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Light scattering in the plastic scintillator

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Optical losses in a standard composition plastic scintillator (PS) (98.5 % PST + 1.5 % *p*-TP + 0.02 % POPOP) have been analyzed numerically. The PS scattering properties have been studied in experiment for PS samples manufactured under two different large-size block polymerization conditions. The total scattering data and bulk attenuation length of light in PS are presented. Contributions from individual scattering components (Rayleigh and Mie scattering) have been estimated basing on a simplified model. The observed Rayleigh scattering component reduction from 1850 to 380 dB/km after additional annealing can be explained by a decrease in local polymer matrix heterogeneity.

Проведен численный анализ оптических потерь в пластмассовом сцинтилляторе (ПС) стандартного состава (98.5 % PST + 1.5 % *p*-TP + 0.02 % POPOP). Экспериментально исследованы рассеивающие свойства ПС, полученного двумя различными режимами полимеризации крупногабаритного блока. Представлены результаты измерения интегрального светорассеяния и объемной длины ослабления света в ПС. На основе упрощенной модели оценены вклады отдельных компонентов светорассеяния — рассеяния Релея и рассеяния Ми. Наблюдаемое уменьшение релеевской составляющей потерь с 1850 до 380 дб/км после дополнительного отжига объясняется уменьшением локальной гетерогенности полимерной матрицы ПС.

Plastic scintillators (PS) are successfully used to detect the fundamental particles in the modern high-energy physics (HEP) experiments. The world production of those inexpensive and efficient scintillation counters is incremented annually almost by 70 %. However, despite of such high production rates, the need for plastic scintillators increases every year. This is due to a trend to continuous increase in energies of particles to be explored and development of more and more complex and multi-purpose designs of detectors. In the largest sandwich type detectors now in use and under construction (with cellular or planar structure), the number of elementary scintillation counters shaped as long-length plates, sheets, or blocks can attain tens and hundreds of thousands. So, for example, the detector CMS (Compact Muon Solenoid) includes about 20000 tiles of 4000 m^2 total area and 16 tons weight [1]. About same number of PS is included in detector LHC (Large Hadron Collider) [2]. The calorimeter ATLAS (A Toroidal Large Hadron Collider Apparatus) is completely made from PS and includes 460000 tiles with the weight exceeding 58 tons [3].

The high transparence is an essential requirement to PS at their use in HEP experiments. This is especially important in calorimetry at measuring the energy of particles in a hadron shower which is passing through wide strips of large-sized PS. Naturally, only a very high transparence of such large-sized scintillator (length up to 5 m) can provide a homogeneous light collection and a high energy resolution of the detector. Now, none of the known PS meets adequately the high transparence requirement.

The bulk attenuation length of light (BAL) in large-sized domestic production PS (UPS-923A) as well as in the best foreign analog (BC-408, BICRON) varies within limits of 250 up to 400 cm. In a 3 to 4 m long scintillation counter, the optical path length of light generated therein will be already comparable to BAL, and the light at PS output is very faint. Thus, an insufficiently high transparence of a scintillator can restrict its applicability essentially. This fact forces to search for the new designs, permitting to raise transparence and light collection efficiency in PS and thus to provide their use in the modern and future HEP designs.

Estimations of optical loss in PS evidence that potential opportunities of PS are far from being exhausted. In fact, at absolute absence of impurities and an ideal microstructure of a polymer matrix, the calculated loss level in PS is several times below the loss limit in real PS [4]. Such a discrepancy is due first to the absorbing impurities usually present in a certain amount in the polymer material, and second, to various kinds of scattering centers (structural defects, inclusions, porosity, etc.), caused by deviations from the polymer synthesis conditions. Those two light-attenuating factors in optically transparent polymers are objects of numerous studies. The manufacturing technology of large-sized polystyrene scintillators (UPS-923A) designed recently at the Institute of scintillation materials (ISMA, Kharkiv, Ukraine) provides a 4 meter transparence that exceeds the former transparence level by a factor of 2 or 2.5. Such a substantial transparence increase became possible due to the solution of some problems associated with the absorption loss in PS [5]. The purpose of this work is to search for ways to decrease the optical loss in PS due to scattering.

It is known that optically transparent and explicitly amorphous polymers polystyrene (PST), polyvinyl toluene, polymethyl methacrylate (PMMA) show only a slight scattering inessential for many applications. However, the transparence thereof depends to a great extent on the light loss caused by the scattering, as the amorphous phase of a polymer matrix is not homogeneous enough. Moreover, the polymer can contain foreign substances (dust, metal ions, dissolved O_2) and pores (of 0.5 up to 10 nm radius). Thus, the PS polymer is as a rule a composite system with distributed in it large and small scattering centers as foreign impurities and intrinsic supramolecular features.

In this work, the study results of optical loss caused by scattering in PS obtained under two various "annealing" regimes of a polymer block. It is shown that the light loss in PS can be almost halved by varying the annealing temperature and time regime of large-sized polystyrene scintillation block. The observed effect is explained, in our opinion, by decreased internal "frozen" strain level of macromolecules in the block and resulting improved optical isotropy of PS.

For the experiments, two series of standard PS composition samples (98.5 % PST + 1.5 % *p*-TP + 0.02 % POPOP), including 98.5 % of polystyrene and two luminescent additives, 1.5 % *p*-terphenyl (*p*-TP) and 0.02 % phenyloxazolylbenzyty (POPOP) were used. The samples were made of two large-sized scintillation blocks prepared using two various polymerization regimes. The basic differences consist in maximal temperature values (T_{max}) achievable in 1-st and in 2-nd cases, in various holding time at T_{max} and at glass transition (T_g ~ 85°C), as well as in the temperature decrease rate near T_g (in the first mode, 3 deg/h while in second, 1.5 deg/h).

To determine the of integrated light transmission characteristics of the samples, a dual-beam sphere photometer (FMSh-56) was used. The intensities of passed and scattered light fluxes (per cent of incident light intensity) were registered. To measure the scattered light flux, the direct light beam was shielded by a light trap (black velvet). The scattering intensity was defined by amount of light deflected from the incident beam direction by about 2.5°.The measurements were carried out in separate spectral regions from 400 nm up to 750 nm using light filters transmission maxima at 400, 434, 490, 540, 582, 612, and 750 nm. The samples were shaped as flat plates of 20 mm thickness with polished surfaces. The plate size (20×30×50 mm^3) was selected so that it overlapped completely the inlet opening of the photometer integrating sphere. The samples were free from inclusions, bubbles and cracks. The polished surfaces had no visible defects (chips, dents, etc.) and was carefully cleaned of polish powder traces and other impurities, and then protected by a polyethylene film (5 to 10 μm). The bulk light attenuation length was measured using a photometric apparatus with a cadmium laser (λ_{max} = 441.6 nm). The samples for BAL measurements were shaped as

50 cm long cylinders. The butts of cylinders were polished thoroughly.

To estimate the total spectral loss in PS, a mathematical model in the form of a simple equation was used. This model represents the sum of discrete mathematical models, each of which corresponds to known light attenuation mechanisms in optical transparent polymers. One of those describes optical loss in visible spectral range of long-wavelength UV-absorption "tail", while another, those in IR absorption edge. The third model corresponds to optical loss associated with light scattering. This equation can be presented as

$$\beta = \beta_s + \beta_{uv} + \beta_{ir}, \quad (1)$$

where β_s is the light loss due to scattering; β_{uv} and β_{ir}, contributions to the loss associated with edges UV and the IR absorption bands, respectively. Here and further, the light loss is characterized by the attenuation index β, expressed in dB per 1 km of the light path in a medium and equal to $4.34 \cdot 10^5$ BAL^{-1} cm^{-1} or $4.34 \cdot \tau \cdot 10^5$ cm^{-1} (BAL is the bulk attenuation length, has dimensionality of cm, τ, the extinction coefficient in cm^{-1}). Usually, the losses due to absorption (UV and IR) are modeled by exponential functions [6, 7]:

$$\beta_{uv} = K_{uv} \cdot \exp(C_{uv}/\lambda), \quad (2)$$

$$\beta_{ir} = K_{ir} \cdot \exp(C_{ir}/\lambda), \quad (3)$$

where K_{uv}, K_{ir} and C_{uv}, C_{ir} are constants. The edge of UV-absorption, according to calculations and experimental data, causes a total loss in transparent polymers no more than 100 dB/km, while the loss associated with the IR absorption edge band does not exceed 1–2 dB/km [7]. In Table 1, presented are typical values of constants K_{uv} and C_{uv}, included in eq.(1) for polystyrene and polymethyl methacrylate [8] as well as for quartz glass [9]. The optical loss values in these materials calculated for $\lambda = 500$ nm are indicated, too. The contribution from optical loss resulting from scattering properties of a material is well-known, too (see, e.g., [8]) and is modeled by the following equation:

$$\beta_s = A \times \lambda^{-4} + B. \quad (4)$$

Table 1. Parameters of the exponential function describing loss associated with UV-absorption edge in optically transparent media [7, 8]

Parameters	Polystyrene	PMMA	Quartz glass
K_{UV} (dB/km)	$1.1 \cdot 10^{-5}$	$1.58 \cdot 10^{-12}$	$1.1 \cdot 10^{-4}$
C_{UV} (nm)	$8 \cdot 10^3$	$1.15 \cdot 10^4$	$4.9 \cdot 10^3$
b_{UV} (dB/km)	100	0.15	2

The first item describes the Rayleigh scattering (scattering on small inhomogeneities $d < \lambda/20$), while the second defines the Mie scattering (scattering on large particles $d \geq \lambda$). A deep purification of initial raw material and a high level of the polymer material synthesis made it possible to exclude essentially the Mie scattering. In usual conditions, the Rayleigh scattering associated with molecular level inhomogeneity is inevitable. The contribution from this factor of light attenuation ($\beta_{Rayleigh}$) is defined by the first item in eq.(4). Precision measurements of loss due to Rayleigh scattering in high-purity polymer fibers [8] at wavelength $\lambda = 633$ nm yield for polystyrene value 55, and for PMMA, 13 dB/km. The considerable difference in the measured values of loss in these polymers, according to [8], accounts for a great anisotropic scattering in the polystyrene matrix caused by presence of bulky phenyl group in its structure.

For PS containing 97.5 % PST, 1.5 % *p*-TP, 0.02 % POPOP and 1 % ST, the absorption loss caused by the polymer matrix itself as well as the loss caused by luminescent additives (1.5 % *p*-TP and 0.02 % POPOP) and sometimes the present residual monomer styrene (~1 % ST) have been estimated using extrapolation of intrinsic electron absorption "tails" of PS components to long-wavelength region under the Gauss law. Using the data on light scattering in polystyrene at $\lambda = 633$ nm [8], loss in PS due to scattering for other wavelengths have been calculated using eq.(4). The plots corresponding to components of loss in PS due to UV absorption and Rayleigh scattering over the range 380 to 480 nm are shown in Fig. 1.

It is seen from Fig. 1 and Table 1, PS with the "optimum" light transmission characteristics in the visible band should have the most part of optical loss peculiar to them in components $\beta_{Rayleigh}$ and β_{UV}. According to the calculations, a limit opti-

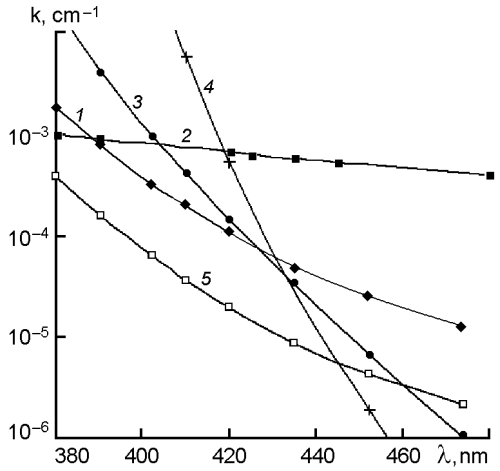

Fig. 1. Indices of light attenuation because of UV-absorption and Rayleigh scattering in PS, containing 97.5 % PST (*1*), scattering and absorption in PST (*2*); ST (*3*); *p*-TP (*4*); and POPOP (*5*) present in the above-mentioned amounts.

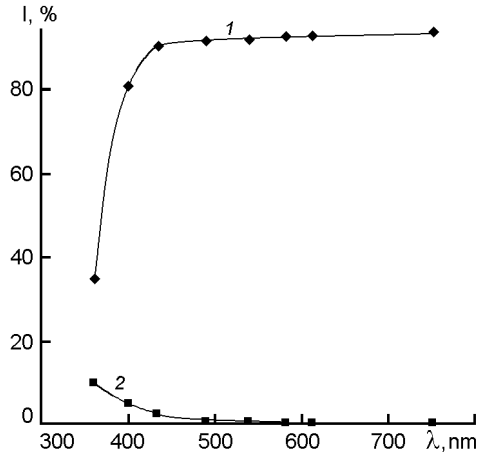

Fig. 2. Integrated PS light transmission (*1*) and the incident light energy loss due to scattering (*2*).

cal loss level in the polystyrene matrix of scintillator at the wavelength of emission maximum (λ = 420 nm) is about 400 dB/km (BAL≈10 m).

Fig. 2 presents the integrated light transmission data for one PS sample of the first series. Besides of the integrated light transmission (curve 1), the light flux fraction dI deflected from the initial direction due to scattering (curve 2) is shown.

The optical loss due to scattering was estimated from the attenuation index β_s

$$\beta_S = 4.34 \cdot \tau \cdot 10^5 (\text{dB/km}). \qquad (5)$$

Here, τ — is the medium turbidity (extinction coefficient in cm^{-1}). Since the turbidity is a measure of light attenuation at passing through medium, it is equivalent to the total scattered radiation, i.e. the extinction coefficient τ and experimentally measured dI are interrelated by a relation

$$\tau = -dI/(I_s \cdot dx). \qquad (6)$$

For resulting optical path x, the following expression is valid:

$$\ln(I_0/I_s) = \tau \cdot x, \qquad (7)$$

where I_0 is the initial light flux intensity; dI, the incident light energy loss due to scattering; I_s, intensity of scattered light transmission. At an absolute measurement method using sphere photometer, the scattered light transmission intensity I_s is defined by the difference between intensities of the incident light and the light flux fraction deflected due to scattering from its initial direction, $I_s = I_0 - dI$. Having determined I_s, it is possible to calculate the extinction coefficient τ from eq. (7) and then the optical loss β_s from eq. (5). For all prepared PS samples (5 samples of each series) the measurements of integrated light transmission and the scattering-deflected light flux fraction have been made using the spectrophotometer. After data processing, profiles of spectral loss $\beta_s(\lambda)$ have been received for PS samples of both series (Fig. 3).

To estimate the Rayleigh and Mie scattering contributions to total light scattering, the spectral loss $\beta_s(\lambda)$ was analyzed using the approximating function from eq.(4). The $\beta_s(\lambda)$ values measured for PS samples of the 1st and 2nd series, transformed from linear scale λ to scale λ^{-4} are shown in Fig. 4. The straight lines calculated by the least square method are shown, too.

To determine the Mie scattering contribution to the total light scattering, of extrapolation the spectral dependence $\beta_s(\lambda^{-4})$ was extrapolated to the long-wavelength spectral region. The line segment cut off on an ordinates axis yields the value of parameter B describing the scattering loss on large particles. From the plot slope, the parameter A was determined and then, the contribution to optical loss due to Rayleigh scattering was calculated for a selected λ value according to eq.(4). As is seen from the Figure, the spectral dependences of

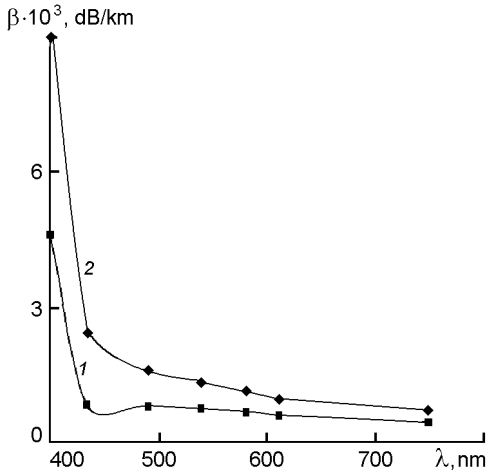

Fig. 3. Spectral losses due to light scattering in samples PS of first (*1*) and the second (*2*) series.

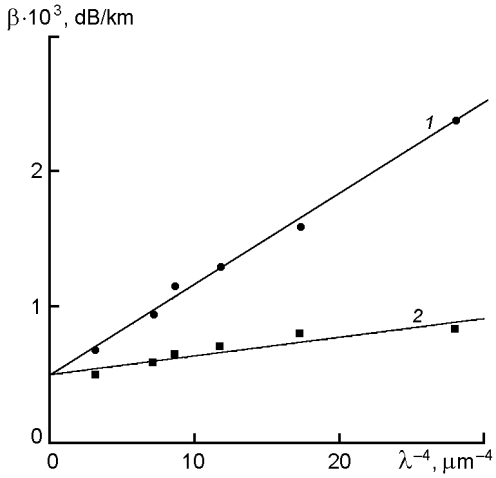

Fig. 4. Spectral dependences of light scattering loss β_s (λ^{-4}) in PS samples of first (*1*) and the second (*2*) series of samples.

light scattering for all PS samples are well described by the selected function (eq.(4).

When comparing two plots in Fig. 4, different slopes of approximating straight lines at essentially the same intersection point with axis β is seen. In fact, the parameter *A*, determined from slopes of these straight lines in Fig. 4, has been found to be 67 dB/km·μm^{-4} for samples of 1-st series and 14 dB/km·μm^{-4} for 2-nd one. Accordingly, the calculated Rayleigh loss for λ near the emission maximum of PS (λ = 434 nm) amounts 1876 dB/km for the first series of samples and 350 dB/km for second one. The parameter *B* defined by cutoff segment on the β axis in Fig. 4 is about 450 dB/km.

The results of measurements and consequent calculations of separate scattering components are shown in Table 2. The determination of total optical loss (β_{total}) was based on measurements of bulk attenuation length in cylindrical PS samples using a laser arrangement. Average BAL value for the first series samples was 150, and for second 350 cm. In Table 2, presented are also the total optical loss β_{total} for PS samples of the both series and the optical loss due to scattering (β_s), determined by the photometer at λ = 434 nm, and values of individual contributions to optical loss from Rayleigh scattering ($\beta_{Rayleigh.}$), and Mie scattering (β_{Mie}). The absorptive loss (β_{UV}), as calculated using eq.(1) and eq.(4) are given, too.

It is seen from Table 2, PS transparence is defined to a greater extent by the level of loss caused by light scattering than by absorptive loss. So, for 1-st series of samples, losses due to scattering have made more than 80 % of the total loss, and for 2-nd, 65 %. However, of the greatest interest are the results on change of separate components of light scattering loss after change of the PS polymerization mode. Changes in β_{Mie} have not exceeded 10 %, and Rayleigh loss $\beta_{Rayleigh}$ have decreased almost by a factor of 5.

Regarding identical requirements of raw material preparation and the same purity degree of the equipment used (the polymerizer, ampoules, room, etc.), the concentration of large scattering centers (a dust, foreign substances and so on) and absorbing impurities in PS can be assumed to be equal in both cases. Such assumption can explain

Table 2. Optical loss in PS samples prepared at various high-temperature annealing regimes of polymerization

PS	Polymerization conditions			Optical loss, β (dB/km)				
	T_{max}, °C	Exposure time at T_{max}, h	Exposure time at T_g, h	β_{total}	β_s	$\beta_{Rayleigh}$	β_{Mie}	β_{UV}
1	160	36	10	2870	2350	1850	500	520
2	170	48	15	1270	830	380	450	400

the fact of an invariance of the absorptive loss and loss due to Mie scattering. An unexpectedly strong influence of PS polymerization conditions on Rayleigh loss component can testify for its structural nature. In fact, according to [10, 11], the arrangement of monomer units in a macromolecule and the spatial arrangement of polymer chains are defined by the final polymerization stage. An insufficiently high annealing temperature and its insufficient duration result in the "frozen" strains of macromolecules in the polymer. Really, during polymerization of the polymer block (because of inevitable temperature gradients), high internal stresses (cramping, shift, stretching) arise. These tensions relax at different rates and their distribution through the whole volume is extremely inhomogeneous. The macromolecules strained under such stresses will form a system with high local inhomogeneity [12, 13]. The clots and rarefications of substance will arise in the micro regions of the polymer matrix. On the contrary, a prolonged annealing and high enough temperature $T_{max} > T_g$, the density fluctuations arising in the polymer block will relax to a homogeneous state and the scattering loss will be considerably dropped. As is seen from results of this work, even a slight T_{max} increase (by 10°C) and increase of the exposure time at T_{max} by 12 h and at T_g by 5 h as well as the slowered cooling of the block has allowed to halve the optical loss level in PS.

So in this work the evaluation of individual contributions of various mechanisms of light attenuation in polymer matrix is made and it is shown that the Rayleigh scattering is a dominant component. It is experimentally determined that by variation of conditions of carrying out of high-temperature annealing in the making polymerization of large scintillation block one may to mprove a local homogeneity of PS greatly and to raise its optical transparency.

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Розсіювання світла у пластмасовому сцинтиляторі

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Проведено чисельний аналіз оптичних втрат у пластмасовому сцинтиляторі (ПС) стандартної сполуки (98.5 % PST + 1.5 % *p*-TP + 0.02 % POPOP). Експериментально досліджено властивості розсіювання ПС, отриманих двома різними режимами полімеризації великогабаритного блоку. Представлено результати вимірювання інтегрального світлорозсіювання та об'ємної довжини ослаблення світла у ПС. На основі спрощеної моделі оцінено внески окремих компонентів світлорозсіювання — релеєвського розсіювання та розсіювання Мі. Зменшення релеєвської складової втрат з 1850 до 380 дб/км після додаткового відпалу пояснюється зменшенням локальної гетерогенності полімерної матриці ПС.