

Large-sized neutron-sensitive plastic scintillator

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The polymerization conditions of a polystyrene-based scintillation composition with a high content of activator (40 wt. %) were selected and optimized. The composition and polymerization mode of a relatively large neutron-sensitive plastic scintillator (mass 1 kg) are proposed.

Keywords: plastic scintillator, activator, polymerization mode, n/γ -discrimination.

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Підбрано та оптимізовано умови полімеризації сцинтиляційної композиції на основі полістиролу з високим вмістом активатора (40 мас. %). Запропоновано склад та режим полімеризації нейтроночутливого пластмасового сцинтилятора відносно великого розміру (маса 1 кг).

1. Introduction

Today, there is a limited set of materials for creating various types of detectors suitable for detecting neutrons. The most common and highly effective, in terms of detecting neutrons in the presence of a gamma background, are detectors based on gas-discharge counters containing helium-3 isotopes [1, 2]. However, a significant problem of these detectors is the limited time of their maintenance (there is no equipment capable of reliably isolating the volume from the leakage of helium atoms). Therefore, any helium-containing detector must be refilled later to restore the helium content. However, the problem is that helium-3 isotopes have become practically unavailable.

An alternative for creating fast neutron detectors can be organic crystals. However, the practical impossibility of obtaining organic single crystals of large sizes does not make it possible to provide the required level of neutron registration

sensitivity. Therefore, there is a problem of searching for other organic scintillation media for detectors capable of detecting fast neutrons. Thus, plastic scintillators (PS) based on polystyrene with a high concentration of activator (up to 40 wt. %) were proposed. The activator in such polymer scintillation compositions is usually 2,5-diphenyloxazole (PPO) molecules, the solubility of which in the polymer medium reaches 36 wt. % [3, 4]. There is no commercially available alternative to PPO as an activator of neutron-sensitive PS in the modern market. However, the use of PPO in such large concentrations does not allow obtaining PS samples of the required size with satisfactory mechanical properties and long-term stability [5]. PPO-like methods were found to modify molecules; they significantly improve the mechanical properties of polymer media with a high content of activator. The effectiveness of alkyl-substituted diaryloxazoles and diaryloxadiazoles was demonstrated on small and medium-sized samples (up to 0.1 kg)

[6, 7]. However, in order to create relatively large-sized samples of neutron-sensitive PS, it is necessary to solve the problem of finding and optimizing the polymerization conditions for significant volumes of polystyrene with a high content of activator. Since a large amount of activator leads to inhibition of the styrene polymerization process, it is necessary to find such initiators and polymerization conditions that would compensate for the inhibition process and not lead to uncontrolled development of the polymerization reaction.

Samples weighing 0.05, 0.25 and 1.0 kg were studied. 2-(4-tert-butylphenyl)-5-phenyloxazole-1,3 (TBPPO) was used as a PS activator, and 1,4-bis(2-(5-phenyloxazolyl))-benzene (POPOP) was used as a shifter.

2. Experimental

All the PS samples were obtained by thermally initiated bulk polymerization. The calculated quantities of the scintillation composition components were loaded into the glass ampoules. The resulting mixture was purged with argon for 10–15 minutes; then the ampoules were hermetically sealed. The initial temperature and polymerization time were chosen depending on the mass of the sample.

The n/γ -discrimination parameter FOM was determined by comparing the total signal charge (Q_{total}) and its ratio to the slow component (Q_{total}/Q_{slow}). For this purpose, the PS samples were irradiated with fast neutrons and γ -quanta from a plutonium-beryllium source ($^{239}\text{Pu}-\text{Be}$) through a 20 mm thick lead plate. After digital processing, the pulse shape and the area values of the slow component (Q_{slow}) in the range from 50 ns to 200 ns and the total pulse (Q_{total}) were stored in the output file for each registered pulse. The initial integration time point for Q_{slow} calculation was chosen for each sample individually. Then, for each event, the ratio $D = Q_{slow}/Q_{total}$ was calculated and the distribution of the number of events over D was constructed, from which the FOM was determined. The method is described in more detail in [8].

3. Results and discussion

Although PS activated by TBPPO has a relatively high long-term stability (compared to samples with a high concentration of unmodified PPO) and satisfactory scintillation characteristics, it has a

rather low microhardness (39 MPa [9]) and, as a result, is difficult to machine. As practice shows, in order to improve the mechanical properties of PS (ensuring rigidity and strength), it is necessary to introduce crosslinking agents into its composition [9, 10]. The following crosslinking agents were used in this work: 1,4-divinylbenzene, 4,4'-bis-(methylene-2-methacrylate)diphenyl (DMABP) and 1,6-hexanediol dimethacrylate (HDDA).

The selection of the crosslinking agent amount and the polymerization mode was tested on samples weighing 0.05 kg.

Samples weighing 0.05 kg. Each polymer composition consisted of 40 wt. % TBPPO, 0.05 wt. % POPOP, X wt. % crosslinking agent and styrene (rest). The concentrations of the crosslinking agent X were 0.1, 0.25, 0.5, 1.0, 2.0, 3.0 and 5.0 wt. %, respectively. Styrene was added to the total mass of 0.05 kg. Each of the PS samples was obtained in triplicate. The initial polymerization mode is 48 h at 90°C, 24 h at 110°C, and 48 h at 125°C, followed by cooling to room temperature at a rate of 5–10°C/h.

1,4-Divinylbenzene. The initial polymerization temperature was 90°C. In the case of divinylbenzene, for each crosslinking agent concentration, cracks appeared in all the PS samples after a certain time interval. Decreasing the initial polymerization temperature from 90°C to 60°C (in steps of 10°C) led to the same result, but with a delay in time. When the temperature increased from 90°C to 110°C (with the same step of 10°C), cracks appeared even faster, in the first hours of polymerization.

4,4'-Bis-(methylene-2-methacrylate)diphenyl (DMABP). At the initial polymerization temperature of 90°C, all the PS samples with DMABP concentrations of 0.1 wt. % to 2.0 wt. % contained opaque inclusions. Samples with 3.0 wt. % and 5.0 wt. % were defect-free. Both an increase and a decrease in the initial polymerization temperature led to the appearance of cracks or white inclusions during the polymerization process in all the samples.

1,6-Hexanediol dimethacrylate (HDDA). In PS samples containing up to 0.5 wt. % HDDA, white inclusions appeared 48 h after the start of polymerization (90°C). In PS samples with a HDDA concentration of 1.0 wt. % and more, 24 hours after the polymerization start (90°C), cracks appeared. Only PS samples

Table 1. The composition and mode of polymerization of the PS sample of neutron-sensitive a mass 1.0 kg

Component PS	Concentration, wt. %	Mode of polymerization
Polymer-based — Styrene	59.4	60°C — 120 h 75°C — 24 h 90°C — 24 h 110°C — 24 h 125°C — 48 h decrease to room temperature by 5°C/h
Activator — TBPPO	40.0	
Shifter — POPOP	0.05	
Initiator — AIBN	0.05	
Cross-linking agent — HDDA	0.5	

with 0.5 wt. % HDDA remained transparent and defect-free during the entire polymerization time at an initial temperature of 90°C. When varying the initial polymerization temperature from 60°C to 90°C (in steps of 10°C), the result was not variable, and when the initial temperature increased above 90°C, cracks and white inclusions appeared in all the samples. Three series of experiments were carried out with repeatable results.

Thus, transparent, defect-free samples were obtained using the cross-linking agents DMABP (3.0 wt. % and 5.0 wt. %) and HDDA (0.5 wt. %). It is known that a high concentration of additional components of PS can lead to a decrease in scintillation properties [11]. In addition, HDDA is a commercially available product, while DMABP requires targeted laboratory synthesis. Therefore, for the further creation of larger samples, taking into account the minimization of the influence of the additional component and its availability, the crosslinking agent HDDA in the amount of 0.5 wt. % was chosen.

As a result, for neutron-sensitive PS weighing 0.05 kg and containing 0.5 wt. % HDDA, the following polymerization mode was chosen: 72 h at 90°C, 24 h at 110°C, 48 h at 125°C, with subsequent cooling to room temperature at a rate of 5–10°C/hour.

Samples weighing 0.25 kg. Next, samples of neutron-sensitive PS weighing 0.25 kg were obtained. The polymer composition consisted of 59.45 t. % styrene, 40 wt. % TBPPO, 0.05 wt. % POPOP and 0.5 wt. % HDDA. Three series of experiments were carried out.

At an initial temperature of 90°C, cracks appeared in the samples a few hours after the start of polymerization. Lowering the initial temperature of polymerization to 80°C made it possible to obtain defect-free samples. Since the polymerization tempera-

ture decreased, the duration of the initial stage of polymerization increased. Finally, to obtain samples weighing 0.25 kg, the following mode was chosen: 96 h at 80°C, 12 h at 90°C, 24 h at 110°C, 48 h at 125°C, with subsequent cooling to room temperature at a rate of 5–10°C/h.

Samples weighing 1.0 kg. At the next stage of the work, samples of neutron-sensitive PS with a mass of 1.0 kg with a composition similar to samples with a mass of 0.25 kg were obtained.

At an initial temperature of 80°C, cracks appeared in the samples a few hours after the start of polymerization. Lowering the initial temperature to 70°C led to a similar result. It seems appropriate to reduce the temperature to 60°C. However, at such a temperature, the rate of styrene thermal initiation is low. In addition, the activator at a high concentration additionally acts as a polymerization inhibitor. Therefore, to ensure the polymerization reaction, 0.05 wt.% of N,N'-azoisobutyronitrile (AIBN) initiator was added to the polymer composition. The working temperature of AIBN is 50–70°C. The following polymerization regime was chosen: 120 h at 60°C, 24 h at 75°C, 24 h at 90°C, 24 h at 110°C, 48 h at 125°C, with subsequent cooling to room temperature at a rate of 5°C/h. Three series of transparent samples without defects were obtained.

Table 1 presents the optimal composition and mode of polymerization of neutron-sensitive PS sample weighing 1.0 kg.

Thus, as a result of the work, the conditions for the polymerization of the polystyrene-based neutron-sensitive scintillation composition with a high content of activator were proposed.

Study of the PS's n/γ -discrimination properties. A sample of neutron-sensitive PS weighing 1 kg was machined by milling,

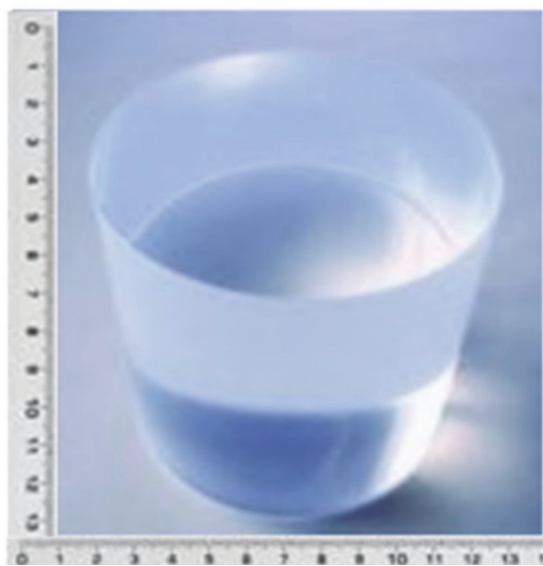


Fig.1. Image of the PS sample with 40wt. % TBPPO, 0.05wt. % POPOP, 0.5wt. % HDDA and 0.05wt. % AIBN.

grinding and polishing. After processing, a cylindrical PS with 100 mm diameter and 110 mm height was obtained and its n/γ -discrimination properties were investigated (a photo of the sample is presented in Fig. 1). Fig. 2 shows the distribution of scintillation signals of neutrons and γ -quanta induced in the sample by the ^{239}Pu -Be source radiation.

Fig. 3 shows the result of processing the signal distribution and approximating it with two Gaussians. From the data of Fig. 3, the FOM n/γ -discrimination factor was calculated as 1.9. In our work [7], the n/γ -discrimination of small and medium-sized plastic scintillator samples was studied. The obtained n/γ -discrimination factor FOM for PS samples of 100 mm×110 mm in size coincides with the value of the FOM of similar composition medium-sized PS obtained without the use of crosslinking agent and initiator.

Based on the results of the studies, it can be concluded that the use of a crosslinking agent and an initiator in the preparation of large size PS does not lead to significant changes in the n/γ -discrimination ability, and even more so to its degradation.

The obtained data allow us to hope that the proposed polymer composition and the polymerization mode will provide the possibility of creating a neutron-sensitive PS of large size and complex geometry.

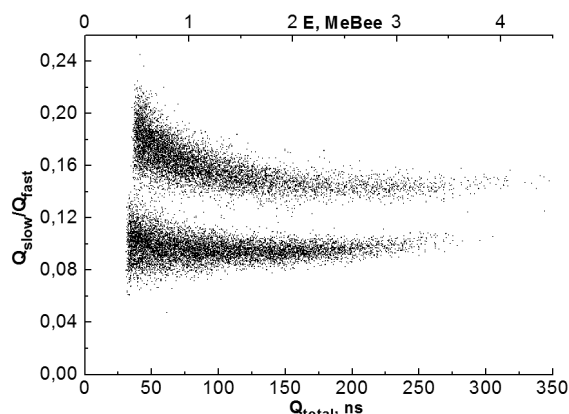


Fig. 2. Neutron-gamma discrimination of the PS with 40 wt. % TBPPO, 0.05 wt. %

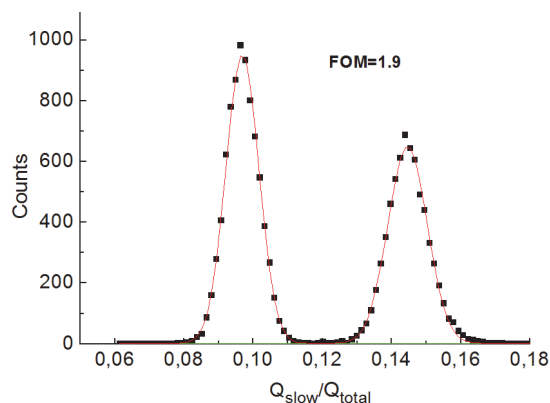


Fig. 3. The n/γ -discrimination form factor of PS with 40 wt. % TBPPO, 0.05 wt. % POPOP, 0.5 wt. % HDDA and 0.05 wt. % AIBN.

4. Conclusions

A polymerization mode is proposed for obtaining a neutron-sensitive scintillation composition based on polystyrene weighing 1 kg with a high content of activator (40 wt%). It is shown that the introduction of a crosslinking agent and an initiator into the composition of a large-sized PS does not lead to decreasing of its n/γ -discrimination ability. The developed PS composition and the proposed polymerization mode are suitable for obtaining large-sized neutron-sensitive PS with complex geometry.

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