

# Preparation and Characterization of Lead Monoxide Filled Unsaturated Polyester Based Polymer Composites for Gamma Radiation Shielding Applications

V. Harish,<sup>1</sup> N. Nagaiah,<sup>2</sup> T. Niranjana Prabhu,<sup>3</sup> K. T. Varughese<sup>4</sup>

<sup>1</sup>Department of Physics, Amrita School of Engineering, Bangalore 560035, India

<sup>2</sup>Department of Physics, Bangalore University, Bangalore 560056, India

<sup>3</sup>Department of Chemistry, East Point College of Engineering and Technology, Bangalore 560049, India

<sup>4</sup>Polymer Laboratory, Central Power Research Institute, Bangalore 560080, India

Received 10 April 2008; accepted 2 November 2008

DOI 10.1002/app.29633

Published online 5 February 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Particulate polymer composites of Isophthalate based unsaturated polyester resin filled with different concentrations of lead monoxide were prepared. These composites were investigated for physical, thermal, mechanical, and gamma radiation shielding characteristics. The results of density evaluation, microscopic studies, and the radiation shielding properties for gamma rays of energy 0.662 MeV from Cs-137 point source have been presented in this article. The results show that, the density of the composites was observed to increase with filler loading. The morphological analysis of the composites made using the scanning electron microscope showed that, the lead monoxide particles were observed to disperse

uniformly in the polymer matrix with an average inter particle distance of about 10  $\mu\text{m}$  and an average size of about 5.36  $\mu\text{m}$ . The linear attenuation coefficient of the composites was found to increase with increased filler content in the composites. The highest value of 0.206  $\text{cm}^{-1}$  was found for 50 wt % of lead monoxide. These composites were observed to exhibit excellent % of heaviness and Half value layer in comparison with other conventional materials. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1503–1508, 2009

**Key words:** composites; density; microstructure; attenuation coefficient; radiation shield

## INTRODUCTION

High energy radiations due to cosmic rays, nuclear reactors, nuclear fuel processing, nuclear weapon tests, controlled fusion reactions, etc. are always harmful and have a degrading effect on both living and non living matter.<sup>1</sup> Hence, to protect life and other matter from such hazardous radiations, an appropriate shielding material made of high density materials such as lead bricks or high density concrete are often used. In addition, other metallic shields include copper, bismuth, tungsten, steel, etc. However lead is superior over all these shielding materials because of its higher atomic number, density, and low cost.<sup>2</sup> But however, lead shields normally lack in service flexibility, chemical stability, mechanical strength, etc.<sup>3</sup> When a flexible shield is required, a protective cloth or an apron which is made of lead or lead oxide filled polymer composites is preferred.<sup>4</sup> Such shields are being used by occupational workers in nuclear reactors, radiotherapy or x-ray radiography, space applications, etc. In performance of radiation shield-

ing, polymer materials are inferior to metals, but there are merits in flexibility, workability, chemical stability, low cost, volume reduction after use, etc.

In view of this, several investigators have used variety of polymers as matrix material with different metal or metal oxides as fillers while fabricating the polymer based composite radiation shields. However, only a few investigators are successful in preparing the composites with lead oxides as filler in polyethylene,<sup>5</sup> copolymers of ethylene with vinyl alkylate, alkyl methacrylate,<sup>6</sup> polyethylene glycol,<sup>7</sup> styrene butadiene rubber,<sup>8</sup> natural rubber,<sup>9</sup> and polystyrene.<sup>10</sup>

The comprehensive literature survey reveals that, the potential properties such as mechanical, thermal and corrosion resistance of Isophthalate resin<sup>11</sup> have not been exploited so far in preparing the polymer based radiation shields using lead monoxide as filler. Hence, in the present study, we attempted to prepare and characterize the polymer based composite radiation shields using isophthalate resin as a matrix element and lead monoxide as filler.

Correspondence to: N. Nagaiah (nagaiah@radiffmail.com).

## EXPERIMENTAL

less than 25 $\mu$ m particle size. Isophthalate resin (KPR6600) along with accelerator (Cobalt Octoate 3%) and Catalyst (MEKP 50%) were procured from KEMROCK Industries, Vadodara, India (An associate company of Georgia-Pacific Resins, Inc. USA). All chemicals were of commercial grade and used without any modifications.

Composites with filler weight % of 0, 5, 10, 20, 30, 40, and 50 were prepared in laminate form using a simple and well established open mold casting technique at room temperature. In this method, filler and resin fractions were carefully weighed and mixed thoroughly for fine dispersion of the filler in a motorized blender at about 1200 rpm. About 2.0% of an accelerator and then 1.5% of hardener were added to the mixture and finally poured into a stainless steel mold of 3 mm thick, 150 mm wide, and 250 mm height. The composites were first allowed to cure in the mold at room temperature for 24 h and post cured in an oven at a constant temperature of 80°C for 6 h. The composite sample designations and the weight % of lead monoxide in the composite are shown in column 1 and 2 of Table I respectively.

Archimedes technique was employed in determining the average density of the composite samples according to ASTM D 792-91.<sup>12</sup> A calibrated (10<sup>-4</sup> gm) single pan electrical balance (Precision Balances, INDIA) and three organic liquids such as toluene, ethanol, and chlorobenzene were used for the purpose. Theoretical values of the density of the composites (void free) were predicted using the following relation and compared with those of experimental values.

$$\text{Density of composite} = \frac{100}{\left[ \frac{M}{\rho_m} + \frac{F}{\rho_f} \right]}$$

Where, M = wt % of the matrix, F = wt % of the filler,  $\rho_m$  = density of matrix and  $\rho_f$  = density of the filler.

Fractured surfaces of the composite samples were examined under a Scanning electron microscope

**TABLE I**  
Filler Fraction, Density, Linear, and Mass Attenuation Coefficients of the Composites

Sample designation	Wt. % of PbO in composite	Density (g cm <sup>-3</sup> )	Linear attenuation coefficient (cm <sup>-1</sup> )	Mass attenuation coefficient (cm <sup>2</sup> g <sup>-1</sup> )
ILM1	0	1.2007	0.0985	0.082
ILM2	5	1.2325	0.0997	0.0809
ILM3	10	1.2891	0.114	0.0842
ILM4	20	1.4285	0.1264	0.0884
ILM5	30	1.6042	0.1422	0.0887
ILM6	40	1.8552	0.1735	0.0935
ILM7	50	2.1721	0.206	0.0948

(S-4700 Cold FE-SEM, Hitachi High Technologies America, Inc.) to understand the binding behavior between the filler particles and the polymer, the nature of dispersion and filler particle size.

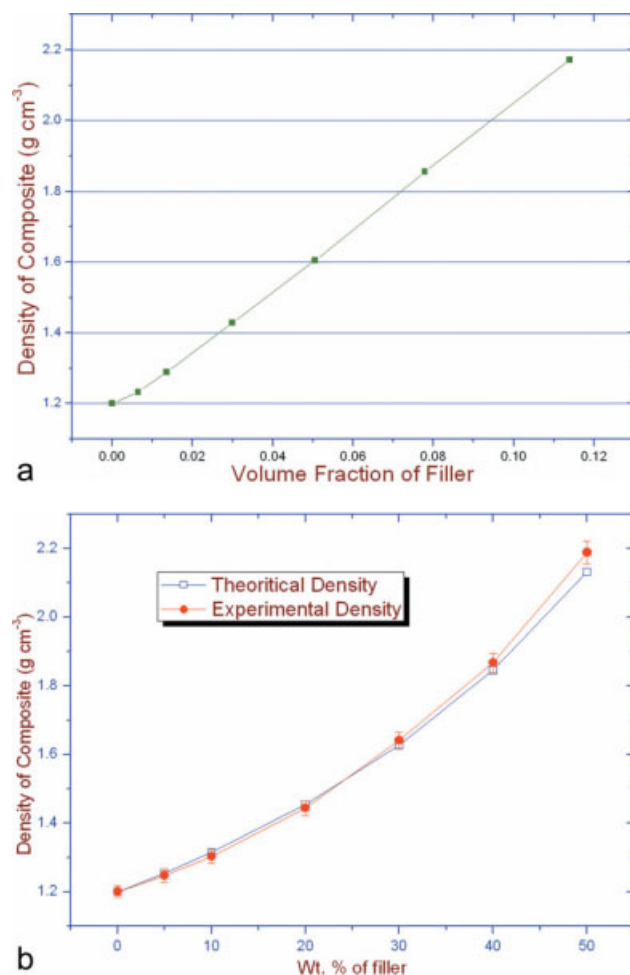
#### Measurement of attenuation coefficient for gamma rays

Gamma photons incident on an absorber material may either be absorbed or scattered in a single event through various interaction processes with atoms, electrons or nuclei of the absorber, due to which a fraction of the incident photons are absorbed completely while the rest transmitted with their full energy. Thus a well collimated beam of gamma rays of initial intensity 'I<sub>0</sub>' after traversing a thickness "x" of absorber will have a residual intensity 'I' of primary photons and is given by the relation  $I = I_0 \exp(-\mu x)$ . Where,  $\mu$  is known as the total linear attenuation coefficient of the absorber (cm<sup>-1</sup>) for  $\gamma$ -rays of appropriate energy.<sup>13</sup>  $\mu$  can be evaluated from a linear graph of  $\ln(I/I_0)$  versus thickness "x" of the absorber. Another important and widely used fundamental quantity known as the mass attenuation coefficient was obtained by dividing  $\mu$  by density ( $\rho$ ) of the absorber.<sup>13</sup> The mass attenuation coefficient (cm<sup>2</sup>/g) represents the efficiency of the absorber and is independent of actual density and physical state of the absorber.

Linear attenuation coefficient of each composite sample was measured for gamma rays of energy 0.662 MeV (Cs-137 point source) using a well calibrated gamma ray spectrometer which consists of 3"×3" NaI-Tl scintillation detector, Amplifier and 16k multi channel analyzer (EG and G- ORTEC). The measurement was made with the narrow beam geometry setup.<sup>13,14</sup> For each composite material, the gamma ray spectrum was recorded as a function of the thickness of the material. In each case, the area under the photo peak of the spectrum was taken to evaluate the intensity I of the transmitted beam. Initially, the intensity I<sub>0</sub> of gamma photons for zero thickness was noted down. The calibration of the experimental setup was confirmed by comparing the experimentally measured attenuation coefficients of the metallic lead, silver, and copper with those of the theoretical values evaluated from the Hubbell's database (NISTR, XCOM).<sup>15</sup>

#### RESULTS AND DISCUSSION

The results of the density of the composites prepared are shown in column 3 of Table I and are observed to increase with the filler loading. The increase in the density of the composite with increasing volume fraction of the filler is shown in Figure 1(a). It confirms that the filler concentrations are below the critical



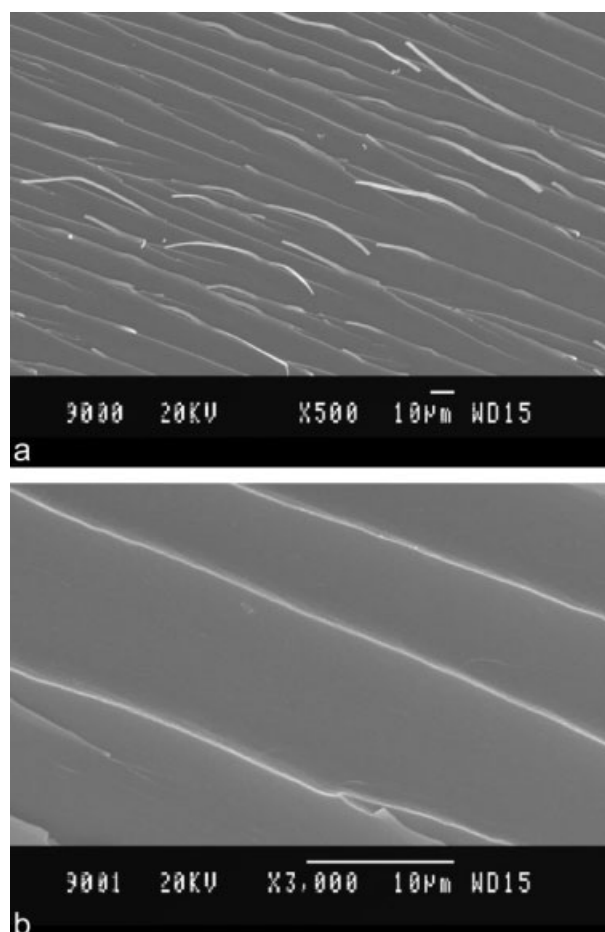
**Figure 1** (a) Plot to represent that the filler fractions are below the critical values. (b) Variation of theoretical and experimental values of density with respect to filler concentration. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

filler loading values. Above the critical concentration of the filler, there might not be enough polymer to cover the filler surface which results in increase of free volume and hence, decrease in density of the composite.<sup>16,17</sup> The experimentally determined densities of composites were observed to be in good agreement with those of theoretical and are as shown in Figure 1(b).

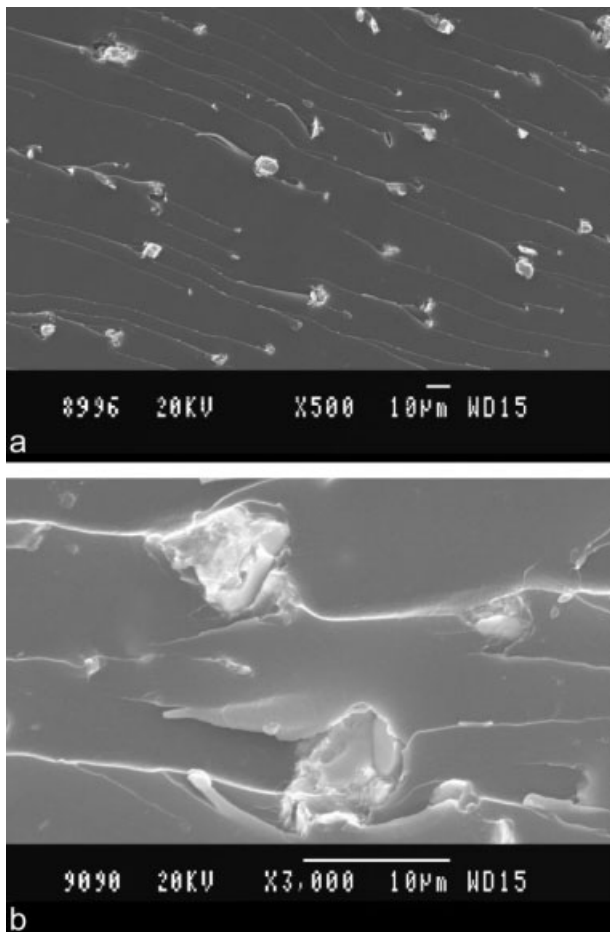
To understand the dispersability of lead monoxide with resin composition, morphological study was made using the scanning electron microscope. The nature of the fractured surfaces has been clearly shown in the photo micrographs of ILM1 [Fig. 2(a,b)], ILM2 [Fig. 3(a,b)] and ILM4 [Fig. 4(a,b)]. Figure 2(a,b) proves the brittle surface fracture of ILM1 with regularly graded ridges with their average widths as 10 microns. In Figure 2(a) there are wider, lighter streaks that depart from the ridges. It represents the fraying or detachment of ribbon-like strands from the ridges during fracture, which is a common fracture

mode in neat thermosets. Figures 3(a,b) and 4(a,b) show the dispersed morphology of the fractured surface at low and high magnification of the composites ILM2 and ILM4. It is clear from these figures that the fillers have a good dispersability with an average inter particle distance of about 10  $\mu\text{m}$  and an average size of about 5.36  $\mu\text{m}$ . Radial fronts involving the lead particle at one end and linking with at least one or the other particle along the ridge path can be seen in Figures 3(b) and 4(b). The presence of lead particles in the matrix makes such a radial path (crack propagation) different from that observed for the neat resin case where due to the absence of filler, the crack propagation is almost straight. On the other hand, for samples involving fillers the direction of the radial front and presence of lead particles in the path influence the progression of the crack. Further, with increased filler loading, there are less pronounced ridges as the tension in the matrix is released more often during fracture resulting in a smoother surface.

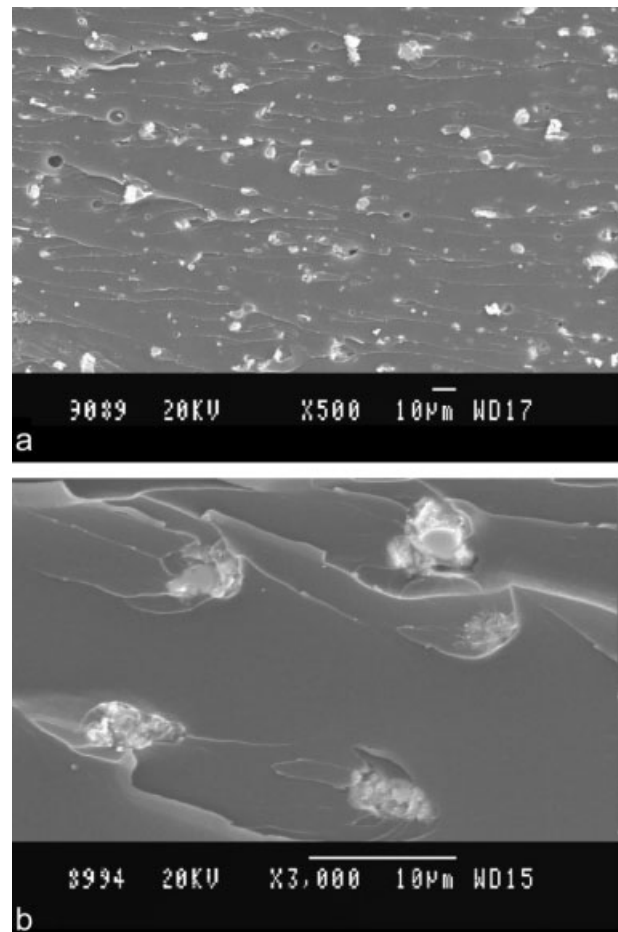
The results of the linear attenuation coefficients of the composites prepared are shown in column 4 of Table I. From the results the linear attenuation coefficient of the composites is found to increase with



**Figure 2** (a) SEM micrograph of ILM1 at low resolution. (b) SEM micrograph of ILM1 at high resolution.



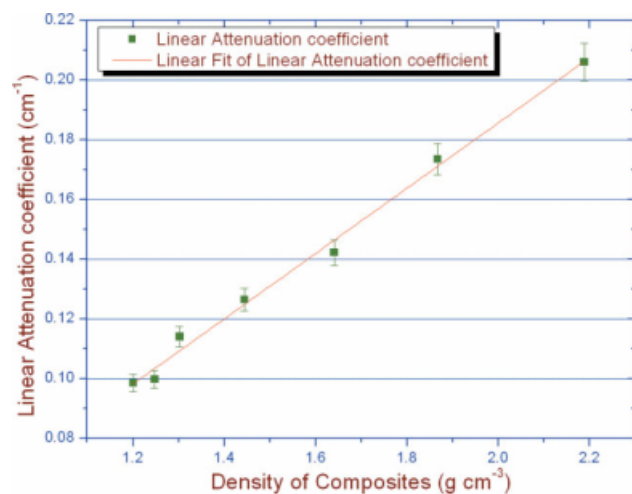
**Figure 3** (a) SEM micrograph of ILM2 at low resolution. (b) SEM micrograph of ILM2 at high resolution.



**Figure 4** (a) SEM micrograph of ILM4 at low resolution. (b) SEM micrograph of ILM4 at high resolution.

increasing filler content. It appears to increase gradually at lower concentrations of filler (up to ILM4) and then rise steeply (up to ILM7). This may be attributed to the fashion by which the filler is dispersed in composites and increase of density of the composites with filler loading. Generally the gamma rays either be absorbed or scattered in a single event through various interaction processes with the different components of the absorber which is a high energy interaction. The total linear attenuation coefficient is the sum of the interaction cross sections/probabilities due to each component of the composite. Further the interaction probability and hence the linear attenuation coefficient is a direct function of density of the material but not of chemical nature (chemical bonding) or structure of the material (crystal structure).<sup>13</sup> Thus composites with a fine dispersion of high density filler should offer more interaction probability for photons and hence better shielding properties. Figures 3(a) and 4(a) clearly reveal the fine dispersion of the filler in the polymer matrix and due to which the composites may have an even distribution of density throughout the samples. Hence such composites were expected to exhibit better shielding properties. Plot

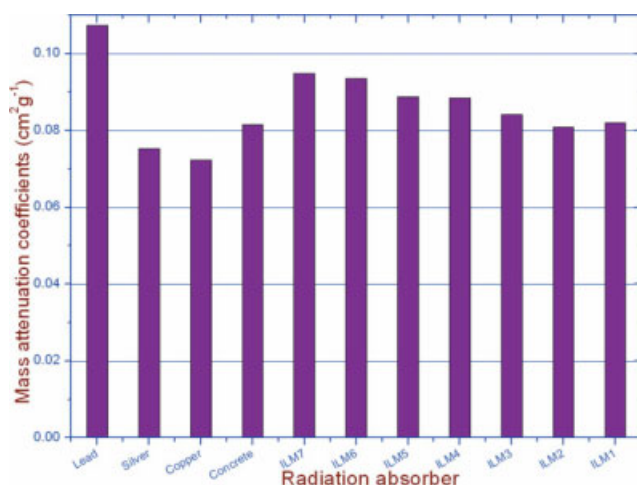
shown in Figure 5 verifies the linear dependence of linear attenuation coefficient on density of composites. Further, from the measured values of the linear



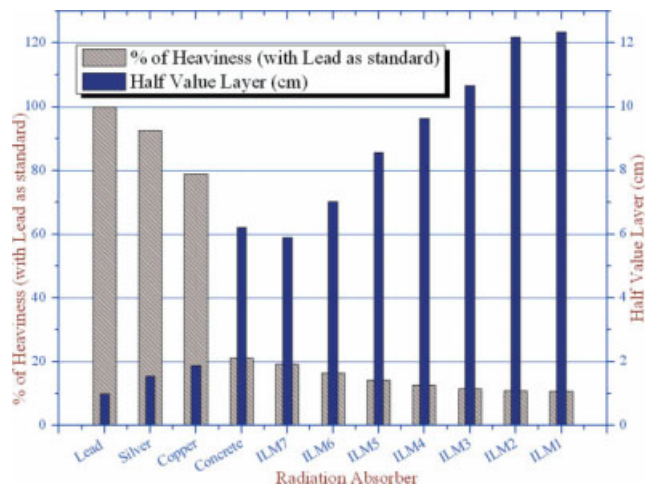
**Figure 5** Plot showing the linear dependence of linear attenuation coefficient on density of composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

attenuation coefficients and the density, the mass attenuation coefficients of the composites (ILM1 to ILM7) were also evaluated and are shown in the last column of Table I. They range from  $0.082 \text{ cm}^2/\text{g}$  (for ILM1) to  $0.0948 \text{ cm}^2/\text{g}$  (for ILM7).

To know the shielding ability of the composites thus prepared with respect to that of the elemental and the conventional shielding materials like lead, silver, copper and concrete, the comparison has been made in terms of a graph (Fig. 6). From the graph, it was found that the composites were observed to exhibit better efficiency (with a peak value of  $0.0948 \text{ cm}^2/\text{g}$  for ILM7) than the other absorbers except lead. Even though, the observed value of the mass attenuation coefficient of the composite ( $0.0948 \text{ cm}^2/\text{g}$  for ILM7) is lower than that of the elemental lead, it is found to possess shielding ability of nearly 86% of that of the latter. It is an appreciable information pertaining to the polymer based radiation shields. The % of heaviness and the half value layer (thickness of the absorber required to reduce the incident intensity to its half) of the various radiation shields by assuming lead as standard (normalized to 100%) are shown in Figure 7. From the figure, the % of heaviness is observed to increase with filler concentration in composites. It is understood from the figure as the composites are much lighter than lead as well as the other metals with only 19.22% of heaviness for the highest filled composite (ILM7). Concrete exhibits a value of 21.15%, slightly higher than that of the composite. The half value layers of the various absorbers with lead as reference (0.57 cm for 0.662 MeV normalized to 1 cm) show that the metals are more superior to concrete and composites because of their high densities. However ILM7 composite exhibits



**Figure 6** Plot showing the comparison of mass attenuation coefficients of various gamma radiation absorbers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 7** Plot showing the comparison of % of heaviness and half value layers of various gamma radiation absorbers with lead as standard reference. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

better properties than concrete in terms of lightness and less half value layer (3.36 cm of ILM7 against 3.54 cm of concrete).

## CONCLUSIONS

Lead monoxide particles were observed to disperse uniformly in the polymer matrix. Isophthalate resin filled with lead monoxide (above 30% filler loading) exhibits good shielding properties for gamma rays of energy 0.662 MeV. Lead content of the filler in the composites may be the major contributor toward the attenuation of gamma rays due to its high atomic number and density. Observed mass attenuation coefficients of the composite samples are sufficiently higher than the metals like silver, copper, and also concrete, but found inferior to lead. These composites may work as good shields at lower and medium gamma energies.

## References

- Holmes-Siedle, A.; Adams, L. *Hand Book of Radiation Effects*, 2nd ed.; Oxford University Press: England, 2002.
- Chilton, A. B.; Shultis, J. K.; Faw, R. E. *Principles of Radiation Shielding*; Prentice Hall Inc.: New Jersey, 1984.
- Spinks, J. W. T.; Wood, R. J. *An Introduction to Radiation Chemistry*; Wiley-Interscience: New York, 1964.
- Bovey, F. A.; *The Effect of Ionizing Radiation on Natural and Synthetic High Polymers*; Wiley-Interscience: New York, 1958.
- Yvan, L.; Pierre, L. Fr 1,384,603, GB 1034533 (1965).
- MacLeod, J. M.; Servant, R. H.; Hector, R. Eur Pat. 372,758, CA 2,003,879, Jpn 02,223,899, U. S. 5,278,219 (1990).
- Hussain, R.; Haq, Z. U.; Mohammad, D. *J Isla Acad Sci* 1997, 10, 81.
- Abdul Aziz, M. M.; Badran, A. S.; Abdel-Hakem, A. A.; Healy, F. M.; Moustafa, A. B. *J Appl Polym Sci* 1991, 42, 1073.

9. Abdul Aziz, M. M.; Gawaily, S. E. *Polym Degrad Stab* 1997, 55, 269.
10. Pavlenko V. I.; Lipkanskii, V. M.; Yastrebinskii R. N. *J Eng Phys Thermophys* 2004, 77, 11.
11. Hansmann, H.; *Compendium-Composites*; ASM Hand Book on Polyester Resins: ASM International, Ohio, USA. 2003.
12. ASTM. Standard Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement (D 792-91), ASTM: West Conshohocken 1997 (Annu Book of ASTM Standards, Vol.08.01).
13. Evans, R. D. *The Atomic Nucleus*; Tata McGraw-Hill Inc.: New York, Ch. 25. 1955.
14. Singh, S.; Kumar, A.; Singh, D.; Thind, K. S.; Mudahar, G. S. *Nucl Instrum Methods Phys Res Sec B* 2008, 266, 140.
15. Berger, M. J.; Hubbell, J. H. XCOM: Photon Cross Sections Database, Web Version 1.2. National Institute of Standards and Technology, Gaithersburg, MD 20899, USA 1999. Originally published as NBSIR 87-3597 1987. Available at <http://physics.nist.gov/xcom>.
16. Katz, H. S.; Milewski, J. V. *Handbook of Fillers for Plastics*; Springer: New York, USA, 1987.
17. Wypych, G. *Handbook of Fillers*; William Andrew Inc.: Chem Tec Publishing, Toronto, Canada, 1999.