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Evaluation of Micro- and Nano-Bismuth(III) Oxide Coated Fabric for Environmentally Friendly X-Ray Shielding Materials

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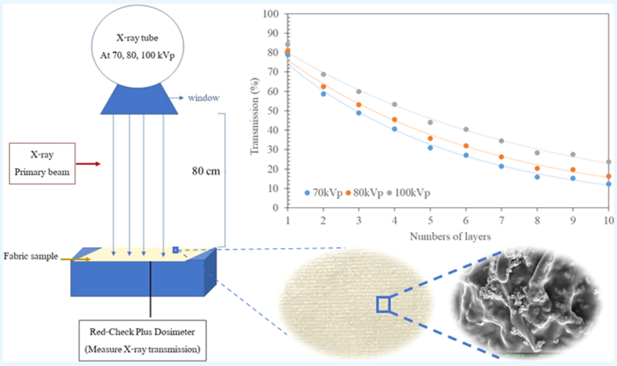
ABSTRACT: This research focuses on the development of environmentally friendly textile-based shielding composites, from micro-sized and nanosized Bi_2O_3 particles, against ionizing radiation. Polyester fabric dyne-coated with either micro- or nano-Bi_2O_3 particles shields some X-rays but the effectiveness is poor. With only ∼58% uptake of micro-sized Bi_2O_3 particles dyeing on polyester fabric, the insufficient amount of Bi_2O_3 leaded to the low density of particles, resulting in only 30% of X-ray shielding at 80 kVp. Cotton fabric coated with either micro- or nano-Bi_2O_3/poly(vinyl alcohol) (PVA) composites, on the other hand, demonstrated the capacity to attenuate X-ray generated by high diagnostic X-ray tube voltages of 70−100 kVp, in compliance with medical protection requirements. The X-ray attenuation performance of cotton fabric coated with either micro-Bi_2O_3/PVA or nano-Bi_2O_3/PVA nanocomposite decreased progressively with increasing tube acceleration voltages, however their ionizing radiation-shielding performance enhanced with the number of fabric layers. Interestingly, for all X-ray tube voltages evaluated, the micro-Bi_2O_3/PVA composite outperformed the nano- Bi_2O_3/PVA composite in terms of X-ray shielding. At a weight ratio of 66.7% Bi_2O_3, 10 layers of cotton fabric coated with micro- Bi_2O_3/PVA composite can attenuate 90, 85, and 80% of X-ray photons at 70, 80, and 100 kVp, respectively. As a result, these less harmful X-ray shielding materials have the potential to replace lead-based composites, which are highly toxic to human health and have negative environmental consequences.



■ INTRODUCTION

Lead (Pb) composites are widely recognized as radiation-shielding materials that attenuate X-ray scatter radiation due to the high atomic number (Z), high density, low cost, ease of processing, and excellent shielding capabilities of lead (Pb) against penetrative γ radiation. Lead composites are used to make a variety of radiation-protective equipment, including lead aprons and thyroid shields, which are the standard shields for the radiation protection of medical personnel in interventional radiology.[1] The disadvantages of lead composites include their weight, human health concerns, and environmental contamination. Researchers are currently concentrating on developing non-lead materials that can successfully replace lead composites as a radiation-shielding material. Numerous experimental studies have focused on creating techniques that can convert metal or mineral powders with adequate content into polymer sheets for efficient shielding and durability to avoid tearing and cracking.

Bismuth(III) oxide (Bi_2O_3), one of the high-Z compounds, was often chosen to incorporate into a polymer at high loading levels to produce X-ray shielding materials because of its relatively low cost, thermal stability, radiopacity, low environmental impact, and absent or low toxicity.[2] Maghrabi et al.[3] studied the shielding effect of barium sulfate ($BaSO_4$) and Bi_2O_3 on the coated fabric samples. The fabric samples were coated with a combination of $BaSO_4$, Bi_2O_3, and poly(vinyl chloride) (PVC) resin using a knife-edge with roller on a Mathis coating machine. They concluded that the shielding capacity of the sample increased due to the high atomic number and high density of bismuth. Later, they investigated the effectiveness of Bi_2O_3 coating using PVC printing resin on polyester and nylon fabrics for X-ray protection[4] and confirmed that coated polyester fabrics with over 50% Bi_2O_3 showed enhanced shielding ability. Evaluation of the effectiveness and shielding performance of a non-lead radiation-shielding fabric containing bismuth oxide was also done by Kang et al.[5] The bismuth nanopowder (containing Bi_2O_3, $BiNaO_3$, and BiN_3O_9; fine spherical particles of <5 μm) with radiation-shielding effects was coated onto a urethane resin to fabricate sheets that can be used as a fabric or cloth. The results showed that the radiation-attenuation capability of one layer of the fabric was 49.9% at a tube voltage of 80 kVp and gradually increased as the number of fabric layers

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increased. Electrospun Bi_2O_3 nanoparticles/poly(vinyl alcohol) (PVA) nanofiber mats with different Bi_2O_3 loadings (0−40 wt %) fabricated for the X-ray shielding purpose were also proposed by Hazlan et al.[6] Their study showed that a 35 wt % Bi_2O_3/PVA nanofiber mat has the highest X-ray attenuation ability. The attenuation characteristics of PVC composites with micro- or nanoparticles of Bi_2O_3 with respect to diagnostic X-rays (40−100 kVp) were revealed by Shik and Gholamzadeh.[7] They also claimed that Bi_2O_3 can be used as a suitable alternative to PbO in shielding designs.

Micro- or nanoparticles dispersed in a polymeric matrix, to the best of our knowledge, can be used to create effective radiation shields. As a result, polymer-based composites are particularly appealing as radiation-shielding materials. There are many types of polymers applied as matrices in non-lead radiation-shielding composites, including PVC,[3,4,7] urethane resin,[5] PVA,[6] silicone,[8] poly(ethylene terephthalate),[9] and epoxy resin.[2] However, most of them are not biodegradable systems.

In the present study, environmentally friendly and biodegradable textile-based shielding composites against ionizing radiation were produced from polyester and cotton fabrics coated with either Bi_2O_3 particles or Bi_2O_3/PVA composites, and their ability to shield diagnostic X-rays (70, 80, and 100 kVp) was investigated. Polyester fabric was dyed using dispersed micro- or nano-Bi_2O_3 particles in heated ethanol. Cotton fabric was treated with NaOH solution before being coated with either Bi_2O_3 particles by the dyeing method or biodegradable PVA composites containing either micro- or nano-Bi_2O_3 particles by a simple hand-coating method. The morphological properties of the fabrics both before and after coating were examined by SEM, and their chemical structures were confirmed by FTIR. The thickness, weight, and color of the samples were also measured. Lastly, the X-ray characteristics of the proposed biodegradable textile-based shielding composites were investigated in terms of the shielding performance of different coated layers of the dyed fabrics as well as the fabrics coated with the Bi_2O_3/PVA composite.

■ EXPERIMENTAL SECTION

Materials. Bismuth(III) oxide (Bi_2O_3) nanopowder with the particle size of 90−210 nm and 99.9% purity and Bi_2O_3 microparticles with the particle size of 10 μm and 99.9% purity were purchased from Aldrich. Poly(vinyl alcohol) (PVA), M_w 89 000−98 000 g/mol with 99% hydrolyzed, was also purchased from Aldrich. Glutaraldehyde (1.2% w/v) was obtained from Fluka. Sulfuric acid, acetic acid, and methanol were purchased from Carlo Erba Reagenti SpA, J. T. Baker, and Fisher Chemicals, respectively. Polyester and cotton fabrics were purchased from a local market in Chonburi Province, Thailand.

Application of Bi_2O_3 on Polyester and Cotton Fabric. Before dyeing, the cotton fabric was immersed in 0.01 M NaOH solution (1 g fabric: 210 mL NaOH solution) for 1 h at 90 °C. After removing the remaining NaOH with distilled water, the treated fabric was air-dried at room temperature for 30 min before being dried in a hot air oven at 70 °C for 30 min.

In the dyeing process, both polyester and cotton fabrics were immersed in a suspension of Bi_2O_3 particles in a suitable solvent at suitable conditions before washing out the excess particles of the fabrics. In order to form a stable dispersion, 2.0 g of Bi_2O_3 powder was mixed with 40 mL of ethanol by slow stirring. Then the fabric was dipped into the resulting suspension and continuously stirred at 90 °C for 2 h. After coating, the excess amount of Bi_2O_3 on the fabric surface was washed thoroughly by ethanol and let to dry at room temperature. The Bi_2O_3-coated fabric was subsequently dried at 70 °C for 30 min in a hot air oven. The %uptake was calculated using the following formula

$$\%\ \text{uptake} = \frac{(W_f - W_i)}{W_i} \times 100 \tag{1}$$

where W_i and W_f are the weights of the fabric before and after coating, respectively.

Bi_2O_3/PVA Composite Coating. A PVA solution (10% w/v) was prepared by dissolving PVA in distilled water at 90 °C under stirring for 2 h. Then 10 mL of PVA solution was mixed with 2.0 g of Bi_2O_3 particles. After well mixing, 2.8 mL of cross-linking solution, prepared from 50% w/v methanol (the quencher), 10% w/v acetic acid (the pH controller), 1.20% w/v glutaraldehyde, and 10% w/v sulfuric acid (the catalyst), with a solution volume ratio of 3:2:1:1, were also added into the mixture under constant stirring for 10 min, in order to obtain a uniform distribution of Bi_2O_3 in the PVA/Bi_2O_3 composite. The mixture was coated on a fabric (10.16 × 10.16 cm^2) using a bar-coater with a short K-Bar No. 200 (K Hand coater, RK Printcoat Instruments, U.K.) and cured at 70 °C for 1 h. The coating was performed twice for each side of the fabric. Samples were named using the following description: NP = nano-Bi_2O_3, MP = micro-Bi_2O_3, C = PVA/Bi_2O_3 composite coating, and 1−10 = numbers of fabric layer.

Characterization. The functional groups presenting on the fabric samples were investigated using a Fourier-transform infrared spectrometer (PerkinElmer Frontier FTIR/NIR system). For each measurement, 12 scans were co-added with a resolution of 4 cm^{-1} and the wavenumbers ranged from 400 to 4000 cm^{-1}.

The surface morphology of the fabric samples was analyzed using an LEO 1450 VP scanning electron microscope (SEM) and Zeiss EVO MA10 SEM. Before the observation, the surfaces were coated with a thin layer of about 10 nm of gold via the sputter coating technique.

Color measurement was carried out using an FRU WR18 colorimeter. The color of the fabric samples was identified using Commission Internationale de l'Eclairage (CIE) $L^*a^*b^*$ coordinates, where L^* indicates lightness (+ = lighter, − = darker), a^* is the red/green coordinate (+ = redder, − = greener), and b^* is the yellow/blue coordinate (+ = yellower, − = bluer).

The fabric mass per unit area of the fabric samples was also calculated using eq 2

$$\text{mass per unit area} = \frac{\text{fabric mass}}{\text{area}} \tag{2}$$

X-Ray Shielding Measurement. Bi_2O_3-coated fabric samples were tested for X-ray attenuation using Radcal 9095, chamber model 10x9-6 S/N 03-0080. In radiography, the source to chamber distance was 80 cm, which is the distance from the X-ray tube (source) to the center of the fabric (the radiation detector was just below the fabric). The fabric samples, with an exposure area of 10.16 × 10.16 cm^2, were exposed to X-rays at tube voltages of 70, 80, and 100 kVp at tube current and a time of 12.5 mA, and the transmission was measured by a dosimeter in mR. Five different positions on each sample were exposed independently and the mean value for each sample was calculated. The same procedure was used on a lead apron, thyroid shield, and uncoated fabrics to compare the shielding abilities among the samples. Each sample's shielding ability was

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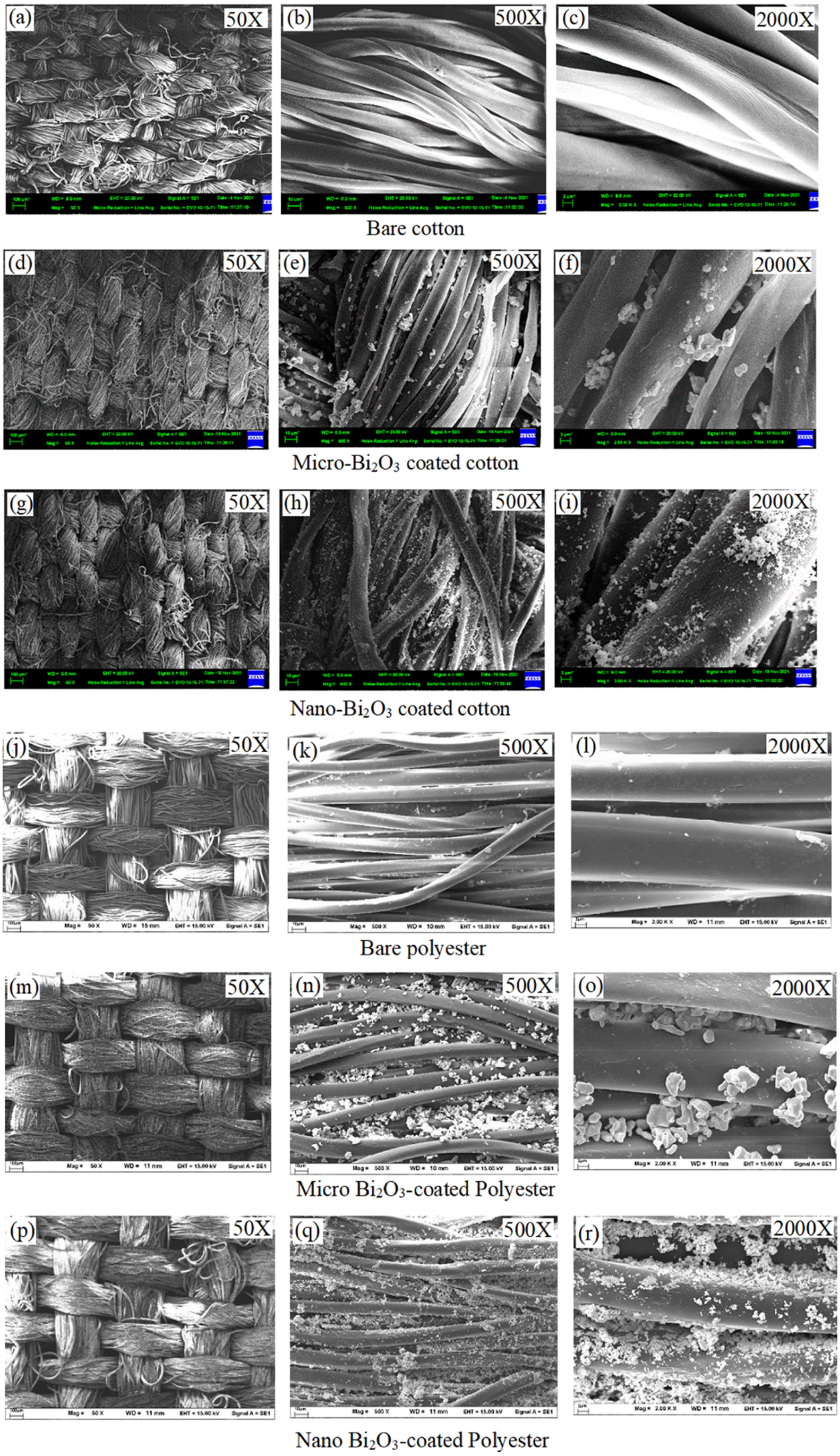

Figure 1. continued

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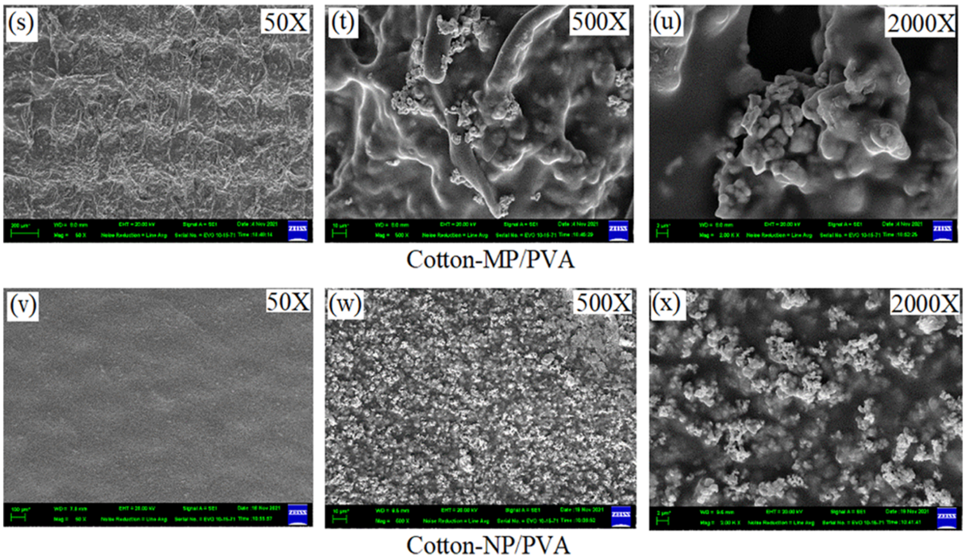

Figure 1. SEM micrographs of the surface of the treated fabric samples: (a−c) bare cotton, (d−f) micro-Bi_2O_3 on cotton, (g−i) nano-Bi_2O_3 on cotton, (j−l) bare polyester, (m−o) micro-Bi_2O_3 on polyester, (p−r) nano-Bi_2O_3 on polyester, (s−u) micro-Bi_2O_3/PVA composite on cotton, and (v−x) nano-Bi_2O_3/PVA composite on cotton.

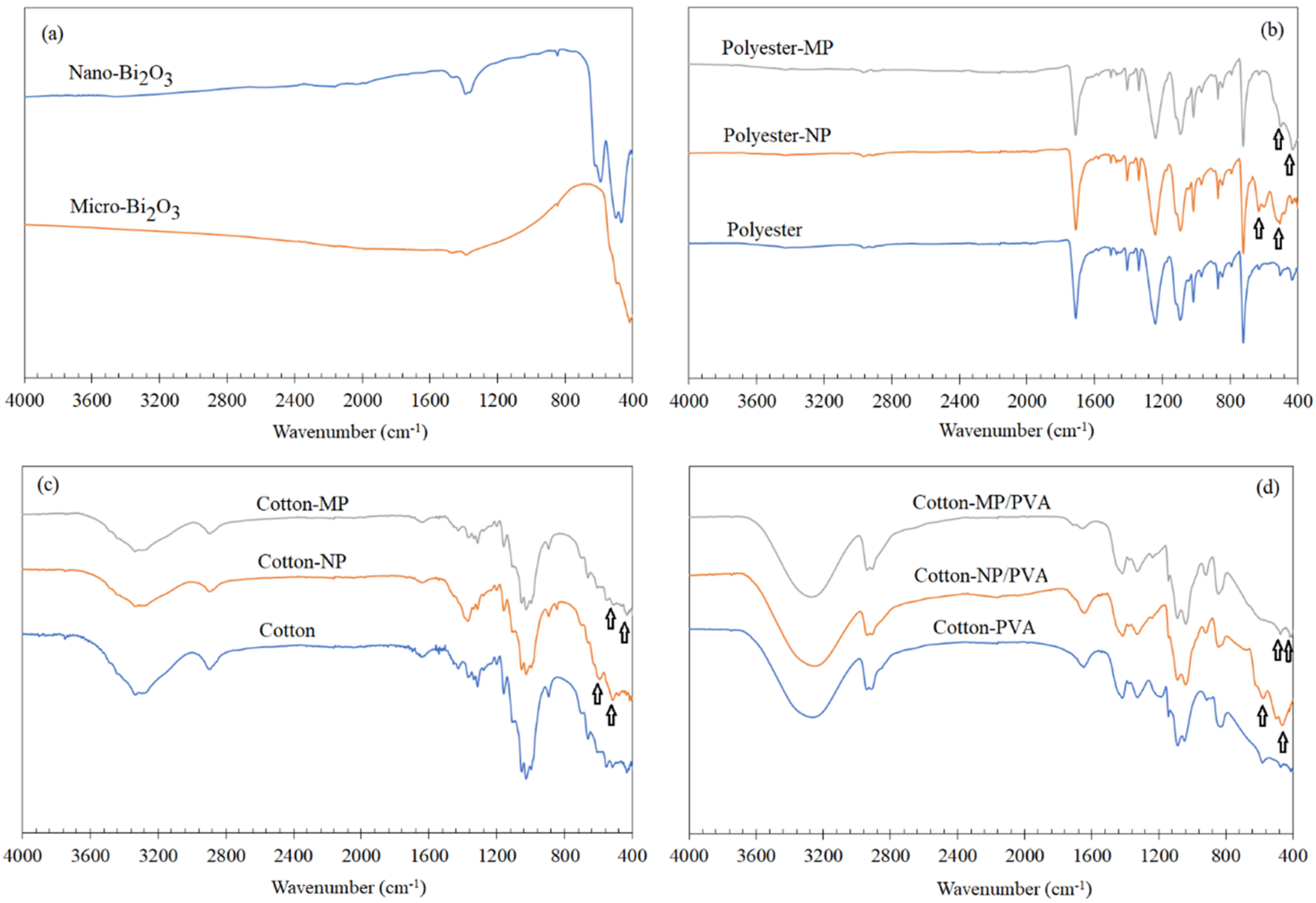

Figure 2. ATR-FTIR spectra of (a) micro- and nano-Bi_2O_3 particles, (b) polyester, micro-Bi_2O_3-coated polyester (polyester-MP), nano-Bi_2O_3-coated polyester (polyester-NP), (c) cotton, micro-Bi_2O_3-coated cotton (cotton-MP), nano-Bi_2O_3-coated cotton (cotton-NP), and (d) PVA-coated cotton (cotton-PVA), micro-Bi_2O_3/PVA composite-coated cotton (cotton-MP/PVA), and nano-Bi_2O_3/PVA composite-coated cotton (cotton-NP/PVA).

assessed by comparing its transmission doses to the measured transmission doses for air reference.

RESULTS AND DISCUSSION

Surface Morphology. In general, dyeing is the primary process by which a white material is colored. In this study, we

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used nano- and micro-sized Bi_2O_3 particles on two different types of fabric: cotton and polyester. The surface of the treated fabric samples was investigated and the SEM images are shown in Figure 1. The pristine cotton and polyester fabrics' surface morphology reveals a smooth longitudinal structure of the textile fibers. It is clearly seen in the figure that both nano- and micro-Bi_2O_3 particles are well distributed on the surface of the fabrics with some degree of aggregation. The size of the particles is crucial in determining their adhesion to the fiber. Large-particle agglomerates should be easily detached from the fiber surface, whereas small particles should penetrate deeper and adhere to the fabric matrix strongly. In addition, both nano- and micro-Bi_2O_3 showed better deposition on the polyester fabric than cotton fabric. This could be because polyester, which contains the ester functional group in its main chain, can interact well with Bi_2O_3.[10]

FTIR Analysis. The chemical structures of the micro- and nano-Bi_2O_3-coated fabrics were examined by ATR-FTIR spectroscopy and the typical FTIR spectra are shown in Figure 2. For nano-Bi_2O_3, the characteristic peaks, showing the presence of the Bi−O bond, appeared at 468−499, 586, 627, and 846 cm^{-1} correspond to the stretching vibration mode of Bi−O−Bi in Bi_2O_3. The peak at 1381 cm^{-1} corresponds to the bending vibrations of O−H bonds of the absorbed water. All of the peaks are typical for α-Bi_2O_3 and are in good accordance with those reported in literature, revealing that the absorption band at 845 cm^{-1} is attributed to the Bi−O−Bi bond, and the strong absorption band recorded at 424 cm^{-1} is due to the stretching mode of Bi−O.[11] Micro-Bi_2O_3, a pale-yellow solid, showed the broad absorption band between 600 and 400 cm^{-1}, peaked at 417 and 498 cm^{-1}, originating from the Bi−O stretching vibration. A small peak at 846 cm^{-1} confirming the Bi−O−Bi vibration is also observed.[12] Figure 2b,c shows the FTIR spectra of the polyester and cotton fabrics coated with micro- and nano-Bi_2O_3, and Figure 2d reveals the FTIR spectra of PVA-coated cotton, micro-Bi_2O_3/PVA composite-coated cotton, and nano-Bi_2O_3/PVA composite-coated cotton. For micro-Bi_2O_3 and nano-Bi_2O_3 particle-coated fabrics and micro-Bi_2O_3/PVA and nano-Bi_2O_3/PVA composite-coated fabrics, the characteristic peaks of Bi_2O_3 are obscured by other high-intensity peaks, characteristic of the fabrics themselves as well as of the PVA matrix. The spectra of the textiles coated with nano-Bi_2O_3 particles and the nano-Bi_2O_3/PVA composite, however, clearly display a characteristic peak at 498 cm^{-1}. Furthermore, other observable evidences, such as SEM pictures, color change after coating, and digital photos of the coated fabrics, confirm the successful deposition of both micro-Bi_2O_3 and nano-Bi_2O_3 on the fabric surfaces.

The results showed that bismuth oxide was successfully deposited on the surface of both types of textiles. Furthermore, the FTIR results show no evidence of a peak shift, a new peak, or the removal of the peaks. This indicates that the Bi_2O_3 and fabric interaction may not be a chemical interaction but instead, a physical type of interaction.[13] Similar results are also proposed by Ambika et al.[14] They reported that bismuth oxide applied to the resin matrix does not experience any chemical reactions and instead occupies the resin network's interstitial gaps.

Deposition Efficiency and Mass Per Unit Area. The deposition efficiency of Bi_2O_3 particles on textile fabrics was confirmed in the dyeing process, after washing out the excess particles of the fabrics, by the value of % uptake, calculated based on the difference between the weights of the fabric before and after coating with respect to the original weight, and the results are shown in Figure 3. The results of mass per unit area are also shown in the same plot. The percent uptake values of Bi_2O_3

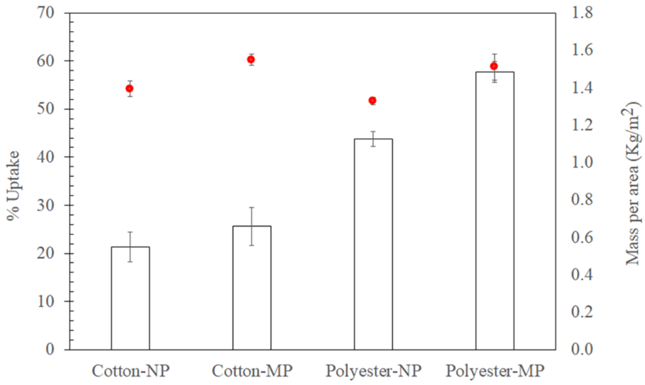

Figure 3. Deposition efficiency of micro- and nano-Bi_2O_3 on cotton and polyester fabrics (columns) and mass per unit area of the coated fabrics (circles): micro-Bi_2O_3-coated polyester (polyester-MP), nano-Bi_2O_3-coated polyester (polyester-NP), micro-Bi_2O_3-coated cotton (cotton-MP), and nano-Bi_2O_3-coated cotton (cotton-NP).

particles on the fabric surfaces are different, depending on both the size of the particles and the types of textile fabric. Micro-Bi_2O_3 particles showed a higher value of % uptake than that of nano-Bi_2O_3 particles on the same type of fabric. Although the larger micro-Bi_2O_3 particle agglomerates detached easier from the fiber surface, their weights are larger, inducing the higher % uptake than that of the nano-Bi_2O_3 particles. The micro- and nano-Bi_2O_3 showed a % uptake of 25.6 ± 4.0 and 21.1 ± 3.1%, respectively, on the cotton fabric, which are lower than those on the polyester fabric (57.7 ± 2.1 and 43.7 ± 1.5%, respectively). These findings are consistent with the FTIR results, suggesting that Bi_2O_3 and the polyester fabric surface have substantial physical interactions. The results are in good accordance with those reported by Syafiuddin et al.,[10] who claimed that the deposition of silver nanoparticles (AgNPs) on polyester fiber showed less particle agglomeration than those that appeared on the surface of cotton fiber due to the soft and fluffy staple fiber of cotton, which has higher flexibility and can agglomerate the AgNPs more effectively. Besides, the more uniform distribution of AgNPs observed on the polyester fabric surface could be due to better interaction between the AgNPs and the polyester fiber.

The mass per unit area of the coated fabric also depended on the particle size of Bi_2O_3. The cotton fabric coated with micro- and nano-Bi_2O_3 showed the mass per unit area of 1.548 and 1.394 kg/m^2, respectively. The polyester fabric coated with micro- and nano-Bi_2O_3 also showed slightly lower values of 1.511 and 1.329 kg/m^2, respectively. Those values are significantly lower than the area density, the minimum mass per unit area, of the commercial lead aprons, which ranks between 2.5 kg/m^2 (the lightest) and 3.3 kg/m^2 (the heaviest).[15]

Color Transformation of the Fabrics. The changed color of the fabrics indicates the adsorption of Bi_2O_3 on the surface of the textile fabric. The values of a^*, b^*, and L^* for micro- and nano-Bi_2O_3, cotton and polyester fabrics, and Bi_2O_3-coated fabrics are shown in Table 1.

The transformation of color of the coated fabrics from the original color of cotton and polyester fabrics indicated the successful adsorption of both micro- and nano-Bi_2O_3 particles on the surfaces of the fabrics. Furthermore, the delta values associated with the color scale, e.g., ΔL^*, Δa^*, and Δb^*, show

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Table 1. Color of Micro- and Nano-Bi_2O_3, Cotton, Polyester, and Bi_2O_3-Coated Fabrics Identified Using CIE L*a*b* Coordinates

samples	CIE *L*a*b** coordinates *L**	*a**	*b**	mass per unit area (kg/m^2)
micro-Bi_2O_3	97.58	−6.17	27.32	1.0 g/cm^3[a]
nano-Bi_2O_3	82.5	10.2	83.61	0.5−1.1 g/cm^3[a]
cotton	91.27	1.04	−1.06	0.1180
polyester	90.81	0.60	1.30	0.0890
cotton-NP	90	−2.77	87.29	1.394
cotton-MP	92.42	−2.3	12.21	1.548
polyester-NP	86.11	7.47	84.77	1.329
polyester-MP	93.22	−4.49	18.85	1.511
cotton-NP/PVA	82.22	11.58	91.07	1.274
cotton-MP/PVA	89.26	−4.92	22.52	1.598

[a]Bulk density. Data were obtained from https://www.sigmaaldrich.com.

that the CIE *L*a*b** coordinates of the coated fabrics are not much different from those of their corresponding Bi_2O_3 particles.

Weight Loss After Washing. In order to investigate the durability of Bi_2O_3 on the coated fabrics, the coated fabric sample was washed three times using distilled water and its weight loss was determined. Figure 4 indicates the loss of the Bi_2O_3-coated fabric weight after three washing cycles. The results specify that for both nano- and micro-Bi_2O_3-coated cotton fabric, the loss of fabric weight after washing is significantly higher than that of the nano- and micro-Bi_2O_3-coated polyester fabric. Moreover, micro-Bi_2O_3-coated fabrics showed a higher weight loss than nano-Bi_2O_3-coated fabrics. This is in good agreement with the SEM results presented previously in Figure 1 and may be due to the fact that the large-particle agglomerates easily separate from the surface of the fabric, while the small particles can penetrate deeper and adhere strongly into the fabric matrix. Moreover, the ester functional groups in polyester can interact well with Bi_2O_3.

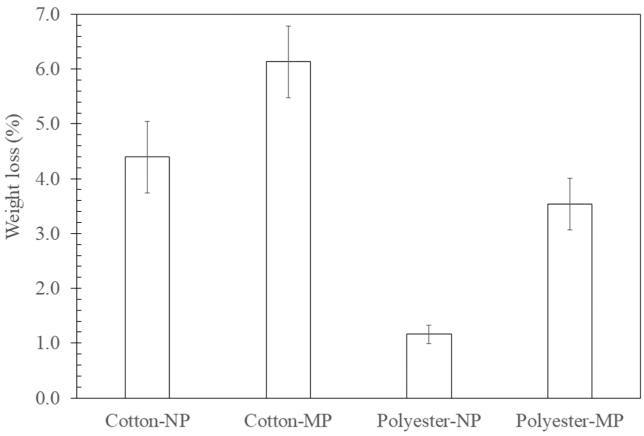

Figure 4. Percent weight loss of nano- and micro-Bi_2O_3-coated cotton fabric (cotton-NP and cotton-MP) and nano- and micro-Bi_2O_3-coated polyester fabric (polyester-NP and polyester-MP) after three washing cycles.

In summary, the experimental results, especially SEM images, deposition efficiency, and weight loss after washing, indicated that the application of Bi_2O_3 on the fabric by the dyeing process is suitable for polyester, but not suitable for the cotton fabric. Therefore, Bi_2O_3/PVA composite-coated cotton fabric was prepared by K-hand coating. The results obtained from SEM micrographs and the FTIR spectra for the cotton fabric coated with the micro-Bi_2O_3/PVA (cotton-MP/PVA) and nano-Bi_2O_3/PVA composite (cotton-NP/PVA), presented in Figures 1s−x and 2d, respectively, confirm the effective application of the Bi_2O_3/PVA composite on the surface of the cotton fabric. A similar application method was also proposed by Kang et al., who applied the Bi_2O_3/urethane resin composite on the surface of a fabric for producing a non-lead radiation-shielding fabric.[5] Therefore, only the coated fabric samples, namely polyester-NP, polyester-MP, cotton-NP/PVA, and cotton-MP/PVA, were chosen for further investigation on their X-ray attenuation performance.

X-Ray Attenuation. The reduction in intensity of an X-ray radiation beam as it travels through a material is referred to as attenuation. The reduction could be due to material absorption, photon scattering, or being deflected off the beam when they hit the particles in the material, or photon−matter interaction involving the atoms of the material absorbing the photons and then re-emitting them.[16]

Figure 5 represents the X-ray transmission of the nano- and micro-Bi_2O_3-coated polyester fabric at 80 kVp, one of the optimal tube acceleration voltages for projection radiographs in clinical practice.[17] The X-ray transmission (I/I_0) was used to assess the photon-shielding properties, where I and I_0 are the intensities of the incident X-ray beam and that transmitted through the thickness direction of the sample composites, respectively. The results showed that the ionizing radiation-shielding performance of both nano- and micro-Bi_2O_3-coated polyester fabrics increases with the number of fabric layers. This is a typical phenomenon since attenuation is dependent on material properties including thickness, density, and effective atomic number (Zeff) number, which represents the total number of electrons surrounding the nucleus of a metal atom in a metal complex.[18] Generally, the amount of bismuth element in Bi_2O_3 is 89%, which is high enough for Bi_2O_3 to perform as a good X-ray absorber. Maghrabi et al.[3] also confirmed that the shielding capacity of the Bi_2O_3-coated fabrics was due to the high atomic number and high density of bismuth. Added to that, the material thickness and mass (Figure 3) have significant

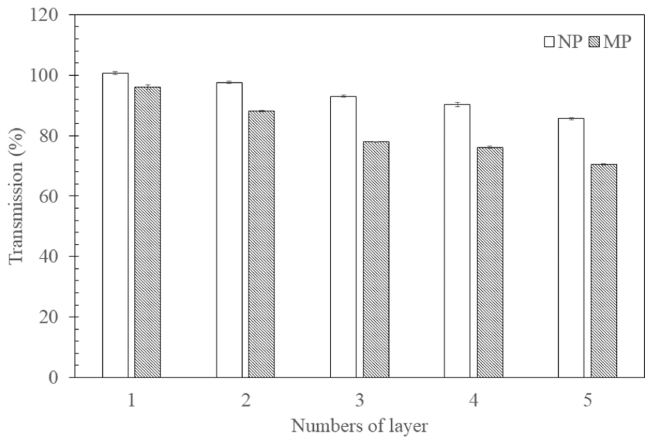

Figure 5. X-ray attenuation performance of nano- and micro-Bi_2O_3-coated polyester fabric at 80 kVp.

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effects on the attenuation strength, because there was greater distance for the X-ray photon to travel through the medium.

It is also evidenced in Figure 5 that the micro-Bi_2O_3-coated polyester fabric showed lower X-ray transmission than that of the nano-Bi_2O_3-coated polyester fabric. This implies that the micro-Bi_2O_3-coated polyester fabric possesses better X-ray attenuation performance than the nano-Bi_2O_3-coated polyester fabric, owing to its higher values of both % uptake and mass per area.

Although the Bi_2O_3 particle-coated polyester fabrics shield some X-rays and have an effect of reducing the transmission, the effectiveness is poor. In their current form, the proposed coated polyester fabrics may not be suitable for use as standard X-ray shielding garments. As previously stated, the poor effectiveness of the coated polyester fabrics was due to an insufficient amount of Bi_2O_3 coated on the fabric surface, resulting in a low particle density. High amounts and densities of Bi_2O_3 particles on the fabric surface should be considered for improvement, as these two factors have a direct correlation with the X-ray attenuation coefficients. Therefore, Bi_2O_3 particles coated on a fabric in a suitable polymer resin matrix with a high Bi_2O_3 concentration of 66.7 wt % were further fabricated and this could provide adequate X-ray shielding.

Biodegradable textile-based shielding composites against ionizing radiation were produced by coating the surface of the cotton fabric with the Bi_2O_3/PVA composite, in which the weight ratio of Bi_2O_3/PVA equals 2:1. Cotton fabrics coated with biodegradable PVA composites containing either micro- or nano-Bi_2O_3 particles were prepared using a simple hand-coating method, and their thickness and ability to shield diagnostic X-rays at tube acceleration voltages of 70, 80, and 100 kVp were examined as functions of the number of fabric layers, as shown in Figures 6 and 7, respectively.

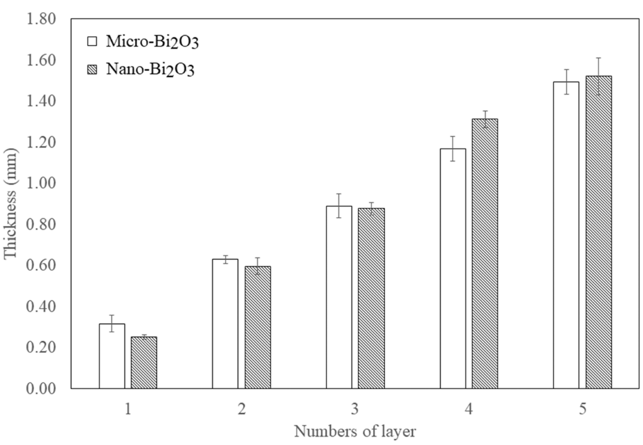

Figure 6. Thickness of the cotton fabric coated with the micro-Bi_2O_3/PVA composite and nano-Bi_2O_3/PVA composite as a function of the number of coated fabric layers.

It can be clearly seen in Figure 6 that the thickness of the cotton fabric coated with either the micro-Bi_2O_3/PVA composite or the nano-Bi_2O_3/PVA composite increased with an increasing number of coated fabric layers. Moreover, there is no significant difference between the thickness of the cotton fabric coated with the micro-Bi_2O_3/PVA composite and that coated with the nano-Bi_2O_3/PVA composite for the same number of coated fabric layers. With 5 layers, the fabric showed a thickness of 1.49 ± 0.06 and 1.52 ± 0.09 mm for the cotton fabric coated with the micro-Bi_2O_3/PVA composite and that coated with the nano-Bi_2O_3/PVA composite, respectively. The results suggest that the 5-layer-coated fabric is thicker than both light lead (0.53 mm) and regular lead samples (0.66 mm). However, the values are in good agreement with the thickness of the polyester fabric coated with micro-Bi_2O_3/PVC (1.33−1.47 mm) that was proposed by Maghrabi et al.

The results of the X-ray attenuation performance of the cotton fabric coated with the micro-Bi_2O_3/PVA composite and nano-Bi_2O_3/PVA composite in Figure 7 showed that with increasing tube acceleration voltages, the X-ray attenuation performance for the cotton fabric coated with either micro-Bi_2O_3/PVA or nano-Bi_2O_3/PVA nanocomposite decreased progressively. It is well known that the output particle energy is equal to the charge on the particle multiplied by the accelerating voltage. Therefore, as the acceleration voltage increased, the output particle energy of the charged particles accelerated through a single potential difference between two electrodes also increased. Subsequently, the high-energy particles can easily penetrate through the coated fabrics. This is in good accordance with the result proposed by Chai et al.[19] for a flexible, lead-free X-ray-shielding composite prepared with methyl vinyl silicone rubber matrix and Bi_2O_3 filler. Besides, it can also be seen in Figure 7 that the ionizing radiation-shielding performance of cotton fabrics coated with either micro- or nano-Bi_2O_3/PVA composites increased with the number of fabric layers. In other words, X-ray attenuation increased with increased material thickness. Hence, the Bi_2O_3/PVA composite-coated cotton fabric with its multilayered forms is an alternative promising means for production of wearable shielding garments.

Furthermore, it was also found that the size of the Bi_2O_3 particles is another factor influencing the X-ray attenuation performance of the Bi_2O_3/PVA composite-coated cotton fabric. Figure 7 shows that the X-ray attenuation performance of the composites produced from micro-sized Bi_2O_3 particles was more effective than that of the nanosized one at all tube voltages (70−100 kVp). The composites with micro-sized Bi_2O_3 show higher values of mass attenuation coefficients than those of the composites with nanosized Bi_2O_3 at all of the investigated tube voltages. This may be due to the differences in absorption and scattering of the incident radiation caused by the particles with different sizes. In radiological physics, the values of mass attenuation coefficients are dependent on the absorption and scattering of the incident radiation caused by several different mechanisms: photoelectric effect, Compton scattering effect, pair production, Rayleigh scattering, and photodisintegration.[20] In the case of Bi_2O_3 (atomic number of Bi = 83), the photoelectric effect is a major mechanism of photons' interactions with matter when the photon energy of 70−100 kVp is applied. Photoelectric effect is a phenomenon in which electrically charged particles are released from or within a material when it absorbs electromagnetic radiation. Hence, the photoelectric effect represents an interaction between light and matter, in which the maximum kinetic energy of the released electrons did not vary with the intensity of the light, but was proportional to the frequency of the light.

This is in contrast with the results proposed by Künzel and Okuno, who studied the effects of the particle size, material concentration, and radiation energy on the X-ray absorption at tube voltages of 25−120 kVp.[21] They reported that the particle grain size influenced the intensity of the transmitted radiation. The X-ray absorption is higher for the nanostructured CuO compared to the microstructured one for low-energy X-ray

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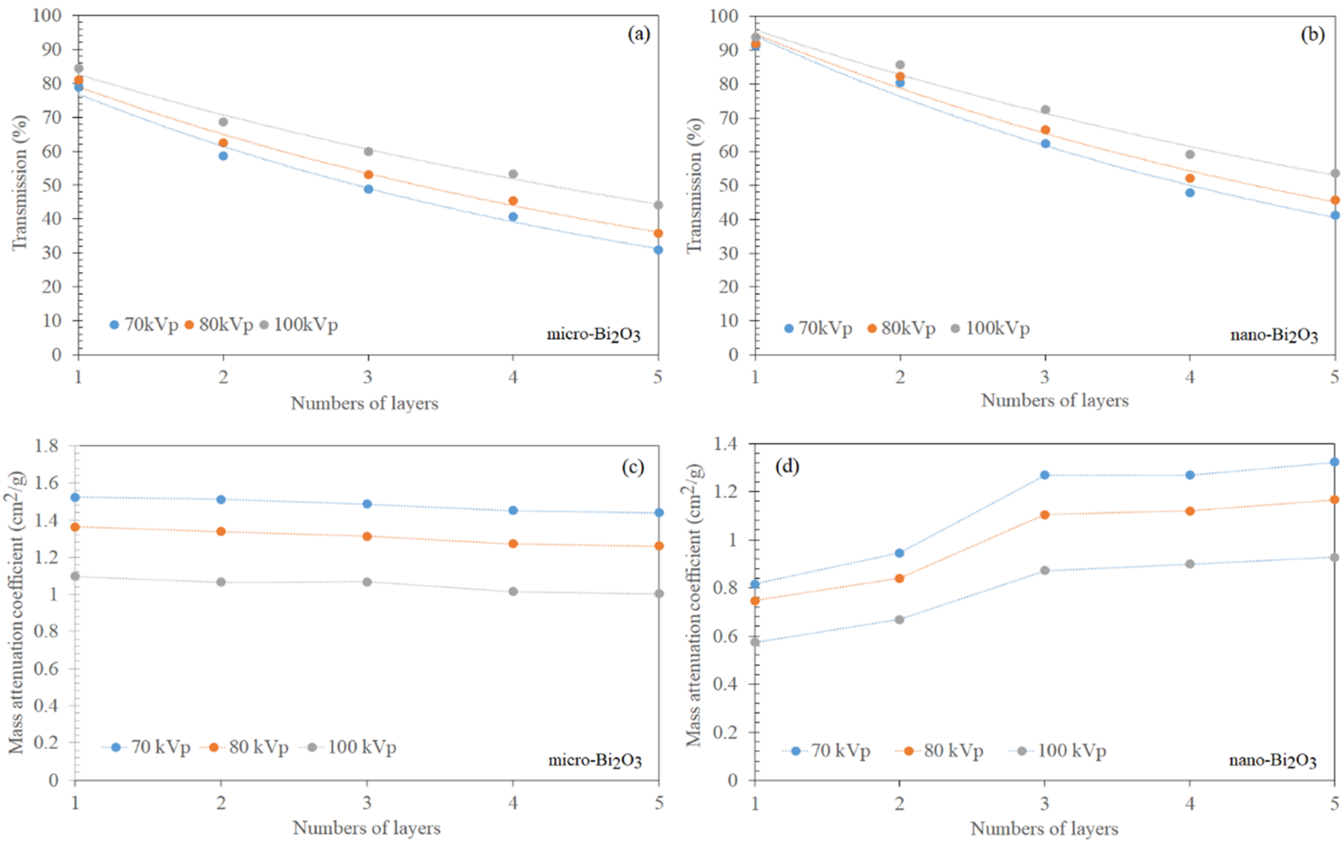

Figure 7. X-ray attenuation performance of the cotton fabric coated with the (a) micro-Bi_2O_3/PVA composite and (b) nano-Bi_2O_3/PVA composite, and mass attenuation coefficients of the (c) micro-Bi_2O_3/PVA composite and (d) nano-Bi_2O_3/PVA composite at various tube voltages of 70, 80, and 100 kVp.

beams (25 and 30 kVp). For the X-ray beams produced at 60 and 120 kVp tube voltages, less than 2% difference in the X-ray transmission through the nanostructured and microstructured materials is observed. Botelho et al.[22] also studied the X-ray transmission performance of plates produced from nano- or micro-sized CuO particles. They proposed that plates produced from nanosized CuO particles were more effective than those from micro-sized copper oxide particles at low tube voltages (26−30 kVp), as the number of Cu particles/g in the nanostructured plates is higher than that for the micro-sized material. Therefore, the probability of a low-energy X-ray photon to interact and to be absorbed may be higher for the nanostructured mixture than for the microstructured material. However, Botelho et al. claimed that for X-ray beams at high tube voltages (60−102 kVp), the X-ray transmission performances of plates produced from nano- or micro-sized copper oxide particles were almost the same. Similar results were confirmed by Low et al.,[23] who investigated the effect of particle size, filler loadings, and X-ray energy on the transmitted X-ray beam intensity by WO_3-epoxy composites. They proposed that nanosized WO_3 has a better ability to attenuate X-rays produced by lower X-ray tube voltages (22−35 kVp) when compared to micro-sized WO_3 of the same filler loading. However, the effect of particle size on the transmitted X-ray beam intensity was negligible in the higher X-ray tube voltage range (40−120 kVp).

Conclusively, our experiment clearly shows that the micro-sized Bi_2O_3 can guarantee a radiation-shielding property. However, it is too early to draw any conclusion on the possible mechanisms of enhanced attenuation of micro-sized Bi_2O_3 particles in the high X-ray tube voltage range of 70−100 kVp. Besides, these findings enhanced our understanding of the important correlation between the metal elements and the required concentration of chemicals, which will have a direct effect on the X-ray attenuation coefficient.

As seen in Figure 7, the 5-layer micro-Bi_2O_3/PVA composite-coated cotton fabric shows a higher level of X-ray protection than that of the 5-layer nano-Bi_2O_3/PVA composite-coated cotton fabric, at all investigated tube voltages. However, such transmittance values (31, 36, and 44% at 70, 80 and 100 kVp, respectively) are quite low and may not be effective for radiation protection. According to Maghrabi et al., the transmittance values for light lead and regular lead at 80 kVp were 18 and 17%, respectively.[4] Therefore, further investigation of the X-ray attenuation performance for 6−10 layers of micro-Bi_2O_3/PVA composite-coated cotton fabric was carried out and the results are shown in Figure 8.

As expected, 10 layers of cotton fabric coated with micro-Bi_2O_3/PVA composite show a high radiation-shielding ability with only 12.2, 16.2, and 23.7% X-rays transmitted at 70, 80, and 100 kVp, respectively. At 80 kVp, the transmittance value of 16.2% is lower than that of both the benchmark lead equivalent samples. Compared with the light lead and the regular lead samples, the X-ray transmittance of the 10-layered cotton fabric coated with micro-Bi_2O_3/PVA composite decreased by 10 and 4.7%, respectively. These findings confirmed that the proposed cotton fabric coated with a micro-sized Bi_2O_3/PVA composite can provide adequate X-ray shielding at high diagnostic voltages.

Comparison of the X-ray attenuation performance for the biodegradable PVA/Bi_2O_3 composite-coated cotton fabric and

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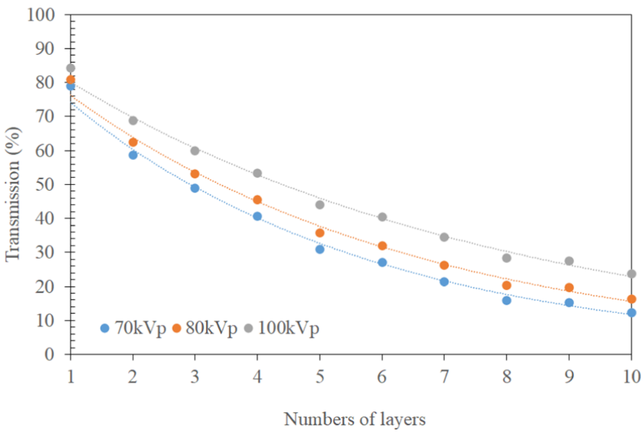

Figure 8. X-ray attenuation performance of cotton fabric coated with 1−10 layers of micro-Bi_2O_3/PVA composite at various tube voltages of 70, 80, and 100 kVp.

other bismuth oxide−polymer composites, especially the non-biodegradable system, is shown in Table 2.

This study concluded that bismuth oxide microparticles can be effective for X-ray attenuation. Bi_2O_3/PVA composites with adequate ability to shield diagnostic X-rays can be used to create environmentally friendly and biodegradable textile-based shielding composites against ionizing radiation. Alternative X-ray shielding materials with lower toxicity have the potential to replace lead-based composites, which are highly toxic to human health and have negative environmental consequences.

CONCLUSIONS

Environmentally friendly and biodegradable textile-based shielding composites against ionizing radiation were successfully produced from fabrics coated with either Bi_2O_3 particles using the dyeing process or Bi_2O_3/PVA composites via the hand-coating method. By the dyeing process, micro- and nano-Bi_2O_3 showed % uptake of 25.6 ± 4.0 and 21.1 ± 3.1%, respectively, on the cotton fabric, which are lower than those of the polyester fabric (57.7 ± 2.1 and 43.7 ± 1.5%, respectively). Moreover, after washing, both nano- and micro-Bi_2O_3-coated cotton fabrics showed higher loss of fabric weights than those of nano- and micro-Bi_2O_3-coated polyester fabrics. Therefore, the application of Bi_2O_3 on fabrics by the dyeing process is suitable for polyester, but not suitable for cotton fabric. The micro- and nano-Bi_2O_3-coated polyester fabric shielded some X-rays and had the effect of reducing the transmission, but the effectiveness is poor owing to insufficient amount of Bi_2O_3 and may not be suitable to be used as a standard X-ray shielding garment. Besides, the results also showed that the micro-Bi_2O_3-coated polyester fabric possesses better X-ray attenuation performance than the nano-Bi_2O_3-coated polyester fabric, owing to its higher values of both % uptake and mass per area. In order to improve the X-ray attenuation performance, a biodegradable textile-based shielding composite against ionizing radiation was produced by coating the surface of the cotton fabric with the Bi_2O_3/PVA composite, in which the weight ratio of Bi_2O_3/PVA equals 2:1. As expected, the cotton fabric coated with the Bi_2O_3/PVA composite exhibited a better ability to attenuate X-rays produced by high diagnostic X-ray tube voltages of 70−100 kVp. With increasing tube acceleration voltages, the X-ray attenuation performance for the cotton fabric coated with either micro-Bi_2O_3/PVA or nano-Bi_2O_3/PVA nanocomposite decreased progressively, while their ionizing radiation-shielding performance increased with the number of fabric layers. The 10-layered cotton fabric coated with the micro-Bi_2O_3/PVA composite shows high radiation-shielding ability with only 12.2, 16.2, and 23.7% X-rays transmitted at 70, 80, and 100 kVp, respectively. At 80 kVp, the transmittance value of 16.2% is lower than that for both the benchmark lead equivalent samples. Hence, the Bi_2O_3/PVA composite-coated cotton fabric with its multilayered forms is an alternative promising means for production of wearable shielding garments. In addition, the micro-sized Bi_2O_3/PVA composite exhibited better X-ray-shielding properties with higher values of mass attenuation coefficients than the nanosized Bi_2O_3/PVA composite at all tube voltages (70−100 kVp).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02578.

Additional experimental details including ATR-FTIR spectra for all compounds and digital photographs for all fabrics (PDF)

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Table 2. Studies on the X-Ray Attenuation Performance of Bismuth Oxide−Polymer Composites

authors	systems	Bi_2O_3 loading (wt %)	voltage (kVp)	transmission (I/I_0)
Kang et al.[5]	nano-Bi_2O_3/urethane resin	no data	60, 80, 100	0.002, 0.04, and 0.09 at 60, 80, and 100 kVp, respectively
Maghrabi et al.[4]	micro-Bi_2O_3/PVC	66.7	80	0.08 at 80 kVp
Chai et al.[19]	micro-Bi_2O_3/methyl vinyl silicone rubber	80	55, 70, 100, 125, 170, 210	0.35 at 100 kVp
Shik and Gholamzadeh[7]	micro-Bi_2O_3/EPVC	20, 40	40−100	mass attenuation coefficient, μ_m = 1.49 and 6.62 cm^2/g for 20 and 40% Bi_2O_3 loading at 100 kVp
Hazlan et al.[6]	nano-Bi_2O_3/PVA	35	8.64−25.20	mass attenuation coefficient, μ_m = 260−65 cm^2/g at 8.64−25.20 kVp
this study	micro-Bi_2O_3/PVA	66.7	70, 80, 100	0.12, 0.16, and 0.24 at 70, 80, and 100 kVp, respectively

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Notes

The authors declare no competing financial interest.

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