JOURNAL OF Applied Polymer SCIENCE

Polymer Nanocomposite-based Shielding Against Diagnostic X-rays

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ABSTRACT: Lead is commonly used in medical radiology departments as a shielding material. Lead-based protective materials are also used by clinical personnel during X-ray image-guided interventional radiology (IVR) procedures. However, lead is extremely toxic and prolonged exposure to it can result in serious health concerns. Polymer composites, on the other hand, can be designed to be lead-free in addition to being lightweight, conformable, cost effective, and potentially capable of significantly attenuating X-rays. Nanomaterials have unique material properties that can be exploited to develop novel lead-free radiation-protection materials. In this study, polydimethylsiloxane (PDMS) nanocomposites were fabricated using different weight percentages (wt %) of bismuth oxide (BO) nanopowder. The attenuation properties of the nanocomposites were characterized using diagnostic X-ray energies from 40 to 150 kV tube potential and were compared to the attenuation characteristics of 0.25-mm-thick pure lead sheet. The PDMS/BO nanocomposite (44.44 wt% of BO and 3.73-mm thick) was capable of attenuating all the scattered X-rays generated at a tube potential of 60 kV, which is the beam energy commonly employed in IVR. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: X-ray shielding; polydimethylsiloxane; bismuth oxide; nanocomposites; radiation protection

Received 4 January 2012; accepted 1 May 2012; published online
DOI: 10.1002/app.37980

INTRODUCTION

High atomic number (Z) materials are capable of attenuating diagnostic X-rays (40–150 kV) predominantly through photoelectric effect. For this reason, lead ($Z = 82$) is considered as the most effective material for protection against X-ray exposure. Hence, it is used as structural material in radiological facilities. Lead aprons and other protective garments containing lead are also commonly used by clinical personnel and patients during interventional radiological (IVR) procedures for protection against direct or scattered X-rays. Protective garments made of high Z materials such as lead, composites of lead or lead-oxide impregnated in polymer matrix,[1,2] and composites of heavy metals,[3–5] have been developed for protection against X-ray exposure during radiological examinations. However, conventional lead aprons are heavy and cause discomfort to the users, especially during prolonged procedures. Alternatively, polymer composites are lightweight, conformable, cost effective, and can be fabricated to effectively attenuate diagnostic X-rays. Earlier investigations on lead-based polymer composites developed by embedding lead powder into elastomer such as natural rubber, showed aging, embrittlement, and cracking of the polymer, resulting in drastically shorter lifetime compared to the projected lifetime of 10 years.[6] Moreover, exposure to lead is very hazardous and may lead to several health problems. For example, long-term exposure to lead or its salts (e.g., lead oxide, lead acetate, etc.) may result in accumulation of the heavy metal within the body which, in turn, may lead to serious (or fatal depending upon the exposure level) health problems such as neuronal disorders, kidney failure, reduced levels of hemoglobin, and red blood cells, etc. Consequently, efforts to replace the conventional lead-based materials have led to the development of "lead-equivalent" materials which, by definition, have radiation-attenuation characteristics as those of lead of a given thickness (typically 0.25 or 0.5 mm).

The advent of nanotechnology and the subsequent availability of nanomaterials have opened up novel applications in numerous industries. Materials with nanometre dimensions tend to exhibit unique chemical and physical properties relative to the same material with dimensions in microscopic or macroscopic range. Nanomaterials are often used as mechanical reinforcement materials in structural applications, and also as high performance, electromagnetic radiation-resistant materials.[7–10] Few

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experimental and theoretical studies have proposed the use of polymer nanocomposites (nanomaterials embedded in polymeric matrix) for X-ray and gamma ray shielding applications.[11–13] Nanomaterials have unique properties that make them excellent candidates as fillers in radiation-shielding materials. Recently, few groups[14–17] have evaluated the radiation resistant properties of the nanocrystalline materials. Owing to the large volume-fraction of grain boundaries, the nanocrystalline materials served as effective sinks for radiation-induced defects. Another study explored the size effects (nanoparticles versus microparticles) on X-ray attenuation properties of copper oxide (CuO) embedded in bee wax.[18] The CuO particles in nanometer range showed enhanced attenuation characteristics at the low energies (26 and 30 kV) in comparison to those of the microparticles of the same material. The selective enhancement of radiation attenuation by the nanomaterials at the lower energies was attributed to the increased number of *particles per gram* and grain-size effects. Therefore, the use of nanomaterials for radiological protection purposes may have important implications in terms of material durability and effective radiation shielding, all of which can be utilized to replace the toxic lead and lead composites.

In this article, we present the X-ray attenuation characteristics of novel, nonlead-based polymer nanocomposites for shielding against X-rays used in IVR and in low-energy diagnostic applications such as mammography. We fabricated nanocomposites of polydimethylsiloxane (PDMS) with different concentrations of bismuth oxide (BO) nanoparticles as filler material. The BO-based PDMS nanocomposites are nontoxic, easy to fabricate, cost-effective, and they can also be used to coat on uneven surfaces. Attenuation-properties of PDMS-based BO nanocomposites for both primary beam and scattered X-rays, at tube-voltages ranging from −40 to 150 kV, are presented in this article.

EXPERIMENTAL

Sample Preparation

PDMS (Sylgard 184, Dow Corning) is used as the polymeric matrix for embedding filler particles of BO nanopowder (Sigma–Aldrich) with particle size ranging from 90 to 210 nm. Samples with 28.57, 37.73, and 44.44 weight percentages (wt %) of BO in PDMS were prepared such that each sample was ~ 1.3-mm thick. The concentration of the filler material (BO nanopowder) was varied in terms of weight percentage (wt %), which is defined as:

$$\text{Wt\% of BO} = \frac{\text{Weight of BO}}{\text{Weight of PDMS} + \text{Weight of BO}} * 100$$

The effective Z of BO was estimated to be 79.27, using the Mayneord "power law" method.[19] For uniform dispersion of the nanopowder, the mixture of PDMS and BO was vortexed for about 15 min. The composite material was then degassed and baked for about 45 min to an hour at 80°C in a vacuum oven. The X-ray attenuation characteristics of the samples were then investigated at X-ray tube-voltages ranging from 40 to 150 kV.

Experimental Set-Up

Investigation of the X-ray attenuation by the samples was conducted for both primary and scattered radiation with a diagnostic X-ray machine (Ysio digital diagnostic X-ray machine, Siemens) for tube-voltages ranging from 40 to 150 kV. The milliampere-second [mAs: product of the X-ray tube current (mA) and the beam on time (s)] and the exposure time in millisecond (ms) were 100 mAs and 250 ms, respectively. When investigating with the primary X-rays, each sample was placed at a distance of about 20 cm from the X-ray source, and the ion chamber (X-ray detector) was placed at least 50 cm from the floor to avoid backscattered radiation [Figure 1(a)]. The field size was maintained at 10 cm × 10 cm. For experiments with scattered X-rays, a lead box was built using a 1–mm-thick lead sheet such that it had an opening with dimensions similar to those of the samples [Figure 1(b)]. The lead box was used to filter out scattered photons (noise) from the background so as to ensure detection of scattered X-rays originating only from a 20-cm-thick solid-water block representing the patient. The lead box was placed perpendicular with respect to the X-ray source and the solid water block. The 0.6 cm^3 Farmer ion chamber (Model: Capintec PR06C, Capintec, Ramsey NJ) was centered at the opening in the lead box and placed right behind the sample(s). The detector was connected to an electrometer (Capintec 192) which was set to "medium" mode for the tests with primary X-rays, and to "low" mode for experiments with scattered X-rays.

Characterization Tests

Machine Characterization. The beam quality of kilovoltage X-rays is usually specified by the first half value layer (HVL) and tube potential (kV_p). Measurements of the HVL of the Ysio diagnostic X-ray machine were determined using technique parameters from 50 to 150 kV_p and 100 mAs in narrow beam geometry. The aluminum attenuators were placed at least 50-cm away from the Farmer chamber (Model: Capintec PR06C, Capintec, Ramsey NJ), and the X-ray collimators (blades) were set at 4 × 4 cm^2 to make a narrow beam measurement. It was ensured that there was no scattering material close to the set-up. The calibration of the 0.6 cm^3 Farmer chamber (Capintec PR06C) together with the electrometer (Capintec 192) is traceable to an accredited National dosimetry laboratory (NRC, Ottawa, Canada). The linearity of mAs and ms with photon intensity were also measured for three different tube-voltages: 40, 60, and 81 kV. The tube output as a function of photon-energy (tube voltage: 40–150 kV) was also investigated using mAs = 100 and ms = 250.

Material Characterization. The dispersion of the BO nanoparticles in PDMS was characterized using a transmission electron microscope (TEM). The nanocomposites with 37.73 and 44.44 wt % of BO in PDMS were sectioned with a diamond knife on a Reichert Ultracut E ultramicrotome fitted with a cryochamber (model FC 4E, Reichert-Jung, Wien, Austria) at 120°C. The sections were then transferred to 100-mesh Formvar-coated grids. The TEM images of the samples were acquired at 80 kV with a Philips CM10 electron microscope.

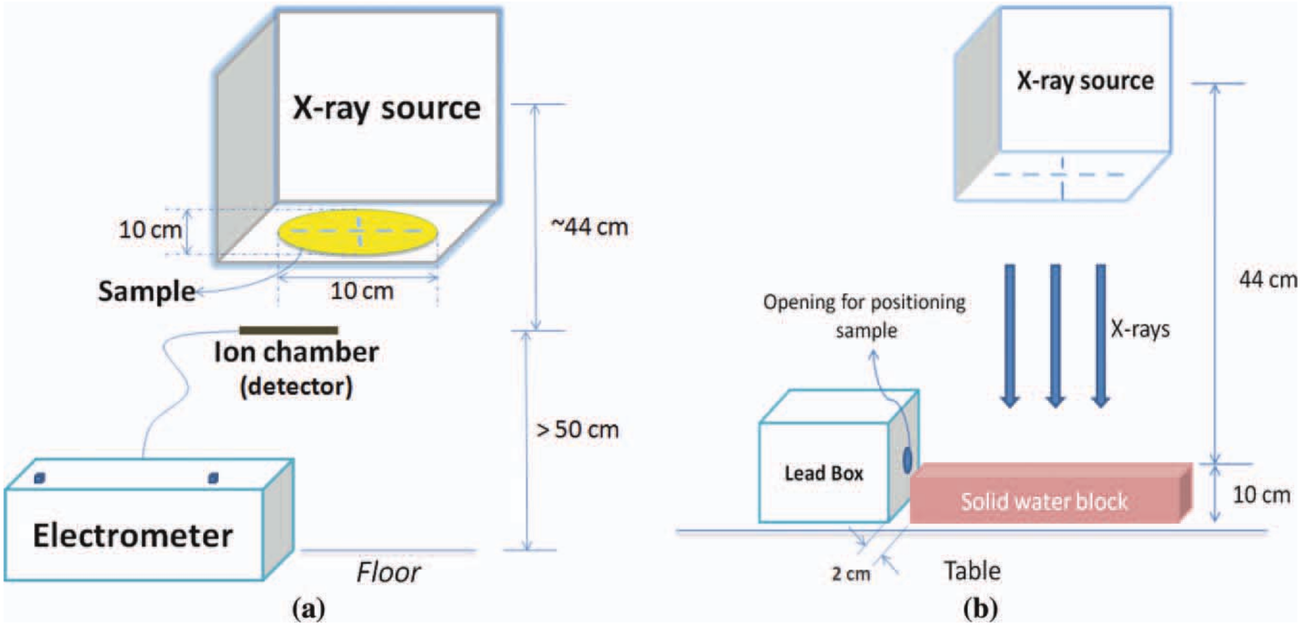

Figure 1. a: Experimental set-up for direct X-rays. b: Experimental set-up for scattered X-rays. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

All X-ray measurements were taken "with" and "without" the samples placed between the X-ray source and the detector. The results were normalized to the electrometer readings obtained with "no sample" between the source and the detector. Percentage attenuation is defined and calculated as follows:

$$\%\text{Attenuation} = \frac{\text{Electrometer reading without sample} - \text{Electrometer reading with sample}}{\text{Electrometer reading without sample}} * 100$$

The effects of concentration of high-Z material, and material thickness on X-ray attenuation were characterized for all energies of interest (40–150 kV). The material thickness was varied by stacking samples of equal sizes. The measurements were repeated for individual samples to ensure reproducibility of samples for a given concentration.

RESULTS AND DISCUSSION

Machine Characterization

The measured half value layers for the Ysio X-ray machine for tube potentials 40–150 kV are presented in Table I. Also included in the table is a measured HVL value for 81 kV.[20] The output of the X-ray machine (Ysio, Siemens) showed a linear trend with both mA and ms (Figures 2 and 3). The electrometer reading as a function of tube potential (40–150 kV) is also shown in Figure 4.

Material Characterization

The TEM images of the samples with 37.73 and 44.44 wt % of BO show spherical morphology of the BO nanoparticles within the size range of 90–210 nm (Figure 5). The nanoparticles seem to be fairly dispersed within the polymer matrix. All the attenuation measurements made with the PDMS/BO nanocomposites indicate that the normalized percentage-attenuation of the X-ray beam decreased with increase in energy for each of the fabricated samples. This is in accordance to the photoelectric interaction between the incident photon and the target material, the attenuation effect decreased with increase in the energy of the incident photons. The effects of the concentration of BO in PDMS and the sample thickness are discussed below.

Table I. First HVL Values for Tube-Voltages 40–150 kV Produced by Ysio Diagnostic X-ray Machine

Tube voltage (kV)	First HVL (mm)
40	1.25
50	1.8
60	2.35
70	2.6
81	3.1 (3 mm[20])
90	3.425
100	3.75
109	4.2
121	4.6
129	4.9
141	5.275
150	5.55

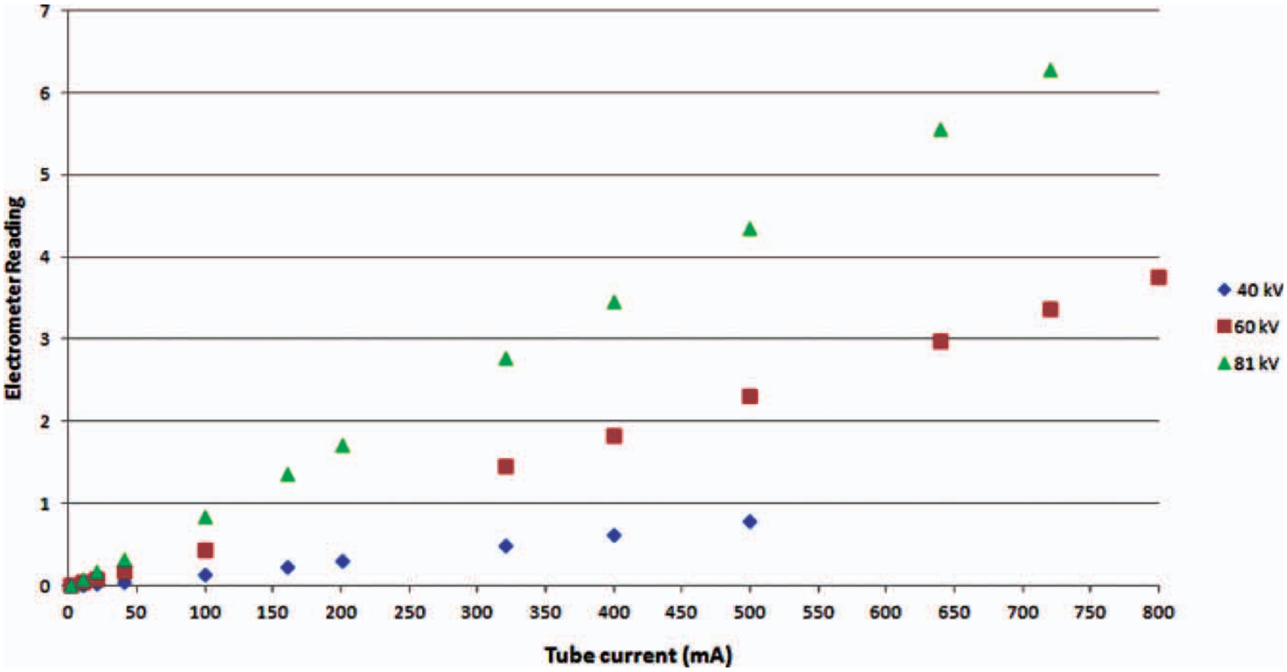

Figure 2. Tube-current linearity test for different tube-potentials with X-ray exposure-time = 500 ms. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Concentration of BO in PDMS (Under Primary X-ray Beam). All samples (of equal thickness) showed an increased attenuation with an increase in the concentration of high *Z* material (BO). Among all the samples, the nanocomposites with 44.44 wt % of BO (sample: BO 44.44) were the most effective for attenuating the X-ray beam (Figure 6).

Effect of Thickness (Under Primary and Scattered X-rays). It is a standard practice to indicate a "lead equivalence value" for a nonlead-based X-ray shield. To determine the "lead equivalence" of our nanocomposites, their attenuation characteristics were compared to 0.25-mm pure lead sheet for both primary and scattered X-rays. The attenuation characteristics of PDMS

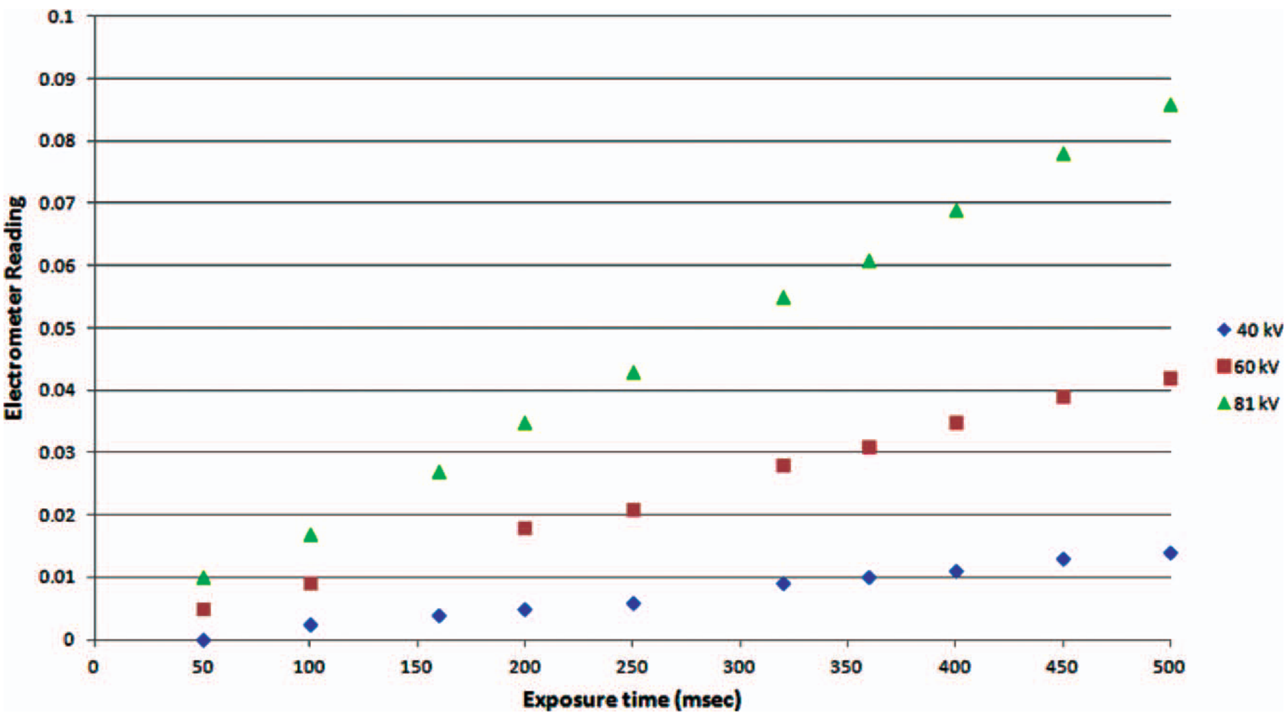

Figure 3. Exposure-time linearity test for different tube-potentials with X-ray tube-current = 10 mA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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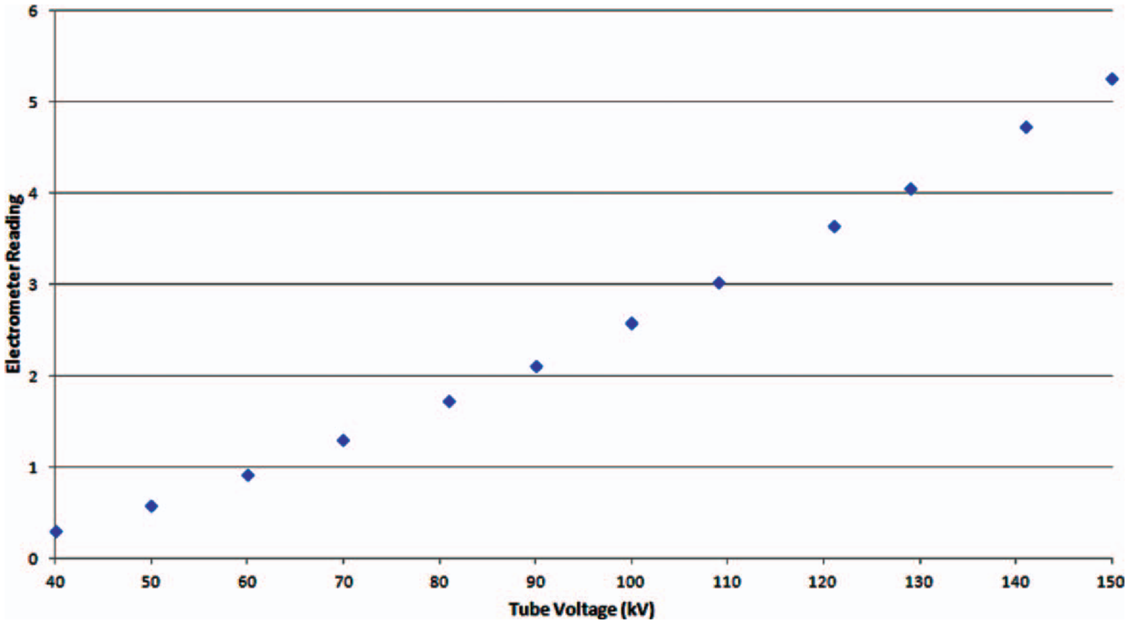

Figure 4. Electrometer reading as a function of tube potential (100 mAs, 250 ms). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanocomposites with different thicknesses under primary X-rays are shown in Figures 7 and 8. The enhanced attenuation by thicker samples of 37.73 and 44.44 wt % of BO in PDMS indicate an increased number of interactions (in the form of absorption or scattering) between the composite material and the X-rays. From Figure 7, it can be observed that the percentage attenuation of “BO 37.73” can be made equivalent to 0.25-mm pure lead sheet for a thickness lying in between 4.92 and 6.15 mm. Moreover, for a higher wt % composite of “BO 44.44” the 0.25-mm lead equivalence can be achieved with a 3.73-mm thick “BO 44.44” (Figure 8).

A more practical scenario of the application of X-ray shielding in IVR is the protection against X-rays scattered from the patient’s body. The 20-cm thick solid-water block was used to emulate the patient’s body. The percentage attenuation of “BO 37.73” and “BO 44.44” nanocomposites exposed to scattered X-rays are shown in Figures 9 and 10. When compared to the attenuation results under primary X-rays, both “BO 37.73” and “BO 44.44” show enhanced attenuation at all energies for a given thickness. This is due to the fact that some of the photons may get absorbed by the water block and only the scattered X-rays actually reach the target material (nanocomposite sample).

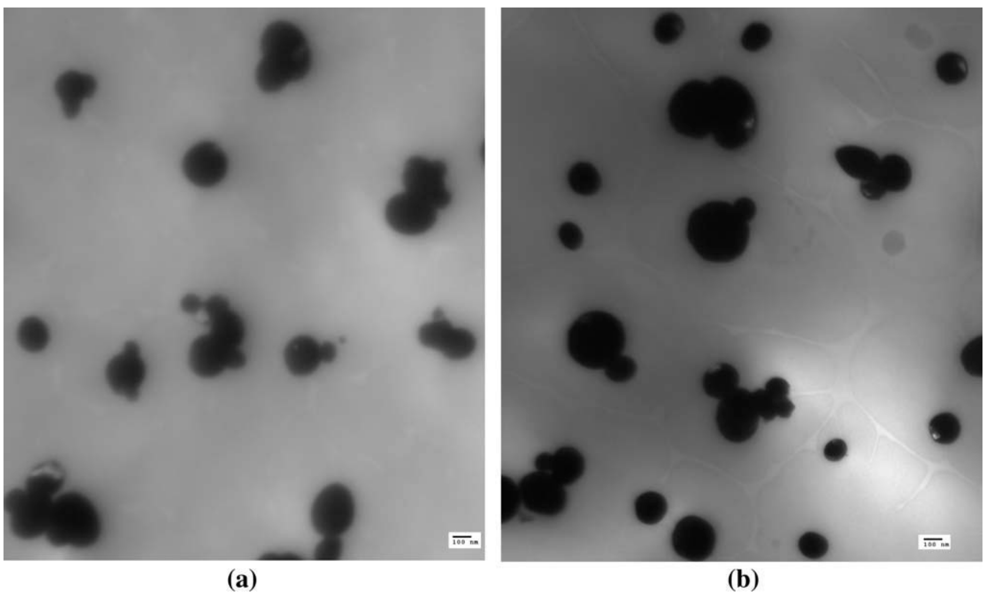

Figure 5. TEM images of PDMS nanocomposites with 37.73 wt% (left) and 44.44 wt% (right) of bismuth oxide nanoparticles taken at 34,000× magnification.

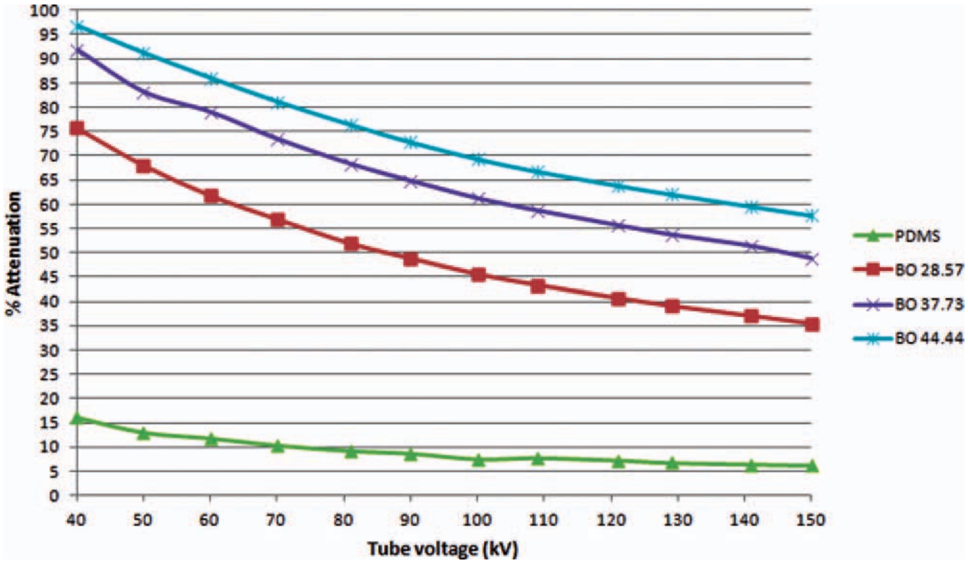

Figure 6. Percentage attenuation for different thicknesses (as indicated in the legend) of 'BO 37.73' nanocomposites using primary X-ray beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

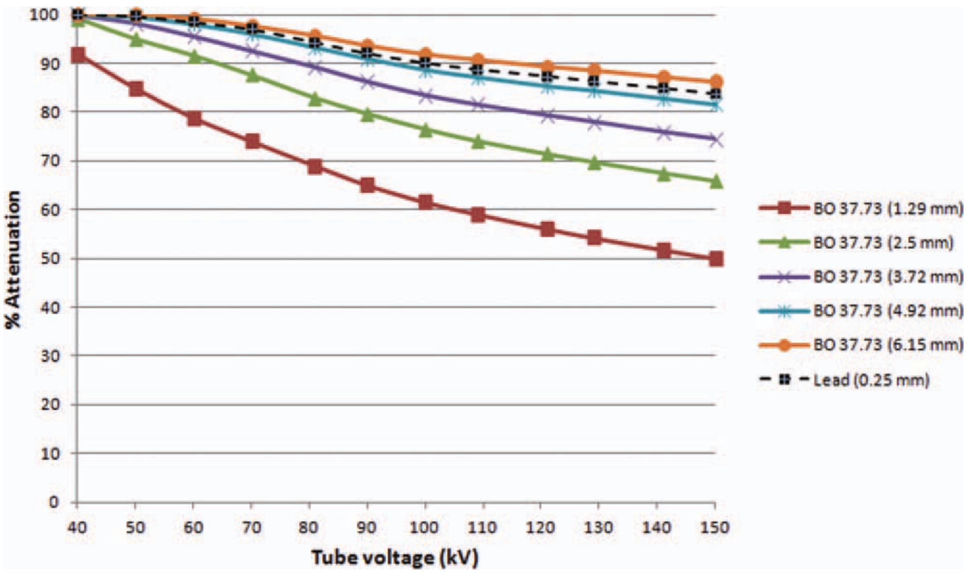

Figure 7. Percentage attenuation for different thicknesses (as indicated in the legend) of 'BO 44.44' nanocomposites using primary X-ray beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

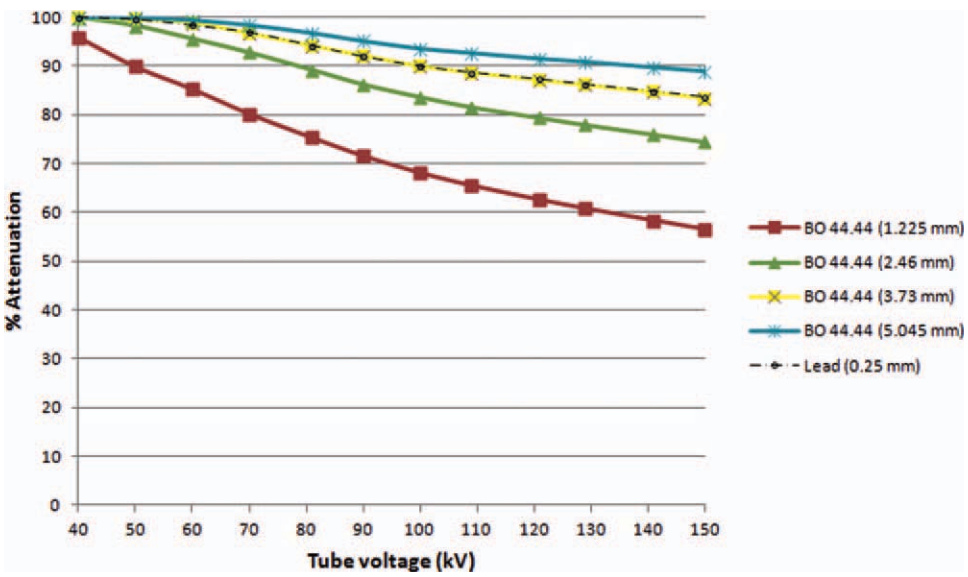

Figure 8. Percentage attenuation for different thicknesses (as indicated in the legend) of 'BO 37.73' nanocomposites using scattered X-rays generated at tube potentials ranging from 40 to 150 kV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

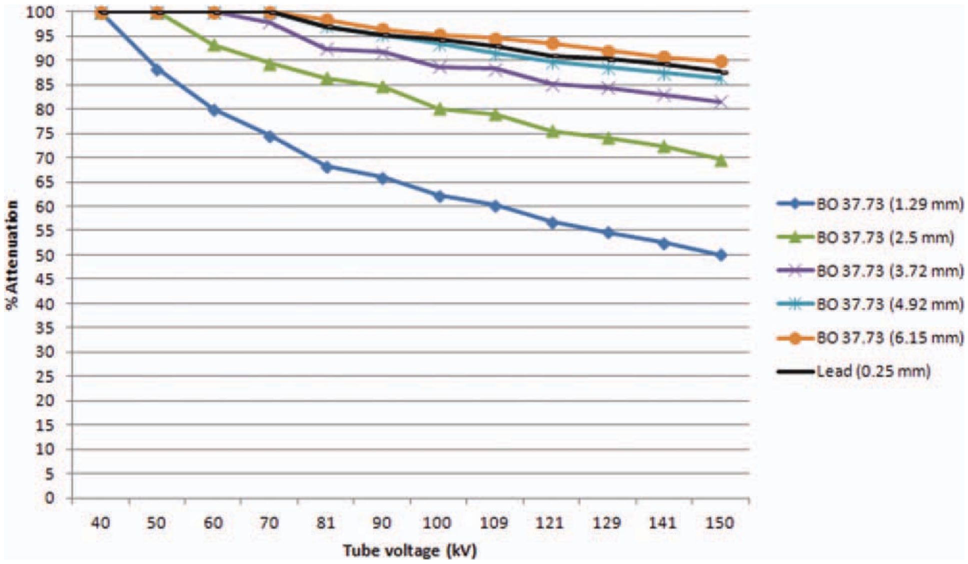

Figure 9. Percentage attenuation for different thicknesses (as indicated in the legend) of 'BO 44.44' nanocomposites using scattered X-rays generated at tube potentials ranging from 40 to 150 kV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The attenuation tests (primary and scattered X-rays) for individual samples of a given wt % and stacked configuration (different thicknesses of samples) were repeated three to four times and the results were completely reproducible.

CONCLUSIONS

We showed that novel PDMS nanocomposites made with different wt % of BO has the potential to effectively attenuate X-rays (primary and phantom-scattered) generated during IVR procedures and hence, can be considered as a protective material during IVR procedures. The attenuation characteristics of the polymer nanocomposite showed good repeatability. However, a detailed examination of the radiation-induced damage is essential for long-term usage of PDMS/BO-based radiation shields. Compared to conventional X-ray shielding materials, PDMS nanocomposites are nontoxic, cost-effective, and easy to fabricate (heavy, industrial-type metal extruders/compressors are not required as is case with most of the commercially available shields). However, to achieve the percentage-attenuation similar (97.5 and 98.7% at 102 kV and 80 mAs) to the commercially available lead/vinyl-based shields,[21] either the wt % of BO or the thickness of the nanocomposites need to be increased. A 0.25-mm lead-equivalent "BO 44.44" (3.73-mm thick) nanocomposite weighed twice as much as 0.25-mm pure lead sheet. It is important to note that these nanocomposites can be coated or painted and can conform to practically any shape of interest. This feature

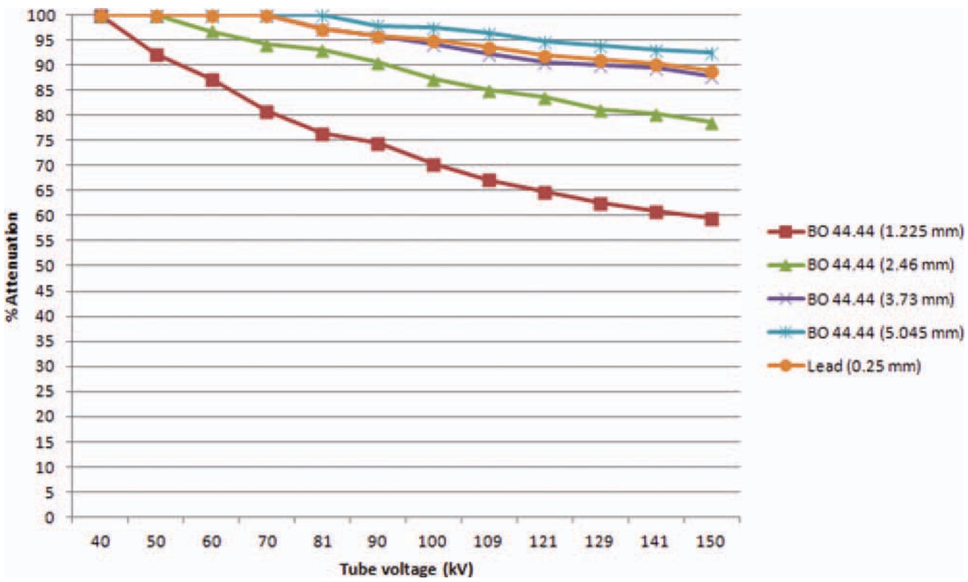

Figure 10. Percentage attenuation for different thicknesses (as indicated in the legend) of 'BO 44.44' nanocomposites using scattered X-rays generated at tube potentials ranging from 40 to 150 kV. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

opens up a range of applications for PDMS/BO nanocomposites and particularly the ones that are not dependent on the weight of the material. For example, the lead-based gonad protection worn by patients can be replaced, or conformable thyroid-shielding during mammography can be offered by the PDMS/BO nanocomposites. Moreover, PDMS composites dry off (polymerizes) at room temperature as well and hence, the extra cost and effort of using any additional equipment to dry/shape the material can be avoided. In conclusion, the material-characteristics of the PDMS/BO radioprotective nanocomposite allow it to be used as a filler-material in the walls (bunkers) of radiation treatment facilities, as a protective-coating on electronic devices, and also as protective shields conformable to specific anatomies of patients undergoing radiological procedures.

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