

Radiation-hard plastic scintillator with increased mechanical strength

*P.N.Zhmurin, V.N.Lebedev, A.I.Bedrik,
V.D.Titskaya, A.F.Adadurov, E.Velmozhnaya*

Institute for Scintillating Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

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This paper describes possibilities of improving mechanical properties of radiation-hard plastic scintillator (PS) with additives by spatial cross-linking their polymer base. This allows improving the mechanical properties of the PS preserving their light yield and transparency. The cross-linked structure is formed in the PS matrix by copolymerization of the main monomer and cross-linking monomer which contains two active vinyl groups. 4,4'-Bis-(methylene-2-metacrylate)-biphenyl (BPBMA) was used as the cross-linking agent and derivatives of biphenyl and naphthalene as diffuse enhancers. Inserting the cross-linking agent and diffuse enhancers facilitate the increase of the PS mechanical strength retaining its functional properties.

Keywords: plastic scintillator, radiation hardness, mechanical strength.

Описуються можливості удешевлення механічних властивостей радіаційно-стійкого пластмасового сцинтилятора з добавками при допомозі просторової зшивки його полімерної основи. Це дозволяє поліпшити механічні властивості пластмасового сцинтилятора, зберігаючи його світловий вихід і прозорість. Зшита структура формується в матриці сцинтилятора в процесі сополімеризації основного мономера і зшиваючого мономера, який містить дві активні винільні групи. 4,4'-Bis-(methylene-2-metacrylate)-biphenyl (BPBMA), використовувався в якості зшиваючого агента, а похідні біфенілу і нафталіну — у якості підсилювачів дифузії. Введення зшиваючого агента і підсилювачів дифузії сприяє підвищенню механічної міцності пластмасового сцинтилятора при збереженні його функціональних властивостей.

Радіаційно-стійкий пластмасовий сцинтилятор з підвищеною механічною міцністю. *П.М.Жмурін, В.М.Лебедев, О.І.Бедрик, В.Д.Тітська, О.Ф.Ададуров, О.С.Вельможна.*

Описано можливості поліпшення механічних властивостей радіаційно-стійкого пластмасового сцинтилятора з домішками за допомогою просторової зшивки його полімерної основи. Це дозволяє поліпшити механічні властивості пластмасового сцинтилятора, зберігаючи його світловий вихід і прозорість. Зшита структура формується в матриці сцинтилятора у процесі сополімеризації основного мономера і зшиваючого мономера, який містить дві активні винільні групи. 4,4'-Bis-(methylene-2-metacrylate)-biphenyl (BPBMA), використано у якості зшиваючого агента, а похідні біфенілу і нафталіну — у якості підсилювачів дифузії. Введення зшиваючого агента і підсилювачів дифузії сприяє підвищенню механічної міцності пластмасового сцинтилятора при збереженні його функціональних властивостей.

1. Introduction

Modern high energy physics experiments require efficient plastic scintillators (PS) with increased radiation hardness and improved mechanical strength. These PS have to retain high scintillation efficiency and transparency to the self fluorescence light.

Polystyrene is the most radiation-hard and mechanically strong plastic base of the PS. But to add special properties to a scintillator, a large amount (20–40 wt. %) of amorphous additives should be inserted to the polystyrene matrix. They usually degrade the mechanical properties of the material. This problem incidental to developing the PS with increased radiation hardness [1–3] and ability to neutron and gamma quanta discrimination by pulse shape (n/γ -discrimination) [4].

The most efficient way to create the radiation-hard polymer bases is the use of plasticizers (diffuse enhancers), which increase the mobility of the polymer chain fragments thus facilitating diffusion of atmospheric oxygen into the PS bulk. This leads to destruction of radicals formed in the PS material under ionizing radiation. Such diffuse enhancers usually are derivatives of naphthalene, biphenyl, and polyvinyl oxides [2–5]. The best results were obtained with 20 % of biphenyloxide. After irradiation by 2.8 Mrad dose this scintillation composition (trade mark UPS-98RH) retains 91 % of the initial light yield, while the PS of traditional content (without diffuse enhancer) — UPS-923A — only 55 % [6]. Therewith, the dose ($D_{1/2}$), which decreases the light yield in a half, is rather small for UPS-923A ($D_{1/2} = 1.2$ Mrad), and in more than four times greater for UPS-98RH ($D_{1/2} = 5.1$ Mrad).

Unfortunately, high content of the diffuse enhancer in the PS (20 wt. %), results in strong plasticizing effect which leads to the PS material softening up to the plastic state (micro hardness $HV < 50$ MPa). Such a small mechanical strength hindered cutting and polishing of the PS material and promotes accelerated diffusion of the additives to the PS surface. This decreases the long-term stability and radiation hardness of the PS. Above drawbacks obstruct production, impair operation characteristics and limit the area of application of the radiation-hard PS with diffuse enhancers.

This paper describes possibilities of improving mechanical properties of the radiation-hard PS by spatial cross-linking their

polymer base. This allows improving the mechanical properties of the PS preserving their light yield and transparency.

A cross-linked structure is formed in the PS matrix by copolymerization of the main monomer and cross-linking monomer which contains two active vinyl groups.

It was shown in [7–9], that the light yield of the cross-linked PS obtained by copolymerization of polystyrene and some derivatives of diacrylates, dimethacrylates, or diisopropenylbiphenyl, actually does not decrease. So, simultaneous inserting the cross-linking agent and plasticizer have to facilitate the increase of the PS mechanical strength retaining its functional properties.

2. Experimental

Polystyrene was used as a base of the radiation-hard PS with improved mechanical properties. It was purified by transmission through chromatographic column with aluminum oxide with further distillation under low pressure ($P = 0.98$ bar) and temperature (85°C). 4,4'-Bis-(methylene-2-metacrylate)-biphenyl (BPBMA) was used as the cross-linking agent and derivatives of biphenyl and naphthalene as diffuse enhancers. All they were synthesized in the Department of Plastic Scintillators, ISMA, NAS of Ukraine. 2,2'-Azobisisobutyronitrile (AIBN) from Aldrich was used as an initiator. It was purified by re-crystallizing from isopropyl alcohol. As scintillation additives, 2-(4-phenyl)-5-(4-biphenyl)-oxadiazole-1,3,4 (PBD) and 1,4-bis(2-(5-phenyloxazolyl))-benzene (POPOP) were used. These substances were produced in the State Plant for Chemical Reagents (Kharkov, Ukraine).

All above substances were selected according to one criterion: possibility of obtaining the firm cross-linked polymer with 25 wt. % of diffuse enhancer. Besides, the PSs made on this base have to have light yield close to that of the PSs based on linear polystyrene. The studies have shown that cross-linking agent 4,4'-bis-(methylene-2-metacrylate)-biphenyl satisfies these conditions. It is possibly due to long monomer chain of BPBMA which allows rather large cells creating in the polymer bulk, which assists the dissolving of required quantity of the diffuse enhancer. Moreover, high compatibility of the polymer composition compounds is also connected with the high boiling temperature (about 300°C) and low freezing point of alkyl substituted naphthalene and biphenyl.

Table 1. Structural formulae, melting temperatures (T_{melt}), boiling points (T_{boil}) and fluorescence maxima (λ_{max}) of compounds used to obtain cross-linked radiation-hard PS

Compound	Structural formula	T_{melt} , °C	λ_{max} , nm
4,4'-Bis-methylene-2-methacrylate-biphenyl (BPBMA)		85	320
2,2'-Azobisisobutyronitrile (AIBN)		104	—
2-(4-Biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD)		—	365
2,2'-(1,4-Phenylene)bis(5-phenyl-1,3-oxazole) (POPOP)		242	418

Structural formulae of all substances used for obtaining the cross-linked radiation-hard compositions are presented in Tables 1 and 2.

Synthesis of 4,4'-bis-methylene-2-methacrylate-biphenyl (BPBMA) was made according to the Scheme 1.

On the first stage, by means of biphenyl bromomethylation in the acetic acid with the presence of sodium bromide, paraformaldehyde and sulfur acid 4,4'-dibromomethylbiphenyl is obtained [10]. On the second stage, in the dimethylphormamide medium with the potassium carbonate under 40°C temperature, the potassium salt of methacrylic acid is obtained. On the third stage, in the dimethylformamide medium, with the methyl alcohol presence, by means of reaction between 4,4'-dibromobiphenyl and potassium salt of methacrylic acid under 55°C temperature 4,4'-bis-(methylene-2-methacrylate)-biphenyl (BPBMA) is obtained as colorless crystal powder. The measured absorption and luminescence spectra of the synthesized BPBMA are presented in Fig. 1,

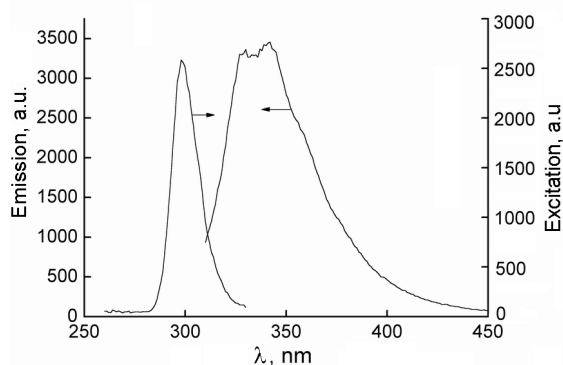
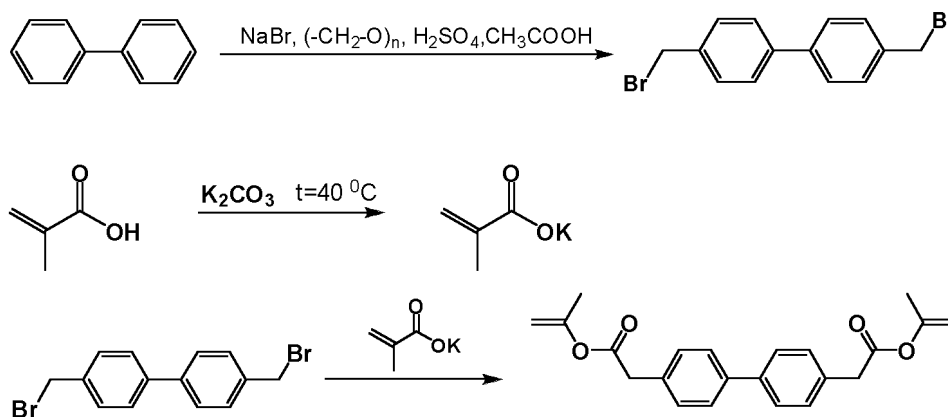


Fig. 1. Absorption and luminescence spectra of 4,4'-bis-(2-methylene-methacrylate) biphenyl.

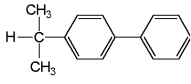
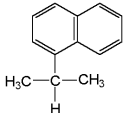
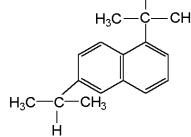

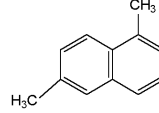
from which it follows that they are close to the corresponding spectra of polystyrene. Therefore, this substance may be involved in the scintillation process.

Purification of 2,2'-azobisisobutyronitrile (AIBN) from impurities was performed by recrystallization from isopropanol. The melting point of purified AIBN is 103°C.



Scheme 1.

Table 2. Structural and molecular formulae, boiling (T_{boil}) and melting (T_{melt}) temperatures of plasticizers

Plasticizers	Structural formula	Molecular formula	T_{boil} , °C
4-Isopropylbiphenyl (IPBP)		$C_{15}H_{16}$	345
1-Isopropyl-naphthalene (IPN)		$C_{13}H_{14}$	—
1,6-Diisopropyl-naphthalene (DIPN)		$C_{16}H_{20}$	306
1-Methylnaphthalene (MN)		$C_{11}H_{10}$	244
1,6-Dimethylnaphthalene (DMN)		$C_{12}H_{12}$	264

Preparation of the samples of spatially cross-linked radiation-hard PS was performed by the copolymerization of styrene monomer with 4,4-bis (2-methylene-methyl) — diphenyl (BPBMA) in the presence of the plasticizer (diffusion enhancer) and the polymerization initiator AIBN. Concentration of the cross-linking agent BPBMA in various samples was ranged from 3 to 15 wt. %. Content of the other additives remained constant: the diffusion enhancer — 25 wt. %, the polymerization initiator (AIBN) — 0.02 wt. %, the primary fluorescent additive (PBD) — 2 wt. %, the secondary fluorescent additive (POPOP) — 0.1 wt. %.

Prepared reaction mixtures with different contents of the cross-linking agent were placed in glass vials in amount of 10 g and dissolved at temperature 65°C. To remove oxygen traces, the reaction mixture was saturated by argon for 10 min., the vials were sealed and mounted in the thermostat. Polymerization was carried out by stepwise temperature-time mode with temperature rise from 65 to 150°C for 150 h and subsequently cooled with 5°C per hour rate. As a result the solid, colorless and transparent preforms were obtained from which the PS samples were made as polished cylinders of 16 mm diameter and of 10 mm height.

Mechanical properties of the samples were evaluated by the value of material microhardness, while scintillation properties

— by the light output. Microhardness was determined by the Vickers Hardness method with PMT-3 microhardnessmeter. The light output was measured by a scintillation spectrometer, performed in the CAMAC standard, using a photomultiplier Hamamatsu R1307 and ^{207}Bi source of electrons. The light output is measured relative to the "standard" PS UPS-923A, which is made on the basis of linear polystyrene and contains two fluorescent additives (2 % of *para*-terphenyl and 0.1 % of POPOP).

The measurement results are shown in Fig. 2–4. Fig. 2 shows the dependence of microhardness of the radiation hard PS with linear structure (without any cross-linking agent) on the plasticizer (IPBP) content. As it is seen in the figure, when the content of IPBP is varied from 0 to 5 wt. %, microhardness of the PS material varies slightly from 124 to 120 MPa, which corresponds to the microhardness of the pure polystyrene. With increasing the plasticizer content up to 10 wt. %, the microhardness decreases slowly, but at content of 20 wt. % microhardness is dramatically reduced to 38 MPa, which corresponds to viscous flowing state, and at 25 wt. % it falls to 2 MPa.

Figure 3 shows a dependence of microhardness of the PS with 25 wt. % of various plasticizers, on the amount of cross-linking agent, i.e. the degree of the polymer "stitching". This figure demonstrates that

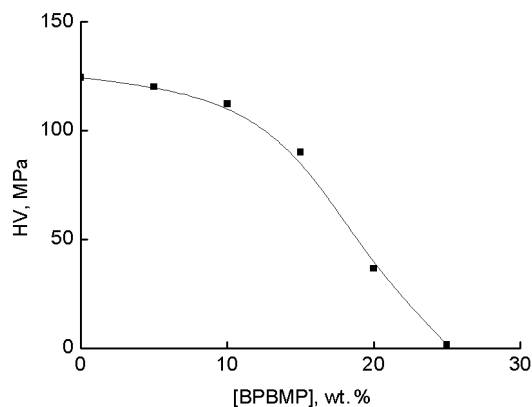


Fig. 2. Dependence of microhardness of radiation hard PS with linear structure (without cross-linking agent) on content of the plasticizer (IPBP).

with increase of the cross-linker content from 3 to 15 wt. % the great increase of microhardness is obtained, regardless of the type of used plasticizer.

It is seen in the figure that when the content of the cross-linking agent BPBMA is 3 wt. %, microhardness of all samples varies from 2 to 11 MPa, which corresponds to the plastic, rubbery-like state. It is also seen that with increasing the cross-linker content from 7 to 10 wt. % microhardness increases faster for the samples in DIMN, IPBP, IPN, DIPN, MN series. Thus, when [BPBMA] = 10 wt. %, microhardness of these samples is 67, 59, 45, 32 and 13 MPa, respectively, and for the DIMN sample virtually reaches its limit (70 MPa). The microhardness of the remaining samples continues to grow with increase of the content of the cross-linking agent, and when [BPBMA] = 15 wt. % it is close to 70 MPa for all samples. This corresponds to the hardness sufficient for material machining (cutting and polishing at the room temperature).

Here we should note that the average microhardness of the polyvinyltoluene based PS BC-408 is 105 MPa, and for the polystyrene-based PS UPS-923A it is 122 MPa. Also it should be noted that these values were obtained within 2 months from the date of manufacture of the PS, because the microhardness of the PS increases in time because of the natural aging processes. Thus, our measurements showed that after 6 months the microhardness of UPS-923A and BC-408 increases from 120–130 to 160–170 MPa and from 100–110 to 130–140 MPa, respectively.

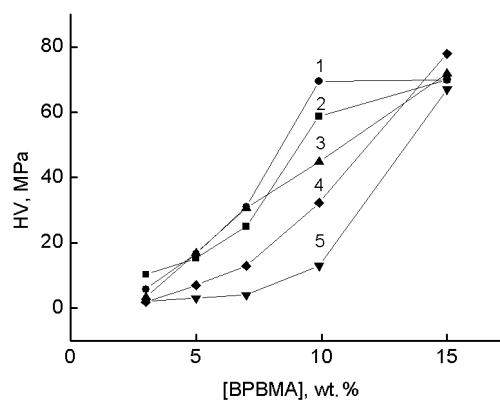


Fig. 3. Dependences of microhardness of PS with 25 wt. % of various plasticizers (1 — DMN, 2 — DIPN, 3 — IPBP, 4 — IPN, 5 — MN) on content of the cross-linking agent BPBMA. For reference-microhardness of the standard UPS-923A is 122 MPa.

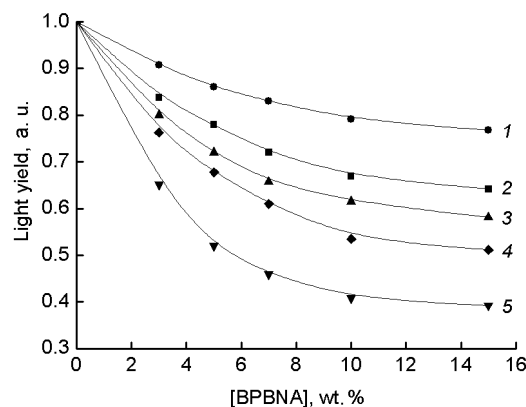


Fig. 4. Relative light output of PS with 25 % wt % of plasticizer (1 — IPN, 2 — IPBP, 3 — MN, 4 — DIPN, 5 — DMN) depending on content of the cross-linking agent BPBMA.

Relative light output was measured on the PS with different content of the cross-link agent BPBMA and 25 wt. % of various plasticizers. Results are shown in Fig. 4. It is seen that the light output of the PS is significantly reduced by increasing the BPBMA content. The PSs with isopropyl-naphthalene (IPN) as a diffusion enhancer retain the largest light output. When the content of the cross-linking agent is 15 wt. %, the light output of this PS is 0.77, and the light output of the PS from IPBP, MN, DPN and DMN series decreases and equals to 0.64, 0.58, 0.51 and 0.39, respectively, with respect to the PS of linear structure (without cross-link agent).

4. Conclusions

Thus, mechanical strength of the PS material with up to 25 % wt. % plasticizers IPBP, IPN, DIPN, MN, DMN can be increased by cross-linking the polymer matrix. Thus, use of 10–15 wt. % of a 4,4'-bis-methylene-2-methacrylate-biphenyl as a cross-linking agent allows increasing the mechanical strength of the PS material with any of the above-mentioned plasticizers up to 70 MPa and higher. The highest light yield of 0.76 and microhardness of 78 MPa are provided in the composition that contains 25 wt % of isopropyl naphthalene in combination with 15 wt % of cross-link agent 4,4'-bis-methylene-2-methacrylate-biphenyl.

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