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Preliminary Study of Alternative Environmentally Friendly X-ray Shielding Materials Based on Nano-bismuth (III) Oxide Coated Fabric

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Abstract

Chest X-ray is the first imaging procedure that play an important role in identification of COVID-19 as well as medical diagnostic and treatment of COVID-19 patients, in order to increase recovery rates and to lower fatality rates. Regardless of their environmental disadvantages and high toxicity, lead aprons are important materials for personal protection of physicians and patients from X-ray radiation during medical operations. Typically, for standard lead protective aprons, the transmittance values for lite-lead (LL) and regular lead (RL) were approximately 18 % and 17 %, respectively. With an aim to find new materials possibly to replace toxic lead-shielding products, in this study, an environmentally friendly and flexible fabric-based radiation shielding material was manufactured. Polyester fabric was coated by Bi_2O_3 nano particles using a simple, scalable, and cost-effective method to deposit the nano-particles onto the textile fabric surface. This application method allows the potential production of nano-Bi_2O_3 coated polyester fabric at the maximum %uptake of 45 and mass per unit area of 0.41 g/cm^2 for 1 layer fabric. Radiation attenuation of the fabric increased with the numbers of fabric layers. Five layers of the fabric showed X-ray transmission of approximately 85% when measured at 80 kVp tube voltage, the medical application standard. To increase X-ray protection ability, the nano-Bi_2O_3 coated polyester fabric surface was recoated with PVA/Bi_2O_3 coating composites using K-hand coater. The potential application of the recoated fabric as environmentally friendly and flexible fabric-based radiation shielding material for X-ray attenuation was also demonstrated. The 5-layer PLA/nano-Bi_2O_3 coated fabric showed the lowest X-ray transmission of 65.7%, implying the moderate improvement of shielding ability. This could lead to an X-ray protection textile garment that can potentially replace lead aprons.

Keywords: X-ray shielding; Coated fabric; Bismuth (III) oxide; Radiation attenuation.

1. Introduction

The spread of the SARS-CoV-2 virus has turned COVID-19 into a pandemic. Images obtained from lung X-rays is increasingly being used to facilitate diagnostic assistance tasks to identify lung problems. Recent findings indicate the presence of COVID-19 in patients with irregular findings on chest X-rays (Osman *et al.,* 2021). Hence, medical professionals around the world have been using lung X-rays to diagnose COVID-19. During medical operations, lead aprons are important materials for personal protection of physicians and patients from X-ray radiation. However, the issue to be concerned is that lead is highly toxic to human health and causes environmental disadvantages. Therefore, alternative X-ray shielding materials with less toxicity has been quested to replace lead-based composites.

Usually, metal elements that have a high atomic number and high density can impart higher X-ray shielding protection. Metals with high atomic number and low toxicity compared with lead such as barium, tungsten, and bismuth have been proposed as a substitute for lead. Among them, bismuth compounds are relatively non-toxic and inexpensive (Kang *et al.,* 2018). In bismuth(III) oxide (Bi_2O_3), the total bismuth element in the component of bismuth oxide is 89% by weight, and therefore can impart enhanced X-ray protection efficiency compared to lead oxide (Maghrabi *et al.,* 2015). Generally, X-rays are attenuated by lead and other powdered metals including Bi_2O_3 by absorption or by deflection (scatter) of photon from the beam and can be affected by different factors such as the beam energy and the absorber atomic number (Maghrabi *et al.,* 2016).

In the present study, an environmentally friendly and flexible fabric-based radiation shielding material was manufactured. Polyester fabric was coated by Bi_2O_3 nano particles and PLA/Bi_2O_3 composite using a simple, scalable, and cost-effective method to deposit the nano-particles onto the textile fabric surface. In addition, the effectiveness of Bi_2O_3 coating and X-ray shielding performance of the proposed materials were evaluated.

2. Materials and Methods

Bismuth (III) oxide (Bi_2O_3) nano-powder with the particle size of 90 - 210 nm and 99.9% purity and poly(vinyl alcohol, PVA, Mw 585,000 – 124,000 g/mol were purchased from Aldrich. Ethanol, analytical grade (99.9% purity), was from QRëC. Glutaraldehyde (1.2% w/v) was obtained from Fluka. Sulfuric acid, acetic acid and methanol were purchased from Carlo Erba Reagenti SpA, J.T. Beaker and Fisher Chemicals, respectively.

2.1 Nano-Bi_2O_3 Coating

In order to form a stable dispersion, 2.0 g of Bi_2O_3 nano-powder was mixed with 40 mL of ethanol by slow stirring. The polyester fabric was dip into the resulting suspension and continuously stirred at 90°C for 2 h. After dip coating, the excess amount of Bi_2O_3 on the fabric surface was washed thoroughly by ethanol and let 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:

$$\%Uptake = \frac{(W_f - W_i)}{W_i} \times 100 \qquad (1)$$

where W_f and W_i are the weights of polyester fabric before and after coating, respectively. Fabric mass per unit area of the coated fabric was also calculated using equation (2)

$$Mass\ per\ unit\ area\ = \frac{Fabric\ mass}{Area} \qquad (2)$$

2.2 PVA/nano-Bi_2O_3 Coating

A PVA solution with a concentration of 10% w/v was prepared by dissolving PVA in distilled water at 90°C under stirring for 2 h. PVA/Bi_2O_3 composite was prepared by mixing 10 mL of PVA solution with 2.0 g of Bi_2O_3 nano particle. After well mixing, 0.3 mL of glycerol was added with 3-min stirring. At that point, 2.8 mL of crosslinking 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 solution volume ratio of 3:2:1:1, was also added into the mixture under constant stirring for 10 min, in order to obtain a uniform distribution of Bi_2O_3. The mixture was coated on a Bi_2O_3-coated polyester fabric using a bar-coater with a short K-Bar No. 200 (K Hand coater, RK Printcoat Instruments, UK) and cured at 70°C for 1 h. The coating was performed twice for each side of the fabric.

2.3 Chemical structure analysis by FTIR

Functional groups presented on coated fabrics were investigated using 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 wavenumbers ranged from 400 to 4,000 cm^{-1}.

2.4 X-ray attenuation performance

Nano-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, source to chamber distance was 80 cm, which is the distance from X-ray tube (source) to the center of the fabric (radiation detector was just below the fabric). Samples were exposed to X-rays at a tube voltage of 80 kVp at tube current and time of 12.5 mAs, 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 fabric sample was 10.16 × 10.16 cm^2. The same procedure was also adopted on fabrics without any coating in order to compare shielding ability among the samples. The shielding ability of each sample was evaluated by comparing their transmission doses with the measured transmission doses for air reference.

3. Results and Discussion

According to Kim, the bismuth-containing shields are environmentally friendly, lead free, and harmless to the human body (Kim, 2016). Moreover, Kang *et al.* (2018) confirmed that because of its high atomic number and low toxicity compared with lead, antimony, and arsenic in the same period of the periodic table, most bismuth compounds are relatively non-toxic. In this present study, Bi_2O_3 nano-particles were applied on to polyester fabric using two different protocols: (1) disperse dyeing and (2) polymer composite coating. Figure 1 shows digital images for the surfaces of non-coated polyester fabric, nano-Bi_2O_3 coated fabric and PVA/nano-Bi_2O_3 coated fabric. It can be seen in Figure 1(b) that by disperse dyeing, the Bi_2O_3 particles homogenously distributed on the polyester fabric surface. In contrast, some degree of aggregation due to agglomerates of Bi_2O_3 particles in the PVA matrix (Figure 1(c) was observed due to a high Bi_2O_3 concentration of 67 %wt in the composite.

3.1 FTIR analysis

Chemical structures of both uncoated- and coated-polyester fabrics were investigated via FTIR measurement and the results are shown in Figure 2.

Generally, various functional groups e.g., ester, alcohol, anhydride, aromatic ring and heterocyclic aromatic rings are found in polyester fabric (Bhattacharya and Chaudhari, 2014). Both uncoated- and coated-polyester fabrics (P and PNP1) showed characteristic peaks at 1712 cm^{-1}, 1409 cm^{-1} and 1340 cm^{-1}, corresponded with C = O stretching vibration, aromatic ring and carboxylic ester or anhydride, respectively. The peak at 1017 cm^{-1} indicates the presence of O = C–O–C.

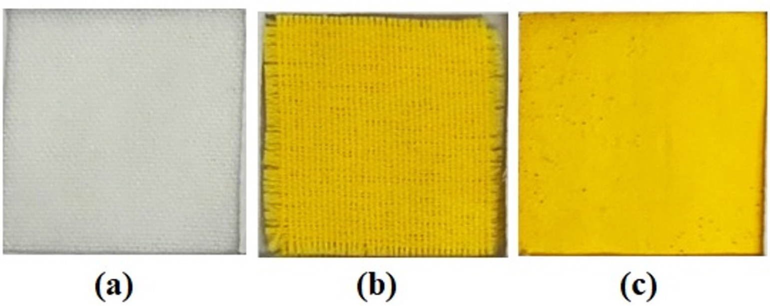

Figure 1. Digital images representing color difference between uncoated and coated polyester fabrics: (a) neat fabric, (b) nano-Bi_2O_3 coated fabric and (c) PVA/nano-Bi_2O_3 coated fabric.

The peaks corresponded with C = C stretching and five substituted H in benzene are found at 970 cm^{-1} and 872 cm^{-1}, respectively. In Bi_2O_3 spectra, the strong band centered at 846 cm^{-1} is related to stretching vibration of Bi–O in $[BiO_3]^{3-}$ polyhedron units and the peaks at 467, 499 cm^{-1} and 590, 620 cm^{-1} are typical Bi^{3+} vibration cause by $[BiO_6]^{9-}$ octahedral units. These peaks are the main characteristic peaks of Bi_2O_3 [Cheng *et al.,* 2006]. In the coated polyester fabrics, Bi–O and Bi^{3+} vibrations were detected around 474, 502 and 610, 629 cm^{-1}, indicating that the Bi_2O_3 nano particles are present in the polyester fabric. In addition, the broad band centered at 3250 cm^{-1} and the band between 2,800 − 2,980 cm^{-1}, found in PNP1C sample, indicating O − H stretching and C − H stretching of PVA, respectively (Jamnongkan and Kaewpirom, 2010).

3.2 Coating efficiency

For easy understanding, samples were named using the description as follows: P = Polyester fabric, NP = nano-Bi_2O_3 , C = PVA/nano-Bi_2O_3 composite, 1 − 5 = numbers of fabric layer. After polyester fabric was dipped coated and the excess amount of Bi_2O_3 on the fabric surface was removed, the averaged %uptake of the dry Bi_2O_3 coated fabric was 42.08 ± 2.5 %. This is in good agreement with the results proposed by Bhattacharya and Chaudharithat (2014), demonstrating that silica nano particles were uniformly distributed on the surface of individual fibers of polyester fabric by pad-dry-cure method. Moreover, the %uptake of Bi_2O_3 presented in our study is relatively higher that the value proposed by Afshari and Montazer (2017). They reported that by using in-situ sonosynthesis of nickel nanoparticles on the polyester fabric surface, %uptake for nickel nanoparticles on the fabric was 2 − 6%. Hence, the coating method used in our study was relatively simple and effective method to deposit the nano-Bi_2O_3 particles onto the polyester fabric surface.

The material thickness and mass per unit area for uncoated- and nano-Bi_2O_3 coated fabrics with various numbers of coated-fabric layers are displayed in Figure 3(a). It can be clearly seen in the figure that the material thickness and mass per unit area increased with increasing number of coated-fabric layer. In other words, the weight of the proposed X-ray shielding fabric increased with number of coated-fabric layer. With 5-layers, the fabric showed thickness and mass per unit area of 1.47 mm and 0.36 g/cm^2, respectively. These imply that the 5-layer coated-fabric is thicker and heavier than regular lead sample (0.66 mm, 0.25 g/ cm^2), which is in accordance with the weight and thickness of PVC/Bi_2O_3 coated polyester fabric, proposed by Maghrabi *et al.* (2015).

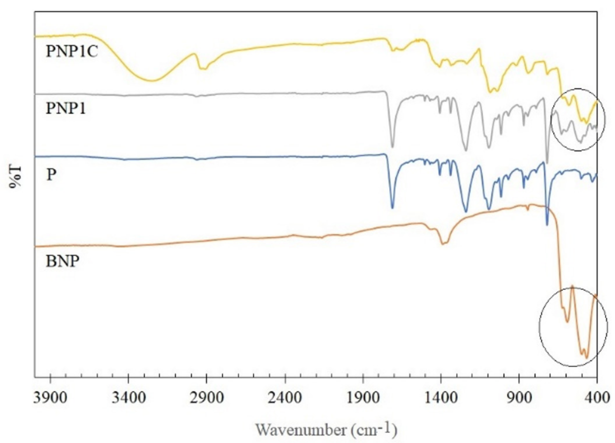

Figure 2. FTIR spectra of Bi2O3 nano particle (BNP), uncoated- and nano-Bi2O3 coated polyester fabric (P and PNP1) and polyester fabrics coated with PVA/Bi2O3 coating composites (PNP1C).

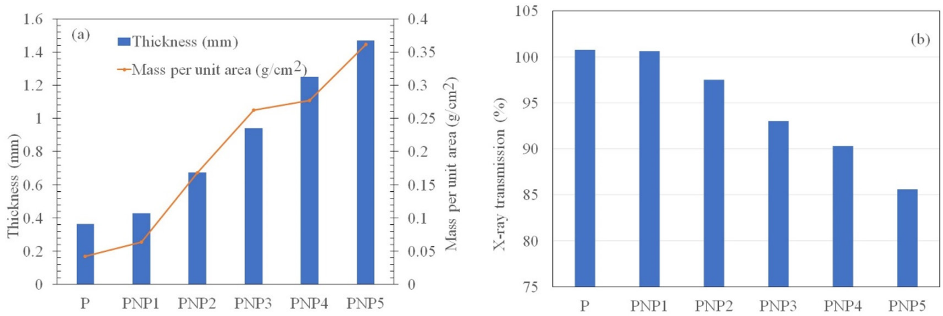

Figure 3. Material thickness, mass per unit area and the X-rays transmission of uncoated fabrics and nano-Bi_2O_3 coated fabrics with various numbers of layers.

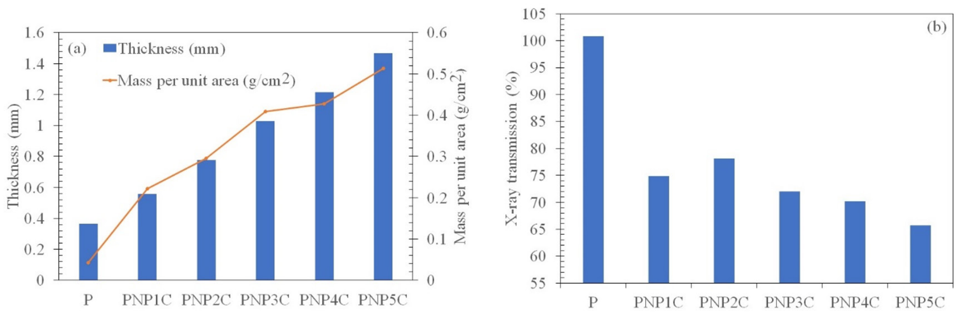

Figure 4. Material thickness, mass per unit area and the X-rays transmission of uncoated fabrics and PLA/nano-Bi_2O_3 coated fabrics with various numbers of layers.

The material thickness and mass per unit area for PLA/nano-Bi_2O_3 coated fabrics with various numbers of layers are also displayed in figure 4. Likewise, the material thickness and mass per unit area increased with increasing number of coated-fabric layer. The highest thickness and mass per unit area are 1.46 mm and 0.51 g/ cm^2, respectively. Again, the 5-layer coated-fabric with PLA/nano-Bi_2O_3 coating is thicker and heavier than regular lead sample.

Although the long-term effect of using Bi_2O_3 coated fabric was not reported in this present study and has not been reported elsewhere. We believe that PLA/nano-Bi_2O_3 coated fabric is more flexible than lead sheets that can easily develop cracks, rips holes and tears due to inflexibility. Therefore, the flexibility and durability of PLA/nano-Bi_2O_3 on the fabric should be further investigated to ensure that the developed fabric is suitable for medical applications.

3.3 X-ray shielding performance

In our study, X-ray exposure via air without any fabric was measured and was taken as control. The uncoated-polyester fabric was also measured as a reference for comparison against the coated-fabric. The shielding ability of nano-Bi_2O_3 coated polyester fabric and PLA/nano-Bi_2O_3 coated fabrics, with 1−5 layers of fabric, was evaluated at a medium level of radiation at 80 kVp. The results are shown in Figure 3(b) and 4(b), respectively. The value of the %transmittance corresponds with the quantity of X-rays that penetrated through the specimen, and designates the shielding performance of the materials. The higher transmittance value, the lower X-ray absorption and the less effective of the material for radiation protection.

It's evidenced in figure 3(b) that both uncoated- and a single-layer nano-Bi_2O_3 coated polyester fabric show no X-ray shielding ability. With 2-layer thick, the nano-Bi_2O_3 coated fabrics shielded some X-rays. The shielding ability increased with the increased number of coated fabric layer. Therefore, the results in figure 3(b) indicate the effectiveness of the nano-Bi_2O_3 coated fabric for radiation protection. However, with 5-layers of nano-Bi_2O_3 coated-fabric, the X-ray transmission showed the high value of 85.6%, which was not suitable to be used as an alternative X-ray shielding materials to replace lead-based composites. This may be due to the low concentration of nano-Bi_2O_3 on the coated fabric as well as the presence of very small apertures inside the coated fabric structure.

With an aim to increase X-ray attenuation of the nano-Bi_2O_3 coated fabric, further coating was carried on with PLA/nano-Bi_2O_3 composites. The nano-Bi_2O_3 coated polyester fabric was further coated with PLA/nano-Bi_2O_3 composites (the weight ratio of PLA: nano-Bi_2O_3 equals 1:2). The X-ray transmission of PLA/nano-Bi_2O_3 coated fabrics with various numbers of layers are shown in figure 4(b). Interestingly, a single-layer PLA/nano-Bi_2O_3 coated fabrics show X-ray shielding ability, with X-ray transmission of 74.8%. Moreover, the shielding ability of the PLA/nano-Bi_2O_3 coated fabrics increased with increasing number of fabric layers. Among the fabric samples, 5-layer PLA/nano-Bi_2O_3 coated fabric showed the lowest X-ray transmission of 65.7%, implying the moderate improvement of shielding ability due to the use of Bi_2O_3, the high atomic number metal compound, as the coating material. Although this transmission value is lower than that proposed by Maghrabi *et al.* (2016), the threshold value of 18 % transmission was not obtained. Hence, the coated fabrics cannot meet satisfactory radiation protection requirement for medical applications. However, this study did bring out a possible solution concerning with the replacement of toxic lead compound by less-toxic bismuth oxide. To achieve the standard level of shielding ability, a larger quantity of Bi_2O_3 and a greater number of coated fabric layers may be required. In our further investigations, we will use the combination of Bi_2O_3 with other high atomic number metal compounds such as tungsten trioxide (WO_3) as coating fillers to demonstrate the suitability of using coated fabrics as an environmentally friendly X-ray shielding apron.

4. Conclusions

In this pilot study, an environmentally friendly X-ray shielding fabric was developed. The shielding ability of the fabrics increased with increasing number of fabric layers. Among the fabric samples, PNP5C, showed the lowest X-ray transmission of 65.7%, implying the moderate improvement of shielding ability due to the use of Bi_2O_3, the high atomic number metal compound, as the coating material. Although this value is lower than the threshold value, this present study did deliver a possible answer concerning with the production of an apron with multi-layered coated fabric as a replacement of toxic lead apron.

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