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Effect of PPO and POPOP activators on the scintillation performance of polystyrene-based scintillator

LIZBETH ALEX[1], RAJESH PAULRAJ[1,*], MOHIT TYAGI[2]
[1]Centre for Crystal Growth, Department of Physics, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, 603110, Tamilnadu, India.
[2]Crystal Technology Section, Technical Physics Division, Bhabha Atomic Research Centre, 400085, Mumbai, India

In this paper, a polystyrene-based plastic scintillator of 4.5 cm diameter and 2.5 cm length doped with 2,5-diphenyloxazole (PPO) and 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP) was synthesized using thermal polymerization reaction carried out at 120°C. Optical transmittance was measured by Perkin Elmer UV-Vis NIR spectrophotometer in the wavelength region of 200-900 nm. The maximum peak of the emission spectra was obtained at 420 nm using Fluorescence spectrophotometer. The radioluminescence measurement of the synthesized sample exhibited a very strong emission band in the wavelength range from 400 to 600 nm, with a peak maximum at 420 nm for different voltages. The fabricated scintillator possessed a linear variation of intensity with respect to the voltage. The fast scintillation decay time of the fabricated plastic scintillator was investigated using γ-rays from ^{137}Cs radiation source. Pulse height spectra were recorded using different gamma ray sources such as ^{137}Cs, ^{60}Co and ^{22}Na. The results showed that the above-mentioned material is a promising and a potential candidate for scintillation and neutron detection applications.

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1. Introduction

The growing needs of modern medical imaging and high energy physics have made scintillators a widely used detectors for spectroscopy of energetic photons (such as X-rays and gamma rays) as well as neutrons. Thus, the research and development of new scintillator materials is a keen interest for many researchers for a while, due to its applications in different fields ranging from homeland security to medical, in material analysis and nuclear energy production [1]. The solutions for low-cost radiation detection for gamma ray spectroscopy have brought organic scintillators to the forefront. Due to fast response time, fair efficiency, relatively low cost as compared to the inorganic scintillators and the pulse shape discrimination capability, organic scintillators took a remarkable position in the field of radiation detection.

Now a days, plastic scintillators have also been extensively used in fast neutron diagnostics because of their availability in large sizes at low cost and fast scintillation decay. In response to this, they are also useful in the detection of high energy X-rays. They are being investigated as a first-line of detectors for ionizing radiation (i.e. gamma and neutron) due to their low cost, mass reproducibility, ease of handling and installation [2]. Thin plastic scintillation detectors are very useful in the field of pulsed fission neutron flux measurements because of its good neutron-to-gamma sensitivity ratio and the relative flat energy response [3]. They are mainly described by the fast response (i.e., short decay time) which is necessary for powerful radiation flux measurements [4]. The choice of the detector will become extremely important in the near future due to the cheapness of plastic scintillators and the necessity for some countries to cover at best their borders with radiation portal monitors [5].

Plastic scintillators consist of an aromatic plastic base, which has a benzene ring attached to its polymer backbone. This is essential for the fluorescence process of absorption and emission to occur in these scintillators. Due to its low fluorescent yield, less transparency to its own emission and the spectral response is too short to match the emission wavelength of the photodetectors, the plastic cannot itself act as a scintillator. The addition of primary fluors makes it an efficient scintillator. A non-radiative energy transfer occurs from the plastic base to the primary fluor, with emission usually in the UV region. Additional fluorescent compound known as wavelength shifter or spectrum shifter is added to increase the attenuation length. At this concentration, a radiative energy transfer (Förster energy exchange) occurs between the primary fluor and the spectrum shifter, with emission of the shifter typically in the blue to blue-green region (visible region) and also maximizes the scintillation yield of the scintillator [6]. So it is very important to eliminate impurities during the fabrication and use of organic scintillators, which degrade the light output by quenching mechanisms for the excitation energy [7]. Due to low density and low atomic number elements, the detection efficiency of plastic scintillator is comparatively low. This problem can be solved by enhancing the detection efficiency by incorporating dopants into the plastic scintillators [8]. Reduction of the effect of self-absorption, prevention of efficiency loss during energy transfer and increasing the wavelength of light output mainly depends on the nature and concentration of the dopants incorporated [9].

Polystyrene based scintillators (PSt) attracted the main attention of many researchers due to their high light yield, low decay time, high resistance to radiation, temperature and moisture and low cost [10, 11]. The studies conducted by Nakamura et. al. showed that the light yield can be controlled by the fluor concentration [12]. It is reported by Zaitseva et. al. [13] that the maximum light output is obtained at relatively lower dye concentrations of about 1 wt% of 2,5-diphenyloxazole (PPO). The increasing of dye concentration above the optimum value can decrease the light output and also the fluorescence intensity due to the effect of concentration quenching [14]. The lifetime of the scintillation light increases with higher fluor concentrations due to radiation trapping (or self-absorption), i.e., the scintillation light emitted is absorbed and re-emitted again [8]. This leads to the slow response time of the scintillation detector.

In this study, we focused on the effect of primary fluor 2,5-diphenyloxazole (PPO) and the wavelength shifter 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP) on the scintillation performance of a polystyrene-based plastic scintillator. The addition of primary dopant 2,5-diphenyloxazole (PPO) in 1 wt. % and 0.05 wt. % of spectrum shifter1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP) to the weak fluorescent styrene polymer matrix increases the scintillator light output [15]. More optimizations done on the purification of the starting materials used and the synthesizing procedures can further improve the scintillation properties and efficiency of the plastic scintillators.

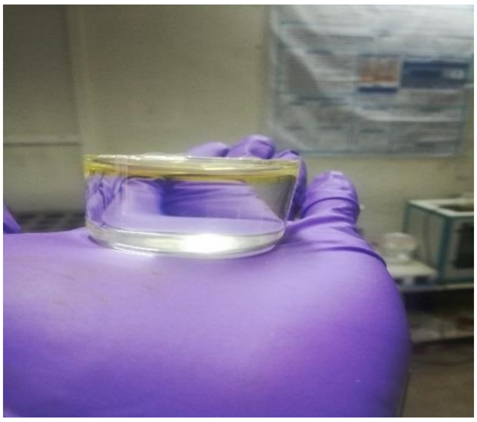
The emission wavelength, radioluminescence, scintillation decay time and pulse height spectra were analysed to explore the scintillation performance of the fabricated plastic scintillator.

2. Materials and methods

A polystyrene based plastic scintillator was fabricated through thermal polymerization reaction to analyse its scintillation properties. All the materials used in the synthesis of the plastic scintillator were purchased from Sigma Aldrich with a purity of 99.5%. The polymer matrix used is the styrene monomer. The primary fluor added is 2,5-diphenyloxazole (PPO) and the wavelength shifter is 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP), which shifts scintillation light from UV to a more convenient wavelength matching with the photodetectors. Vacuum distillation was performed to improve the purity of styrene monomer to remove the small particulates and inhibitors present.

The distilled styrene was then mixed with the primary fluor and the wavelength shifter. The mixture was poured into a 100 mL beaker and stirred using a magnetic stirrer constantly for 6 hours, and was afterwards stirred inside a water bath maintained at a constant temperature of 60°C. The homogeneously stirred solution was filtered by Grade 1 Whatman filter paper of pore size 11 μm and degassed through bubbling method with high purity nitrogen gas. The solution was then covered with aluminium foil in an air-free atmosphere provided by a glove box and placed inside a high temperature heater (muffle furnace) for the polymerization reaction to take place. The temperature was increased gradually from room temperature 30°C and maintained at 120°C for the thermal polymerization reaction to occur. After the polymerization reaction has ended, the temperature was gradually cooled down to the room temperature for about 60 hours [16]. This slow cooling is done to avoid the formation of air bubbles on the top and the bottom surfaces as a result of internal stress occurred inside the polystyrene material. Fig. 1(a) and (b) show the photographs of the polystyrene-based plastic scintillator fabricated using this method taken under white and UV illumination. The temperature profile of the synthesis process is depicted in Fig. 2.

The top and bottom surfaces of the fabricated plastic scintillator were cut by South Bay Tech-low speed Diamond wheel cutter to remove the air bubbles. The surfaces were then polished with 320-1500 grit sandpaper and the final polishing was done in high grade polishing sheet using alumina powder of 9 micron and with diamond paste (10-SFDC-EC) in velvet cloth. For protection, it is then wrapped inside a Teflon Tape, which acts as a reflector. The cut and polished samples are in Fig. 3 (a) and (b).



(a)

(b)

Fig. 1. Polystyrene based plastic scintillator under white (a) and UV illumination (b) (color online)

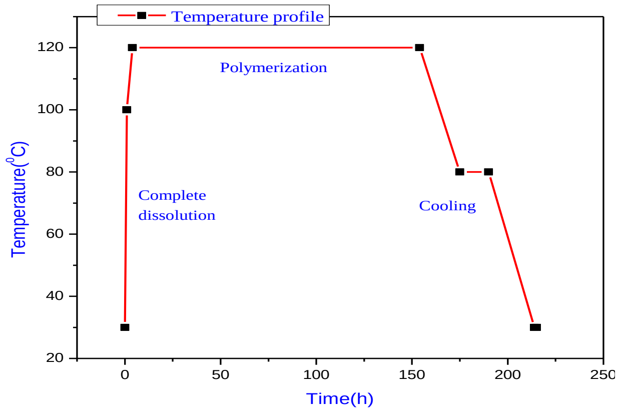
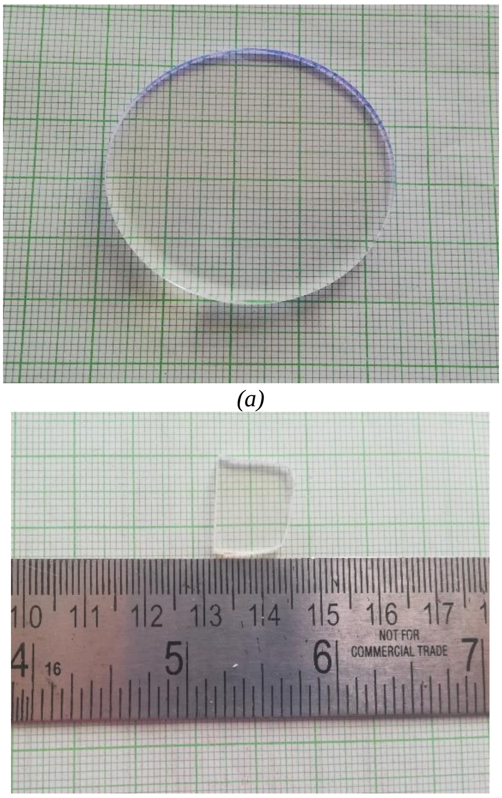


Fig. 2. Temperature profile of the synthesis process (color online)



(a)

(b)

Fig. 3. (a) Cut and polished scintillator, (b) cut and polished prepared sample (color online)

3. Characterisations

The plastic scintillator sample was cut into small pieces for further characterizations. The optical transmittance of the fabricated plastic scintillator of 2 mm thickness was studied using the Perkin Elmer UV-Vis NIR Spectrophotometer in the region of 200-900 nm. The Fourier Transform Infrared Spectroscopy (FTIR) spectrum was recorded by Bruker AXS FTIR spectrometer with ATR mode in the region from 600 to 3200 cm^{-1}. The X-ray induced luminescence spectra was measured at room temperature using Edinburg FLS- 980 Time-Resolved Fluorescence Spectrometer. A 450W Xe arc continuous lamp was used as the light source and a cooled PMT tube as the detector. Radioluminescence spectra was measured for different voltages ranging from 70 to 140 V by Avantes Spectrograph, using X-ray as the source. The scintillation decay time was measured using ^{137}Cs γ-source at room temperature. The sample was optically coupled using Hamamatsu H3378-50 PMT. A CAEN DT5790 digitizer was employed to convert the PMT analog output signal.

4. Results and discussion

4.1. UV-Vis NIR Study

The transmittance spectra of the polystyrene-based plastic scintillator doped with PPO and POPOP is shown in Fig. 4. The UV-Vis NIR study reveals that the scintillator possesses higher transmittance (90%) in the visible region with a cut-off wavelength at 390 nm, showing its good transparency and making it worth for scintillation applications. The absorptions in organic materials are due to the π-π* transition from the ground state to the excited energy state of individual molecules [7].

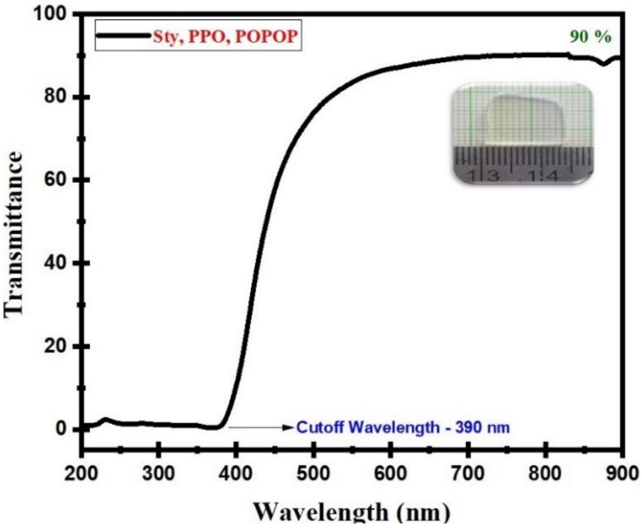


Fig. 4. Transmittance of the synthesized plastic scintillator (color online)

4.2. FTIR analysis

Fig. 5 shows the FT-IR spectrum of the fabricated polystyrene-based plastic scintillator. The peak at 3050 cm^{-1} indicates C-H stretching of benzene ring CH groups on the polystyrene side chain [17]. The peak at 3024 cm^{-1} is due to aromatic C-H stretching vibration [18]. The C-H asymmetric and symmetric stretching bands are shown at 2920 and 2848 cm^{-1} respectively [19]. The peak at 1598 cm^{-1} reflects the carbon-carbon stretching vibration in the aromatic ring [20]. The two peaks at 1494 and 1444 cm^{-1} correspond to aromatic C-H bond stretching vibration. The aromatic C-H deformation vibration is observed at 1020 cm^{-}

^{1} [19]. The out-of-plane (“oop”) aromatic C-H band appears at 903, 745 and 686 cm^{-1} [19,20].

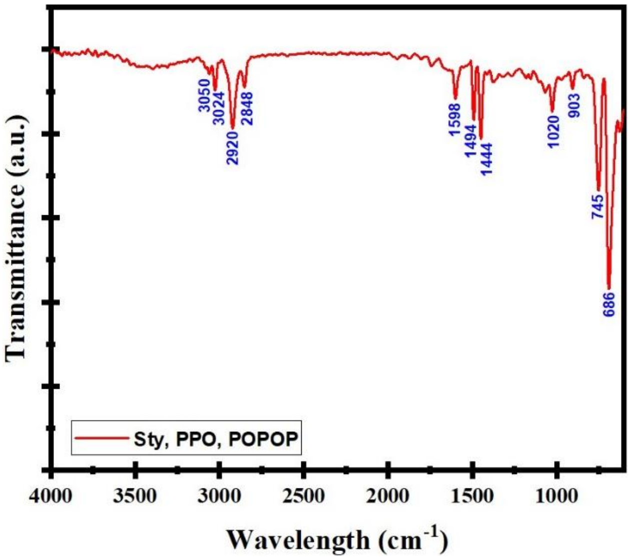


Fig. 5. FTIR spectrum of the fabricated scintillator (color online)

4.3. Emission wavelength

Considering the scintillation applications, there exist two main categories of emission mechanisms, one is intrinsic emission obtained from the characteristic transitions of the host compound itself such as self-trapped exciton and the other is extrinsic emission which is obtained from the dopants in the host matrix [21]. Here the emission spectrum of the as-synthesized sample comprises a strong luminescence band from 400 to 600 nm and centered at 420 nm, which strongly agrees with the reported data [16]. Fig. 6 shows the emission wavelength of the scintillator.

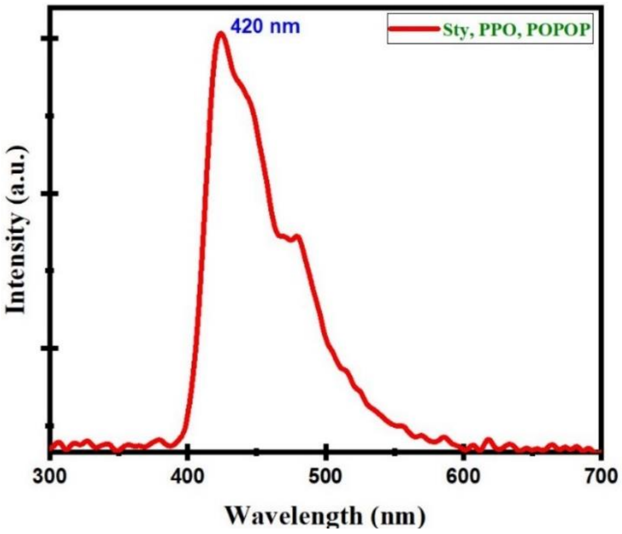


Fig. 6. Emission wavelength of the plastic scintillator (color online)

Thus, it can be understood that the fabricated scintillator shows the same properties compared to that of the commercial plastic scintillators available, since they have almost similar emission wavelength spectrum and also the spectral range matches well with the conventional photomultiplier tube efficient regions, which makes it suitable for scintillation detectors.

3.4. Radioluminescence

The radioluminescence spectra of the polystyrene based plastic scintillator doped with 2,5-diphenyloxazole (PPO) and 1,4-bis[2-(phenyloxazolyl)]-benzene (POPOP) was measured by Avantes Spectrograph, using X-ray as the source. The scintillation light was dispersed through a monochromator equipped with a holographic grating and then detected with a photomultiplier tube. Fig. 7 shows a typical radioluminescence spectra of a polystyrene based scintillator doped with PPO and POPOP for different voltages ranging from 70 to 140 V. The spectrum consists of a broad emission band between the regions of 400 and 600 nm, showing a maximum peak at 420 nm for all voltages.

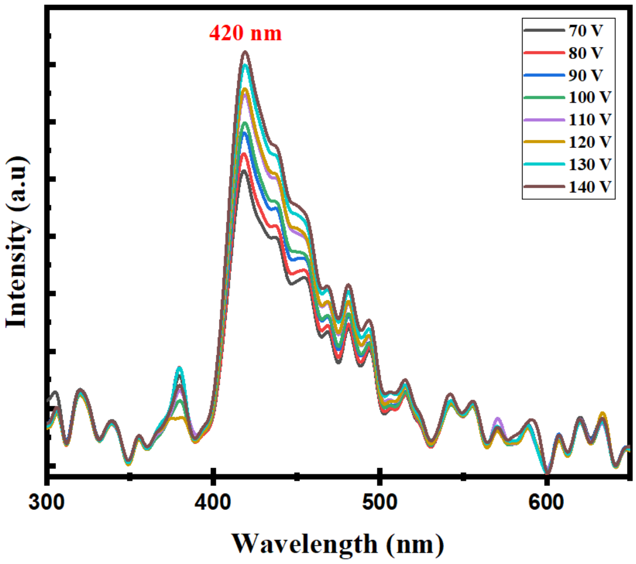


Fig. 7. Radioluminescence spectra for different voltages (color online)

The emission is associated to the de-excitation of the PPO and POPOP molecules in the plastic after excitation by the ionizing radiation. Depending on the variations in the concentrations of the primary fluor PPO and the wavelength shifter POPOP, the peak emission wavelength can be found in a range from 400-600 nm [8,22]. Due to the addition of fluorescent additives, the peak emission shifts towards the longer wavelengths. Absorption and re-emission processes occur multiple times, which results in an emission that is shifted towards the longer wavelength side. Higher the concentration of the additives, more efficient will be the energy transfer. Fig. 8 shows the linearity of integrated intensity with respect to different voltages.

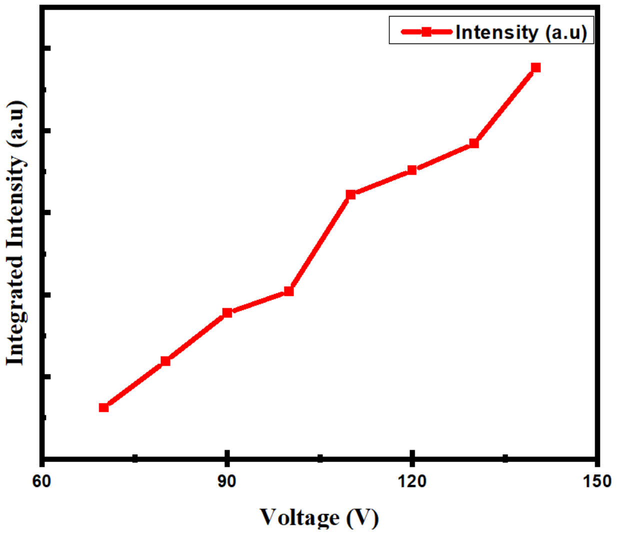


Fig. 8. Integrated intensity Vs voltage (color online)

4.5. Scintillation decay time

The experimental setup for studying the decay time characteristics of the polystyrene-based scintillator doped with PPO and POPOP is shown in the Fig. 9. The scintillator was coupled to a fast PMT (Hamamatsu H3378-50) using an optical grease. In all the measurements, both scintillator and PMT were exposed at room temperature. High voltage was provided by CAEN DT5790 digitizer for the PMT. To have good signal-to-noise ratio without reaching the maximum anode to cathode voltage, the voltage had been set at negative 1490 V. The decay time was measured using 1 GHz digital storage oscilloscope by measuring the direct anode pulse from a fast PMT (Hamamatsu H3378-50) which has risen time lesser than 1 ns. The signal distortions were avoided by directly feding fast PMT anode pulses to the digital oscilloscope. The digitized data was then stored in the memory and then sent to the host computer through an ethernet cable.

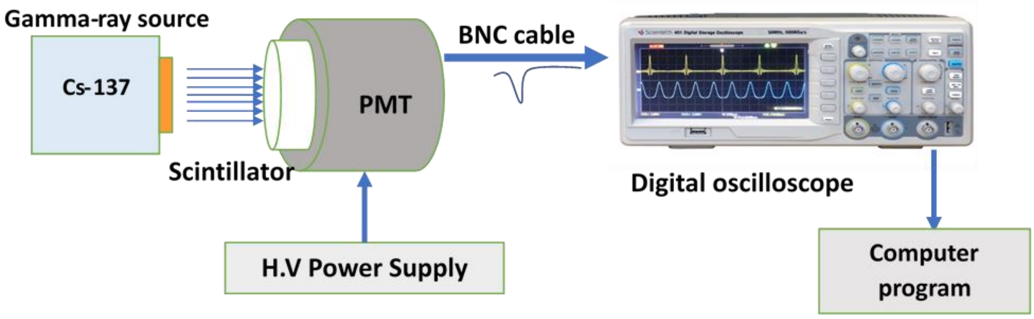


Fig. 9. The experimental setup for measuring the decay time of the plastic scintillator (color online)

The data was analysed using a custom script written in MATLAB. The first part of the script reads the waveform of each pulse from the digitized data and then store them in the form of a matrix with dimension N×M, where N gives the number of sampling points for each acquisition window and M is the number of acquired pulses. The datas of clipped or piled-up pulses were not used. The baseline was calculated separately for each pulse [23].

The monitoring channel shows a fast scintillation decay by recording the trailing edge of the time response waveform. Thus, it can be considered that this time response waveform displayed by the measurement channel is attenuated or constricted in the same minus exponential rule approximately [24].

$$I = A_0 + I_0 e^{(-\frac{t}{t1})} \tag{1}$$

where t_1 is the decay time of the scintillator. Therefore, it is found out that the decay constant estimated from the measurement channel by recording the trailing edge of the time response waveform is equivalent to the decay time of the fabricated scintillator [25]. The decay time was obtained by fitting the trailing edge of the waveform in accordance with the equation (1).

The decay time of the fabricated scintillator was evaluated to be 6 ns by exciting ^{137}Cs gamma ray source. This was measured slightly higher than that of the commercial plastic scintillators available such as BC-408, EJ-200 (2-4 ns). It can be due to the difference occurred in the preparation process such as mass ratio, polymerization time etc. Fig. 10 depicts the decay time graph of the polystyrene based plastic scintillator.

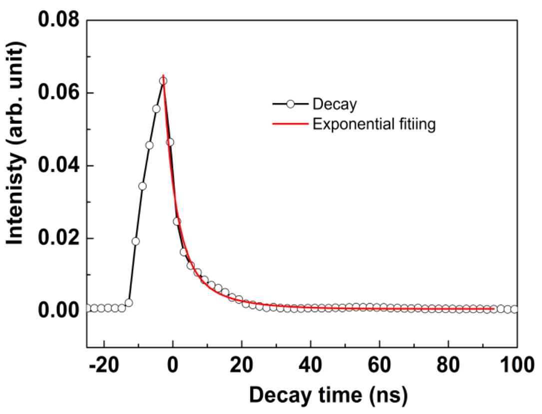


Fig. 10. Decay time curve of the polystyrene based plastic scintillator (color online)

4.6. Pulse height spectra

Pulse height analysis or energy spectrometry is used to examine the amplitudes of signals from a radiation detector to sort out different radiation energies striking the detector or to select for counting only those energies within a desired energy range. The spectrum recorded from a radiation source depends not only on the emission energy of the source but also on the type of radiation detector used. The amplitude of the signal depends on the amount of radiation energy deposited in the detector, which may be less than the full energy of the incident particle or photon.

Pulse height spectra was recorded by optically coupling the scintillator sample using Hamamatsu H3378-50 photomultiplier tube. A CAEN DT5790 digitizer was used to convert the PMT analog output signal [21]. Gamma ray sources such as ^{137}Cs, ^{60}Co and ^{22}Na were placed near the scintillator and the setup was completely isolated from light. Fig. 11 shows the pulse height spectra of the polystyrene based plastic scintillator measured using ^{137}Cs, ^{60}Co and ^{22}Na sources at room temperature.

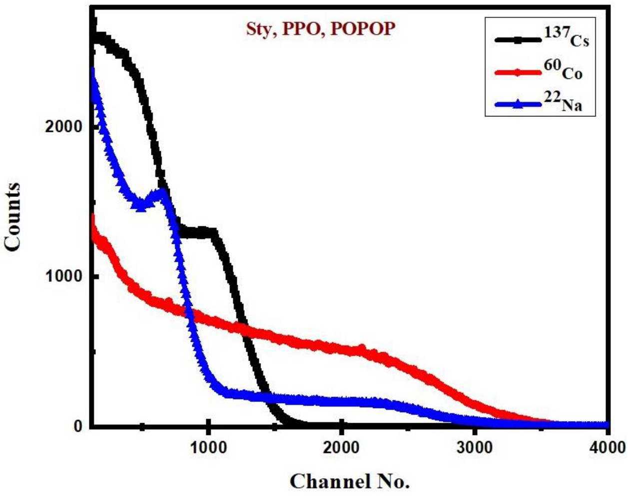
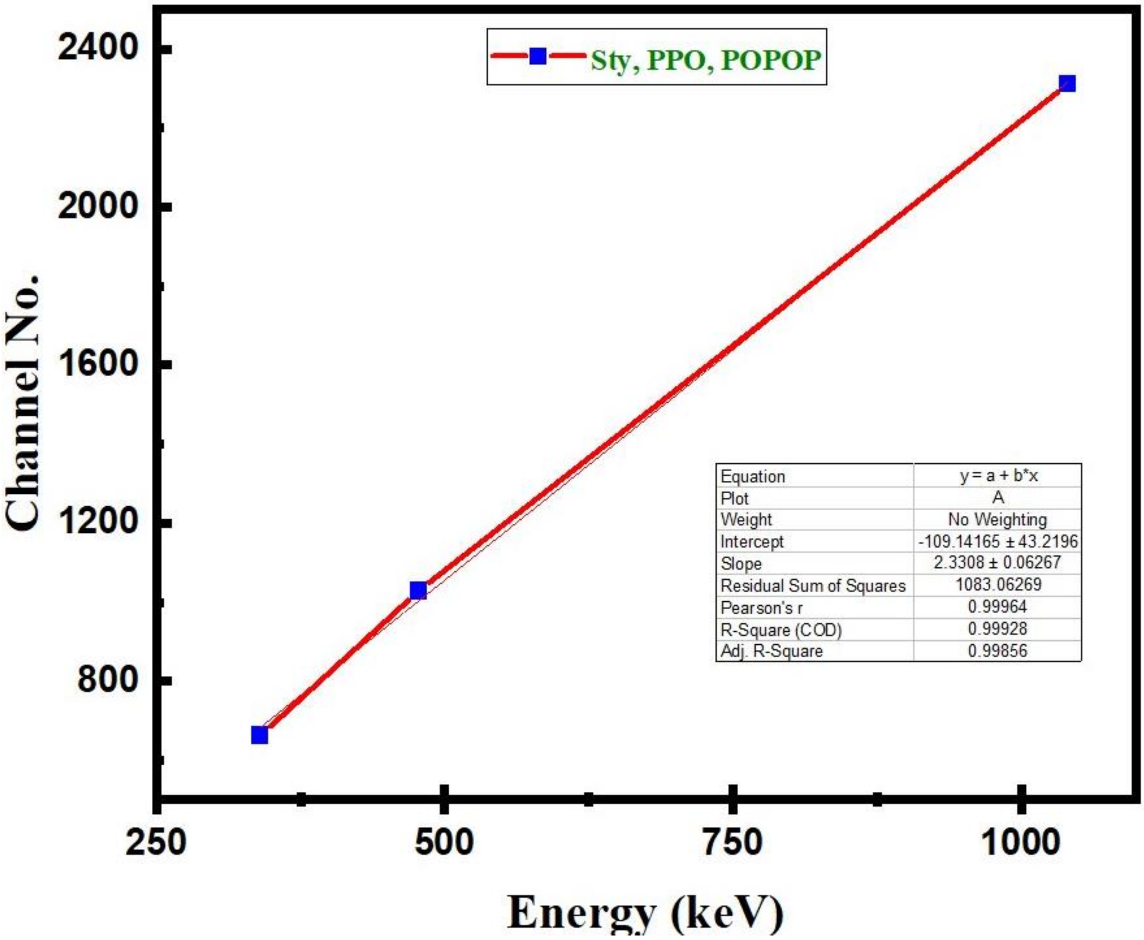


Fig. 11. Pulse height spectra using ^{137}Cs, ^{60}Co and ^{22}Na sources (color online)

The behaviour of the spectra indicates a strong dependence with the nature of the dopant. It is observed in Fig. 12 that an excellent energy linearity of 99.85% is exhibited by the plastic scintillator, obtained through the energy calibration corresponding to the Compton edges in the pulse spectra.



Equation	y = a + b*x
Plot	A
Weight	No Weighting
Intercept	-109.14165 ± 43.2196
Slope	2.3308 ± 0.06267
Residual Sum of Squares	1083.06269
Pearson's r	0.99964
R-Square (COD)	0.99928
Adj. R-Square	0.99856

Fig. 12. Energy calibration via linear fit corresponding to the Compton edges

5. Conclusion

A large sized good transparent polystyrene based plastic scintillator with high fluorescence intensity and fast response time was successfully synthesized using thermal polymerization reaction in high temperature furnace. Various functional groups were analysed using FTIR spectroscopy. The emission spectrum revealed a strong luminescence band at 420 nm, which matches the peak emission wavelength of a typical commercial plastic scintillator. The radioluminescence spectra analysed for different voltages ranging from 70 to 140 V showed a broad emission band between 400 and 600 nm, peaking at 420 nm. It was also found out that the intensity varies linearly with voltage. The fabricated polystyrene-based plastic scintillator exhibited a short decay time of 6 ns by exciting ^{137}Cs gamma ray source, which is a promising characteristic of the plastic scintillators. Pulse spectra were measured via PMT, amplifier, high voltage power supply and MCA using different radiation sources such as ^{137}Cs, ^{60}Co and ^{22}Na and the excellent energy linearity were observed through the spectral analysis. Thus, the polystyrene-based plastic scintillator doped with PPO and POPOP is worth to be considered for scintillation and neutron detection applications.

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[*] Corresponding author: rajeshp@ssn.edu.in