting, then the vials were sealed and placed into thermostat. The polymerization was performed by the stepping temperature-temporal regime with temperature growth from 65 to 150°C for 150 h with the following cooling at rate of 5°C per h. As a result, hard, colorless and transparent PS workpieces were obtained, of which the samples with a shape of polished cylinders with diameter of 16 and height of 10 mm were fabricated.

Mechanical properties were estimated by the microhardness value, and scintillation properties — by the light yield. The microhardness was determined by the Vickers method with a microhardnessmeter PMT-3 (Russian Federation). The light yield was determined with a scintillation spectrometer, adapted to the CAMAC standard. A signal from a photomultiplier tube Hamamatsu R1307 was fed to input of a charge digital converter QDC LeCroy 2249A. The studied PS registered a flux of monoenergetic electrons with energy of 975 keV from a radioisotope electron source Bi-207. The PS light yield was measured relatively to the "standard" PS sample UPS-923A, made on the base of linear polystyrene without filler, containing two luminescent additives (2 % paraterphenyl and 0.1 % POPOP).

3. Results and discussion

The obtained samples microhardness and light yield measurements results are given in Tables 3, 4 and Fig. 1, 2. In Tables 3 and 4 the microhardness by the Vickers (HV) and light yield (LY) values for the PS with different diffusion enhancers at different cross-linking agent content [DVBP] are given. The light yield values are given rela-

Table 3. Microhardness by the Vickers (HV, MPa) for the PS with different diffusion enhancers (DE), at different cross-linking agent contents [DVBP]

[DVBP], wt.%	Microhardness, MPa					
	[DE] = 0 wt.%	[IPDP] = 25 wt.%	[*p*-xylene] 25 wt.%	[IPN] 25 wt.%	[1,6DMN] 25 wt.%	[DIPN] 25 wt.%
0	122	9	22	5	6	16
3	124	67	105	20	30	27
5	133	107	147	36	56	45
7	155	149	139	90	120	106
10	179	116	124	110	126	126

Table 4. Normalized light yield (LY) for the PS with different diffusion enhancers (DE) at different cross-linking agents contains [DVBP]

[DVBP], wt.%	The normalized light yield				
	[IPDP] 25 wt.%	[*p*-xylene] 25 wt.%	[IPN] 25 wt.%	[1,6DMN] 25 wt.%	[DIPN] 25 wt.%
0	1	1	1	1	1
3	0.62	0.81	0.71	0.52	0.57
5	0.51	0.69	0.60	0.41	0.45
7	0.45	0.63	0.54	0.35	0.41

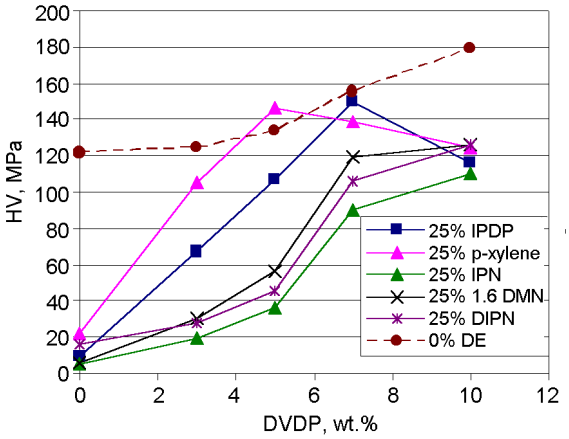


Fig. 1. Microhardness change of the PS samples with different diffusion enhancers on cross-linking agent content [DVBP]; downward: 0 wt. % DE (without DE), — 25 wt. % IPBP, — 25 wt. % p-xylene, — 25 wt. % IPN, — 25 wt. % 1.6DMN, — 25 wt. % DIPN.

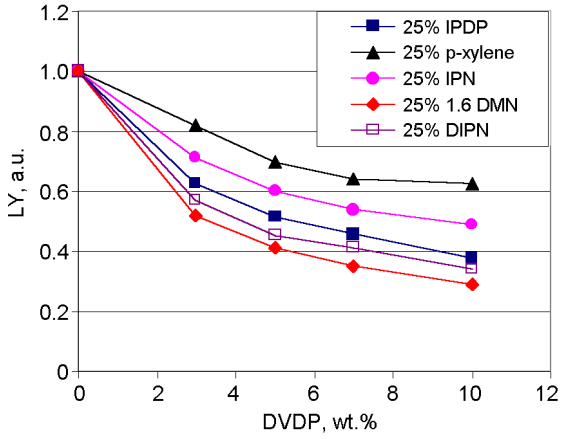


Fig. 2. Light yield change of the PS samples with different DE on cross-linking agent content [DVBP]; downward: 0 wt. % DE (without DE), — 25 wt. % IPBP, — 25 wt. % p-xylene, — 25 wt. % IPN, — 25 wt. % 1,6DMN, — 25 wt. % DIPN.

tively to the values at [DVBP] = 0 wt. % (i.e. relatively to the light yield of the PS without any cross-linking agent). As the diffusion enhancer, isopropylbiphenyl (IPBP), *p*-xylene, isopropylnaphthalene (IPN), 1,6-dimethylnaphthalene (1,6DMN) and diisopropylnaphthalene (DIPN) were used. For clearness, these results are also presented in Fig. 1 and 2.

Fig. 1 presents microhardness dependences of the PS samples with different DE (IPBP, *p*-xylene, IPN, 1,6DMN, DIPN) and without them on cross-linking agent content [DVDP]. This figure demonstrates, that for the PS with 25 % of isopropylbiphenyl (IPBP) at linking agent content increase from 0 to 7 wt. %, the multiple PS material microhardness increase from 7 to 150 MPa is observed. However, the microhardness of

the PS material, containing 25 % *p*-xylene as diffusion enhancer, reaches its maximal value of HV = 145 MPa at quite little cross-linking agent content [DVBP] = 5 wt. %. Noteworthy, at even lower cross-linking agent content [DVBP] = 3 wt. % the microhardness value reaches HV = 102 MPa, close to the microhardness of the "standard" PS UPS-923A with linear structure (HV = 122 MPa), not cross-linked and without any diffusion enhancers. At the same time, as it is seen in Fig. 1, the microhardness of the PS without any diffusion enhancer increases to 178 MPa at DVDP content increase up to 10 wt. %. However, at the same linking agent content ([DVDP] = 10 wt. %), but in presence of 25 wt. % any diffusion enhancer, the PS microhardness falls to the value of HV ~ 110–126 MPa. But, for the PS with 25 wt. % of diffusion enhancers on the naphthalene base (IPN, 1,6DMN, DIPN), the significant microhardness increase is reached at the higher linking agent content, then for the PS with 25 wt. % of IPBP and *p*-xylene.

The normalized light yield of the same PS samples, which were in microhardness measurments, is presented in Fig. 2. It is seen in Fig. 2, that the light yield of all PS significantly decreases with cross-linking agent content [DVDP] growth. Wherein, the PS with the biggest light yield contains *p*-xylene as the diffusion enhancer. Let's note, at the linking agent content [DVBP] = 3 wt. % the PS light yield is still significantly high and amounts LY = 0.82. At the same time, as Fig. 1 shows, at [DVBP] = 3 wt. %, the PS material already has the high microhardness HV = 102 MPa, enough to its cutting and polishing.

4. Conclusions

The highest microhardness and light yield belong to the obtained PS, which contains *p*-xylene as the diffusion enhancer, and DVDP as the linking agent at amounts 25 and 3 wt. % accordingly. Given compound has the mechanical strength HV = 102 MPa, equal to the commercial PS BC-408, and the light yield LY = 0.82 relatively to the PS without linking agent.

Thus, the combination in the PS compound of 25 wt. % p-xylene, as the diffusion enhancer and 3 wt. % DVBP, as the cross-linking agent, allows to create the unique PS material. It has the mechanical strength equal to the commercial PS BC-408 (HV = 102 MPa), and high light yield (LY = 82 %) relatively to the PS without linking agent, at the low cross-linking agent content and high diffusion enhancer content.

Notably, this result exceeds the parameters of the best PS, obtained in the work [1]. In that work the highest light yield LY = 0.76 and microhardness HV = 78 MPa belong to the compound, which contains 25 wt. % isopropylnaphtalene with 15 wt. % 4,4′-bis-methylene-2-methacrylate-biphenyl linking agent.

Apparently, the use of BVBP as the linking agent is better than 4,4′-bis-methylene-2-methacrylate-biphenyl (BPBMA), because it allows to obtain the higher mechanical strength of the PS with DE at the lower linking agent content. In its turn, the lower linking agent content gives an opportunity to obtain the higher light yield due to decrease of the cross-linking degree of polymeric matrix.

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