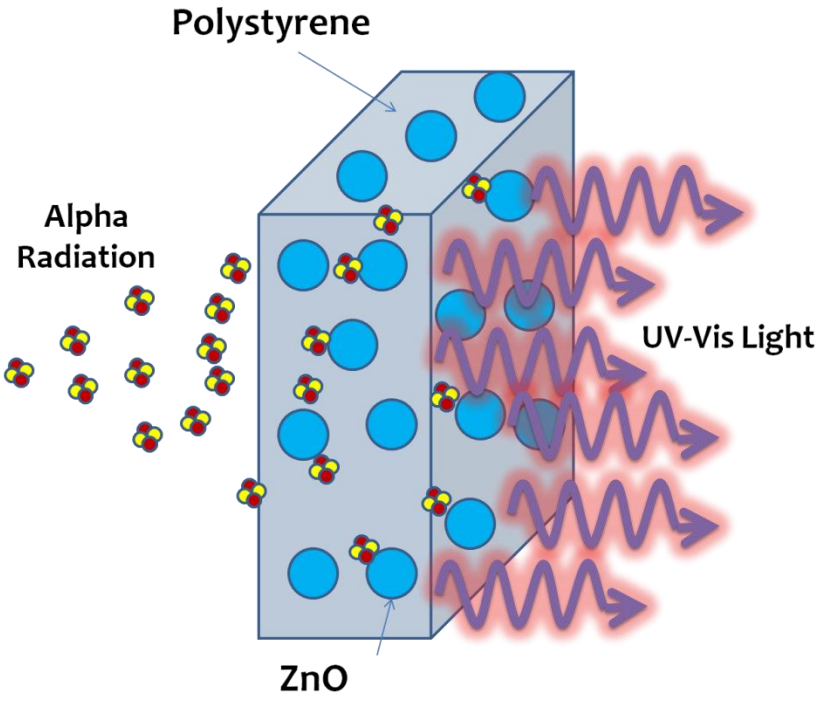

ZnO-Polystyrene Composite Scintillator for Alpha Radiation Detection

Chapter 6 ZnO-Polystyrene Composite Scintillator for Alpha Radiation Detection

6.1 Introduction

Polymer composite materials are micro/nanoparticles embedded in a polymer medium, suitable for wide applications, including optical and sensing applications. Polymer medium is usually a transparent medium that holds micro/nanoparticles, typically halide, oxides and can be prepared in different shapes and sizes due to flexibility with the polymer. Composite scintillators consist of inorganic or organic materials distributed with transparent polymer, cast in desired shape and size. The dopant size varies from 100 nm-1000 μm depending upon the applications(Boyarintsev et al., 2017). Various materials such as BaF_2, Gd_2O_3:Eu, CeF_3, $CaWO_3$, LSO, SrF_2 polymer composites have been reported for radiation detection applications (Coura et al., 2021; Demkiv et al., 2017, 2018; Hamroun et al., 2019; Novais et al., 2018; Oliveira et al., 2015). Zinc Oxide/ Polystyrene composites are also used in UV shielding applications, Tribo-electric generators and other applications (Gupta et al., 2020; Tu et al., 2010). Zinc oxide-polystyrene composites are cost-effective alternative of ZnO single crystal or ceramic scintillators and can be easily fabricated in a large area for alpha particle detection applications.

In this chapter, zinc oxide polystyrene composite synthesis is reported together with their optical, luminescence and alpha-induced scintillation properties. Loading of Zinc oxide varied from 5-50% and the effect on material properties was investigated. Photoluminescence shows 386-390 nm emission from the composite film characteristics of zinc oxide, which matched with alpha-induced radio-luminescence showing the sensitivity to the alpha particle. Alpha-induced scintillation pulse height linearly increases with the loading of zinc oxide in polystyrene. The minimum detectable activity (MDA) was ~ 0.4 Bq for 50% loading of zinc oxide and a linear response with various activities.

6.2 Experimental Procedure

Zinc Oxide/Polystyrene composite scintillator prepared using solution mixing method. Zinc oxide (99.999%, NOAH Technology Corporation, particle size < 5 microns) was added in toluene with 0, 5, 10, 20 and 50% w/w fine polystyrene granules in separate glass vials and mechanically stirred to obtain a uniform milky white solutions. Further, 0.2 g of solution was then poured and spread on a quartz glass substrate and dried at room temperature for 12 hrs. The preparation process is schematically shown in figure 6.1 a and the optical photograph of each sample is shown in figure 6.1 b. Optical properties such as transmittance and absorbance are studied using SPECORD photodiode array spectrophotometer. The diffused reflectance measurements are carried out using Perkin–Almer Lambda 900 UV-Vis-NIR spectrophotometer and the bandgap is estimated using the measured reflectance data. The luminescence properties are characterized using photoluminescence measurements by JASCO-FP 6500 spectrofluorometer. Alpha Radiation measurements are carried out using PMT coupled with commercial 1K MCA with inbuilt high voltage divider for PMT, preamplifier and spectroscopy amplifier. ^{241}Am is used to analyze the relative alpha response of the film, as schematically shown in Figure 6.1 c. Absolute detection efficiency and minimum detectable activity are evaluated for the prepared samples.

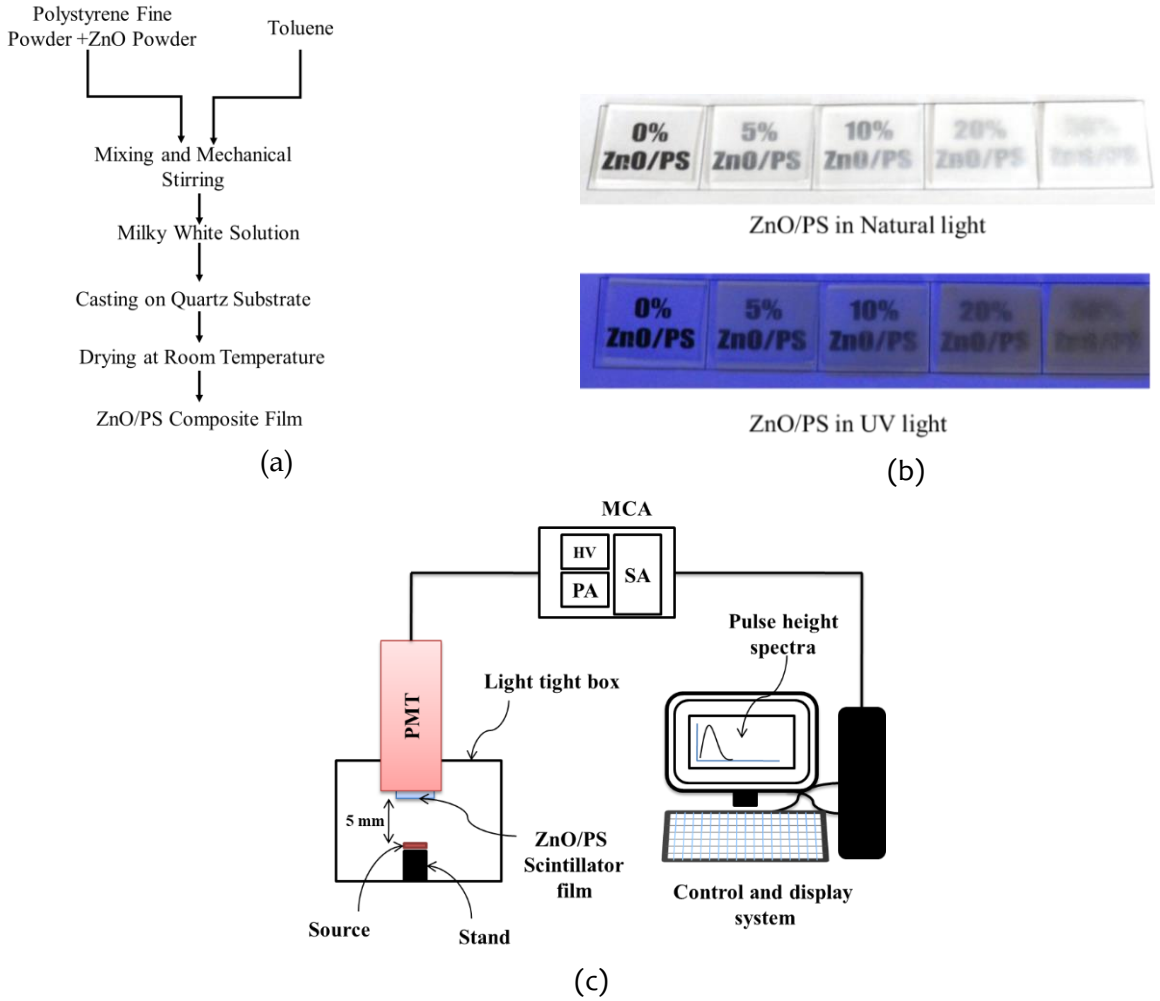

Figure 6.1: (a) Schematic diagram of Process for preparation of ZnO-Polystyrene scintillator film (b) Actual prepared film in natural and UV light (c) Experimental Setup Schematic for alpha measurement

6.3 Results and Discussion

6.3.1 Absorbance and Transmittance

Figure 6.2a shows the transmittance of the ZnO/Polystyrene composite along with bare polystyrene in the range of 200-1000 nm. The pristine polystyrene is ~ 92 % transparent beyond 280 nm and loading of 5% w/w of zinc oxide reduces the transmittance to 35% at 300 nm together with a dip at 385 nm. It is attributed to the near-band edge absorption of zinc oxide. The transmittance is gradually increasing in the visible region and beyond. The decrease in transmittance is exponential with an increase in wt% of zinc oxide in polystyrene as shown in figure 6.2 b. The absorbance of bare polystyrene and zinc oxide composites with 5-50% w/w is shown in figure 6.3c. Strong absorption of wavelength ~ 280 nm and below is observed in bare polystyrene and the composite samples as well. For 5-10% zinc oxide in polystyrene, absorbance peaks at 385 nm and as the weight percentage increases, the additional absorbance peaks at 388 nm starts appearing. This redshift may be attributed to agglomeration of zinc oxide in composites with high weight%.

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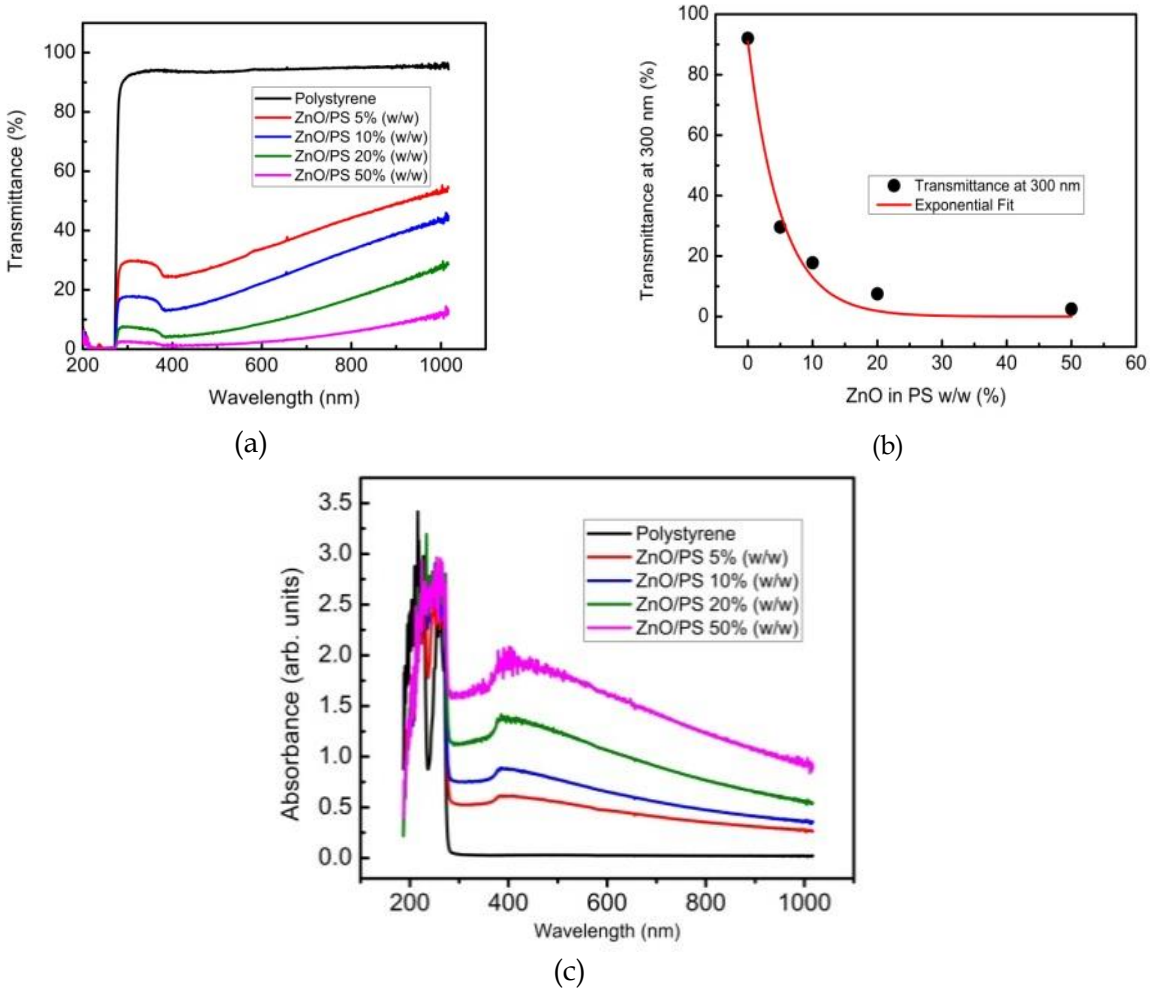
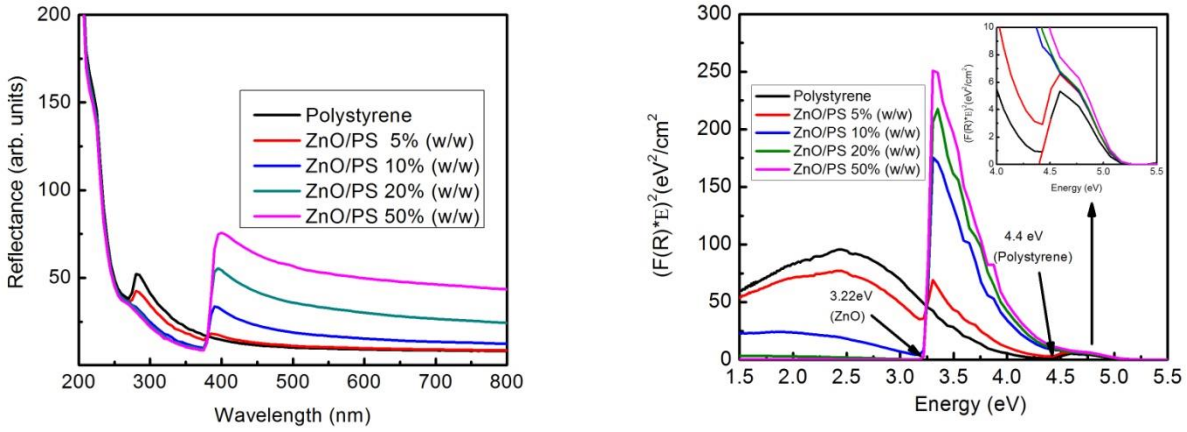


Figure 6.2: Optical properties of Zinc Oxide/Polystyrene composites (a) Transmittance of zinc oxide/polystyrene composite with different % (w/w) of ZnO in 200-1000 nm range (b) at 300 nm (c) Absorbance of ZnO/PS composite with different % (w/w) of ZnO in 200-1000 range (Sahani et.al. 2021)

6.3.2 Diffused Reflectance Measurements:

Diffused reflectance recorded for zinc oxide/polystyrene composites with 5-50 % w/w of ZnO in polystyrene is shown in figure 6.3a. Absorption of 270-280 nm due to bare polystyrene leads to a decrease in reflectance spectra. On loading 5% w/w zinc oxide in polystyrene, absorption at 375-390 nm was observed along with 270-280 nm due to polystyrene absorption. Further increase of zinc oxide in polystyrene from 10 to 50% w/w, change in reflectance in 375-390 nm region is observed because of strong absorption by zinc oxide. Using the reflectance R for photon energy hv, Kulbeka-Munk function defined as $F(R) = \frac{(1-R)^2}{2R}$ (Paul and Munk, 1931; Roy Choudhury, 2014) is calculated to estimate bandgap E_g using Davis and Mott's relation $F(R) * h\nu = B(h\nu - E_g)^{1/n}$; (n=2 for direct transition, B is constant). $(F(R)*E)^2$ vs. energy plots are shown in figure 5.3b, The bandgap of bare polystyrene is ~ 4.4 eV, which is in agreement with earlier studies on Polystyrene film(Ismail et al., 2017). Zinc oxide/polystyrene composites with 5% w/w ZnO, showing two band edges at ~ 3.22 eV and ~ 4.4 eV, corresponding to ZnO and Polystyrene, respectively (figure 6.3b and inset). At higher 10-50 % w/w of ZnO, the bandgap at 4.4 eV is not observed because of enhanced ZnO absorption.

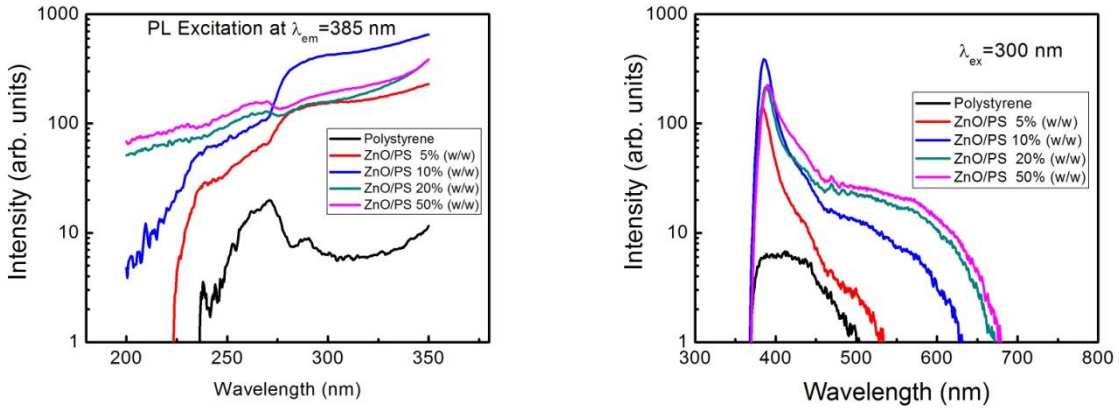


(a) (b)

Figure 6.3: UV-Vis spectroscopy of ZnO/Polystyrene Composites (a) Diffused Reflectance spectra (b) Band Gap Measurement of ZnO/Polystyrene Composite films

6.3.3 Photoluminescence and Radio-luminescence

Figure 6.4 shows the excitation and emission spectra of bare polystyrene and zinc oxide/polystyrene composites obtained using the spectro-fluorometer. Bare polystyrene shows excitation at 271 nm, which is very near to its bandgap ~ 4.57eV. Due to this excitation, the electronic transition from the ground state to a higher molecular orbital takes place with subsequent emission of 380-500 nm with some energy loss in the vibrational molecular orbital (figure 6.4 b). This emission is attributed to phenyl dimmers or multimers due to π-stacking interactions (Kuo, 2011). 5 % w/w ZnO loading in polystyrene changes the excitation wavelength, which dominates at ~300 nm, consistent with its absorbance spectra (figure 6.2 c). After this excitation is obtained at 385 nm, which corresponds to ZnO bandgap ~ 3.22 eV energy, the near band edge emission (NBE). Apart from this emission at 385 nm, a broad emission in the visible range is also observed, corresponding to the PS emission and ZnO defect-related emissions. These emission intensities increase with increasing ZnO loading to 10 % w/w. Further, increase in ZnO % w/w, leads a redshift in near band edge emission, i.e., 388 nm, consistent with the observed redshift in absorbance spectra of these samples. This is attributed to the agglomeration of ZnO particles. NBE intensity decreases in higher wt% (20 & 50%), which may be due to absorption of 388 nm emission causing higher visible emission.



(a) (b)

Figure 6.4: Photoluminescence properties of ZnO/Polystyrene composite scintillator (a) PL Excitation Spectra at 385 nm emission (b)PL Emission Spectra at 300 nm excitation of ZnO/PS composite films

Figure 6.5 shows the alpha-induced radioluminescence measured with ^{239}Pu alpha particle excitation. The emission at ~ 350-500 nm with a peak at ~431 nm is observed for bare polystyrene film. 5% w/w ZnO loaded composite shows the emission at ~ 387 nm, which increases with higher ZnO % w/w in a polystyrene matrix.

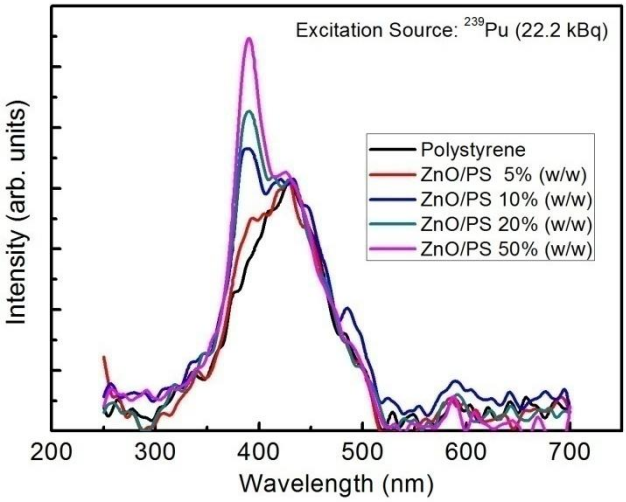


Figure 6.5: Radio-luminescence obtained by 239Pu Alpha radiation excitation

6.3.4 Alpha Induced Scintillation

Alpha particle when incident on ZnO/polystyrene composite, three main interactions occurs: (i) Molecular excitation of polystyrene and subsequent decay leading to emission of 382 nm which corresponds to excimer emission (ii) Excitation of zinc oxide which results in the scintillation and (iii) Non-radiative absorption of alpha particles energy in polystyrene and subsequent transfer to ZnO particles through Forster Energy Transfer (FRET)(Burešová et al., 2016), producing the emissions ~ 385 nm and ~ 550 nm, corresponding to ZnO NBE and DBE transitions, respectively. All these three alpha particle interaction processes in Zinc oxide/polystyrene samples are schematically shown in Fig 6.6a and the respective NBE and DBE excitations are shown in Fig 6.6b.

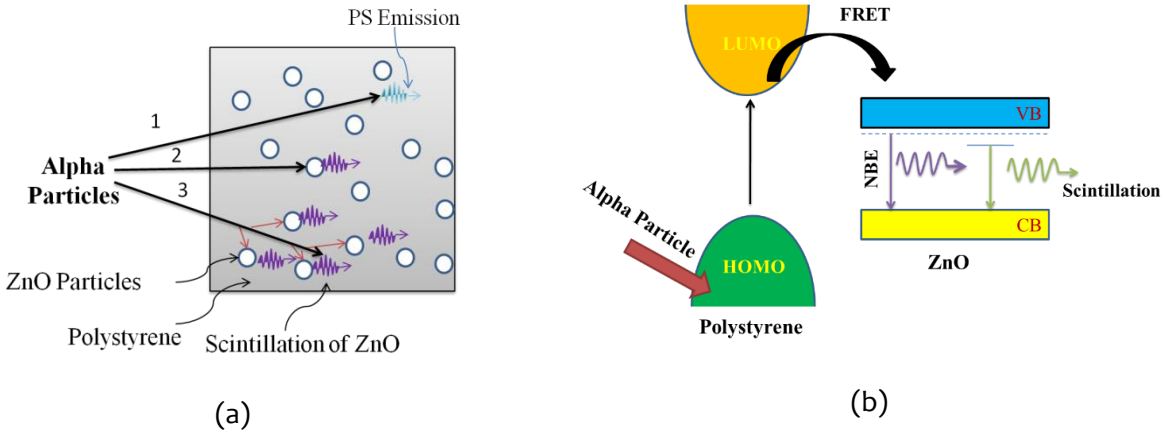


Figure 6.6:(a) Interaction of Alpha Particle to ZnO/PS composite and scintillation (b Mechanism of Nonradioactive Energy transfer in ZnO/PS Composite Scintillator)

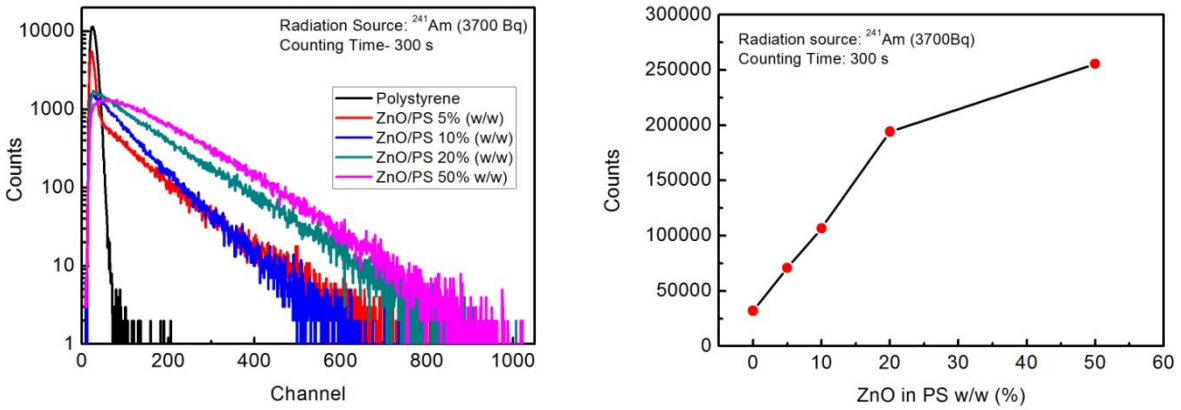
Scintillation light emitted from ZnO/PS composite due to alpha particle excitation is converted into electrical pulses, further processed by amplifiers. The distribution of the voltage pulse height collected by MCA is shown in figure 6.7 a. The distribution of pulse height obtained due to pristine polystyrene is extended to 100 channels only. In 5% w/w ZnO loaded polystyrene, the obtained pulses are of large pulse heights are extending to 650 channels, with

the contribution from polystyrene in initial channels. In 10% w/w ZnO in polystyrene composite sample, polystyrene contribution in initial channels has disappeared completely.

Further increase in ZnO 20-50% w/w composites, the intensity of pulse height increases. The integrated counts in channels from 40-1020 are plotted for different % w/w of ZnO in figure 6.7b for comparing the relative performance of different wt% ZnO loaded Polystyrene composite samples. The integrated count increases with increasing zinc oxide % w/w in polystyrene linearly up to 20% and at 50 % response deviates from linearity as transparency of the composite film has reduced drastically.

Table 6.1: Integral counts obtained in 40-1020 with differently doped ZnO/PS composites using ^{241}Am alpha source (3700Bq), calculated detection efficiencies and MDA

Composite	Int. Background Counts (GB) (40-1020 Channel)	Int. Source Counts with ^{241}Am 3700 Bq (GS) (40-1020 Channel)	Background Count rate (cps) NB=GB/t	Source Count rate (cps) NS=GS/t	Detection efficiency (cps/Bq) $\varepsilon = \frac{N_S - N_B}{A_\alpha}$	Minimum Detectable Activity (Bq) AMD= $\frac{2.71+4.66\sqrt{N_B * t}}{\varepsilon * t}$
5% (w/w) ZnO/PS	34	70955	0.113333	236.4033	0.063893	1.558978
10% (w/w) ZnO/PS	30	106738	0.1	355.6933	0.096133	0.978983
20% (w/w) ZnO/PS	23	194126	0.076667	647.01	0.174868	0.495804
50% (w/w) ZnO/PS	28	255612	0.093333	851.9467	0.230256	0.396203



(a) (b)

Figure 6.7: Alpha Induced Scintillation Measurement (a) Pulse height distribution obtained with differently loaded ZnO/PS composites using 241Am Alpha source, (b) Integrated Counts in 40-1020 channels

6.4 Detection Efficiency and MDA

Background counts and counts due to ^{241}Am alpha source obtained from 5-50% ZnO/polystyrene composites are tabulated in table 6.1. The absolute detection efficiency $\varepsilon = \frac{N_S - N_B}{A_\alpha}$;(N_s is count rate (in cps) due to source of Activity A_α, N_B is the background count rate (in cps) and $A_\alpha$is the activity of alpha source (in Bq)) and minimum detectable activity (MDA) $A_{MD}(Bq) = \frac{2.71+4.67\sqrt{N_B * t}}{t * \varepsilon}$ is computed and summarized in table 6.1. The calculated efficiency

and MDA for different % w/w ZnO/PS composite samples are plotted in figure 6.8. The detection efficiency varies from 6.3% to 23% for 5 to 50% w/w ZnO in polystyrene. The corresponding minimum detectable activity also varies from 1.6 Bq to 0.4 Bq. MDA depends on the background count rate N_B, which is very low for ZnO/PS detectors, making it sensitive to low activities, usually the case for radioactive contaminants.

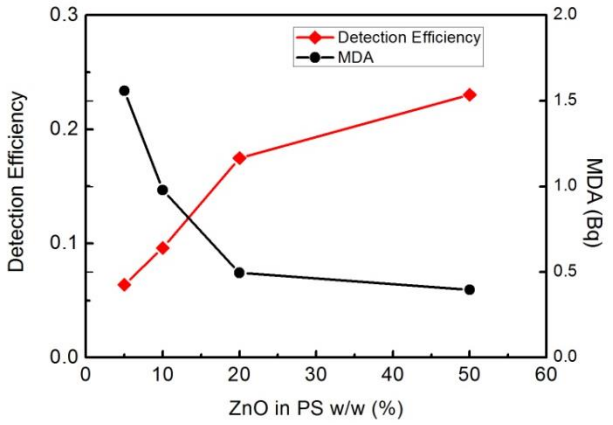


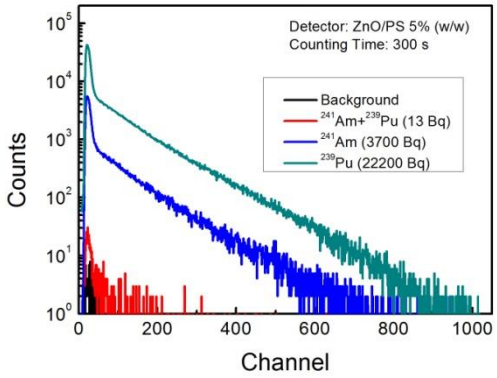
Figure 6.8: Alpha detection efficiency and MDA of 5-50% w/w ZnO loaded in Polystyrene

6.5 Linearity

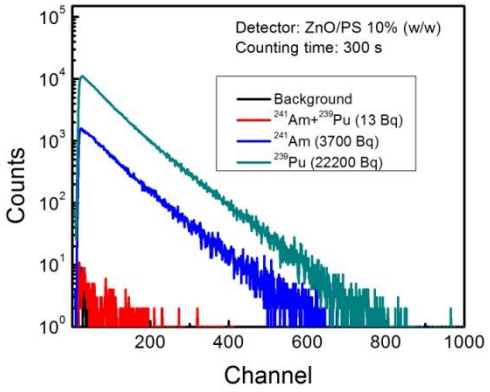
The response of a scintillator detector should be linear to the activities of the source. To understand the variation of ZnO/polystyrene in the composite scintillator response with the activity of alpha source, pulse height spectra are recorded with the different activities of alpha sources $^{241}Am+^{239}Pu$ (13 Bq), ^{241}Am (3700 Bq) and ^{239}Pu (22200 Bq) along with the background using all samples of ZnO/polystyrene. These spectra are plotted in figure 6.9 (a-d) and integral counts in 40-1020 channels are summarized in table 6.2 are plotted in 6.9 e. The pulse height intensity is increasing the activity of the source. The alpha radiation response is linear with activity for all ZnO/polystyrene samples, figure 6.9 e.

Table 6.2: Integrated Counts in 40-1020 channels with different activity alpha sources

Composite	Integrated Counts with Source (40-1020 Channel)			
	Background	**241Am+239Pu (13 Bq)**	**241Am (3700 Bq)**	**239Pu (22200 Bq)**
5%(w/w) ZnO/PS	34	269	70955	520279
10% (w/w) ZnO/PS	30	294	106738	560608
20% (w/w) ZnO/PS	23	461	194126	668208
50% (w/w) ZnO/PS	28	778	255612	1388043



(a)



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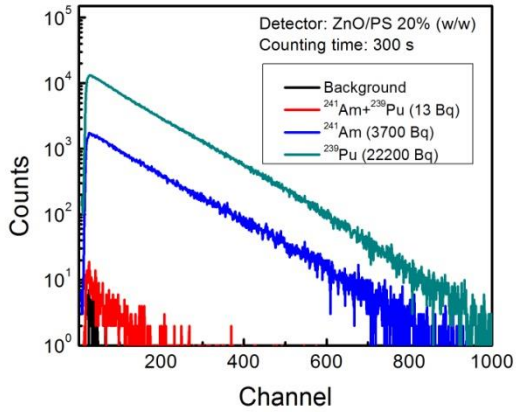

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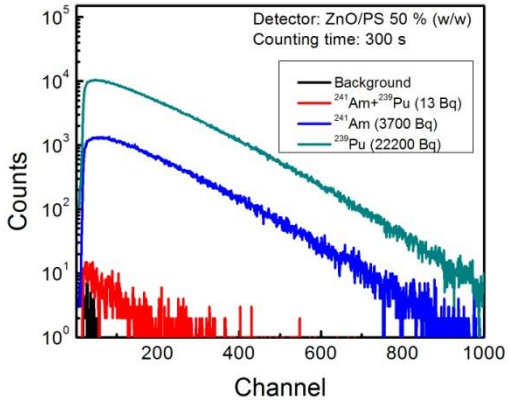
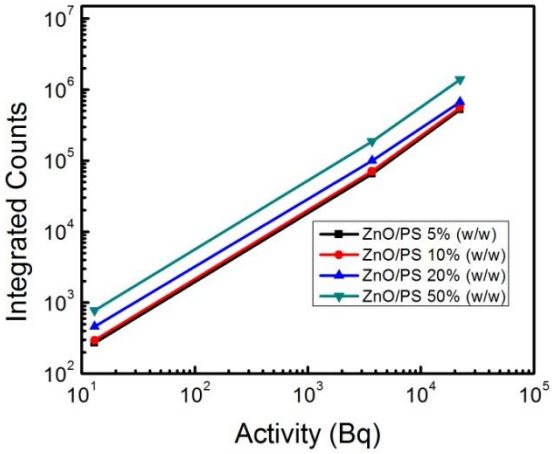


(d)



(e)

Figure 6.9: Pulse height spectra of (a) 5% ZnO-PS (b)10% ZnO/PS (c) 20% ZnO/PS (d) 50% ZnO/PS Composite Film with different activities of Alpha sources (e) Integrated Counts in 40-1020 Channels

6.6 Repeatability and Reproducibility

Repeatability and reproducibility in the performance are two important parameters showing variation of response of single detector in multiple runs and variation in response of multiple detectors in single run respectively. Pulse height spectrum recorded in five run of single ZnO/PS 50% (w/w) in shown in figure 6.10 a and corresponding count rate integrated in channels 40-1020 channels are shown in the inset. It is evident that pulse height spectra are highly overlapping and the variation in count rate ~ ±0.5%, showing the highly repeatable performance of ZnO/PS detector. Figure 6.10 b shows pulse height spectra obtained from four ZnO/PS 50% (w/w) samples and count rate are shown in the inset. The variation in count rate is found to be within ~ ±5%.

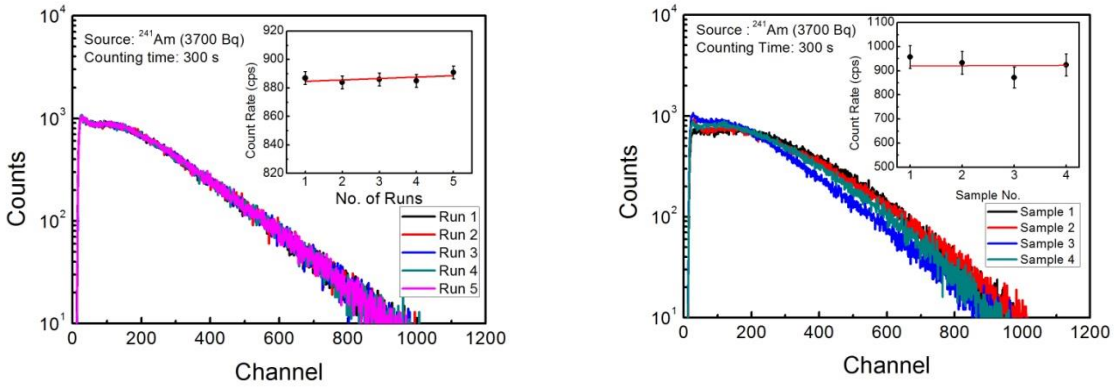
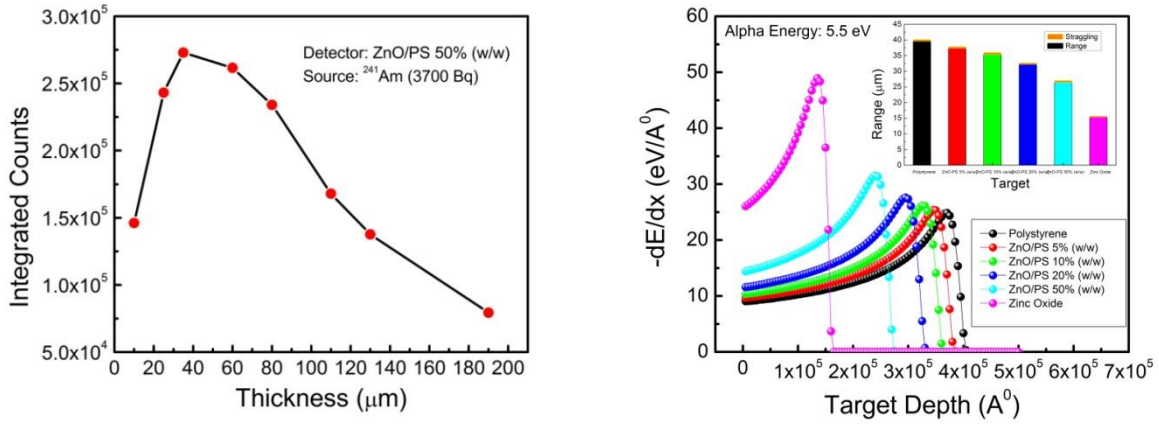


Figure 6.10: (a) Repeatability of Alpha detection of single ZnO/PS 50% (w/w) sample (b) Reproducibility of alpha detection of four ZnO/PS 50 % (w/w) samples

6.7 Alpha Response with variation in Thickness

Alpha particles lose their energy very rapidly in matter. This makes it important to study the scintillation with detector thickness. Integrated counts obtained from 50%w/w ZnO/polystyrene composite of 10-190 μm with ^{241}Am (3700 Bq) and plotted vs. thickness in figure 6.10 a. Integrated counts increase up to detector thickness ~35 μm and decreases afterward.



(a) (b)

Figure 6.11 (a) Alpha radiation response versus thickness for ZnO/PS 50% (w/w) composite sample (b) Range of 5.5 MeV alpha particle in Polystyrene, ZnO/PS 5-50% (w/w) and ZnO calculated using SRIM-2008.04 version(Ziegler et al., 2010)

When detector thickness is low, the total energy is not transferred in the ZnO/Polystyrene composite, leading to lesser scintillation events; as the thickness increases, scintillation events increase up to 35 μm. Further increase in detector thickness leads to attenuation of scintillation light passing through the sample reaching PMT, causing a decrease in the integrated counts. Alpha particle absorption in polystyrene and ZnO/polystyrene composite studied using SRIM-2008.04 version (Ziegler et al., 2010). The stopping power of polystyrene and ZnO/PS composites for the 5.5 MeV Alpha particle at various target depths is plotted in figure 5.10. The corresponding range is shown by the bar diagram in the inset. The range of alpha particle in polystyrene is ~39.6±0.6μm. (Where 0.6 μm is straggling) and for ZnO/PS composite range varies from 37.4±0.5 μm to 26.5±0.5μm. Range of alpha particle decreases with increasing zinc oxide % w/w in polystyrene and for pure zinc oxide, the range is obtained as ~15.4±0.3 μm. The range calculated by SRIM in ZnO/Polystyrene 50% w/w is ~ 27 μm, for the maximum counts; however, the maximum counts were for ~35 μm. This difference is because of the assumption that the theoretical range obtained for ZnO/PS composites is calculated on the assumption in theoretical range calculation that ZnO particles are uniformly distributed at the atomic/molecular level in polystyrene. However, as the detector is composite, being a mixture of two materials, such ideal distribution is difficult to achieve and thus, a deviation is observed.

6.8 Conclusion

ZnO/Polystyrene (ZnO/PS) composite thin scintillator samples are prepared using a simple, cost-effective process. The optical properties, such as absorbance, transmittance and diffused reflectance are studied. Further, luminescence properties such as photoluminescence and alpha-induced radio-luminescence are intensively investigated. The alpha particle induced scintillation is studied by analyzing pulse height intensity, which is significantly higher than the pristine polystyrene host material. The pulse height also increases with the loading of ZnO particles in polystyrene. The maximum detection efficiency is observed for 50 % w/w ZnO/PS and is ~23% together with the minimum detectable activity < 0.4 Bq. The response increases linearly with the activity for all ZnO/PS composite samples. Thus, the promising alpha response in ZnO/PS composite samples makes it worthy for radioactive contamination measurement even for very low detection limits.