Silicone rubber composite reinforced by bismuth tungsten oxide as an effective gamma ray protective materials

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Abstract

The workers’ continual exposure to nuclear radiation makes it indispensable to invent and form lightweight materials as flexible radiation shields. So, in this article, silicone rubber SR inlaid with varying filler ratios of bismuth tungsten oxide Bi2(WO4)3 was produced. Mechanical properties, hardness, tensile strength, tensile modulus, and elongation at break, of the SR/Bi2(WO4)3 composites were studied as a function of filler concentration and irradiation dose. The Bi2(WO4)3 filler enhanced these properties. On the other hand, with augmentation of irradiation dose, hardness of the SR/Bi2(WO4)3 composites increased and the other mechanical properties decreased. Under accurate geometry conditions, the gamma ray attenuation coefficients of the SR/Bi2(WO4)3 composites were studied at the energies 661.66, 1173.24, and 1332.5 keV. The attenuation parameters, linear attenuation coefficients $\mu$, experimental mass attenuation coefficients $\sigma_{\text{exp}}$, and half value layer HVL results revealed that the attenuation ability of the composite was enhanced with the increase of Bi2(WO4)3 concentration. The results of $\sigma_{\text{exp}}$ were confirmed through their congruence with the theoretical calculations of mass attenuation coefficients $\sigma_{\text{theo}}$. Considering the merits of lightweight, high mechanical properties, superior attenuation ability, and appropriate irradiation resistance, the produced SR/Bi2(WO4)3 composite is suitable as durable and flexible gamma ray shields such as anti-radiation coats, gloves, shoes.

Keywords Bi2(WO4)3 silicone rubber · Shielding materials · Gamma irradiation · Mechanical properties

Introduction

In the nuclear domains, shielding materials are one of the most important nuclear safety measures [1, 2]. Critical criteria of the shielding materials selection are high attenuation efficiency, lightweight, adequate chemical, mechanical, and thermal properties, and stability under the influence of high irradiation doses [1–5]. In this regard, the various properties of polymeric composites such as lightweight, the large degree of flexibility, suitable chemical, thermal, and mechanical properties as well as low cost have enabled them to play a pivotal role [6–9]. But, it is well known that the polymeric materials by themselves have not adequate capabilities to attenuate nuclear radiation. So, they are inlaid by a high-efficiency filler to resist nuclear radiation, such as high Z-elements in gamma rays case and high cross-section elements for neutrons. High-Z elements such as Bi, W, Ba, Fe, etc. become a potential substitute for the Pb due to their low toxicity and effective physical, chemical, and mechanical properties [10–13]. Many researchers have studied the various polymeric composites with various fillers and still in order to achieve high attenuation capabilities and appropriate physical, chemical, and mechanical properties for the applications [5–12]. In 2002, Gwaily studied the attenuation of 661.66 keV gamma ray in Galena-rubber composites and reported 0.295 cm$^{-1}$ as a linear attenuation coefficient and 2.3 cm as a HVL at the highest value of Galena [14]. In their study to silicone rubber/Bi2O3 composites (2015), El-Fiki et al. found that 60 phr of Bi2O3 is the optimal composition although they studied up to 80 phr and this is due to the deterioration of mechanical properties above 60 phr [15]. In 2018, Pin Gong et al. studied the transmission of gamma rays energies 661.66, 1173.24, and 1332.5 eV and the transmission of thermal neutron for methyl vinyl silicone rubber (VMQ) filled by of B4C, PbO, and benzophenone (BP). They also studied the morphological observations, crosslinking density, mechanical properties, and thermal stability [16]. In 2019, Hoda Alavian et al. were...
used a MCNP code to study the attenuation ability of polymer composites reinforced by different sizes and proportions of tungsten particles. The authors concluded that the filler proportion more efficient than the filler size in attenuating gamma rays [17]. And finally, there are a large number of other studies primarily focused on investigating the attenuation of gamma rays of different types of polymers reinforced with different elements [18–24].

In our study, we used a bismuth tungsten oxide \( \text{Bi}_2(\text{WO}_4)_3 \) compound as a filler to inlay the silicone rubber SR composite because it collects between the properties of W and Bi. The mechanical properties of the considered SR/Bi\(_2\)(WO\(_4\))\(_3\) composite were examined. The attenuation performance was tested using three different energies of gamma rays. Finally, the two best composites of SR/Bi\(_2\)(WO\(_4\))\(_3\) were chosen and the effect of gamma ray irradiation on their mechanical properties was studied. The novelty of the current study stems from the inlaying of the polymer by \( \text{Bi}_2(\text{WO}_4)_3 \) for the first time and its access to high concentrations within the polymer reached 40 phr. We obtained unique results for the ability of the newly produced SR/Bi\(_2\)(WO\(_4\))\(_3\) to attenuate gamma rays along with its manifesting high flexibility that was clearly observed in the mechanical properties results. In addition, the SR/Bi\(_2\)(WO\(_4\))\(_3\) composite showed an efficient resistance to high irradiation doses.

**Experimental procedures**

Silicone rubber SR (Polydimethylsiloxane PDMS, ELASTOSIL R 401/20) as a host material was filled by different ratios 10, 20, 30, and 40 phr (parts per hundred) of bismuth tungsten oxide \( \text{Bi}_2(\text{WO}_4)_3 \) [99% purity]. In the synthesized composite as listed in Table 1, 5 phr of zinc oxide and 2 phr of stearic acid were used as activators, 2.5-bis-(tert-butylperoxy)-2.5 dimethylhexane was utilized as the cross-linker, and peroxide was used as curing agent. All chemicals were used as received without any further purification.

The proposed materials were weighed and then mixed using two-roll mills (outside diameter 470 mm, working distance 300 mm, and speed of slow roll 24 rpm). The mixture was well stirred mechanically at 300 rpm at room temperature for 30 min. The SR/Bi\(_2\)(WO\(_4\))\(_3\) composite were subjected to sheeting on the mill and are cured in an electrically heated hydraulic press at 150° ± 1 °C and a pressure of about 4 MPa for 5 min. The SR/Bi\(_2\)(WO\(_4\))\(_3\) composites were produced with dimensions 10 × 10 × 0.3 cm\(^3\). The mechanical strength of the produced composites was measured using Universal Testing Machine (LR 50 K-Lloyd Instruments, UK) according to ASTM D412-06 standard testing. The tensioned specimens were in the form of rectangular bars of dimension 300 mm × 30 mm × 3 mm placed between the grips of the UTM and were pulled until failure. The hardness was measured using a hardness durometer (Shore A) according to ASTM D 2240–05. The density of the produced composites was measured by Archimedes principle [7, 25]

\[
\rho = \frac{W_a}{W_a - W_w} \times \rho_w
\]

where, \(W_a\) is the weight of the composite in the air, \(W_w\) its weight in the distilled water, and \(\rho_w\) is the distilled water density = 0.998 g/cm\(^3\).

![Fig. 1 Measuring system of the transmitted gamma-ray](image)
A collimated beam of the three gamma ray energies 661.66, 1173.24, and 1332.5 keV that emitted from $^{137}$Cs and $^{60}$Co radioactive point sources were used to study the attenuation capability of the produced SR/Bi$_2$(WO$_4$)$_3$ composites. A 3in. × 3in. NaI(Tl) detector placed inside a thick lead sheet as shown in Fig. 1 was used to measure the transmitted gamma ray beam.

A $^{60}$Co gamma ray cell (2000 Ci) was used to irradiate the produced SR/Bi$_2$(WO$_4$)$_3$ composites. The activity of the irradiation facility was 11,994.8 Ci at the time of installation (2002). The absorbed dose rate was found to be in the range $5.03565 \pm 60.078$ kGy.h$^{-1}$ overall the time of the experimental part of the present work. The overall uncertainty of the absorbed dose rate is $\pm 2.2\%$ at the 95% confidence level. Mechanical properties, hardness, tensile strength, tensile modulus, and elongation at break of the SR/Bi$_2$(WO$_4$)$_3$ composites were studied at different irradiation doses.

Results and discussion

Ingress of Bi$_2$(WO$_4$)$_3$ filler to the SR composite matrix significantly increases the hardness, tensile strength, tensile modulus, and elongation at break as shown in Fig. 2. Permeation of the Bi$_2$(WO$_4$)$_3$ filler that is considered the hardest surface metal in the synthesized SR composite increases the SR matrix-filler bonding causing the surface hardness augmentation. The increase in the density with the increase in the filler ratio is due to that the Bi$_2$(WO$_4$)$_3$ filler creating a Bi$_2$(WO$_4$)$_3$ – SR network connection, which causes a tighter package, Bi$_2$(WO$_4$)$_3$ – SR chemical interaction and interface adhesion, and closeness in the gaps of the neighboring grains. Hence, the density results confirm the formation of a strong connection between the Bi$_2$(WO$_4$)$_3$ filler and SR matrix. The density and hardness results are in tune and confirm each other.
The values of density were increased as 1.773, 2.418, 3.062, 3.707, 4.352 gm/cm³ for 0, 10, 20, 30, and 40 phr of Bi₂(WO₄)₃, respectively. The addition of Bi₂(WO₄)₃ filler increases the crosslinking density of the SR composite leading to a decrease in the chain mobility. The domination of Bi₂(WO₄)₃ filler on the SR matrix restrains the chains crosslink joints resulting in augmentation of tensile strength, tensile modulus, and elongation at break. The mechanical properties of the synthesized SR composite were enhanced by 91.335%, 131.404%, 162.963%, and 168.602% for elongation at break, tensile modulus, hardness, and tensile strength, respectively at 40 phr of Bi₂(WO₄)₃.

By drawing the attenuation curves between the transmitted gamma ray intensity and the different thicknesses of the SR/Bi₂(WO₄)₃ composites barriers, the linear attenuation coefficients µ were obtained, where the slope of the curve represents the linear attenuation coefficient. The linear attenuation coefficients values were used to deduce the experimental values of mass attenuation coefficients σ_exp based on the relation µ/ρ and the half value layers HVL by 0.693/µ. On the other hand, the theoretical values of mass attenuation coefficients σ_theo were calculated from the WinXcom computer program (Version 3.1). The obtained values of µ, σ_exp, and σ_theo, and HVL as a function in the Bi₂(WO₄)₃ filler concentration for the studied energy lines.
of γ-rays are shown in Figs. 3, 4, and 5 respectively. The observed augmentation in the linear and mass attenuation coefficients and the dwindling in the half-value layer with the increase of the Bi$_2$(WO$_4$)$_3$ filler concentration indicates an improvement in the attenuating ability of the composite. It is known that the gamma ray with energies less than 3 MeV interact directly with the atomic electrons, photon-electron interaction. Therefore, by increasing the high-Z element, here we mean Bi$_2$(WO$_4$)$_3$, the material becomes crowded by electrons and thereby the composite becomes denser. This electronic overcrowding leads to an increase of the gamma ray interaction with SR/Bi$_2$(WO$_4$)$_3$ composites and therefore increases the attenuating capability. The values of HVL improved by 67.784%, 61.672%, and 63.923% for 661.66, 1173.24, and 1332.49 keV, respectively.

The comparison between experimental and theoretical values of mass attenuation coefficient showed a quite satisfactory agreement between them, with some divergence. The relative deviation RD between experimental and theoretical results of mass attenuation coefficients was calculated using the following relation \[ [\text{RD} = \left(\frac{\text{Theoretical} - \text{Experimental}}{\text{Experimental}}\right) \times 100 \]

For 661.66 keV gamma ray energy that emitted from monoenergetic source ($^{137}$Cs), the difference between experimental and theoretical results is in the range of the experimental error values. On the other hand, the divergence between the experimental and theoretical for some points of two gamma-ray lines of $^{60}$Co may be attributed to the multi-energetic lines of the source and the impurities in the commercial ores of the produced materials.

The 30 and 40 phr of Bi$_2$(WO$_4$)$_3$, which are the highest attenuator in the SR/Bi$_2$(WO$_4$)$_3$ composite were selected to study the effect of irradiation on the mechanical properties. The mechanical properties were influenced by the increase of irradiation dose as shown in Fig. 6. The hardness was slightly increased while tensile strength, tensile modulus, and elongation at break were decreased for irradiated SR/Bi$_2$(WO$_4$)$_3$ composites relative to that of the un-irradiated. In rubber composites, both crosslinking and degradation reactions side-by-side are induced by gamma irradiation. The growth of the hardness was attributed to the increase of the crosslinking, which causes difficulty in the mobility of the chain segments. The downturn in tensile properties arose out of the aggregations induced inside the SR/Bi$_2$(WO$_4$)$_3$ composite by gamma irradiation, which lead to structural deformation. In the SR/Bi$_2$(WO$_4$)$_3$ composites, the predominance of aggregations breaks the main chain and reinforces the crosslink of the branch chains, which reduces the tensile strength, tensile modulus, and elongation at break. For 30 phr of Bi$_2$(WO$_4$)$_3$, the 200 kGy of gamma irradiation dose caused a reduction by 70.837% in tensile strength, 89.222% in tensile modulus, and 91.724% in elongation at break. In the same respect, for 40 phr of Bi$_2$(WO$_4$)$_3$, 71.243, 82.478, and 88.494 reductions were observed in tensile strength, tensile modulus, and elongation at break respectively. However, the hardness enhanced by 42.188 and 30.986% for 30 and 40 phr of Bi$_2$(WO$_4$)$_3$ respectively.

| Bi$_2$(WO$_4$)$_3$ concentration | RD%       |
|-------------------------------|----------|
|                               | $E_{\gamma}=661.66\text{keV}$ | $E_{\gamma}=1173.24\text{keV}$ | $E_{\gamma}=1332.49\text{keV}$ |
| 0                             | 10.885   | 13.730   | 17.634   |
| 10                            | 0        | 7.435    | 1.869    |
| 20                            | 2.554    | 8.436    | 9.018    |
| 30                            | 4.574    | 6.453    | 0.929    |
| 40                            | -3.330   | 7.022    | 3.238    |
Conclusion

A new formulation of non-toxic and lightweight SR/Bi2(WO4)3 composite has been studied to be used as gamma ray flexible protective materials. An improvement in the mechanical properties of SR/Bi2(WO4)3 composites was observed with the increase of the used Bi2(WO4)3 filler. The 40 phr of Bi2(WO4)3 owns utmost attenuating ability, which means only a small thickness is needed. Gamma irradiation of the SR/Bi2(WO4)3 composites increased the hardness and deteriorated the tensile strength, tensile modulus, and elongation at break. The 40 phr of Bi2(WO4)3 of the new SR/Bi2(WO4)3 composite has many advantages that qualify it to be flexible radiation shields in many nuclear applications such as anti-radiation coats, gloves, shoes.

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Declarations

Conflicts of interest The authors declare no conflict of interest.

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