

ORIGINAL ARTICLE

Synthesis and Characterization of a Polystyrene-based Scintillator for Gamma Detection

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ABSTRACT – This study aimed to create and examine plastic scintillators made from a polystyrene matrix, which are widely used in radiation detection due to their favorable properties, such as rapid decay time, low cost, resistance to moisture, and ease of fabrication. The scintillators were doped with p-terphenyl (PTP) and 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP) using an injection method with an extruder machine. The materials were characterized using various techniques. Fourier transform infrared spectroscopy (FTIR) revealed the presence of aromatic chains, which are essential for the scintillation process. Differential scanning calorimetry (DSC) analysis showed stable thermal properties with a glass transition temperature of approximately 100°C. Scanning electron microscopy (SEM) showed that the surface of the polymer is amorphous with small bumps and protrusions likely caused by the PTP and POPOP dopants. The optical evaluation indicated that the sample could absorb UV photons up to 340 nm and emit photons in the wavelength range of 400–500 nm with a peak at 421 nm. Gamma spectra analysis indicated that the plastic scintillators performed well in gamma detection and could be used in a radiation portal monitor (RPM).

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INTRODUCTION

Plastic scintillators are detectors that can be used to detect gamma rays. Gamma rays are a type of high-energy radiation that can come from natural sources like cosmic rays or radioactive materials or from man-made sources like nuclear power plants, medical imaging devices, and radiation therapy equipment [1]–[3]. Plastic scintillators have become more popular for gamma-ray detection because they have many advantages. Plastic scintillators are lightweight, durable, relatively inexpensive, and can detect gamma rays with energies ranging from a few keV to several MeV [4], [5]. It is also easily molded into different shapes and sizes, making them useful for various applications [6], [7].

The most common method for preparing plastic scintillators is the thermal polymerization of a solution containing a liquid monomer. The liquid styrene base matrix is used, with 2,5-diphenyloxazole (PPO) as the primary dopant and 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP) as the wavelength shifter. Dopant molecules are formed by replacing hydrogen atoms in an aromatic molecule's phenyl-ring with one or more phenyl, oxazole, or other groups [8]–[10].

The emission spectrum of POPOP is crucial to its use as a wavelength shifter in plastic scintillators because it determines the spectral overlap with the primary scintillator material's emission spectrum. Polystyrene is typically used as the primary scintillator material doped with fluorescent dyes such as p-terphenyl (PTP) [11]. Optimizing the emission spectra of the wavelength shifter and the primary scintillator improves the overall detection efficiency and energy resolution of the scintillator [12].

In this study, plastic scintillators were made using a polystyrene matrix with an injection method using an extruder machine. PTP was used as the primary dopant, and POPOP was used as the secondary dopant. The thermal properties of the material were evaluated with differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) was used to analyze the functional groups that make up the polystyrene. The scanning electron microscope (SEM) was used to examine the morphology of the polystyrene (PS) scintillator sample. The optical characterization of the scintillator was conducted using a UV-Vis spectrophotometer and a fluorescence spectrophotometer. Gamma-ray detection characterization was analyzed using a module made up of a photomultiplier tube (PMT) and a multichannel analyzer (MCA) using gamma cesium 137 sources. The results of this study are expected to be valuable for making large plastic scintillators for use in radiation portal monitors (RPM).

EXPERIMENTAL METHOD

Sample Preparation

The study utilized a commercial grade of general-purpose polystyrene (PS) obtained from Trinseo Materials Indonesia, along with primary and secondary dopants, p-terphenyl (PTP), and 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP), respectively, purchased from Sigma-Aldrich. A commercial plastic scintillator from Epic Crystal in China was also used.

Table 1 shows six batches of PS-based scintillator samples, with different dopant compositions. The samples were created using an injection method with a screw extruder machine, as shown in schematic Figure 1, following a similar process as a preliminary study [13]. The material was melted in three heating stages, with the pellets melting at around 220°C and then being pushed into a mold and cooled. The resulting plastic scintillator was in the form of a plate-sized 65 × 50 × 3 mm.

Table 1. The ratio of dopants on plastic scintillators

Sample	PTP (%wt)	POPOP (%wt)
PS01	1.0	0.01
PS02	1.0	0.03
PS03	1.0	0.05
PS04	1.5	0.01
PS05	1.5	0.03
PS06	1.5	0.05

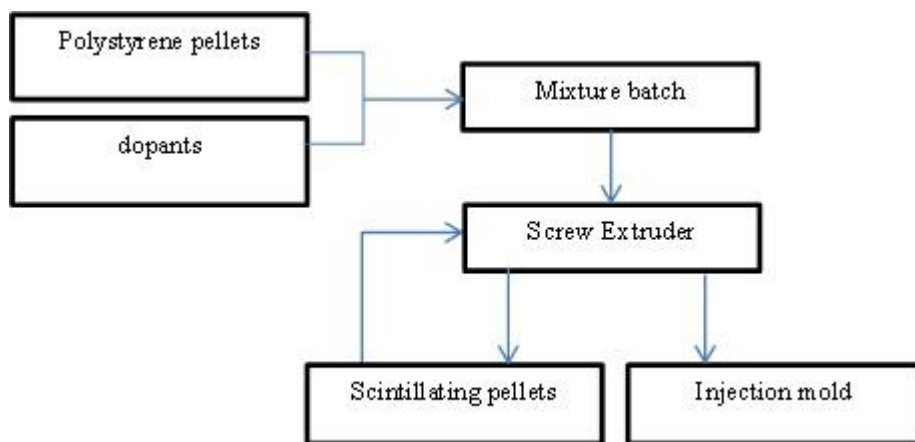


Figure 1. Schematic process of PS-based scintillator fabrication [13]

Characterization

To analyze the functional groups present in the PS-based scintillator, Fourier transform infrared (FTIR) analysis was performed. The analysis was conducted using a spectrometer (Bruker-Tensor II) in the 500–4000 cm^{-1} frequency range with the reflectance technique and a KBr prism. Scanning electron microscopy (SEM) was used to evaluate the morphology of the PS-based scintillator sample, and high-vacuum backscattered electron images were obtained using polished samples at 10kV. Differential scanning calorimetry (DSC) was performed using a simultaneous thermal analyzer (STA) Labsys, where samples of approximately 25 mg were placed in aluminum cartridges in a nitrogen flow of 20 mL min^{-1} . In the first scan, samples were heated stepwise to 300°C at a rate of 10 $^{\circ}\text{C min}^{-1}$.

The absorption spectra of the scintillator sample were measured using the Hitachi UH5300 UV-Vis spectrophotometer to determine its absorbance in the ultraviolet (UV) region (200–350 nm) and visible light region (350–800 nm). The fluorescence spectrophotometer fluoromax-Horiba was used to evaluate the emission spectra of PTP and POPOP dissolved in a PS matrix. The measurement was performed over a wavelength range of 350 to 600 nm.

Gamma spectra analysis was conducted using the gamma detector module, following the experimental apparatus scheme shown in Figure 2, which included (1) a gamma source ^{137}Cs (4.86 μCi), (2) a scintillator sample placed in an aluminum

tube, (3) a Hamamatsu R878 PMT (also in an aluminum tube), (4) a Spectacular MCA, and data acquisition by (5) the personal computer [13]. The gamma source was measured at 2 cm perpendicular to the center photomultiplier tube (PMT) detector setup with a scintillator sample. Each measurement was repeated three times for 300 seconds. This analysis determined the number of gamma photon counts passing through the scintillator and the Compton spectra resulting from the interaction of photons and scintillator material.

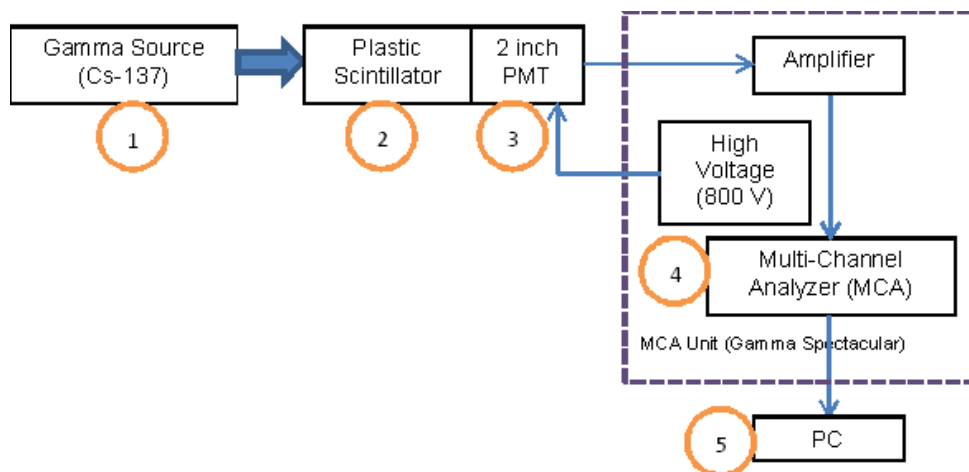


Figure 2. Schematic for gamma spectra evaluation [13]

RESULTS AND DISCUSSION

Figure 3 shows a 3 mm thin plate polystyrene (PS)-based scintillator in which p-terphenyl (PTP) and 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP) as dopants have been dissolved. For measuring the gamma spectra, the prepared plastic scintillator was shaped rounds following the photomultiplier tube (PMT) shape with a diameter of 50 mm.

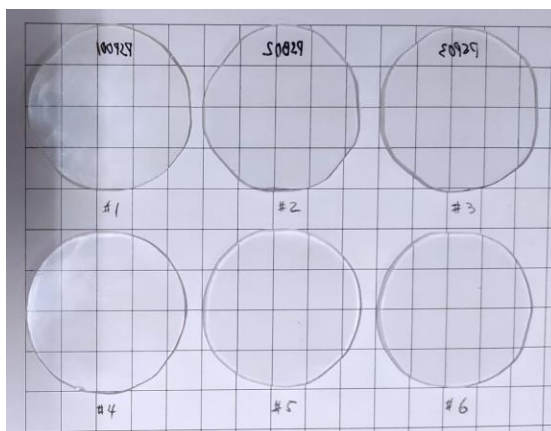


Figure 3. Photograph of scintillator sample $\text{\O} 50\text{mm} \times 3\text{mm}$

IR spectra

As depicted in Figure 4 (a), PS has specific infrared (IR) bands in the range of $3050\text{--}3020\text{ cm}^{-1}$, corresponding to the stretching vibration of aromatic C-H bonds. The absorption band at 1601 cm^{-1} corresponds to the stretching vibration of the C=C bond in the aromatic ring. The bending vibration of the aromatic C=C bond can be observed at 1492 cm^{-1} , while the CH_2 bending vibrations appear as two bands at 1450 cm^{-1} (symmetric) and 1450 cm^{-1} (asymmetric). The bending vibration of the aromatic C-H bond can be observed at $1200\text{--}1000\text{ cm}^{-1}$. Finally, the out-of-plane bending vibration of the aromatic C-H bond appears as a band at 698 cm^{-1} , in accordance with the reference literature [14], [15].

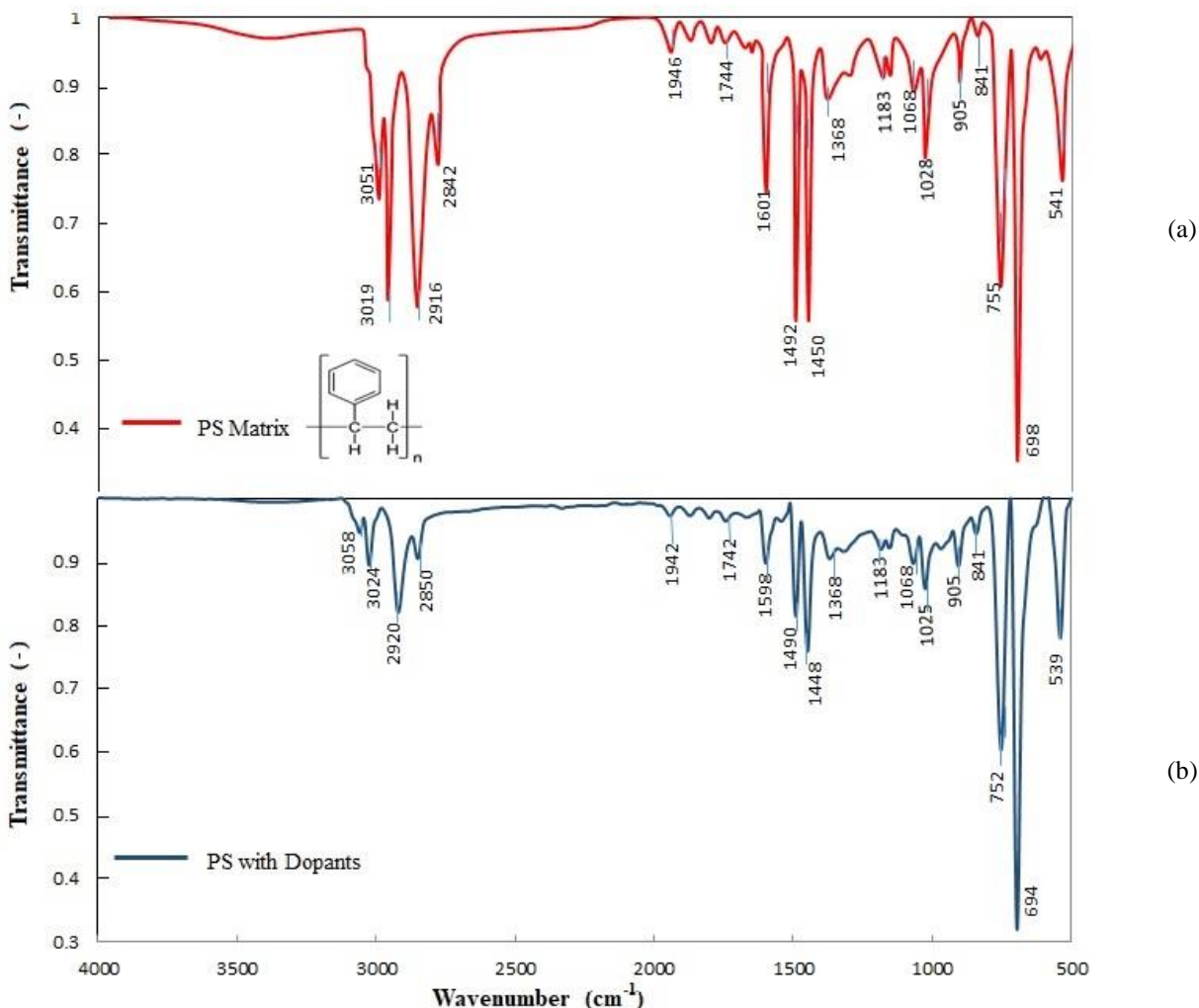


Figure 4. FTIR spectra of (a) PS matrix and (b) PS-based scintillator sample

The FTIR results for the PS-based sample (PS02), as shown in Figure 4 (b), reveal that the absorbance peaks are spread over a wide range of spectra scales. The first peak at 3058 cm⁻¹ indicates the aromatic C-H stretching vibration, while the second peak at 2920 cm⁻¹ is due to the presence of impurities in the sample. The following three peaks at 1598, 1490, and 1448 cm⁻¹ correspond to the aromatic C-H bond stretching vibration. The peaks at 1183, 1025, 752, and 694 cm⁻¹ correspond to the aromatic C-H deformation vibration. The IR spectra of the PS-based scintillator sample (with dopants) in Figure 4 (b) demonstrate that the absorption positions are nearly identical to those of the PS raw material. This is because the dopant does not undergo chemical reactions but is merely dispersed within the PS matrix. This observation applies to all samples. The IR spectra characterization supports the presence of aromatic chains in the samples, as the dominant fluorescence phenomenon is influenced by these aromatic molecules. This finding is further supported by the literature [10]. Polystyrene alone is unable to convert ionizing energy into optical photons effectively due to its short average free path. However, the addition of a 1% aromatic dopant can enhance its performance by increasing the attenuation length and light output [16].

DSC curve and SEM

The differential scanning calorimetry (DSC) curve of the PS-based sample (PS02) shown in Figure 5 (a) indicates a broad glass transition region rather than a sharp melting peak [17]. The glass transition temperature (T_g) for this PS-based sample is around 90–140°C, indicating that the thermal characteristics of the sample are nearly identical to those of the matrix, which is atactic polystyrene. This observation holds true for all concentration variations of the samples. Atactic polystyrene is a random arrangement of the styrene monomer units, where the phenyl groups of the monomers are arranged randomly along the polymer chain. Due to this irregular arrangement, atactic polystyrene has lower melting and glass

transition temperatures and is more amorphous [18]. In contrast, the melting point of crystal-type polystyrene, represented by an endothermic heat flow pulse, appears at a temperature of 270°C for syndiotactic as a reference [14].

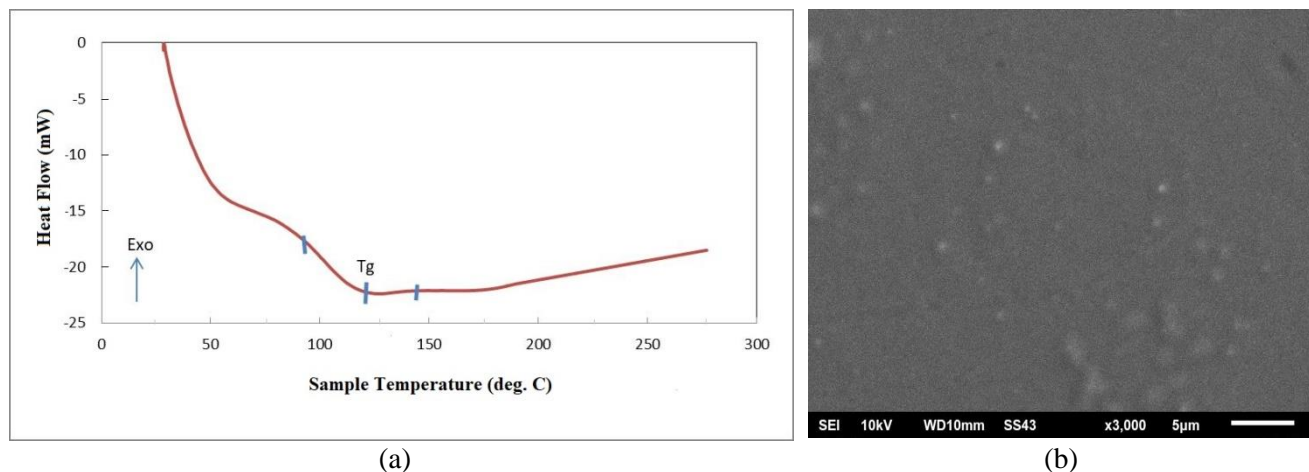


Figure 5. (a) DSC curve and (b) SEM photograph of PS-based scintillator

The surface morphology of amorphous polystyrene can be observed using scanning electron microscopy (SEM). Since amorphous polymers have a disordered, random arrangement of molecular chains, their surface morphology can reflect this [19]. As shown in Figure 5 (b), the surface of the amorphous PS-based scintillator sample appears smooth with a uniform texture that lacks any distinct patterns or features. However, the presence of PTP and POPOP as dopants can result in small bumps, protrusions, or rougher areas on the surface. The results of the DSC and SEM analyses, depicted in Figures 5 (a) and Figure 5 (b), respectively, corroborate the findings of the IR spectra analysis, indicating that the addition of the dopant does not result in a chemical reaction but rather the dispersion of the dopant within the PS matrix.

Emission and absorption spectra

In Figure 6, increasing the PTP concentration from 1% to 1.5% wt did not show a significant increase in intensity, and this confirmed the report that became the reference for this study which stated that 1% primary dopant was sufficient to make PS-based scintillator [2]. Although the concentration of POPOP increases, the emission spectra do not show a consistent trend, and the maximum intensity is obtained at 0.03 wt% POPOP as on sample PS02. In all samples, emission was observed in 400–500 nm at a peak wavelength of 421 nm, attributed to the influence of the wavelength shifters POPOP, which emitted at that wavelength [20]. For comparison, a commercial plastic scintillator from Epic produces an emission spectrum with a peak wavelength of 415 nm [21].

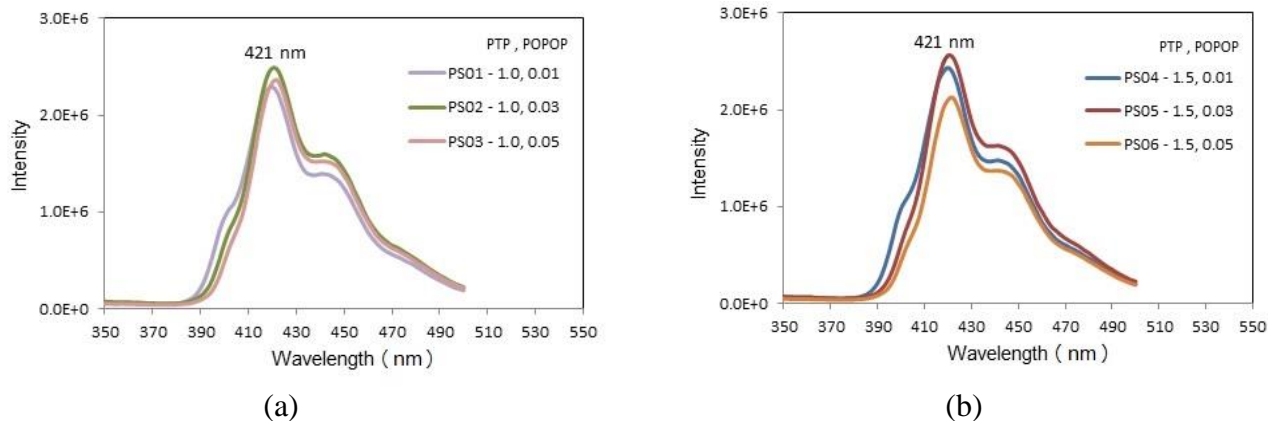


Figure 6. Emission spectra of scintillator samples with (a) PTP 1% wt and (b) PTP 1.5% wt

In a scintillator material, primary dopants and wavelength shifters (WLS) play important roles in converting ionizing radiation into detectable light. Primary dopants, such as PTP, are molecules added to the scintillator material to enhance its light yield and improve energy transfer efficiency between the scintillator's excited state and the primary dopant. POPOP is

a common WLS used in organic scintillators because it absorbs light in the ultraviolet (UV) range and emits light in the blue-violet range, which is closer to the maximum sensitivity of many photodetectors [10].

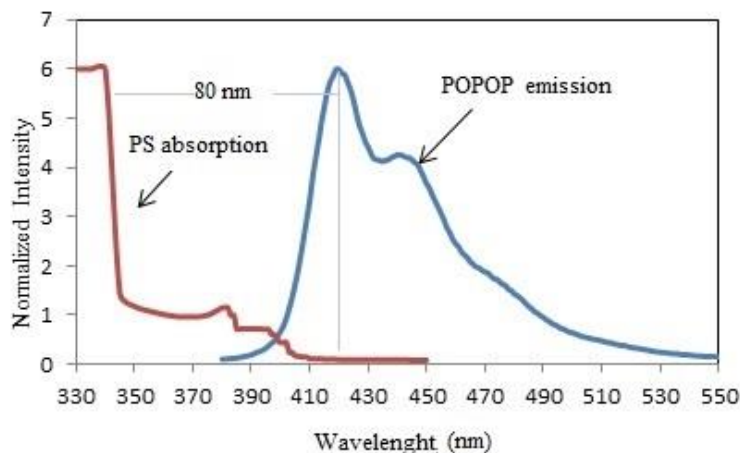


Figure 7. Stokes shift of PS-based scintillator sample

The Stokes shift is a phenomenon commonly observed in fluorescence spectroscopy, where the emission wavelength of fluorescent material is at a longer wavelength than the excitation wavelength. In other words, the energy of the emitted photons is lower than that of the absorbed photons. Figure 7 shows the results of the absorption spectra combined with the emission spectra. The result indicates that the sample absorbs UV photons until 340 nm and emitted photons at a wavelength range of 400–500 nm with a peak at 421 nm, which creates enough space for Stokes shifts. The Stokes shift distance of around 80 nm is sufficient to reduce the spectral overlap area, which also prevents the re-absorption of photons emitted by dopants in the sample. The Stokes shift can vary depending on the specific material and the nature of the transitions involved, but it is typically in the range of tens to hundreds of nanometers [22]. The Stokes shift is an important parameter for the design and optimization of luminescent materials, as it affects the light output of the scintillator [23].

Gamma spectra

Compton scattering becomes the dominant interaction when high-energy photons of gamma rays collide with the organic matter. In this process, the photon collides with an electron in the scintillator material, causing it to scatter at an angle and lose some energy. The scattered photon then moves in a new direction with lower energy and a longer wavelength than the original photon [24], [25]. This process can occur multiple times, with the scattered photons producing scintillation light that is detected and measured.

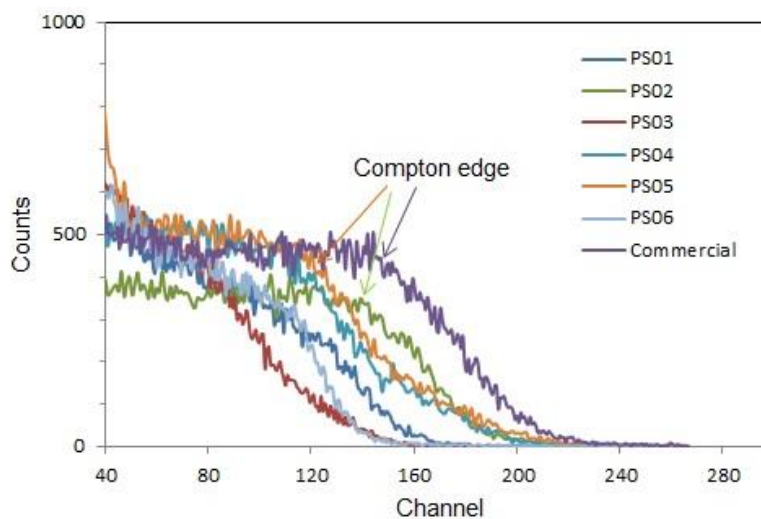


Figure 8. The spectra of PS-based scintillators obtained by Cesium 137 compared to the commercial plastic scintillator

The graph shown in Figure 8 indicates that the Compton spectra shape of the sample is similar to that of the commercial scintillator. However, the Compton edge of the PS02 and PS05 scintillators falls in channels 135 and 122, respectively, while the commercial scintillator falls in channel 147. This suggests that the scintillator samples detect lower energy levels compared to the commercial scintillator. Based on the position of the Compton edge, it can be inferred that the scintillator samples can detect energy levels between 60% to 89% relative to commercial plastics. Moreover, the PS02 sample, which has a PTP concentration of 1% and POPOP wt of 0.03%, emits a strong light intensity, resulting in a relatively higher energy output (channel) than the other samples.

CONCLUSION

Plastic scintillators are materials used for detecting ionizing radiation. In this study, plastic scintillators were made using a polystyrene (PS) matrix with an injection method. P-terphenyl (PTP) and 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP) were used as the primary and secondary dopants, respectively. The Fourier transform infrared spectroscopy (FTIR) analysis revealed the presence of aromatic chains, which play a crucial role in the scintillation process by affecting the efficiency of converting high-energy radiation into a visible light signal. In the characterization of the IR spectra, differential scanning calorimetry (DSC), and scanning electron microscope (SEM), it is evident that the character of the sample (PS + dopants) is predominantly determined by the PS matrix. The added aromatic dopants do not undergo chemical reactions but are only dispersed within the matrix. Any chemical changes would be reflected in the FTIR and DSC analyses through observable alterations in IR absorption. The dispersion of the dopants within the PS matrix can be observed from the surface morphology, where distinct molecular spots are still visible under SEM. Based on the optical evaluation, the sample was found to absorb UV photons up to 340 nm and emit photons in the wavelength range of 400–500 nm, with a peak at 421 nm. This provides enough space for Stokes shifts, with a distance of 80 nm, which effectively reduces the spectral overlap and prevents the re-absorption of photons emitted by dopants in the sample. Gamma spectra analysis showed that the plastic scintillators had good gamma detection performance. The PS-based scintillator sample with a 1%wt PTP and 0.03%wt POPOP composition had the best performance. Based on the position of the Compton edge, it can be inferred that the sample is capable of detecting energy levels until 89% relative to commercial plastics. In conclusion, the plastic scintillators produced in this study using the injection method have good potential for radiation portal monitors (RPM) use. The combination of PTP and POPOP as dopants in the polystyrene matrix has shown promising results in terms of gamma detection performance.

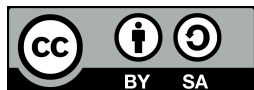
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