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Role of bismuth oxide as a reinforcer on gamma shielding ability of unsaturated polyester based polymer composites

M. R. Ambika,[1] N. Nagaiah,[1] S. K. Suman[2]
[1]Department of Physics, Bangalore University, Bengaluru, Karnataka 560056, India
[2]Radiation Safety Systems Division, BARC, Trombay, Mumbai, Maharashtra 400085, India
Correspondence to: N. Nagaiah (E-mail: nagaiah@bub.ernet.in)

ABSTRACT: Unsaturated Polyester resin is reinforced with Bi_2O_3 up to 60% filler weight. The effect of bismuth oxide on gamma shielding ability of the composites is studied in terms of attenuation parameters using Ba-133, Cs-137, and Co-60 gamma ray sources. The results reveal that, the shielding property of the composite material increases with increase in the filler concentration and decreases with energy. The HVL, TVL, and relaxation length of the composites are found to decrease with increase in the filler concentration. It is found that, the shielding ability of 60% filled polymer composite is comparable to that of barite at low energy. The above polymer composite performs well at all energies and can act as an excellent gamma radiation shield for low energies and also proved to be light weight when compared to the conventional shielding materials. Thus, the gamma shielding ability of the UP resin is enhanced due to the addition of Bi_2O_3. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *134*, 44657.

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INTRODUCTION

Composite materials are the materials that consist of two or more substances with different chemical and physical characteristics. They comprise of matrix (ceramic, polymeric, or metallic) and the reinforcement (fibrous, particulate, or laminate). A polymer composite consists of a polymer as a matrix and any of the reinforcement as per the requirement. Variety of polymers such as thermoplastic, thermosets and elastomers have been used as matrix material with different metal or metal compounds as fillers while fabricating polymer composites.[1–5] Polymer composites find their place in several fields such as biomedical, automobile industry, aerospace, construction applications, electrical, and electronic field, sanitary applications, sports and many more. In addition, polymer composites are finding their application in nuclear science and technology especially in radiation protection.[6,7] The common shielding material in practice, for protecting from the radiation exposure is lead, but, do lack in chemical stability, heaviness, flexibility, and moreover is toxic. To overcome these demerits of lead, researchers are in ease to fabricate a lead free shielding material, which is light weight and effective in absorbing high energy radiations. Research efforts is enhancing day by day, such that, a few studies have been reported on polymer composite radiation shields over the globe,[8–11] whereas in India, studies are being carried out mainly on glass based radiation shields,[12–14] and a very few on polymers composites.[15,16] The chief advantage of using polymers as a matrix is the low cost, easy processability, good chemical resistance, low specific gravity and light weight. Thermoset polymers are those which are being widely used due to the presence of cross linked or network structures with covalent bonds with all molecules and have good prospects of long performance in the radiation environment of doses upto 10 MGy.[17] They do not soften but decompose on heating. Once solidified by cross linking process, they cannot be reshaped. While fabricating polymer based radiation shielding composites, the matrix material and the filler are selected based on the application. Hence, polymer composites have become an attractive tool for developing materials that can be designed to attenuate high energy radiation effectively. Especially, unsaturated polyesters (UPs) as a matrix in composite shields can offer excellent flexibility and shielding efficiency as they are radiation resistance.[16,18] They represent the thermoset composites market having their application in construction and marine industry. In general, the polymers as such are inferior to metals in the performance of radiation shielding. However, with the reinforcement or any other additives into the polymer matrix, UPs based composites can exhibit excellent radiation shielding ability.[16]

In this study the authors have made an attempt to reinforce bismuth oxide into the UP resin matrix to improve its gamma shielding ability. Bismuth oxide was selected as the

Table I. Comparison of the Properties of the Reinforcer with the Conventional Shielding Materials

Sl. No.	Material	Nature	Density (g/cc)	Molecular weight (g/mol)	Melting point (°C)
1.	Bi_2O_3	Non toxic	8.9	465.96	817
2.	Lead	Toxic	11.34	207.2	327.46
3.	Baryte	Non toxic	4.48	233.39	1580
4.	Steel	Non toxic	7.85	~55.845	1370

reinforcement by looking into its potential properties such as high density, high melting point, low conductivity and its availability in fine powder form,[11] which are mentioned in Table I and compared with those of the conventional materials, as high dense materials are suitable for absorbing high energy radiations such as X/Gamma rays which are highly penetrating and poses various harmful effects.[19,20] As mentioned in the table, Bismuth Oxide is a high Z metal oxide with density 8.9 g/cc which is less than that of lead and greater than that of barite and steel. Its melting point is better than that of lead and moreover is non toxic. This nontoxicity overcomes the other properties of the material. Hence, Bi_2O_3 was selected as the Reinforcer.

MATERIALS AND METHODS

Materials

Isophthalic resin is basically an UP, which is commercially available and was procured from M/s Ashland, Mumbai. With reference to the suppliers details, Isophthalic polyester precursor is a viscous, pale colored liquid, which is prepared using Maleic anhydride [$C_4H_2O_3$], Isophthalic acid [$C_6H_4(COOH)_2$], propylene Glycol [$CH_3CHOH{-}CH_2OH$] and styrene [$C_6H_5CH{=}CH_2$] in the molar ratio 0.5, 0.5, 1.0, and 1.2, respectively.[21,22] The first three components undergo reaction forming linear chains, whereas styrene performs the vital function of enabling the resin to cure from a liquid to a solid by cross-linking the molecular chains of the polyester without the evolution of any by-products. The addition of styrene in amounts of up to 50% helps to make the resin easier to handle by reducing its viscosity.[23] The structure of UP is as shown in Figure 1.

The Polyester precursor will set by itself, if enough time is given. But, for the practical purposes, this rate of polymerization is too slow. Hence, suitable accelerator and catalyst are being added to achieve the process of polymerization within the stipulated time. Bismuth oxide (Product code: 223891), which is acting as reinforcement was procured from Sigma Aldrich. The density, molecular weight, and average particle size are 8.9 g/cc, 465.96 g/mol, and ≤ 10 μm respectively. All the chemicals are of analar grade and were used as procured without any modifications.

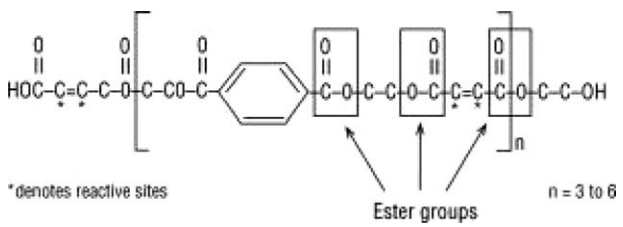

Figure 1. Structure of UP.

Fabrication of Composites

Finely powdered bismuth oxide of different wt % was reinforced into the UP matrix by open mould cast technique.[16] The matrix and the filler were initially stirred carefully to mix the components evenly. Further, the filler was dispersed effectively into the polymer matrix using an ultrasonicator. Two percent of Cobalt octoate acting as catalyst was added to the mixture to initiate the polymerisation reaction and does not take part in the chemical reaction. Later, Methyl ethyl ketone peroxide (1.5%) was added to the catalysed resin to enable the reaction to take place at a greater rate to complete the process of polymerization. Finally, the mixture was poured into a stainless steel mould and allowed to cure at room temperature for 12–15 h and then in a vacuum oven at 80 °C for 6 h.

Gamma Attenuation Measurements

When gamma rays are incident on a material medium, they get either absorbed or scattered through the process of photoelectric effect, Compton scattering, and pair production by transferring their energy. The attenuation of photons by various absorbing materials under ideal narrow beam condition satisfies the relationship $I = I_O\ e^{-\mu x}$, where, I_O is the initial photon intensity, I is the photon intensity after passing through an absorber of thickness x cm and μ is the total linear attenuation coefficient (cm^{-1}), which accounts for all the interaction processes.[24,25] The schematic representation of the gamma ray shielding mechanism is shown in Figure 2.

The gamma ray attenuation measurements were performed using a gamma ray spectrometer set up consisting of 3″ × 3″ NaI(Tl) detector, photomultiplier tube, pre-amplifier and PC based 4k MCA with a resolution of 8% for 662 keV gamma rays from Cs-137. The experimental set up was designed in such a way, so as to obtain a good collimated beam of photons. The gamma radiation sources used in this study are Ba^{133} (80 and 356 keV), Cs^{137}(662 keV), and Co^{60}(1170 and 1332 keV) of good strength, which were procured from Board of Radiation

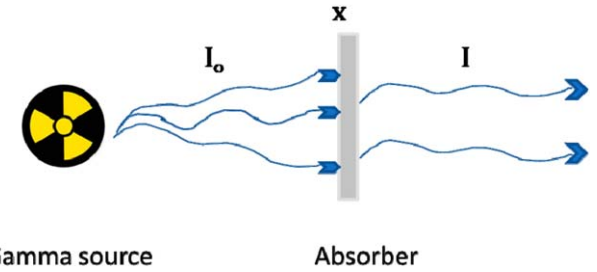

Figure 2. Schematic Representation of Gamma ray shielding Mechanism. [Color figure can be viewed at wileyonlinelibrary.com]

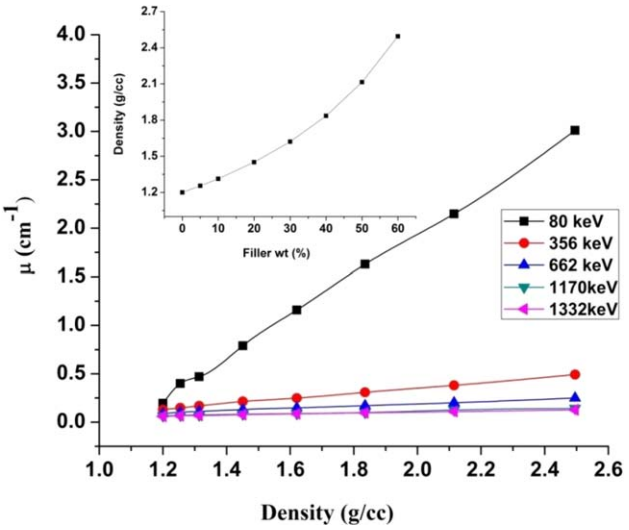

Figure 3. Effect of density on Linear attenuation coefficients of the polymer composites. [Color figure can be viewed at wileyonlinelibrary.com]

and Isotope Technology, Mumbai, India. The gamma energy range 80–1332 keV was selected as it covers the low, medium, and high energy gamma photons. The usage of polymer composites as shielding materials is based on their performance for different gamma energy, which are being used for various applications such as, low and high energy gamma radiations in medical field and industrial applications, high energy gamma radiations in the vicinity of the nuclear reactors, to safeguard the electronic devices in spacecrafts and many more. The performance of the experimental set up was studied using lead, silver and copper absorbers. The dimension of the samples was 4×4 cm^2 of 3 mm thick. The gamma ray spectrum was recorded for each polymer composition by varying the thickness, and for gamma rays of different energy. The background subtracted counts were used to evaluate the linear attenuation coefficient μ of the polymer composites. From the measured value of μ, the other attenuation parameters such as mass attenuation coefficient (μ_m), half value layer (HVL) thickness, tenth value layer (TVL) thickness, and relaxation length (λ) were established.

RESULTS AND DISCUSSION

Linear Attenuation Coefficient (μ)

Linear attenuation coefficient is the simplest parameter which is being used to measure experimentally the absorbing ability of any material for the incident radiation. It is defined as the probability of a gamma photon interacting with a material medium per unit path length.[24,26] Gamma rays interact primarily with atomic electrons; therefore, the linear attenuation coefficient is proportional to the electron density, which is proportional to the bulk density ρ of the absorbing material. The density of the pristine and the composites were measured using Archimedes technique as per the ASTM standards. The density of the pristine sample is 1.2 g/cc, whereas that of the composites ranges from 1.25 to 2.5 g/cc. The linear attenuation coefficient of the composites increases with increase in the wt % of the reinforcer which is due to the increase in the density of the composites and decreases with increase in energy as evident from Figure 3. The attenuation coefficient for the pristine sample is found to be 0.195, 0.127, 0.087, 0.065, and 0.06 cm^{-1} at 80, 356, 662, 1170, and 1332 keV gamma photon energy, respectively, and has been increased to 3.011, 0.492, 0.249, 0.142, and 0.127 cm^{-1} at the corresponding gamma photon energy for the composite reinforced with 60% bismuth oxide. Since, bismuth oxide is used as a reinforcement consisting of bismuth, a high Z metal, which plays a vital role in attenuating the gamma photons.

Mass Attenuation Coefficient (μ_m)

Mass attenuation coefficient is another shielding parameter which is essential to compare the shielding ability of various materials. It is defined as the probability of gamma photon interacting with the medium per unit mass of the absorber. It is independent of density and was obtained by dividing the linear attenuation coefficient with the density of the material. μ_m increases with increase in the filler concentration, which may be due to the increasing bismuth content in the composites as shown in Figure 4. The bismuth oxide added to the resin matrix do not undergo any chemical reaction, instead occupies the interstitial spaces within the network. In addition, it is evident from Figure 5 that, uniform distribution and dispersion of the reinforcer within the polymer matrix might have influenced for the increase in the attenuation coefficient of the composites.

Figures 4 and 6 reveal that, with increase in the energy of the gamma photons, the mass attenuation coefficients tend to decrease at each filler concentration which is due to decrease in the interaction cross sections with increase in photon energy.[27,28] The probability of interaction for photoelectric absorption strongly depends on gamma energy and atomic number Z of the medium where complete absorption of photons takes place and is dominant for energies lower than 100 keV. The cross sections for Compton scattering are significant between 100 keV to 10 MeV, whereas pair production process becomes dominant above 2 MeV.[24]

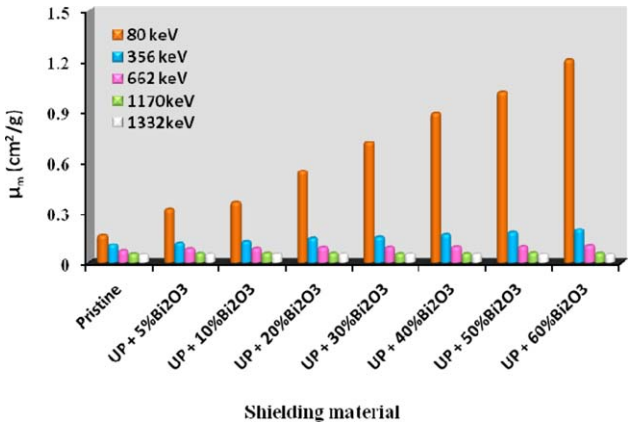

Figure 4. Effect of filler wt % on mass attenuation coefficient of the polymer composites for different energies. [Color figure can be viewed at wileyonlinelibrary.com]

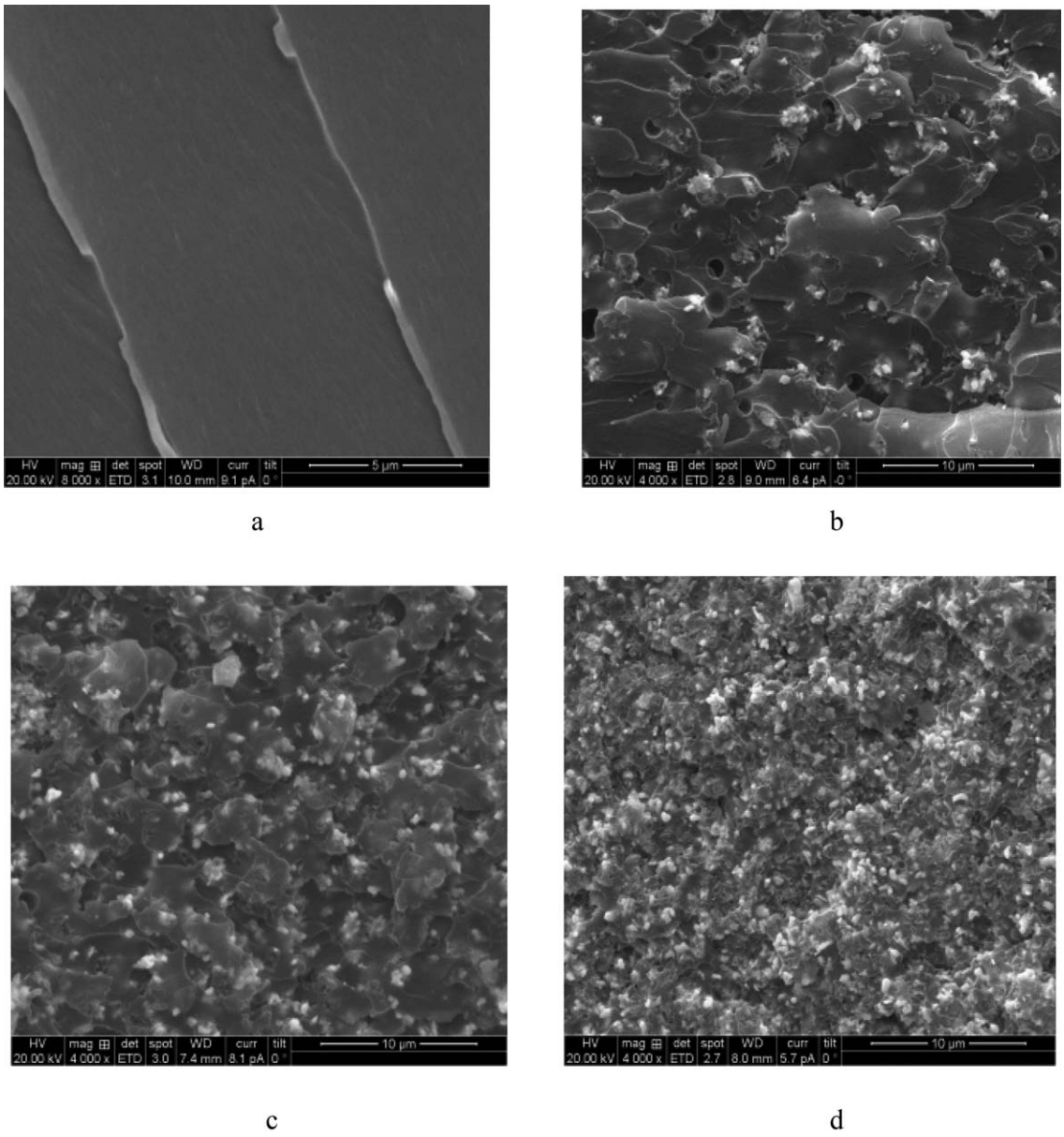

Figure 5. (a–d) SEM images of pristine (a) and the reinforced polymer composites (20, 40, and 60% Bi_2O_3; b–d).

The reinforced polymer composites do perform well at all the energies but excel in performance at low energies. The shielding ability of the pristine and the reinforced polymer composites are compared with the conventional materials and are shown in Figure 7. It is clear from the figure that, the gamma shielding ability of the 60% Bi_2O_3 reinforced polymer composite is almost comparable to that of barite.

Effect of Bismuth Content

The UP resin and the reinforced polymer composites consist of various elements such as carbon, oxygen, hydrogen, and bismuth of different proportion. The authors have made an attempt to study the contribution of each element in gamma attenuation process using a computer code WinXCom and XMuDat. Theoretical mass attenuation coefficient for each element was obtained using this code for different gamma energies from 30 to 1500 keV and is shown in Figure 8. It is clear from the figure that, the contribution of carbon, oxygen, and hydrogen are almost the same and do not vary appreciably with an increase in energy as well as the concentration due to the absence of absorption edges for photoelectric absorption. For high Z materials such as, bismuth present in the polymer composite, the attenuation coefficient significantly varies with respect to gamma energy. As energy increases, the attenuation coefficient decreases and is found to be maximum at 90.5 keV due to the presence of k—absorption edge for photoelectric absorption.[9] In this process, a photon interacts with an absorber atom in which the photon completely disappears by ejecting an energetic electron from one of the bound shells of the atom. The interaction probability increases rapidly as energy decreases, but then becomes much smaller at gamma-ray energy just below the binding energy of the K electron. This discontinuity

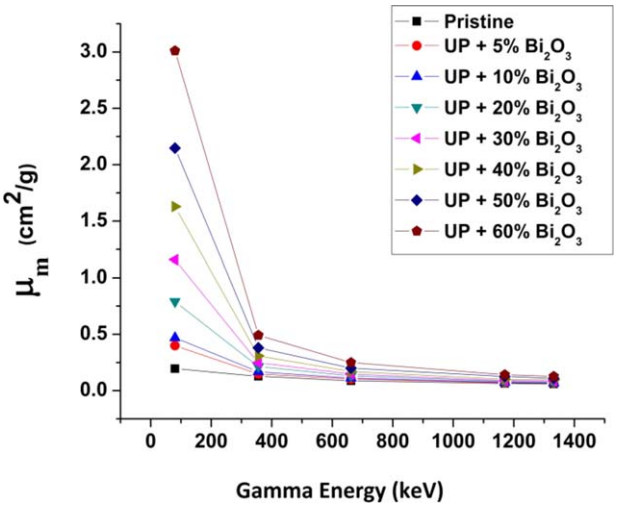

Figure 6. Variation of Mass attenuation coefficients of the polymer composites with respect gamma photon energy. [Color figure can be viewed at wileyonlinelibrary.com]

is called the K edge below this energy the gamma ray does not have sufficient energy to dislodge a K electron. Below the K edge, the interaction probability increases again until the energy drops below the binding energies of the L electrons, these discontinuities are called the L absorption edges.[9,25] Thus, the presence of absorption edge plays a vital role in the attenuation process especially in high *Z* material medium. Hence, the gamma attenuation in the bismuth oxide reinforced polymer composites is expected mainly because of the presence of bismuth and thus μ_m increases with increase in the bismuth content in the composites.

HVL and TVL Thickness

The shielding ability of any material for the practical applications is decided based on its HVL thickness HVL and TVL thickness TVL. HVL is defined as the thickness of a material required to reduce the intensity of the incident radiation to half of its original value, whereas TVL is to one tenth of its original intensity.[29] These were evaluated using the following relations

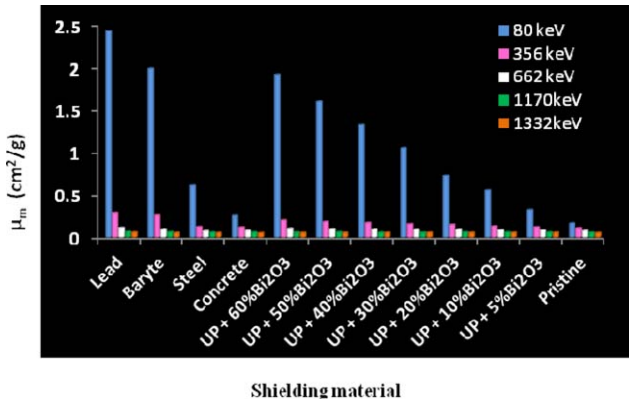

Figure 7. Comparison of shielding ability of UP + Bi_2O_3 Polymer Composites with the conventional shielding materials. [Color figure can be viewed at wileyonlinelibrary.com]

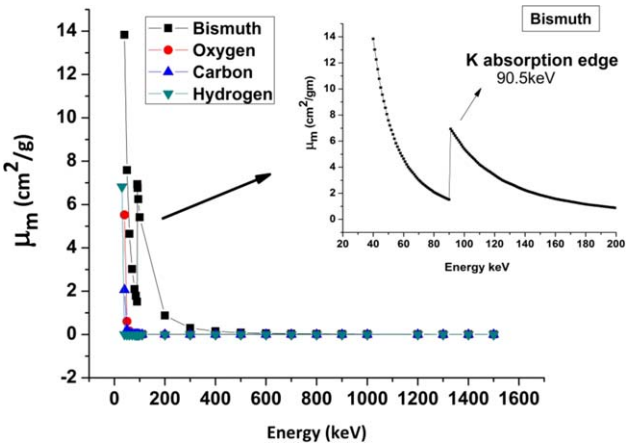

Figure 8. Theoretical Mass attenuation coefficients of various elements present in the composites with respect to gamma photon energy. [Color figure can be viewed at wileyonlinelibrary.com]

$$\mathrm{HVL} = \frac{Ln\ 2}{\mu} = \frac{0.693}{\mu} \quad (1)$$

$$\mathrm{TVL} = \frac{Ln\ 10}{\mu} = \frac{2.3026}{\mu} \quad (2)$$

The results reveal that, the values of HVL and TVL decreases with increase in the filler weight % and increases with increase in energy and are as shown in Figures 9 and 10. The HVL for the maximum filled composite (60 wt %) is found to be 0.23 and 1.4 cm, respectively, for gamma rays of energy 80 and 356 keV and which lies between that of Concrete and steel and thus proves to be better than concrete and poor than steel. This high filled reinforced composite also possess HVL value better than that of concrete at higher gamma energies say 662, 1170, and 1332 keV. Any shielding material finds its usefulness, if it exhibits lower HVL and TVL values as small as possible.

Relaxation Length (λ)

The shielding property of a material can also be understood in terms of relaxation length, which is also called as mean free path and is defined as the average distance travelled by a gamma photon during various collisions with the atoms of the medium. It was measured using the following relation and the result is as shown in Figure 11.

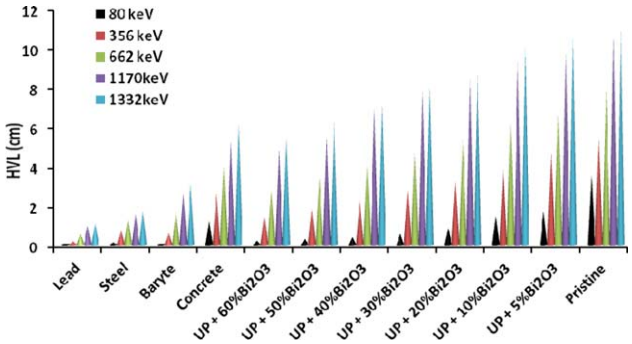

Figure 9. HVL thickness of the polymer composites and conventional shielding materials. [Color figure can be viewed at wileyonlinelibrary.com]

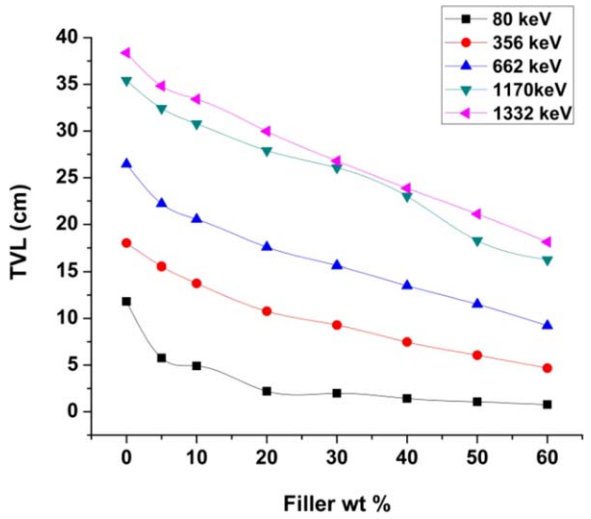

Figure 10. TVL thickness of the polymer Composites with respect to filler wt %. [Color figure can be viewed at wileyonlinelibrary.com]

$$\lambda = \frac{1}{\mu} \quad (3)$$

where μ is the linear attenuation coefficient.

It can be seen from the figure that, λ decreases with increase in the filler wt %, whereas it increases with increase in gamma energy. The low energy photons lose their energy over a short distance, whereas the high energy photons require a relatively longer distance to lose their energy.[24,26] λ is found to range from 5.12 to 0.33, 7.82 to 2.03, 11.49 to 4.0, 15.38 to 7.04, and 16.66 to 7.87 cm for 80, 356, 662, 1170, and 1332 keV gamma rays. Thus, smaller the relaxation length of a material better is the shielding property.

% of Heaviness

Heaviness is also very much essential for the application of any shielding material. The beauty of the polymer composites lies in their lightness. Polymers are known to be light weight in general, but in this study, since UP resin was reinforced by bismuth oxide which is a high dense metal oxide, an attempt has also been made by the authors to evaluate the heaviness of the polymer composites. By assuming lead (Pb) as standard and normalizing it to 100%, the % of heaviness of the polymer composites was obtained using the following relation[16]

$$\%\ \text{of Heaviness} = \frac{\text{Density of the material}}{\text{Density of Lead}} \times 100 \quad (4)$$

The % of heaviness of the pristine, reinforced polymer composites and the conventional shielding materials are as shown in Figure 12. It is evident from the figure that, with lead at 100% heavy, barite, steel and concrete are 39.5, 69.22, and 20.28% heavy relative to lead. Whereas, in case of Bi_2O_3 reinforced UP resin based polymer composites, the 60% filled composite is 22% of lead while, the pristine is 10.58% of lead. Thus, the filled composites are light weight when compared to the conventional shielding materials such as lead, barite, and steel.

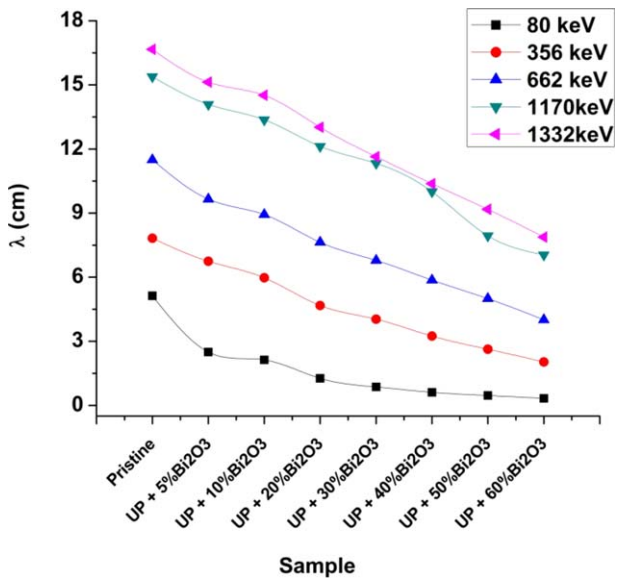

Figure 11. Relaxation length of the polymer composites with respect to filler wt %. [Color figure can be viewed at wileyonlinelibrary.com]

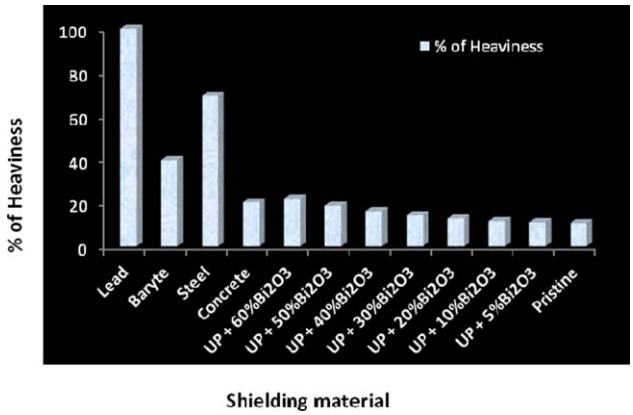

Figure 12. % of Heaviness of polymer composites and conventional shielding materials. [Color figure can be viewed at wileyonlinelibrary.com]

CONCLUSIONS

UP resin was reinforced with bismuth oxide upto 60 wt %. Gamma attenuation studies were carried out to study the shielding ability of the composites for different photon energies. The results revealed that, the attenuation coefficient increases with increase in the filler wt % and decreases with increase in the gamma photon energy. Various shielding parameters such as HVL, TVL, and λ were also evaluated. These were found to decrease with increase in the filler wt % and increase with increase in the gamma photon energy, which is required essentially for any shielding material. Experimental and theoretical results proved the role of bismuth oxide in the process of gamma attenuation. The shielding efficiency of the pristine and the reinforced composites were compared with the conventional shielding materials such as lead, barite, concrete, and steel. The composites do perform well at all the energies but excel their ability at low energies and are comparable to barite in performance. In addition, the polymer composites exhibit excellent lightness and is reflected in their low % of heaviness (22%). Thus, the UP resin was successfully reinforced with Bi_2O_3 to

improve its gamma shielding ability. Hence, UP-Bi_2O_3 polymer composites can be used for gamma shielding applications to protect from harmful effects of X/Gamma rays.

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